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VOLUME **98**

Editor

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PREFACE

Volume 98 of *Advances in Heterocyclic Chemistry* commences with an overview of the use of dimedone as a versatile precursor for annulated heterocycles, authored by El Sayed H. El Ashry, Laila F. Awad, Yeldey El Kilany, and Elsayed I. Ibrahim, all from the Alexandria University in Egypt. This topic has not previously been covered in a comprehensive fashion; the authors now show how dimedone can be used for the preparation of many classes of annulated heterocycles, classified in a systematic fashion.

We have published a series of updates on the chemistry of pyrazol-3-ones, derivatives important particularly in the chemistry of pharmaceuticals and dyestuffs. Part I, which was published in 2001 in Volume 80, describes syntheses of pyrazol-3-ones. Part II (Volume 87, 2004) summarizes reactions at ring atoms at pyrazol-3-ones. Part III (Volume 95, 2008) discusses the reactivity of ring substituents of pyrazol-3-ones. Chapter 2 covers more recent syntheses and a variety of applications of pyrazol-3-ones. Together this four-part series updates the major work on pyrazolones that was published by Wiley in the series of monographs *The Chemistry of Heterocyclic Compounds* back in 1964. All the four parts of this mini series are authored by George Varvounis of the University of Ioannina, Greece.

The third and final chapter in this volume is by Alexander P. Sadimenko of the University of Fort Hare, Republic of South Africa. It represents a further installment in his wide-ranging survey of organometallic complexes formed by heterocyclic ligands. It covers complexes of polypyridine ligands and their analogues, which are of increasing importance in many areas of chemistry, in particular catalytic reactions, structural diversity, and many areas of analytical chemistry.

Alan R. Katritzky
Gainesville, Florida

Dimedone: A Versatile Precursor for Annulated Heterocycles

**El Sayed H. El Ashry^{a,b}, Laila F. Awad^a,
Yeldey El Kilany^c and Elsayed I. Ibrahim^d**

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1. INTRODUCTION

Dimedone (**1**) is an alicyclic compound having 1,3-dicarbonyl groups flanked by a methylene group and exists in a tautomeric *trans*-enolized form where intramolecular hydrogen bonding is not possible (05S3468). The inherent structural features in **1** have created various reactive centers: C-1, C-2, and to a less extent C-6 in addition to C-3 in or 3-O (Figure 1). Such phenomenon attracted much attention for using it as a synthetic reagent for the characterizations of aldehydes, since its discovery, by the formation of readily crystalizable derivatives; determination of formaldehyde in textiles has been done by a colorometric method (04MIa79). Moreover, dimedone is an excellent precursor for partially hydrogenated fused heterocycles (04CUOC695), where two of the carbon-atoms of dimedone are part of the backbone of the formed heterocycles. Its structural features and its reactivity to form more functionalized derivatives have led to the construction of a wide range of fused or spiral biheterocycles.

This chapter will emphasize the role of **1** in the synthesis of fused heterocycles, classified according to the size of the ring and the number of heteroatoms in the heterocycle fused to the cyclohexane ring and subdivided according to the heteroatoms and their arrangement in the ring. The titles are given as annulated heterocycles to **1**, which are mostly saturated or partially saturated heterocycles. However, for the simplicity the subtitle is given between two brackets as benzoheterocycles.

2. DIMEDONE-ANNULATED THREE- AND FOUR-MEMBERED HETEROCYCLES

Only few examples were reported related to these ring systems. Moreover, only those fused with three-membered ring mainly containing one heteroatom oxygen were reported. No examples can be found with a four-membered ring containing two heteroatoms.

The epoxide ring in such fused ring systems has been formed by the epoxidation with *t*-butylhydroperoxide/Triton-B of the respective double bond in **6** and **7**, which were prepared from **2** *via* the formation of

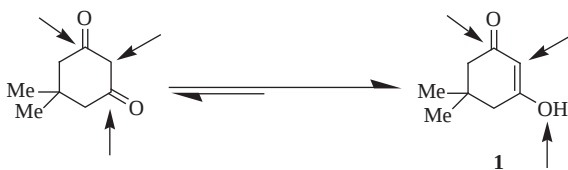
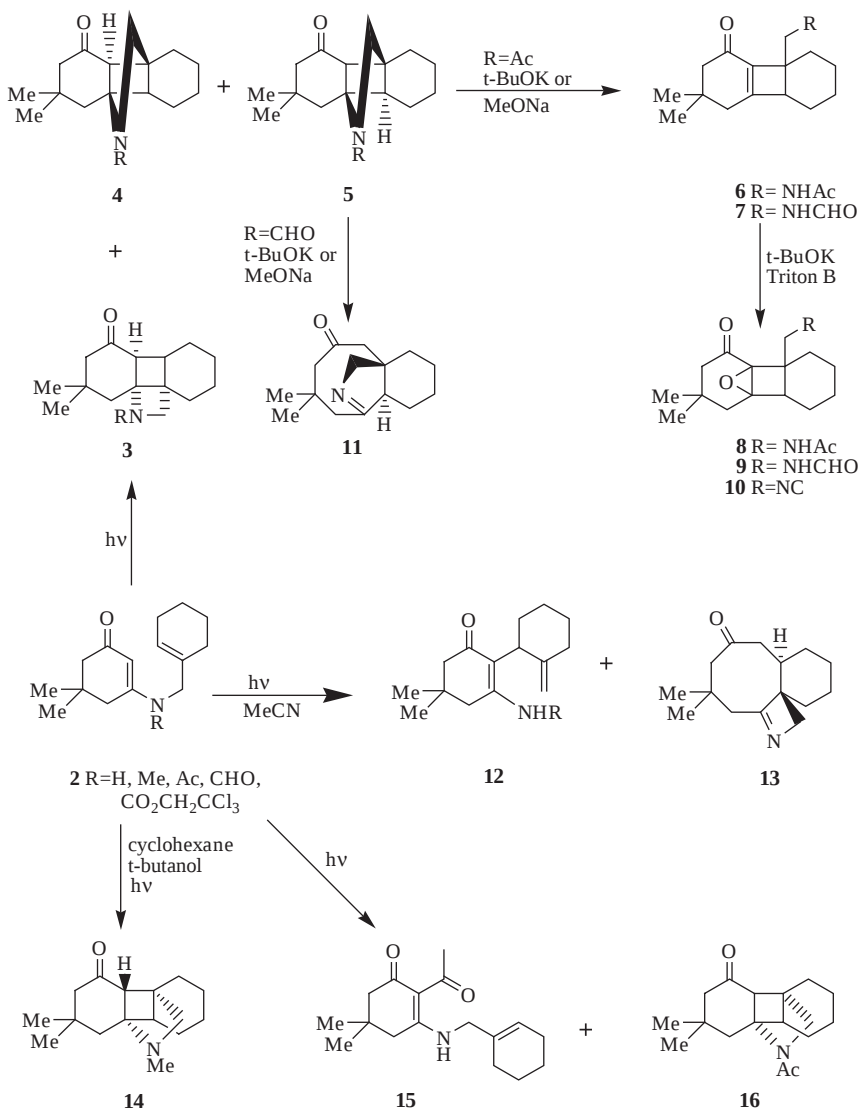


Figure 1 Arrows directed to the most reactive centers of dimedone (**1**).

a fused pyrrole ring, as it will be shown latter, to give **8** and **9**, respectively (87JOC2346). Treatment of **9** with MsCl/Py gave isocyanide **10** (87JOC2346) (Scheme 1).

Compounds **3** and **13** represented fused four-membered heterocycles, that have been formed by the photochemical irradiation of **2** (R = H) to give **12**, *via* a photo-aza-Claisen rearrangement, in addition to the four-membered ring **13** in a very poor yield. The formation of which has been



Scheme 1

explained to take place from **2** via a [2+2] photoadduct followed by a retro-Mannich fragmentation (89JOC4165).

3. DIMEDONE-ANNULATED FIVE-MEMBERED HETEROCYCLES WITH ONE HETEROATOM

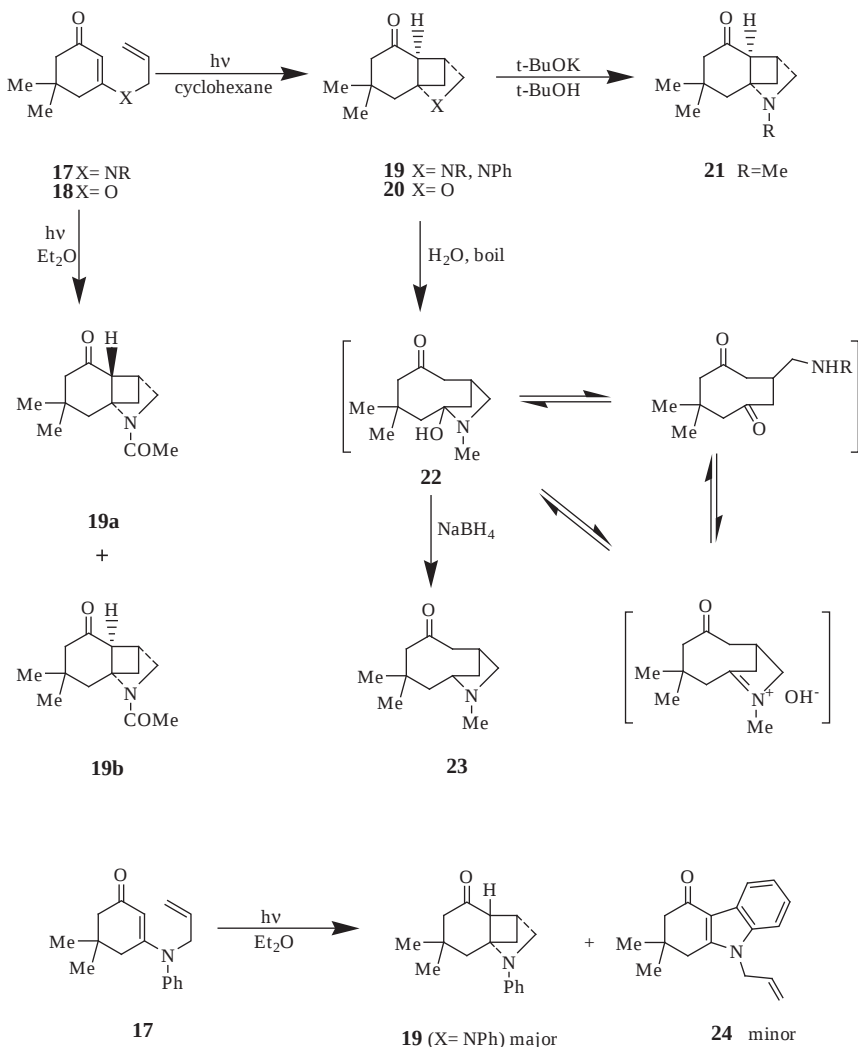
There are three classes of compounds that can be categorized under this title.

3.1 Annulation with pyrrole (synthesis of indoles and carbazoles)

There are two main approaches for constructing indole rings from **1**. Starting either with enamines and introducing the two carbons on C-2 and then amination at C-3 followed by cyclization. Photolysis of enamine **2** gave, depending on the substituent R, a variety of products containing the tetrahydropyrrole ring fused with a cyclobutane and a cyclohexane ring. Thus, irradiation of **2** (R = Me) gave **4** (R = Me) and the “crossed” [2+2] cycloadduct **14** (89JOC4165). In contrast, irradiation of the *N*-acetyl **2** (R = Ac) resulted in an acyl migration to form **15** as a minor product and azabicyclo[2.1.1]hexane **16** as a major one (79JOC1380). Reinvestigation of the irradiation of **2** (R = Ac) led to the isolation of **5** in addition to less amounts of **4** and **3**, whose structures were proven by X-ray analysis; **15** was not detected (79JOC1380). Similarly, photolysis of **2** (R = CHO) gave **3**, **4**, and **5**, whereas **2** (R = CO₂CH₂CCl₃) gave **5** as a major product. Ring expansion of **5** (R = CHO) and **5** (R = Ac) with or *t*-BuOK MeONa gave **11** and **6**, respectively (87JOC2346).

Photoirradiation of 3-allylamino and 3-allyloxy-5,5-dimethylcyclohex-2-en-1-one **17** and **18** in cyclohexane generated 2-aza and 2-oxabicyclo[2.1.1]hexanes **19** and **20**, respectively (71MI1167, 75JOC2702). Epimerization of **19** (R = Me) with *t*-BuOK gave **21**. Ring enlargement of **19** in boiling water afforded **22**, existed in equilibrium with its open form, whose reduction with sodium borohydride gave **23** (72TL1977, 75JOC2702). Photoirradiation of the ethereal solution of **17** (X = NCOMe) afforded two epimers **19a** and **19b**. Similar irradiation of **17** (X = NPh) afforded in addition to the major product **19** (X = NPh), carbazole **24** as a minor product (75JOC2702) (Scheme 2).

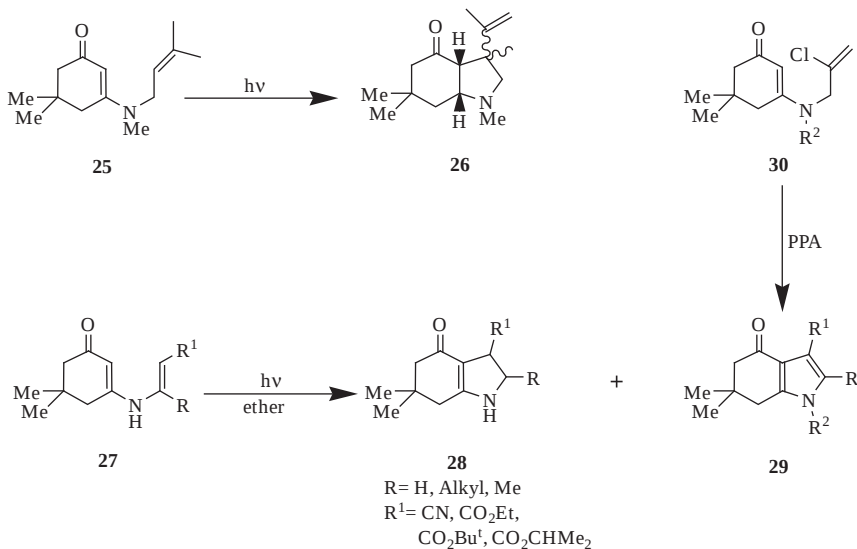
Photoirradiation of *N*-allyl enamine **25** afforded perhydro indole **26** (76JOC1277). Irradiation of an ethereal solution of **27** (R = CO₂CH(CH₃)₂, R¹ = H) gave the tetra- **29** and hexa-hydroindolones **28**, whereas its analog with other substituents (R = CO₂Et, CN, R¹ = Me) afforded only the respective tetrahydroindolone **29** (87JOC5395). The 3-methyltetrahydroindole **29** (R = H, R² = Me) can be obtained by ring closure of the



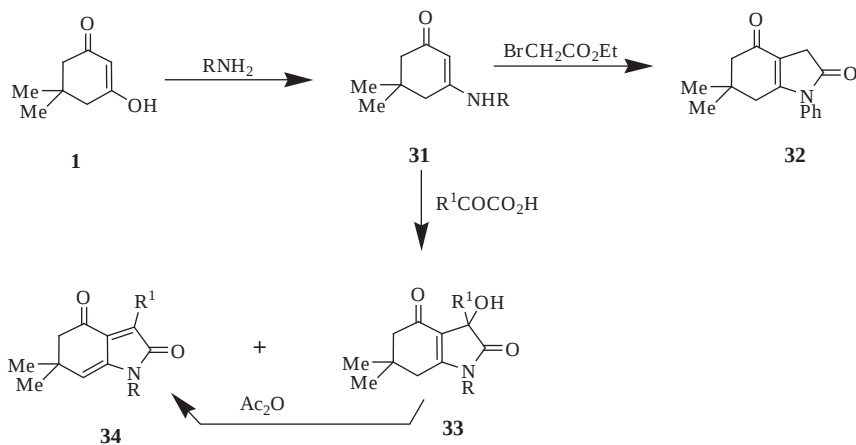
Scheme 2

chloroallyl enamine **30** upon treatment with polyphosphoric acid (75JCS(P1)1446) (Scheme 3).

Condensation of enaminone **31** ($R = \text{Ph}$) with ethyl bromoacetate gave hexahydroindolone **32** (91MI197), whereas with pyruvic acid gave the indole derivatives **33** ($R^1 = \text{Me}$) and **34** ($R^1 = \text{Me}$) as the major and minor products, respectively. The two diastereoisomers of **33** ($R = 2,3$ -dichlorophenyl) were separated, when 2,3-dichlorophenyl-enamine **31** was used (85JCR(S)244) whose dehydration with acetic anhydride



Scheme 3



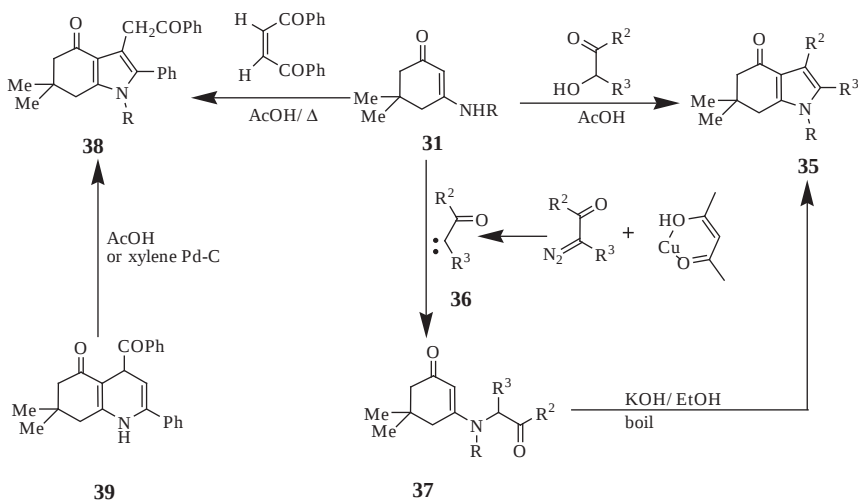
Scheme 4

afforded **34** (Scheme 4). Reaction of phenylglyoxalic acid with enamine **31** ($R = \text{Ph}$) gave indole **33** ($R = R^1 = \text{Ph}$) in addition to 3,3,6,6-tetramethyl-9,10-diphenyloctahydroacridine-1,8-dione, whereas similar reaction with 2-oxoglutaric acid afforded indole **34** ($R = \text{Ph}$, $R^1 = \text{CH}_2\text{CH}_2\text{CO}_2\text{H}$) with a trace of 3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8,9,10-decahydroacridine-1,8-dione (85JCR(S)244).

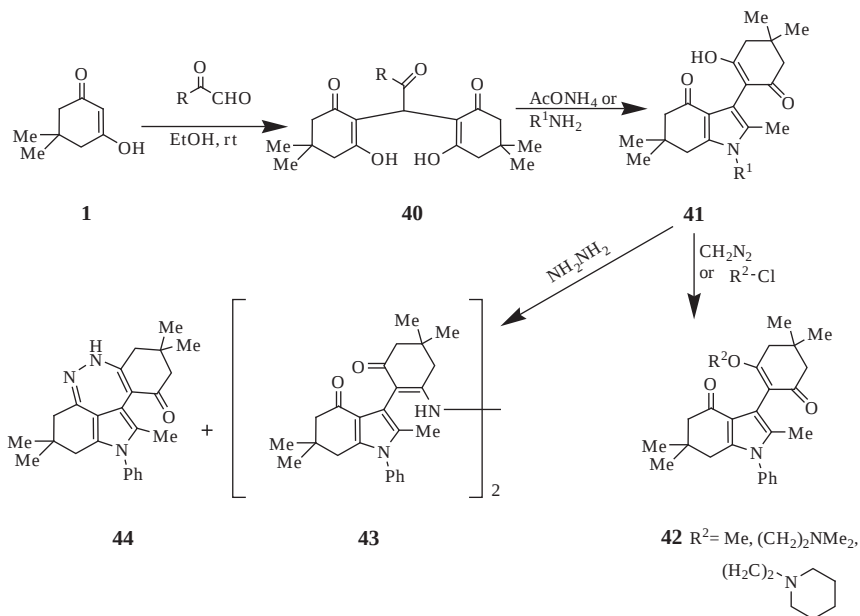
4-Benzoyl-1-phenyl-5-methoxycarbonyl-2,3-dihydro-pyrrole-2,3-dione was reacted with 5,5-dimethyl-3-*p*-methoxyphenylamino-2-cyclohexen-1-one in boiling benzene to afford 6,6-dimethyl-1-*p*-methoxyphenyl-2,4-dioxo-2,3,4,5,6,7-hexahydro-1H-indole-3-spiro-2-(3-benzoyl-5-oxo-4-phenyl-amino-2,5-dihydrofuran) in high yield. The reaction proceeded by the enamine addition to the 2-carbonyl group with ring opening, followed by double cyclization (06RJOC772).

When the enamionone **31** ($R = H$) was reacted with copper(II)-stabilized keto carbenes **36**, derived from the reaction of the respective diazo-ketones and copper(II) acetylacetonate, it afforded the uncyclized *N*-alkylated products **37** that were cyclized with potassium hydroxide in boiling ethanol to give the indoles **35** (88JOC2084), that also obtained from the condensation of **31** with α -hydroxyketones (71AP73). Similarly, *N*-methyl-enamionone **31** ($R = Me$) gave tetrahydroindole **35** ($R = Me$) (88JOC2084). Reaction of enamine **31** with dibenzoyl ethylene (DBE) in boiling acetic acid afforded tetrahydroindoles **38** (76CPB1160), which were also obtained when 5-oxotetrahydroquinoline **39** was heated in acetic acid or xylene in the presence of Pd-C (76CPB1160) (Scheme 5).

Condensation of **1** with glyoxal derivatives or 1,3-dichloroacetone gave the *bis*(dimedonyl)methane **40** whose fusion with an equimolar amount of ammonium acetate or heating with primary amines in chlorobenzene gave 4,5,6,7-tetrahydroindole **41** (89IJC(B)326). Reaction of **41** ($R^1 = Ph$) with diazomethane or amino-alkylchloride afforded ethers **42**, and with hydrazine gave the disubstituted hydrazine **43** as the major product and the indole derivative **44** as a minor one (89IJC(B)326) (Scheme 6).



Scheme 5



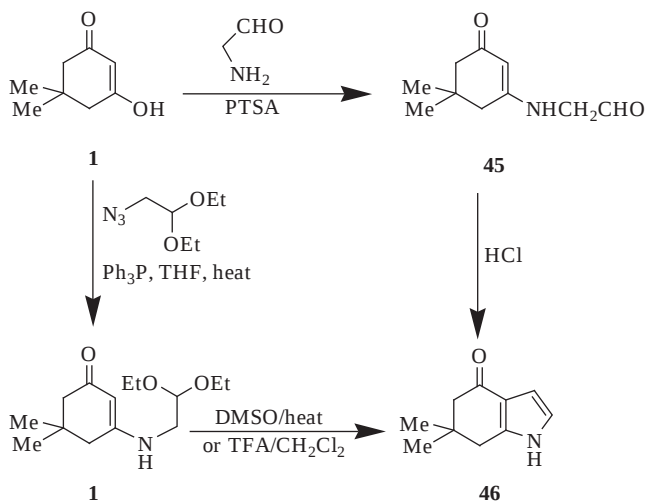
Scheme 6

The indole **46** was obtained by reaction of **1** with aminoacetaldehyde in the presence of *p*-toluene sulfonic acid to give the enamine intermediate **45**, which subsequently cyclized with hydrochloric acid. An increase in acid concentration led to the formation of dimers, while less concentrated acid gave no products (33IJCS663) (Scheme 7). The condensation of **1** with 2-azido-1,1-diethoxyethane followed by cyclization gave indolone **46** (06TL2151) (Scheme 7).

2-Amino-2-deoxy-D-glucose (**47**) and **1** produced 2-deoxy-2-(5,5-dimethyl-3-oxo-cyclohex-1-en-1-ylamino)-D-glucose (**48**), which was cyclized to 2-(D-arabino-1,2,3,4-tetrahydroxybutyl)-6,6-dimethyl-1,5,6,7-tetrahydroindol-4-one (**49**) (66QS471, 74JCS(P1)1237). Acetylation of the later gave **50** and its periodate oxidation gave aldehyde **51**, whose oxidation with silver oxide gave indole-2-carboxylic acid **52** (66QS471).

(D-Galactopentitol-1-yl)indolone **53** was obtained from reaction of 2-(benzylamino)-2-deoxy-D-glycero-L-gluco-heptose with **1**. Its kinetically controlled dehydration catalyzed by acid gave the furanosyl C-nucleoside **54**, whereas under thermodynamically controlled conditions, a mixture of the α - and β -D-lyxopyranosyls was obtained (83CAR255). The above reaction has been extended to other analogues and derivatives of **53** (80CAR17) (Scheme 8).

Functionalization of dimedone at C-2 provided derivatives suitable for constructing the pyrrole ring. Thus, tetrahydroindole **56** was obtained

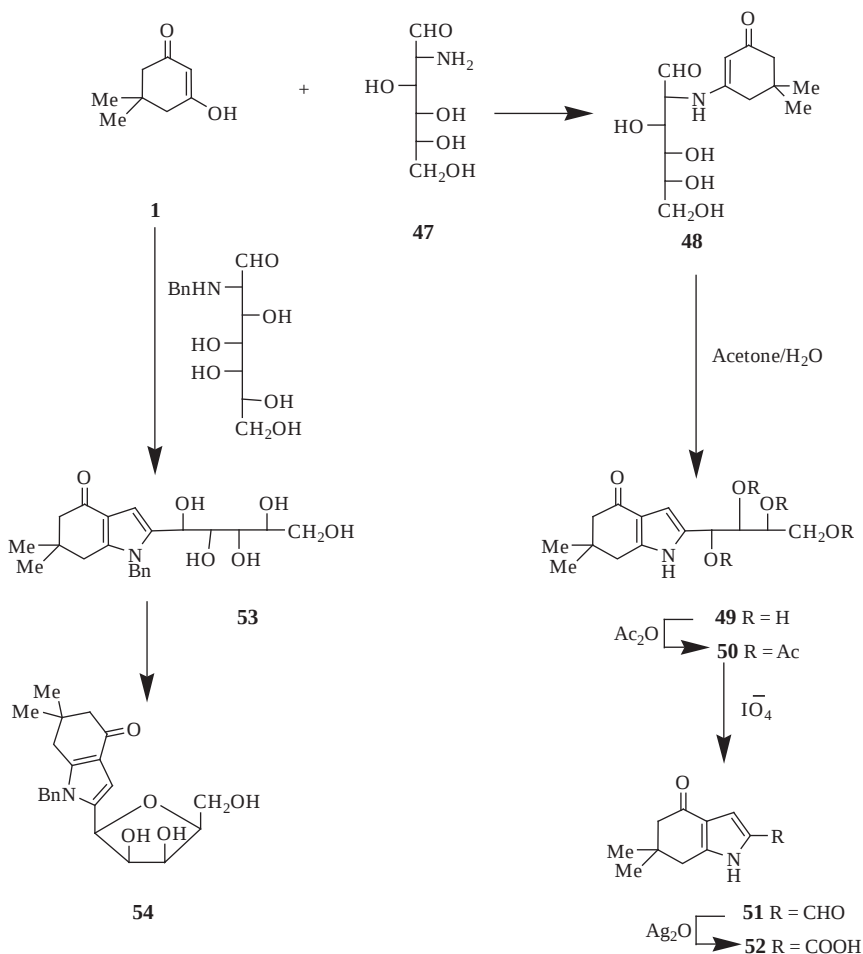


Scheme 7

from 2-allyl dimedone **55** by reaction with benzylamine followed by iodination in the presence of triethylamine and subsequent deiodination with DBU in toluene (99T10915) (Scheme 9).

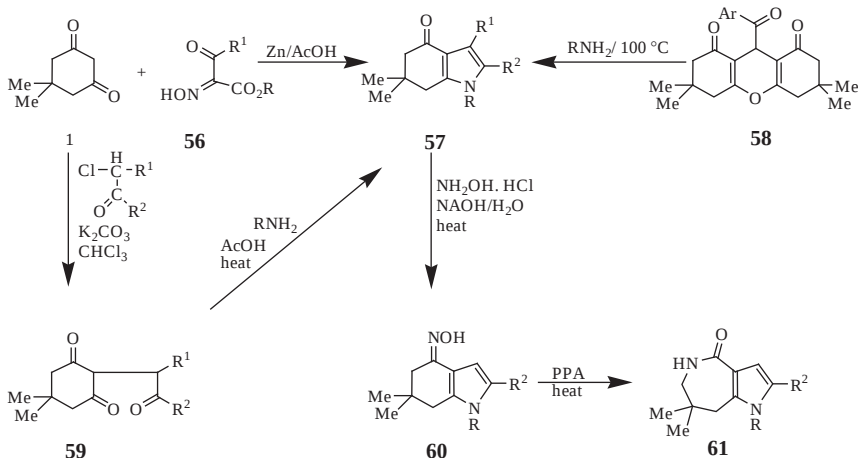
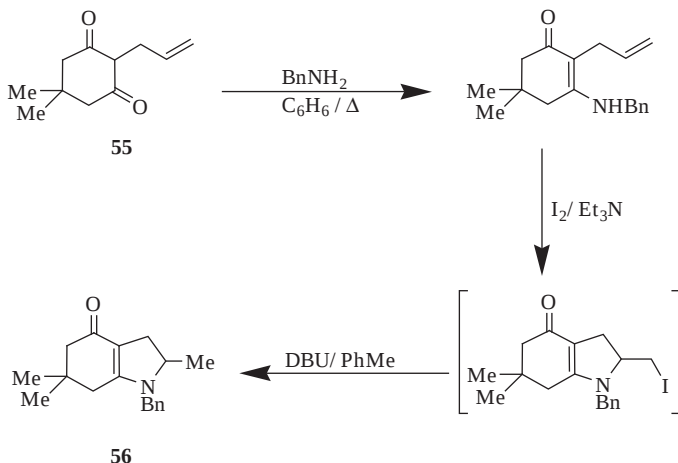
Condensation of **1** with functionalized oximes derived from acetoacetic esters under Knorr pyrrole reaction conditions afforded tetrahydro-1H-indoles **57**, which have been used as precursors for porphyrins bearing six-membered exocyclic rings (92JOC4809, 05T11628). The tetrahydroindole skeleton could also be constructed upon heating 9-aryloctahydroxanthene-1,8-dione **58** with ammonia or methyl amine (87CHE89). Alkylation of **1** with 3,5,5-tetrachloropentan-2-one afforded 2-alkyl **59**, which underwent cyclization with primary amines to give tetrahydroindole **57** ($R^1 = \text{CH}_2\text{CCl}_3$, $R^2 = \text{Me}$). Acid hydrolysis gave indolylacetic acid **57** ($R^1 = \text{CH}_2\text{COOH}$, $R^2 = \text{Me}$) (01RCB1259). Oximation of **57** gave **60** whose Beckmann rearrangement yielded azepinones **61** (06BMC4007) (Scheme 10).

Alkylation of dimedone with phenacyl bromide in the presence of potassium carbonate afforded triketone **62**, which upon further alkylation at the same site with MeI in the presence of DBU gave **63**. Subsequent treatment of **63** with liquid ammonia afforded hydroxypyrroline **64** whose dehydration with *p*-toluenesulfonic acid in boiling benzene, hot acetic acid, dry HCl in EtOH and 4A molecular sieves or Florisil in benzene afforded indolizine **65** rather than the expected **66**. Alternatively, **65** was obtained upon heating **64** to its melting point or by treatment of **63** with ammonium acetate in boiling acetic acid. Different mechanisms were proposed for this rearrangement (88JCS(P1)161) (Scheme 11).



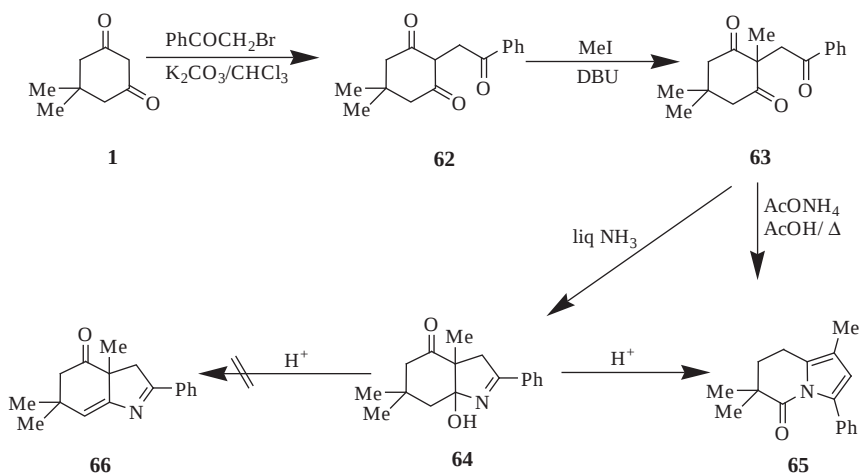
Scheme 8

The carbazole ring can be formed either by introducing an *N*-aryl amine or hydrazine functionalities in **1** and subsequent cyclization. Reaction of **1** with aryl hydroxylamines in benzene gave adducts **67** in low yield, but the yield has been improved by the addition of a small amount of ascorbic acid. Cyclization occurred by the acetylation of its hydroxyl group to give **68** whose acid catalyzed elimination of the acetoxy group and then hydrogen rearrangement gave 1,2,3,4-tetrahydro-4-oxo-carbazole **69** ($R^1 = R^2 = \text{H}$). Carbazole **69** was directly obtained from **67** under strongly acidic conditions (73TL4533), or by catalytic cyclization of bromo-*N*-substituted amines **70** with a triphenylphosphine–palladium acetate complex in DMF (80JOC2938).

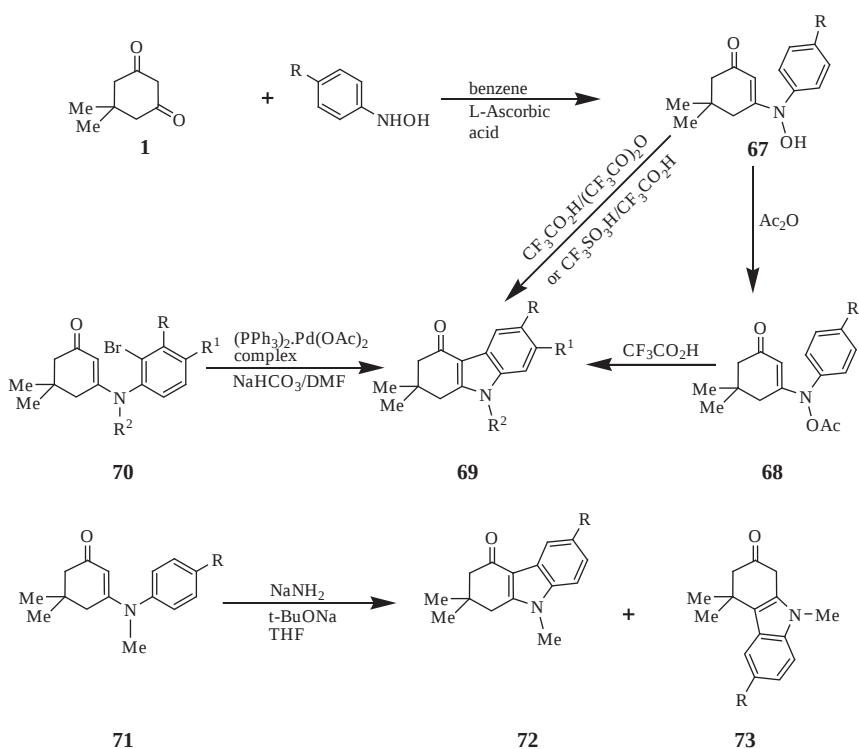


The complex base NaNH_2 -*t*-BuONa allowed the cyclization of **71** to **72** and **73** (94T11903) (Scheme 12).

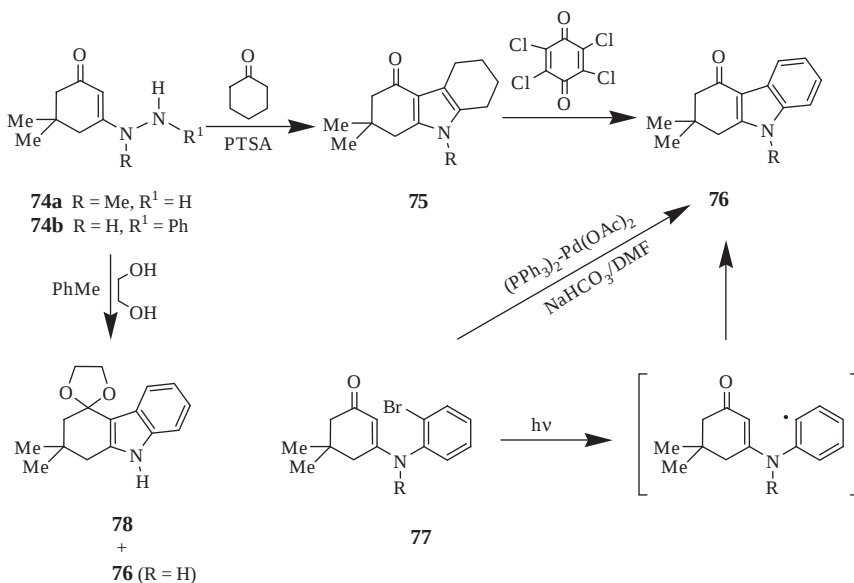
Fischer-type reaction of enhydrazine **74a** with cyclohexanone in the presence of *p*-toluenesulfonic acid afforded octahydrocarbazole **75** ($\text{R} = \text{Me}$), which can be oxidized with chloranil to tetrahydrocarbazole **76** ($\text{R} = \text{Me}$) (70CB1767). The carbazole **76** ($\text{R} = \text{H}$, Et) were obtained from the enamines **77** ($\text{R} = \text{H}$, Et) by photolysis in dioxane-acetonitrile containing triethylamine or by treatment with triphenylphosphine-palladium acetate complex (2:1) in DMF in the presence of NaHCO_3



Scheme 11



Scheme 12

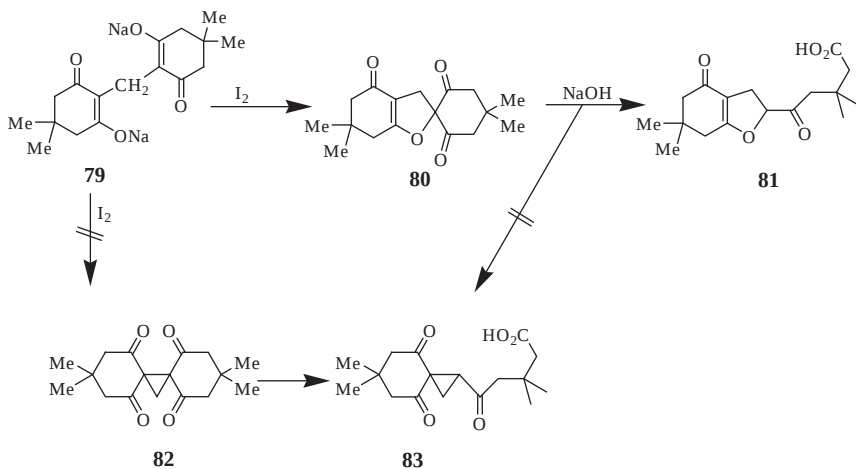


Scheme 13

(78CC766, 80JOC2938). The tetrahydrocarbazole **76** (R = H) was also obtained when the **74b** (R = H, R¹ = Ph) was treated with *p*-toluenesulfonic acid in toluene. When the latter reaction was carried out in ethylene glycol-toluene, it gave **76** (R = H) and **78** (73JOC2729), (Scheme 13).

3.2 Annulation with furan (synthesis of benzofurans)

The synthesis of this ring has been mainly based on C-alkylation at C-2 with a suitable functional group to add the two carbons of the furan ring. Reaction of the disodium salt of *bis*(dimedonyl)methane **79** with iodine was reported to give cyclopropane **82** (25BSF187, 27MI129). Later, the structure of **82** was revised to isomeric dihydrofuran **80** based on its spectral properties. Consequently, cleavage of the product with alkali was also revised to yield the benzofuran **81** instead of the formerly reported **83**. The formation of **80** rather than **82** may be due to the greater stability of **1** in the enol rather than in the keto form (65JOC1251) (Scheme 14). The attempted bromination of **1** with Dess–Martin periodinane (DMP) in the presence of triethyl ammonium bromide, methanol, and chloroform gave **80**. Its formation was due to the presence of a dimedone-formaldehyde adduct *in situ*; formaldehyde resulted from the oxidation of methanol during the reaction (07SC275).

**Scheme 14**

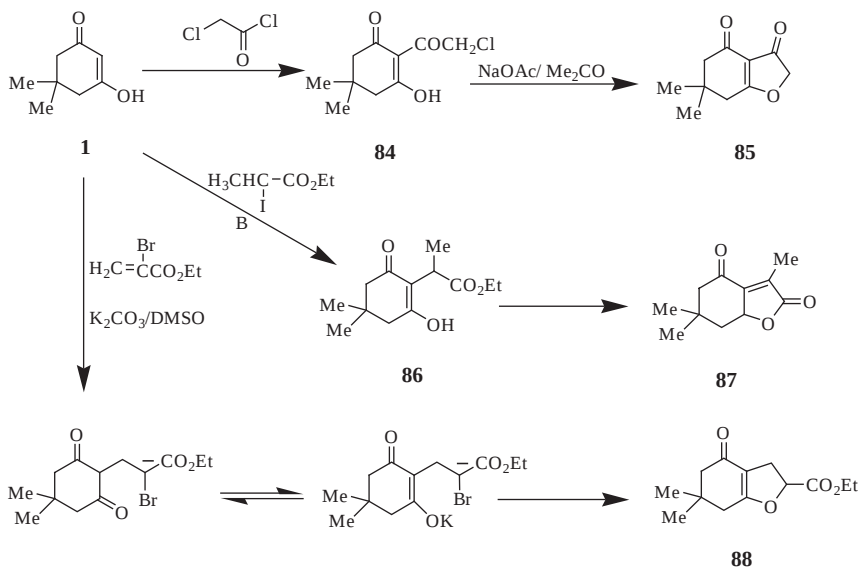
Hexahydro-3,4-dioxobenzo[*b*]furan **85** was obtained by intramolecular nucleophilic heterocyclization of 2-chloroacetyl-5,5-dimethylcyclohexane-1,3-dione **84** (85KGS1130). Cyclization was also achieved in the presence of sodium nitrite, sodium methoxide, sodium acetate, or silver acetate. The nucleophiles acted as basic deprotonating agents and did not interact with the chloroacetyl group (89ZOR1882).

C-Alkylation of **1** with ethyl 2-iodopropionate gave **86** whose lactonization afforded 3,6,6-trimethylbenzofuran-2-one **87** (84CPB2249). While **1** with ethyl α -bromoacrylate in the presence of potassium carbonate in DMSO gave benzofuran **88**. The reaction is due to a Michael addition of the carbanion obtained from **1** to the activated double bond of the acrylate ester to give an intermediate C-alkylated adduct that spontaneously cyclized to **88** (86ZOR2262) (Scheme 15).

Reaction of **1** with ethylene glycol **89** (R = H) in the presence of a dichlorotris(triphenylphosphine)ruthenium catalyst gave a mixture of benzofuran **90** (R = H), 3,3-dimethylcyclohexanone, 3,3-dimethylcyclohexanol, and 3,3-dimethylcyclohexanone ethylene ketal, while **1** with propan-1,2-diol **89** (R = Me) afforded a mixture of the two isomeric benzofurans **90** (R = Me) and **91** (75JOC2402) (Scheme 16).

Condensation of dimedone with D-ribose or glucose in the presence of Sc(OTf)₃ in water gave acyclic C-alditolyl analogue **92**. The use of small amount of catalyst in the reaction with glucose gave cyclic C-glycosyl analog **92a** (07CAR913) (Scheme 16).

The ethyl ether of **1** was obtained by reaction of **1** with ethanol in boiling benzene in the presence of *p*-toluenesulfonic acid. A Stork–Danheiser alkylation of which with lithium diisopropylamide and methyl iodide and then with ethyl bromoacetate gave **93**. Reduction of **93** with

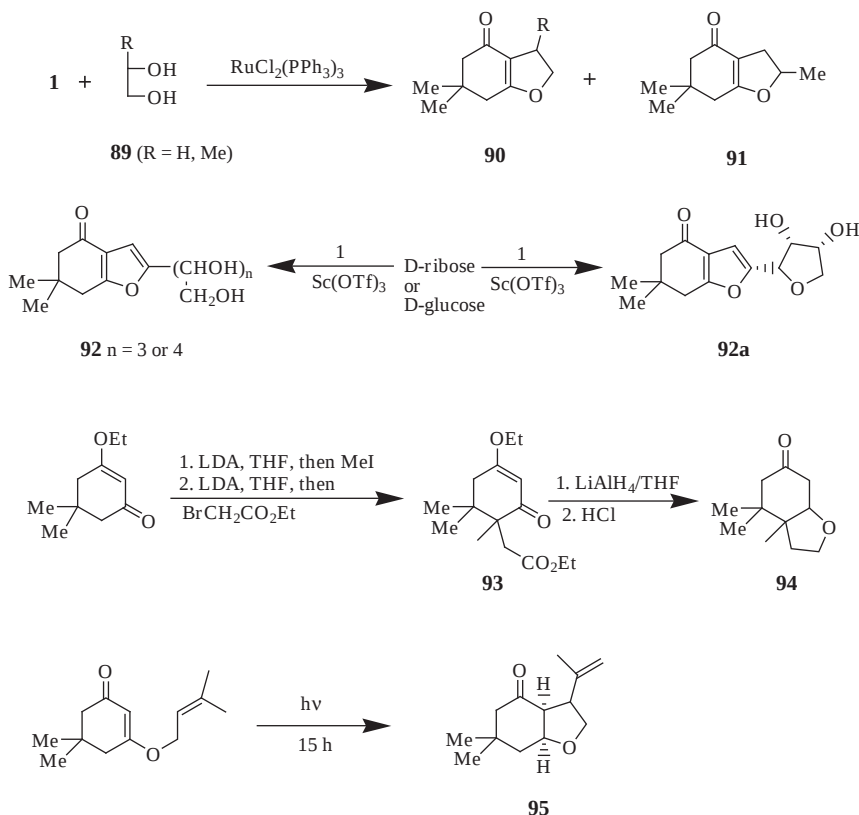


lithium aluminum hydride afforded an unstable diol that was immediately reacted with hydrochloric acid to give **94**; a useful precursor for the total synthesis of the natural product pygaeocin (05SL417).

Photocyclization of 5,5-dimethyl-3-(3-methylbut-2-enyloxy)-cyclohex-2-en-1-one by irradiation with a 350-W high-pressure mercury lamp in a Pyrex tube resulted in the formation of perhydrobenzofuran **95** (76JOC1277). The allyl derivative **18** gave **20** upon photolysis (75JOC2702) (Scheme 16).

Radical oxidative cyclization of **1** with acyclic alkenes using ceric ammonium nitrate (CAN) or $\text{Mn}(\text{OAc})_3$ -mediated reactions gave hexahydrobenzo[*b*]furans **96** (95JCS(P1)187, 01H171, 01SC3871, 05MI579). Although, both reagents were very efficient, the CAN-mediated reaction was reported to give a higher yield compared to $\text{Mn}(\text{OAc})_3$ (95JCS(P1)187). In another report $\text{Mn}(\text{OAc})_3$ was slightly more efficient than CAN (01H171). Regio- and stereoselective synthesis of hexahydrobenzo[*b*]furan **97** and not **97a** was accomplished by oxidative [3+2] cycloaddition of **1** and cinnamate ester in the presence of CAN and NaHCO_3 (96T2193).

Oxidative radical-mediated cycloaddition of **1** with vinylsulfides was carried out by using silver carbonate/celite or CAN in acetonitrile to give hexahydrobenzo[*b*]furan **98** (97TL5671, 03S1977). Subsequent oxidation of **98** with periodate followed by syn-elimination using active alumina afforded tetrahydrobenzo[*b*]furan **99** (97TL5671). The *cis*-cycloadduct **100** was also obtained by using CAN in THF (03S1977).

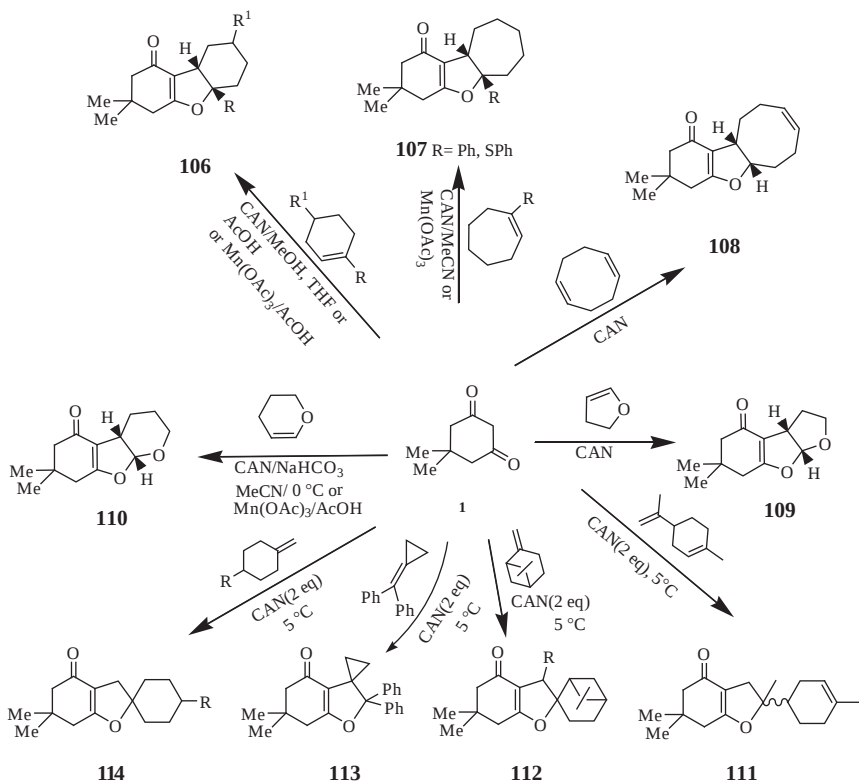


Scheme 16

Oxidative cycloaddition of **1** with cyclopentene or cyclopentadiene in the presence of CAN in THF afforded benzofuran **101** and **102** ($\text{X} = \text{CH}_2$), respectively (96SC4531, 00TL1913), and with cyclohexadiene it gave the hexahydro derivatives **101** ($\text{X} = \text{CH}_2\text{--CH}_2$) (95JCS(P1)187, 96SC4531) (Scheme 17). Also, CAN mediated the oxidative addition of 2,3-dimethyl-1,3-butadiene to **1** to give **103** (00IJC(B)352, 00T8845). The reaction of **1** with 1,4-dihydroxybut-2-ene dicarbonate in the presence of Pd-catalysts gave **104**. Similarly, cyclopentene and hexene diacetate gave **105** (88S60, 95JCS(P1)187, 96SC4531, 99SL1925, 05EJO1568, 06S865).

The decahydrodibenzofuran derivatives **106** having the *cis*-configuration were obtained by oxidative addition of dimedone to cyclic alkenes mediated by either CAN, in methanol, acetic acid or THF, or by $\text{Mn}(\text{OAc})_3$ in acetic acid (95JCS(P1)187, 96JCS(P1)1487, 01H171, 03S1977). Similarly, **1** with cycloheptenes afforded cyclohepta[*b*]benzofuran **107** (01H171, 03S1977), and with 1,5-cyclooctadiene gave cycloocta[*b*]benzofuran **108** in low yield; a *trans*-annular addition of such species was



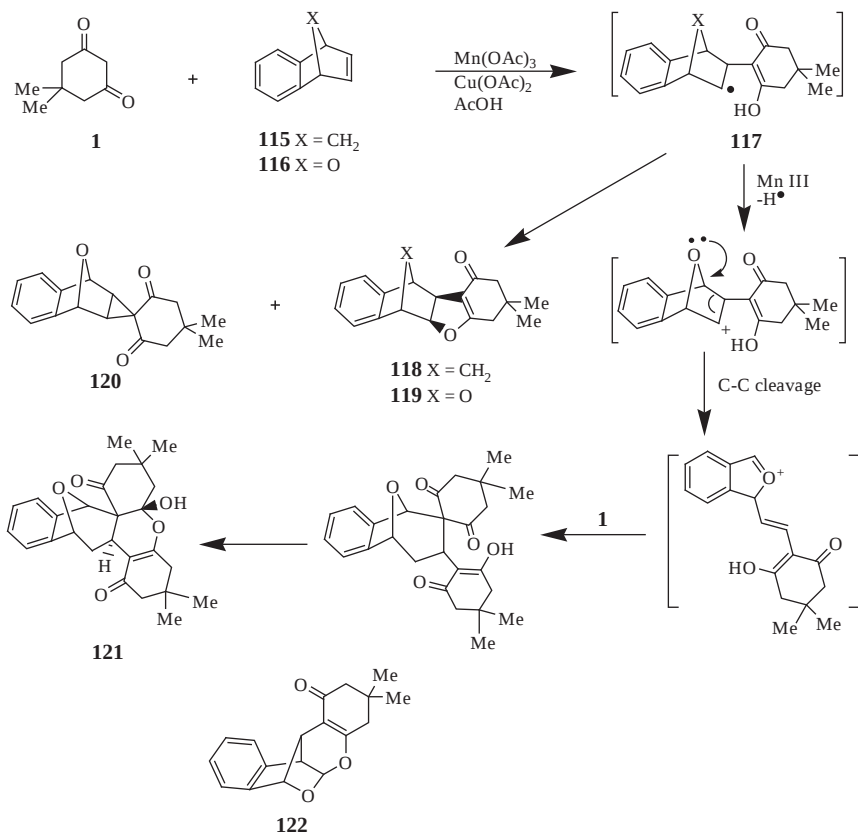


Scheme 18

disfavored due to steric factors (96SC4531). The cycloaddition of **1** with dihydrofuran or dihydropyran was catalyzed by either $\text{CAN}/\text{NaHCO}_3$ in acetonitrile at 0°C or by $\text{Mn}(\text{OAc})_3/\text{AcOH}$ to give furo and pyrano[2,3-*b*]benzofurans **109** and **110**, respectively (93T7557, 96T12495).

The addition of dimedone to limonene mediated with CAN was expected to proceed by tandem radical additions to the two double bonds but the only isolated product was dihydrofuran **111** (96SC4531). The oxidative addition of **1** can also occur similarly to exocyclic alkenes to afford spiroannulated dihydrofurans **112**–**114** in moderate to good yields, whereas $\text{Mn}(\text{OAc})_3$ mediated addition gave low yields (95SC3981, 06S609, 06S2335) (Scheme 18).

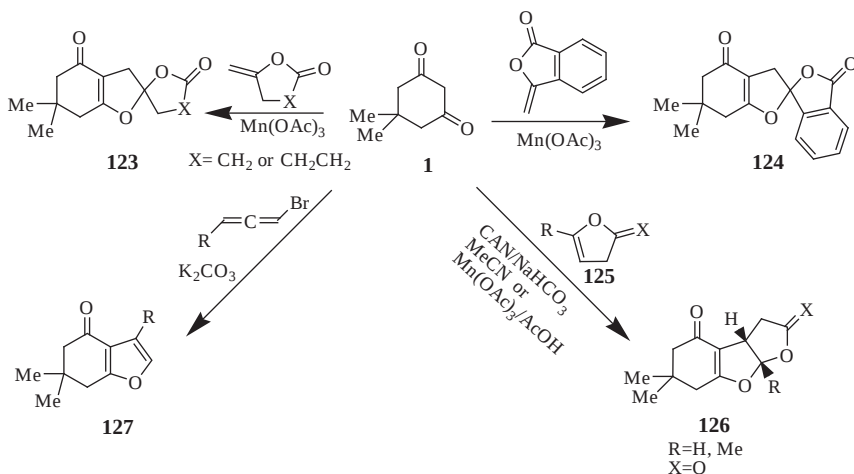
Benzonorbornadiene (**115**) with **1** in the presence of $\text{Mn}(\text{OAc})_3$ or $\text{Cu}(\text{OAc})_2$ gave **118**, whereas its oxa analog **116** gave **119**, **120**, and **121** (05TL6227, 07JOC3353) (Scheme 19); this difference was attributed to the bridging oxygen. It was assumed that the addition of **1** to **116** resulted in the formation of radical **117** where the enol functionality in dimedone can interact with the bridge oxygen forming a hydrogen bonding that



Scheme 19

resulted in a restricted conformation that under the oxidative condition gave the cyclopropane product **120**. Further oxidation of radical **117** gave a cation whose fragmentation relieve a ring strain to give a stable oxonium ion that added a molecule of **1** to form **121**. In the absence of cupric acetate a different product **122** was obtained in addition to the major **121** (07JOC3353).

Exocyclic enolates were also oxidatively added to **1** in the presence of Mn(OAc)₃ in acetic acid to give spirolactones **123** (X = CH₂) and **124** in good yield, whereas **123** (X = CH₂-CH₂) was obtained in low yield as a result of its sensitivity to acid (93T7547). Oxidative cycloaddition of **1** with dihydrofuranone **125** was promoted either by CAN and excess of NaHCO₃ or Mn(OAc)₃ in acetic acid to give **126** (93T7557, 96T12495). Monoaryl bromoallenes with **1** afforded substituted furans **127** (06OL5061) (Scheme 20).

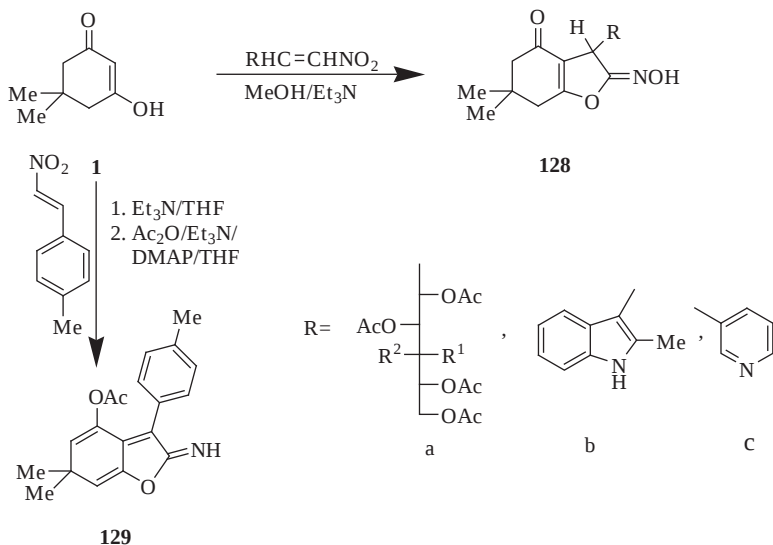


Scheme 20

Three-component condensation reactions of cyclic 1,3-diketones, 4-nitrobenzaldehyde, and alkyl or aryl isocyanides in water afforded the corresponding tetrahydrobenzofuran derivatives (04M441).

Reaction of **1** with an equimolar amount of 3,4,5,6,7-penta-*O*-acetyl-1,2-dideoxy-1-nitrohept-1-enitol in boiling methanol containing a catalytic amount of triethylamine gave 3,5,6,7-tetrahydro-2-hydroxyimino-3-(penta-acetoxy-alditol-1-yl)benzofuran-2H-one **128a** as the main product (85JCS(P1)2695). The furanone oxime **128b** ($\text{R} = 2\text{-methylindol-3-yl}$) was obtained by the formation of a Michael adduct from **1** and 2-methyl-3-(2-nitrovinyl)indole in the presence of sodium methoxide followed by heterocyclization (01RJOC1505). The X-ray analysis of **128c** showed a planar five-membered hetero-ring with the pyridine ring almost perpendicular to it while the cyclohexane ring has a sofa conformation (04RJGC1394) (Scheme 21). A domino process took place upon reaction of **1** and a nitro-olefin followed by acetylation to give **129** (05OL1211) (Scheme 21).

2-Nitro-propene or 2-butene and **1** gave ketofuran adduct **130** and **131** ($\text{R} = \text{Me}$), respectively (75CC726, 80JOC2945). A stereoisomeric mixture of hydroxyimino dihydrofuran **132** was obtained in the presence of KF. Reaction of **1** with 1-nitro-1-(phenylthio)-propene in the presence of KF afforded a diastereomeric mixture of dihydrofuran **133** along with 2-phenylthiofuran **133a** (80JOC2945). Desulfenylation of **133** afforded 3-methyltetrahydrobenzofuran **131** ($\text{R} = \text{H}$) (80JOC2945), that was obtained when **1** was treated with diethylprop-2-ynylsulfonium bromide (93JOC3960, 94JOC5970). 1-Bromo-2-(*p*-chlorophenyl)-1-nitroethene with **1** gave 3-(*p*-chlorophenyl)-2-nitro-2,3,4,5,6,7-hexahydrobenzofuran-4-one **134**. The reaction involved Michael addition to form an intermediate



Scheme 21

adduct, which subsequently underwent O-alkylation (98RJOC59). Reaction of two molecules of **1** with trichloronitroethylene under basic condition at room temperature formed 2-nitrobenzofuran **135** *via* a mechanism shown in the scheme (77ZOR972) (Scheme 22).

Ethyl phenylpropiolate and **1** in the presence of tributyl phosphine gave cinnamate **136a** in only 10% yield in addition to **136** and **136b** in 13% and 7% yield, respectively. The latter was obtained due to the cyclization of **136a** *via* an intramolecular Michael addition of the enolate to the vinyl ester followed by migration of the double bond (05T2287) (Scheme 23).

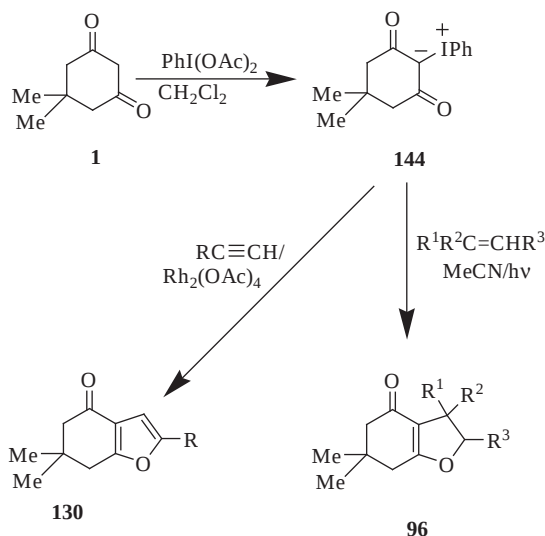
Base promoted C,O-dialkylation of **1** with 4a,6,7,8a-tetrachloro-1,4-methanenaphthalene-5,8-dione gave **137** in high yield. Similarly, 2,3-dichloro-1,4-naphthalene-5,8-dione was cyclized with **1** in moderate yield (05S1605) (Scheme 23).

Electrochemical oxidation of catechol derivatives in the presence of **1** gave **138** *via* a Michael addition of the formed quinones to **1** (04JOC2637, 06CPB959) (Scheme 23).

Copper acetate and manganese acetate-mediated radical reactions of [60]fullerene with **1** gave dihydro furan-fused fullerene **139** *via* a radical mechanism (05OBC794) (Scheme 23).

Solvent-free reaction of **1** with C60 in the presence of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ and CAN under high-speed vibration milling conditions afforded dihydrofuran-fused[60]fullerene. CAN was a better oxidant than $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ in these mechanochemical reactions (05MI1327).





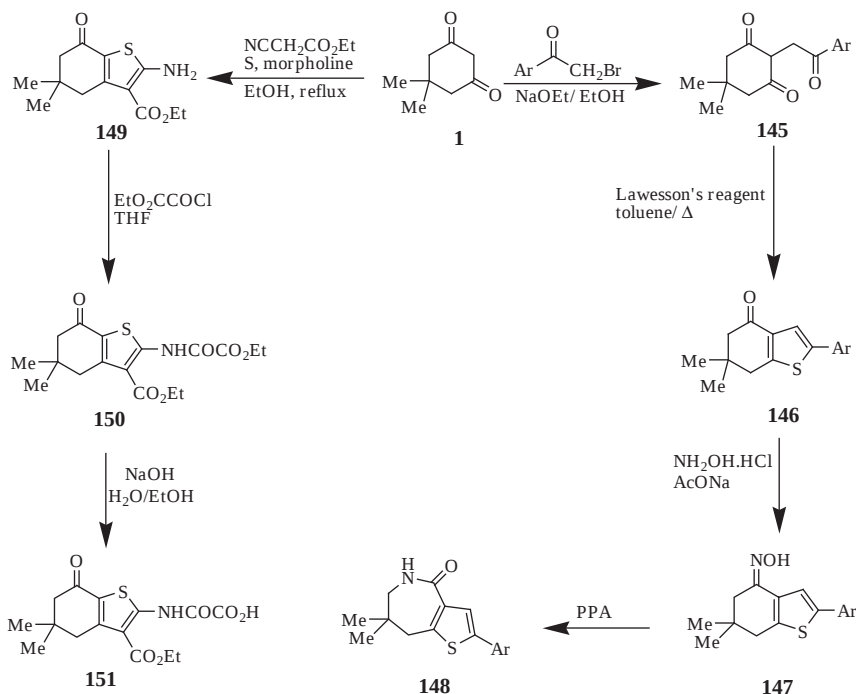
Scheme 25

Photochemical cycloaddition of ylide **144** and excess styrenes in acetonitrile exhibited high regio- and diastereoselectivity leading to one isomer of 2,3-dihydrofuran **96** in much better yield than that from a Rh-catalyzed thermal reaction (00TL9299). Alternatively, one-pot reaction of olefins with **1** at 0°C in the presence of diacetoxyiodobenzene gave **96** (03TL6729). Reaction of **144** with alkynes in the presence of a catalytic amount of $\text{Rh}_2(\text{OAc})_4$ without solvent and under an inert atmosphere at reflux proceeded through a thermal [3+2] cycloaddition to give only regioisomers **130**. The high regioselectivity can be explained by addition of the oxygen atom of the iodonium ylide exclusively onto the more substituted atom of the triple bond to afford a 2-substituted benzofuran (00TL9299) (Scheme 25).

3.3 Annulation with thiophene (synthesis of benzothiophenes)

Alkylation of **1** with phenacyl bromide derivatives in the presence of sodium ethoxide gave tricarbonyl **145**, which were cyclized to benzo[*b*]thiophenes **146** upon treatment with Lawesson's reagent (99JHC687). Tetrahydrobenzothiophenes **146** with hydroxylamine hydrochloride afforded syn/antioximes **147**, which upon treatment with PPA underwent a regiospecific ring expansion to thieno[3,2-*c*]azepinones **148** (99JHC687).

The analogue **149** was prepared from **1** with ethyl cyanoacetate and sulfur. Its reaction with ethyl oxalyl chloride gave **150** whose hydrolysis

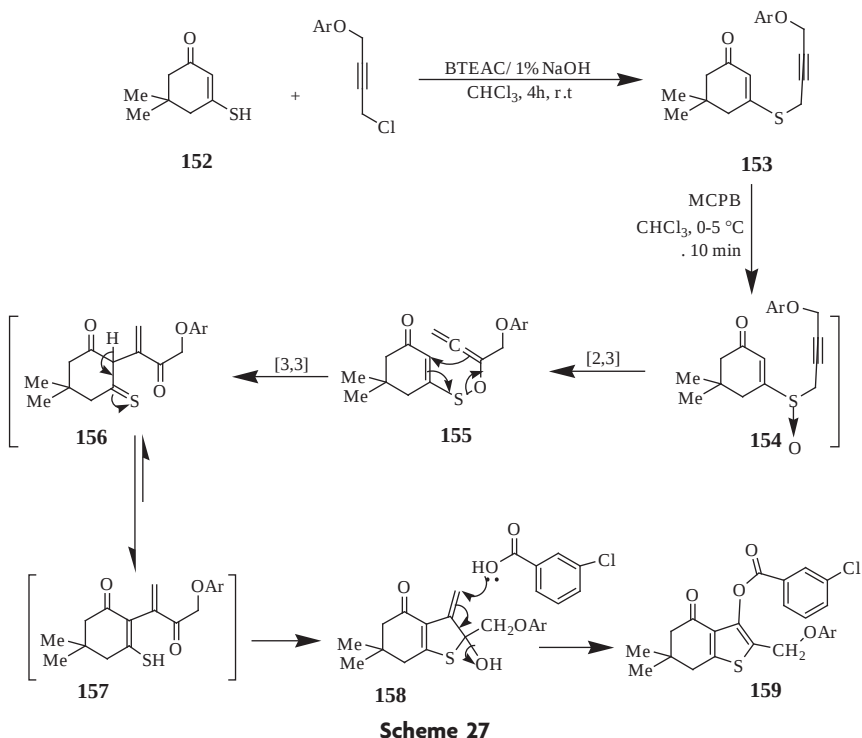


Scheme 26

gave **151**; an inhibitor of protein tyrosine phosphatase (06BMCL4002) (Scheme 26).

Phase transfer catalyzed alkylation of 5,5-dimethyl-3-mercaptocyclohex-2-en-1-one (**152**) (74ACS(B)1077) with 1-aryloxy-4-chlorobut-2-yne in chloroform and 1% aqueous NaOH in the presence of benzyltriethylammonium chloride (BTEAC) at room temperature afforded thioether **153**. Chemoselective oxidation of which with 3-chloroperoxybenzoic acid in chloroform gave **159**. The reaction was explained to proceed *via* sulfoxides **154**, which could not be isolated but underwent a [2,3] and then a [3,3] sigmatropic rearrangement to give unstable allenesulfenates **155** that tautomerized to **157** *via* **156**, and then cyclized to give the benzo[*b*]thiophene **158**. An $\text{S}_{\text{N}}2$ displacement in **158** with *m*-chlorobenzoic acid afforded **159** (02T4551) (Scheme 27).

Alkylation of the sodium salt of **152** with allyl bromide in DMSO afforded the 3-*S*-allyl **160** ($\text{R} = \text{H}$), which underwent a thio-Claisen rearrangement in the presence of *p*-toluenesulfonic acid to give 2-allyl-3-mercapto **161** ($\text{R} = \text{H}$) that cyclized partially during purification to hexahydrothiophene **162** ($\text{R} = \text{H}$). Alternatively, acetylation of **161** ($\text{R} = \text{H}$) gave **163**, which cyclized on heating in quinoline to afford **162** ($\text{R} = \text{H}$). Similarly, 2-butenyl **160** ($\text{R} = \text{Me}$) gave **161** ($\text{R} = \text{Me}$) but the



Scheme 27

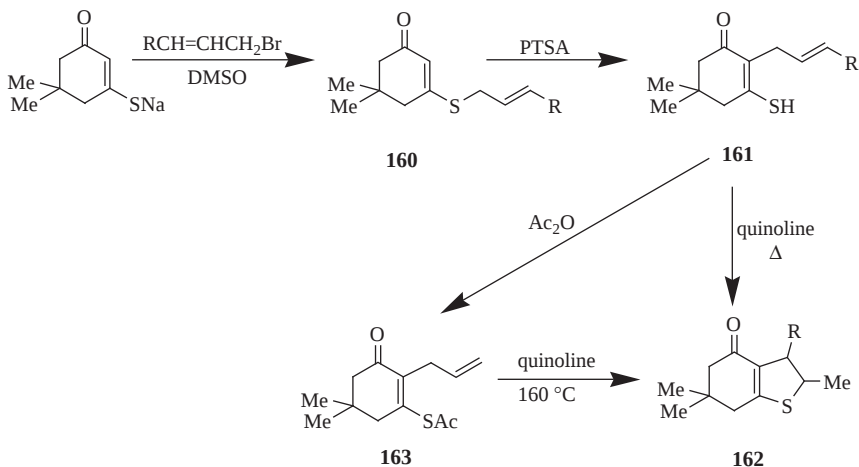
reaction was slower. Cyclization then gave **162** (R = Me) (74ACS(B)1077) (Scheme 28).

Condensation of **1** with carbon disulfide in the presence of potassium carbonate in DMF afforded dithioketene anion **164** that upon reaction with ethyl bromoacetate and methyl iodide in DMF led to the formation of 4,5,6,7-tetrahydrobenzo[*c*]thiophene **165** (95SC2449). Derivative **166** was reported in a patent (06WOP98).

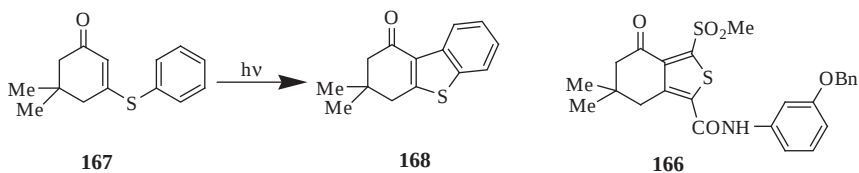
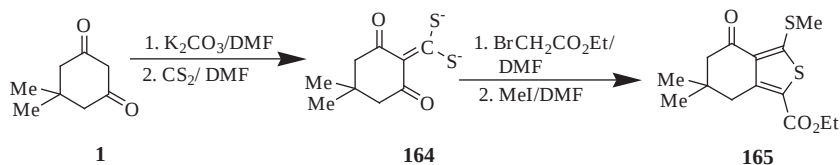
Photolysis of 5,5-dimethyl-3-phenylthio-cyclohex-2-en-1-one (**167**) afforded tetrahydrodibenzothiophene **168** in poor yield through an intramolecular cyclization-oxidation (74ACS(B)1077) (Scheme 29).

4. DIMEDONE-ANNULATED FIVE-MEMBERED HETEROCYCLES WITH TWO HETEROATOMS

There are six classes of compounds, which can be presented under this heading. These include the partially hydrogenated benzo-five-membered-heterocycles with nitrogen, oxygen or sulfur.



Scheme 28



Scheme 29

4.1 Annulation with pyrazole (synthesis of indazoles)

Two main approaches were known for the synthesis of this ring from **1**; both started with 2-acyldimedones either through their enehydrazine or ene-amine derivatives (98TL1603). 2-Acetyldimedone **169** ($\text{R} = \text{Me}$) gave, upon reaction with hydrazine, indazolone **171** ($\text{R} = \text{Me}$, $\text{R}^1 = \text{H}$) (66MI680, 72JPR31, 96AJC163, 06T11704). Indazole **171** ($\text{R} = \text{H}$) was obtained from 2-acyldimedone **169** with primary amines followed by TFA and then hydrazine hydrate (93JCSCC778, 97TL5391).

2-Formyldimedone **169** ($\text{R} = \text{H}$) with arylhydrazines gave hydrazino intermediates **170** ($\text{R} = \text{H}$, $\text{R}^1 = \text{aryl}$), which were cyclized to indazolone

172 (R = H) on heating with PPA (75JCS(P1)2438) (Scheme 30). Similarly, either 2-hydrazinopyridine or 2-hydrazinobenzimidazole with 2-acetyldimedone **169** (R = Me) afforded tetrahydroindazoles **173** and **174**, respectively (94MI738, 96CHE221). 2-Hydrazinobenzimidazole and **169** at room temperature in ethanol gave **170** whereas in refluxing 2-propanol in the presence of HCl **174** were obtained rather than **175** (96CHE221) (Scheme 30). Reaction of **1** with dimethyl formamide dimethyl acetal (DMFDMA) gave the enaminone **176** (R = H) (82JHC1355) whose reaction with hydrazine afforded the tetrahydroindazole **171** (06T11704) (Scheme 30).

Phenylhydrazine and benzaldehyde with **1** gave tetrahydro and hexahydro-indazoles **177** (Ar = Ph) and **178**, respectively (01MI24) (Scheme 30). Dimedone-phenylhydrazone **179** with aromatic and heterocyclic aldehydes gave 2,3-diaryl-4-oxo-4,5,6,7-tetrahydroindazoles **180** (R = Ph) whereas dimedone tosylhydrazone gave 3-aryl-4-oxo-4,5,6,7-tetrahydroindazoles **180** (R = H) (05CHE1398, 05CHE1405). Treatment of diketoester **181** with hydrazine hydrate gave pyrazolo[4,5-*f*]indazole **182** (92JHC1375). Examples of **173** were tested as inhibitors against PC-3 cell proliferation and HSP-90 (06WOP264). Derivatives of **177** showed inhibitory activities against the growth of tumor cells (06WOP110).

Sequential acylation of **1** by the carboxylic acid functionality of protected aspartic or glutamic acids gave **183**, which upon regioselective cycloaddition with dinucleophile hydrazine gave indazole **184** (R = H) whose deprotection afforded pseudoaromatic α -amino acids **185** (R = H) as homochiral amino acids with a tetrahydroindazole as a side chain (04TL1237). Fmoc **186** and thiourea **187** as well as the 1-benzyl derivatives **184a**, **185a**, and **186a** (R = Bn) were synthesized (04TL1237) (Scheme 31).

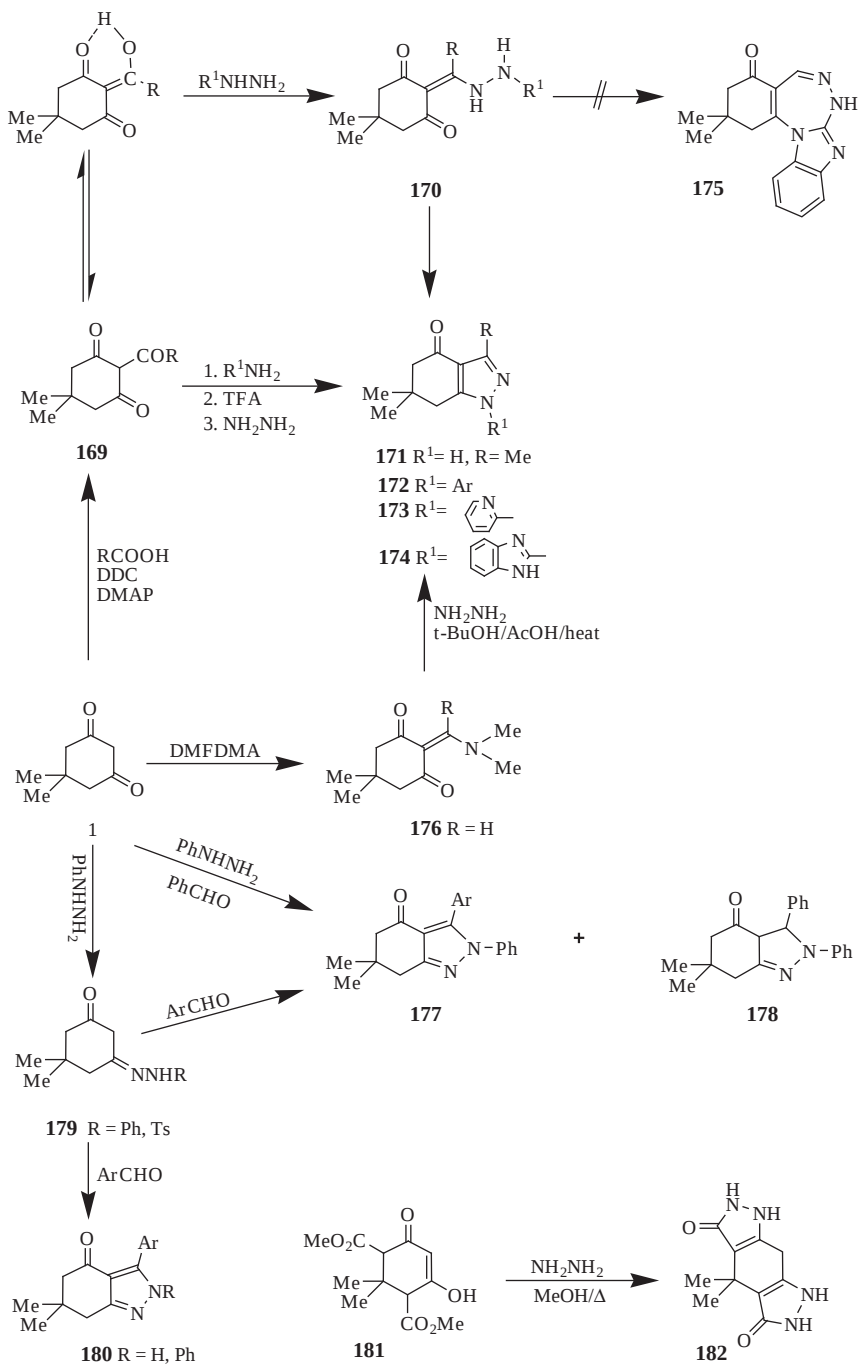
4.2 Annulation with imidazole (synthesis of benzimidazoles)

3-Amino-5-phenyl-1,2,4-oxadiazole and **1** gave enamino-ketone **188** that on irradiation with a low-pressure mercury lamp gave benzimidazole **189** as a result of a photoinduced rearrangement of the 1,2,4-oxadiazole ring (88JHC1551) (Scheme 32).

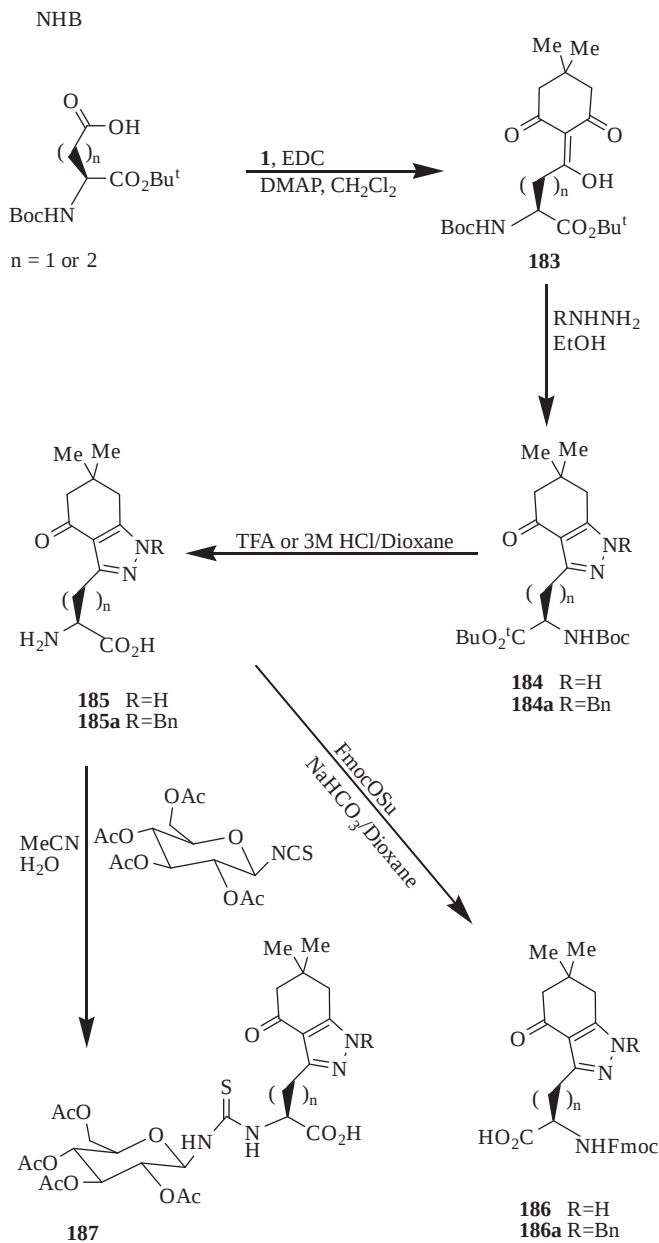
4.3 Annulation with dithiole (synthesis of benzodithioles)

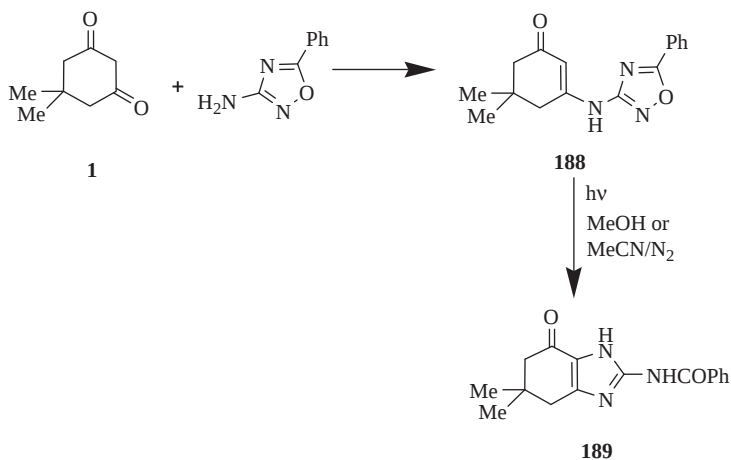
3-(*o*-Aminoanilino)-5,5-dimethylcyclohex-2-en-1-one **190** can be readily prepared from **1** and *o*-phenylenediamine. Its reaction with carbon disulfide in the presence of DMSO gave benzo[1,2]dithiol-3-thione **191** (91JHC1245) (Scheme 33).

Photolysis of thiol **152** (R = H) gave disulfide **192**, 1,3-benzodithiole **193**, and thianthrene **194**, whereas the photolysis of the acetyl, alkenyl,

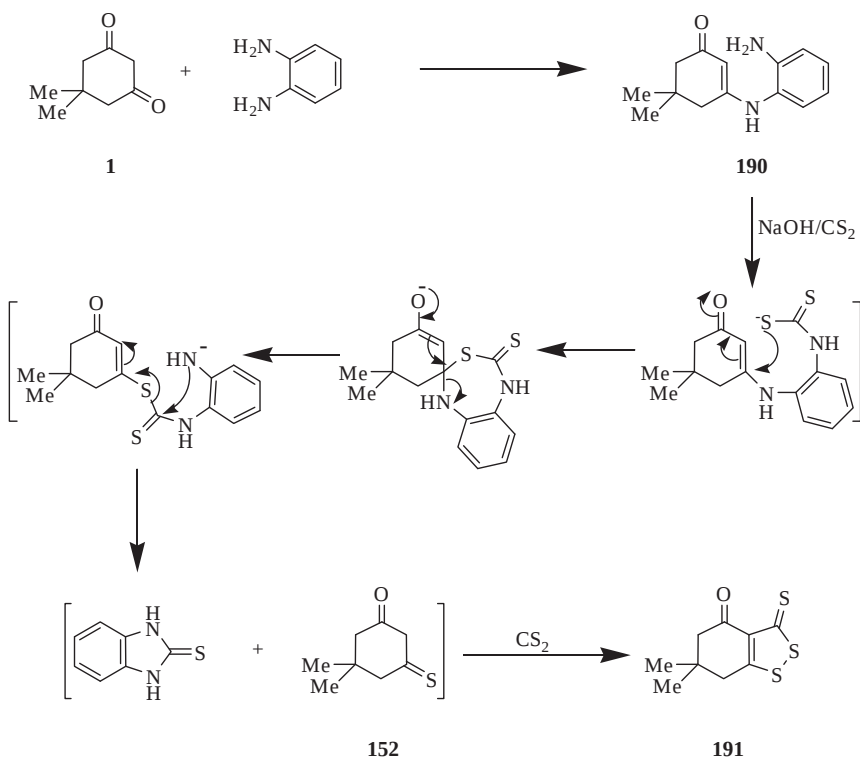


Scheme 30

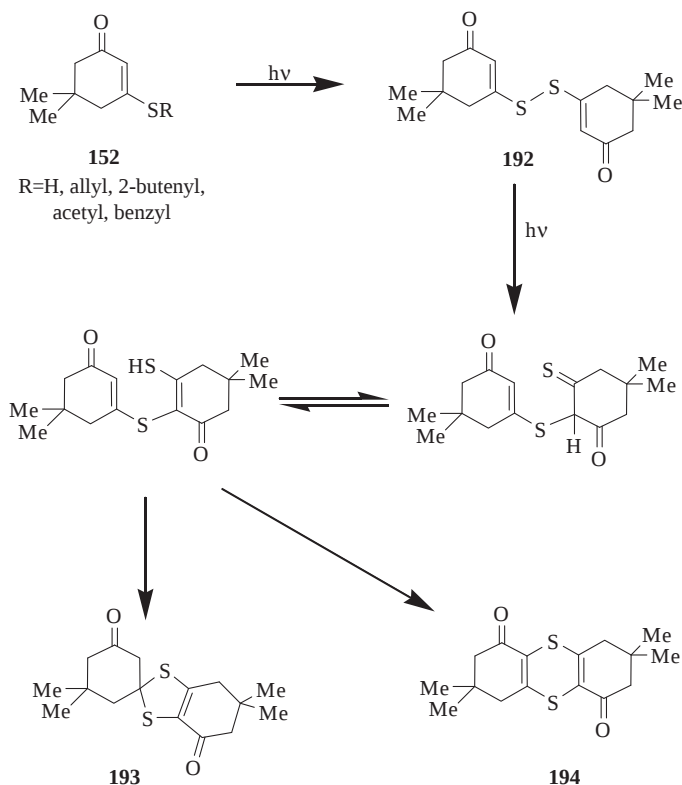




Scheme 32



Scheme 33



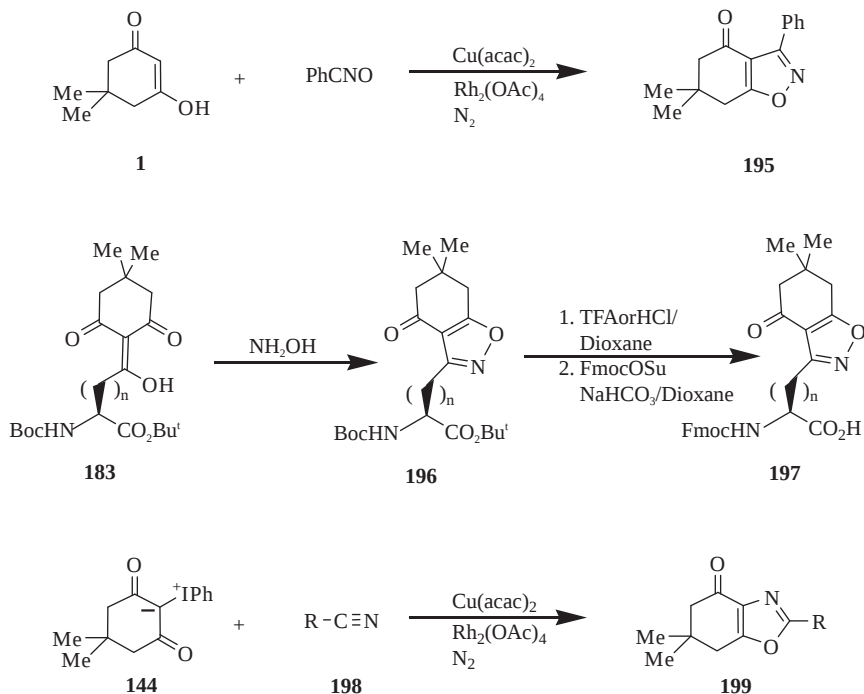
Scheme 34

benzyl derivatives of **152** gave **192** and **193** in variable ratios. The rearrangement was ruled out under thermal conditions in darkness (74ACS(B)1077) (Scheme 34).

4.4 Annulation with isoxazole and oxazole (synthesis of benzoisoxazoles and benzoxazoles)

1,3-Dipolar cycloaddition of benzonitrile oxide with **1** led to the formation of tetrahydrobenzoisoxazole **195** (74KGS901). Acyldimedone **183** with hydroxylamine afforded benzoisoxazole **196**. Subsequent protecting group manipulation afforded the N-Fmoc **197** (04TL1237).

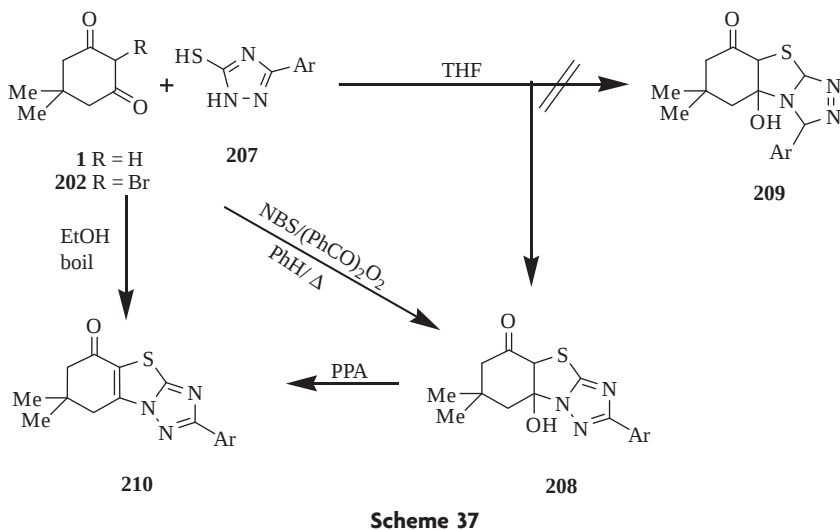
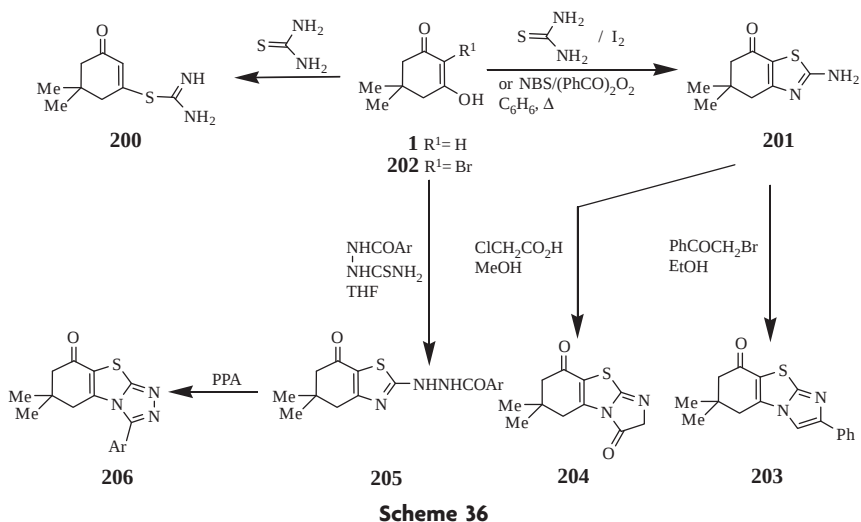
Thermal [3+2] cycloaddition of the iodonium ylide of dimedone **144** to nitriles **198** in the presence of $\text{Rh}_2(\text{OAc})_4$ or $\text{Cu}(\text{acac})_2$ catalyst under an inert atmosphere without solvent gave the regioisomers of benzoxazoles **199** (87TL4449, 00TL9299) (Scheme 35).



4.5 Annulation with thiazole (synthesis of benzothiazoles)

Addition of thiourea to **1** gave the isothiurea **200** (82CZP082). In the presence of iodine, or NBS and traces of benzoyl peroxide, the thiazole **201** was obtained (64MI65, 89IJC(B)81]. Also **201** was obtained from the reaction of thiourea with 2-halodimedone **202**. 2-Aminobenzothiazole **201** and phenacyl bromide or chloroacetic acid afforded imidazo[2,1-*b*]benzothiazoles **203** and **204**, respectively [89IJC(B)81]. Tetrahydrobenzothiazoles **205** were obtained from 2-bromodimedone **202** ($R^1 = \text{Br}$) and aroyl thiosemicarbazides in THF at room temperature (95M759). Dehydrative cyclization of 2-aryllhydrazinobenzothiazole **205** was achieved by heating in PPA at 160 °C to give 3-aryl-6,6-dimethyl-8-oxo-5,6,7,8-tetrahydro-1,2,4-4*H*-triazolo[3,4-*b*]benzothiazole **206** (95M759) (Scheme 36).

Condensation of 2-bromodimedone **202** and 3-aryl-5-mercapto-1,2,4-4*H*-triazoles **207** in THF at room temperature afforded intermediates 5*a*-hydroxy-1,2,4-4*H*-triazolo[3,2-*b*]benzothiazoles **208** rather than [3,4-*b*] isomers **209**; polarity of different solvents did not affect the outcome (95M759). A one-pot synthesis of **208** was achieved by heating a mixture of **1**, NBS, and **207** in benzene containing traces of benzoyl peroxide. Dehydration of **208** on heating in PPA at 150 °C afforded **210**, which also



could be obtained from simultaneous condensation and dehydrocyclization when a mixture of **202** and **207** was refluxed in absolute ethanol (95M759) (Scheme 37).

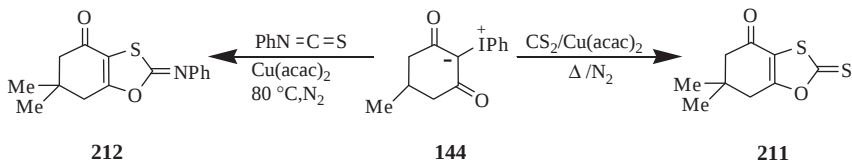
4.6 Annulation with oxathiole (synthesis of benzoxathioles)

4-Oxo-4,5,6,7-tetrahydro-6,6-dimethyl-1,3-benzoxathiole-2-thione **211** was obtained from the reaction of iodonium ylide **144** with carbon disulfide in

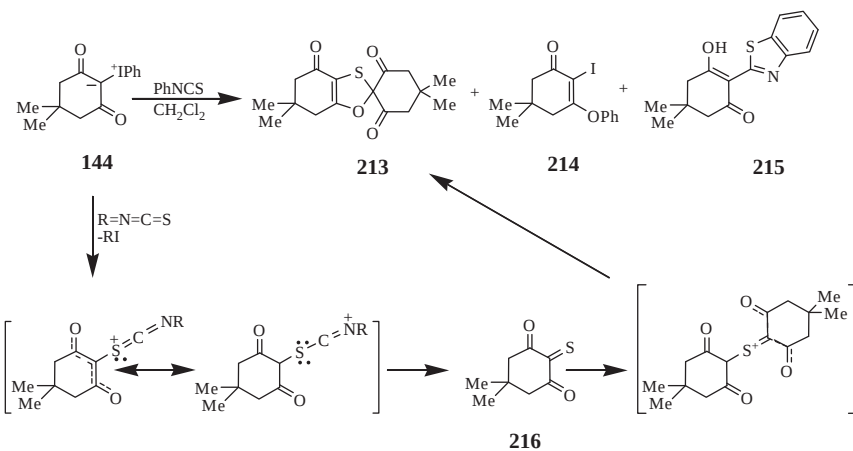
the presence of Cu(acac)₂. 2-Phenylimino **212** was obtained from reaction of **144** with phenyl isothiocyanate under similar conditions (87TL4449) (Scheme 38).

When **144** was reacted with phenyl isothiocyanate in dichloromethane at room temperature, 4-oxo-6,6-dimethyl-tetrahydro-1,3-benzoxathiole-2,2-dimethylcyclohexane-2',6'-dione **213** was obtained together with phenyl-2-iododimedonyl ether **214** and 2-(2-benzothiazolyl)dimedone **215** (76JOC125). Both **213** and **214** were obtained when **144** was treated with methyl isothiocyanate. Both reactions may proceed through common intermediate **216**. An attempt to synthesize **216** by treatment with hydrogen sulfide was unsuccessful, but compound **213** was isolated in higher yield (40%) (76JOC125) (Scheme 39).

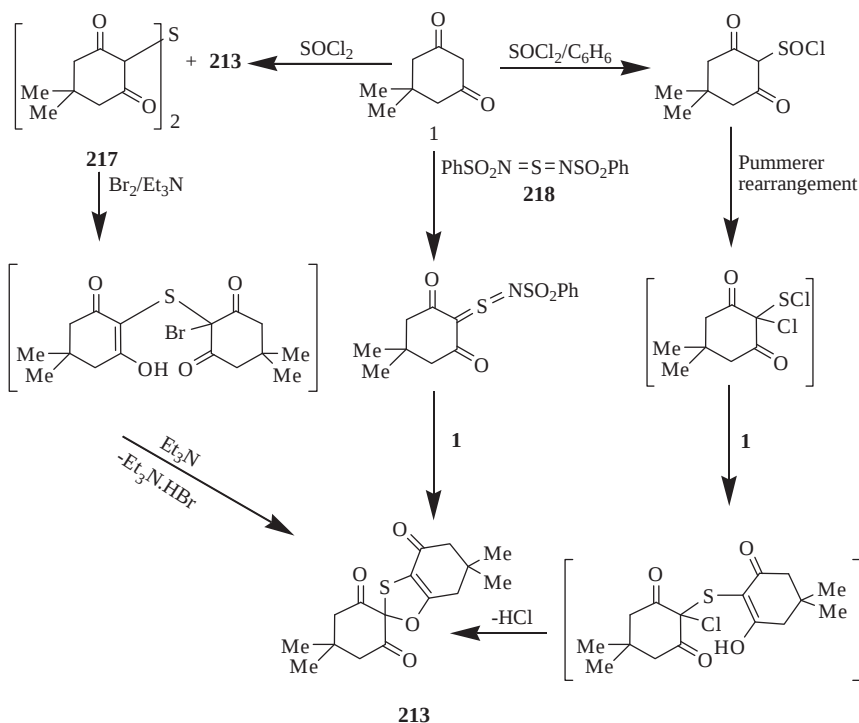
Alternatively, **213** was synthesized from **1** upon treatment with thionyl chloride in benzene (81JOC4911) or in pyridine (81ZOR990). The reaction involved an initial attack at C-2 followed by a Pummerer rearrangement (81JOC4911). *N,N'*-bis(phenylsulfonyl)sulfurdiimide **218** or *N*-sulfinylbenzenesulfonamide with **1** gave **213**, which also was obtained by bromination of the sulfide **217** (81ZOR990) (Scheme 40).



Scheme 38



Scheme 39



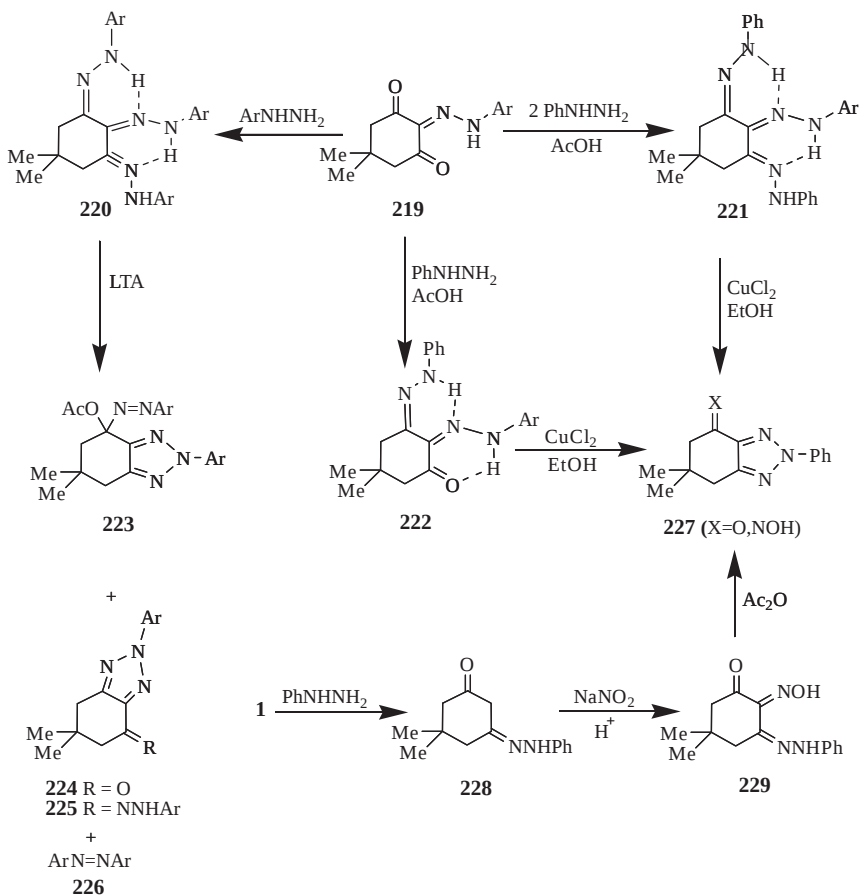
Scheme 40

5. DIMEDONE-ANNULATED FIVE-MEMBERED HETEROCYCLES WITH THREE HETEROATOMS

5.1 Annulation with triazole (synthesis of benzotriazoles)

Aryldiazonium chlorides and **1** gave 5,5-dimethylcyclohexan-1,2,3-trione-2-arylhydrazones **219** (85JCR(M)1076, 07MI570) which upon reaction with excess arylhydrazines in ethanol gave 5,5-dimethylcyclohexan-1,2,3-trione-1,2,3-tris(arylhydrazones) **220**. Reaction of **219** with two equivalents of phenylhydrazine gave the mixed *tris*-hydrazones **221**, and with one equivalent of phenylhydrazine gave mixed *bis*-hydrazone **222** (93OPP569, 07MI570). Oxidation of **220** gave benzo[*d*]-1,2,3-triazoles **223–225** in addition to **226** (85JCR(M)1076). Both **221** and **222** with an ethanolic solution of cupric chloride afforded the same **227** ($\text{X} = \text{O}$) (93OPP569). This proved that the substituted aniline and not aniline itself was lost in each case.

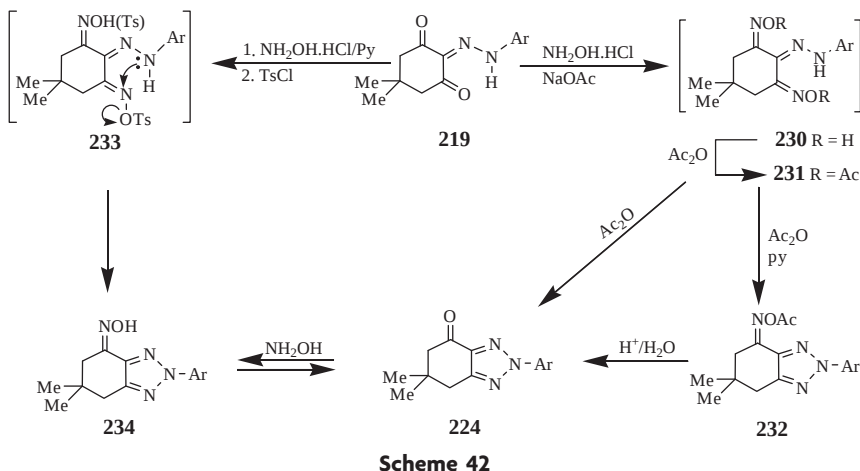
Phenylhydrazine and **1** gave **228**, which with sodium nitrite afforded hydrazone oxime **229**. Its treatment with acetic anhydride gave **227**



Scheme 41

(X = O). The latter with hydroxylamine gave the corresponding oxime **227** (X = NOH) (86JHC443) (Scheme 41).

Reaction of **219** with hydroxylamine followed by acetic anhydride gave the benzo[*d*][1,2,3]triazole **224** rather than **232** or **234**; the initially formed dioxime **230** was converted to **231**, which lost acetic acid to give triazole **232**. Subsequent cleavage of the oxime to give ketone **224** may be due to the presence of the acetic acid formed during the dehydration (93OPP569). However, under the same condition **219** (Ar = antipyrine) gave **232** rather than **224** (07MI570). Moreover, **219** (Ar = *p*-Me-C₆H₄, antipyrine) with hydroxylamine hydrochloride in pyridine as acid scavenger followed by acetic anhydride afforded *N*-acetyloxime **232** (Ar = *p*-Me-C₆H₄, antipyrine), which confirmed the proposed pathway (93OPP569, 07MI570). Alternatively the dehydrative cyclization of the



hydrazone oxime from **219** (Ar = *p*-Me-C₆H₄) was carried out with *p*-toluenesulfonyl chloride to give **234** (Ar = *p*-Me-C₆H₄). Perhaps the cyclization took place between the hydrazone and oxime residue *via* tosylate intermediate **233** (93OPP569) (Scheme 42).

5.2 Annulation with oxadiazole (synthesis of benzoxadiazoles)

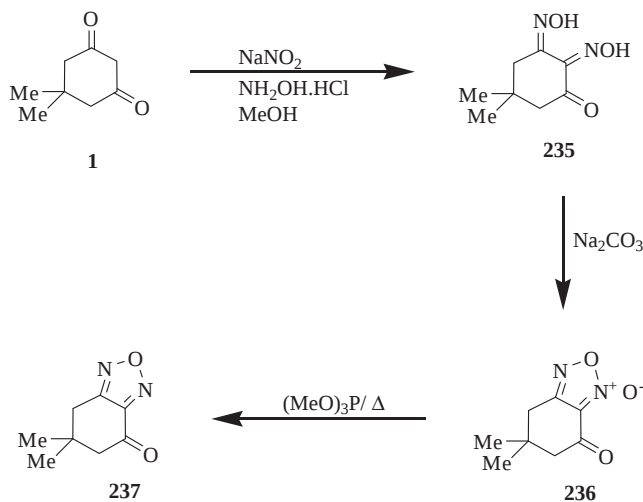
The oxadiazole ring was added onto **1** on stirring a saturated solution in methanol with sodium nitrite and hydroxylamine hydrochloride to give dioxime **235**. On treatment with sodium carbonate it gave furazan oxide **236** that upon heating in trimethylphosphite gave 2,1,3-benzoxadiazole **237** (73JCS(P)351). (Scheme 43).

5.3 Annulation with thiadiazole (synthesis of benzothiadiazoles)

p-Toluenesulfonylhydrazine was reacted with **1** to give monotosylhydrazone **238** (73JOC3637) that upon treatment with thionyl chloride in methylene chloride at room temperature gave 6,6-dichloro-5,5-dimethyl-4,5,6,7-tetrahydro-7-oxo[1,2,3-*b*]benzothiadiazole-1,1-dioxide (**239**) (88SUL125). In an earlier report (87SUL109), the structure 5,5-dimethyl-4,5,6,7-tetrahydro-7-oxo[1,2,3-*b*]benzothiadiazole **240** was given for the product.

Condensation of **239** with thiourea in refluxing ethanol gave 7-amino-5,5-dimethyl-4*H*,5*H*-1,2,3-benzothiadiazolo[7,6-*d*]thiazole (**241**) (88SUL125); thiourea effected a facile reduction of the sulfone to a sulfide.

Addition of vinyl magnesium bromide to bicyclic ketone **240** under normant conditions (60AdvOC1) gave the anticipated allyl alcohol **242**



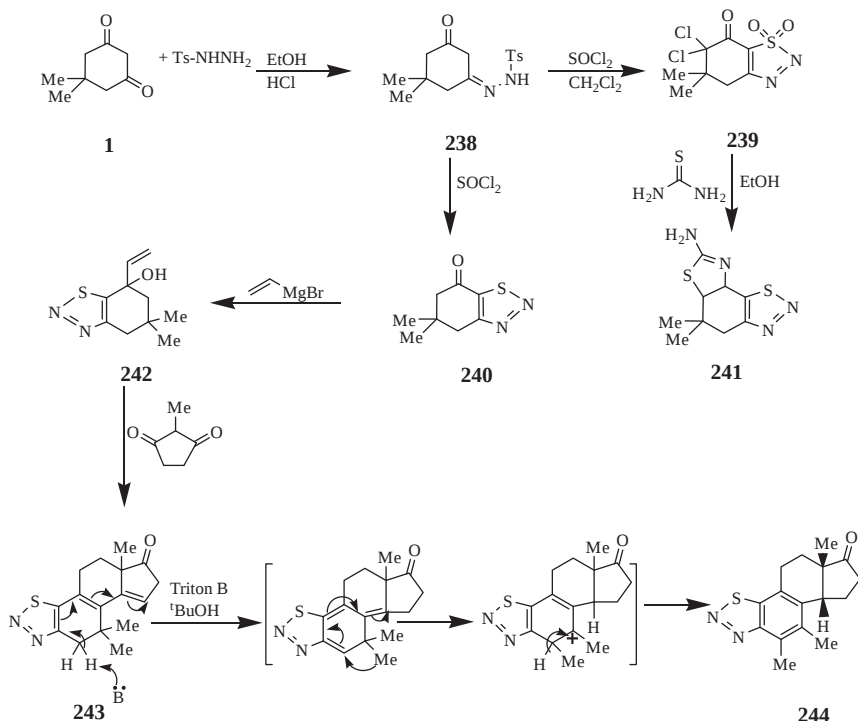
Scheme 43

that upon condensation with 2-methylcyclopentane-1,3-dione in boiling xylene containing *tert*-butanol and catalytic amount of Triton-B gave 6,7-dimethyl-1-thia-2,3-diaza-A-nor-14-isoestra-2,5-(10),6,8-tetraen-17-one **244**. The formation of **244** was rationalized by assuming the initial formation of the expected cyclodehydrated product **243**. The inherent strain caused by the gem-dimethyl group at C-7 in **243** may be responsible for the shift of one methyl group at C-7 to C-6 leading to the aromatization of the ring and the saturation of the 14,15-olefinic bond (87SUL109) (Scheme 44).

6. DIMEDONE-ANNULATED SIX-MEMBERED HETEROCYCLES WITH ONE HETEROATOM

6.1 Annulation with pyridine (synthesis of quinolines)

Dimedone has been extensively used in the synthesis of partially hydrogenated quinoline rings. Thus, 1,4,5,6,7,8-hexahydroquinolines **245** were prepared by Hantzsch-like synthesis starting from **1**, aromatic or aliphatic aldehydes and β -aminocrotonates or β -aminocrotonamide (66CHE583, 89AF1393, 94IJC(B)526, 06MI109). Hexahydroquinolines **245** were also obtained by ultrasound or microwave (MW) irradiation of a mixture of **1**, aromatic aldehydes and β -aminocrotonates or ethyl acetoacetate in the presence of ammonium acetate (97JCR(S)266, 01MI313, 02MI99, 06MI60) or in water in the presence of triethylbenzylammonium (TEBA) chloride (05MI696, 06MI263). Quinolines **245**



Scheme 44

($\text{R} = \text{Ar}$) also can be obtained from the *bis*(dimedonyl)methane derivative with β -aminocrotonates or from arylalkylidene acetoacetate in the presence of aqueous ammonia or ammonium acetate (94IJC(B)526).

Condensation of **1** with either the *bis*-acetonitrile or the enamines of acetylacetone or benzoylacetone imine in ethanol and paraformaldehyde, acetaldehyde, or benzaldehyde afforded the respective 3,4-disubstituted-hexahydroquinoline derivatives **245**. Benzaldehyde gave good results, but condensation did not take place with acetaldehyde and benzoylacetone or acetylacetone imines. When paraformaldehyde was used, *bis*(dimedonyl)methane was isolated as a byproduct (67KGS1118).

The Hantzsch cyclocondensation of the four components **1**, aldehydes, ketoesters, and ammonium acetate has attracted much attention for the synthesis of polyhydroquinolines **246**. Various catalysts have been used, such as molecular iodine (05TL5771), CAN (06T7293), HY-zeolite (06CPB1044, 06T7293), bakers yeast (07TL3887), Montmorillonite K10 clay in methanol (05SC2875), L-proline in water, or solvent-free condition (07T1946), $\text{HClO}_4\text{-ScO}_2$ under solvent-free condition (06ARK201), triethylbenzylammonium chloride in water (04MI1569), scandium triflate (06JMOC309), $\text{Yb}(\text{OTf})_3$ (05T1539), and ionic liquids under solvent-free

conditions such as hexamethylimidazolium tetrafluoroborate {[hmim]BF₄}, decylmethylimidazolium tetrafluoroborate {[dmim]BF₄}, hexamethylimidazolium hexafluorophosphate {[hmim]PF₆}, as well as hexamethylimidazolium bromide {[hmim]Br}, where the former was the optimum one. Aliphatic aldehydes (04SL831, 06MI698) may be used also.

X-ray study of the 4-(3-chlorophenyl) derivative showed that the N containing ring adopted a boat conformation and the cyclohexene has a half-chair conformation (05AX(E)01634). The corresponding 4-(2-chloro-5-nitrophenyl) derivative has the chloro substituent in a syn-periplanar orientation with respect to the pyridine ring plane with the nitro group over it (04AX(E)0711).

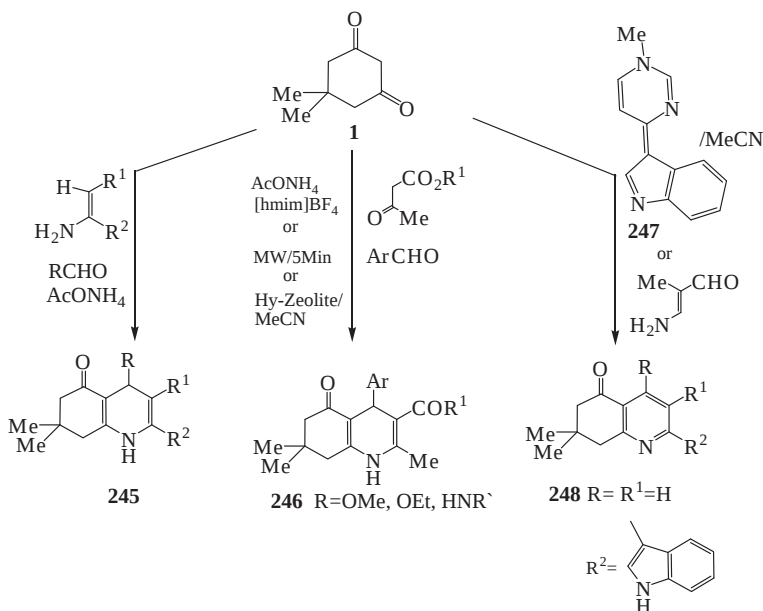
The use of terephthalaldehyde or isophthalaldehyde as an aldehyde allowed the presence of two polyhydroquinolines on the benzene ring; the synthesis was achieved under MW irradiation (05JHC29).

Four-component cyclocondensation of **1**, aromatic aldehydes, malononitrile, and ammonium acetate proceeded under MW irradiation in solvent-free conditions to give highly functionalized hexahydroquinolines in excellent yield. The crystal structure of 2-amino-3-cyano-4-phenyl-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline was determined (06JHC985).

Oxidation of **245** with chromic acid gave tetrahydro derivatives **248** (67KGS1118), that can be also obtained from reaction of **1** with 3-amino 2-methylacrylaldehyde (76JCS(P1)975), or 4-(3-indolyl)pyrimidine **247** (83KGS555). Various derivatives of **246** and **248** were reported for treatment of cardiovascular and cellular proliferative diseases (05WOP294, 06MIP24, 06MIP25, 06WOP50) (Scheme 45).

A solution phase approach has been developed on the basis of an ionic liquid-phase strategy with a protocol of coupling, detachment, and purification. The attachment of ionic liquid phase bound β -keto ester **249** was performed under MW which by heating with **1**, aldehyde and ammonium acetate afforded the hexahydroquinoline bound ionic liquid **250** whose oxidation gave the tetrahydroquinoline **251** that upon transesterification or hydrolysis gave **252** (06JCO829). The Hantzsch polyhydroquinoline ionic liquid synthesis was also performed by using ionic liquid bound aldehyde **253** to give **254** whose transesterification gave **255** (05T12386) (Scheme 46).

When the triketones **256** was boiled with ammonia in ethanol, they afforded the respective hexahydroquinolines **257**, but in individual cases additional oxidized products, tetrahydroquinolines **258** were formed (03CHE1121). Moreover, the triketone **256** ($R^3 = 4\text{-NO}_2\text{-C}_6\text{H}_4$, $R^2 = \text{H}$, $R^1 = \text{Ph}$) gave upon treatment with ammonium acetate in glacial acetic acid at 150 °C, the tetrahydroquinolin-5-one **258**. When the triketones **256** ($R^1, R^3 = \text{Ph}$ or $4\text{-MeO-C}_6\text{H}_4$) were reacted with excess hydroxylamine hydrochloride, the expected 2,4-diaryl-5,6,7,8-tetrahydroquinoline-5-oxime



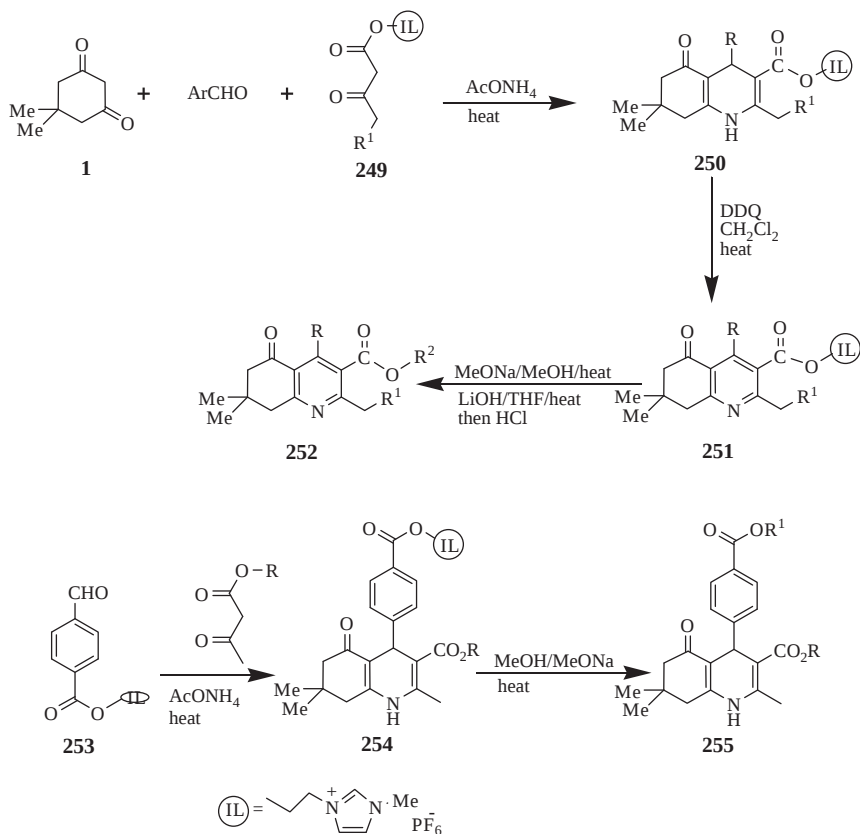
Scheme 45

259 and their isomeric 2,3-diaryl **260** were formed as a result of anionotropic rearrangement (03CHE1121) that was promoted by the presence of electron-donating group R^1 and R^3 of **256** where the yield of the isomer **260** was increased, whereas the rearrangement did not occur by the presence of an electron-withdrawing nitro group in R^1 or R^3 (90KGS209) (Scheme 47).

The partially hydrogenated 5-oxo-quinoline **257** ($\text{R}^2 = \text{H}$) have been synthesized from the reaction of **1** with 1,3-diaryl-2-propen-1-ones (chalcones) in DMF in the presence of ammonium acetate (02SC3449). The reaction was also done under MW (05JCR697) or by solid-state reaction (06ARK28). Using ammonium formate under solvent-free conditions gave the same polyhydroquinoline derivatives; X-ray crystallography of one of them has been reported (06MI317).

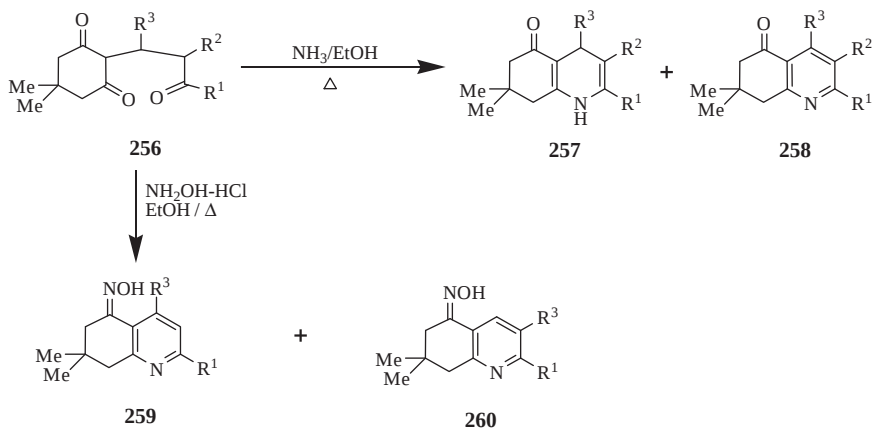
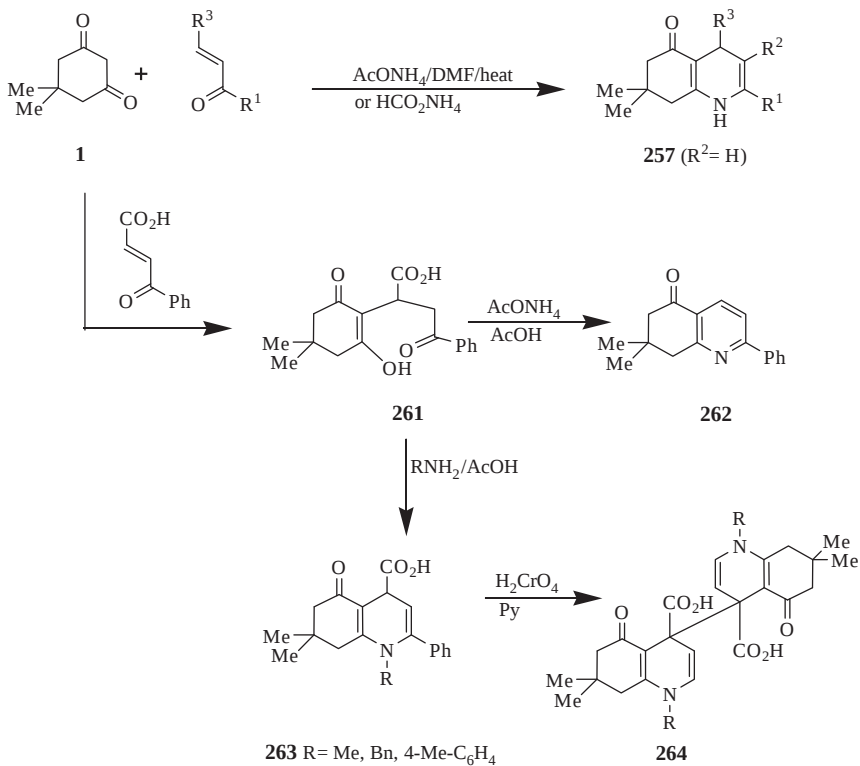
The adduct 2-(4,4-dimethyl-2,6-dioxocyclohexyl)-4-oxo-4-phenylbutanoic acid **261** was obtained from the reaction of dimesityl 1,4-cyclohexanedione and β -benzoylacrylic acid, which upon reaction with ammonium acetate in acetic acid led to the pyridine ring that accompanied by decarboxylation to give **262**. When the reaction was done in the presence of methylamine, benzylamine, or *p*-toluidine, it gave quinolines **263** whose oxidation by chromic acid in pyridine gave **264** (01CHE1111) (Scheme 48).

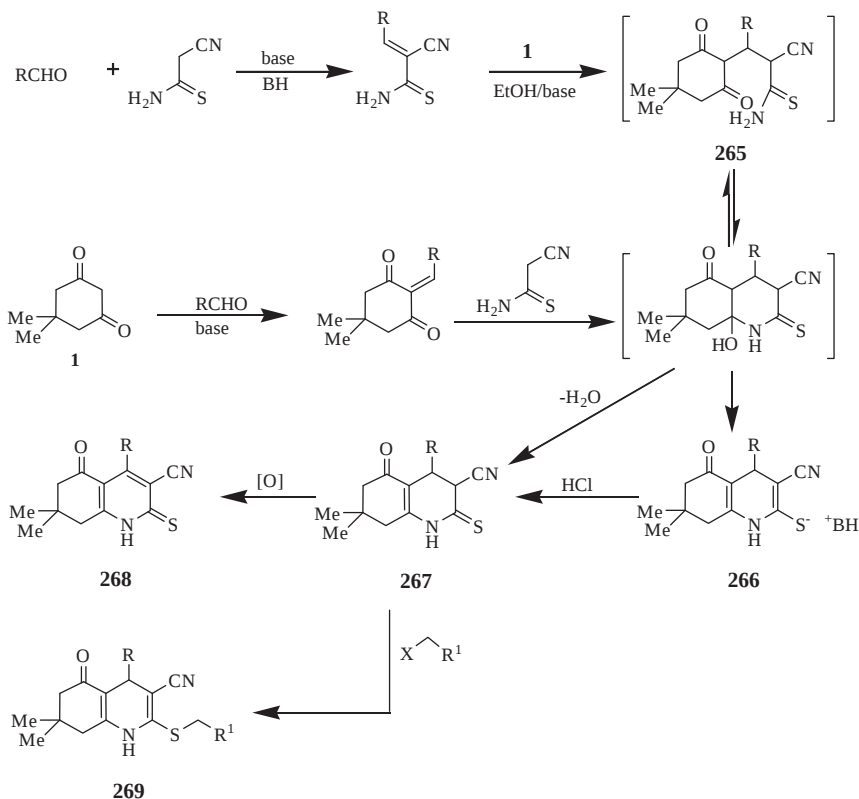
The hexahydroquinolines were obtained by addition of the active methylene group of dimesityl 1,4-cyclohexanedione to the double bond of



Scheme 46

arylmethylenecyanothioacetamide or cyclohexylidenecyanothioacetamide in boiling ethanol containing catalytic amount of piperidine, diethylamine, or morpholine to form the intermediate **265**, which cyclized to **267** and then oxidized to give **268** (85ZOR2470, 86ZOR1962, 97RJOC1501, 97T17441). A one-pot reaction of dimedone, aliphatic aldehydes, and cyanothioacetamide in the presence of *N*-methylmorpholine at room temperature gave **266**, which upon acidification gave **267** (90ZOR1578, 97CHE684, 98RJOC707, 99CHE1485). In contrast, with aromatic aldehydes, the adducts **265** were obtained as ammonium salts and their cyclization to **267** was achieved by heating (98RJOC707) while with 4-chlorobenzaldehyde in the presence of piperidine, it gave the piperidinium 3-(4-chlorophenyl)-2-cyano-3-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-enyl)thiopropionimide that was used for the synthesis of partially hydrogenated quinolin-2-thiones **267** (00RCB736). Alkylation of which with methyl iodide, chloroacetonitrile, or phenacyl bromide

**Scheme 47****Scheme 48**

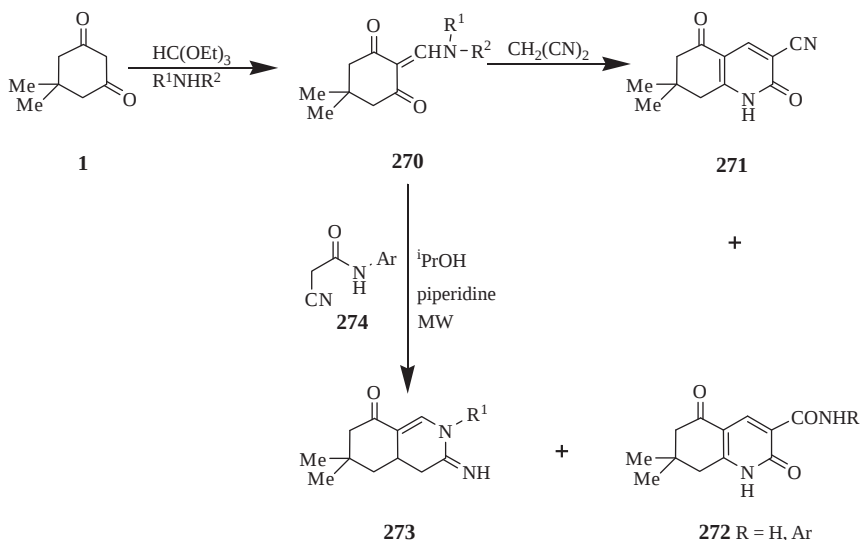


Scheme 49

under basic condition afforded sulfide **269** (85ZOR2470, 86ZOR1962, 98RJOC707, 05RJGC1537) (Scheme 49).

When the aminomethylene **270** ($R^1 = R^2 = H$ or Me), obtained from reaction of **1** with triethoxymethane in the presence of amine, was reacted with malononitrile, it gave the quinolines **271–273** (74M1283; 03JHC689) and with cyanoacetamide **274** gave quinolines **272** ($R = Ar$) (04T8633) (Scheme 50).

The enaminones **31** have proved to be good precursors for the synthesis of quinoline derivatives. Thus, condensation of **31** ($R = Ph$) with diethyl malonate afforded the octahydroquinoline **275** ($R = Ph$) (91MI197). C-Alkylation of **31** ($R = H$) with ethyl acrylate in the presence of sodium hydride in diglyme or in the presence of 15-Crown-5 in THF followed by ring closure gave the quinolinedione **276** (84JCS(P1)287). Reaction of **31** ($R = H$) with 1,1,3,3-tetraethoxypropane or 3-ethoxy-2-methylacrylaldehyde at $120^\circ C$ without solvent afforded the respective tetrahydroquinolinone **277**, whose reduction gave tetrahydroquinoline

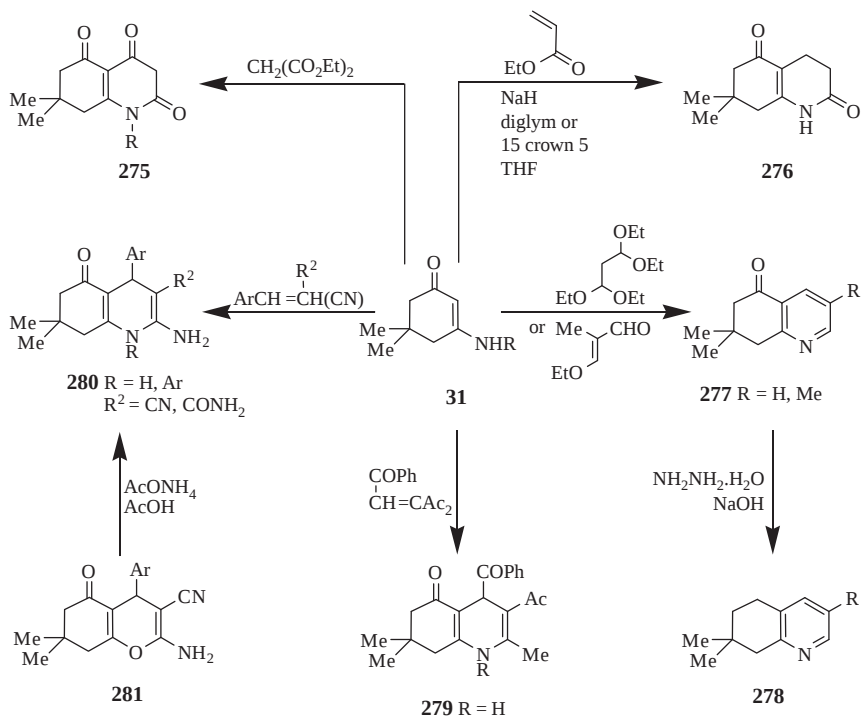


Scheme 50

278 (76JCS(P1)975). Reaction **31** with 1,1-diacetyl-2-benzoyl ethylene afforded hexahydroquinolines **279**, and with arylidene malononitrile or cyanoacetamide gave the quinolines **280** (89JPR971, 96IJC(B)608, 00JHC735, 01ARK73, 02SC3449, 06MI77), which can be obtained by aminolysis of benzo[*b*]pyran derivatives **281** with ammonium acetate in acetic acid (89JPR971). A one-pot reaction of dimedone, benzaldehyde and malononitrile in the presence of ammonium acetate under MW irradiation gave **280** (Ar = Ph) (05AX(E)0983). Palladium-catalyzed oxidation of the enamine **31** (R = $(\text{CH}_2)_3\text{-OH}$) and subsequent cyclization followed by aromatization gave **277** (R = H) (02TL7929) (Scheme 51).

Reaction of 3-amino-5,5-dimethylcyclohex-2-en-1-one **31** (R = H) with methylvinyl ketone under acidic condition gave a mixture of **283** and **284**; presumably *via* the intermediates **282** and **282a**. The intermediate **282** would be formed by C-2 alkylation followed by dehydration to give **283** and **284**, however N-alkylation followed by ring closure gave the isomeric products **283a** and **284a** (79JCS(P1)1411). In contrast, when the trione **285**, obtained from dimedone and methylvinyl ketone, was heated with ammonia in toluene gave isomeric mixture of **283** and **284** (79JCS(P1)1411). Heating of **31** (R = H) with 3-benzoylacrylonitrile in toluene gave **284** (R = H, $\text{R}^1 = \text{Ph}$) (84CPB2824) (Scheme 52).

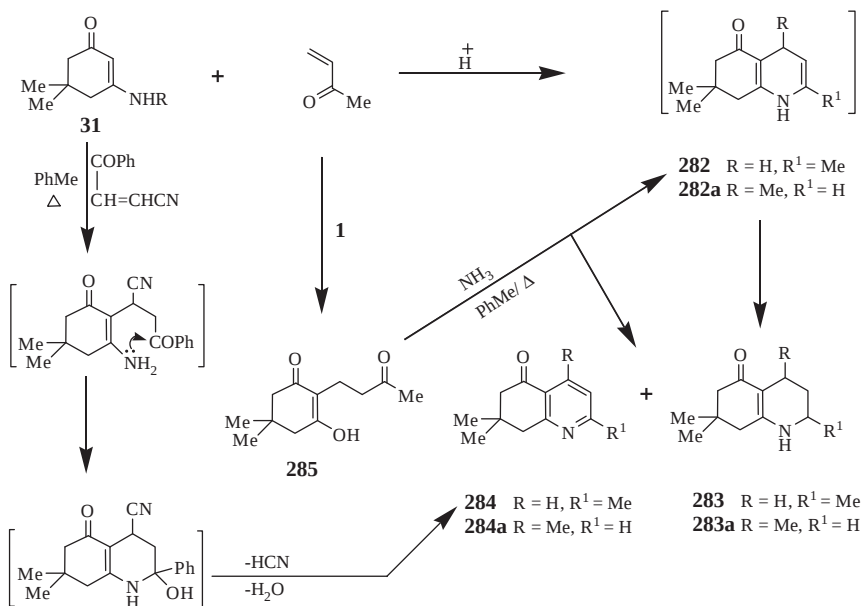
Quinoline **289** was obtained as a byproduct from the acid catalyzed reaction of **31** (R = H) with 3-ethoxy-2-methylacrolein to give **286** whose further reaction with **31** (R = H) gave **287** that upon oxidation gave **288**, which cyclized to **289** (81JCR(S)66, 84JCS(P1)287). Enamine **31** (R = H,



Scheme 51

Me) with formaldehyde under neutral conditions gave the bienaminone **290**, which on treatment with aqueous acidic formaldehyde gave the spiroquinoline **291** that can be directly obtained from **31** ($\text{R} = \text{H, Me}$) (71JCS(C)2699) (Scheme 53).

Condensation of **31** ($\text{R} = \text{H, Me}$) with 5-arylidene-2,2-dimethyl-1,3-dioxane-4,6-dione in boiling ethanol afforded the octahydroquinoline **292** in 60–70% yield (93KGS1227). Alternatively, **292** ($\text{R} = \text{H}$ or Me) were obtained from Meldrum's acid by heating with equimolar amount of **1** and aromatic aldehydes in the presence of excess ammonium acetate in acetic acid (99T875) or with **31** and aromatic aldehyde in ethanol (90KGS786). The reaction was assumed to take place through a Hantzsch-like mechanism *via* conjugated addition of enamine **31** (obtained from **1** and ammonia released from ammonium acetate) to the arylidene derivative followed by imino-enamine tautomerism and subsequent ring cyclization and loss of acetone and carbon dioxide (99T875). The MW irradiation was used for the synthesis of **292** in a shorter time (01SC2657, 01MI313, 06BMCL2925). Similarly, the quinolinediones **293** were also prepared under MW irradiation (05AX(E)03536, 05AX(E)04372).

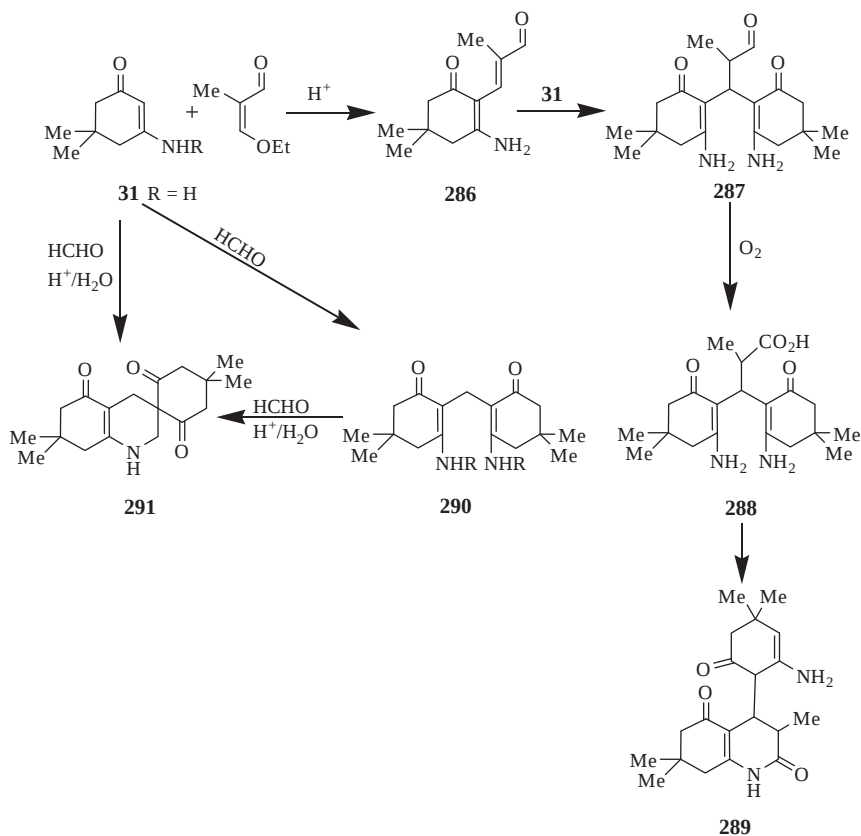


Scheme 52

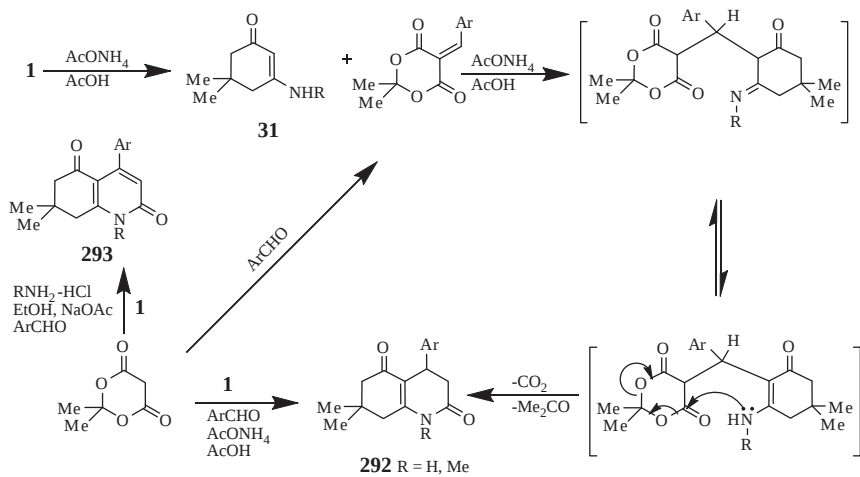
The structures of a number of **292** and **293** have been studied by X-ray crystallographic analysis and semiempirical molecular orbital calculation (AMI) and *ab initio* (HF/3-21G) methods (99T875, 06MI599, 05AX(E)04372, 05AX(E)03536) (Scheme 54).

Chlorination of **1** with phosphorous trichloride afforded 3-chloro-5,5-dimethylcyclohex-2-enone (74ACS(B)1077) which upon treatment with a number of 1-aryloxy-4-*N*-methylaminobut-2-ynes (**294**) gave **295**. Heating of which in chlorobenzene led to [3,3]sigmatropic shift at the propargyl vinyl amine moiety to form the allene intermediate **296**, which tautomerized to **296a** that underwent [1,5]proton shift to give **296b** whose electrocyclic ring closure gave unstable endocyclic intermediate **296c** that upon [1,3] prototropic shift gave 7,7-dimethyl-1,2,3,6,7,8-hexahydro-4-aryloxymethylene-1-methylquinolin-5-one **297**. Otherwise one more [1,5] proton shift in **296b** gave **296d** followed by a 6-endocyclization to give **297** (01T4955) (Scheme 55).

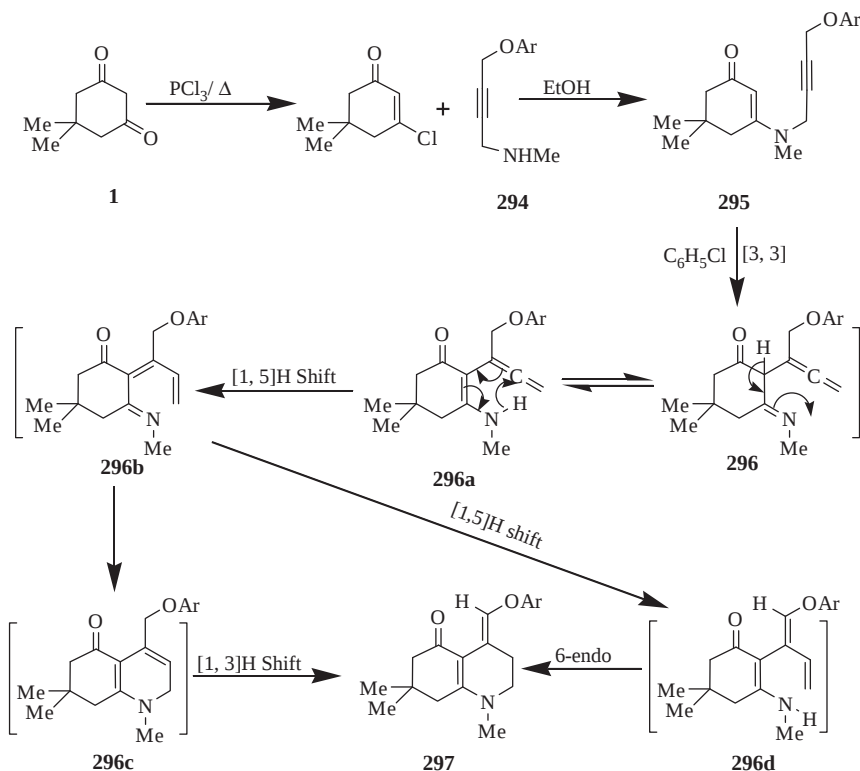
Chiral quinolines can be prepared by using chiral auxiliary. Thus, asymmetric Michael addition of the arylidenemalonate to the enhydrazone **298**, obtained from a chiral hydrazine with **1**, in the presence of *n*-butyllithium in THF afforded the adduct **299** in high diastereomeric purity which underwent ring closure to the quinoline-2,5-dione **300** (R = H). The chiral auxiliary was removed by N–N bond cleavage with



Scheme 53



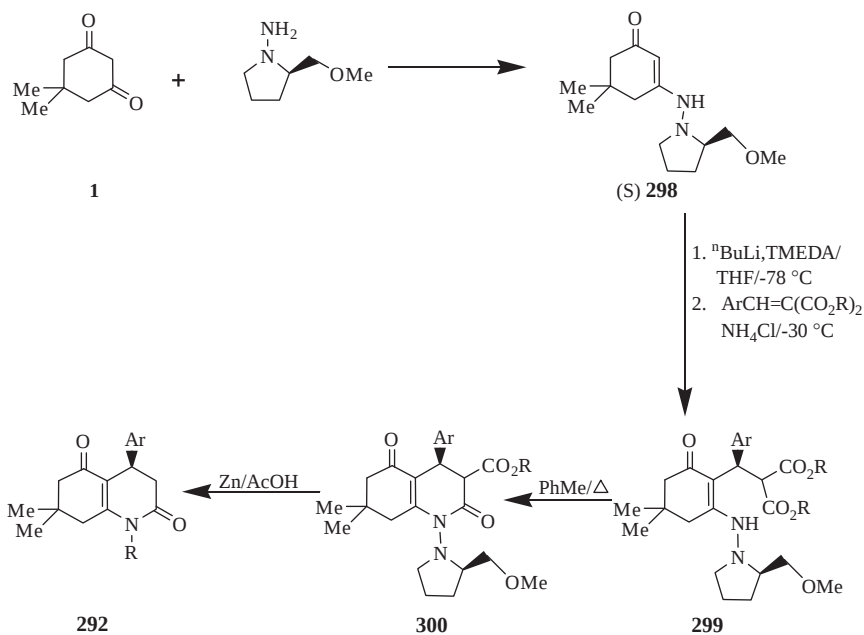
Scheme 54



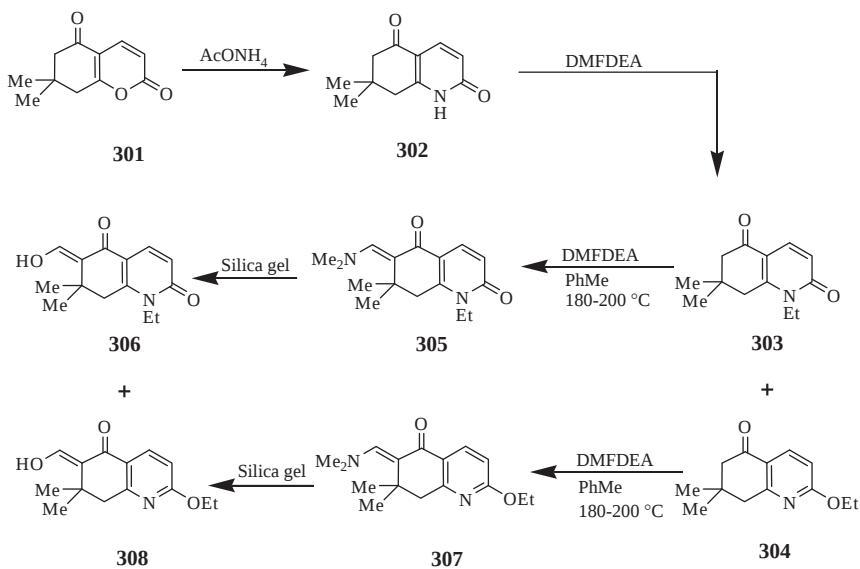
Scheme 55

Zn/AcOH with simultaneous loss of ester group to give (R)-**292** ($\text{R} = \text{H}$) in very high enantiomeric purity ($\text{EE} \geq 98\%$) (87TL3795); the absolute configuration was based on the X-ray structural analysis. The (S)-enantiomer was obtained by changing the chiral auxiliary (Scheme 56).

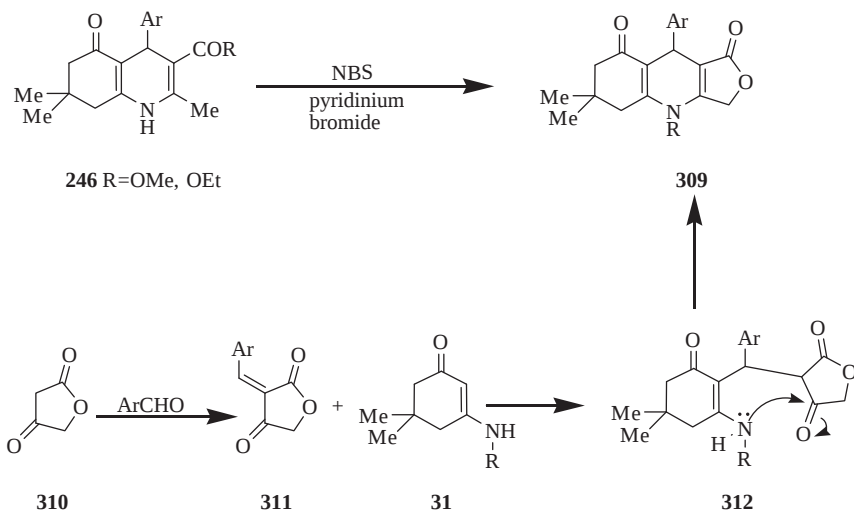
Aminolysis of benzopyran **301** with ammonium acetate afforded the quinoline **302**, which upon reaction with DMF diethyl acetal (DMFDEA) produced a mixture of the respective N- and O-alkylated derivatives **303** and **304**. The latter compound was also prepared by chlorination of **302** with PCl_5 followed by reaction with sodium ethoxide. Further treatment of **303** and **304** with DMFDEA in toluene at $180\text{--}200^\circ\text{C}$ resulted in C-alkylation to give **305** and **307**, respectively. Column chromatography on silica gel resulted in the formation of **306** and **308**, respectively with the recovery of the starting material **303** (91KGS86) (Scheme 57).



Scheme 56



Scheme 57



Scheme 58

6.2 Synthesis of quinoline-fused with heterocycles

6.2.1 Synthesis of furo-quinolines

Intramolecular cyclization of the hexahydroquinolines **246** (Ar = 2-trifluoromethyl, nitro, or methoxyphenyl) with *N*-bromosuccinimide and pyridinium bromide gave furoquinolines **309** (R¹ = H) (89AF1393) (Scheme 58).

Three-components reaction of an aldehyde, enamine **31** and tetronic acid **310** in glacial acetic acid under MW irradiation without a catalyst gave the furoquinolines **309** (06S3874), *via* the formation of the arylidene derivative **311** (Scheme 58).

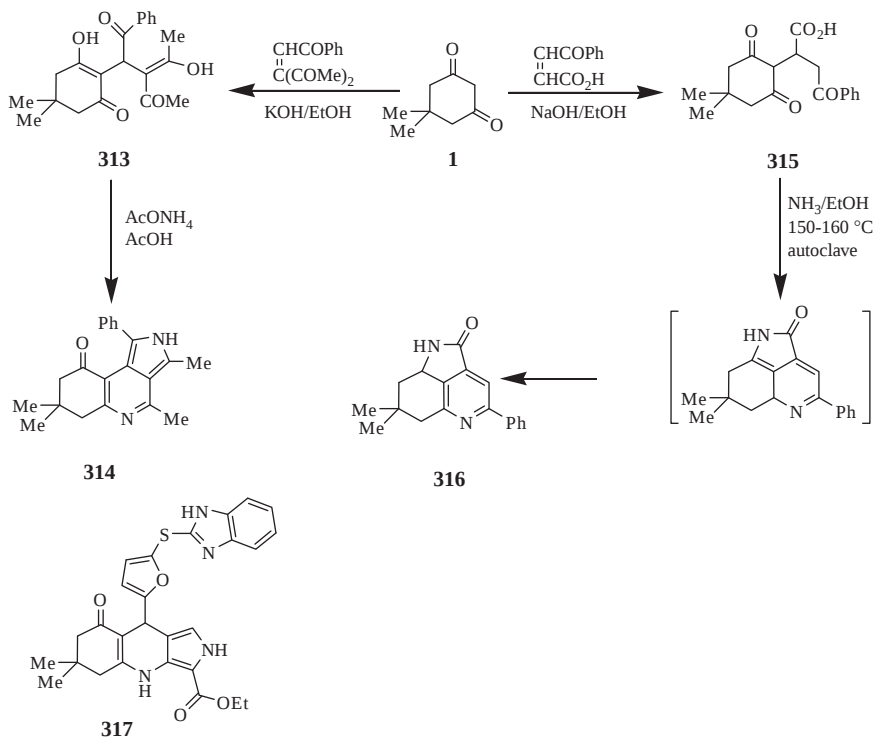
6.2.2 Synthesis of pyrrolo-quinolines

Condensation of **1** with 1,1-diacetyl-2-benzoylethylene in ethanol gave the adduct **313**, which upon treatment with ammonium acetate in acetic acid gave pyrrolo[3,4-*c*]quinoline **314** (01HCO155).

Michael condensation of **1** and *trans*- β -benzoylacrylic acid afforded butanoic acid derivative **315** that can be cyclized, with ammonia in an autoclave at 150–160 °C, to give 7,7-dimethyl-4-phenyl-1,2,6,7,8,8a-hexahydro-pyrrolo[4,3,2-*d,e*]quinolin-2-one (**316**) (97JOU1048). The pyrrolo[3,4-*b*]quinoline **317** was reported as inhibitor of Aurora A Kinase (07EUP60) (Scheme 59).

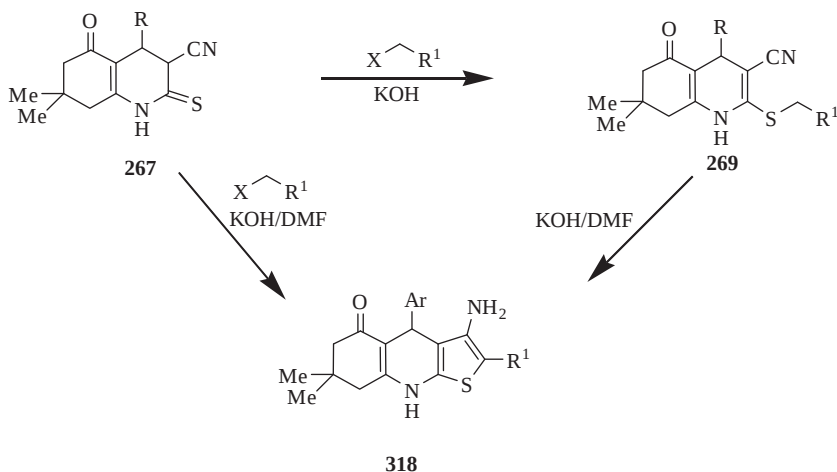
6.2.3 Synthesis of thieno-quinolines

Heating 2-alkylthioquinolines **269** with KOH/DMF afforded thieno-[2,3-*b*]quinolines **318** (85ZOR2470, 86ZOR1962, 98RJOC707, 99CHE1485).



Scheme 59

Alternatively, **318** were obtained in a one-pot reaction when **267** were treated with the respective alkyl halide in excess of KOH (98RJOC707) (Scheme 60). Thus the 4-fluorophenyl derivative of **318** was synthesized by the cycloalkylation of 3-cyano-4(4-fluorophenyl)-2-mercapto-7,7-dimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline with chloroacetonitrile. Treatment of **318** with formic acid, formamide, thioacetamide, or phenyl isothiocyanate furnished the corresponding quinolino[3',2',4,5]thieno[3,2-d]pyrimidines. Reaction of **318** with triethylorthoformate gave the ethoxymethylene derivative and with boiling acetic anhydride for a short time afforded monoacetamide derivative, whereas prolonged reaction time furnished the diacetyl derivative. Fusion of **318** with urea or thiourea yielded the corresponding quinolino[3,2,4,5]thieno[3,2-d]pyrimidines. When **318** were reacted with urea in the presence of sodium ethoxide, the substitution of the amino group by ureido fragment took place. Treatment of **318** with sulfuric acid hydrolyzed the cyano group to the amido group, while upon heating the corresponding carboxylic acid was obtained. Reaction of **318** with hydroxylamine afforded pyrazolothienoquinoline, whereas the reaction

**Scheme 60**

with ethyl cyanoacetate, benzylidene malononitrile, or acetaldehyde and malononitrile gave the corresponding pyrido[2,3,4,5]thieno[2,3-*d*]quinolines. On preliminary screening, the pyrazolo- and pyrido-thienoquinoline exhibited *in vitro* inhibitory activity against *Saccharomyces cerevisiae*, when compared with the standard fungicide Mycostatine, whose structure remain unchanged when exposed to gamma irradiation (06PS279) (Scheme 60).

6.2.4 Synthesis of pyrazolo-quinolines

Friedlander condensation of 5-aminopyrazole-4-carboxaldehydes **319** with dimedone furnished pyrazolo[3,4-*b*]quinolines **320**. Subsequent Vilsmeier Hack formylation and sequential cyclocondensation with phenylhydrazine gave *bis*-pyrazolo[3,4-*b*:4,3-*f*]quinolines (06JHC1169).

Dimedone with arylidene aminopyrazoles **319a** in ethanol gave the intermediate adduct **321** that spontaneously cyclized to hexahydropyrazolo[3,4-*c*]isoquinolines **322**. The cyclization of the adduct **321** took place at C-4 only even for the N-1-unsubstituted arylidene derivatives **319a** (93M893).

A one-pot cyclocondensation of 5-amino-3-substituted pyrazole derivatives **319b** with **1** and substituted benzaldehydes in ethanol afforded the tricyclic linear tetrahydropyrazolo[3,4-*b*]quinoline derivative **323** rather than the angular isomer **322** ($R^1 = \text{Me}$). The same products were obtained under MW irradiation as energy transfer agent (98JHC575, 01AX(E)0151, 01T6947, 05MI209, 05MI1610, 05WOP56, 07JCO14).

Cyclocondensation of 3-amino-5-methylpyrazole with 2-arylmethylidene-5,5-dimethylcyclohexane-1,3-diones or 9-aryl-3,3,6,6-tetramethyl-2,3,4,5,6,7,8,9-octahydro-1H-xanthene-1,8-diones, in DMF or methanol gave 4-aryl-3,7,7-trimethyl-1,4,6,7,8,9-hexahydropyrazolo[3,4-*b*]quinolin-5-ones **323** whose structure was proved by the X-ray diffraction data (06RJOC1015).

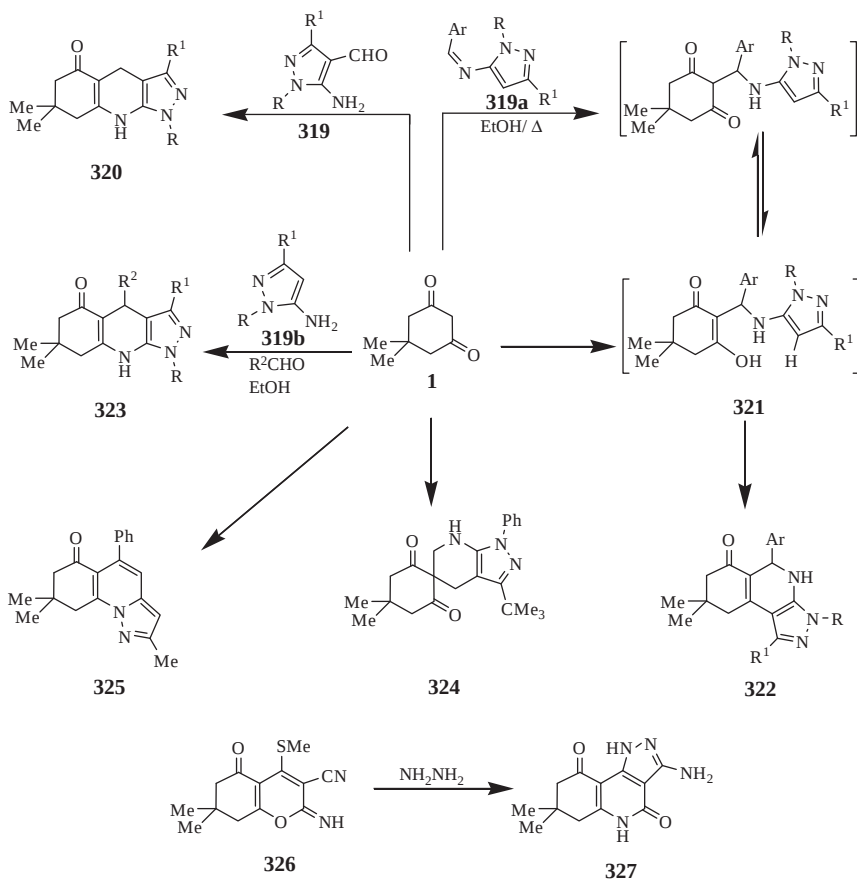
The reaction proceeded through a first Knoevenagel condensation between **1** and the aldehyde followed by a Michael addition of the aminopyrazole to these adducts and further cyclization to give the pyrazolo[3,4-*b*]quinolines. This pass way was preferred rather than starting by the reaction of **1** with the aminopyrazole to give the eneamine because the latter failed to react with aldehydes. NOESY experiments and X-ray analysis were used to conclude the structure of the product (01T6947). The nonaromatic carbocyclic ring in 3-(4-methoxyphenyl)-7,7-dimethyl-1,6,7,8-tetrahydropyrazolo[3,4-*b*]quinolin-5-one, adopts an envelope conformation. The molecules are linked by a combination of hydrogen bonds into a chain of centrosymmetric ring (06AX(C)0525). In both **322** and **323**, the two heterocycles were planar whereas the carbocyclic ring adopted envelope conformation. The pyrazoloquinoline derivatives **323** ($R = \text{Ph}$, $R^1 = t\text{-butyl}$, $R^2 = \text{H}$) was similarly prepared but under MW and its X-ray crystallography confirmed the structure. When formaldehyde units have incorporated in the reaction, the spiro compound **324** was obtained (04AX(C)0265), whereas, using orthobenzoic acid trimethyl ester as carbon inserting agent instead of formalin, **325** was obtained whose structure was confirmed by X-ray (04AX(C)0479).

The other angular pyrazoloquinoline derivative **327** was obtained by hydrazinolysis of 2-imino-7,7-dimethyl-4-methylsulfanyl-5-oxo-5,6,7,8-tetrahydro-2H-benzopyran-3-carbonitrile (**326**). The reaction can be proceeded by substitution of the methylsulfanyl group by hydrazine followed by cyclization to give **327** (97JCR(S)256) (Scheme 61).

6.2.5 Synthesis of imidazo-quinolines

Condensation of endione **328** with aminal **329** in acetonitrile gave the imidazo[1,2-*a*]quinoline **330** *via* the formation of a C–C bond intermediate. Alternatively, **330** was prepared in a one-pot reaction by refluxing **1** with **329** and benzaldehyde in acetonitrile (99JCS(P1)2087). When the enamine **31** ($R = \text{CH}_2\text{CO}_2\text{Et}$), obtained from reaction of **1** and ethyl glycinate, was reacted with 2-(3-nitrobenzylidene)malononitrile, it gave **330** ($R = \text{CN}$, $Y, X = \text{O}$) *via* the formation of 2-aminoquinoline **331** that spontaneously cyclized to **330** (01ARK73) (Scheme 62).

The benzimidazolo-quinolines **332** were obtained *via* a molecular-sieves-promoted three-component domino reaction, and *in situ* aerobic oxidation, of dimedone, *o*-phenylenediamine, and acrylaldehyde (06SL1671).



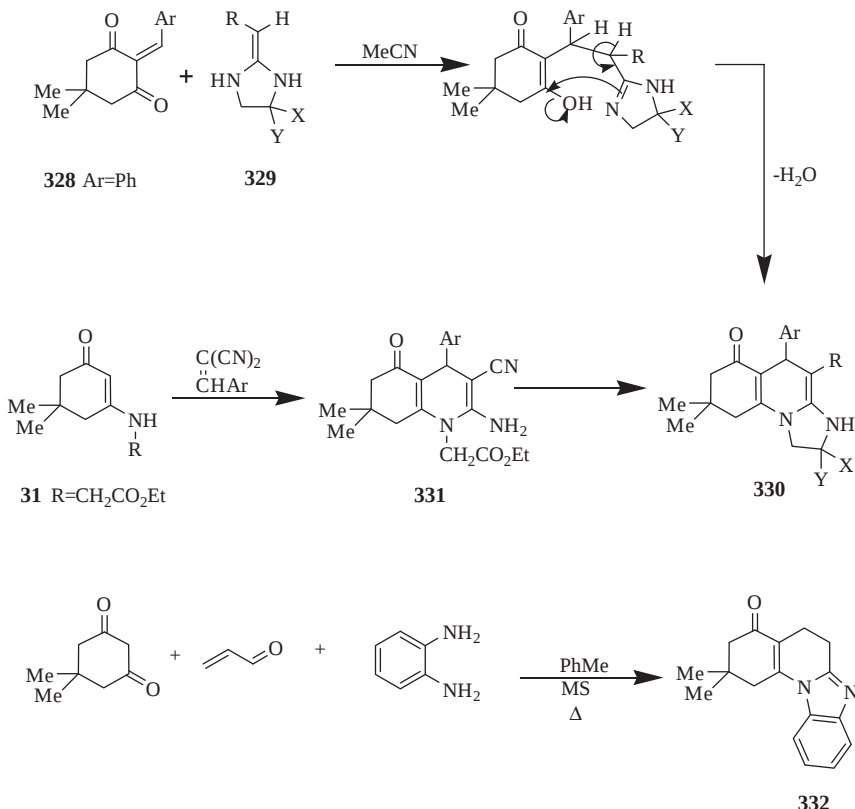
Scheme 61

6.2.6 Synthesis of benzofuro, benzothiopheno, and benzoselino-quinolines

Boiling the pyrylium salts **333** (X = O, S, or Se) in aqueous ethanol afforded the tricarbonyl compounds **334**, which could be cyclized to the fused quinolines **335** by alcoholic ammonia (94CHE283). Reduction of **335** with LiAlH₄ afforded the alcohols **336**, and their reaction with hydrazine hydrate gave the respective hydrazones whose reaction with KOH in ethylene glycol gave **337** (94CHE283) (Scheme 63).

6.2.7 Synthesis of pyrano-quinolines

Treatment of the enamine **31** (R = H) with excess methylvinyl ketone in the absence of acid afforded the adduct **338**, *via* the intermediate **282** and subsequent condensation with another molecule of methylvinyl ketone



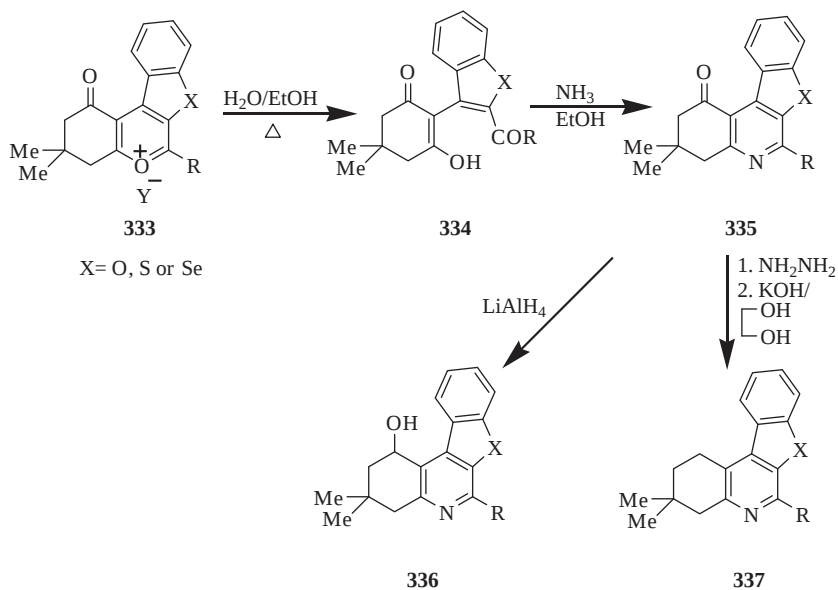
Scheme 62

(79JCS(P1)1411). The condensation reaction of the trione **285** with ammonia in refluxing xylene afforded the tetracyclic product **339**, by the deprotonation of **285** to split acetone anion to give methylenedimdone and **282** that condensed with ammonia to give **339** (79JCS(P1)1411) (Scheme 64). Functionalized benzochromones were condensed with dimedone to give **340** (06HAC2) (Scheme 64).

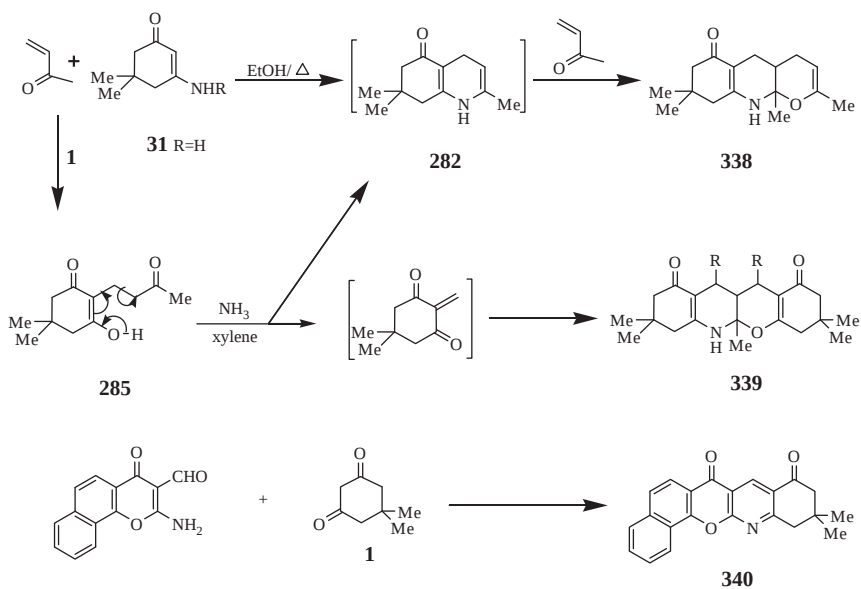
6.2.8 Synthesis of pyrido-quinolines

2-Amino-4-aryl-3-cyano-7,7-dimethyl-5,6,7,8-tetrahydro-4H-benzo[b]pyran **281** were reacted with benzylidene malononitrile in the presence of piperidine at 160 °C to afford pyrido[3,4-*b*]quinolines **341** (89JPR971) (Scheme 65).

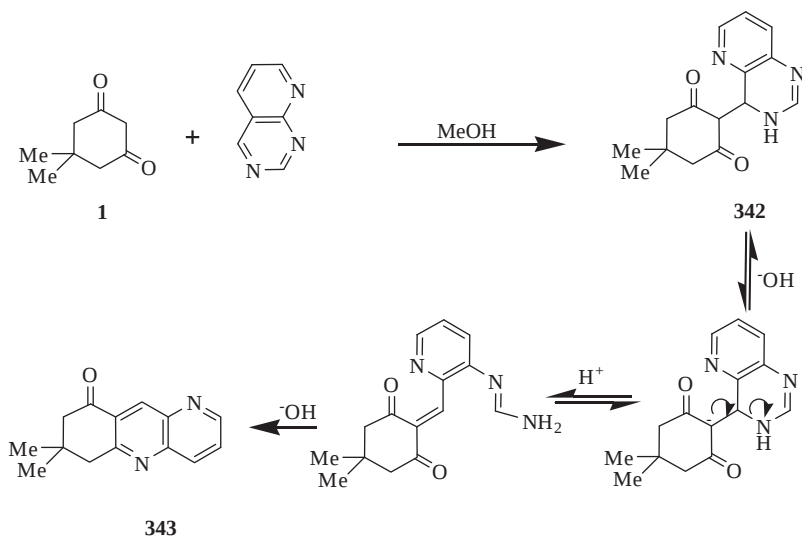
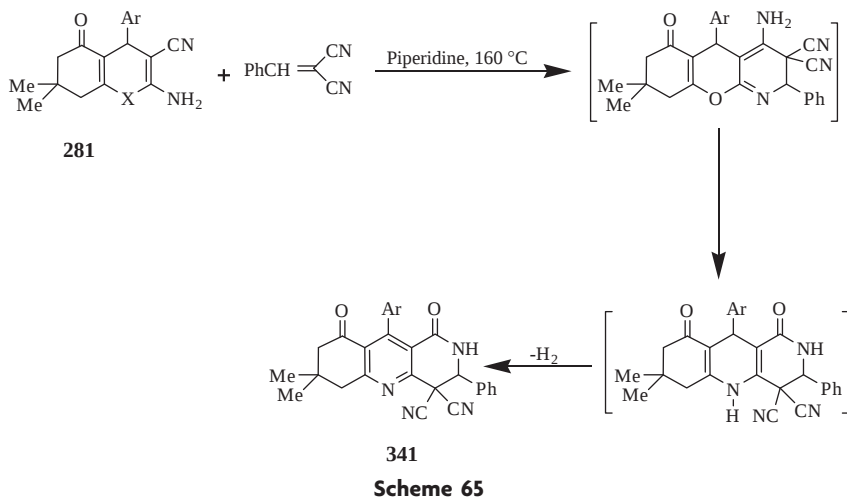
Reaction of **1** with pyrido[3,2-*d*]pyrimidine in methanol afforded the adduct **342** that with NaOH gave the pyrido[2,3-*b*]quinoline **343** (73JCS(P1)1794) (Scheme 66).



Scheme 63



Scheme 64



6.2.9 Synthesis of pyrimido-quinolines

Pyrimido[4,5-*b*]quinolines **344** were obtained from 2-amino-3-cyanoquinoline **280** ($R = Ar^1$) upon reaction with benzoyl isothiocyanate (96IJC(B)608) (Scheme 67). Reaction of enamine **31** ($R = o\text{-CNC}_6\text{H}_4$) with benzylidene malononitrile in the presence of DBU gave the pyrimidoquinoline **345** *via* the respective quinoline **280** (01ARK73). A series of pyrimidoquinolines were prepared by cyclization of the



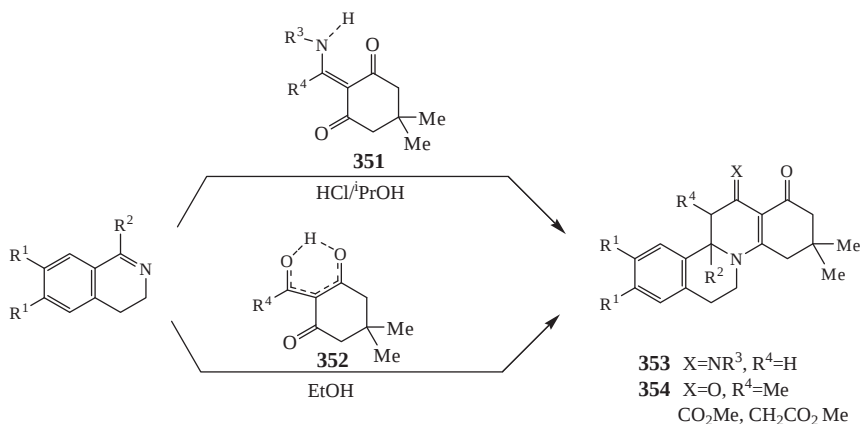
The linear hexahydro-pyrimido[4,5-*b*]quinolines **347** were obtained regiospecifically by a one-pot reaction of equimolar amounts of 6-aminopyrimidine **346**, dimedone and benzaldehyde derivatives; the

angular isomers **347a** were not formed (98JHC231) (Scheme 67). In contrast, MW irradiation of a mixture of **1**, **346** ($R = H, Me$) and excess of formaldehyde in the presence of triethylamine afforded pyridopyrimidine-spirocyclohexanetriones **348** (06TL27). However, when equimolar amount of paraformaldehyde was used, the linear pyrimido[4,5-*b*]quinoline **347** was obtained by either irradiation or heating in ethanol whereas, further irradiation afforded **349** (06TL27). The ratio of formaldehyde played a role on the product whereby **348** was formed in the presence of triethyl amine whereas **348a** and **348b** were formed as byproducts with excess formaldehyde (04AX(C)0438). Similarly, the linear pyrimido[4,5-*b*]quinoline-trione **349** was obtained when **1**, 6-amino-1,3-dimethyluracil and formaldehyde were reacted in the presence of piperidine (01H1315), or using MW irradiation of the three components on a solid support to give **350** that upon subsequent removal of the support gave **350a** (05TL1345) (Scheme 67).

A series of pyrimidoquinoline derivatives were synthesized in good yield and short reaction time through a similar one-pot condensation using 2,6-diaminopyrimidin-4-one, in glycol under MW irradiation without catalyst (05JHC707). The solvent-free multicomponent reaction using 6-aminopyrimidin-4(3H)-ones with dimedone and *N,N*-dimethylformamide dimethylacetal under MW irradiation yielded pyrimido[4,5-*c*]isoquinolines, whereby, the intermediate of cyclization was isolated (06JHC463).

6.2.10 Synthesis of quinolino-isoquinolines

Annulation of 3,4-dihydroisoquinolines with either the enamine diketone **351** or the β -triketones **352** afforded the isoquinolino[1,2-*a*]quinoline (8-aza-D-homogonanes) **353** and **354**, respectively (91ZOR213, 94RJGC1382) (Scheme 68).



Scheme 68

6.2.11 Synthesis of acridines and phenanthridines

Simultaneous reaction of dimedone, formaldehyde, and aromatic amines in nitrobenzene and in the presence of perchloric acid gave 10-aryldecahydroacridines **356** ($R = H$) together with the perchlorate salts **357** (82ZOR1460). The same products **356** and **357** ($R^1 = Ph$) were obtained in much higher yield from reaction of *bis*(dimedonyl)methane **355** ($R = H$) with aniline (82ZOR1460). The 10-arylacridines **356** were also obtained from the reaction of dimedone **1** with arylamines in formic acid at 150 °C (94JOU1109). Boiling ethanolic solutions of **356** in atmospheric oxygen gave the oxidized products **358**, which were also obtained by treatment of the salts **357** with alkali (82ZOR1460). One-pot condensation of **1** with acetaldehyde followed by aromatic amines afforded the acridine **356** ($R = Me$) while at higher temperature in the presence of perchloric acid the perchlorate salt **357** was obtained (03MI142, 04MI78). In the case of naphthylamines, however, the predominating products were the salts **357** ($R^1 = 1\text{- or }2\text{-naphthyl}$). The low yield in case of using 1-naphthylamine was explained to be due to the steric hindrance in the reaction of *bis*(dimedonyl)methane with 1-naphthylamine. Reaction of **355** with *o*-aminophenol gave only compound **356** ($R^1 = o\text{-hydroxyphenyl}$) (04CHE1550).

Boiling of **1**, aromatic aldehyde and arylamine in water and in the presence of *p*-dodecylbenzenesulfonic acid gave high yield of the acridine **356** ($R, R^1 = Ar$) (04S2001). In contrast, condensation of **1** with secondary aromatic amines and formaldehyde in an acid medium afforded the tetrahydroacridinium salts **359** (79ZOR2226, 04MI59).

MW irradiation activated the reaction of dimedone with aniline or *p*-chloroaniline in formic acid to give the acridines **356**, which can be derivatized as the respective *bis*-oxime and *bis*-phenylhydrazone. However, under the same reaction condition 2-aminopyridine gave the corresponding xanthene derivative (06ARK178).

Acridine derivatives **356** ($R^1 = Me, cyclopropyl$) were obtained when dimedone was treated with aldehydes and methyl or cyclopropylamine hydrochloride in the presence of sodium acetate in glycol or water under MW irradiation (04AX(E)0187, 04AX(E)02328, 05MI1646, 05JHC1155). The X-ray analysis of 10-cyclopropyl acridine was studied (04AX(E)02328). Reaction of **1** with glycine and aromatic aldehyde in glycol under MW without catalyst gave the acridine **356** ($R^1 = CH_2CO_2H$) (05AX(E)03743, 06JHC1647). The reaction was also suitable for aromatic dialdehydes (06JHC1647). MW irradiation was also used for the synthesis of 9,10-diarylacridine **356** ($R = R^1 = Ar$) (03AX(E)01139, 03MI1291, 04MI91).

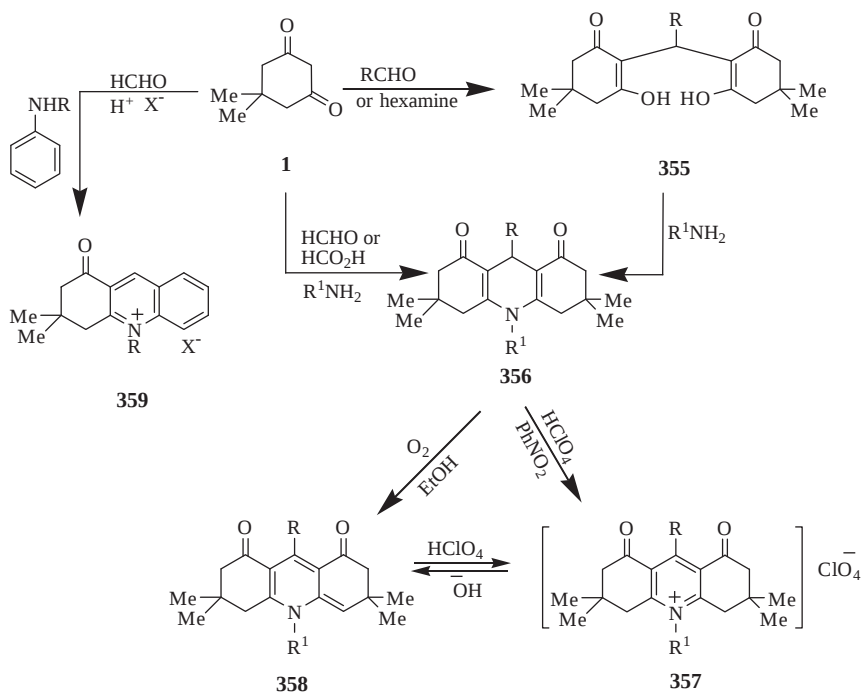
MW-assisted synthesis of acridine and quinazolines was performed on thin layer chromatographic plates that were readily amenable to parallel synthesis of their libraries (05JHC703).

Reaction of the tetraketone **355** with nitroanilines in the presence of catalytic amount of P_2O_5 in ethanol gave **356**. Reduction of the *m*-nitro group to the amine with Zn/HCl was successful whereas the *p*-nitro was unsuccessful. The reaction of **355** with *N*-amino ethyl piprazine or thiosemicarbazides in acetic acid gave the respective *N*-substituted acridines **356** (04ARK124).

Amberlyst-15 has been found to be an efficient catalyst for the synthesis of 1,8-dioxodecahydroacridines, **356** ($R^1 = Ph$, $R = m\text{-NO}_2C_6H_4$) in excellent yield (06JMOC233).

Decahydroacridine-1,8-dione **356** ($R = R^1 = H$) was synthesized by firstly reacting dimedone with hexamine in aqueous methanol solution to give *bis*(dimedonyl)methane. Subsequent treatment with concentrated ammonia and ammonium carbonate in autoclave gave **356** (95MI19) (Scheme 69).

A convenient one-pot method for the synthesis of acridine derivatives was carried out by supporting a mixture of dimedone, aromatic aldehydes, and ammonium bicarbonate (02SC2181) or ammonium acetate (99H21), as a nitrogen donor, on neutral or better basic alumina and catalytic amount of DMF to give upon MW irradiation good yields of **356** ($R = Ar$, $R^1 = H$) within very short time (99H21). The reaction can



Scheme 69

also take place under conventional heating using acetic acid and ammonium acetate (04MI511). Alternatively, ammonium hydroxide was used instead of ammonium acetate under conventional heating to give **356** (95JHC235).

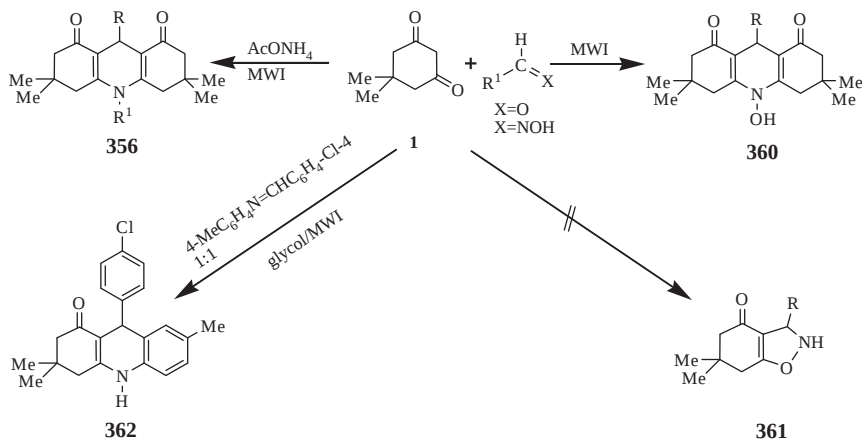
MW irradiation of dimedone with aromatic or aliphatic aldehydes or their oxime derivatives and ammonium acetate either without solvent or in glycol or ethanol afforded the acridines **356** ($R^1 = H$) (01CHE506, 02MI37, 02MI313, 03IJC(B)3145, 04SC1289, 04JHC767, 04CHE475, 06BCJ454). The TEBA chloride in water (04MI430) and inorganic solid support without solvent catalyzed the reaction (05HAC138).

Ionic liquids catalyzed one-pot condensation of dimedone, aromatic aldehyde, and ammonium acetate under MW to give **356** ($R^1 = H$) (05JCR600, 06MI874). However, when dimedone and oxime derivatives were MW irradiated in glycol and in the absence of ammonium acetate, *N*-hydroxyacridines **360** were obtained instead of the expected product **361** (04SL255). Alternatively *N*-hydroxyacridines **360** ($R = Ar, Et$) were obtained when the three components dimedone, aromatic or aliphatic aldehyde, and hydroxylamine hydrochloride were MW irradiated in glycol (04AX(E)01677, 05MI255) or by using TEBA chloride as a catalyst in H_2O (05MI1223).

A cascade reaction of Schiff's base such as 4-MeC₆H₄N:CHC₆H₄Cl-4 with dimedone in the ratio 1:2 or 1:1 in glycol under MW irradiation gave the acridines **356** and **362**, respectively. When NH₄OAc was added to the reaction system, the *N*-unsubstituted acridine was obtained. A possible mechanism involved the breaking and formation of new bond between carbon and nitrogen atoms (06MI58, 07JHC83).

Condensation of **1**, aromatic aldehydes and substituted acetophenone in the presence of NH₄OAc under MW irradiation in DMF gave the acridines **356** ($R = Ar, R^1 = H$) instead of the expected 2,4-diaryl-7,7-dimethyl-1,4,5,6,7,8-hexahydroquinolin-5-one (07TL1369) (Scheme 70).

Direct condensation of dimedone with urea, mono or diarylurea in formic acid afforded the hydrogenated acridine-1,8-dione derivatives **356** ($R = H$) (89ZOR1579, 94JOU1109). Alternatively, they were obtained when dimedone was reacted with arylidene *bis*-ureas in glacial acetic acid (91ZOR859). 9,10-Disubstituted acridines **356** ($R^1 = Ph, R = Ar$) were obtained from the condensation of dimedone with diarylurea and aromatic aldehydes in formic acid (94JOU1109). Condensation of **1** with urea and a series of aliphatic and aromatic aldehydes in acetic acid afforded the respective 9-substituted acridines **356** ($R^1 = H$) (91ZOR855). In case of using acetaldehyde the octahydro derivative **363** rather than **356** ($R^1 = H, R = Me$) was obtained. Diarylureas underwent a reverse thermal and catalytic dissociation to give aryl isocyanates and arylamines, which can act as heterocyclizing agents in the reaction of **1** with diarylureas, where arylamines were more likely to be the



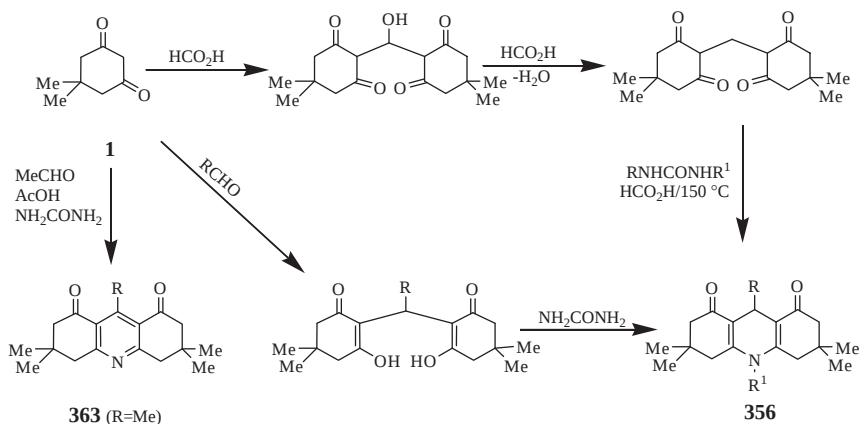
Scheme 70

heterocyclizing agents (89ZOR1579). In contrast, the reaction of **1** with methylurea in formic acid led to a mixture of acridines **356** ($\text{R}^1 = \text{H}$) and **356** ($\text{R}^1 = \text{Me}$) in a ratio 1:3 whereas with symmetrical dimethylurea gave only **356** ($\text{R}^1 = \text{Me}$) (91ZOR855); the reaction took place through the intermediate formation of *bis*-dimedonyl methane.

When reaction of dimedone with urea, phenylurea, aniline, benzyldeneaniline, or benzyldenebenzylamine was carried out in the presence of dimethyl or diethylsulfoxide, the acridine-1,8-dione derivatives **356** ($\text{R} = \text{H}$, $\text{R}^1 = \text{H}$, Me, Ph, Ar) were obtained (91ZOR223, 91ZOR1519). Compound **356** ($\text{R}^1 = \text{H}$, $\text{R} = 9\text{-ethylcarbazol-3-yl}$) was obtained from reaction of **1** with 9-ethyl-3-formylcarbazole and urea (98MI113). The 10-phenyl-acridine **356** ($\text{R}^1 = \text{Ph}$, $\text{R} = \text{H}$) was obtained from reaction of **1** and phenyl isocyanate or aniline in formic acid (89ZOR1579); the possibility that aniline has acted as heterocyclizing reagent cannot be ruled out (94JOU1109), as a result of hydrolysis of phenyl isocyanate by traces of water or as a result of reaction with formic acid and subsequent decarboxylation (Scheme 71).

The octahydro derivative **363** ($\text{R} = \text{H}$) was prepared from the reaction of enamine **31** ($\text{R} = \text{H}$) with triethyl orthoformate (75ZN(B)249), but **356a** ($\text{R}^1 = \text{COOH}$) was obtained from reaction of **31** ($\text{R} = \text{Ph}$) with glyoxalic acid (85JCR(S)244). The acridines **356** ($\text{R}^1 = \text{H}$, Me, $\text{R} = \text{Me}$, Ph) were obtained when **31** ($\text{R} = \text{H}$, Me) was treated with either acetaldehyde or benzaldehyde in ethanol and dilute hydrochloric acid (71JCS(C)2699).

Green syntheses of unsymmetrical 9,10-diarylacridine-1,8-dione and indenoquinoline were accomplished by the reaction of 3-anilino-5,5-dimethylcyclohex-2-enones **31** ($\text{R} = \text{Ph}$), aromatic aldehydes and 1,3-dicarbonyl compounds in the ionic liquid medium $[\text{bmim}^+][\text{BF}_4^-]$. A possible mechanism of the reaction *via* Knoevenagel condensation and



Scheme 71

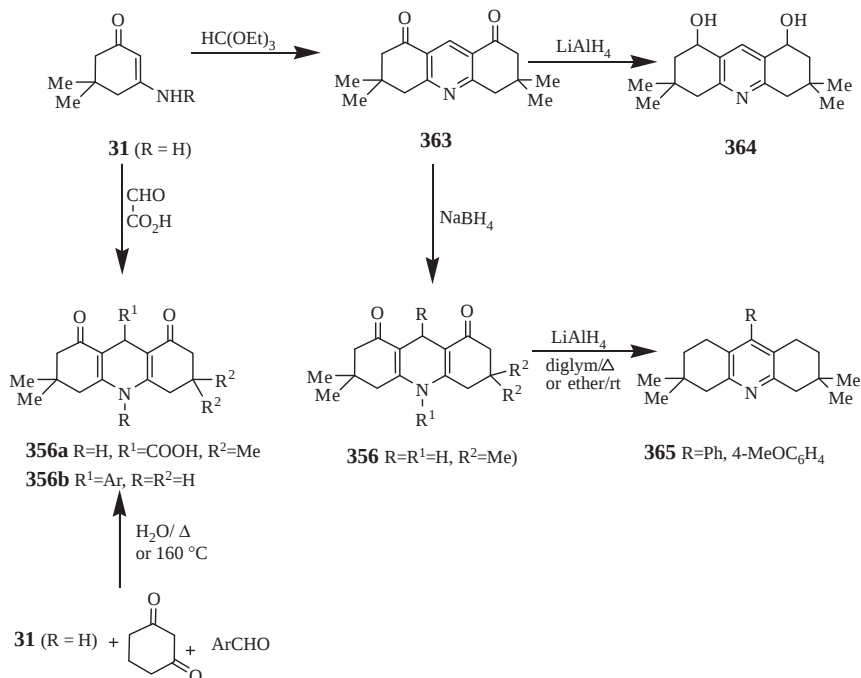
Michael addition was reported and the crystal structure of an acridinedione, and an indenoquinoline were presented (06S4187).

Unsymmetrical acridines **356a** were obtained when equimolar amounts of enamine **31** ($\text{R} = \text{H}$, Me , $4\text{-MeC}_6\text{H}_4$), aromatic aldehydes and 1,3-cyclohexanedione were allowed to react in water under reflux for 3–10 h, however, comparable yields were achieved when the reaction mixture was heated for 2–5 min at 160°C under solvent-free conditions (06GC1080). The structure of the product was confirmed by X-ray crystallography.

Reduction of **363** with NaBH_4 gave **356** ($\text{R} = \text{R}^1 = \text{H}$) as a result of reduction of the pyridine ring (61IZV223), but its reduction with LiAlH_4 afforded octahydroacridinediol **364** (99KGS774). In contrast, reduction of **356** ($\text{R} = \text{H}$, Ph , $4\text{-MeO-C}_6\text{H}_4$) with LiAlH_4 in boiling diglyme or in ether at room temperature gave octahydroacridine derivatives **365** (03CHE1029) (Scheme 72).

A series of 9-(aryl)acridines have been synthesized by reaction of ethyl(arylmethylene)(cyano) acetate with dimedone in AcOH and in the presence of ammonium acetate (05MI76).

A number of papers dealt with the X-ray analysis of acridines (05AX(E)02570, 06AX(E)01326, 06AX(E)0226, 05AX(E)02296, 05MI131). The X-ray analysis of **356** ($\text{R} = m\text{-nitrophenyl}$) revealed a boat conformation for the dihydropyridine ring and envelope conformation for the cyclohexenone ring (07MI54). Structures of **356** ($\text{R}^1 = \text{H}$, $\text{R} = \text{Aryl}$) and **356** ($\text{R}^1 = \text{OH}$, $\text{R} = \text{Aryl}$) were also confirmed by X-ray diffraction study (04MI91, 04SL255, 04SC1289). X-ray crystallography of **356** ($\text{R}^1 = \text{Ph}$, $\text{R} = 4\text{-Cl-C}_6\text{H}_4$) revealed that the 1,4-dihydropyridine ring adopted a boat conformation and the other two partially saturated six-membered rings adopt half-chair conformations (03AX(E)01139). In another report,



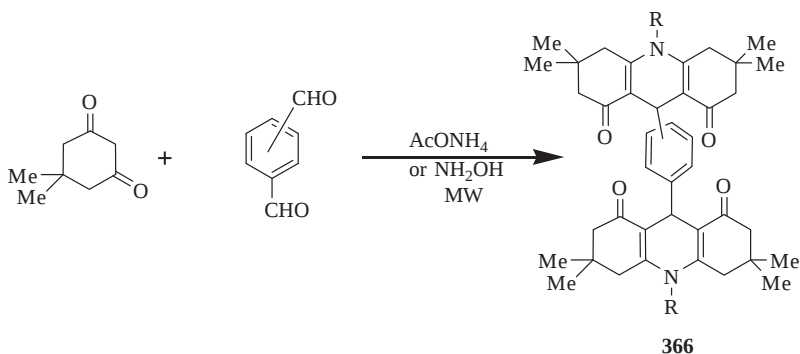
Scheme 72

the X-ray analysis of **356** ($R^1 = \text{H}$, $R = 4\text{-Cl-C}_6\text{H}_4$) showed that the dihydropyridine plane has approximately bisected by the plane of the orthogonal phenyl ring and the two fused rings are in the same boat main plane (01AX(E)0383). In contrast, the central dihydropyridine ring in the 9-(4-pyridyl) derivative **356** ($R^1 = \text{H}$, $R = 4\text{-pyridyl}$) adopted a flattened boat conformation while the outer cyclohexene rings adopted sofa conformations (03AX(E)0659). X-ray of **356** ($R^1 = \text{OH}$, $R = \text{Et}$) showed that dihydropyridine ring adopt boat conformation whereas cyclohexanone rings were in an enveloped conformation (05MI255). The X-ray crystallographic data of 9-(2-chlorophenyl)-1,2,3,4,5,6,7,8,9,10-decahydro-3,3,6,6-tetramethylacridine-1,8-dione showed that the dihydropyridine ring adopted a half-chair conformation (06AX(E)02380).

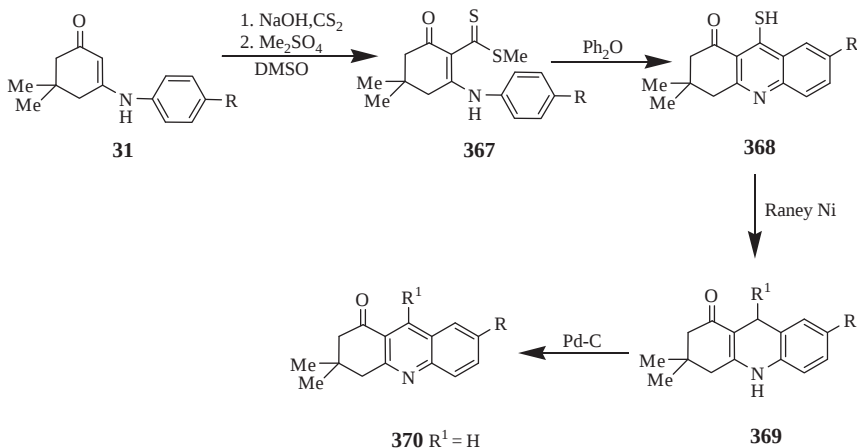
Bifunctional acridine derivative **366** ($R = \text{H}$) has been synthesized by condensation of tere- or iso-phthalaldehyde with dimedone in the presence of ammonium acetate under MW irradiation (04BMCL1533, 04SC2617) (Scheme 73). The *N*-hydroxyacridine **366** ($R = \text{OH}$) has been synthesized by using hydroxylamine instead of ammonium acetate (04SC2617, 04MI950). X-ray analysis of an example of **366** revealed that the dihydropyridine and cyclohexenone rings adopt half-boat conformation (04AX(E)02022).

Tetrahydroacridine thiols **368** were obtained from the enaminodithiocarboxylates **367**, readily available from enamine **31**, upon boiling in diphenyl ether. Desulfurization of **368** with Raney nickel in ethanol afforded **369** ($R^1 = H$), which were dehydrogenated to give **370** (91JHC1245) (Scheme 74).

Solvent-free BiCl_3 or trifluoroacetic acid promoted the synthesis of the acridines **370** ($R^1 = \text{Ar}$) when 2-aminoaryl-ketone or aldehyde were condensed with dimedone at 60–90 °C (06MI289, 07SC629). At room temperature, the reaction was catalyzed with either $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (06TL813), $\text{Bi}(\text{OTf})_3$ (04SL963), or $\text{SnCl}_3 \cdot 2\text{H}_2\text{O}$ (05CL314). The reaction was also done in aqueous hydrochloric acid to give **371** ($R^1 = \text{Ar}$) (06TL1059). Similarly, the condensation was done in the presence of



Scheme 73



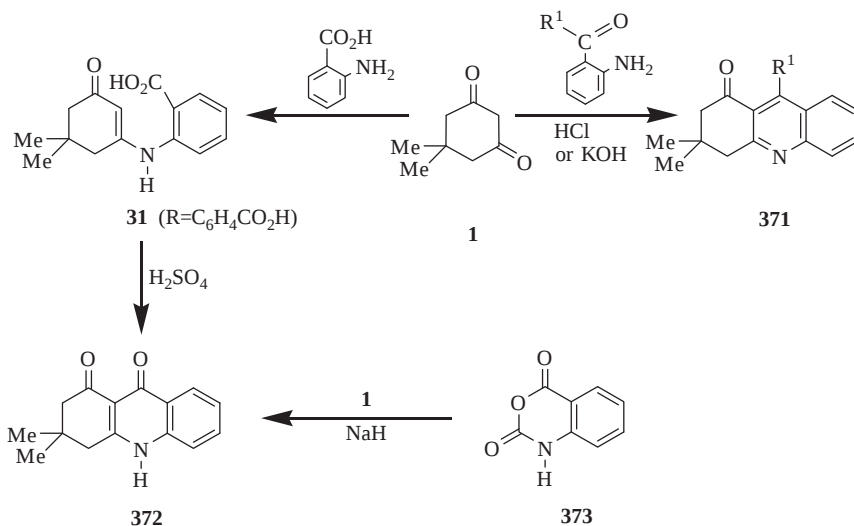
Scheme 74

sulfamic acid as recyclable catalyst without solvent (05TL7249), catalytic amount of $\text{Yb}(\text{OTf})_3$ (05TL1647), neodymium nitrate (06S3825), or KHSO_4 (06JHC1379). Condensation of **1** with *o*-aminobenzaldehyde in the presence of potassium hydroxide afforded 3,3-dimethyl-1-oxo-tetrahydro-acridine **371** ($\text{R}^1 = \text{H}$) (32MI141). In contrast, the reaction with anthranilic acid gave the enamine **31**, which upon dehydration with sulfuric acid gave 3,3-dimethyl-1,9-dioxo-1,2,3,4,9,10-hexahydro-acridine **372** (60MI180). The latter acridone was also synthesized by the reaction of isatoic anhydride **373** with **1** in the presence of sodium hydride (86GEP835) (Scheme 75).

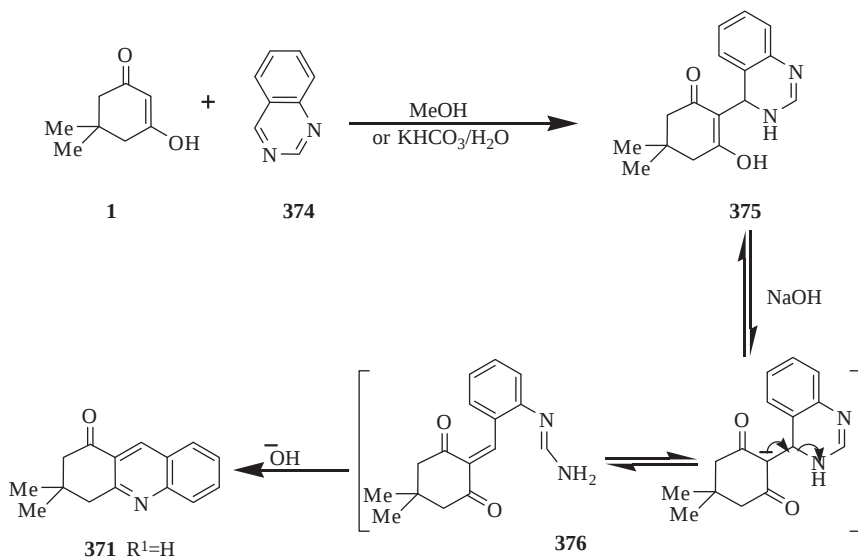
A carbon–carbon bond can be generated between C-2 of **1** and C-4 of quinazoline **374** to yield the addition product **375**, which could be cyclized with sodium hydroxide to give 3,3-dimethyl-1-oxo-1,2,3,4-tetrahydroacridine **371** *via* a possible intermediate **376** (73JCS(P1)1794) (Scheme 76).

Heating either the dimedonylmethane **377** or 9-aryloctahydro-xanthene **58** with ammonia at 130–150 °C led to the formation of pyrrolo-acridine **378**. But, at lower temperature, 90–120 °C, the tetrahydroindoles **379** were initially formed which can be converted to **378** (88CHE417) (Scheme 77).

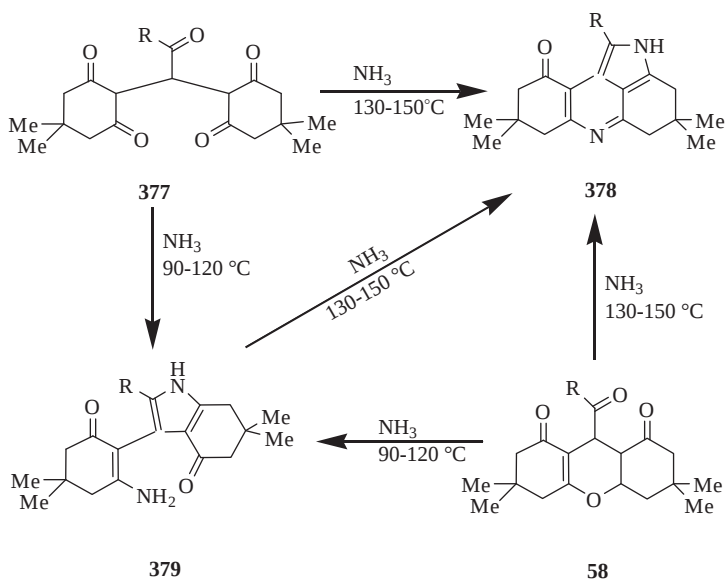
Photoirradiation of the bromobenzyl-enamine **380** ($\text{R} = \text{H}$) in a solution of dioxan-acetonitrile containing triethylamine gave the dihydrophenanthridine **381** (78CC766), which was also obtained when **380** was treated with lithium diethylamide (LDEA) in THF (78JA3598). Under the same conditions, the *N*-ethyl derivative **380** ($\text{R} = \text{Et}$) gave the



Scheme 75



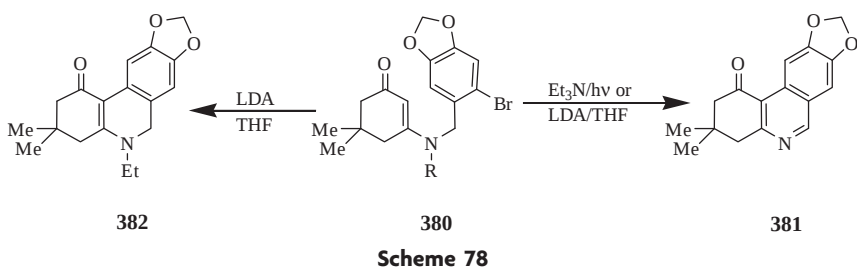
Scheme 76



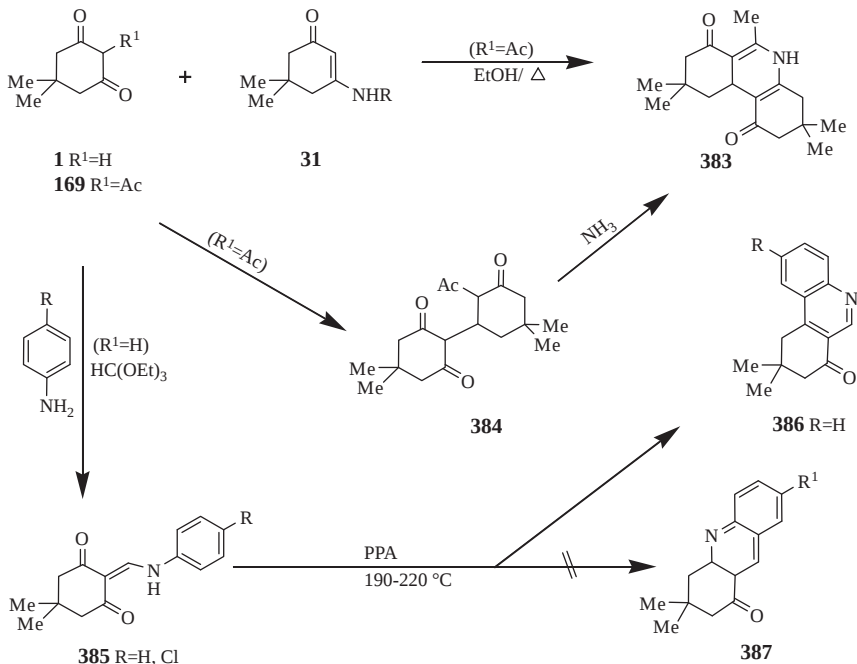
Scheme 77

phenanthridine **382** (78JA3598), through a benzyne intermediate (79JOC1074) (Scheme 78).

Reaction of 2-acetyl-5,5-dimethyl-cyclohexandione **169** ($R^1 = \text{Ac}$) with enaminone **31** ($R = \text{H}$) in refluxing ethanol afforded the phenanthridine-1,7-dione **383** (90KGS66). Alternatively, **383** was obtained from bicyclic tetraketone **384** on treatment with ammonia (83ZOR2322). The 9,10-dihydrophenanthridine **386** rather than the rearranged product **387** was obtained by thermolysis of 2-arylaminomethylene derivative **385**, obtained from the reaction of dimedone and arylamine in the presence of triethyl orthoformate and polyphosphoric acid (77S723, 96JHC905) (Scheme 79).



Scheme 78



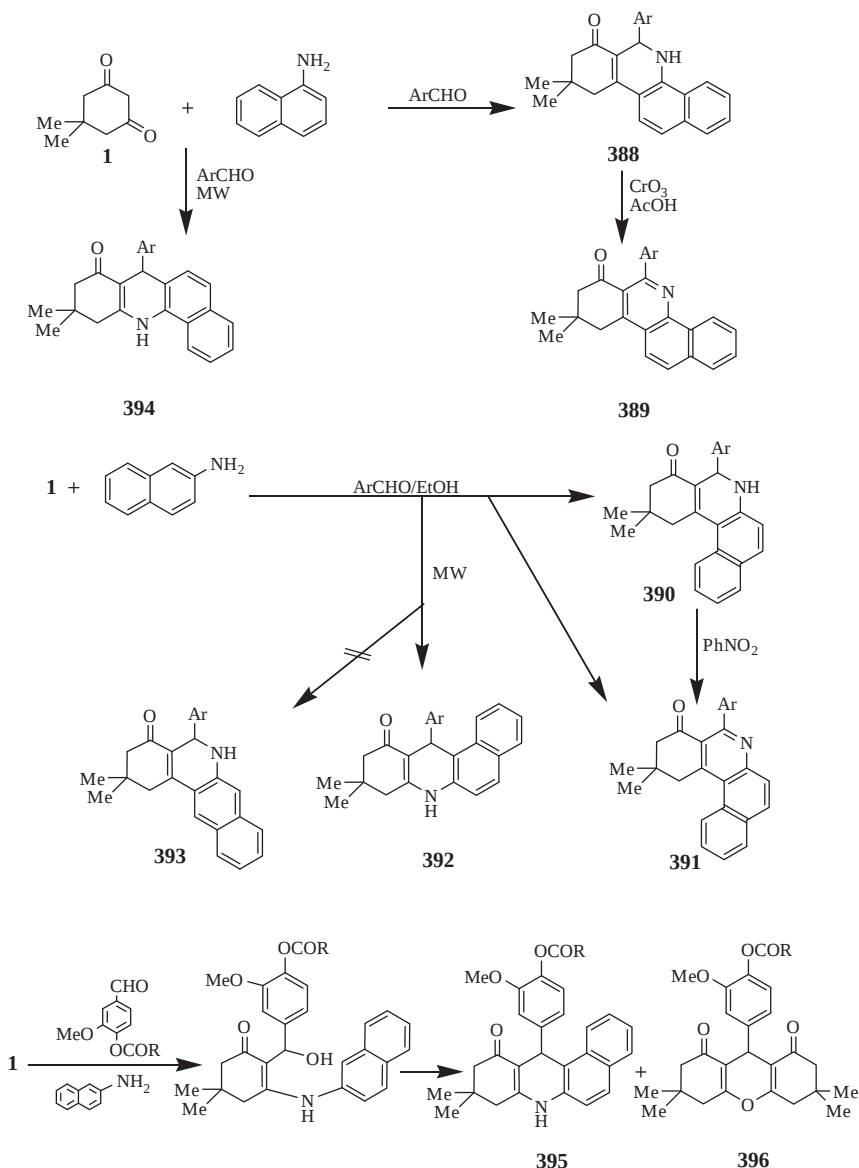
Scheme 79

Heating aromatic aldehydes with equimolar amounts of 1-naphthylamine and **1** gave the respective hexahydrobenzo[*a*]phenanthridines **388**. Oxidation of **388** with CrO₃ in AcOH gave the corresponding dehydro derivatives **389** (71MI39). In contrast, reaction of 2-naphthylamine with aromatic aldehyde and dimedone gave the benzo[*a*]phenanthridin-4-one **390** or its dehydro derivative **391** depending upon the substituent on the aromatic ring of the aldehyde. Thus, the aldehydes that carry *o*-, *m*-, or *p*-nitro groups led to the formation of **391**, whereas those carrying *p*-dialkylamino groups led to **390** (69MI193, 69MI197) (Scheme 80). However, reaction of 2-naphthylamine, and 1-naphthylamine with aromatic aldehydes and **1** under MW irradiation (06JHC1621) gave benzo[*a*]acridine derivatives **392**, rather than the benzophenanthridine **393**, and hexahydrobenzo[*c*]acridine **394**, respectively (90JHC363).

The reaction of long-chain vanillyl ester aldehydes with 2-naphthylamine and **1** afforded the benzo[*c*]acridines **395** (04MIb79, 05RJGC617) along with xanthene **396** (05RJGC617) (Scheme 80). The condensation using vaniline ester of substituted benzoic acid afforded hexahydrobenzo[*a*]acridines (06RJOC266). The condensation of 2-hydroxy[1,1',3',1'']terphenyl-5-carbaldehyde with 2-naphthylamine and **1** gave 7,8,9,10,11,12-hexahydrobenzo[*a*]acridin-11-ones (06RJOC107). In contrast, the three-component condensation of dimedone, 2-naphthylamine, and formaldehyde in alcohols under mild conditions gave high yields of the *N*-(alkoxymethyl)benzo[*f*]quinoline derivatives having a substituted 2-azaspiro[5.5]undecane fragment (06RJOC855).

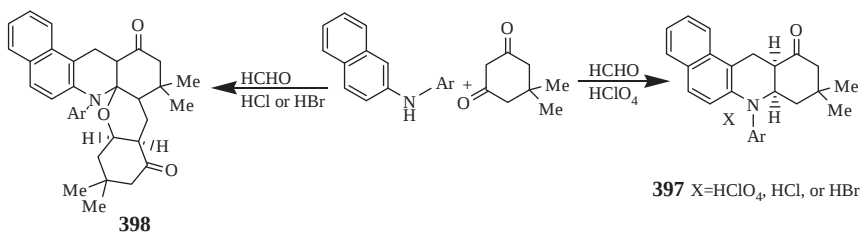
Reaction of *N*-aryl-2-naphthylamine with formaldehyde and dimedone in the presence of perchloric acid gave regioselectively the angular 7-aryl-9,9-dimethyl-11-oxo-8,9,10,11-tetrahydrobenzo[*a*]acridine perchlorates **397** (80ZOR1875). In contrast, when the reaction was carried out in the presence of hydrochloric acid or hydrobromic acid, appreciable amount of chromeno[2,3-*q*]benzoacridine **398** was obtained in addition to the respective salts of **397** (90KGS1230) (Scheme 81).

A synthesis of 10,10-dimethyl-7-aryl-7,9,10,11-tetrahydro-9H-benzo[*c*]acridin-8-ones **394** was accomplished in high yield *via* the reaction of arylidene derivatives or 1-naphthylamine **399** with **1** in aqueous medium catalyzed by TEBA chloride (05TL7169, 06ARK117, 06JHC989). Similarly, the reaction of arylidene-2-naphthylamine **400** afforded hexahydrobenzo[*a*]phenanthridines **390** that upon boiling in nitrobenzene gave **391** (68MI67). However, the benzo[*a*]acridine **390a** was resulted as product under the same reaction conditions (05TL7169). It was assumed that the first step involved the addition of methylene group of dimedone to the azomethine C=N bond to form the intermediate amino-diketone **401** that cyclized upon losing a molecule of water (68MI67, 96CHE30) (Scheme 82).

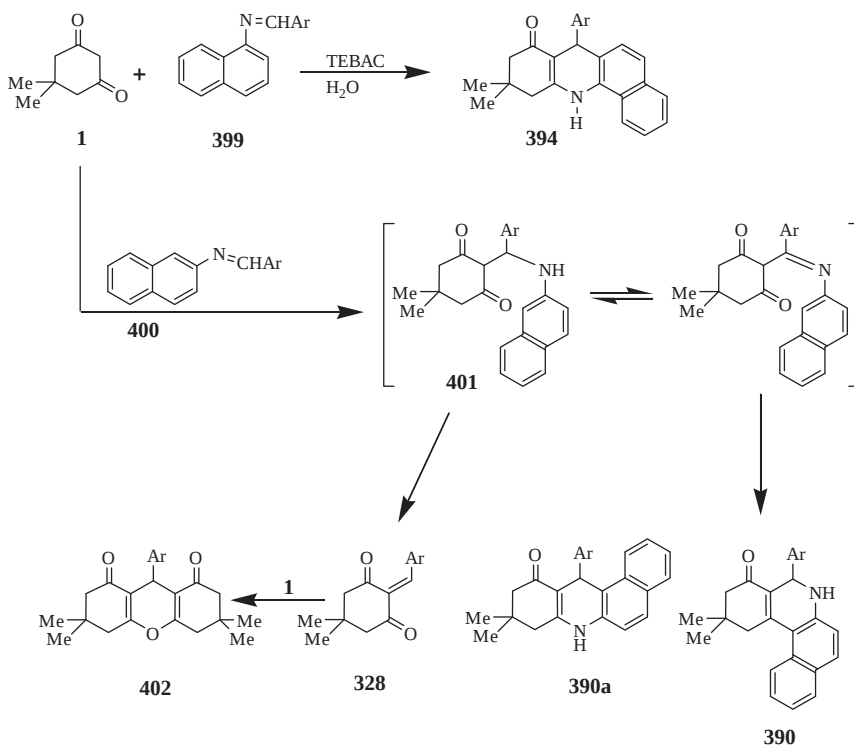


Scheme 80

The condensation of the *o*-hydroxyarylidene-2-naphthylamines **400** ($\text{Ar} = o\text{-HOC}_6\text{H}_4$) with **1** gave the octahydro-xanthene **402** along with the benzo[*a*]phenanthridines **390**. It was assumed that the *ortho*-hydroxyl group caused a steric hindrance toward cyclization of the intermediate amino-diketone **401** as a result of which it underwent fission to give



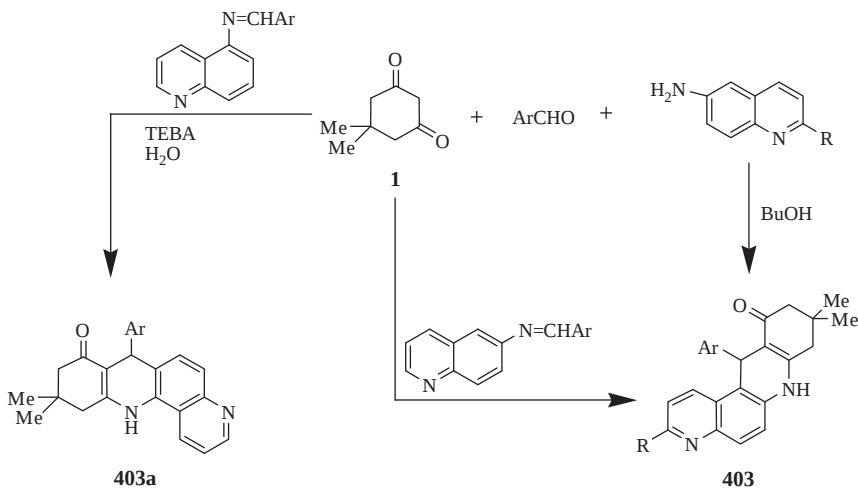
Scheme 81



Scheme 82

2-naphthylamine and α,β -unsaturated ketone **328**. Subsequent condensation of the latter with **1** gave the xanthenes **402** (96CHE30) (Scheme 82).

The synthesis of hexahydrobenzo[*a*]phenanthrolin-9-ones **403** were similarly achieved by condensation of 6-aminoquinolines with aromatic aldehyde and **1** (01RJOC1495, 04RJOC705, 04RJOC1662) (Scheme 83). Alternatively, they were obtained by condensation of 6-(arylideneamino)-quinoline with **1** (01RJOC1495), whereas in the presence of TEBA in water the pyrido[2,3-*c*]acridine **403a** was obtained (05TL7169). When the



Scheme 83

vaniline ester of substituted benzoic acids, were used, the hexahydrobenzo[*b*][4,7]phenanthrolines were obtained (06RJOC266). Partially hydrogenated benzo[*b*][4,7]phenanthrolines were prepared by condensation of 6-aminoquinoline with formaldehyde and **1** and subsequent oxidative dehydrogenation (06RJOC1388).

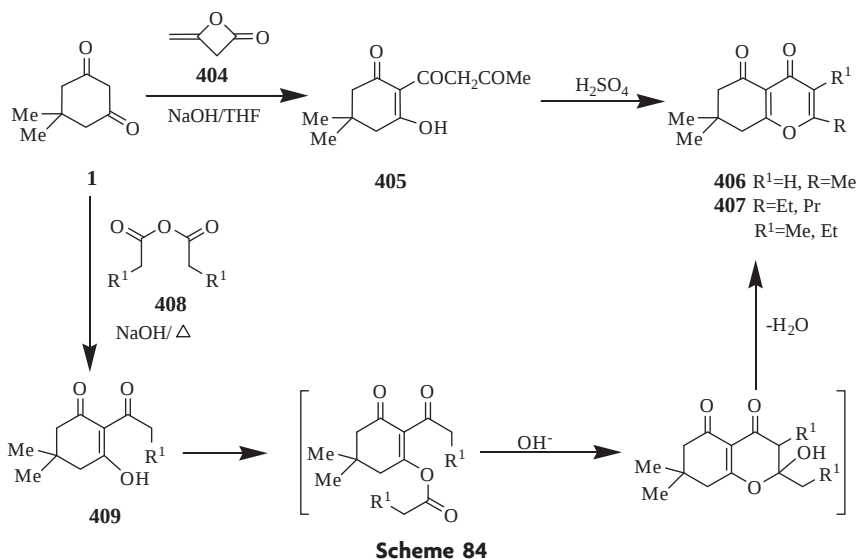
Oxidation of 1,3-diphenyl[4,7]phenanthroline with potassium permanganate in alkaline medium resulted in transformation of the 4,7-phenanthroline ring system into 1,8-diazafluorenone. Oxidation of 12-aryl-9,9-dimethyl-8,9,10,12-tetrahydro-7H-benzo[*b*][4,7]phenanthroline-11-ones, resulting from the condensation of 6-arylmethyleneaminoquinolines and **1** with sodium nitrite in acetic acid led to 12-aryl-9,10-dihydro-8H-benzo[*b*][4,7]phenanthroline-11-ones (04RJOC1322) (Scheme 83).

Aromatization of 9-(2-nitrophenyl)tetrahydroacridine 1,8-dione **356** ($R = 2\text{-NO}_2\text{-C}_6\text{H}_4$, $R^1 = \text{H}$) with active MnO_2 afforded **363** ($R = 2\text{-NO}_2\text{-C}_6\text{H}_4$), which on reductive cyclization with Fe/HCl gave 3,3,7,7-tetramethyl-1,3,4,5,5a,6,7,8-octahydroquino[2,3,4-*kl*]acridine (05SC1781).

6.3 Annulation with pyran

6.3.1 Synthesis of benzopyrans

Reaction of **1** with diketene **404** in the presence of sodium hydroxide in tetrahydrofuran gave 2-acetoacetyl dimedone **405**. Cyclization of which to the benzopyran-4,5-dione **406** was performed with acid (73CPB1840).

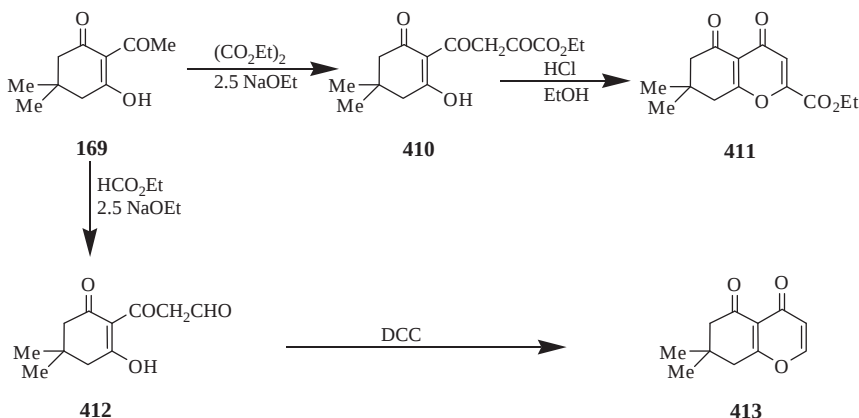


Acylation of **1** with acid anhydrides **408** in the presence of sodium hydroxide gave the expected 2-acyl derivatives **409** as major products and the pyran derivatives **407** as the minor ones. The formation of the pyrans **407** have been explained to proceed by O-acylation of the initially formed **409** followed by an intramolecular base catalyzed aldol condensation and loss of H₂O (75TL2491) (Scheme 84).

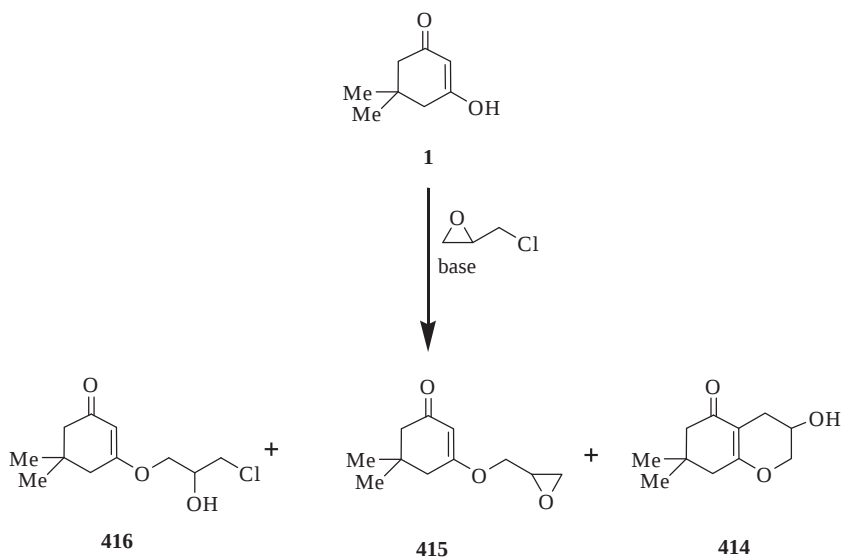
Carbethoxycabonylation and formylation of the disodium salt of 2-acetyldimedone **169** gave the corresponding tetracarbonyl derivatives **410** and **412**, whose dehydrative cyclization gave the corresponding tetrahydrobenzopyrans **411** and **413** (72JOC1337) (Scheme 85).

Alkylation of dimedone with chloromethyloxirane in basic medium afforded hexahydrobenzo[*b*]pyran **414** along with the expected alkylation products **415** and **416** (89IJC(B)316) (Scheme 86).

Reaction of an α,β -unsaturated acid chloride with the anion of **1** gave either the enol ester **417** when the acid chloride was used in excess whereas in the presence of excess anion, the product was 4,6,7,8-tetrahydro-2H-1-benzopyran-2,5-(3H)-diones **418** (69JHC917). Reaction of **1** with Meldrum's acid **416** and aldehydes under MW without catalyst afforded **418** (R = Ar) (01SC3729), whereas the 4-aryl derivatives of **418** were resulted when the reaction was catalyzed by TEBA chloride (03AX(E)01265, 03JCR(S)674) or hexadecyltrimethyl ammonium bromide (04JCR457) as catalyst in water and also under solvent-free conditions using grinding (07SC183). Alternatively, **418** could be synthesized from reaction of **1** with the alkylidene derivative of Meldrum's acid **420** (64M53), which can be catalyzed by TEBA (04MI43).



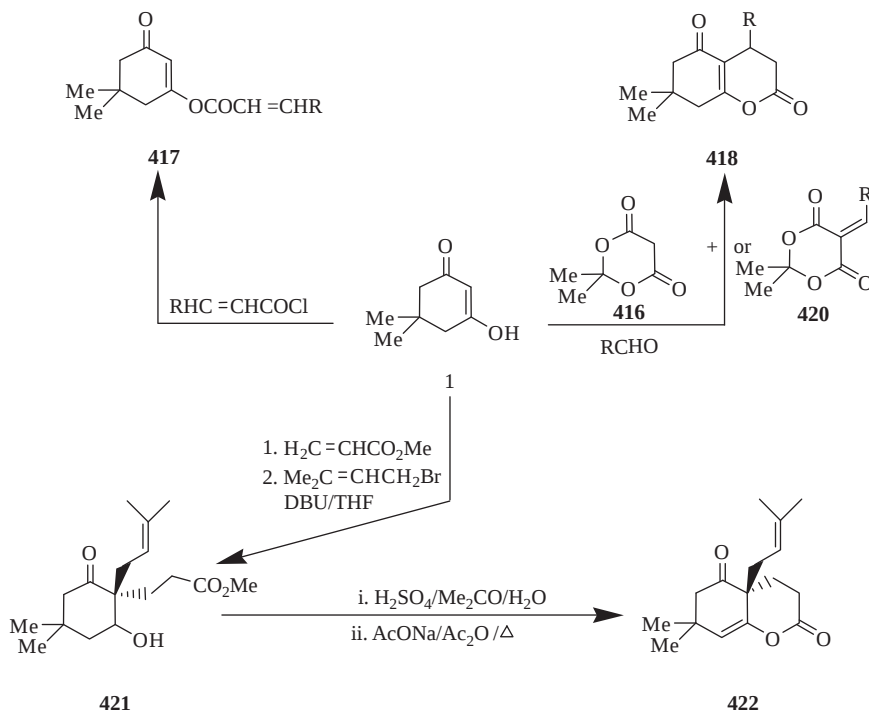
Scheme 85



Scheme 86

Sequential addition of methylacrylate and prenyl bromide to **1** in the presence of DBU furnished the *bis*-alkylated derivatives **421**. Hydrolysis of which to the respective acid followed by enol-lactonization gave **422** (06TL689) (Scheme 87).

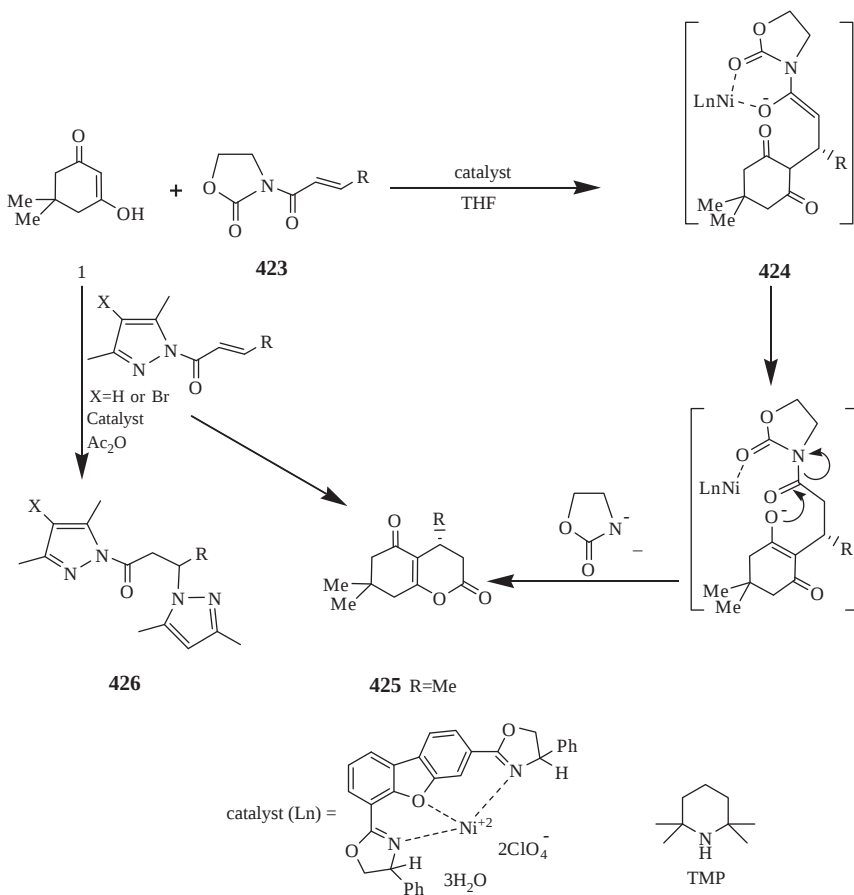
Enantioselective addition of 3-crotonyl-2-oxazolidinone **423** to **1** under double catalytic conditions using 2,2,6,6-tetramethylpiperidine (TMP) and R,R-complex of nickel(II) perchlorate hexahydrate in THF



Scheme 87

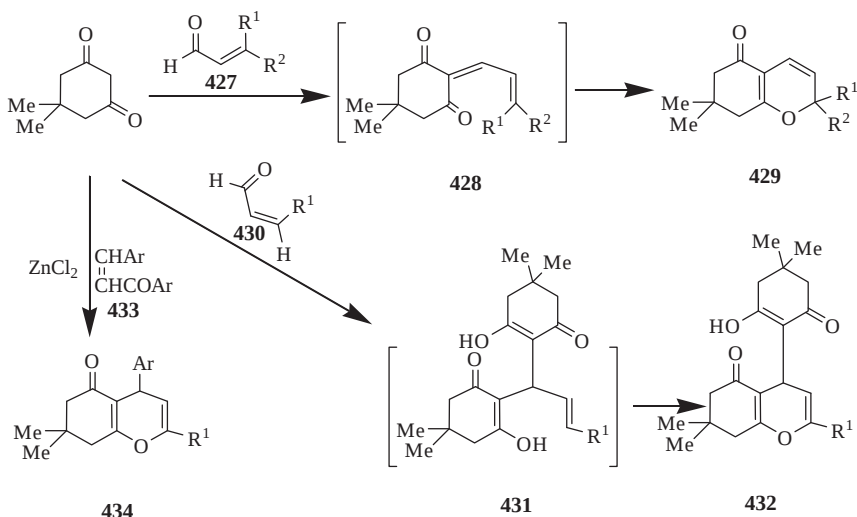
afforded **425** through the Michael adduct anion **424** that subsequently cyclized with splitting of 2-oxazolidinone auxiliary (**05OL979**). Using 1-crotonyl-3,5-dimethylpyrazole under the same reaction conditions, afforded **425** in higher enantioselectivity but lower yield as a result of the formation of the undesired byproduct **426** (**05OL979**). The presence of acetic anhydride has prevented the formation of **426** and led to improved yield and enantioselectivity (**05OL979**). In contrast, 1-(2-alkenoyl)-4-bromo-3,5-dimethylpyrazoles under the same reaction conditions gave **425** ($\text{R} = \text{alkyl, aryl}$) in high yield and excellent enantioselectivity (**05OL979**). Also under double catalytic activation condition using nickel(II)perchlorate and TMP, dimedone was reacted with 4-bromo-1-crotonyl-3,5-dimethylpyrazole in THF to give **425** in good yield (**03TL1799**) (Scheme 88).

A synthesis of benzopyrans **429** was performed by condensation of disubstituted α,β -unsaturated aldehydes **427** with **1** (**75TL3407**); the firstly formed dienones **428** underwent valence isomerization to give the stable 2H-benzopyrans **429**. When the reaction was carried out at room temperature in pyridine, a small amount of **428** was isolated together with the major product **429** (**75TL3407**). When the monosubstituted



α,β -unsaturated aldehydes **430** were reacted with **1**, the benzopyrans **432** were formed through the intramolecular cycloaddition of the intermediate **431** (87ZOB935). Reaction of the α,β -unsaturated ketone **433** with dimedone in the presence of anhydrous ZnCl_2 afforded 2,4-disubstituted benzo[b]pyran **434** (02IJC(B)368, 05IJC(B)622). The pyran derivatives have been also synthesized by using indium trichloride as a catalyst under MW irradiation and solvent-free conditions (06CJC1054, 05MI886) (Scheme 89).

The 5,6,7,8-tetrahydro-7,7-dimethyl-2,5-dioxo-2H-1-benzopyran-4-carboxylic ester **435** was prepared from **1** and sodium diethyl oxalacetate in trifluoroacetic acid. Hydrolysis of the ester group in **435** gave **436** whose decarboxylation afforded the 7,8-dihydrobenzopyran **437** (72JOC1337).



Scheme 89

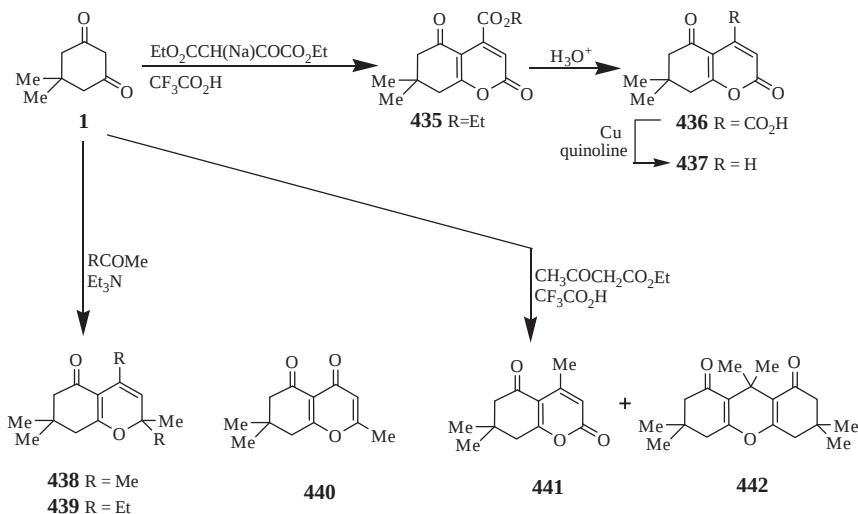
Condensation of **1** with acetone or ethylmethyl ketone in the presence of triethylamine afforded 2,2,4,7,7-pentamethyl- and 2,4-diethyl-2,7,7-trimethyl-5-oxo-2,6,7,8-tetrahydrobenzo[*b*]pyran **438** and **439**, respectively [89]JC(B)81].

With ethyl acetoacetate in the presence of trifluoroacetic acid dimedone gave the benzopyran **440** (69JOC2796). In another report, under the same conditions, the structure was found to be the benzopyran **441** together with the xanthene **442** (72JOC1337) (Scheme 90).

2-Amino-3,4-disubstituted-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydrobenzo[*b*]pyrans **281** were obtained by equimolar condensation of aldehydes, malononitrile, and dimedone under basic conditions (95JCR(S)178, 97CHE684, 98RJOC707, 99CHE1183). A green approach using water as a solvent has been recently reported for its synthesis (05TL6453, 07SC491). S-Proline (06SL263), rare earth perfluorooctanoate (06JFC97), 4-dodecylbenzenesulfonic acid (DBSA) (04MI1598), or hexadecyltrimethylammonium bromide (MIMAB) in water (04SL871) have been found to be efficient catalysts for the formation of **281**.

The synthesis of **281** (X = CN) from the same reactants was achieved by ultrasonic irradiation without catalyst (03MI488, 04MI562), and under MW irradiation in the presence of sodium bromide or piperidine under solvent-free conditions (04TL8625, 01MI742) as well as heterogeneous amines grafted on silica such as *N,N*-diethylamino-propylated silica (06H889).

Ionic liquids as reaction medium and promoter without any catalyst have been also used (04AJC1067, 06JHC685, 05MI1085).



Scheme 90

The condensation of dimedone with aromatic aldehydes and malononitrile was also performed under solvent-free and solid-state conditions using $\text{KF}/\text{Al}_2\text{O}_3$ (06IJC(B)470), TEBA chloride as catalysts in aqueous medium (04JCR821) to give **281** ($\text{R}^1 = \text{Aryl}$).

A range of tetrahydrobenzo[*b*]pyrans were synthesized in good yields under solvent-free conditions by grinding α -cyanocinnamionitriles or β -cyano- β -carbomethoxy styrene and **1** in the presence of TEBA (06SC2363).

Condensation of cinnamionitrile or arylidene malononitrile with dimedone under basic conditions afforded **281** (80ZOR2188, 89JPR971, 89ZOR1331, 98RJOC554, 03MI63). A high yield was reported in water in the presence of TEBA chloride as catalyst (03MI877). Rare earth perfluorooctanoate $[\text{RE}(\text{PFO})_3]$ such as $\text{Yb}(\text{PFO})_3$, $\text{La}(\text{PFO})_3$, and $\text{Sm}(\text{PFO})_3$, catalyzed such reaction to give good to high yields (06JFC97). Also the reaction with arylmethylene cyanoacetate was catalyzed by TEBA (05MI1570).

The $\text{KF}/\text{Al}_2\text{O}_3$ was used for the condensation of cyanoacetic ester, aromatic aldehydes, and dimedone at room temperature under ultrasound irradiation to give **281** ($\text{X} = \text{COOR}$) (04SC4565). In contrast, **281** ($\text{X} = \text{CN}$, $\text{R}^1 = \text{Ph}$) was obtained on MW irradiation of dimedone with **443** without catalyst under solvent-free conditions (02SC2137). The reaction was also achieved in DMF under MW (07SL480) or ultrasound irradiation (04MI562).

In contrast, when benzylidene malononitriles **443** ($\text{X} = \text{CN}$) were melted with dimedone in stoichiometric amounts without catalyst at 97–130 °C for 1 h, it gave **444** that afforded quantitative yields of **281**

($R^1 = \text{Ph}, 4\text{-OH-C}_6\text{H}_4, 4\text{-NO}_2\text{-C}_6\text{H}_4, 4\text{-Cl-C}_6\text{H}_4$) (03T3753). These compounds were previously obtained under catalysis with acids or bases in lower yields (01MI742, 02T953, 01MRC105, 86JOU1185, 96T14273, 89JPR971) even under MW irradiation for 6 min (01MI742). Alternatively, they were obtained on heating the mixture in ethylene glycol at 80 °C without catalyst (02MI393; 01MI505). Compounds **281** ($X = \text{CN}, \text{CO}_2\text{Me}, \text{CO}_2\text{Et}$, $R^1 = \text{aryl, hetryl}$) were also prepared from reaction of arylidene-malononitrile or cyano-3-aryl-1-acrylate with dimedone in DMF at room temperature using KF-alumina as catalyst (03SC119).

Cyclohexanecarboxaldehyde with dimedone afforded 1-benzopyrans such as 2-amino-4-cyclohexyl-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-1-benzopyran-3-carboxylic acid ethyl ester (06RJGC282).

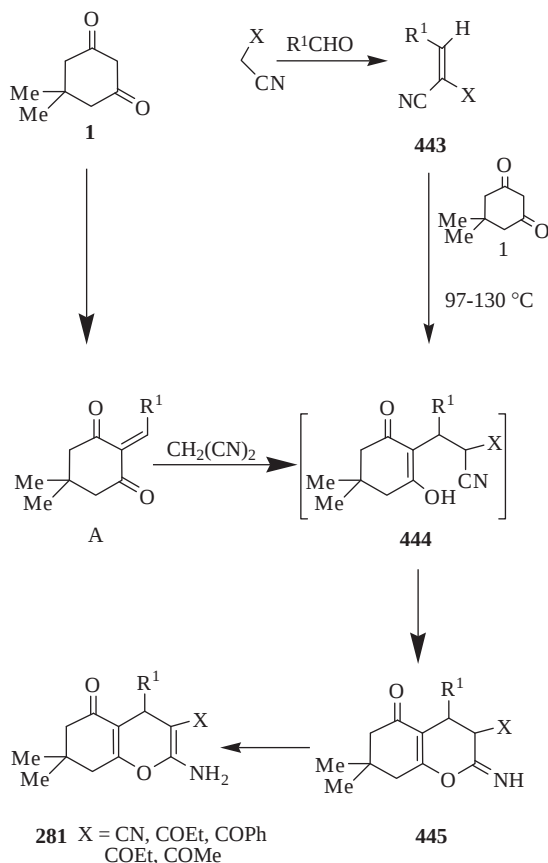
The electrochemical-induced catalytic multicomponent transformation of **1**, aldehydes and malononitriles in alcohols gave tetrahydro-4*H*-chromenes in high yields (06EJO4335).

Indolylbenzopyrans were prepared from indolecarboaldehydes, PhCH_2CN and **1**. These indoles showed antipyretic activity; the starting indoles have analgesic and anticonvulsant activity (04MI225).

When methyl 4-chloro- α -cyanocinnamate was condensed with dimedone, it afforded **281** ($X = \text{CO}_2\text{Me}$, $R = 4\text{-Cl-C}_6\text{H}_4$) in which the two six-membered rings adopted a boat and half-chair conformations with intramolecular hydrogen bonds in the crystal structure (02MI597). Compound **281** ($X = \text{CO}_2\text{Et}$, $R = 4\text{-F-C}_6\text{H}_4$) was obtained either by the condensation of 4-fluorobenzaldehyde with dimedone and ethyl acrylate or ethyl (4-fluorobenzylidene)cianoacetate and dimedone in water in the presence of TEBA (03MI46). Crystallographic data of this compound showed that the pyran ring adopted a boat conformation while the fused six-membered ring adopted a distorted boat conformation (03AX(E)01501). Crystallographic examination of 4-(3,4-methylenedioxyphenyl)-7,7-dimethyl-2,5-dioxo-3,4,5,6,7,8-hexahydrobenzo[*b*]pyran (02MI146) showed that both of the pyran and fused six-membered rings adopted distorted boat conformations (03AX(E)01265) (Scheme 91).

Syntheses and X-ray structural studies were carried out for the 2-amino-7,7-dimethyl-4-(1-naphthyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile where the heterocyclic ring has a flattened boat conformation. The fused cyclohexenone ring adopted a sofa conformation. Intermolecular $\text{N-H}\cdots\text{N}$ and $\text{N-H}\cdots\text{OH}$ bonds linked the molecules and a centrosymmetric dimer *via* $\text{N-H}\cdots\text{NH}$ bonds with only one H atom of NH_2 donor group taking part in H bonding (04AX(C)0334).

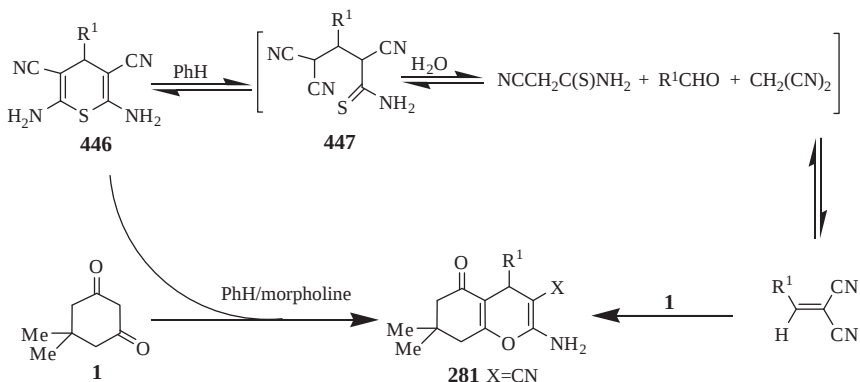
Reaction of **1** with the 4*H*-thiapyran **446** in benzene and in the presence of morpholine as a base afforded **281** ($R^1 = 4\text{-F-C}_6\text{H}_4$, 2-furyl, $X = \text{CN}$) (89ZOR1331). The thiapyran **446** underwent ring opening in benzene to give the intermediate **447**, which in water can form the aldehyde and malononitrile with the elimination of cyanothioacetamide.

**Scheme 91**

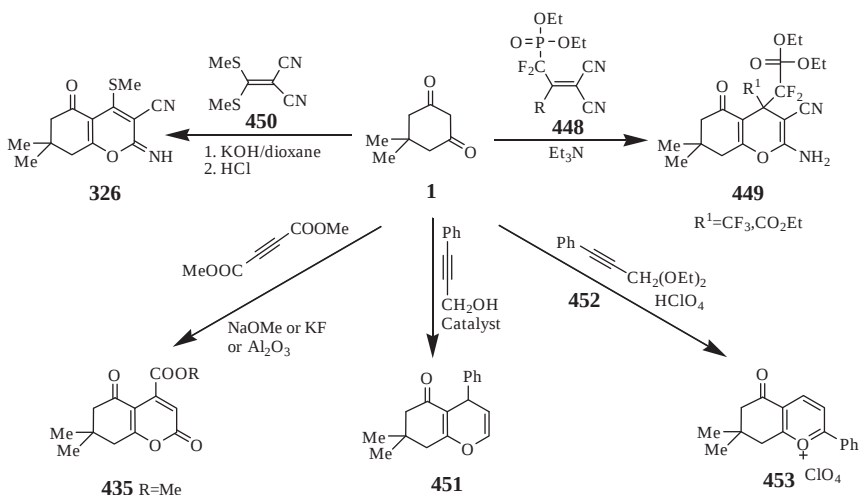
Subsequent reaction of the aldehyde with malononitrile gave the arylidenemalononitrile which upon reaction with dimedone afforded **281** (Scheme 92).

Reaction of alkenes **448** with **1** in the presence of Et_3N gave the benzopyran **449** (04JFC1853). When **1** was condensed with [bis(methylsulfanyl)methylidene]malononitrile **450** in the presence of potassium hydroxide in 1,4-dioxane, it gave 2-iminotetrahydrobenzopyran **326** (97JCR(S)256) (Scheme 93).

Michael addition of **1** to dimethyl acetylene dicarboxylate in the presence of sodium methoxide, potassium fluoride, or aluminum trioxide gave **435** ($\text{R} = \text{Me}$) *via* an intermolecular cyclocondensation (89MI87). Regioselective cycloaddition of propargylic alcohol and dimedone in the presence of thiolate-bridged diruthenium complex afforded the tetrahydrobenzo[*b*]pyran **451** (04JOC3408).



Scheme 92



Scheme 93

Cyclocondensation of **1** with 3,3-diethoxy-1-phenylpropyne **452** in the presence of HClO_4 gave the perchlorate **453** (90ZOR2609) (Scheme 93).

The dimethyl 2-(*tert*-butylamino)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3,4-dicarboxylate was synthesized by the reaction of *tert*-butyl isocyanide and dimethyl acetylenedicarboxylate with dimedone in cold CH_2Cl_2 . Its structure was established by X-ray analysis which revealed that it was stabilized by one intramolecular hydrogen bond and the pyran ring had a distorted boat conformation (05MI545).

Condensation of **1** with 2,3-disubstitutedamino-propenoates **454** or *N*-(2,2-dicyanoethenyl)-2,2-dimethylaminoethyl)aminoacetonitrile in acetic

acid gave tetrahydrobenzo[*b*]pyrans **456** *via* the intermediate **455**, which was cyclized without isolation (97HCA2418, 97JHC247, 97JHC263, 97JHC813, 98T9799, 99JHC225, 90JHC1021, 01ARK85, 05H207, 06JOC95, 06RJOC1380).

Reaction of **1** with triethoxymethane and various ureas afforded 2-ureidomethylenes **457**, which were reacted with activated acetonitriles in the presence of a strong base to give 5-oxo-5,6,7,8-tetrahydrobenzo[*b*]pyrans **458** (81S225).

Reaction of *N*-methyl-2-pyrrolidine diethylacetal with 2-aminomethylene-dimedone **457** ($R = R^1 = H$ or Me) afforded the dienediamine **459**, which on heating in dilute hydrochloric acid gave 7,7-dimethyl-3-(β -methylamino)ethyl-5,6,7,8-tetrahydrobenzo[*b*]pyran-2,5-diones **460** (87KGS1477).

The spiro compound **461** was obtained by condensation of isatin, malononitrile, and dimedone (95JCR(S)178) (Scheme 94).

A synthesis of 3-benzoylamino-5,6,7,8-tetrahydrobenzopyran-2,5-dione **456** ($R = \text{NHCOPh}$) was carried out using equimolar ratios of dimedone, hippuric acid, and one carbon synthon such as triethyl orthoformate, diethoxymethylacetate, or *N,N*-dimethylformamide dimethylacetal in the presence of excess acetic anhydride (89SC1713). Similarly, the *N*-(isonicotinoyl)glycine was reacted with **1** and one carbon synthon $\{\text{CH}(\text{OEt})_3, \text{MeCO}_2\text{CH}(\text{OEt}_2) \text{ or } \text{Me}_2\text{NCH}(\text{OMe})_2\}$ in acetic anhydride to give **456** ($R = \text{NHCOPy}$) *via* the mechanism shown in the scheme. Its reaction with nitrogen nucleophile gave the quinolines **462** (97JHC1753) (Scheme 95).

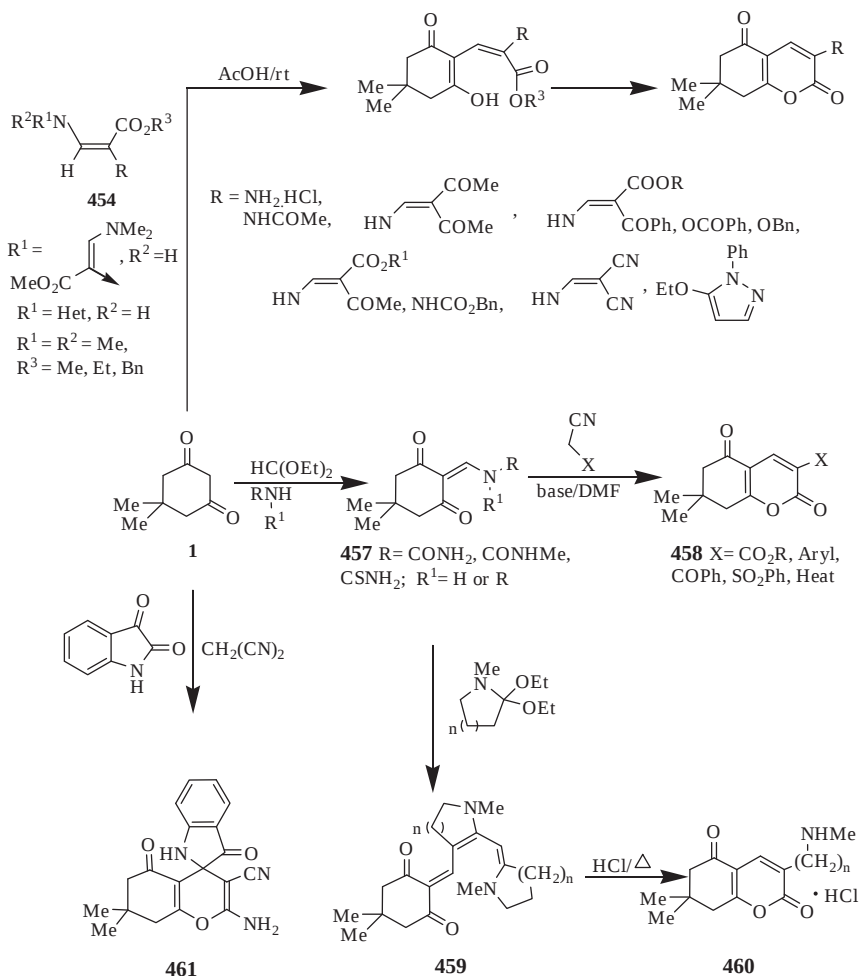
Reaction of 1,2-allenyl esters and **1**, catalyzed by potassium carbonate, gave **456a** through a tandem nucleophilic addition–lactonization process (06S2731). The (chlorocarbonyl)phenyl ketene was condensed with **1** to give **456** ($R = \text{Ph}$) (04T5931).

The *bis*-benzopyrans **463** were prepared from dimedone, malononitrile and 1,3- or 1,4-benzenedicarboxaldehyde under MW irradiation (04MI622).

Michael reaction of two molars of **1** and diarylideneacetone in a mixture of boiling toluene and *n*-heptane in the presence of anhydrous ZnCl_2 afforded 2,2'-spirobis(4-aryl-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydrochromane) **464** (05TL8217) (Scheme 96).

6.3.2 Synthesis of dibenzopyran (xanthenes)

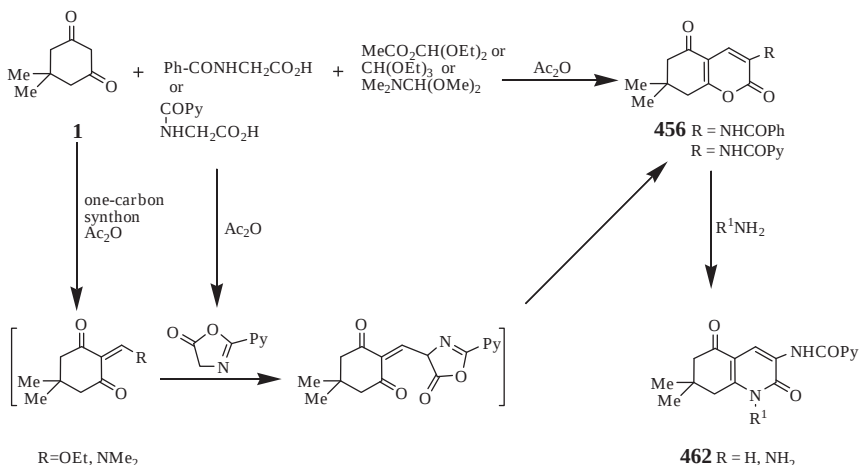
Dimedone is a well-known reagent for the characterization of aldehydes by giving *bis*(dimedonyl)methanes **355**, that can be cyclized into the corresponding xanthene derivatives **402** by the action of acids such as sulfuric, hydrochloric acid (25BSF187, 29MI204, 46JOC95, 89IJC(B)326, 92IJC(B)73, 01MI1164, 02SC3063), *p*-DBSA (04SL866) in water. TEBA chloride was used to catalyze the reaction to afford **355**, which were



Scheme 94

cyclized to the xanthenes by the action of PTSA (03MI694). The condensation of **1** and aromatic aldehydes in ethylene glycol gave the xanthenes **402** (02SC3063, 04CHE43).

A variety of aldehydes including those derived from heterocyclic compounds such as theophyllin-7-acetaldehyde and 2-formylfuro-[3,2-*b*]pyrrolo-5-carboxylates afforded **355**, which on boiling with dilute hydrochloric acid afforded the xanthenes **402** (99CCCC1135, 01JCR(S)129). In contrast, the *bis*(dimedonyl)methane **355** ($\text{R} = \text{H, Ph}$) was obtained when **1** was reacted with benzaldehyde and 2-aminopyridine (06ARK178). Better yield of **355** were obtained when a mixture of dimedone, benzaldehyde, acetic anhydride, and sodium acetate was MW

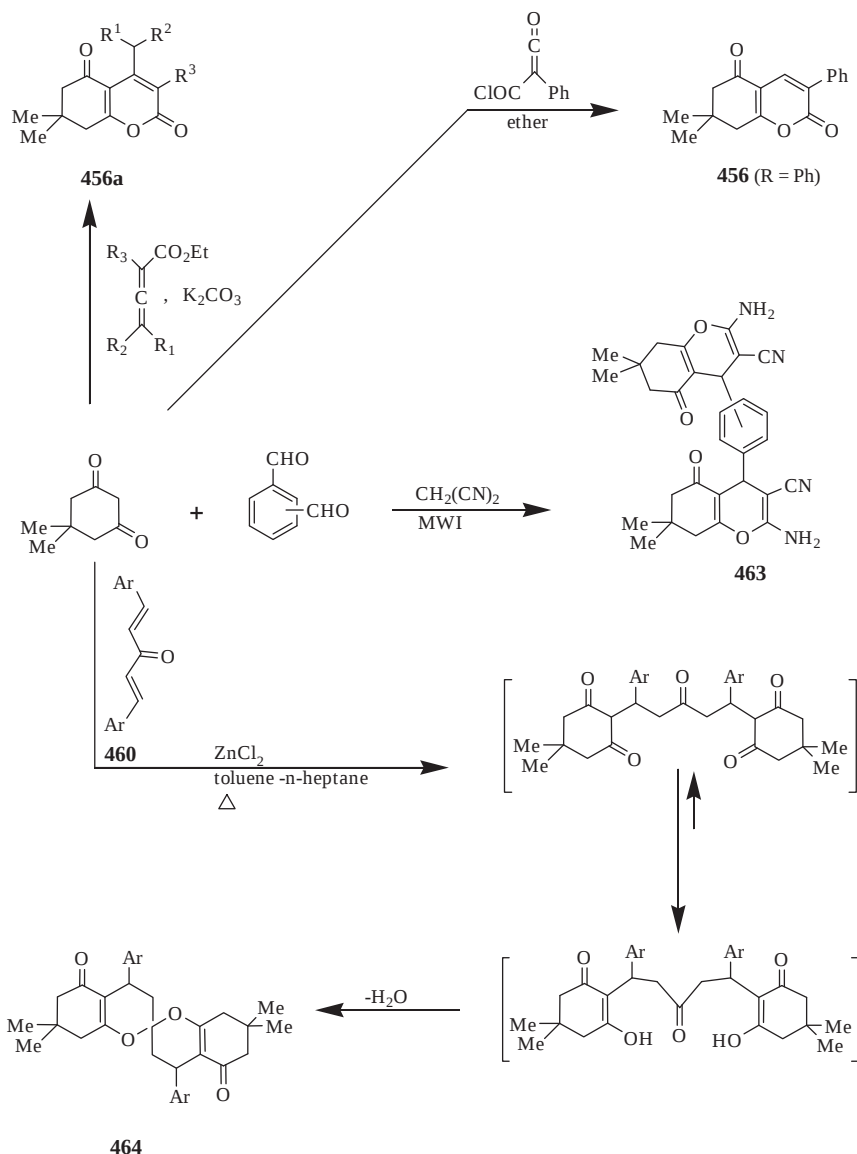


Scheme 95

irradiated for 5 min (06ARK178). MW irradiation of a mixture of methyl 4-benzyl-2-formylfuro[2,3-*b*]-pyrrole-5-carboxylate, dimedone, acetic anhydride and potassium acetate afforded **328**, which on further condensation with dimedone afforded the respective *bis*(dimedonyl)-methane **355**. This proved that the reaction proceeded through the intermediate **328**, which in a fast step added to another molecule of dimedone *via* Michael addition to give **355** (99CCCC1135).

The Knoevenagel condensation, Michael addition and cyclodehydration of **1** with aliphatic or aromatic aldehydes in the solid state by grinding without catalyst or with KF/Al₂O₃ as catalyst at room temperature was limited to give **355** (R = alkyl or aryl) (05SC2339, 06IJC(B)470). Similarly the HClO₄-SiO₂ catalyzed the reaction to give **355** (07JMOC53). When the reaction was carried out on solid state using TiO₂/SO₄²⁻ superacid or silica sulfate (05SC2339, 06IJC(B)470), PPA-SiO₂ neat or in acetonitrile (07JMOC53), NH₂SO₃H and SDS (05MI335), Fe³⁺-montmorillonite (07MI673) as catalysts, it afforded the respective xanthenes **402**. InCl₃·4H₂O promoted the preparation of xanthenediones in ionic liquids, whereas in absence of the catalyst both **355** and **402** were formed (05CJC16, 05MI293). Similarly [bmim][BF₄] in the presence of FeCl₃·6H₂O gave xanthenediones in high yield. However, when a combination of trimethylchlorosilane (TMSCl) and FeCl₃·6H₂O afforded ring-opened derivatives of xanthenediones with high efficiency (05MI897, 05MI1482), whereas TMSCl in MeCN/DMF gave the xanthenes **402** (06ARK136).

Reaction of imines with **1** in methanol and in the presence of iodine and a catalytic amount of zinc powder gave xanthenediones in excellent



Scheme 96

yields (06SC2345). In contrast, without a catalytic amount of iodine, ring-opening derivatives of xanthenediones were obtained in high yields.

An efficient approach to the synthesis of 3,3,6,6-tetramethyl-9-aryl-1,8-dioxooctahydroxanthene **402** [R = Ph, styryl] using *p*-DBSA as the catalyst in water has been done under ultrasonic irradiation (06MI220).

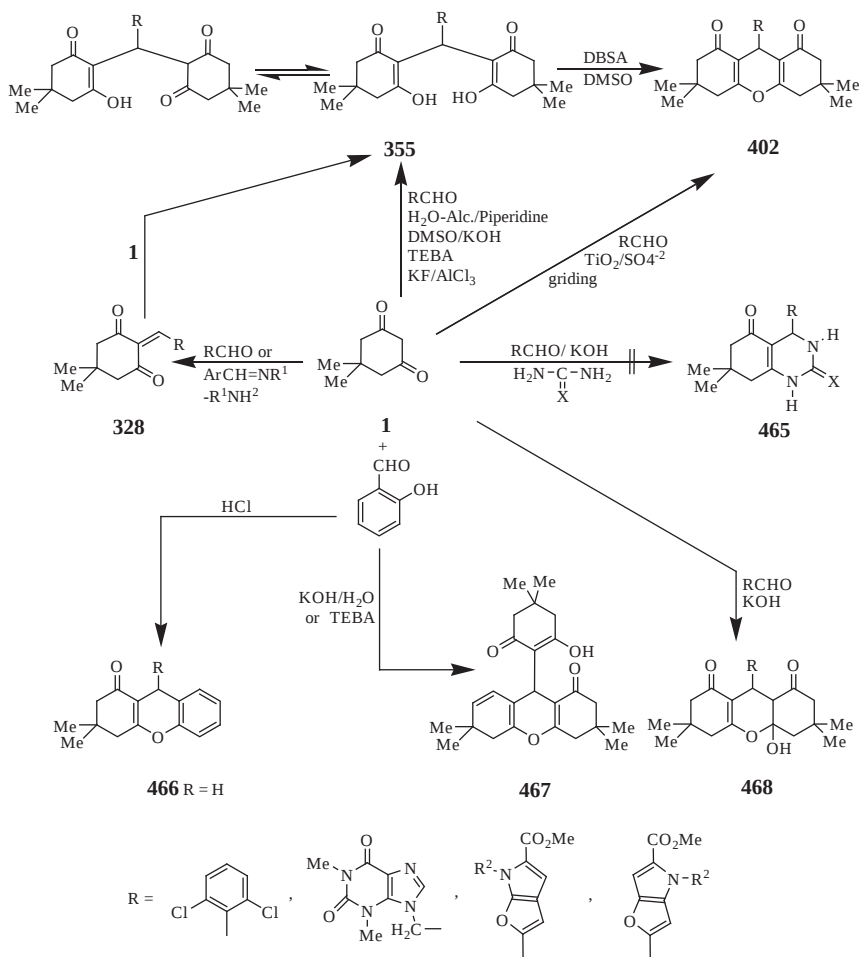
Coupling of **1** with urea and aldehydes gave the xanthene **402** ($R = Ar$) rather than the quinazoline **465** (04IJC(B)135). Reaction of **1** with aromatic aldehydes and thiourea using MW irradiation afforded the xanthenedione as a major product (06MI527). When arylglyoxals were used as aldehydes in a mixture of acetic acid and acetic anhydride, 9-aryl-octahydro-xanthenes **402** ($R = ArCO$) were obtained (82URP115). Reaction of α,β -acetylenic aldehydes with **1** led to the corresponding ethynyl-*bis*(dimedonyl)methanes **355** ($R = -C \equiv CR$), which underwent dehydrative cyclization upon heating in presence of sulfuric acid to afford **402** (82ZOR1999). It has been reported that crystallization of 3,3,6,6,9-pentamethyl-2,3,4,5,6,7,9,10-octahydroacridine **356** ($R^1 = H$, $R = Me$) from ethanol afforded the xanthene **402** ($R = Me$) (03MI142).

Azomethines behave like synthetic equivalents of benzaldehyde in the reaction with **1** (68MI67), reaction of **1** with aromatic azomethine gave **402** ($R = Ar$) *via* intermediate formation of **328**. Thus reaction of **1** with aromatic aldehydes was found to be dependent on the substituent on the aromatic ring. Dimedone with benzaldehyde in the presence of potassium hydroxide gave a mixture of benzal dimedone **328** and 9-phenyl-3,3,6,6-tetramethyl-1,2,3,4,5,6,7,8-octahydro-xanthene-1,8-dione **402** ($R = Ph$) (32MI141, 33IJCS663) (Scheme 97). The presence of functional groups on the *ortho* position of benzaldehyde led to the formation of different types of heterocyclic compounds. Thus, reaction with salicylaldehyde (32MI141) under acidic condition gave **466**, whereas in aqueous potassium hydroxide (32MI141) or TEBA in water (05SC97) the product was **467** ($R = H$). The reaction of substituted salicylaldehydes with dimedone catalyzed by KF/Al_2O_3 gave **467** ($R = Me$) (05MI846). The reaction with *m*-methoxybenzaldehyde gave **402** (93PS73), and with 2,6-dichlorobenzaldehyde gave **468**, which existed as two enantiomeric pairs of diastereomers (01AX(C)0444). Compound **466** was obtained from the condensation of **1** with *o*-hydroxybenzyl alcohol in the presence of hexamethylphosphoramide (HMPA) (72CC839).

Treatment of dimedone with sodium hydride followed by β -bromostyrene and CuI in HMPA at $120^\circ C$ gave **355** ($R = Bn$) that was cyclized to **402** upon treatment with H_2SO_4 (90CL937).

Dimedone **1** did not change in DMSO at temperatures up to $150^\circ C$, but at $180^\circ C$ methylation took place with the formation of **402** ($R = Me$) (91ZOR1519). When the reaction was carried in the presence of KOH , **355** ($R = Me$) was isolated in low yield which by fractional crystallization readily underwent cyclization to **402**; KOH inhibited heterocyclization of **355** (91ZOR1519).

Single-crystal X-ray diffraction of 3,3,6,6-tetramethyl-9-(3,4-methylenedioxyphenyl)-1,8-dioxo-2,3,4,5,6,7-hexahydroxanthene revealed that the pyran ring adopted a boat conformation, while the two cyclohexenone rings have envelope conformations (04MI187). The

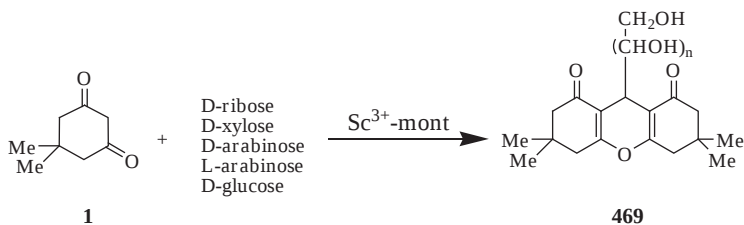


Scheme 97

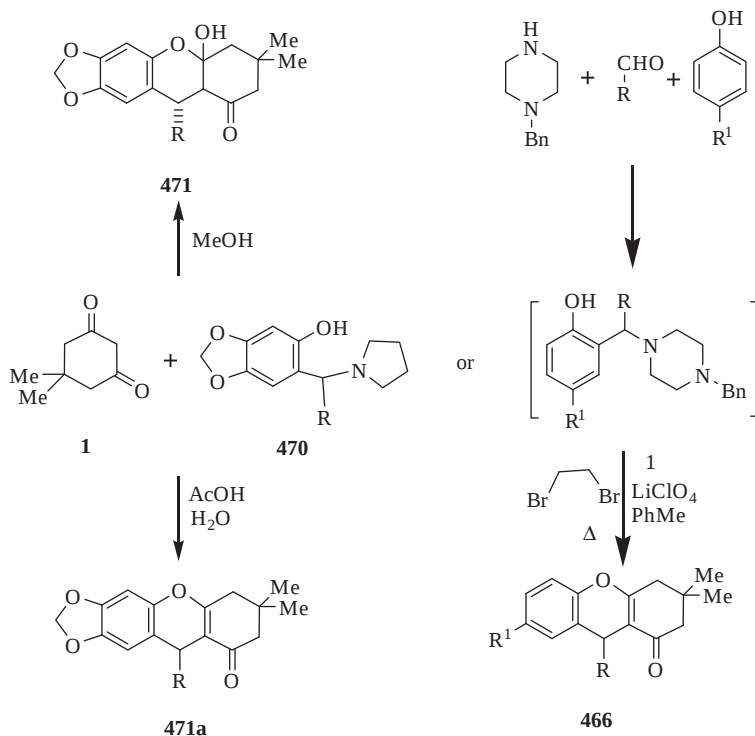
3,3,6,6-tetramethyl-9-(2-oxo-1,2-dihydroquinolin-3-yl)-1,2,3,4,5,6,7,8-octa-hydro-9H-xanthene-1,8-dione has a planar central ring of the xanthene moiety and the two outer rings are in half-boat conformations. The molecular packing in the crystal structure has been stabilized by N-H $\cdots$ O and C-H $\cdots$ O bonds in addition to van der Waals forces (05AX(E)03701).

The condensation of **1** with unprotected sugars in aqueous solution in the presence of a catalytic amount of Sc^{3+} -montmorillonite gave the acyclic C-alditolyis of xanthenedione **469** (07CAR913) (Scheme 98).

Pyrrolidinyl Mannich bases **470** were reacted with **1** in methanol to give the hydroxydibenzopyrans **471** whereas when aqueous acetic acid



Scheme 98



Scheme 99

was used instead of methanol the dehydrated products **471a** were obtained (89JHC1349).

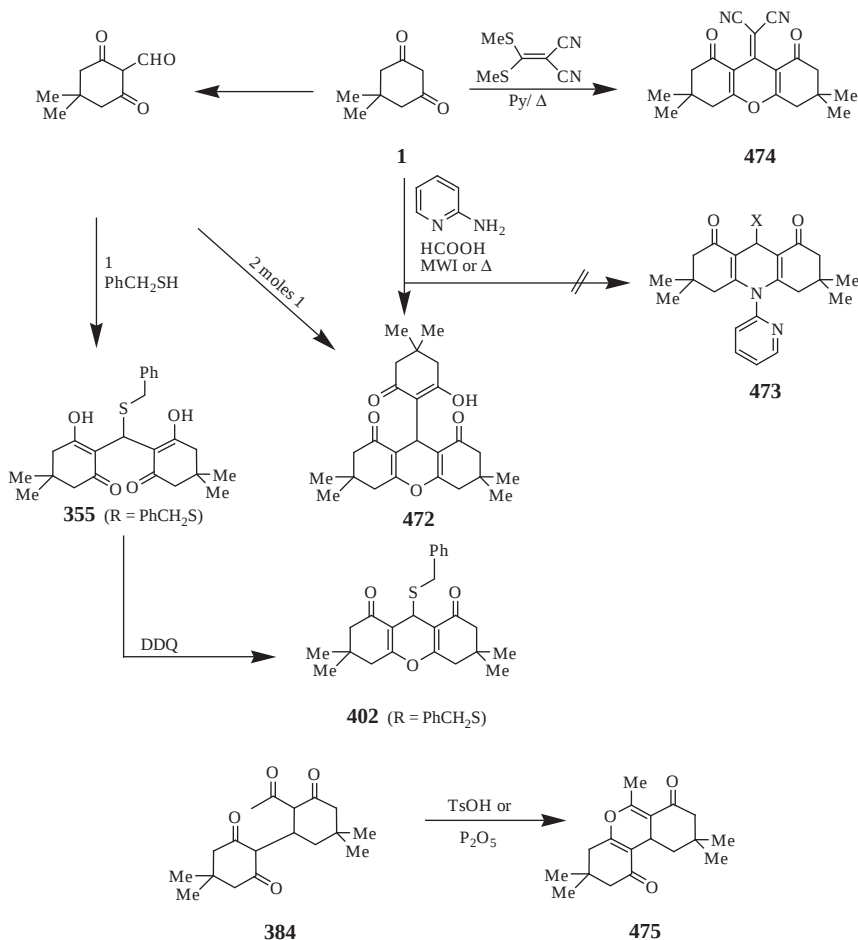
Three-component coupling of phenols, aldehydes, and dimedone in the presence of benzyl piperazine gave the respective xanthene **466** (06OBC3410) (Scheme 99).

Formylation of dimedone using ethyl orthoformate in the presence of acetic anhydride gave the 2-formyldimedone whose condensation with two moles of dimedone gave the xanthene **472** (57JCS4798), which can also be obtained directly from reaction of dimedone with triethyl

orthoformate (73TL4905). Alternatively, **472** was obtained instead of **473** when **1** was treated with 2-aminopyridine in formic acid, either under conventional heating or by MW irradiation (06ARK178).

Reaction of 2-formyldimedone with **1** under acid-catalysis in the presence of phenylmethanethiol produced the adduct **355** ($R = \text{SCH}_2\text{Ph}$). Reaction of which with DDQ afforded the xanthene derivative **402** ($R = \text{PhCH}_2\text{S}$) (99JCS(P1)847). Condensation of **1** with *bis*[(methylsulfonyl)methylidene]malononitrile in boiling pyridine afforded **474** (97JCR(S)256).

Dibenzo[*b,d*]pyran **475** was obtained when the tetraketone **384** was treated with phosphorous pentaoxide or *p*-toluenesulfonic acid in boiling benzene (83ZOR2322) (Scheme 100).

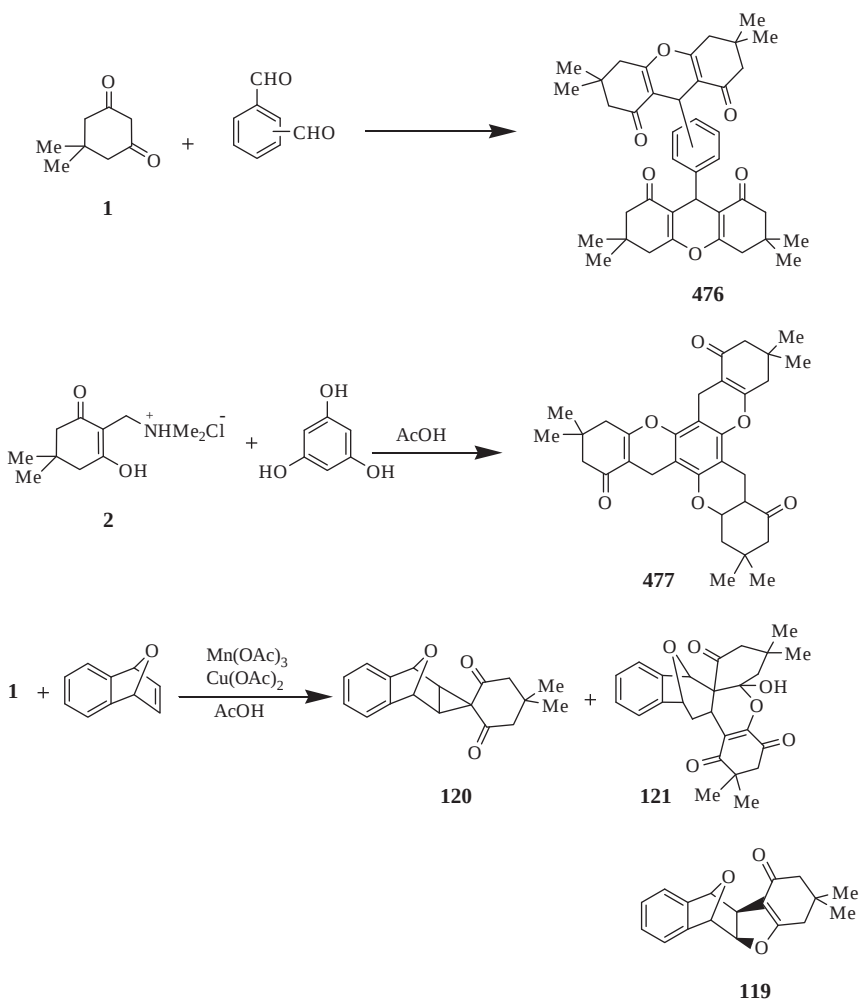


Scheme 100

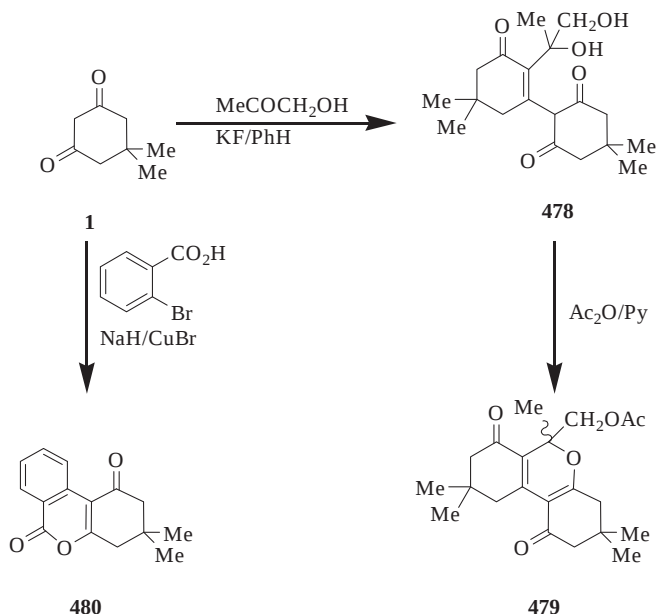
The *bis*-xanthenes **476** were prepared by condensing **1** with iso- or tere-phthalaldehyde (04SC2617). Phase transfer catalysts were used in water to prepare such compounds (05SC2379).

Reaction of the Mannich base 2-(trimethylammoniummethylene chloride)-dimedone with phloroglucinol gave the xanthene **477** (04H2615). Oxabenzonorbornadiene was reacted with **1** in the presence of $\text{Mn}(\text{OAc})_3$ and $\text{Cu}(\text{OAc})_2$ to give unusual products, the cyclopropanated compound **120** and **121** in addition to the furan **119** (05TL6227) (Scheme 101).

C-Alkylation of **1** with hydroxyacetone in presence of potassium fluoride in benzene afforded the dimeric condensation product **478**,



Scheme 101



Scheme 102

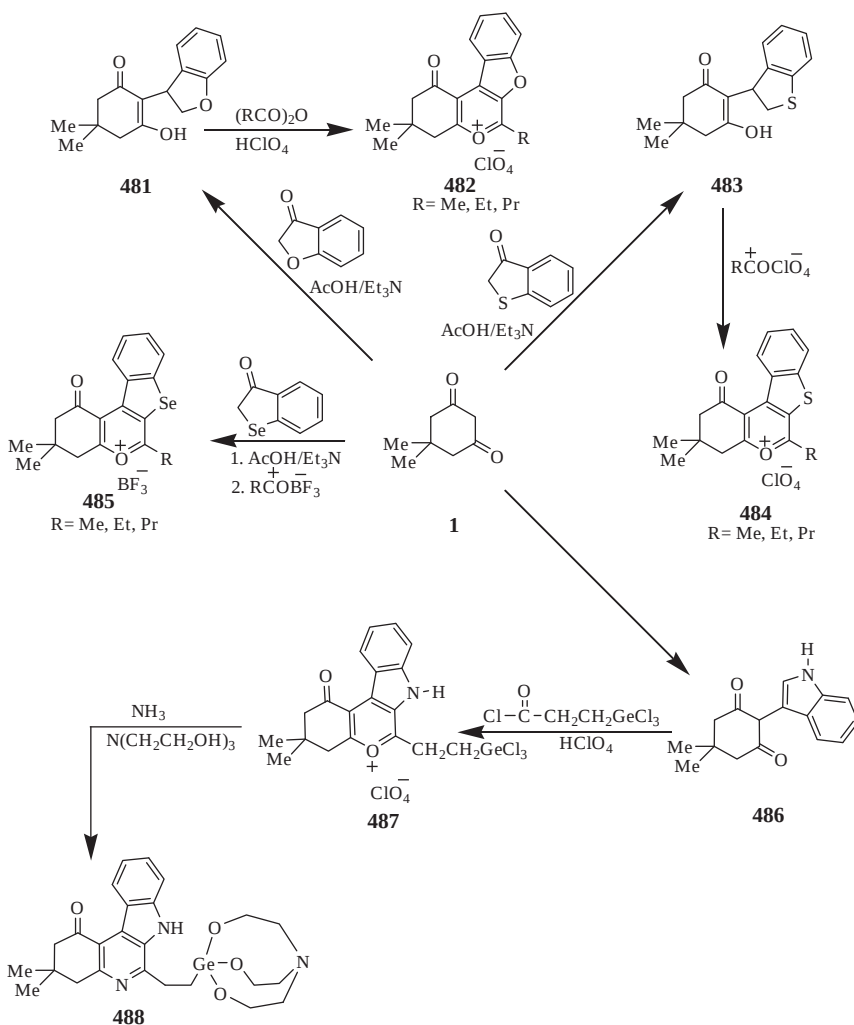
which upon acetylation with acetic anhydride in pyridine gave the tricyclic dibenzo[b,d]pyran **479** (99CPB897). The dibenzo[b,d]pyran **480** was obtained when **1** was reacted with 2-bromobenzoic acid and sodium hydride in presence of CuBr (77S759) (Scheme 102).

6.3.3 Synthesis of benzofuro, thieno, seleno, and indolo[2,3-c]chromenes

Condensation of benzo[b]furan-3(2H)-one with **1** in acetic acid in the presence of triethylamine afforded 2-(3-benzo[b]furyl)dione **481**, which upon acylation with acid anhydrides in the presence of 70% perchloric acid led to the corresponding tetrahydrobenzo[b]furo[2,3-c]pyrylium perchlorate **482** (94CHE283). Similarly, benzo[b]thieno[2,3-c]pyrylium perchlorate **484** (94CHE283) and benzo[b]seleno[2,3-c]pyrylium salt **485** were prepared (94CHE283).

Indolo[2,3-c]pyrylium salt **487** was obtained by acid catalyzed acylation of 2-(indol-3-yl)dione **486** with trichlorogermlypropionyl chloride (98CHE592). Treatment of **487** with ammonia and triethanol amine gave the indoloquinoline **488** (98CHE592) (Scheme 103).

Domino Knoevenagel hetero-Diels–Alder reaction of **1** with sugar aldehyde **489** gave, in a stereoselective manner, the fused furo[2',3':5,6]-pyrano[3,4-c]chromen-1-one **491** presumably *via* the aldehyde adduct **490** (04TL3493, 04S1150) (Scheme 104).

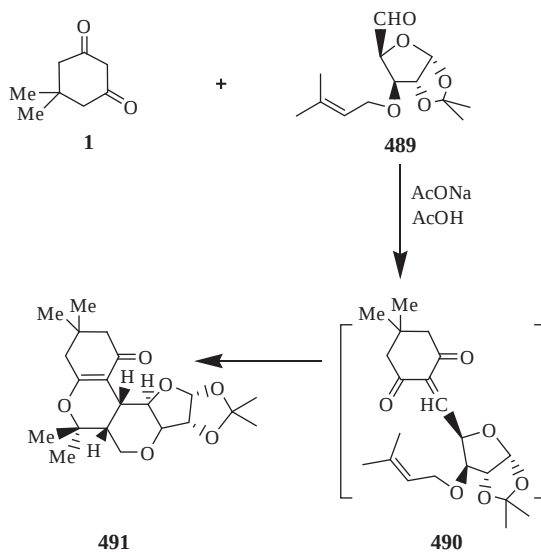


Scheme 103

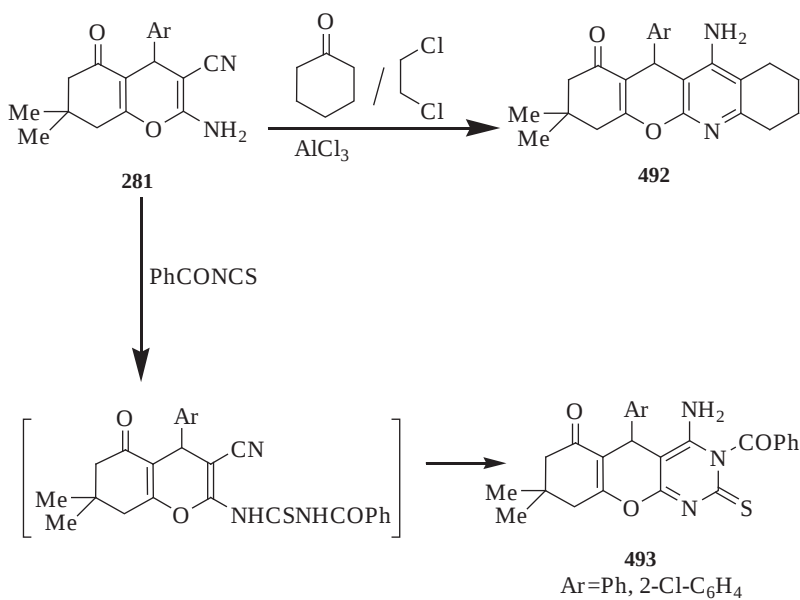
6.3.4 Synthesis of quinolino- and pyrimido-benzopyrans

Condensation of 2-amino-3-cyano-benzo[*b*]pyran **281** with cyclohexanone in presence of aluminum trichloride gave the tetracyclic ring **492**, having neuroprotective activity (06BMC8176).

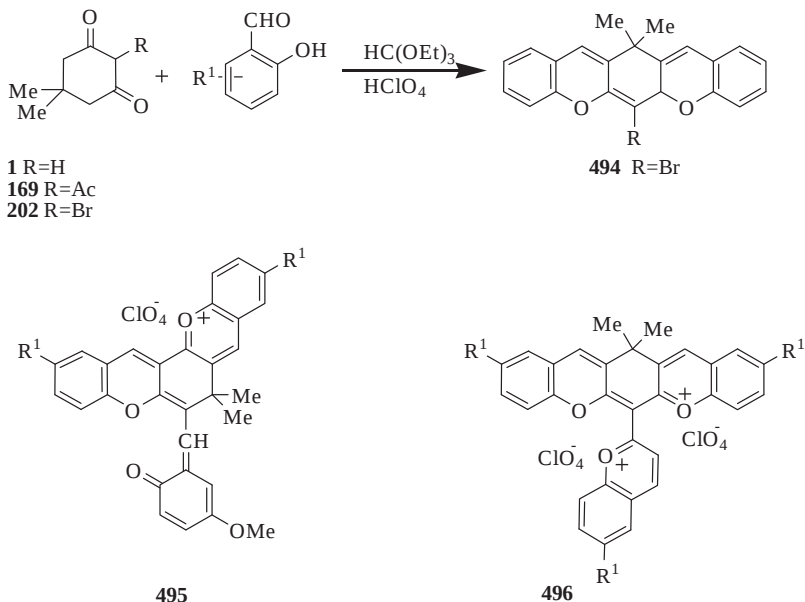
Reaction of **281** with benzoylthiocyanate afforded pyrimido[4,5-*b*]benzo[*b*]pyran **493**, which was assumed to be formed *via* the respective open-chain thiourea derivative (89JPR971) (Scheme 105).



Scheme 104



Scheme 105



Scheme 106

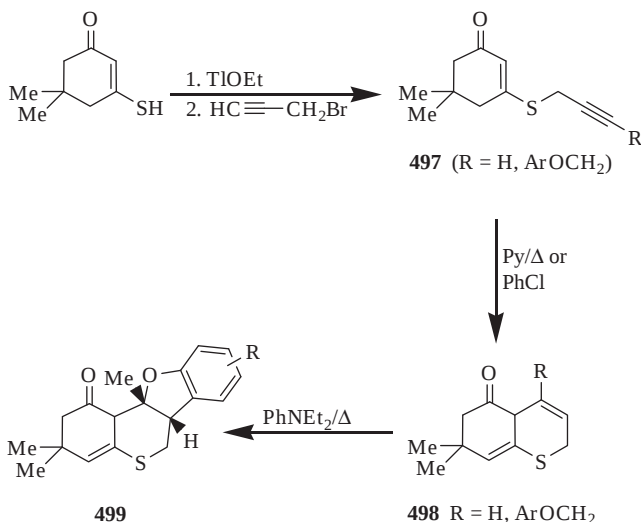
6.3.5 Synthesis of chromeno-xanthenes

Reaction of 2-bromodimedone **202** (R = Br) with salicylaldehyde in triethylorthoformate and perchloric acid furnished the chromeno[2,3-*a*]-xanth-5-ylum perchlorate **494** (01RJOC527). Under similar conditions, **1** and 2-acetyldimedone **169** (R = Ac) were reacted with 2-hydroxyarylaldehydes to give chromeno[2,3-*a*]xanth-13-ylum perchlorate **495** and chromeno[2,3-*b*]xanth-5-ylum diperchlorate **496** (01RJOC527) (Scheme 106).

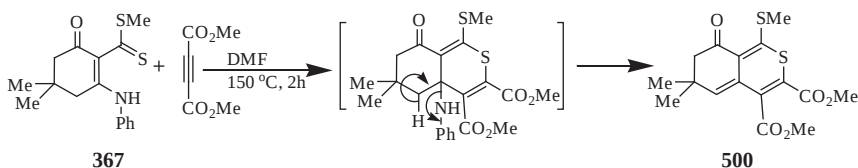
6.4 Annulation with thiapyran

Thio-Claisen rearrangement of 5,5-dimethyl-3-(2-propynylthio)cyclohex-2-en-1-one **497** followed by cyclization to the pentahydro-benzothiopyran **498** was performed by heating **497** in pyridine (74ACS(B)1077). Sequential [3,3]sigmatropic rearrangement of **497** (R = ArOCH₂) upon heating in chlorobenzene gave **498**, which on heating in diethylaniline gave **499** in a stereoselective manner (06SC1299) (Scheme 107).

The enamino dithiocarboxylate **367** (R = H), acting as hetero-diene was reacted with dimethyl acetylenedicarboxylate in DMF at 150 °C to give the corresponding benzothiapyran **500**. The reaction proceeded through the formation of a cycloadduct that upon losing an aniline moiety gave **500** (91JHC1245) (Scheme 108).



Scheme 107



Scheme 108

7. DIMEDONE-ANNULATED SIX-MEMBERED HETEROCYCLES WITH TWO HETEROATOMS

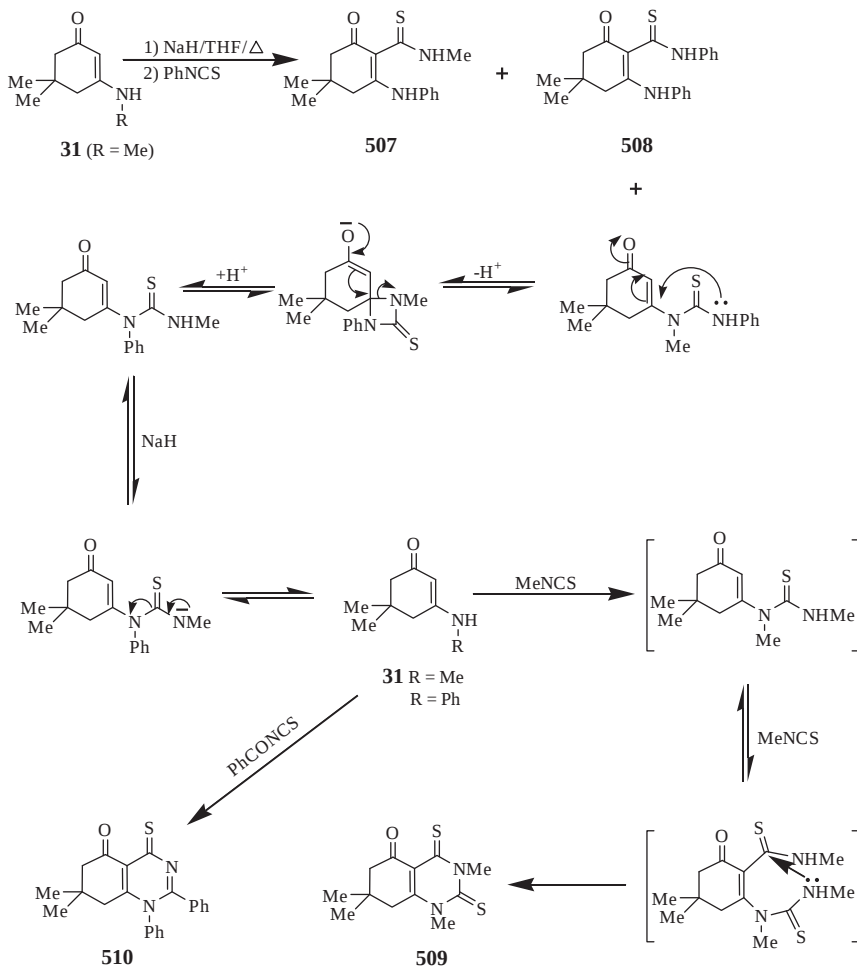
7.1 Annulation with pyridazine (synthesis of cinnolines)

This ring system can be constructed by introducing the hydrazine moiety on C-1 or C-2 of dimedone and then heterocyclization with functionalized carbon reagents. Thus, reaction of 2-arylhydrazono-5,5-dimethylcyclohexane-1,3-dione **219**, prepared from reaction of **1** with aryldiazonium chlorides, with Wittig reagents **501** afforded the respective tetrahydrocinnolinones **503**. Alternatively, **503** were synthesized by the coupling of **504**, obtained from reaction of **1** with Wittig reagent **501**, with benzenediazonium chloride followed by boiling in ethanol and piperidine (97JCR(S)236); the reaction proceeded through the intermediates **502**. In contrast, reaction of **1** with 1,1-diacetyl-2-benzoyl ethylene in the presence of KOH afforded the adduct **505** that upon treatment with hydrazine hydrate gave the cinnolinone **506** (01HCO155) (Scheme 109).



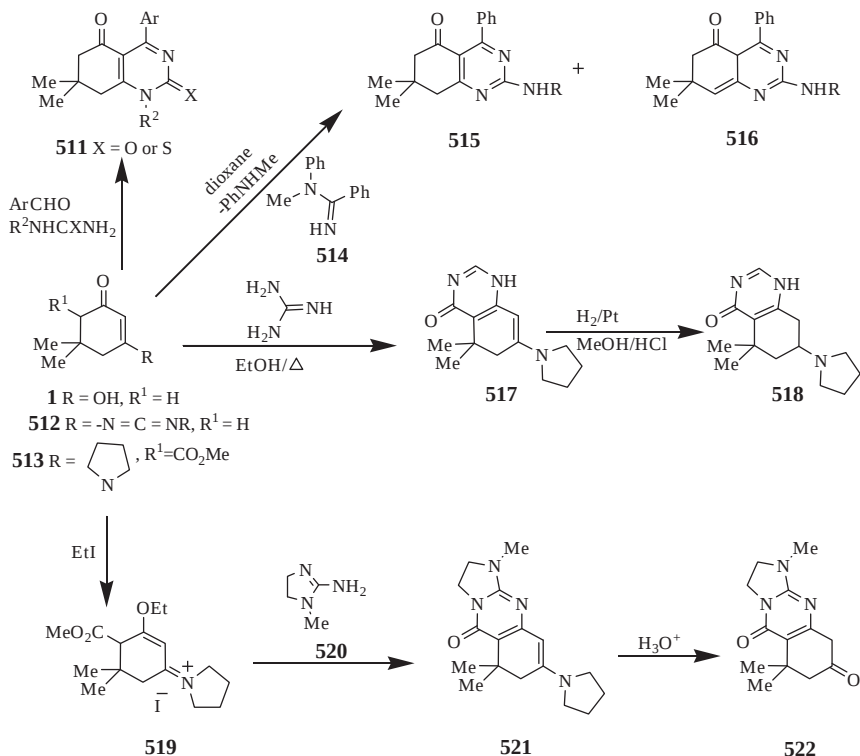
When the enaminone **31** (R = Me) was reacted with sodium hydride in THF under reflux followed by phenyl isothiocyanate, it afforded a mixture of products among them the enaminones **31** (R = Ph), **507**, **508**, and the quinazoline derivative **509** (90JCS(P1)1869). Similarly, reaction of **31** (R = Ph) with methyl isothiocyanate under the same reaction conditions afforded **507**, **508**, **509** with recovery of **31** (R = Ph) (90JCS(P1)1869). In contrast, reaction of enaminone **31** (R = Ph) with benzoyl isothiocyanate afforded the quinazoline **510** as a single product (96IJC(B)608) (Scheme 110).

A series of 4-aryl-7,7-dimethyl and 1,7,7-trimethyl-octahydroquinazolin-2,5-diones **511** (R² = H; or Me, X = O) were synthesized by condensation of urea or *N*-methylurea with **1** and aromatic aldehydes



Scheme 110

(03FES17, 04CHE43); the xanthene **402** was obtained as a minor product. However, **511** can be the only product when the condensation was carried out under solvent-free conditions (05EJM816). Condensation of **1** with urea or thiourea and aromatic aldehydes in the presence of H_2SO_4 was achieved in water to give **511** ($X = \text{O}, \text{S}; R^2 = \text{H}$) (06BMCL4479). Tangstophosphoric acid both in bulk form or supported on silica gel efficiently catalyzed the three-component condensation of aldehyde, dimedone and urea or thiourea to afford 3,4-dihydropyrimidin-2(1H)-ones in high yields under solvent-free conditions (06MI843). Also TMSCl mediated such condensation in MeCN to give **511** ($R^2 = \text{H}, X = \text{O}, \text{S}$) (06ARK136).



Scheme 111

The thio analogue of **511** with $\text{R}^2 = \text{H}$ and $\text{Ar} = m$ -hydroxyphenyl named dimethylenastron was prepared as a racemic mixture by the reaction of *m*-hydroxy benzaldehyde with **1** and thiourea in the presence of polyphosphate ester under MW irradiation. It has a distinct cell permeable inhibition of the mitotic Kinesin, Eg5 which was more potent than monastrol (05MI1173).

The conjugated carbodiimide **512** was reacted with amidine **514** in dioxane to give quinazolines **515** and **516** in moderate yields (95HCO421).

Reaction of the enamine-ester **513** with guanidine in boiling ethanol afforded the quinazolone **517**. Hydrogenation of which gave the dihydro derivative **518** (92JHC1375) (Scheme 111).

7.3 Annulation with heterocyclo-quinazolines

7.3.1 Synthesis of pyrazolo-quinazolines

X-ray analysis of 2-(4-chlorophenyl)-5,8,8-trimethyl-6,7,8,9-tetrahydropyrazolo[2,3-*a*]quinazolin-6-one, 2-(4-methoxyphenyl)-5,8,8-trimethyl-6,7,8,

9-tetrahydropyrazolo[2,3-*a*]quinazolin-6-one, and 8,8-dimethyl-2-(4-methylphenyl)-6,7,8,9-tetrahydropyrazolo[2,3-*a*]quinazolin-6-one monohydrate indicated that the nonaromatic carbocyclic ring adopted a half-chair conformation, while this ring adopted a conformation intermediate between the envelope and scew-boat forms in 2-(4-chlorophenyl)-8,8-dimethyl-5-phenyl-6,7,8,9-tetrahydropyrazolo[2,3-*a*]quinazolin-6-one (06AX(C)0364).

In 2,8,8-trimethyl-6,7,8,9-tetrahydropyrazolo[2,3-*a*]quinazolin-6-one, the heterobicyclic system was planar and in 3-*tert*-butyl-4',4'-dimethyl-1-phenyl-4,5,6,7-tetrahydro-1H-pyrazolo[3,4-*b*]pyridine-5-spiro-1-cyclohexane-2',6'-dione, the pyrazole ring exhibited marked bond fixation, while the reduced pyridine ring adopted a half-chair conformation (04AX(C)0265).

7.3.2 Synthesis of imidazo-quinazolines

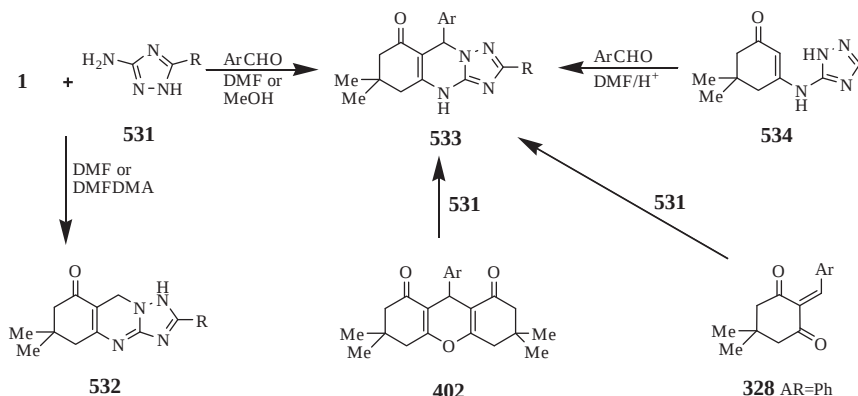
Ethylation of the enamine **513** with iodoethane afforded the *O*-ethylated salt **519**, which was reacted with 2-amino-1-methylimidazoline **520** to give **521** that upon hydrolysis gave **522** (92JHC1375) (Scheme 111).

Condensation of 2-aminobenzimidazole **523** with aromatic aldehydes and **1** in DMF or ethanol afforded the tetrahydro-benzimidazo[2,1-*b*]quinazolines **525** rather than **524** (03CHE1041, 04HCO399). The reaction has been also achieved under MW irradiation (07MI287227). Alternatively, compounds **525** were obtained when 2-aminobenzimidazole **523** was reacted with the xanthenes **402** (*R* = Ar) or the arylidene **328** in the absence of aromatic aldehydes (03CHE1041). Reaction of **1** with **523** in boiling DMF afforded **527** rather than **528** through the intermediate **526**. The product **527** was obtained exclusively when 2-formyldimedone was heated with **523** in ethanol in the presence of catalytic amount of *p*-toluenesulfonic acid. The intermediate aminomethylene derivative **529** was obtained when the reaction was performed in ethanol at 20 °C. Oxidation of **527** with selenious acid afforded the α -diketone **530** (96CHE221). X-ray structural analysis showed that the tricyclic pyrimido[1,2-*a*]benzimidazole fragment was planar and the cyclohexene fragment existed in a half-chair conformation (03CHE1041) (Scheme 112).

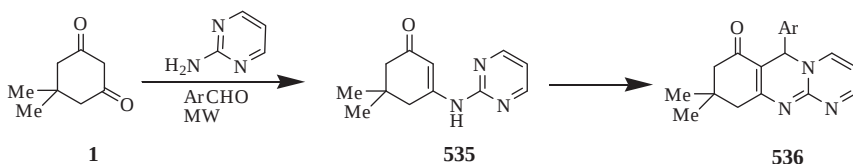
7.3.3 Synthesis of triazolo-quinazolines

The 1,2,4-triazolo[2,3-*a*]quinazoline **532** was obtained by reaction of **1** with 3-amino-1,2,4-triazole **531** in DMF (05RJOC114). In the presence of *p*-substituted benzaldehyde, the condensation with equimolar amounts of **531** and **1** in DMF or methanol gave 1,2,4-triazolo[5,1-*b*]quinazolin-8-ones **533** (03CHE1213, 07MI11). Also, the reaction can take place under MW irradiation (07MI287227). Alternatively, **533** were obtained from the condensation of **531** with arylidinedimedone **328** or xanthenedione **402** (*R* = Ar), *via* a loss of a molecule of dimedone from the latter compound





Scheme 113



Scheme 114

(03CHE1213). The **533** (R = SMe) were also synthesized from **531** (R = SMe), **328** (02MI10) and enamine **534** (03CHE1213). Condensation of **1**, aromatic aldehydes and **531** (R = NH₂) in DMF afforded **533** (R = NH₂) (05RJOC114) (Scheme 113).

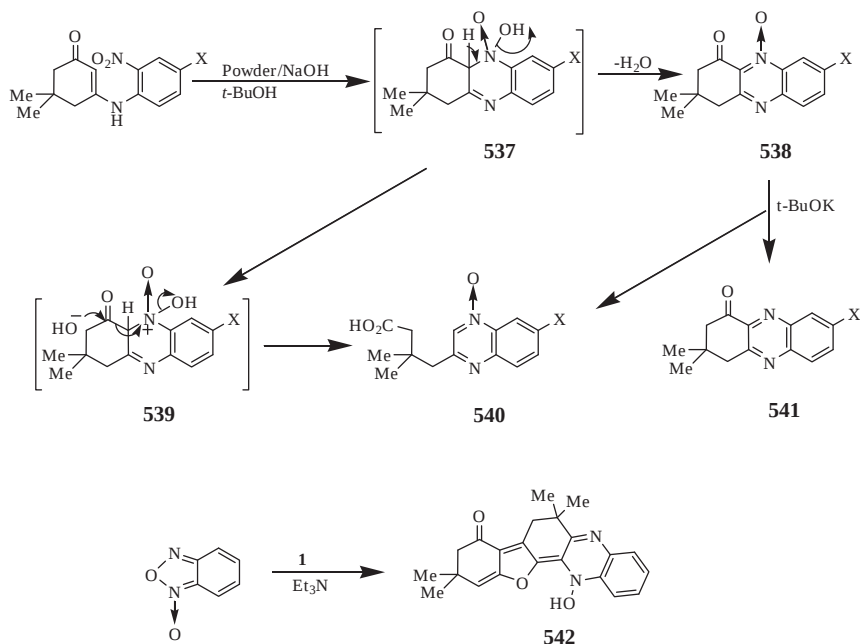
A three-component condensation of 3-amino-1,2,4-triazole (or its 5-Me and 5-methylthio derivatives), **1** and DMF-dimethylacetal afforded 8,9-dihydro[1,2,4]triazolo[1,5-a]quinazolin-6(7H)-ones (06RCB1224). Condensation of 3,4,5-triamino-1,2,4-triazole with aromatic aldehydes and dimedone afforded partially hydrogenated 9-aryl-[1,2,4]triazolo[5,1-b]quinazolin-8-ones. The structure of 2-amino-6,6-dimethyl-3-(4-nitrobenzylidene)amino-9-(4-nitrophenyl)-5,6,7,9-tetrahydro[1,2,4]triazolo[5,1-b]quinazolin-8-one was confirmed by X-ray analysis (05RCB2903).

7.3.4 Synthesis of pyrimido-quinazolines

When 2-aminopyrimidine was reacted with aromatic aldehydes and dimedone, it gave pyrimido[1,2-a]quinazolinone **536** presumably *via* **535**, under MW irradiation (02HCO299) (Scheme 114).

7.4 Annulation with pyrazine (synthesis of quinoxalines)

Treatment of 3-(2-nitroanilino)-5,5-dimethyl-2-cyclohexenone with powdered sodium hydroxide in *t*-butanol gave the quinoxaline-1-oxide **538**,



Scheme 115

via the intermediate **537** or **539**. When potassium *t*-butoxide was used instead of sodium hydroxide, the dihydrophenazine **541** was obtained as a byproduct in addition to **540** (81S60).

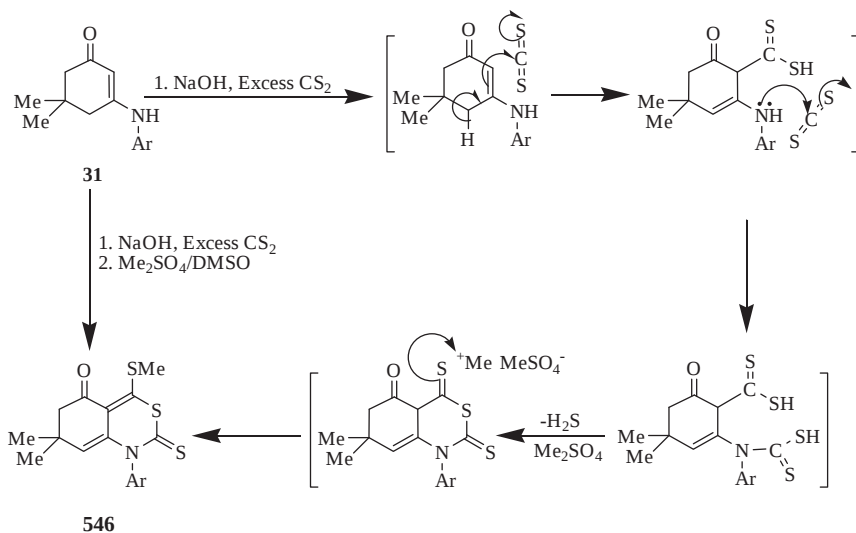
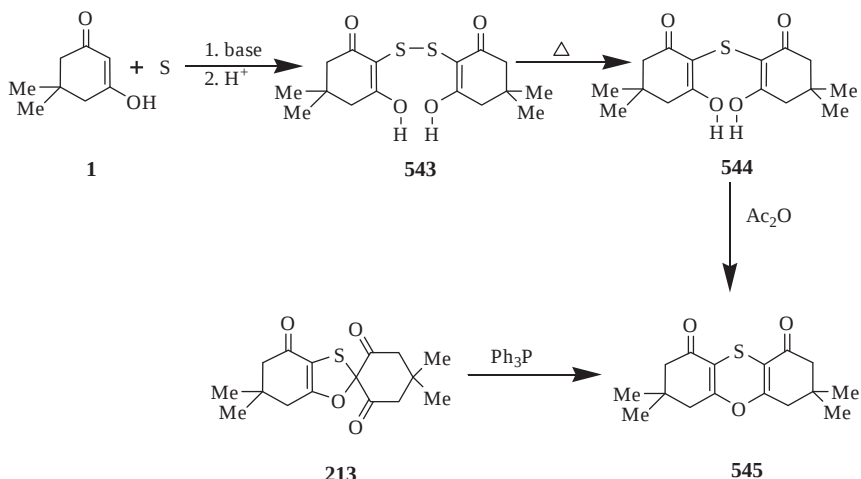
Dimedone was reacted with benzofuraxan in the presence of Et_3N to give the unexpected product **542** in low yield. Its formation was proposed on the basis AM1 type semiempirical calculation (02JST143) (Scheme 115).

7.5 Annulation with oxathiin (synthesis of dibenzo-1,4-oxathiin)

Reaction of **1** with sulfur in the presence of amines followed by neutralization with acid gave the disulfide **543**, which upon heating at a temperature higher than its melting point gave *bis*(dimedone)sulfide **544**. Reaction of the latter with acetic anhydride gave the dibenzo-1,4-oxathiine **545** (81ZOR990, 81KGS563). Alternatively, **545** was obtained upon reacting 4-oxo-6,6-dimethyl-tetrahydro-1,3-benzoxathiole-2-spiro-4',4'-dimethylcyclohexane-2',6'-dione **213** with triphenylphosphine (81ZOR990) (Scheme 116).

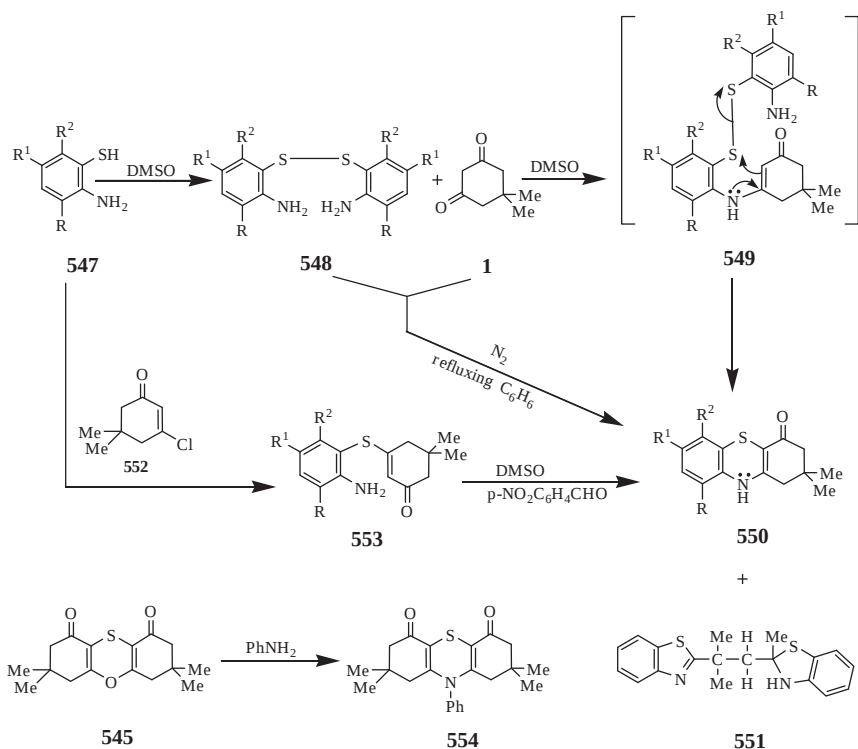
7.6 Annulation with thiazine (synthesis of benzothiazines)

Reaction of *N*-aryl-enamine **31** with excess of carbon disulfide in the presence of sodium hydroxide followed by dimethylsulfate afforded the



benzo[3,1]thiazines **546**, through the suggested mechanism in the scheme (91JHC1245). Other alkylating agents were used to give the respective **546** with different alkyl, aralkyl, and glycosyl groups instead of the methyl (El Ashry and Amer, unpublished results) (Scheme 117).

Condensation of *o*-aminobenzenethiol **547** with **1** in dimethyl sulfoxide gave the phenothiazinone **550** (76JCS(P1)1146, 83S933,



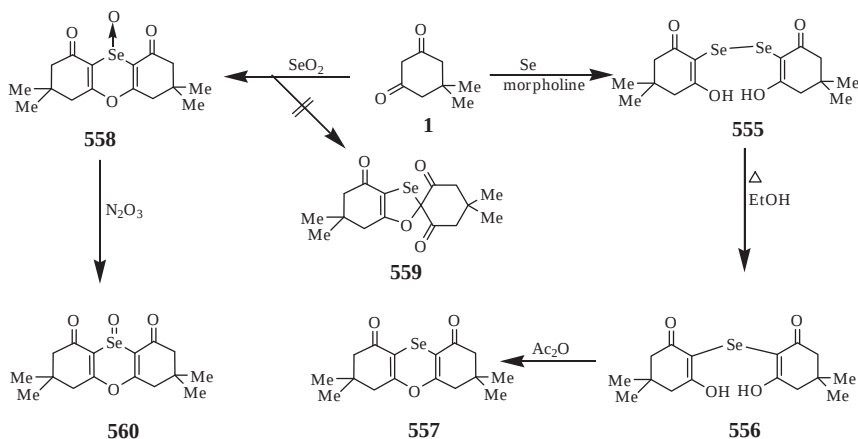
Scheme 118

93PHA546, 04IJC(B)413), *via* the oxidation of **547** to the disulfides **548** that condensed with **1** to yield the enamino-ketones **549** the phenothiazine that cyclized to **550** (93PHA546). Reaction of **548** with two molar equivalents of dimedone gave **550** in addition to **551** (76JCS(P1)1146).

Compound **547** was condensed with **552** and *p*-nitrobenzaldehyde in DMSO to give the sulfide **553** that underwent oxidative cyclization in DMSO to give **550** ($\text{R}, \text{R}^1, \text{R}^2 = \text{H}$) without utilizing the *p*-nitrobenzaldehyde (76JCS(P1)1146). The condensation of dimedone with 2-nitrobenzenesulfonyl chloride and subsequent reductive cyclization gave **550** (72KGS1901). Synthesis of benzothiazine **554** can be carried out by treatment of **545** with aniline (81KGS563) (Scheme 118).

7.7 Annulation with oxaselenin (synthesis of dibenzo-1,4-oxaselenin)

When dimedone was allowed to react with selenium in morpholine, it gave a diselenide **555** that upon heating in ethanol gave



Scheme 119

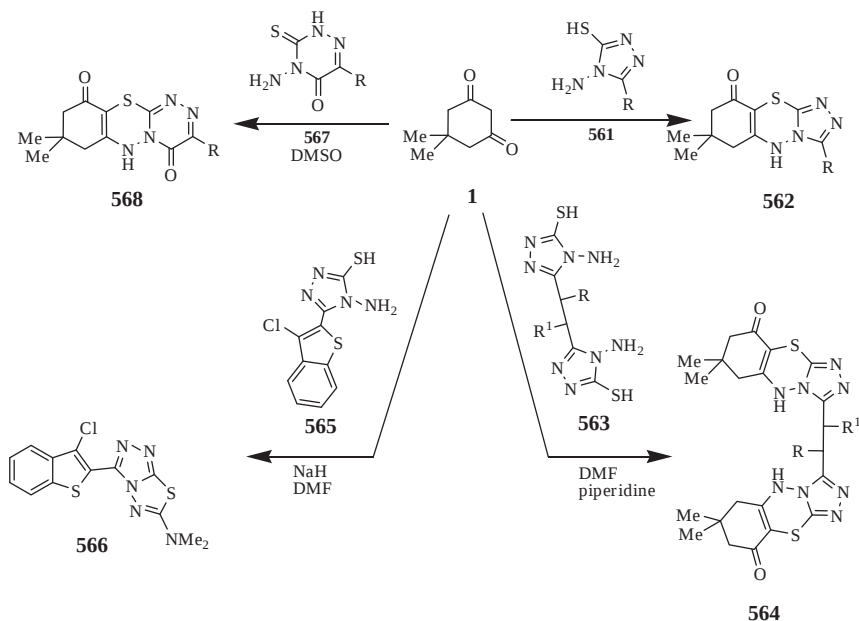
bis(dimedone)selenium **556** (85MI206). Reaction of the latter with acetic anhydride afforded dibenzo-1,4-oxaselenin **557**. Reaction of dimedone with selenium dioxide gave anhydro *bis*(dimedone)selenium oxide **558** and not **559** (33CB1558, 40CB839, 79MI145, 82MI15). The product **558** could be oxidized with nitrogen trioxide to give dibenzo-1,4-oxaselenon **560** (Scheme 119).

8. DIMEDONE-ANNULATED SIX-MEMBERED HETEROCYCLES WITH THREE HETEROATOMS

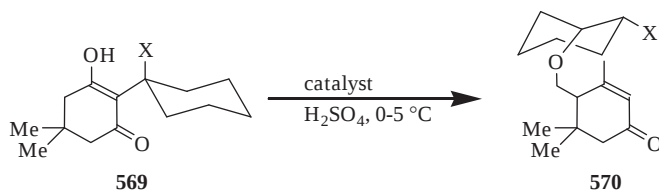
8.1 Annulation with thiadiazine (synthesis of benzothiadiazines)

Reaction of 3-substituted-4-amino-5-mercapto(4*H*)-1,2,4-triazoles **561** with **1** gave 6,7,8,9-tetrahydro-3-substituted-1,2,4-triazolo[4,3-*b*][1,3,4]benzothiadiazin-9-ones **562** (90H2147, 01IJC(B)828, 95MI297). The reaction can be achieved also under MW irradiation in DMF (97IJC(B)782). The *bis*-triazolo-benzothiadiazine **564** flanked by dihydroxyethyl was prepared from **1** and **563** (05NNN1885). However, reaction of 4-amino-5-(3-chlorobenzo[*b*]thien-2-yl)-1,2,4-triazole-3-thiol (**565**) with **1** in the presence of NaOH, NaOEt, NaOAc, or NaH in different solvents led to recovery of the starting material, but in DMF as a high boiling solvent, the unexpected product **566** was obtained (El Ashry, unpublished results).

Dehydrative cyclization of 4-amino-3-mercapto-6-substituted-1,2,4-triazin(2*H*)-ones **567** with **1** in DMSO gave 8,8-dimethyl-7,8,9,10-tetrahydro-3-substituted-1,2,4-triazino[3,4-*b*][1,3,4]benzothiadiazin-4,10-diones **568** (01PHA376) (Scheme 120).



Scheme 120



Scheme 121

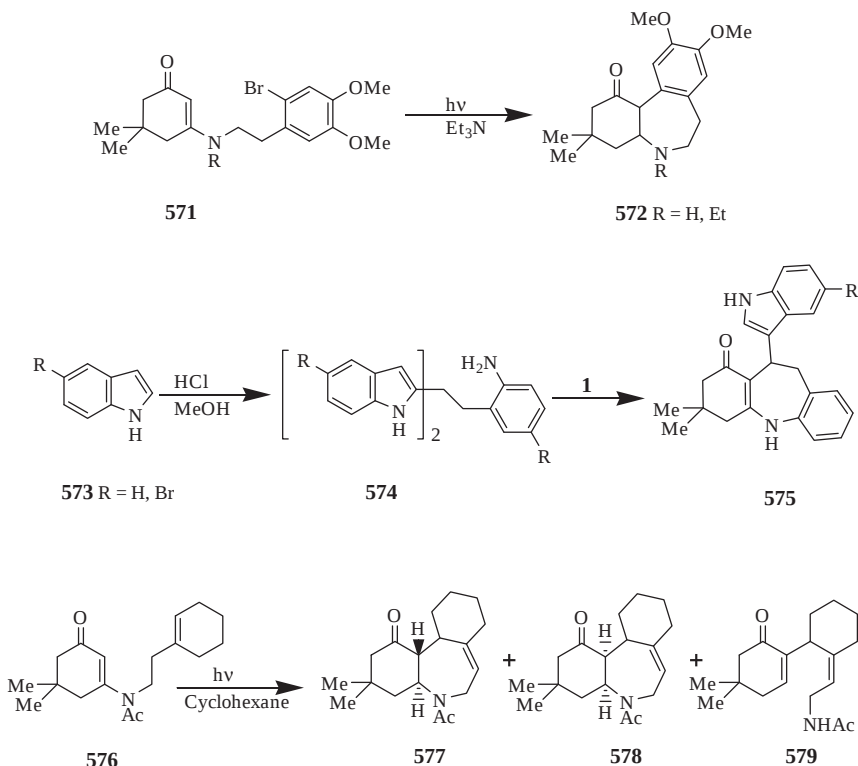
9. DIMEDONE-ANNULATED SEVEN-MEMBERED HETEROCYCLES WITH ONE HETEROATOM

9.1 Annulation with oxepin (synthesis of benzoxepin)

Regioselective heterocyclization of **569–570** has been taken place on treatment with pyridine hydrotribromide, hexamethylenetetramine hydrobromide, elemental bromine, or NIS in acetonitrile and H_2SO_4 at $0-5^\circ\text{C}$ (03SC679) (Scheme 121).

9.2 Annulation with azepine (synthesis of benzazepines)

Photocyclization of the enamine **571** with a high-pressure mercury lamp in dioxane-acetonitrile in the presence of Et_3N gave the azepine **572** (78CC766).



Scheme 122

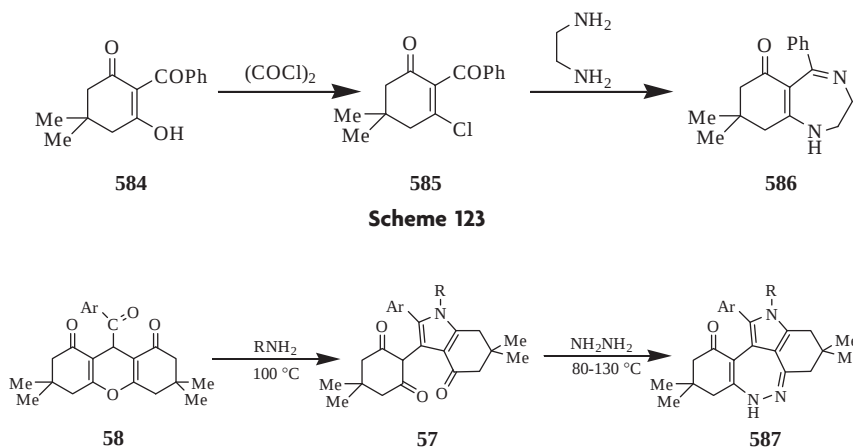
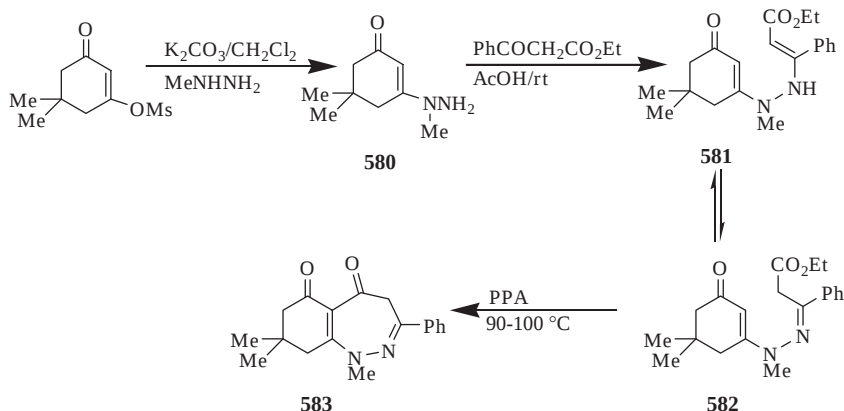
Condensation of **1** with 5-bromoindole **573** (R = Br) in the presence of hydrochloric acid gave indolyl dibenzazepinone **575** (72CR(C)965; 73CR(C)117). The reaction involved the trimerization of **573** to give **574**, which upon reaction with dimedone gave **575**. Similarly **575** (R = H) was obtained when **1** was reacted with indole **573** (R = H) in the presence of 47% HBr (03IJ(C)2573).

Stereoisomeric dibenzazepines **577** and **578** were obtained when a cyclohexane solution of the enamine **576** was photoirradiated (78JOC4420). Irradiation of a dilute solution produced the diastereomeric photoadducts **577** and **578** in addition to the enone **579** (78JOC4420) (Scheme 122).

10. DIMEDONE-ANNULATED SEVEN-MEMBERED HETEROCYCLES WITH TWO HETEROATOMS

10.1 Annulation with diazepine (synthesis of benzodiazepines)

Reaction of hydrazino-cyclohexenone **580** with ethyl benzoylacetate in acetic acid afforded an equilibrium mixture of the hydrazine form **581** and the enhydrazone form **582**, which upon heating in PPA produced

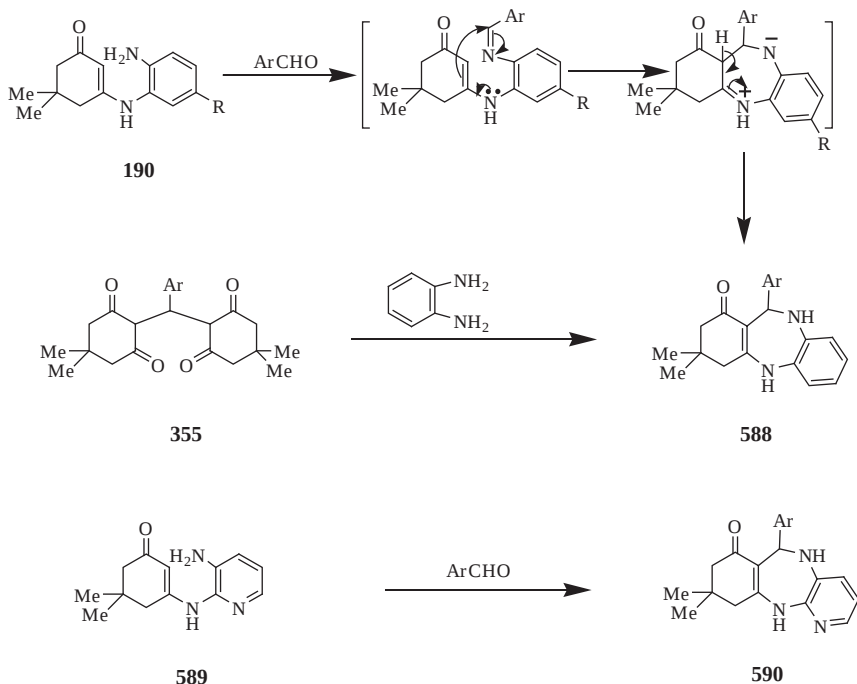


3-phenyl-1,8,8-trimethyl-4,5,6,7,8,9-hexahydro-1,2-benzodiazepine-5,6(1H)-dione (**583**) (98H315).

Chlorination of 2-benzoyldimedone **584** with oxalyl chloride afforded the 3-chloro derivative **585**, which upon treatment with ethylenediamine gave the respective hexahydro-1,4-benzodiazepine **586** (95JHC655) (Scheme 123).

Reaction of tetrahydroindoles **57** (R^1 = dimedone-2-yl, R^2 = Ar), obtained from **58** upon reaction with primary amines, with hydrazine at 80–130 °C in autoclave led to the formation of 1-aryl-4,4,9,9-tetramethyl-2,3,4,5,8,9,10,11-octahydro-7H-benzof[1,2]diazepino[5,4,3-*c,d*]-indol-11-one (**587**) (97HCO73) (Scheme 124).

Cyclization of enaminones **190** to dibenzo[*b,c*][1,4]diazepines **588** was achieved upon treatment with aldehydes (72CPB1588, 90JIC609,



Scheme 125

93MI189, 02JHC55, 04CHE949, 04JHC277; 07JHC183). Alternatively, one-pot reaction of **1**, *o*-phenylenediamine and aryl aldehyde afforded the dibenzodiazepines **588** (01MI24). Compounds **588** were obtained when aryl-*bis*-(dimedonyl)methanes **355** ($R = Ar$) were reacted with *o*-phenylenediamine (04CHE1550).

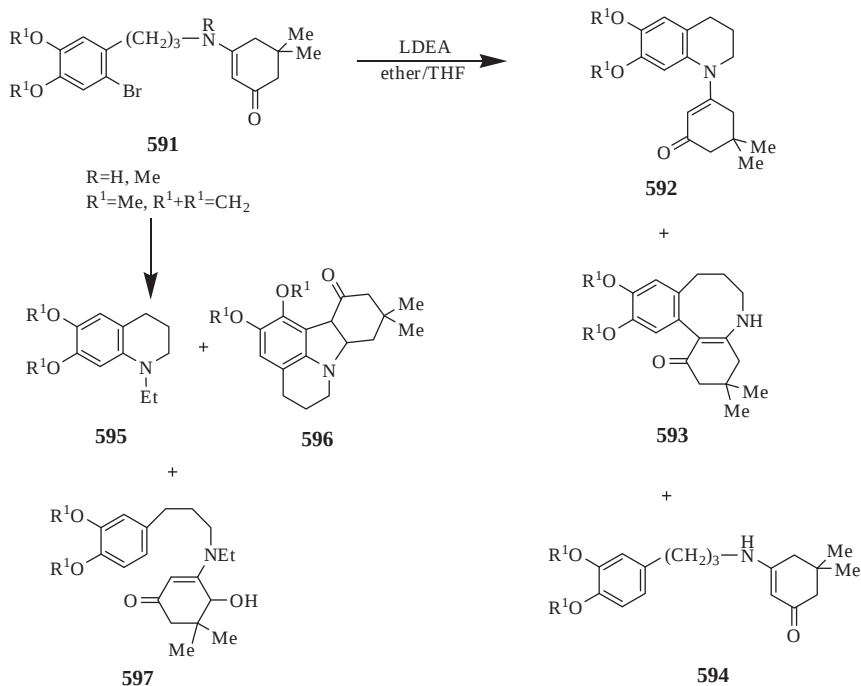
Pyrido[3,2-*b*][1,4]benzodiazepines **590** were obtained when enamine **589** was reacted with aromatic aldehydes (04CHE944) (Scheme 125).

Acetylation of 11-(2,4-dichlorophenyl)-2,3,4,5,10,11-hexahydro-3,3-dimethyl-1H-dibenzo[*b,e*][1,4]diazepin-1-one and its analogues with acetic anhydride gave a series of *N*-acetyl derivatives, which were evaluated for their HCV inhibitory activity (07WOP196).

11. DIMEDONE-ANNULATED EIGHT-MEMBERED HETEROCYCLES WITH ONE HETEROATOM

11.1 Annulation with azocine (synthesis of benzoazocines)

Treatment of the enaminone **591** ($R = H$) with LDEA in ether-THF afforded the tetrahydroquinoline **592**, the benzazocine **593** ($R = H$) and a debrominated product **594** ($R = H$) (79JOC3985). Under similar reaction



Scheme 126

conditions the *N*-ethyl **591** (R = Et) gave the quinoline **595** and pyridocarbazole **596** in addition to the debrominated alcohol **597** (Scheme 126).

The dibenzazocine **599** was prepared from the photoirradiation of the enaminone **598** (78JOC4420). In contrast, irradiation of a benzene solution of 5,5-dimethyl-3-(3-methoxyanilino)cyclohex-2-en-1-one **600** with a high-pressure mercury lamp gave the benzazocine **601** (74TL1741) (Scheme 127).

12. MISCELLANEOUS

3,3,7,7-Tetramethyl-1*a*,2,3,4,6,7,8,8*a*-octahydrobenzofuro[4,3,2-*b,c,d*]benzofuran **604** was obtained in a one-pot reaction of **1** with lithium ethylenediamine (Li/EDA), through the enolization of dimedone in the alkaline medium to give the dienol, which underwent dehydration to the diether **602**. The latter formed two free-radical sites at 2,2'-positions upon attack by the nascent hydrogen formed by Li/EDA, which led to the formation of a C–C bond to give the intermediate **603** that on isomerization furnished **604** (92IJC(B)762) (Scheme 128).

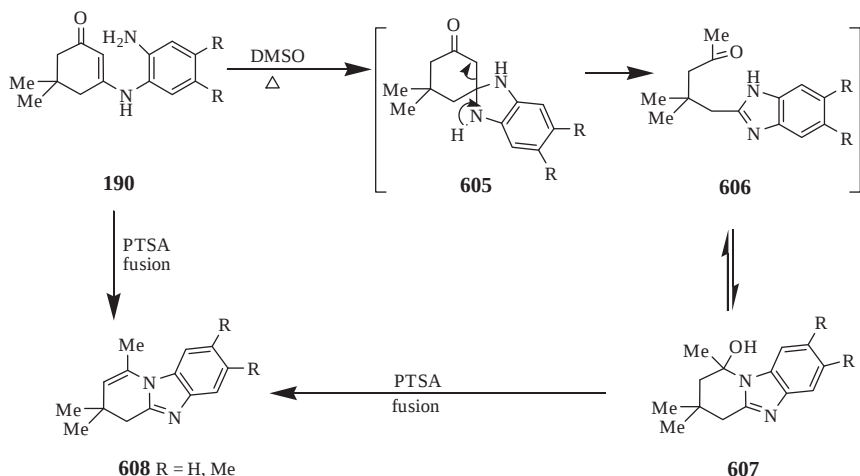


Scheme 127

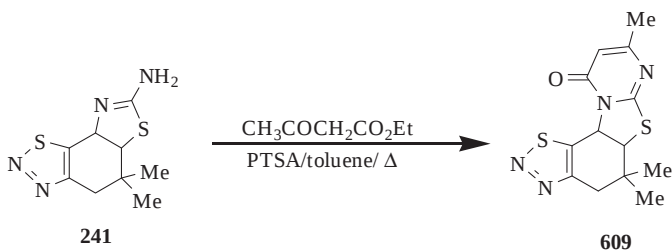


Scheme 128

Condensation of 2-amino[1,2,3]benzothiadiazolo[7,6-*d*]thiazole **241** with ethyl acetoacetate in the presence of PTSA in boiling toluene afforded 5,5,8-trimethyl-4*H*,5*H*-1,2,3-benzothiadiazolo[7',6':4,5]thiazolo[3,2-*a*]pyrimidin-10-one **609** (88SUL125) (Scheme 130).



Scheme 129

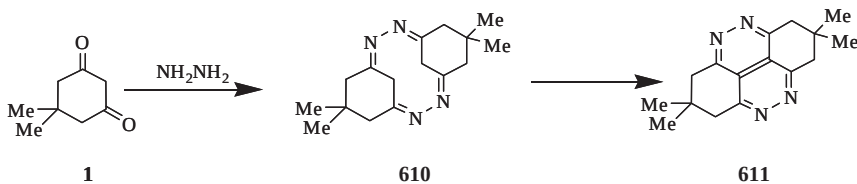


Scheme 130

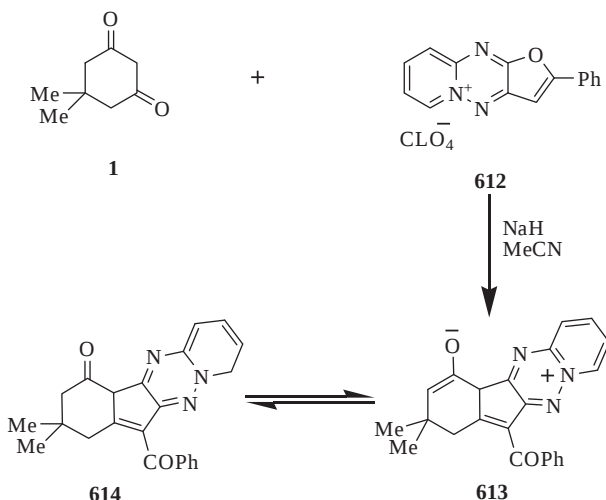
Reaction of dimedone with excess hydrazine hydrate afforded 1,4,5,8-*bis*-dimethyl-trimethylene pyridazino[4,5-*d*]pyridazine **611**. The formation of **611** presumably proceeded through the formation of the intermediate azine **610**, which was oxidized under the reaction conditions to **611** (64JA661) (Scheme 131).

Tricyclic furo[2,3-*e*]pyrido[1,2-*b*][1,2,4]triazinium salt **612** underwent ring transformation by reaction with carbon nucleophiles. Thus, the sodium salt of **1** generated from reaction of **1** and sodium hydride in acetonitrile, was treated with **612** to give 7-benzoyl-8,9,10,11-tetrahydro-9,9-dimethylindeno[1,2-*e*]pyrido[1,2-*b*]1,2,4-triazin-11-one (94CB1799), which because of the enhanced delocalization of the π electronic system, it existed in two equilibrium forms **613** and **614** (Scheme 132).

2-Substituted benzothiazoles **201** ($\text{R} = \text{NH}_2$) were rearranged to thiazolo[5,4-*c*]azepin-8-one **615** under the conditions of Schmidt reaction.



Scheme 131



Scheme 132

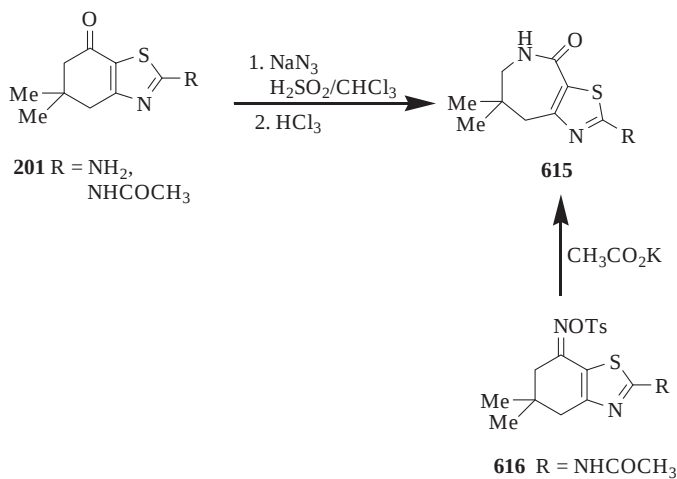
Compound **615** ($\text{R} = \text{NHCOCH}_3$) was also obtained from *N*-*p*-toluenesulfonate **616** by the Beckman rearrangement (89KGS277) (Scheme 133).

Irradiation of the enamine **617** in either methylene chloride or acetonitrile gave the expected aza-DeMayo products **618** (89JOC4165).

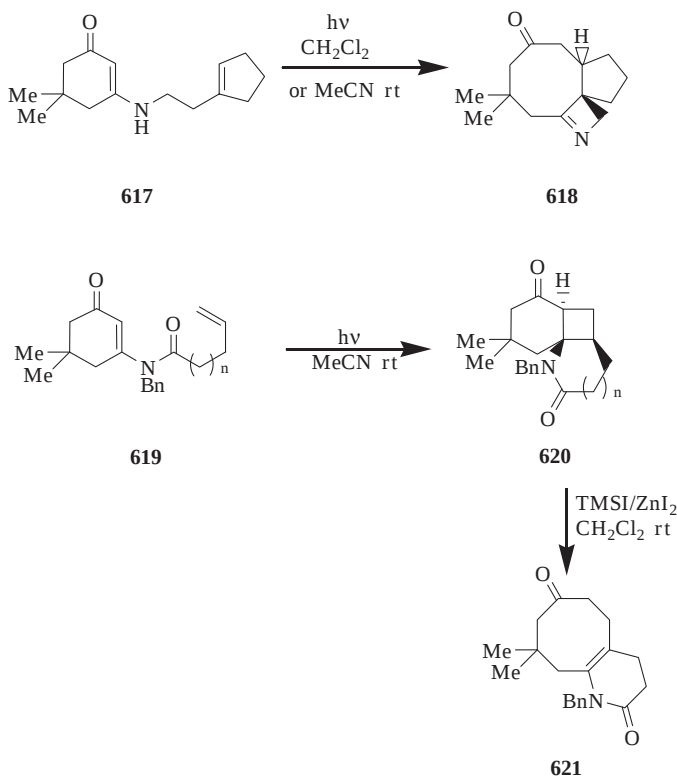
Photoirradiation of β -enamine **619** in argon-flushed acetonitrile solution afforded the regioisomeric [2+2] cycloadduct **620**. Selective ring opening of the cycloadduct **620** with trimethylsilyliodide in methylene chloride gave the pyridocyclooctane **621** (92TL7347) (Scheme 134).

Reaction of **1** and arylidenedimedone **328** with Lawesson's reagent in different molar ratios gave oxathiaphosphole **622**, the disulfide **623** and the dithione analogs of arylidenedimedone (00PS123) (Scheme 135).

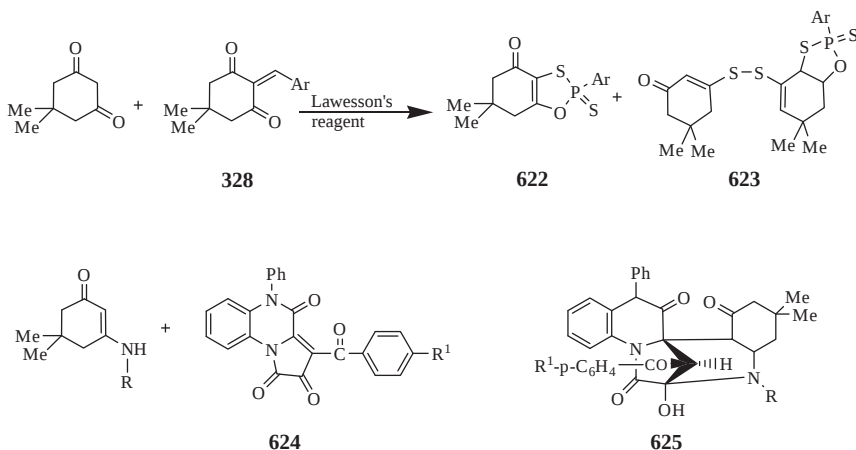
Dimedone was treated with two equivalents of bromine in glacial acetic acid to yield 2,2-dibromo-5,5-dimethylcyclohexane-1,3-dione. The dibromo compound was subjected to reaction with substituted 2-aminothiophenols, 2-aminophenol, thiocarbohydrazones, and triazoles to furnish spiro-(2',6'-dioxo-4',4'-dimethylcyclohexane)-6-substituted-1,



Scheme 133



Scheme 134



Scheme 135

3-benzothiazole, spiro-(2',6'-dioxo-4',4'-dimethylcyclohexane)-6-substituted-1,3-benzoxazole, Schiff base of 1-thia-2-hydrazino-3,4-diaza-4*H*-6,10-dioxo-7,9-dihydro-8,8-dimethyl-spiro[4,5]dec-2-ene and spiro-(2',6'-dioxo-4',4'-dioxo-4',4'-dimethylcyclohexane)-1,3,4-thiadiazolo[2,3-*d*]-4-substituted-1,2,4-triazoles. All compounds were synthesized by also under the MW irradiation technique (06HCO241).

1-Alkylamino-5,5-dimethyl-1-cyclohexen-3-ones **31** was reacted with pyrrolo[1,2-*a*]quinoxaline-1,2,3-triones **624** to form **625** (R = Allyl, Bn, R¹ = Br, MeO) (05MI163) (Scheme 135)

ACKNOWLEDGMENTS

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CHAPTER 2

Pyrazol-3-ones. Part IV: Synthesis and Applications

George Varvounis

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1. INTRODUCTION

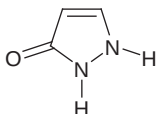
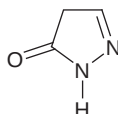
The present chapter is Part IV of a four-part series which aims to follow up the major work on pyrazolones published by Wiley and Wiley in *The Chemistry of Heterocyclic Compounds* series of monographs (64MI1) and specifically comprises an update of Part I. In Part I (01AHC(80)73), the synthesis and applications of pyrazol-3-ones **I** and **II**

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are described covering literature from 1964 up to 2000. In Part II (04AHC(87)141), the reactions of the ring atoms of pyrazol-3-ones **I** and **II** are treated for literature from 1964 up to 2003. In Part III (08AHC(95)27), the reactivity of the ring substituents of pyrazol-3-ones **I** and **II** has been presented from 1964 up to 2007. The literature of the present chapter (Part IV of the series) has been searched up to December 2008.

**(I)****(II)**

1,2-dihydro-3H-pyrazol-3-one

2,4-dihydro-3H-pyrazol-3-one

Following the trend of Parts I, II and III, and throughout Part IV, all pyrazolones have been named according to the IUPAC recommendations as pyrazol-3-ones and not as pyrazol-5-ones. The IUPAC nomenclature numbers the ring clockwise, whereas most organic chemists are used to an anticlockwise numbering.

2. SYNTHESIS

Since the publication of Part 1, the majority of pyrazol-3-ones have been synthesized from open chain precursors, and relatively few from 5-, 6-, 5,6-, 6,6- and 5,6,7-membered rings. Moreover, due to the growing use of combinatorial chemistry in various applications, uses of polymer-supported methodologies have increased.

2.1 Syntheses from aliphatic compounds

2.1.1 From β -keto esters

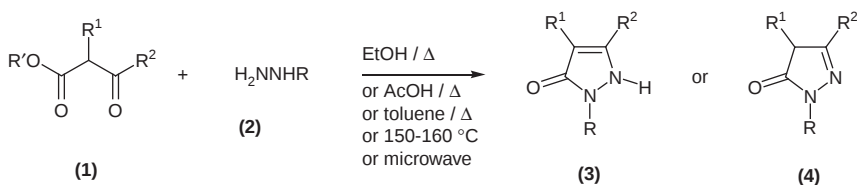
2.1.1.1 By reaction with hydrazine hydrate or monosubstituted alkyl, aryl or heterocyclic hydrazines. The cyclocondensation of simple β -keto esters and their derivatives with hydrazine hydrate or monosubstituted hydrazines is today still the most frequently used method for the synthesis of 1,2- and 2,4-dihydro-3H-pyrazol-3-ones **3** and **4**, respectively. The reactions take place in refluxing methanol (99BSCQ367, 98JHC1281, 01CHE127), methanol and a catalytic amount of hydrochloric acid (01CHE127), ethanol (01BSCQ459, 01HC493, 01SC1335, 02CC1896,

02EJC947, 02IJC(B)394, 02JHC877, 02JOM134, 02SC3767, 02ZN(B)668, 03BMCL3983, 03H2323, 04APH143, 04HYN64, 04JIC(I)32, 04JMC3111, 04YH1300, 05AP167, 05H77, 05HYN195, 05JCCS1205, 05USP272794, 06BMCL5939, 06PCT12934, 06PCT114213, 08AR112(xi)), ethanol and a catalytic amount of acetic acid (06IJC(B)1041), ethanol and a catalytic amount of hydrochloric acid (03CHE749), ethanol and a catalytic amount of sulfuric acid (04MOL109), aqueous ethanol and ethyl acetate (02AP99), ethanolic potassium hydroxide (04M45), ethanolic sodium ethoxide (00PS1), acetonitrile (07BMCL4228), toluene (98BMCL2689), toluene and 3 Å molecular sieves (96JMC3920), acetic acid (01RJOC1228, 00TL4713, 01JMC3730, 02SC3767), aqueous acetic acid (06BMCL3713), xylene and sodium (01BCF140), neat reactants (99JOC2814), neat reactants at 100, 160 or 180 °C (03H197, 02PJS69, 06HEC225, 07DP387), neat reactants in the presence of potassium hydroxide at 150–160 °C (99JOM344) and neat reactants under microwave (MW) irradiation (01SC3175). In Scheme 1 and Table 1, the syntheses of 1,2-dihydro-3*H*-pyrazol-3-ones **3** and 2,4-dihydro-3*H*-pyrazol-3-ones **4** are presented in chronological order.

Formation of the dianion of ethyl 3-oxobutanoate **5** with two equivalents of lithium diisopropylamide (LDA) in tetrahydrofuran followed by alkylation with allyl or propargyl bromide provided β -keto esters **6a,b** in 62% and 75% yield, respectively. Condensation of these esters with methyl or phenyl hydrazine in refluxing ethanol yielded the corresponding pyrazol-3-ones **7a,b** in excellent yield (99TL3535) (Scheme 2).

A direct way of obtaining (*E/Z*)-4-[(pyrazolo[3,4-*b*]pyridin-3-yl)hydrazono]pyrazol-3-ones **9a,b** was reported by El-Dean et al. (91IJC(B)878) (Scheme 3) who heated (*E/Z*)-3-oxobutyric acid ethyl ester **8** with hydrazine hydrate **2a** or phenylhydrazine **2b** in glacial acetic acid. The products were isolated in 60% and 55% yield, respectively.

Diazotization of 4-[(4-aminophenyl)sulfonamido]-2,6-dimethyl pyrimidine **10**, followed by coupling of the diazonium salt with ethyl 3-oxobutanoate **11a** or 1,3-diphenyl-1,3-propanedione **11b**, afforded hydrazones **12a,b**. Reaction of hydrazone **12a** with aminoguanidine nitrate in refluxing acetic acid yielded the pyrazol-3-one **13a** in 55% yield (00JIC42) (Scheme 4).



Scheme 1

Table 1 1,2-Dihydro-3*H*-pyrazol-3-ones (**3**) and 2,4-dihydro-3*H*-pyrazol-3-ones (**4**)

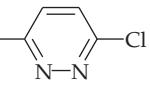
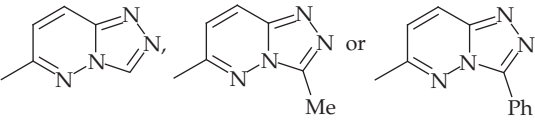
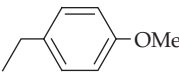
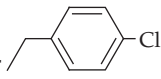
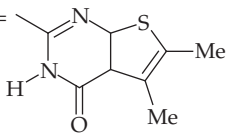
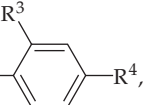
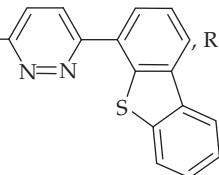
Characteristic substitution	Product	References
$R = H, R^1 = CH_2-4-MeSC_6H_4, R^2 = CF_3$ or $R^1 = CF_3$	(4)	96JMC3920
$R = Me, R^1 = CH_2-4-MeSC_6H_4, R^2 = CF_3$ or $R^1 = CF_3$	(3)	96JMC3920
$R = 4-ClC_6H_4, R^1 = 4-FC_6H_4, R^2 = 4-pyridyl$ or $R^1 = 4-pyridyl, R^2 = 4-FC_6H_4$	(3)	98BMCL2689
$4-NO_2C_6H_4$, or 	(3)	98JHC1281
		
$R = H, R^1 = H, R^2 = Ph$	(4)	99BSCQ367
$R^1 = H, R^2 = Bz, R = Ph$,  or 	(4)	99JOC2814
$R = 4-CF_3C_6H_4, R^1 = H, R^2 = Me$	(3)	99JOM344
$R^1 = H, R^2 = Me, R =$ 	(4)	00PS1
$R = NO_2, R^1 = H, R^2 = Me, R^2 = CH(Me)_2$	(4)	00TL4713
$R =$  , $R^3 = R^4 = H, R^3 = Me, R^4 = H, R^3 = H$		
$R^4 = CO_2Et, R^3 = H, R^4 = H, SO_2NH_2, R^1 = CH_2-1H$ -benzoimidazol-2-yl, $R^2 = Me$	(4)	01BCF140
$R = R^1 = H, R^2 = Me$ or Ph	(4)	01BSCQ459
$R = 1H$ -benzoimidazol-2-yl, $R^1 = H, R^2 = CF_3$	(3)	01CHE127
$R = 1H$ -benzoimidazol-2-yl, $R^1 = H, R^2 = Me$	(4)	01CHE127
$R =$  , $R^1 = H, R^2 = Me$	(4)	01HC493

Table 1 (Continued)

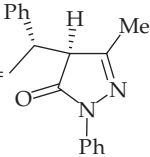
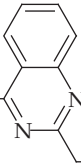
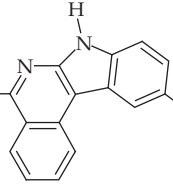
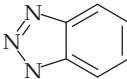
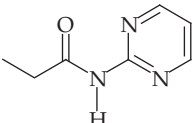
Characteristic substitution	Product	References
$R^1 = R^2 = H, R^3 = Me, R = (CH_2)_2OH, Bn, 2-MeC_6H_4,$ $3-MeC_6H_4, 3-(Me_3)CC_6H_4, 4-(Me_3)CC_6H_4, 2-(F_3)CC_6H_4, 4-$ $(F_3)CC_6H_4, 2-(F_3)CC_6H_4, 4-BnOC_6H_4, 2-NO_2C_6H_4,$ $4-NO_2C_6H_4, 4-SO_2MeC_6H_4, 3,4-Me_2C_6H_4, 3,4-Cl_2C_6H_4,$ $4-IC_6H_4$ or 2-pyridin-2-yl or $R^1 = R^2 = H, R^3 = Ph,$ $R = 3,4-Me_2C_6H_4$	(4)	01JMC3730
 $R^1 = H, R^2 =$, $R^3 = Me, R = Ph$	(4)	01SC1335
$R^1 = R^2 = H, R^3 = (CH_2)_2Me$ or $Ph, R = Ph$	(4)	01SC3175
$R^1 = R^2 = H, R^3 = Me, R = 4-FC_6H_4$	(4)	02AP99
$R^1 = R = H, R^2 = Ph$	(3)	02CC1896
 $R^1 = H, R^2 = Me, R =$	(3)	02EJC947
 $R^1 = R^2 = H, R^3 = Me, R =$, $R^4 = Me$ or Cl	(4)	02IJC(B)394
 $R^1 = R^2 = H, R^3 =$, $R = H$	(4)	02JHC877
$R = H, R^2 = Ph, R = Cl$ or $R^2 = 4-NO_2C_6H_4$	(4)	02JOM134
 $R^1 = H, R^2 = Me, R =$	(3)	02PJS69

Table 1 (Continued)

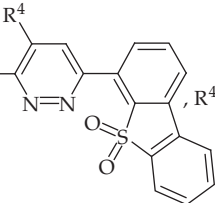
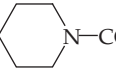
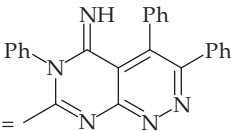
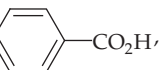
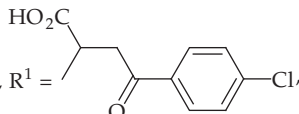
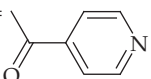
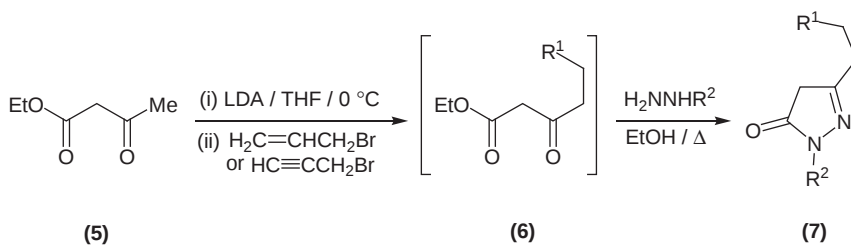
Characteristic substitution	Product	References
$R^1 = \text{CO}_2\text{Et}$, $R^2 = \text{Et}$, $(\text{CH}_2)_5$, $(\text{CH}_2)_9$, PhCH_2 or $\text{Ph}(\text{CH}_2)_2$, $R = \text{H}$	(3)	02SC3767
$R^1 = R^2 = \text{H}$, $R^3 = \text{Me}$, $R =$  , $R^4 = \text{NHCH}_2\text{Ph}$	(4)	02ZN(B)668
$R^1 = R^2 = \text{Me}$, $R^3 = 4\text{-HNCO}_2\text{BnC}_6\text{H}_4$, $R = \text{H}$	(4)	03BMCL3983
$R^1 = R^2 = \text{H}$, $R^3 = \text{Me}$, $R = 3,5\text{-Cl}_2\text{pyridin-2-yl}$	(4)	03CHE749
$R^1 = R^2 = \text{H}$, $R^3 = \text{CH}_2\text{CO}_2\text{R}'$, $\text{R}' = \text{Me}$ or Et , $R = \text{Ph}$	(4)	03H197
$R = \text{Ph}$, $R^1 = \text{H}$, $R^2 = \text{Me}$ or Ph	(3)	03H2323
$R = 2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3$, $R^2 = \text{Me}$, $R^1 = \text{N} = \text{NAr}$ where $\text{Ar} = \text{Ph}$ or $4\text{-ClC}_6\text{H}_4$	(4)	04APH143
$R = 4\text{-NO}_2\text{C}_6\text{H}_4$, $R^1 = \text{H}$, $R^2 = \text{Me}$	(4)	04HYN64
$R^1 = R^2 = \text{H}$, $R^3 =$  , $R = \text{H}$	(4)	04JMC3111
$R^1 = R^2 = \text{H}$, $R^3 = \text{Me}$, $R =$ 	(4)	04M45
$R^1 = R^2 = R = \text{H}$, $R^3 = \text{CF}_3$	(4)	04MOL109
$R = 3\text{-MeC}_6\text{H}_4$, $R^1 = \text{H}$, $R^2 = \text{Me}$	(3)	04JIC(I)32
$R = 4\text{-ClC}_6\text{H}_4$, $R^1 = \text{H}$, $R^2 = \text{Ph}$	(3)	04YH1300
$R = 4\text{-MeC}_6\text{H}_4$, $4\text{-FC}_6\text{H}_4$, $4\text{-SO}_2\text{NH}_2\text{C}_6\text{H}_4$ or $4\text{-SO}_2\text{NHAcC}_6\text{H}_4$		
$R^1 = \text{N} = \text{N}$ -  - CO_2H , $R^2 = \text{Me}$	(4)	05AP167
$R = \text{H}$, $R^1 = \text{CO}_2\text{Et}$, $R^2 = \text{Me}$	(3)	05H77
$R = 4\text{-MeC}_6\text{H}_4$, $R^1 = \text{H}$, $R^2 = \text{Me}$	(4)	05HYN195
$R = \text{Ph}$, $R^1 =$  , $R^2 = \text{Me}$	(4)	05JCCS1205

Table 1 (Continued)

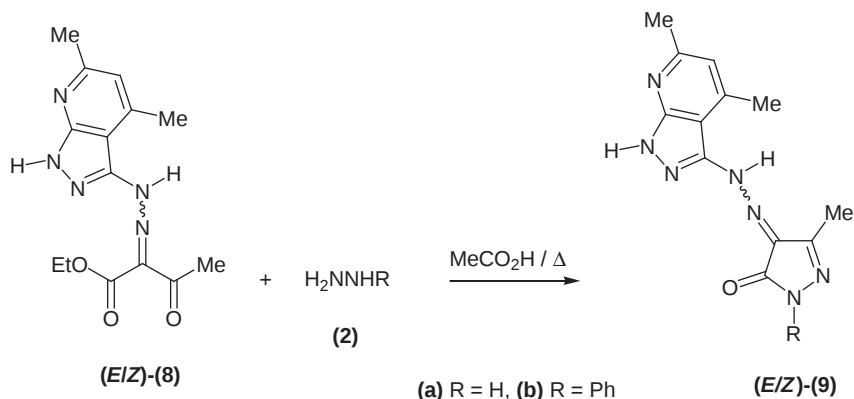
Characteristic substitution	Product	References
R = CH(Me)-4-CO ₂ EtC ₆ H ₄ , R ¹ = H, R ² = 3,5-Cl ₂ C ₆ H ₃ ,	(4)	05USP272794
R = Ph, R ¹ = H, R ² = Et, <i>i</i> -Pr or <i>i</i> -Bu	(4)	06BMCL3713
R ¹ = H, R ² = Me, R = cyclohexyl, 4-MeOC ₆ H ₄ or	(4)	06BMCL5939
2-pyridyl R = Ph, R ¹ = H, R ² = CF ₃ , Ph, 4-NO ₂ C ₆ H ₄ or		
4-MeOC ₆ H ₄ , R = Ph, R ¹ = H, R ² = PhCH ₂ or isopropenyl,		
R ² = Me,		
R ¹ = Ph, cyclopropyl or isobutyl		
R = H or Ph, R ¹ = H or Et, R ² = Me, R = H or Ph,	(4)	06HEC225
R ¹ = H, R ² = <i>n</i> -Pr or 2-furyl		
R = Ph, R ¹ = CO ₂ Et, R ² = Ph or 4-NO ₂ C ₆ H ₄	(4)	06IJC(B)1041
R = 1,3-benzothiazol-2-yl, R ¹ = H, R ² = Me	(4)	06PCT12934
R = pyrimidin-2-yl, R ¹ = =CHOH, R ² = pyridin-3-yl	(3)	06PCT114213
R ¹ = H, R ² = Me, R = Ph, 2-pyridyl, cyclohexyl,	(3)	07BMCL4228
2-FC ₆ H ₄ , 3-FC ₆ H ₄ , 4-FC ₆ H ₄ , 4-ClC ₆ H ₄ , 4-HOC ₆ H ₄ ,		
4-NO ₂ C ₆ H ₄ , 4-CNC ₆ H ₄ , 4-MeOC ₆ H ₄ , 4-NH ₂ C ₆ H ₄ ,		
4-CO ₂ HC ₆ H ₄ , 4-MeCONHC ₆ H ₄ , 4-(Me) ₂ NC ₆ H ₄ ,		
4-Cl(3-pyridyl) or 4-MeO(3-pyridyl)		
R ¹ = H, R ² = Ph, R = 2-pyridyl, 4-MeOC ₆ H ₄ or 4-ClC ₆ H ₄	(4)	07DP387
R =  , R ¹ = H, R ² = Me	(4)	08AR112(xi)



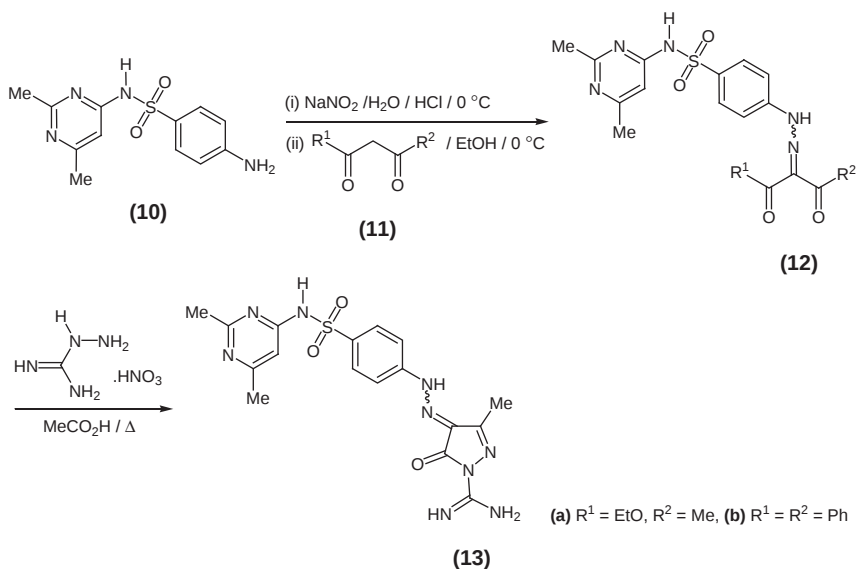
(a) R¹ = HC=CH, R² = Me or Ph, (b) R¹ = C≡CH, R² = Me or Ph

Scheme 2

An efficient and selective procedure for the synthesis of spiro-fused isoxazolinopyrazol-3-ones **23** from 2-(spiro-isoxazolino) β -keto esters **21**, starting from methyl acrylate **14**, has been developed by Kurth and co-workers (02JOC876) (Scheme 5). The process consists of utilizing the Baylis–Hillman reaction, or a quicker stepwise Michael addition, Aldol reaction and Cope elimination (MAC) procedure, 1,3-dipolar

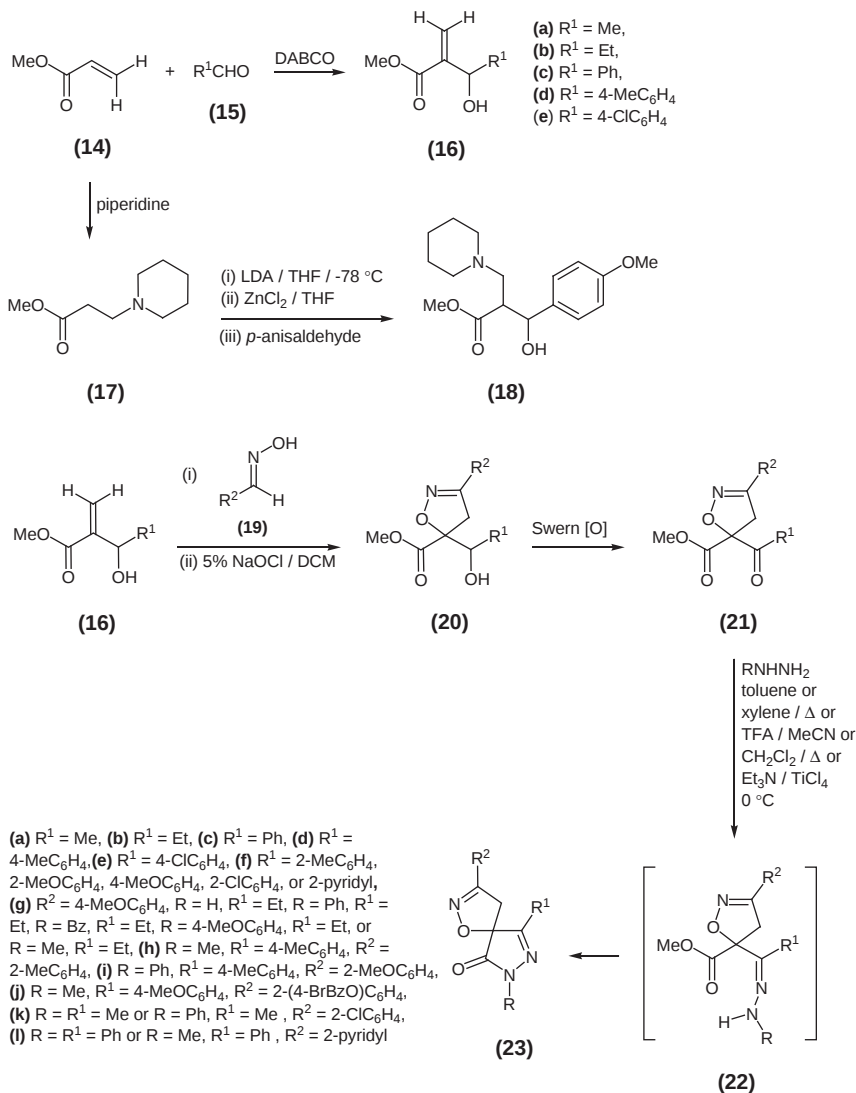


Scheme 3



Scheme 4

cycloaddition with nitrite oxides, Swern oxidation and hydrazone formation with concomitant cycloelimination. The key intermediates are the allylic alcohols **16a–e**. With the exception of allylic alcohol **16e**, they were synthesized from aldehydes **15a–d** and methyl acrylate **14** in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) for 7–10 days. The problems encountered with *p*-anisaldehyde led to the use of the following method. Methyl acrylate **14** underwent a Michael addition with piperidine to give methyl-3-piperidine-1-yl-propanoate **17**, and then treated consecutively with LDA to form the lithium enolate, ZnCl_2 , to

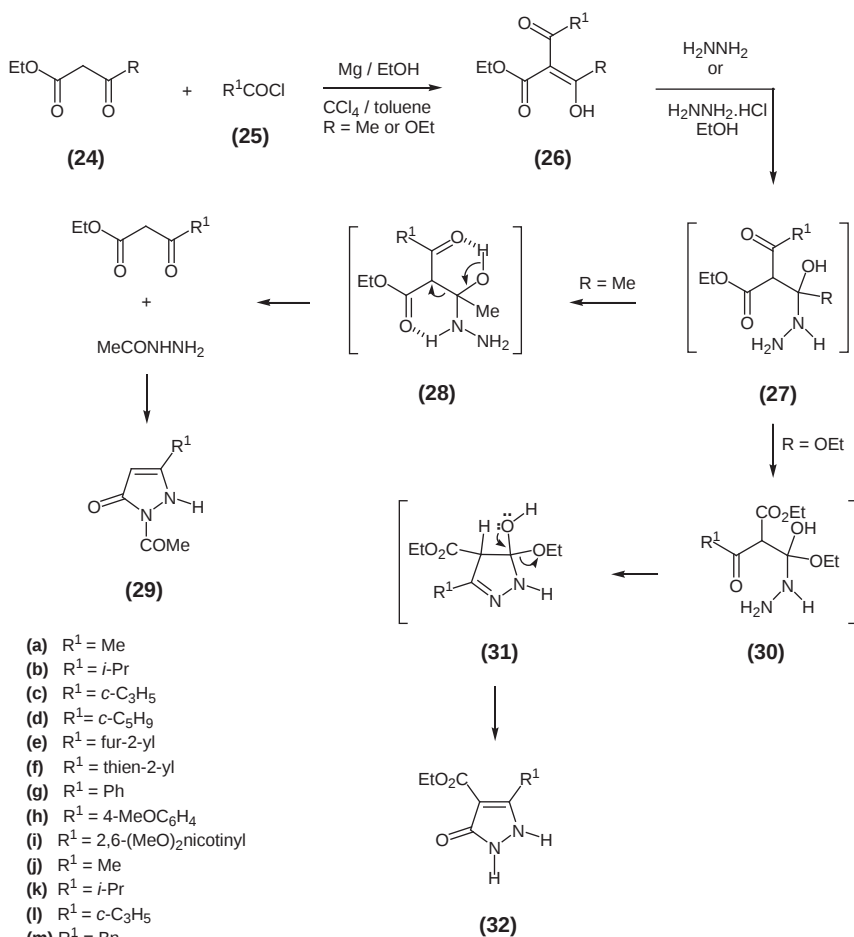


Scheme 5

form the zincate, and *p*-anisaldehyde to form the aldol adduct **18**. Treatment of **18** with MCPBA in DCM caused N-oxide formation from the γ -amino alcohol followed by Cope elimination to afford **16e** in 58% yield. In the next step, the allylic alcohols **16a–e** were reacted with the corresponding nitrite oxides generated *in situ* from aldoxides in the presence of 5% sodium hypochlorite solution. The resulting 1,3-dipolar cycloaddition gave isoxazolines **20a–f**. Diastereoselectivity for these

cycloadducts ranged from 1.4 to 2.6 with a preference for the *syn* diastereomer. Compounds **20a–f** then were used without separation of diastereomers or purification. The subsequent Swern oxidation removed the second stereocenter and proceeded efficiently to give β -keto esters **21a–f** in yields ranging from 64% to 76%. These compounds were converted to spiro-isoxazolinopyrazol-3-ones **23g–l** with hydrazines by three methods: refluxing in toluene or xylene in the presence of triethylamine, in acetonitrile or dichloromethane in the presence of trifluoroacetic acid (TFA), or in dichloromethane in the presence of titanium tetrachloride first at 0 °C and then to refluxing temperature.

Avery and co-workers (02T3639) (Scheme 6) developed an efficient synthesis of 5-substituted and 4,5-disubstituted pyrazol-3-ones **29a–m**

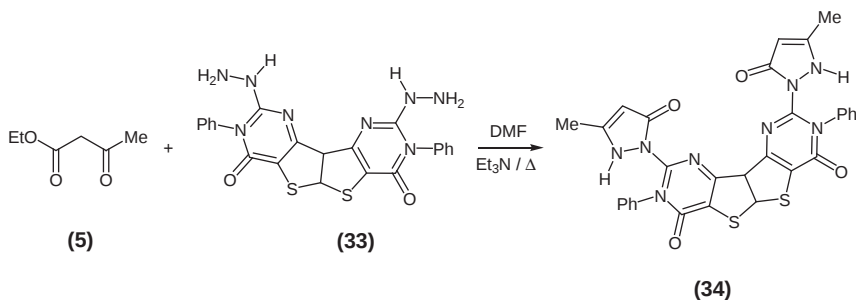


Scheme 6

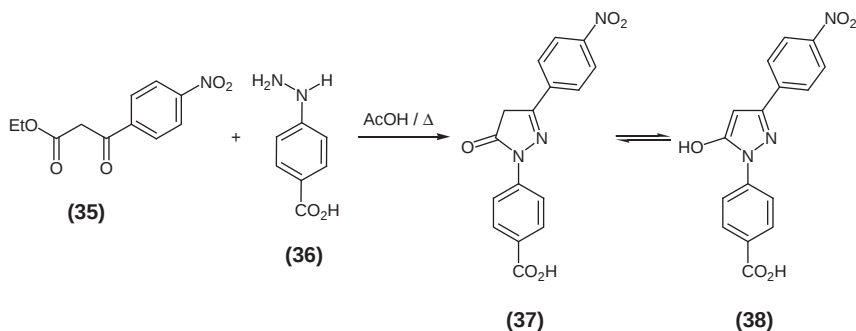
and **32a–d** from α -acylated β -keto esters and diethyl malonates. The required α -acylated esters **26a–m** could be synthesized in high yields from ethyl 3-oxobutanoate **24** ($R = \text{Me}$) or diethyl malonate **24** ($R = \text{OEt}$) with the appropriate acyl chlorides **25a–m** and magnesium diethoxide in carbon tetrachloride/toluene. The acylated β -keto esters **26a–i** were easily and cleanly converted to 5-substituted pyrazol-3-ones **29a–i** with 98% hydrazine in ethanol at room temperature, while acylated diethyl malonates **26j–m** were cleanly transformed into 4-ethoxycarbonyl-5-substituted pyrazolones **32j–m** with hydrazine hydrochloride in ethanol. The postulated mechanisms for these two reactions are shown in Scheme 6.

Khodairy (03PS893) (Scheme 7) heated 3,6-hydrazino-2,7-diphenyl-2*H*,7*H*-9,10-dithia-2,4,5,7-tetraazaindeno[1,2-*a*]indene-1,8-dione **33** with two equivalents of ethyl 3-oxobutanoate **5** in *N,N*-dimethylformamide containing triethylamine and obtained the *bis*-pyrazol-3-one derivative **34** in 30% yield.

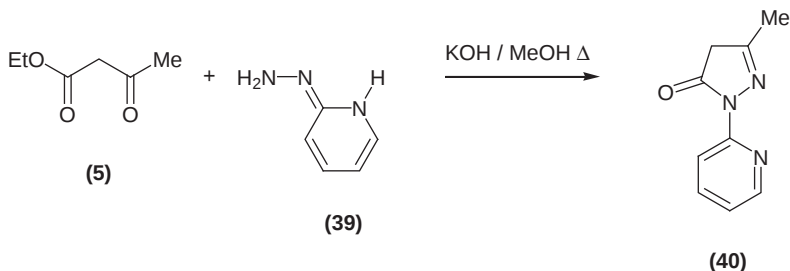
The preparation of pyrazol-3-one **37** involved heating 4-hydrazino-*benzoic acid* **36** and 4-nitrobenzoyl acetate in acetic acid (03TL8063) (Scheme 8). It was found by NMR spectroscopy that in non-polar



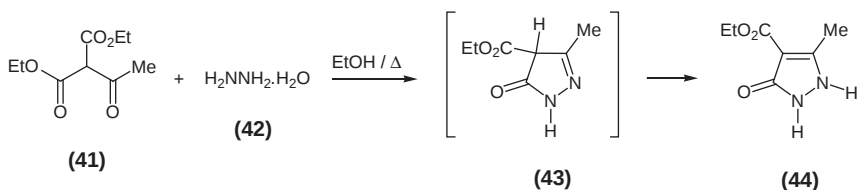
Scheme 7



Scheme 8



Scheme 9



Scheme 10

solvents, the pyrazol-3-one **37** existed in near 1:1 ratio with its enol form pyrazol **38**. In polar solvents, however, the enol was predominant.

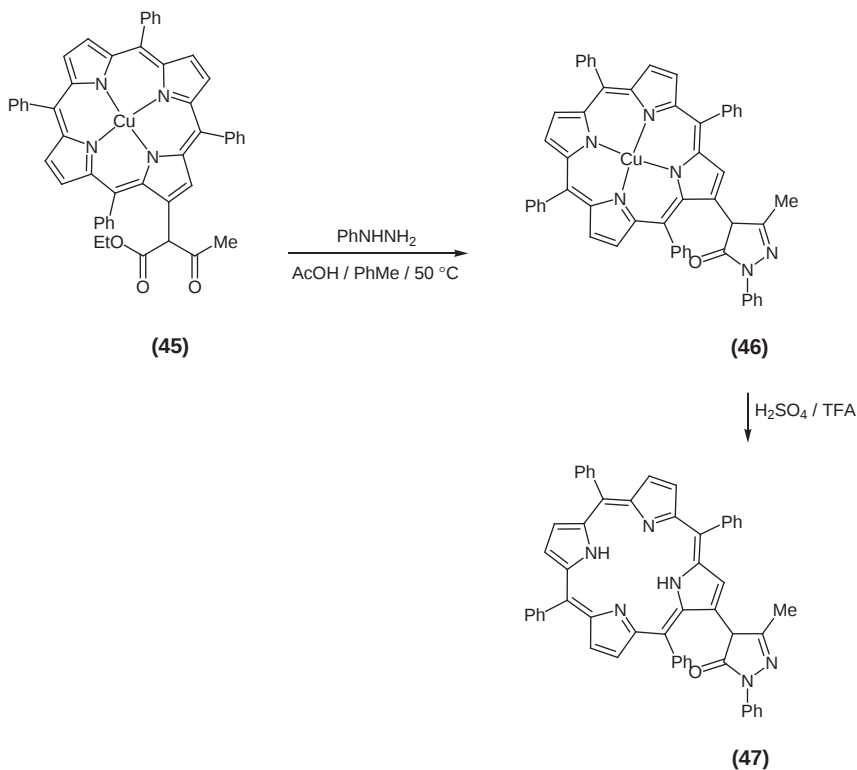
5-Methyl-2-pyridin-2-yl-2,4-dihydro-pyrazol-3-one **40** was synthesized by heating ethyl 3-oxobutanoate **5** and (1*H*-pyridin-2-ylidene)-hydrazine **39** in methanol containing potassium hydroxide (04IC4387) (Scheme 9). Compound **40** was used to synthesize, among others, silver(I) complexes.

The cyclocondensation of 2-acetylmalonic acid diethyl ester **41** with hydrazine hydrate **42** gave pyrazol-3-one **44**, after tautomerism of the initially formed intermediate **43** (05H77) (Scheme 10).

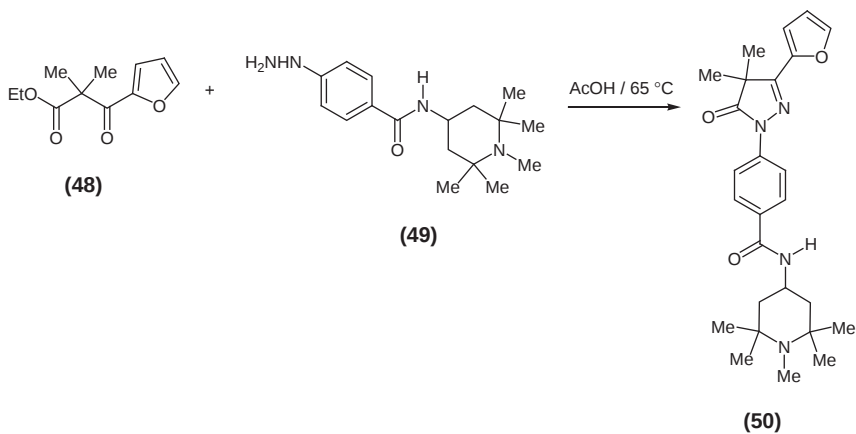
Cavaleiro and co-workers (05T10454) (Scheme 11) showed that the β -keto ester **45** could be converted into pyrazol-3-one **46** in 60% yield by reacting it with phenyl hydrazine in a mixture of glacial acetic acid and toluene at 50 °C. The free base **47** was obtained in 94% yield by treating the metallated porphyrin **46** with a 5% solution of concentrated sulfuric acid in TFA.

Although 2,2-disubstituted β -keto esters are less common than 2-substituted β -keto esters, the direct introduction of two methyl groups in position 4 of pyrazol-3-ones was considered important and was patented (05PCT46679) (Scheme 12). Thus, ethyl 3-(2-furyl)-2,2-dimethyl-3-oxopropanoate **46** was heated with 4-hydrazino-*N*-(1,2,2,6,6-pentamethylpiperidin-4-yl)benzamide **49** in glacial acetic acid at 65 °C to give 4,4-dimethylpyrazol-3-one **50** in good yield.

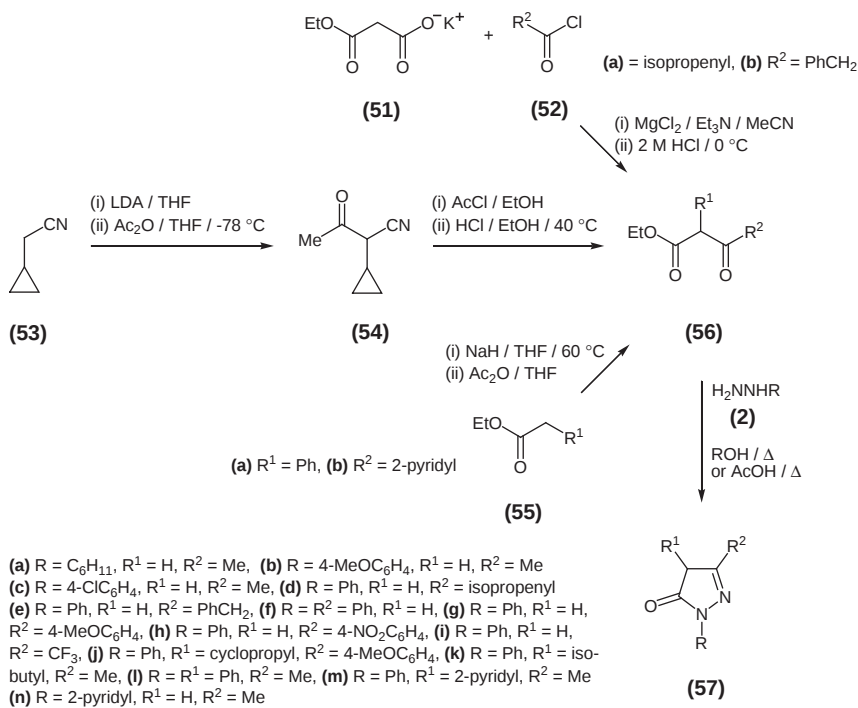
Recently, Nakagawa and co-workers (06BMCL5939) (Scheme 13) prepared a small focused library of edaravone derivatives. Edaravone (5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one), also known as



Scheme 11



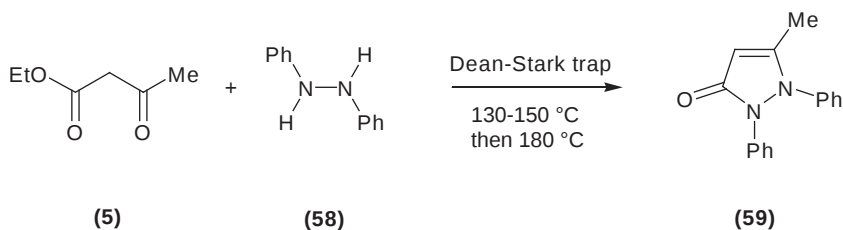
Scheme 12



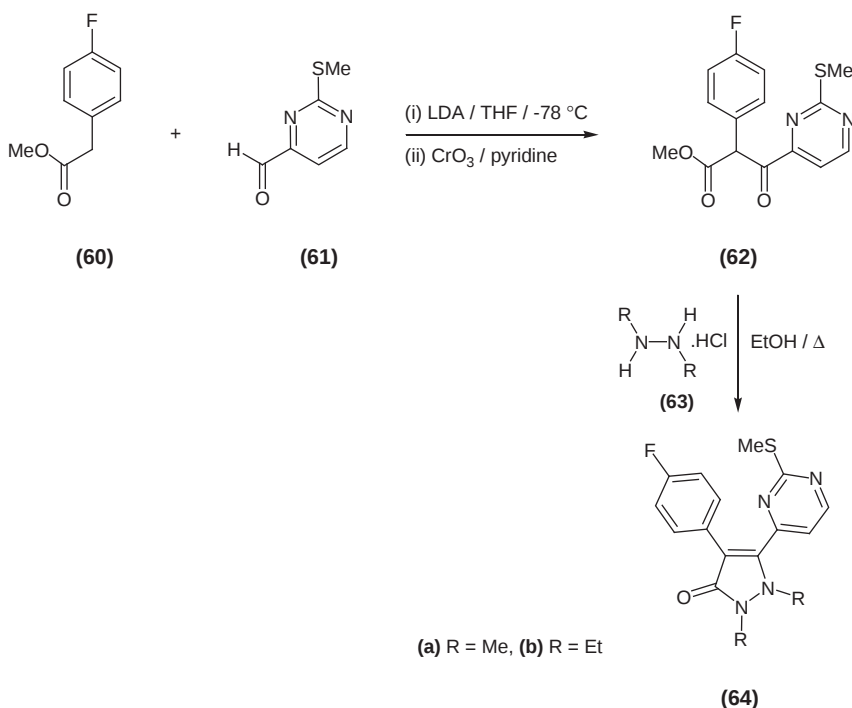
Scheme 13

MCI-186, has been developed as a medical drug for brain ischemia. The preparation of pyrazol-3-ones **57a–m** was achieved by refluxing β -keto esters **56a–m** and hydrazines **2a–m** in ethanol or acetic acid. β -Keto esters **56d,e,j,l,m**, which are not commercially available, were synthesized from acyl chlorides **52a,b**, nitrile **53** or ethyl esters **55a,b** with the appropriate reagents (Scheme 13). Ethyl 2-acetyl-3-methylbut-3-enoate **56k** was prepared in 43% yield from ethyl 3-oxobutanoate **56a** by first forming ethyl 3-oxobutanoate sodium salt and then treating the salt with isobutyl iodide in THF at 80°C .

2.1.1.2 By reaction with *N,N'*-disubstituted alkyl or aryl hydrazines. The condensation of β -keto esters with *N,N'*-disubstituted hydrazines is an obvious route when 1,2-disubstituted 1,2-dihydro-3*H*-pyrazol-3-ones are required. This method introduces the same substituent in positions 1 and 2 of the ring and may be the reason why it has not been widely used. Synthesis of 1,2-diphenyl-5-methylpyrazol-3-one **59** required heating ethyl 3-oxobutanoate **5** with 1,2-diphenylhydrazine **58** in a Dean-Stark trap first at $130\text{--}150^\circ\text{C}$ and then at 180°C (05AF251) (Scheme 14).



Scheme 14

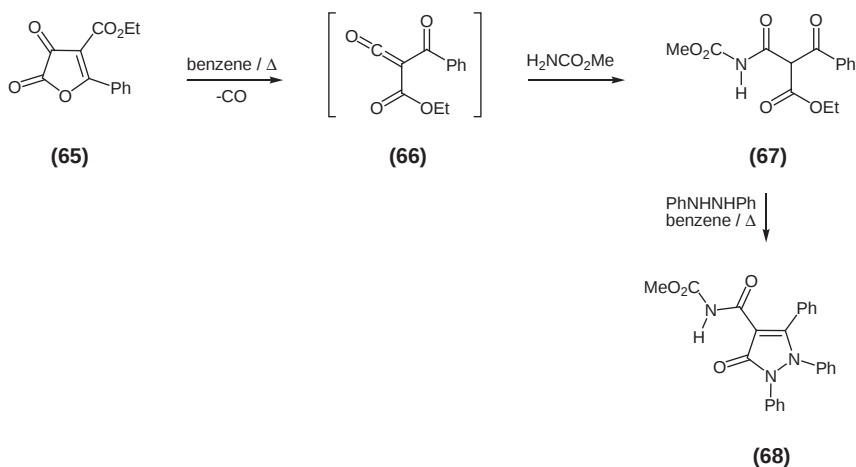


Scheme 15

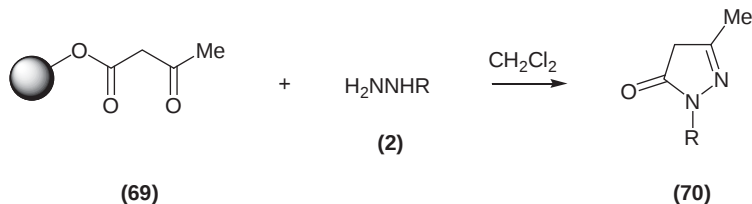
The use of 1,2-disubstituted hydrazine hydrochlorides with β -keto esters seems to work well under milder conditions. The condensation of 1,2-dimethyl- or 1,2-diethylhydrazine hydrochlorides **63a,b** with methyl 2-(4-fluorophenyl)-3-[2-(methylthio)pyrimidin-4-yl]-3-oxopropionate **62** required heating under reflux in ethanol to give pyrazol-3-ones **64a,b** (05BMCL2285) (Scheme 15). The β -keto ester **62** was synthesized by coupling methyl (4-fluorophenyl)acetate **60** with 2-(methylthio)pyrimidine-4-carboxaldehyde **61** in tetrahydrofuran with LDA at $-78\text{ }^{\circ}\text{C}$, followed by chromium(VI) oxide oxidation.

The introduction of a carbonyl carbamate group at position 4 of the pyrazol-3-one ring can be done directly by fusion of appropriately 2-substituted β -keto ester with a hydrazine (04TJC659) (Scheme 16). The β -keto ester **67** was synthesized in two steps from ethyl 4,5-dioxo-2-phenyl-4,5-dihydrofuran-3-carboxylate **65** by decarbonylation to ethoxy-carbonylbenzoylketene intermediate **66** in refluxing benzene and then nucleophilic addition by methyl carbamate. Ethyl 2-benzoyl-3-[(methoxy-carbonyl)amino]-3-oxopropanoate **67** with diphenylhydrazine on heating in benzene gave 4-substituted pyrazol-3-one **68** in 44% yield.

2.1.1.3 Solid-phase synthesis: by reacting polymer-bound β -keto esters with hydrazine hydrate or monosubstituted hydrazines. Schön et al. (03SL983) (Scheme 17) developed a new 1,3-diketone resin and compared it with β -keto ester resin **69** as the basis for a selective scavenger for hydrazines and for the selective removal of primary amines in the presence of



Scheme 16



(a) $\text{R} = \text{H}$, (b) $\text{R} = (\text{CH}_2)_2\text{CN}$, (c) $\text{R} = \text{Ph}$

Scheme 17

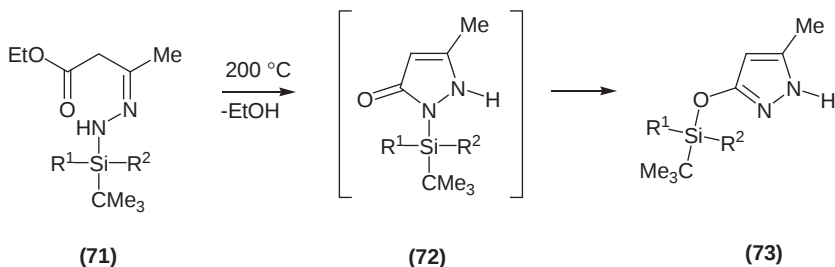
secondary amines. Part of their studies involved the preparation of pyrazol-3-ones **70a–c** from **69** and the corresponding hydrazines **2a–c**.

2.1.1.4 By the cyclization of hydrazones. A common characteristic of hydrazone cyclizations is the requirement of high temperatures when no solvents are used. Under these conditions, heating 3-[(Z)-2-(*t*-butyl-substituted silyl)hydrazono]butanoates **71a–c** at 200 °C initially formed pyrazol-3-ones **72a–c** which were not stable at that temperature but underwent a 1,3-*N,O*-silyl group migration to the *O*-silylpyrazoles **73a–c** (99JOM341) (Scheme 18).

Tautomeric lactose hydrazone **77/78** was obtained from 2,2,2-trifluoroethyl-3-oxobutanoate **76** with hydrazine tautomers **74/74** in a 1:3 ratio using acetonitrile and water to give, after lyophilization, a mixture of pyrazol-3-one **79** and 1-lactosylpyrazol-3-one **80** (00CAR169) (Scheme 19). They were identified by HPLC–ESIMS, their stability being limited due to rapid atmospheric oxidation. Further reaction of this mixture with 4-methylbenzenediazonium chloride in aqueous sodium bicarbonate followed by addition of 2,4-pentadione gave, after purification by HPLC, stable 2- β -D-lactosyl-4-[2-(methylphenyl)diazenyl]pyrazol-3-one **81** in 15% yield.

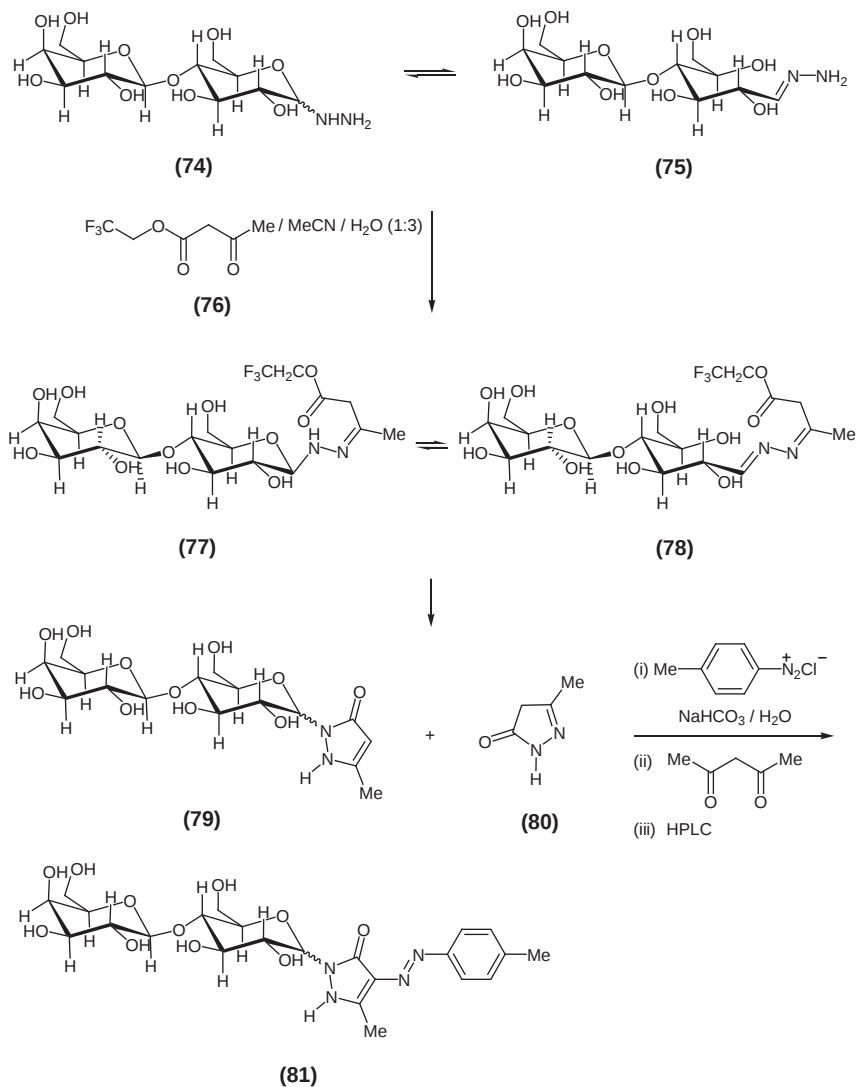
2- β -L-Fucopyranosylpyrazol-3-one **84** was prepared in 25% yield from fucosehydrazone **82** and β -keto ester **83** in a similar manner (00CAR169) (Scheme 20).

Wejroch et al. (02PJC1577) (Scheme 21) heated 3-[(4,4-dimethyl-6-oxopyridazin-3-yl)hydrazono]butanoate **85** at 140–175 °C and obtained a mixture of 6-(3-oxo-pyrazol-2-yl)pyridazin-3-one **86** and [1,2,4]triazolo[4,3-*b*]pyridazin-6-(5*H*)-one **87** in 24% and 68% yield, respectively. Interestingly, 3-[(5-phenyl-6-oxopyridazin-3-yl)hydrazono]butanoate **88** was heated at a higher average temperature to give 6-(3-oxopyrazol-2-yl)-pyridazin-3-one **89** as the only detected product in 37% yield. The authors



(a) R¹ = CMe₃, R² = Ph, (b) R¹ = CMe₃, R² = Me, (c) R¹ = R² = CHMe₂,

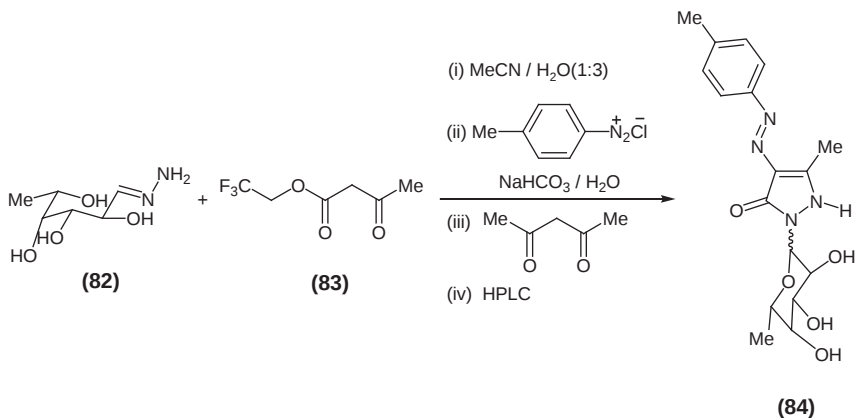
Scheme 18



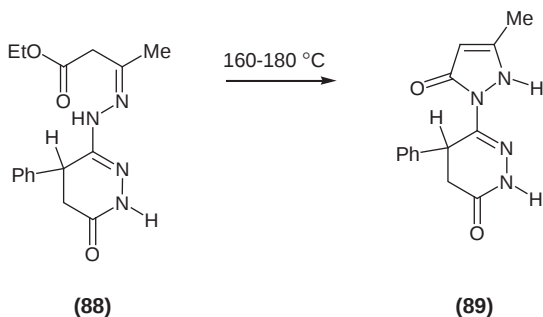
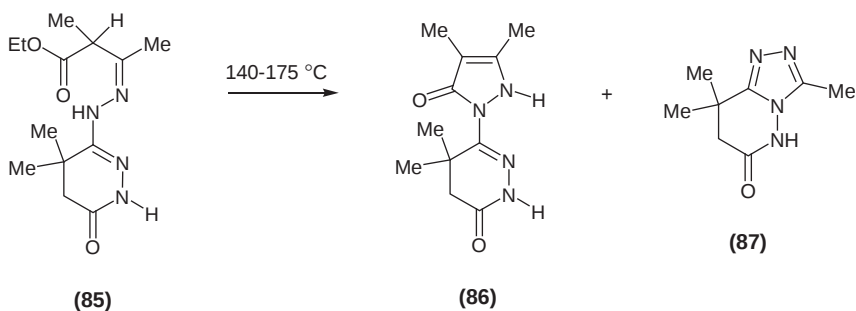
Scheme 19

are unclear why the phenyl group on the pyridazinone ring plays a role in the outcome.

Krivonogov et al. (02RJOC308) (Scheme 22) used basic conditions, *N,N*-dimethylformamide and methanol with sodium methoxide, to cyclize *bis*-hydrazone **90**, whereas Filippone and co-workers (02S1546) (Scheme 22) used acidic conditions, tetrahydrofuran with TFA, to cyclize



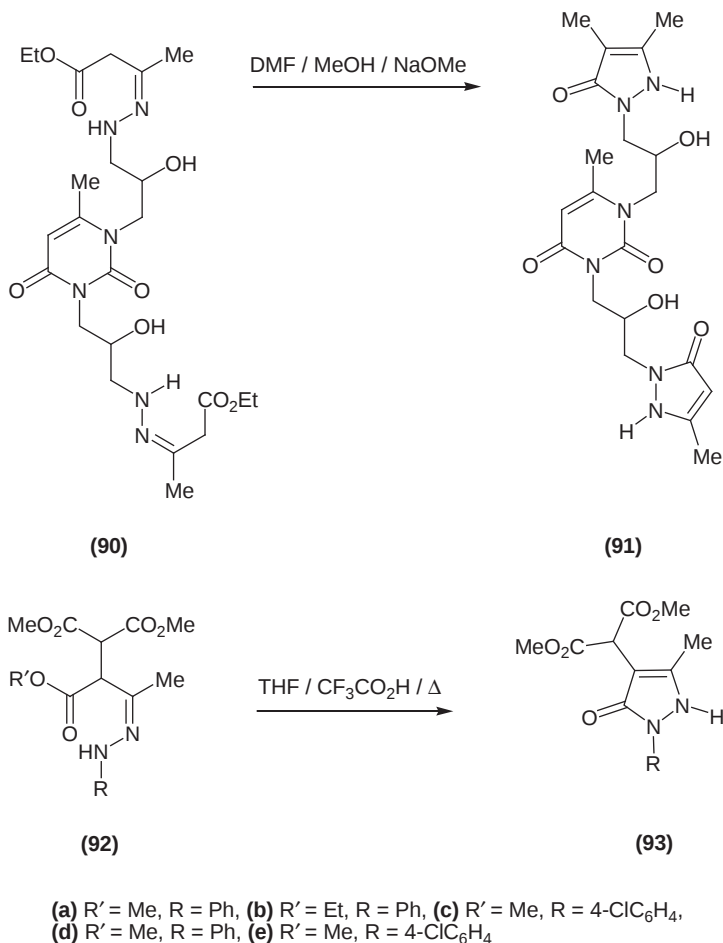
Scheme 20



Scheme 21

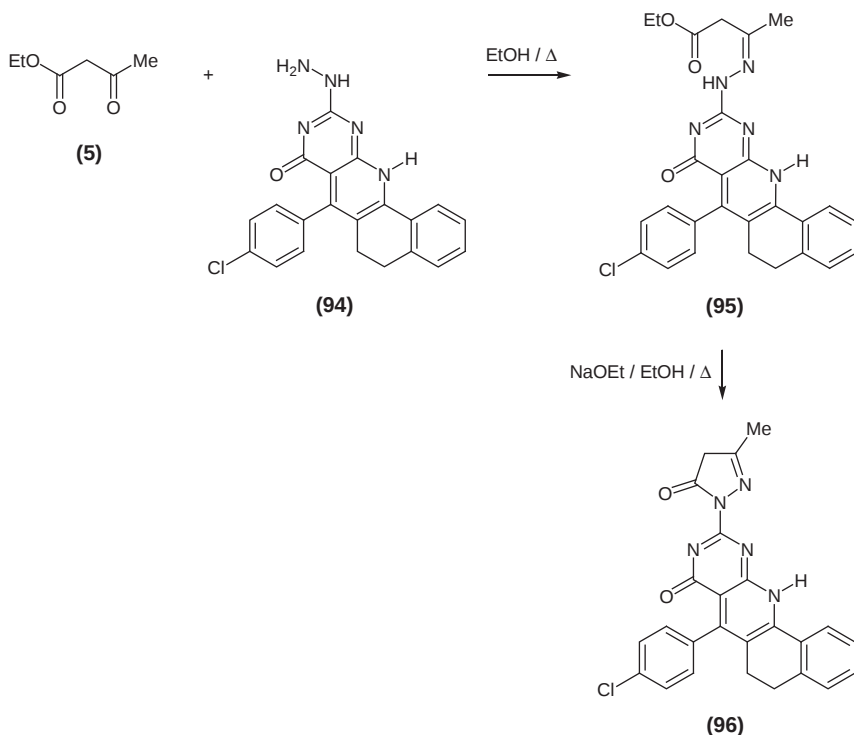
3-(arylhydrazono)butane-1,1,2-tricarboxylates **92a-c**. The corresponding pyrazol-3-ones **91** and **93d,e** were obtained in average to good yields.

Elgazzar et al. (06PS1859) (Scheme 23) prepared the 2-benzopyrimidoquinolinone derivative of pyrazol-3-one **96** by heating ethyl

**Scheme 22**

3-oxobutanoate **5** with 7-(4-chlorophenyl)-10-hydrazino-6,12-dihydrobenzo-[h]pyrimido[4,5-*b*]quinolin-8(5*H*)-one **94** in ethanol and then heating the resulting hydrazone **95** in the same solvent but in the presence of sodium ethoxide.

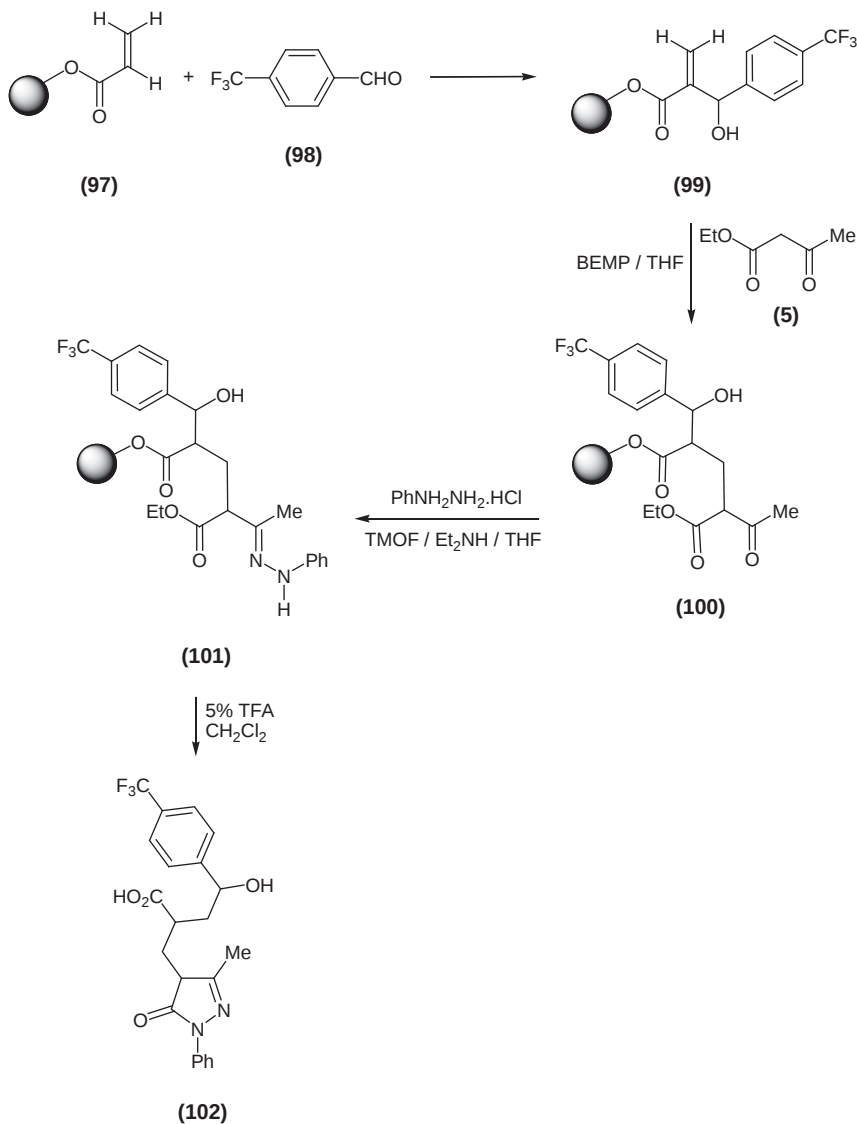
2.1.1.5 Solid-phase synthesis: by the cyclization of polymer-bound hydrazones of β -keto esters. Jung and co-workers (99JOC1362) (Scheme 24) have reported the synthesis of pyrazol-3-one **102** from polymer-bound β -keto ester **100** and phenyl hydrazine. In the first step, polymer-bound 3-hydroxy-2-methylidenepropionic acid **99** is derived from a Baylis–Hillman reaction between polymer-bound allylic alcohol



Scheme 23

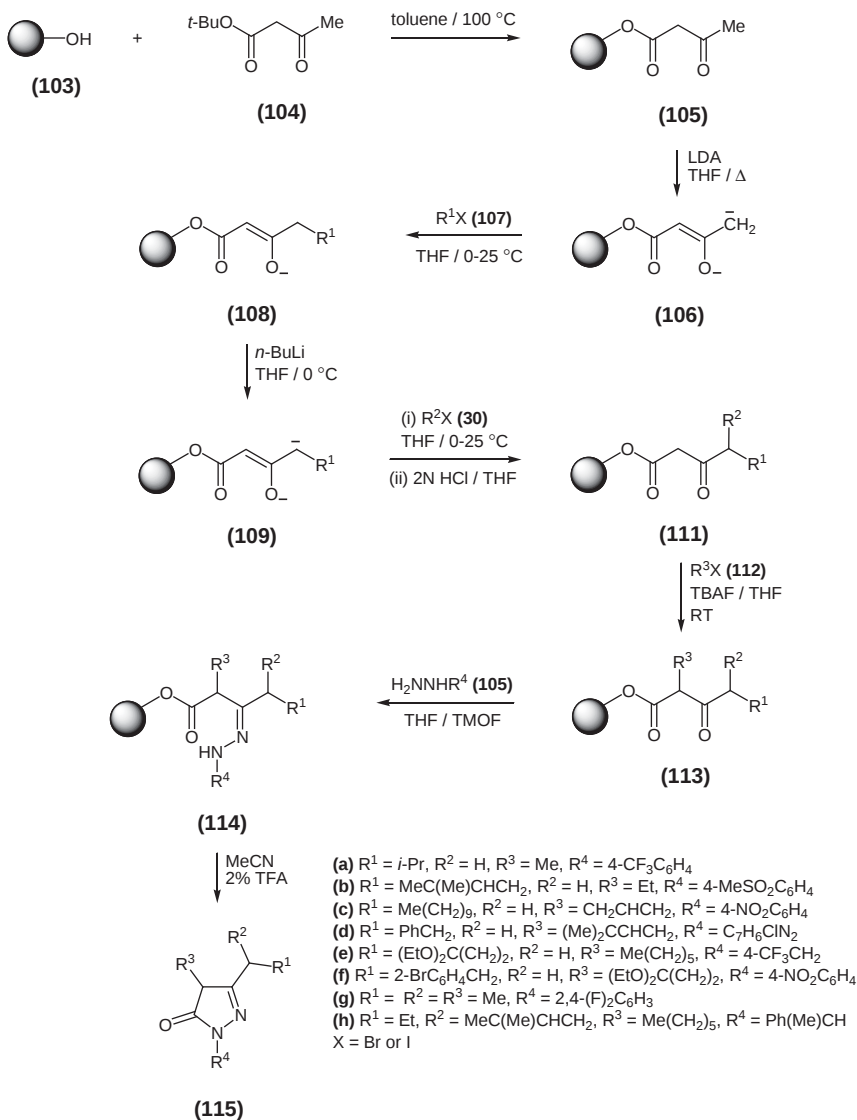
97 and 4-(trifluoromethyl)benzaldehyde **98**. In the second step, a Michael addition between ethyl 3-oxobutanoate **5** and compound **99** in the presence of BEMP afforded polymer-bound β -keto ester **100**. The latter was then transformed into hydrazone **101** with phenylhydrazine hydrochloride in the presence of TMOF and diethylamine. In the last step, cyclization of **101** occurred with 5% TFA in dichloromethane to give pyrazol-3-one **102** (80%) after cleavage of the polymer.

Using polymer-bound β -keto esters with hydrazines, Tietze et al. continued their work on the solid-phase synthesis of substituted pyrazol-3-ones. Polymer-bound β -keto esters **113** were prepared by a six-step reaction sequence from spacer-modified Merrifield resin **103** and *t*-butyl acetoacetate **104** (01EJOC1631) (Scheme 25). In the first step, polymer-bound acetoacetate **105** was prepared by *trans* acetoacetylation on heating resin **103** and ester **104** in toluene. Various polymer-bound β -keto esters **106a–h** were prepared by treating polymer-bound **105** with LDA to give dianion **106**, which, after removal of unreacted base, was alkylated with a variety of haloalkanes **107a–h**. In the next step, the γ -alkylated β -keto ester monoanions **108** were deprotonated with *n*-BuLi to the dianions **109**, which were again alkylated with various haloalkanes



Scheme 24

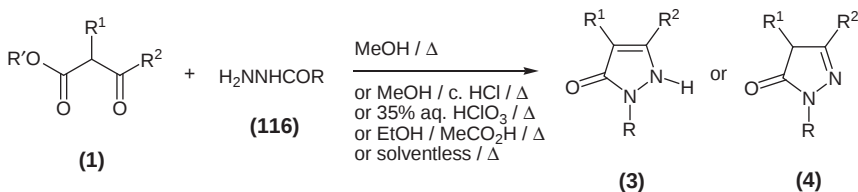
110a–h to yield polymer-bound β -keto esters **111a–h** after protonation with acid. α -Monoalkylation of esters **111** required treatment with haloalkanes **112a–h** in the presence of TBAF. The resulting trisubstituted keto esters **113a–h** were condensed with hydrazines **105a–h** and trimethylorthoformate to give the corresponding hydrazones **114a–h**. The latter underwent cyclization and concomitant cleavage from the



Scheme 25

polymer in acetonitrile containing TFA to yield pyrazol-3-ones **115a–h** in very good yields.

2.1.1.6 By reaction with hydrazides. In these reactions, aliphatic, aromatic and heteroaromatic hydrazides **118** condense and cyclize with ethyl (or methyl) 3-oxobutanoate **1** to give pyrazol-3-ones **3** or **4** in one



Scheme 26

step (Scheme 26). The conditions vary from simply boiling in methanol or ethanol (01HC493, 01IJC(B)37, 01IJC(B)43, 02BCF389, 02EJC205, 02EJC881, 02JIC770, 03AP95), heating in methanol with concentrated hydrochloric acid (03IJC(B)1975) and 35% aqueous perchloric acid (04PS411), heating in ethanol with glacial acetic acid (02M255) or simply heating together the two reactants (03PHA99, 04JCCS147) (Scheme 26 and Table 2).

2.1.1.7 By the cyclization of acylhydrazones. In certain cases, the reaction of β -keto esters with hydrazides can be selectively controlled so that heating in ethanol gives the acylhydrazones which can be isolated and then converted into pyrazol-3-ones by heating in ethanol containing glacial acetic acid, in glacial acetic acid alone, in PPA and glacial acetic acid or even by the action of sodium hydride in tetrahydrofuran.

Recent work on reactions of β -keto esters with hydrazides is presented by Meng and co-workers (01CHJC398) (Scheme 27) involving the condensation of ethyl 3-oxobutanoate **5** with hydrazides **117a–d** in refluxing ethanol. The resulting acylhydrazones **118a–d** were obtained in high yields and cyclized to the corresponding pyrazol-3-ones **119a–d** by heating in a mixture of PPA and acetic acid.

Sarhan (01M753) (Scheme 28) condensed 1*H*-indole-3-carboxylic acid hydrazide **120** with ethyl 3-oxobutanoate **5** without solvent and isolated hydrazone **121** in 70% yield. Compound **121** could be cyclized to 1-(1*H*-indole-2-carbonyl)pyrazol-3-one **122** in 67% yield by heating in a mixture of ethanol and acetic acid (10:2 ratio). Using this solvent, mixture pyrazol-3-one **681** was obtained independently in 34% yield by heating hydrazide **120** with ethyl 3-oxobutanoate **5**.

Aiming at synthesizing 1,2-dihydro-3*H*-pyrazol-3-one, Attanasi et al. (01T1387) (Scheme 29) reported a NHCOCH -bridged and a *N*-bridged pyrrole-pyrazol-3-one. In the first of five steps, all the reactions were run at room temperature, methyl or ethyl 2-chloroacetoacetate **123a,b** was treated with ethyl 3-hydrazino-3-oxopropionate **124a** and acetic acid hydrazides **124b–f** in tetrahydrofuran to afford the corresponding α -chlorohydrazone derivatives **125a–f**. In the presence of sodium

Table 2 1,2-Dihydro-3*H*-pyrazol-3-ones (3) and 2,4-dihydro-3*H*-pyrazol-3-ones (4)

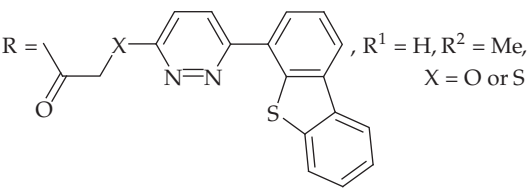
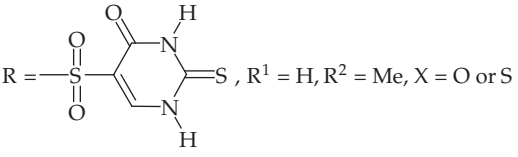
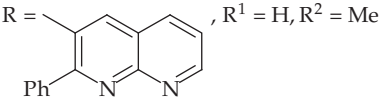
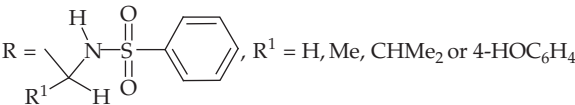
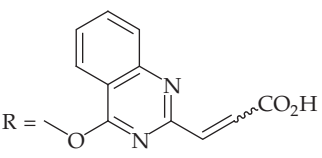
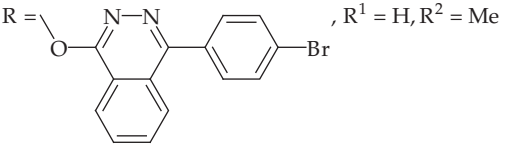
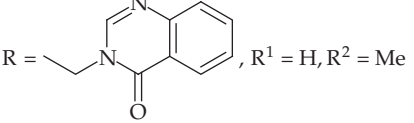
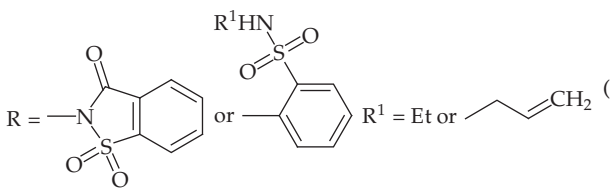
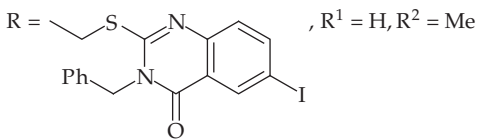
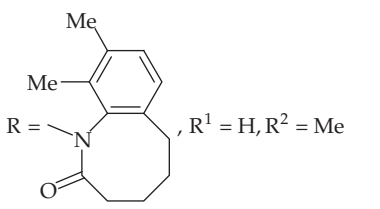
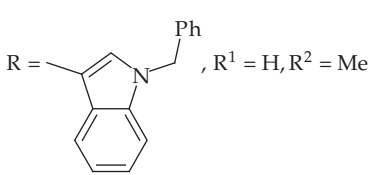
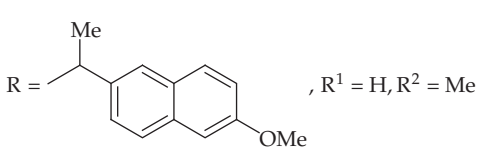
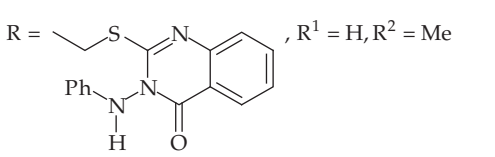
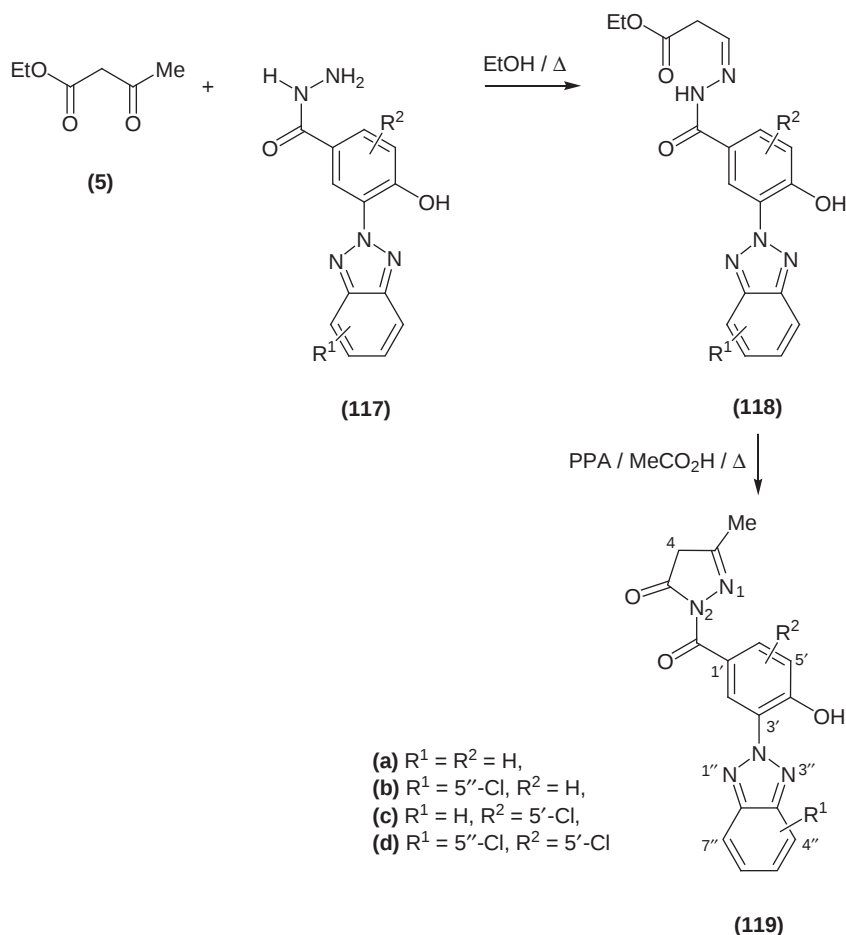
Characteristic substitution	Product	References
 $R = -C(=O)CH_2X$, $R^1 = H, R^2 = Me$, $X = O \text{ or } S$	(4)	01HC493
 $R = -SO_2NH_2$, $R^1 = H, R^2 = Me, X = O \text{ or } S$	(4)	01IJC(B)43
 $R = -Ph$, $R^1 = H, R^2 = Me$	(4)	01IJC(B)43
 $R = -NHSO_2Ph$, $R^1 = H, Me, CHMe_2 \text{ or } 4-HOC_6H_4$	(4)	02BCF389
 $R = -OCH_3$, $R^1 = H, R^2 = Me$	(4)	02EJC205
 $R = -OCH_3$, $R^1 = H, R^2 = Me$	(3)	02EJC881
 $R = -CH_2CH_3$, $R^1 = H, R^2 = Me$	(4)	02JIC770

Table 2 (Continued)

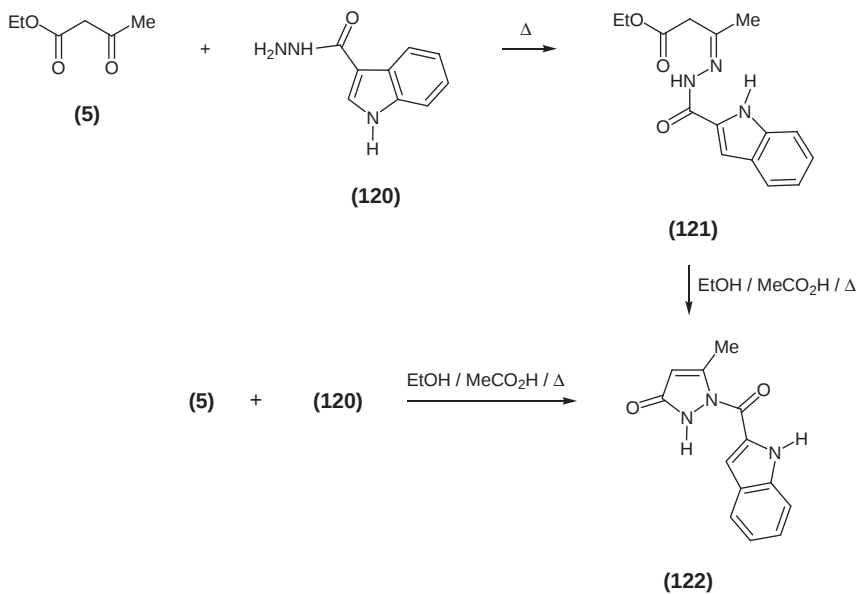
Characteristic substitution	Product	References
	(4)	02M255
	(4)	03AP95
	(4)	03IJC(B)1975
	(3)	03PHA99
	(3)	04JCCS147
	(4)	04PS411



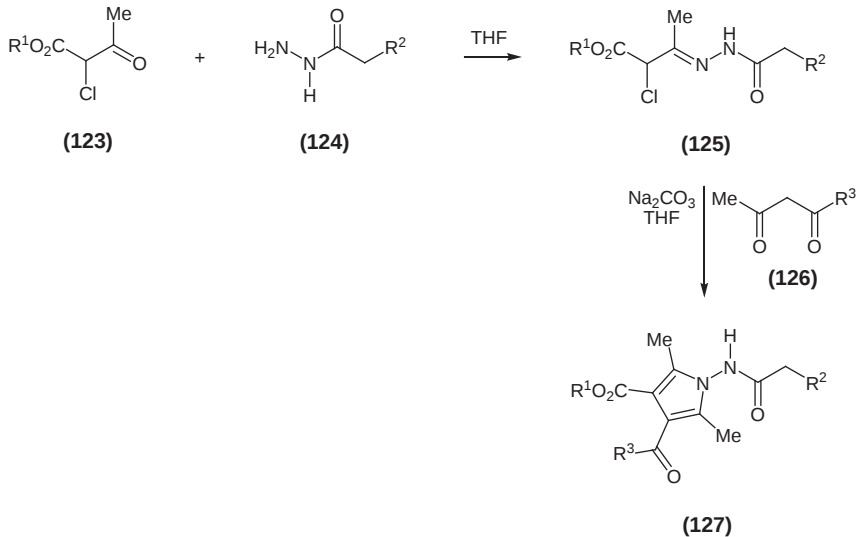
Scheme 27

carbonate, these latter compounds reacted under similar conditions with acetoacetanilide **126a** or 2,4-pentanedione **126c** in tetrahydrofuran to give the relevant 1-aminopyrroles **127a–g**, in good to excellent yields.

Heating ethyl 3-oxobutanoate **5** with 2-phenylamino[1,4]naphthoquinone-3-sulfonylhydrazide **128** in ethanol gave sulfonylhydrazone **129** which then required heating under reflux in glacial acetic acid to cyclize to pyrazol-3-one **130**. The latter was obtained in 65% yield (04PS1907) (Scheme 30). However, Fathalla (01IJC(B)37) heated ethyl 3-oxobutanoate **5** with 2-thio-4-onepyrimidine-5-sulfonylhydrazide **131** to the boiling point, without solvent, to give directly the pyrazol-3-one **132**, in 68% yield.

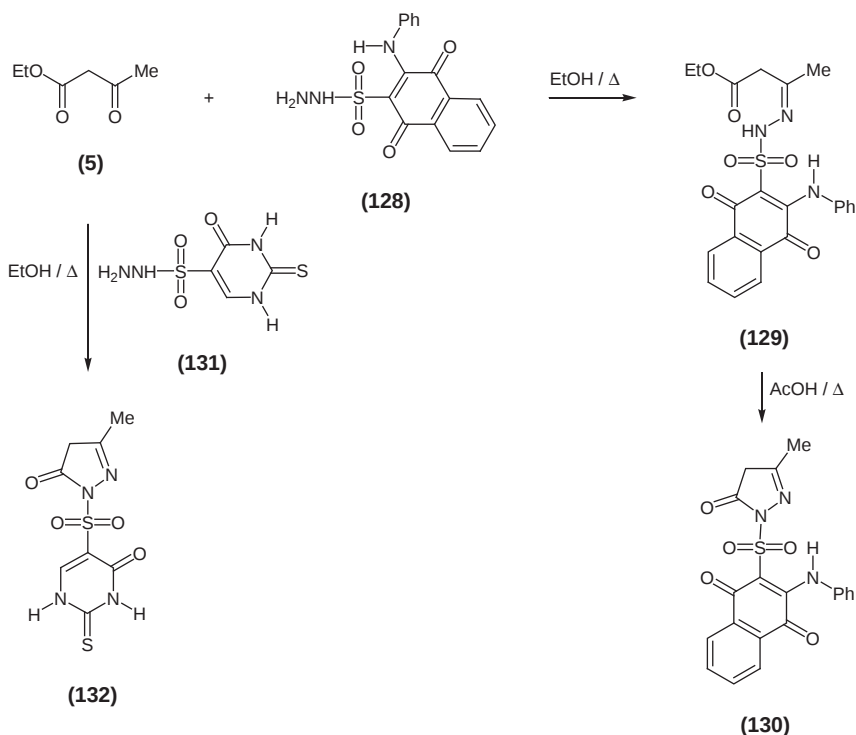


Scheme 28



- (a) R¹ = Me, R² = COEt, R³ = NHPh, R⁴ = OBU^t, (b) R¹ = Me, R² = COEt, R³ = NHPh, R⁴ = OBU^t
 (c) R¹ = Me, R² = COEt, R³ = Me, R⁴ = OMe, (d) R¹ = Et, R² = 4-NO₂C₆H₄, R³ = Me, R⁴ = OBU^t
 (e) R¹ = Et, R² = 4-NO₂C₆H₄, R³ = Me, R⁴ = NH₂, (f) R¹ = Et, R² = Ph, R³ = Et, R⁴ = NHPh
 (g) R¹ = Et, R² = Ph, R³ = Me, R⁴ = NH₂

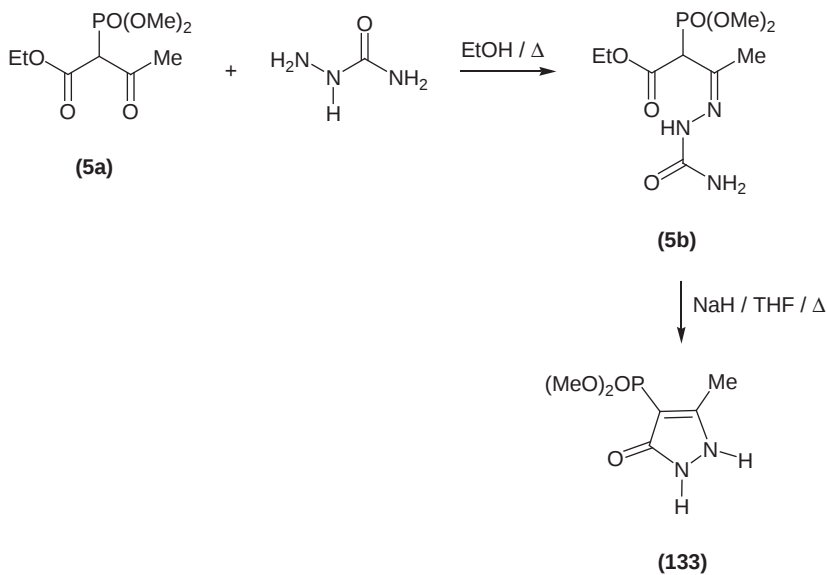
Scheme 29



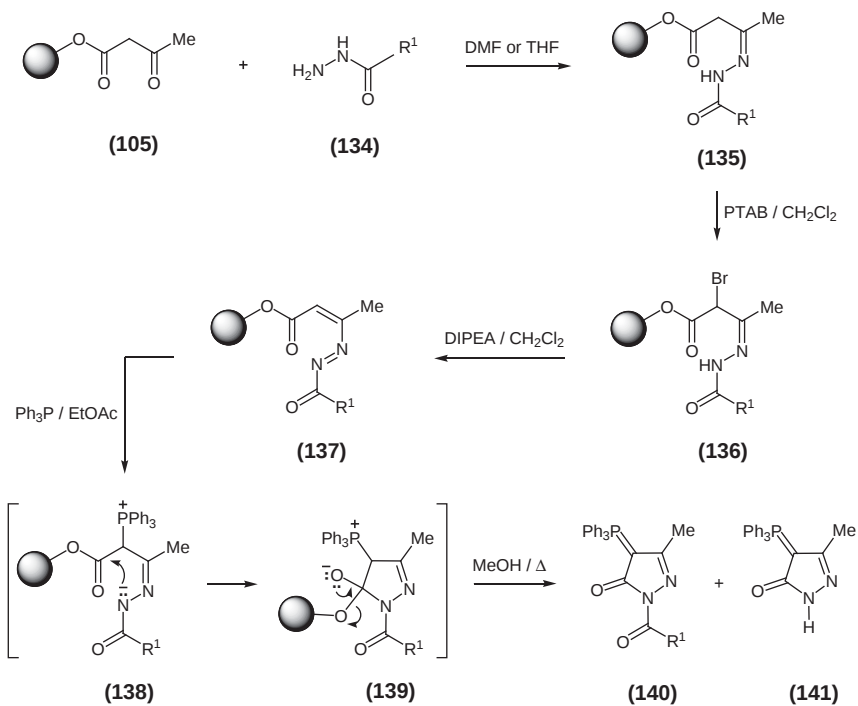
Scheme 30

Filippone and co-workers (05JOC4033) (Scheme 31) obtained hydrazone **5b** by heating 2-(dimethoxyphosphoryl)-3-oxobutyrlic acid ethyl ester **5a** with semicarbazide in ethanol. Cyclization of **5b** to pyrazol-3-one **133** required heating in tetrahydrofuran with sodium hydride which caused cleavage of the amide moiety at position 2 of the initially formed pyrazol-3-one.

2.1.1.8 Solid-phase synthesis: by the cyclization of polymer-bound acylhydrazones of β -keto esters. Both Merrifield and Wang resins were used by Filippone and co-workers (01T5855) (Scheme 32) to prepare polymer-bound 1,2-diaza-1,3-butadienes **1327a–e** that were used for the synthesis of 4-(triphenyl-*l*-5-phosphanylidene)pyrazol-3-ones **140a–e** and **141**. This multistep synthesis to **137a–e** involved reaction of the resin with *tert*-butylacetoacetate in refluxing toluene to give the polymer-bound β -keto ester **105**. The keto esters were then reacted with hydrazine derivatives **134a–e** in *N,N*-dimethylformamide or tetrahydrofuran to



Scheme 31



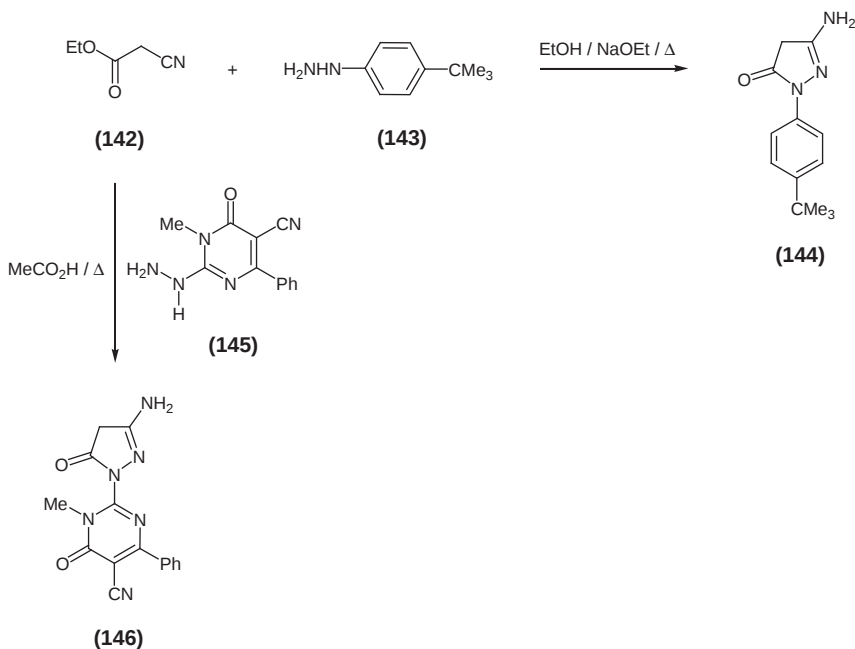
(a) $\text{R}^1 = \text{NH}_2$, (b) $\text{R}^1 = \text{NHPh}$, (c) $\text{R}^1 = \text{OMe}$, (d) $\text{R}^1 = \text{OEt}$, (e) $\text{R}^1 = \text{Ot-Bu}$

Scheme 32

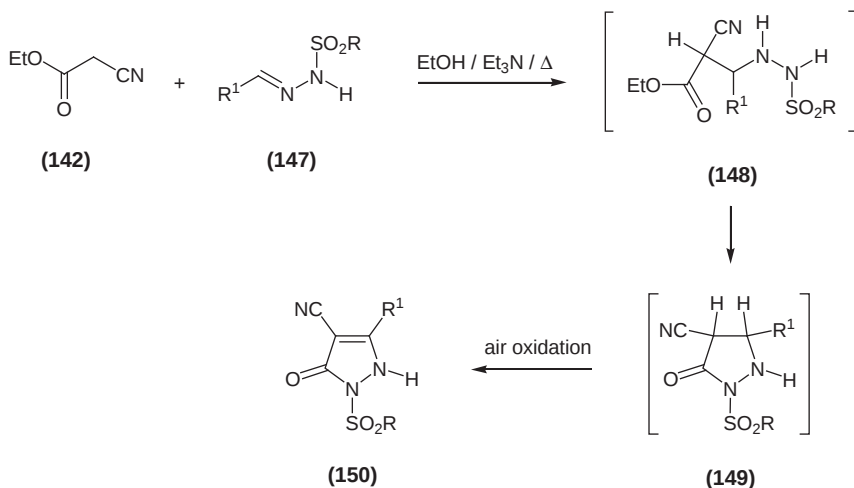
give the corresponding hydrazones **135a–e** which were subjected to bromination by phenyltrimethylammonium tribromide (PTAB) in dichloromethane, and then treatment of the resulting brominated hydrazones **136a–e** with *N,N*-diisopropylethylamine (DIPEA) in dichloromethane. On addition of triphenylphosphine in ethyl acetate to modified Merrifield or Wang resin, the polymer-bound 1,2-diaza-1,3-butadienes **137a–e** produced the zwitterionic intermediates **138a–e** that cyclizes to betaine **139**. The latter release pyrazol-3-ones **140a–e** and **140** by methanolysis in about a 1:1 ratio. The yields of **140** and **141** vary from 12% to 42% and are comparable using Merrifield or Wang polymer-bound **137a–e** as starting material.

2.1.2 From β -cyano esters

2.1.2.1 From ethyl 2-cyanoacetate. 5-Aminopyrazol-3-ones can be conveniently prepared from β -keto esters with hydrazines. Thus, heating ethyl 2-cyanoacetate **142** with (4-*tert*-butylphenyl)hydrazine **143** in ethanolic sodium ethoxide afforded 5-amino-2-(4-*tert*-butylphenyl)-2,4-dihydropyrazol-3-one **144** (01JMC3730) (Scheme 33). The reaction that takes place under acidic conditions, between ethyl 2-cyanoacetate **142** and 2-hydrazino-6-oxopyrimidine-5-carbonitrile **145** in boiling acetic



Scheme 33



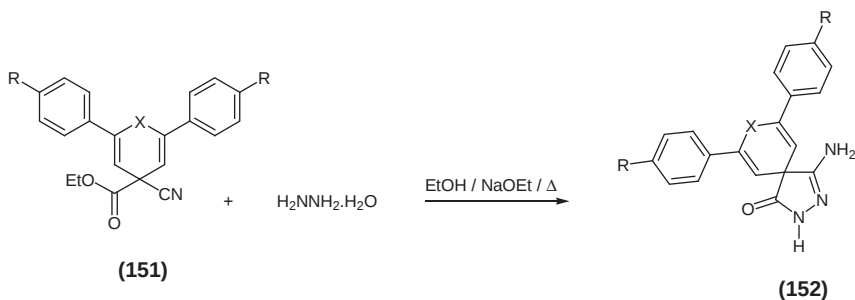
R = naphthalen-2-yl, R¹ = 4-MeOC₆H₄

Scheme 34

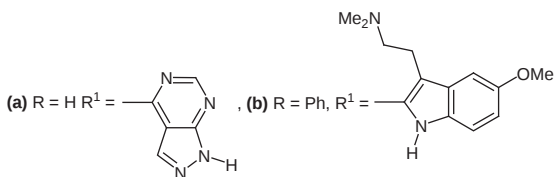
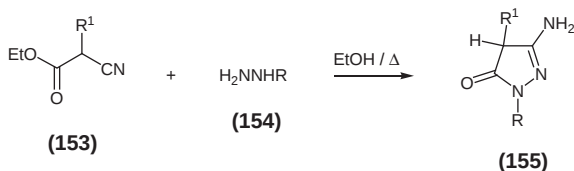
acid, gives 5-amino-1,2-dihydropyrazol-3-one **146** in 70% yield (04JCCS547) (Scheme 33).

A completely different approach initially involves the addition of the carbanion of ethyl 2-cyanoacetate **142** in the presence of base to the imine group of 2-naphthylsulfonyl hydrazone **147** followed by cyclization and oxidation to pyrazol-3-one **150** (02NN469) (Scheme 34). The reaction requires heating in ethanol with triethylamine and it is suggested that intermediate **148** is first produced, and then undergoes an intramolecular acyl substitution resulting in the unstable pyrazol-3-one **149**. The latter is prone to oxidation by molecular oxygen and is converted to stable pyrazol-3-one **150**.

2.1.2.2 From 4-cyano-1,4-dihydropyridine(or 4H-pyran)-4-carboxylic acid ethyl ester. Reddy and co-workers (03HC513) (Scheme 35) obtained spiroaminopyrazol-3-ones **152a–d** in moderate yields from β -cyano esters **151a–d** and hydrazine hydrate in refluxing ethanolic sodium ethoxide. Ghorab et al. (04HC57) found there was no need to add sodium ethoxide in the reaction of cyano-(1*H*-pyrazolo[3,4-*d*]pyrimidin-4-yl)-acetic acid ethyl ester **153a** with hydrazine hydrate **154a** which required only heating in ethanol to give 5-aminopyrazol-3-one **155a** in 75% yield. However, Doss et al. (03PHA607) found that condensation and cyclization of cyano[3-(1*H*-indol-2-yl)]acetic acid ethyl ester **153b** with phenylhydrazine **154b** to give 5-aminopyrazol-3-one **155b**



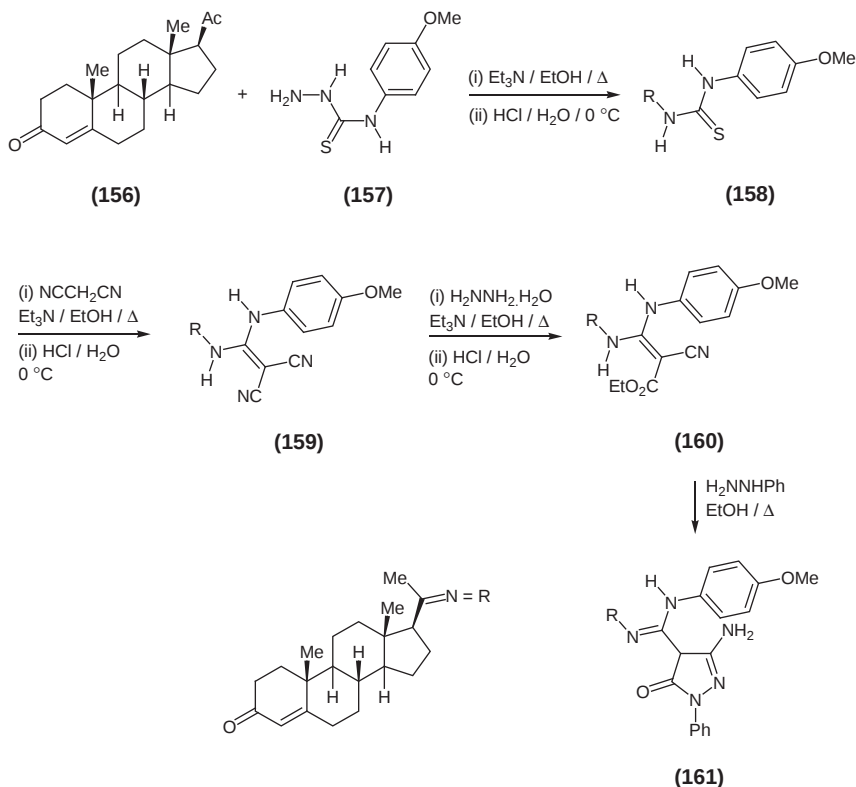
(a) R = H, X = N, (b) R = OMe, X = N, (c) R = Cl, X = N, (d) R = Cl, X = O



Scheme 35

(72% yield) required heating with *N,N*-dimethylformamide containing piperidine.

2.1.2.3 From the condensation product of progesterone with ethyl 2-cyano-3-hydrazino-3-[(4-methoxyphenyl)amino]acrylate. Elmegeed and Wardakhan (05EJC407) (Scheme 36) reported the synthesis of steroidal heterocycles, one of which contained a pyrazol-3-one ring. Progesterone **156** reacted with 4-methoxyphenylthiosemicarbazide **157** in refluxing ethanol containing triethylamine to afford, after neutralization with dilute hydrochloric acid, the progesterone thiosemicarbazone **158** in 77% yield. Thiosemicarbazone **158** was condensed with malononitrile under similar conditions to give the progesterone malononitrile **159** in 72% yield. The latter was converted into the progesterone β -cyano ester **160** in 70% yield by heating with hydrazine hydrate and triethylamine in ethanol followed by neutralization with acid. The progesterone pyrazol-3-one **161** was obtained in 74% yield by heating β -cyano ester **160** with phenylhydrazine in ethanol.

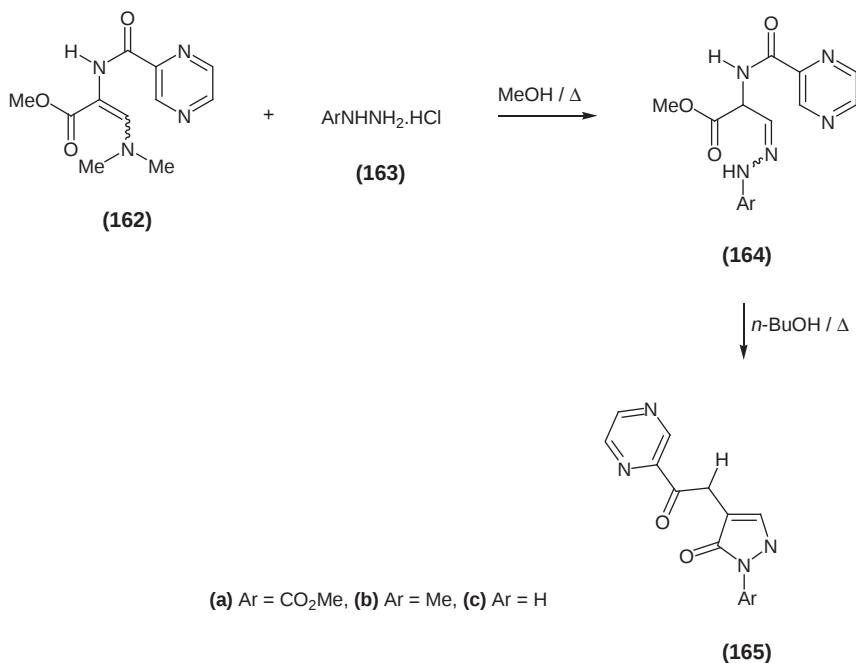


Scheme 36

2.1.3 From β -enamino esters

2.1.3.1 From methyl (*Z/E*)-3-dimethylamino-2-[(pyrazin-2-ylcarbonyl)amino]-prop-2-enoate. (*Z/E*)-Prop-2-enoate **162** reacts with arylhydrazine hydrochloride **163a–c** in refluxing methanol to yield the corresponding hydrazinoprop-2-enoates **164a–c**. When propenoates **164a–c** were heated in *n*-butanol, intramolecular acyl substitution afforded pyrazol-3-ones **165a–c** in high yields (00H443) (Scheme 37).

Conjugate substitution of the dimethylamino group of 2-(benzoimidazol-2-yl)-3-dimethylaminoacrylic acid methyl ester **166a** with phenylhydrazine **154a** required heating for 2 h at 150 °C to give pyrazol-3-one **168a**, in 92% yield (01S581) (Scheme 38). At 80 °C under MW irradiation for 30 min, **166a** with methylhydrazine **154b** afforded pyrazol-3-one **168b** in 96% yield. By contrast, the reaction of 2-(oxazol-2-yl)-3-dimethylaminoacrylic acid methyl ester **166c** with phenylhydrazine **154c** at 60 °C was very sluggish, and it required 11 days to give pyrazol-3-one **168c** in 74% yield.



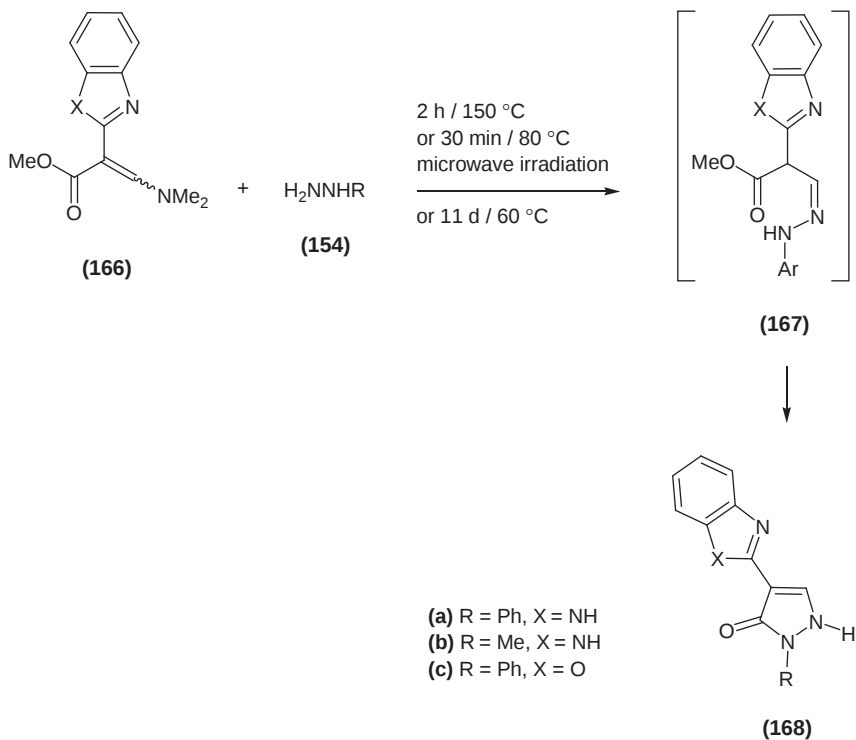
Scheme 37

2.1.4 From α,β -unsaturated esters

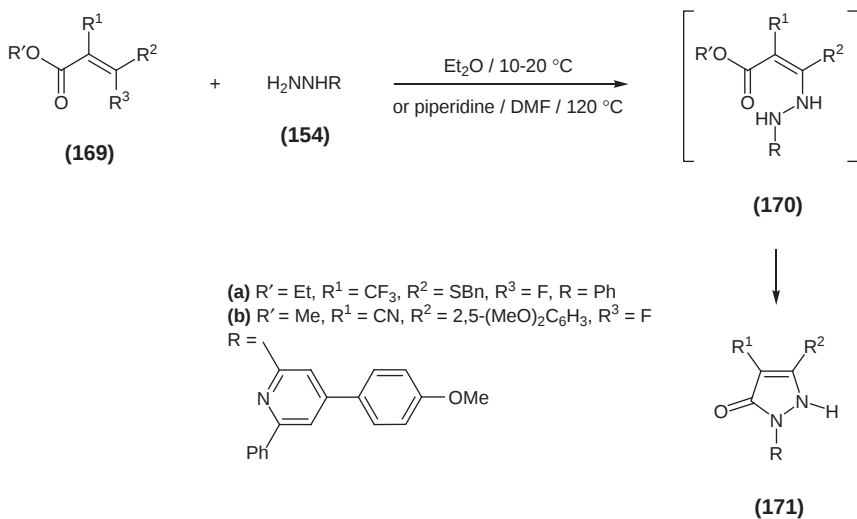
There are three reports on the synthesis of pyrazol-3-ones from α,β -unsaturated esters since 1999 (02RCB1020, 04APP55, 02SC3767) (Scheme 39).

2.1.4.1 From 3-fluoroacrylic acid esters. The first report (02RCB1020) describes the synthesis of pyrazol-3-one **171a** from 3-benzylsulfanyl-3-fluoro-2-trifluoromethylacrylic acid ethyl ester **169a** and phenylhydrazine **154a** in diethyl ether at 10–20 °C. The second report (04APP55) describes the synthesis of pyrazol-3-one **171b** from 2-cyano-3-(2,5-dimethoxyphenyl)-3-fluoroacrylic acid methyl ester **168b** and [4-(4-methoxyphenyl)-6-phenyl-pyridin-2-yl]hydrazine **154b** in N,N -dimethylformamide containing piperidine at 120 °C. The reaction may take place in two steps, conjugate addition–elimination to give intermediate **170** followed by intramolecular acyl substitution to the products.

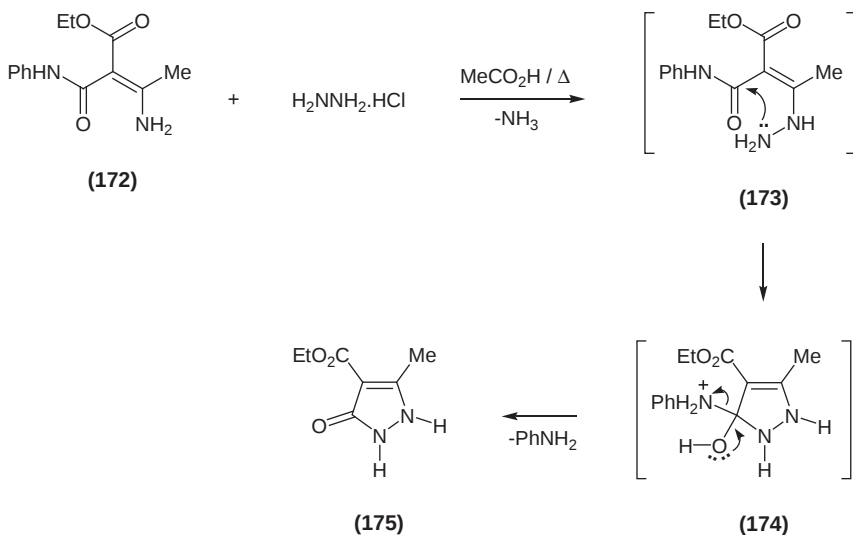
2.1.4.2 From 3-amino-2-phenylcarbamoyl-but-2-enoic acid ethyl ester. Here (02SC3767) (Scheme 40), 3-oxopyrazole-4-carboxylic acid ethyl ester **175** was obtained in 91% yield by heating the carbamoyl ester **172** with hydrazine hydrate hydrochloride in glacial acetic acid. The reaction



Scheme 38



Scheme 39



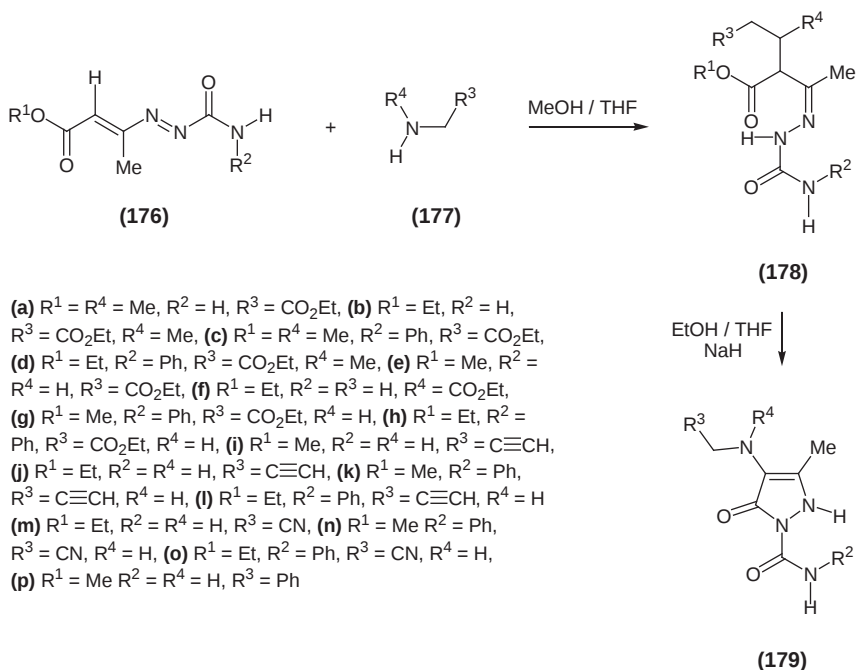
Scheme 40

may occur by an addition–elimination of hydrazine to the β -carbon of the alkene where elimination of ammonia gives intermediate **173**. Intramolecular addition of **173** leads to intermediate **174** from which aniline is eliminated to **175**.

2.1.5 From conjugated azoalkenyl esters

2.1.5.1 From ethyl or methyl [(acetyl or phenylacetyl)diazenyl]but-2-enoates. Attanasi and co-workers (01T2031) (Scheme 41) continued their previous work on the synthesis of pyrazol-3-ones from conjugated azoalkenyl esters by demonstrating that 1,2-diaza-1,3-butadienes **176a–d** react with amines **177a–e** to give α -aminohydrazones **178a–p**, which then can undergo base-promoted heterocyclization to 1-aminocarbonylpyrazol-3-ones **179a–e**.

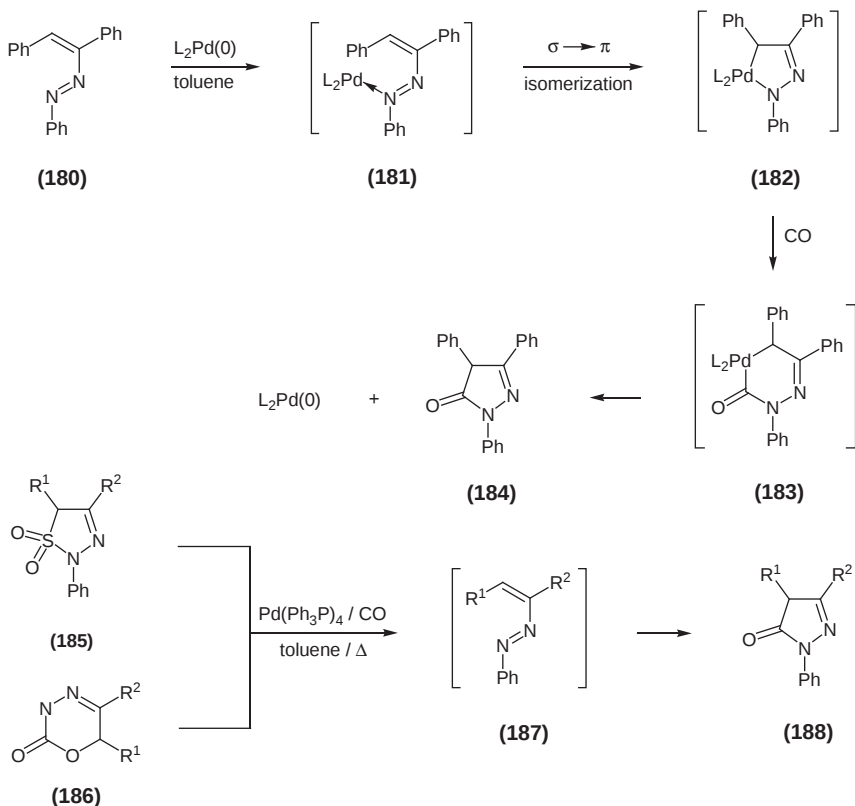
2.1.5.2 By palladium (O)-catalyzed carbonylation of 1,2-diaza-1,3-butadienes. Boeckman et al. (01OL3651) (Scheme 42) reported that stable 1-(1,2-diphenylethenyl)-2-phenyldiazene **180** when treated with 10 or 1 mol% of $\text{Pd}(\text{Ph}_3\text{P})_4$ or $\text{Pd}(\text{dppe})_2$ catalysts, respectively, in toluene under 1 or 2 atm of carbon monoxide, at room temperature or 100°C for 0.25–30 h, afforded pyrazol-3-one **184** in excellent yields. Although no intermediates were detected, by analogy to the previously studied cyclopalladation of azobenzene, the mechanism shown in Scheme 42 was proposed. The mechanism involves formation of a σ -complex **181** between **180** and $\text{Pd}(0)$ -catalyst, cycloaddition by $\sigma \rightarrow \pi$ isomerization to



Scheme 41

intermediate **182**, migratory insertion of carbon monoxide to intermediate **183** and finally reductive elimination of the Pd(0)-catalyst to give pyrazol-3-one **184**. The authors suggested it is also possible that carbon monoxide enters the ligand sphere of palladium prior to $\sigma \rightarrow \pi$ isomerization so that migratory insertion of carbon monoxide could precede cyclopalladation.

Because the overall transformation seems feasible, a route to pyrazol-3-ones from heterocyclic precursors that are known to thermally decompose to 1,2-diaza-1,3-butadienes under conditions where cyclopalladation/carbonylation would be rapid was investigated. Thus, thiadiazole dioxides **185a–c** noted to decompose with rapid gas evolution at 90–100 °C were carbonylated in CO-saturated hot toluene (110 °C) in the presence of Pd(PPh₃)₄ generated *in situ* from Pd(OAc)₂ and four equivalents of PPh₃. The pyrazol-3-ones **188a–c** were isolated in 78%, 54% and 74% yield, respectively. Oxadiazinone **186d**, known to decompose rapidly at ~140 °C, and Pd(dppe)₂ (5 mol%) were heated at 135 °C in toluene under CO (2 atm) to give pyrazol-3-one **188d** in 58% yield. To determine whether heteroatoms were tolerated at C-5 of the oxadiazinone ring, oxadiazinone **186e** was carbonylated at 110 °C using Pd(PPh₃)₄. It afforded the expected pyrazol-3-one **188e** in 62% yield.



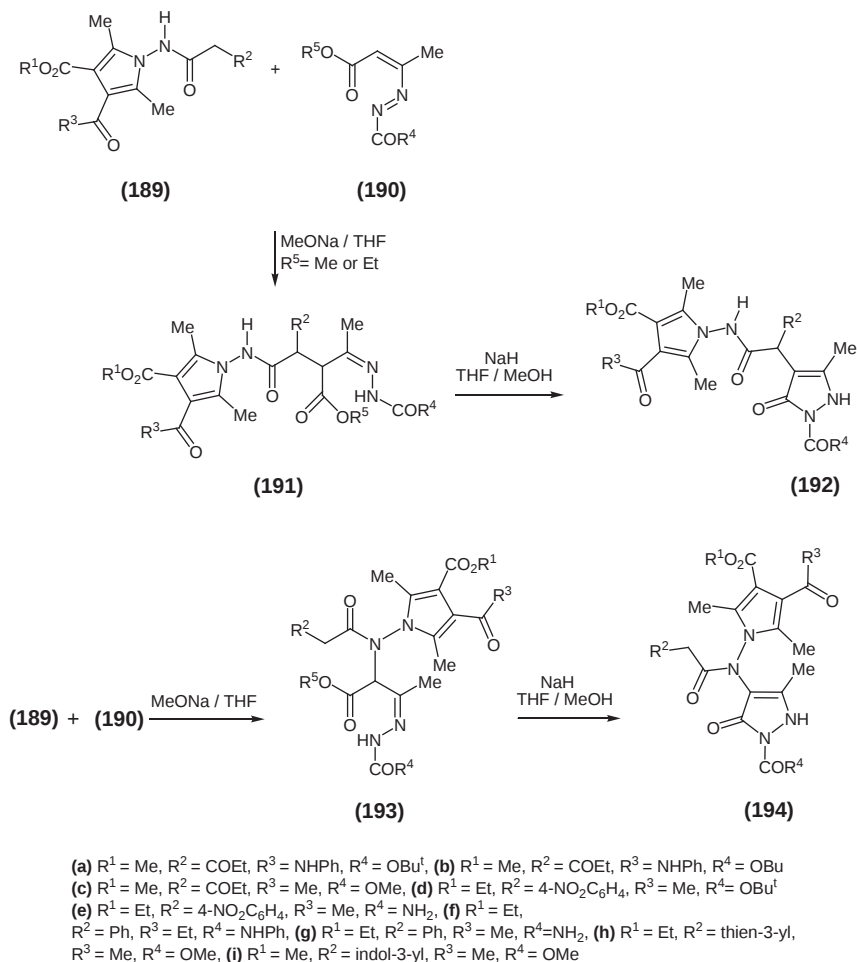
(a) $R^1 = R^2 = Ph$, (b) $R^1 = Ph$, $R^2 = H$, (c) $R^1 = Me$, $R^2 = Ph$, (d) $R^1 = R^2 = Ph$, $Y = X = O$, (e) $R^1 = Ph$, $R^2 = 4-ClC_6H_4O$, $Y = X = O$, (f) $R^1 = Ph$, $R^2 = OPh$, $Y = X = O$, (g) $R^1 = R^2 = Ph$, $Y = O$, $X = S$

Scheme 42

When the related aryloxy derivative **186f** was employed, the yield of product **188f** decreased to 40%. Knowing that substitution of sulfur for one or more of the oxygen atoms of oxadiazinones **186** had the beneficial effect of lowering the temperature at which decomposition to the diazadiene occurred, oxadiazinethione **186g** was treated with CO (2 atm) in the presence of $Pd(dppe)_2$ (5 mol%) at 110 °C to afford **188g** in 81% yield.

2.1.5.3 From activated methylene compounds and 1,2-diaza-1,3-butadienes.

The activated methylene group of pyrroles **189a,b,d**, under basic conditions in tetrahydrofuran, attacked C-4 of 1,2-diaza-1,3-butadienes **190a–d** to give the hydrazones **191a–e** as diastereomeric mixtures (02S1546) (Scheme 43). Cyclization of these derivatives in the presence

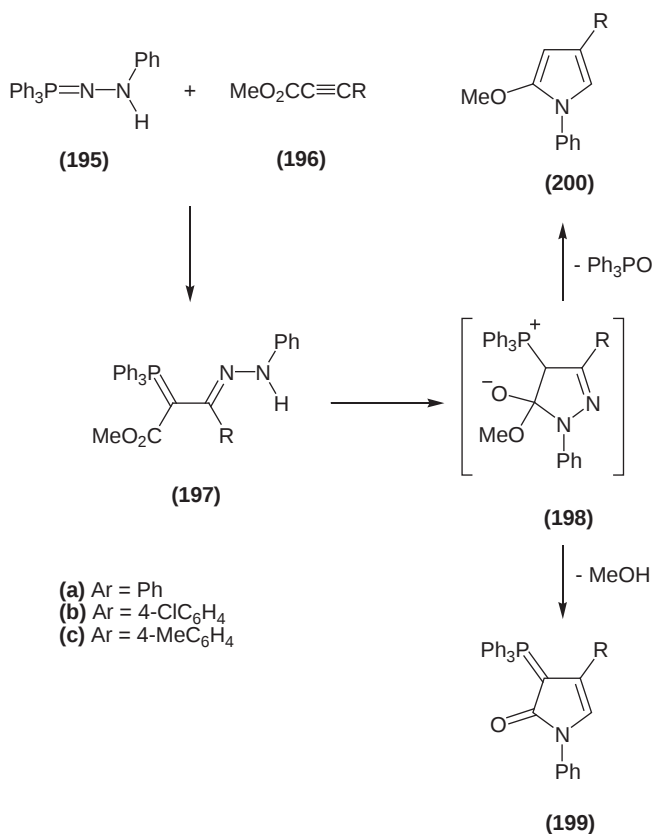


Scheme 43

of sodium methoxide in tetrahydrofuran/methanol provided pyrrole-pyrazol-3-ones **192a-e**. Less activated pyrroles **189e-g** reacted with 1,2-diaza-1,3-butadienes **190c,e-g** *via* the amide nitrogen of the former to afford conjugated adducts **193f-i** (Scheme 43). The latter cyclized to pyrrole-pyrazol-3-ones **194f-i** with sodium hydride in tetrahydrofuran/methanol. The different behavior between hydrazides **189** and 1,2-diaza-1,3-butadienes **190** is attributed to the electronic effects of the substituents attached to the methylene group of the hydrazide derivatives.

2.1.6 From acetylenes

2.1.6.1 From dimethyl but-2-ynedioate, methyl butynoate or methyl propiolate. Phosphazene **60** reacts with dimethyl but-2-ynedioate **196a** in acetonitrile at room temperature to give the conjugated hydrazone **197a** in 80% yield (99T14451) (Scheme 44). Heating hydrazone **197a** in ethanol yielded a mixture of phospharanylidene pyrazol-3-one **199a** and pyrazol **200a** in a 35:65 ratio. On the other hand, treatment of **197a** with *n*-butyllithium in tetrahydrofuran at 0 °C gave, regioselectively, pyrazol-3-one **199a** in 70% yield. When the initial reaction in acetonitrile was repeated with phosphazene **195** and methyl butynoate **196b**, pyrazol-3-one **199b** and pyrazol **200b** were obtained in a ratio of about 1:1. A 70% yield of hydrazone **197c** was obtained when phosphazene **195** was treated with methyl propionate **196c**. Hydrazone **197c** cyclized easily in hot ethanol to give exclusively pyrazol-3-one **199c**. A possible intermediate prior to the formation of **199** or **200** is pyrazoline **198**.



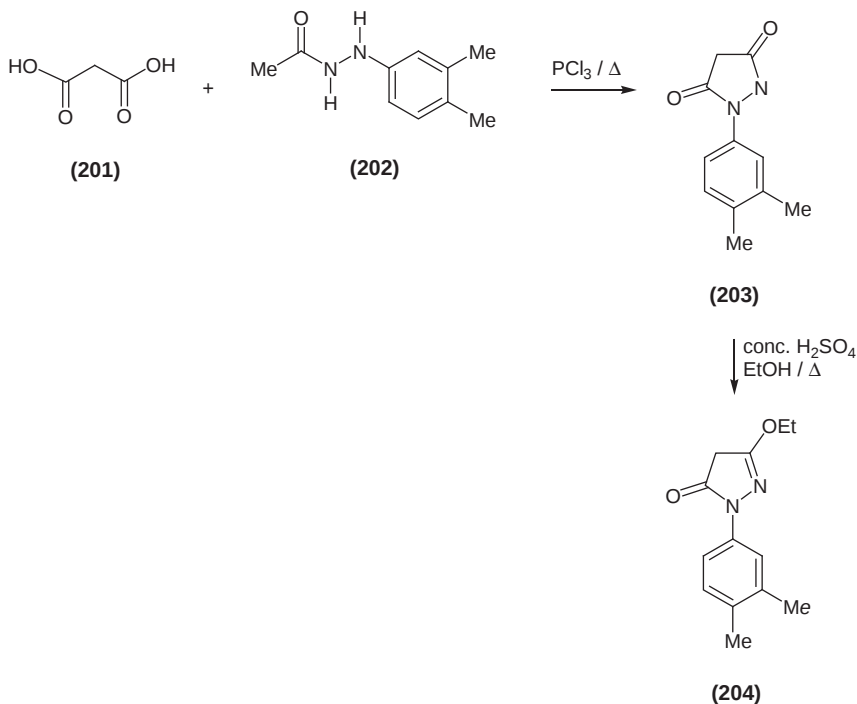
Scheme 44

2.1.7 From malonic acid or dialkylmalonates

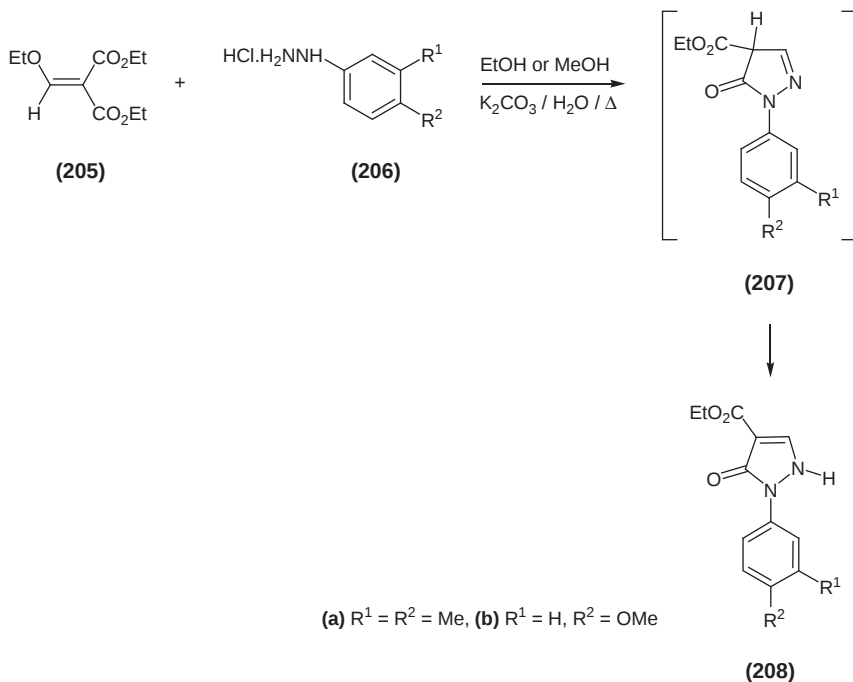
2.1.7.1 From malonic acid or diethyl (ethoxymethylene)malonate. Malonic acid **201** underwent nucleophilic acyl substitution with *N*-acetyl-3,4-dimethylphenylhydrazine **202** and phosphorus trichloride *via in situ* generated malonyl dichloride to afford pyrazoline-3,5-dione **203** which then underwent acid-catalyzed condensation with ethanol over molecular sieves to give 4-ethoxyrazol-3-one **204** (01JMC3730) (Scheme 45).

Less vigorous conditions than those described above converted diethyl (ethoxymethylene)malonate **205** and (3,4-dimethylphenyl)hydrazine monohydrochloride **206** into pyrazol-3-one **208** (01JMC3730, 04H2537) (Scheme 46). The reaction took place in ethanol or methanol containing aqueous potassium carbonate *via* conjugate substitution of ethoxide ion, intramolecular acyl substitution and tautomerization of intermediate pyrazol-3-one **207**.

To prepare 5-amino-4-[(3-phenyl-1*H*-pyrazol-4-yl)hydrazono]-2,4-dihydropyrazol-3-one **212**, Al-Mousawi et al. (08ARK268(xvi)) diazotized 3-phenyl-1*H*-pyrazol-4-ylamine **209** in hydrochloric acid to yield, *in situ*, diazonium chloride **210** which then coupled with malononitrile to give 2-pyrazolylhydrazonomesoxalonitrile **211**. Compound **211** then could be



Scheme 45



Scheme 46

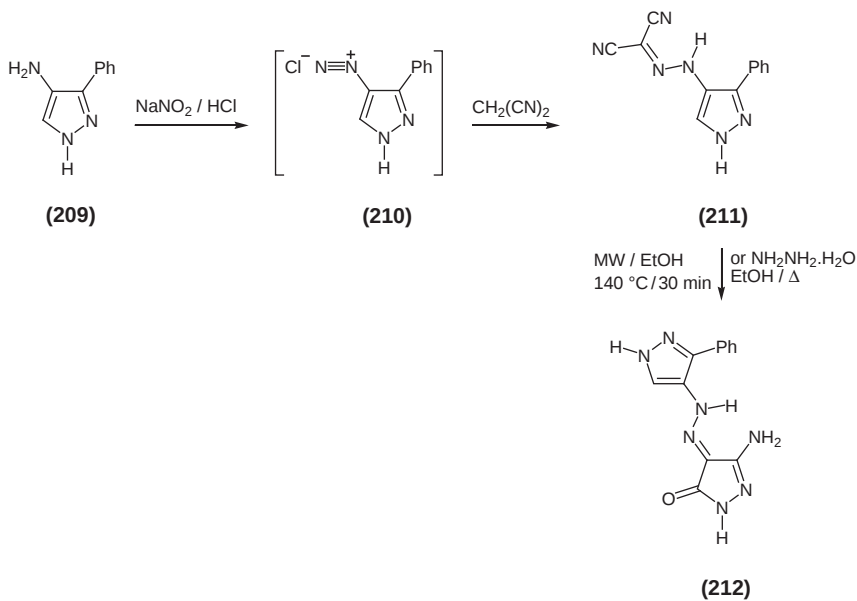
converted into aminopyrazol-3-one **212** with hydrazine hydrate either by refluxing in EtOH for 6 h or by MW irradiation with the same solvent at 140°C for 30 min, in 37% and 87% yield, respectively (Scheme 47).

2.1.8 From 2-oxosuccinic acid or succinates

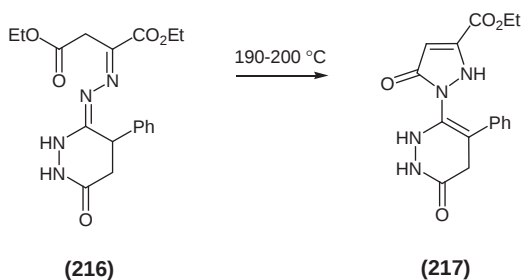
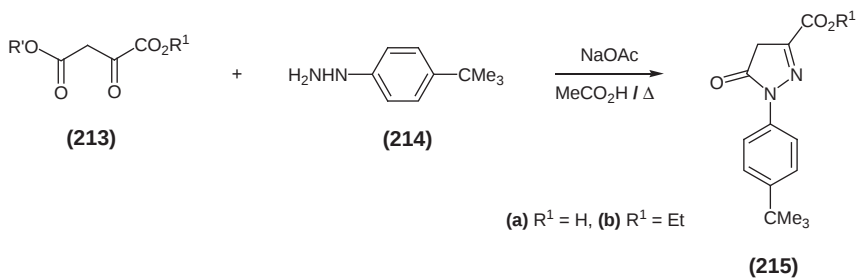
2.1.8.1 From 2-oxosuccinic acid or diethyl 2-oxosuccinate. 2-Oxosuccinic acid **213a** and diethyl 2-oxosuccinate **213b** each were heated with (4-*tert*-butylphenyl)hydrazine **214** in glacial acetic acid containing sodium acetate to afford the corresponding pyrazol-3-ones **215a,b** in 70% and 96% yield (01JMC3730) (Scheme 48). Succinate **216** cyclized to the pyrazol-3-one **217** (60%) on forcibly heating at $190\text{--}200^\circ\text{C}$ (01JHC877).

2.1.9 From β -keto amides

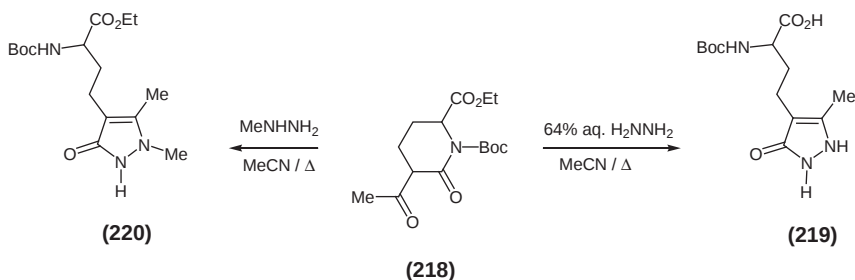
2.1.9.1 From 1-*tert*-butyl 2-ethyl 5-acetyl-6-oxopiperidine-1,2-dicarboxylate. Treatment of Boc-protected 5-acetyl-6-oxopiperidine-2-carboxylic acid ethyl ester **218** with a 64% aqueous solution of hydrazine in acetonitrile gave (*R,S*)-2-*tert*-butoxycarbonylamino-4-(3-oxopyrazol-4-yl)butyric acid **219**, in 67% yield. The corresponding 1-methyl derivative **220** was obtained in only 17% yield by treating **218** with methylhydrazine under similar conditions (99EJMC967) (Scheme 49).



Scheme 47



Scheme 48



Scheme 49

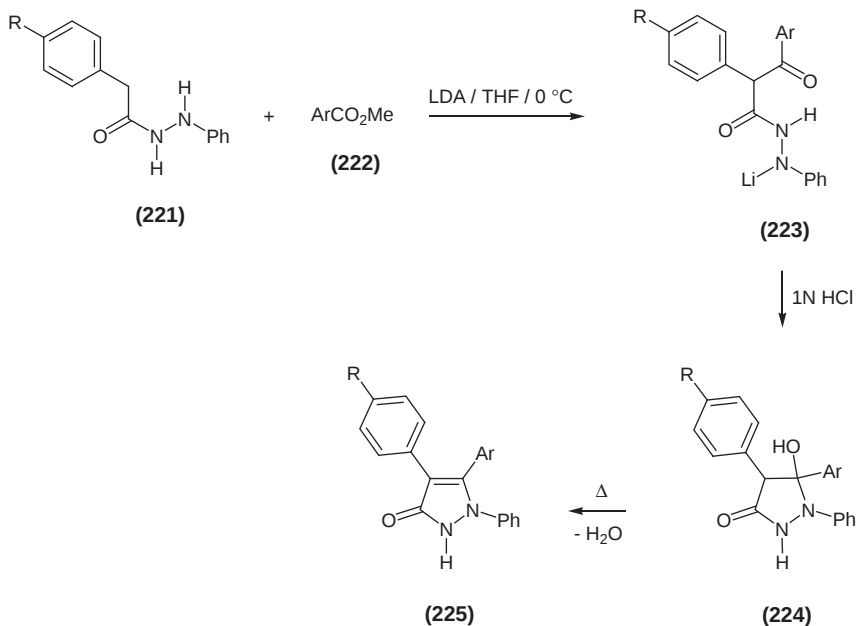
2.1.10 From hydrazides

2.1.10.1 From 2-aryl-*N*-phenylacetohydrazides. An expedient route to 1,4,5-trisubstituted pyrazol-3-ones **73** consists of condensing polyolithiated 2-aryl-*N*-phenylacetohydrazides **221a–e** with aromatic esters **222a–e** and excess LDA. The reaction most probably proceeds *via* polyolithiated C-acyl intermediates **223** that cyclize to pyrrolidinones **224**, after addition of hydrochloric acid, which on heating dehydrate to pyrazol-3-ones **225a–e** (01JHC695) (Scheme 50).

2.1.10.2 From 3-oxopropionic acid arylidenehydrazides. Irradiation of 3-oxo-3-(4-oxo-1,4-dihydro[1,8]naphthyridin-3-yl)propionic acid arylidenehydrazides **226a–f** over acidic alumina for 1–5 min afforded the corresponding pyrazol-3-ones **227a–f** in excellent yields (02IJC(B)427) (Scheme 51).

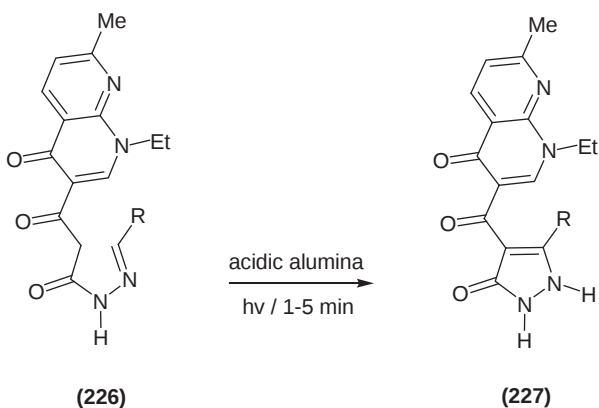
2.1.10.3 From (*N*'-benzhydrylidene-*N*-phenylhydrazinocarbonyl)acetic acid ethyl ester. Haddad and Baron (02TL2171) (Scheme 52) prepared pyrazol-3-one **231** by cyclization of hydrazinocarbonyl ester **230**. Overall, the synthesis is a three-step procedure where hydrazone **229** is synthesized first from bromobenzene **227** and benzophenone hydrazone **228** by a coupling reaction using $\text{Pd}(\text{OAc})_2/\text{BINAP}$ catalyst, as described by Buchwald and co-workers (98JA6621). In the second step, **229** was treated with ethyl malonyl chloride in refluxing 1,4-dioxane to give hydrazinocarbonyl ester **230** in 83% yield. In the final step, **230** was cyclized in refluxing ethanol containing *p*-TsOH catalyst to afford pyrazol-3-one **231** in 70% yield.

2.1.10.4 From thiohydrazides or 3-ethoxyacrylic acid *N*'-phenylhydrazide. Thiohydrazides **231a,b** were heated in methanol containing a catalytic amount of aqueous sodium hydroxide and then treated with aqueous TFA to give 3-oxopyrazole-2-carbothioic acid amides **232a,c** (04DT2019).



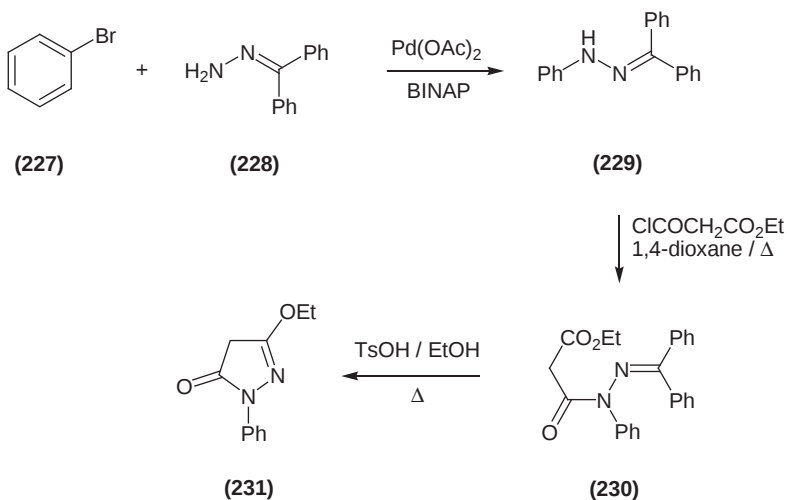
(a) $\text{R} = \text{H}$, $\text{Ar} = 2\text{-HOC}_6\text{H}_4$, (b) $\text{R} = \text{H}$, $\text{Ar} = 4\text{-MeOC}_6\text{H}_4$, (c) $\text{R} = \text{H}$, $\text{Ar} = 2\text{-HO}$, $3\text{-MeOC}_6\text{H}_4$,
 (d) $\text{R} = \text{MeO}$, $\text{Ar} = 4\text{-MeOC}_6\text{H}_4$, (e) $\text{R} = \text{Cl}$, $\text{Ar} = \text{Ph}$

Scheme 50

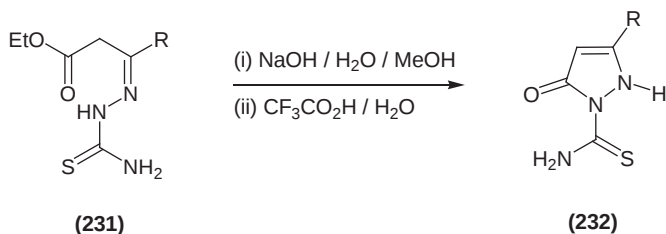


(a) $\text{R} = \text{Ph}$, (b) $\text{R} = 4\text{-HOC}_6\text{H}_4$, (c) $\text{R} = 4\text{-MeOC}_6\text{H}_4$, (d) $\text{R} = 4\text{-ClC}_6\text{H}_4$,
 (e) $\text{R} = 3\text{-NO}_2\text{C}_6\text{H}_4$, (f) $\text{R} = \text{furan-2-yl}$

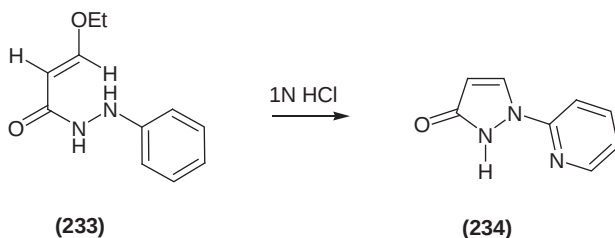
Scheme 51



Scheme 52



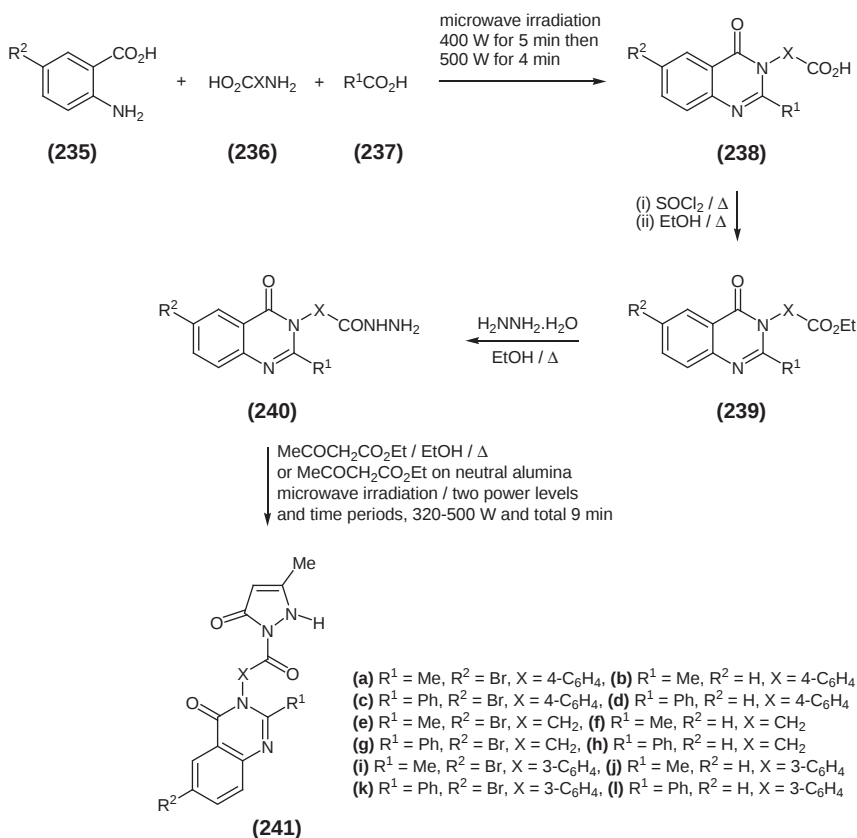
(a) R = Et, (b) R = Ph



Scheme 53

(Scheme 53). 3-Ethoxyacrylic acid *N'*-phenylhydrazide **233** cyclized by intramolecular conjugate substitution of ethoxide ion when treated with aqueous hydrochloric acid to give 1-pyridin-2-ylpyrazol-3-one **234** in 45% yield (04JMC4645).

2.1.10.5 From (4-oxoquinazolin-3(4H)-yl)aceto(or benzo)hydrazides. Desai and Desai (05ARK98(xiii)) (Scheme 54) reported a modified Niementowski reaction using conventional and MW-induced conditions, leading to quinazolinone hydrazides that were then condensed with ethyl acetoacetate to give 1,2-dihydro-3H-pyrazol-3-ones. Thus, 2-aminobenzoic acid **235** ($R^2 = H$) or 2-amino-5-bromobenzoic acid **235** ($R^2 = Br$), acetic acid **235** ($R^2 = Me$) or benzoic acid **237** ($R^2 = Ph$) and aminoacetic acid **236** ($X = CH_2$) or 4-aminobenzoic acid **236** ($X = C_6H_4$) were appropriately mixed and irradiated using MWs (400 W for 5 min and 500 W for 4 min) to yield 2,3-disubstituted-4(3H)-quinazolinonecarboxylic acids **238a–l**. Yields were much higher when compared to the conventional procedure. The quinazolinone carboxylic acids **238a–l** were converted to quinazolinone esters **239a–l** first with thionyl chloride to give the corresponding acid chlorides, followed by heating in ethanol. Heating esters **239a–l** with hydrazine hydrate in ethanol afforded the quinazolinone hydrazides **240a–l**. Finally, condensation of **240a–l** with ethyl acetoacetate on neutral alumina followed by microwave irradiation afforded the 1,2-dihydro-3H-pyrazol-3-ones **241a–l**.

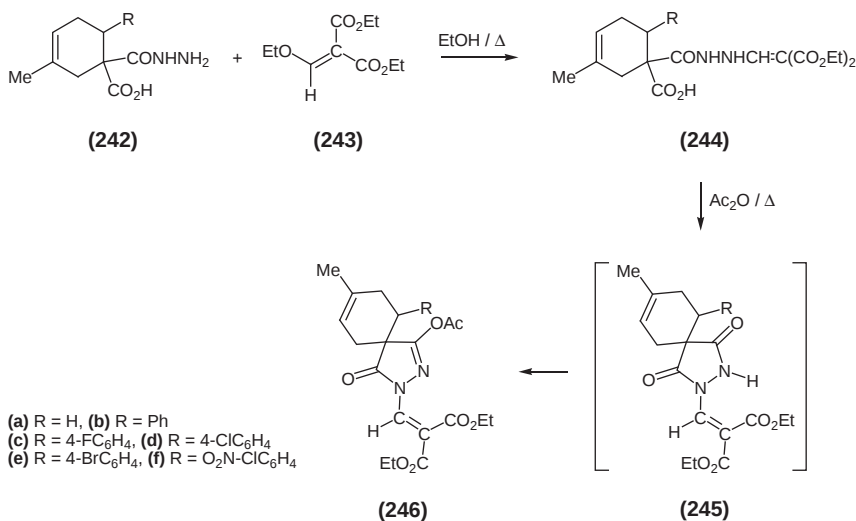


Scheme 54

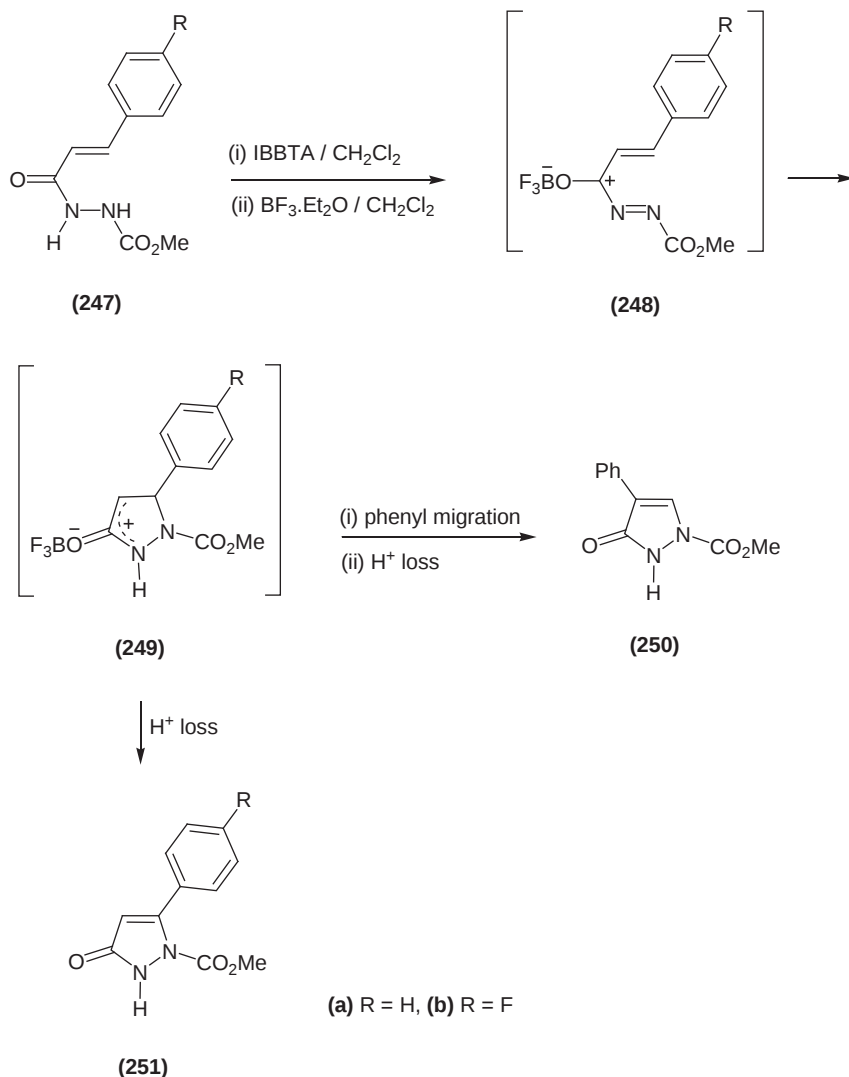
240a–l. The latter were either subjected to heating with ethyl acetoacetate in ethanol or irradiated under MWs (in two power levels ranging from 320 to 500 W and two time periods totaling about 9 min) with ethyl acetoacetate on neutral alumina to give 1,2-dihydro-2-substituted-5-methyl-3*H*-pyrazol-3-ones **241a–l** in yields of 26–82% and 85–95%, respectively.

2.1.10.6 From monohydrazides of cyclohexenedi-carboxylic acids. The synthesis of spiropyrazol-3-ones **244a–f** can be carried out by a two-step reaction (05CHE187) (Scheme 55). First, 1-(hydrazinocarbonyl)-3-methylcyclohex-3-ene-1-carboxylic acids **242a–f** are heated with ethoxymethylenemalonic acid diethyl ester **243** in ethanol to give *N*-(2,2-diethoxycarbonyl-ethylenyl)hydrazides of 3-methylcyclohex-3-ene-1,1-dicarboxylic acids **244a–f**. The latter are then heated with acetic anhydride to afford spiropyrazol-3-ones **246a–f** (61–91%) *via* the intermediate spiropyrazolidine-3,5-diones **245a–f**.

2.1.10.7 From *N,N'*-diacyl-*N,N'*-disubstituted hydrazides. Diacylhydrazide derivatives **247a,b** were oxidized (02JCS(P1)513) (Scheme 56) by iodobenzene *bis*(trifluoroacetate) (IBBTA) in dichloromethane followed by addition of boron trifluoroetherate to afford, in the case of **247a**, a mixture containing pyrazol-3-one **250** in 9% yield and pyrazol-3-one **251a** in 43% yield, and in the case of **247b** pyrazol-3-one **251b** as the only product in 23% yield. Apparently a Nazarov reaction formed cyclic



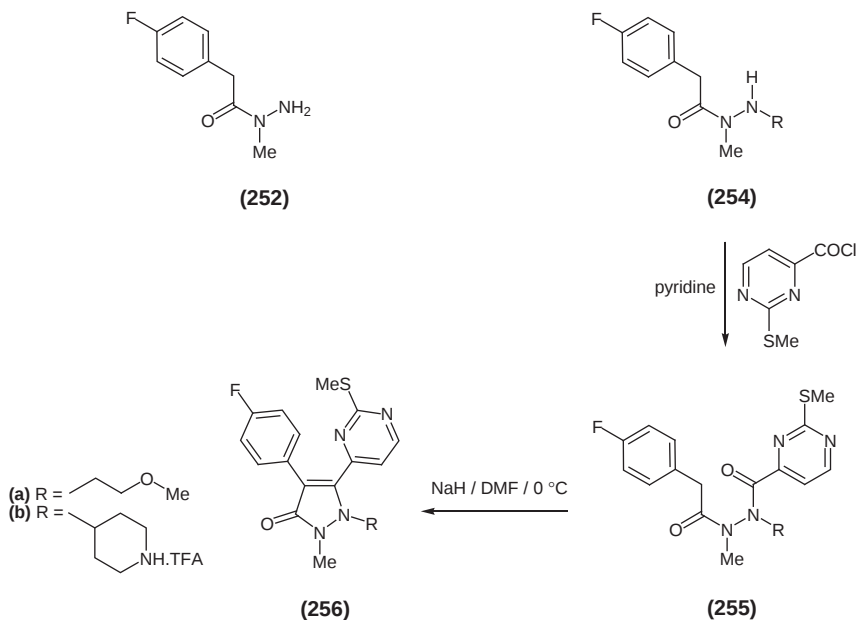
Scheme 55



Scheme 56

cation **249** via the initially formed azodicarbonyl **248**. Proton loss from the former gives pyrazol-3-ones **251a,b**. A similar proton loss subsequent to phenyl migration in **249a** produces pyrazol-3-one **250**.

The formation of pyrazol-3-ones by an intramolecular aldol condensation of *N,N'*-diacyl-*N,N'*-dimethylhydrazides with either phenyllithium or lithium *bis*(trimethylsilyl)amide bases was reported earlier (08AHC(95)27). Recently, Golebiowski et al. (05BMCL2285) (Scheme 57) described the synthesis of *bis*-acylated hydrazines **255a,b** and their

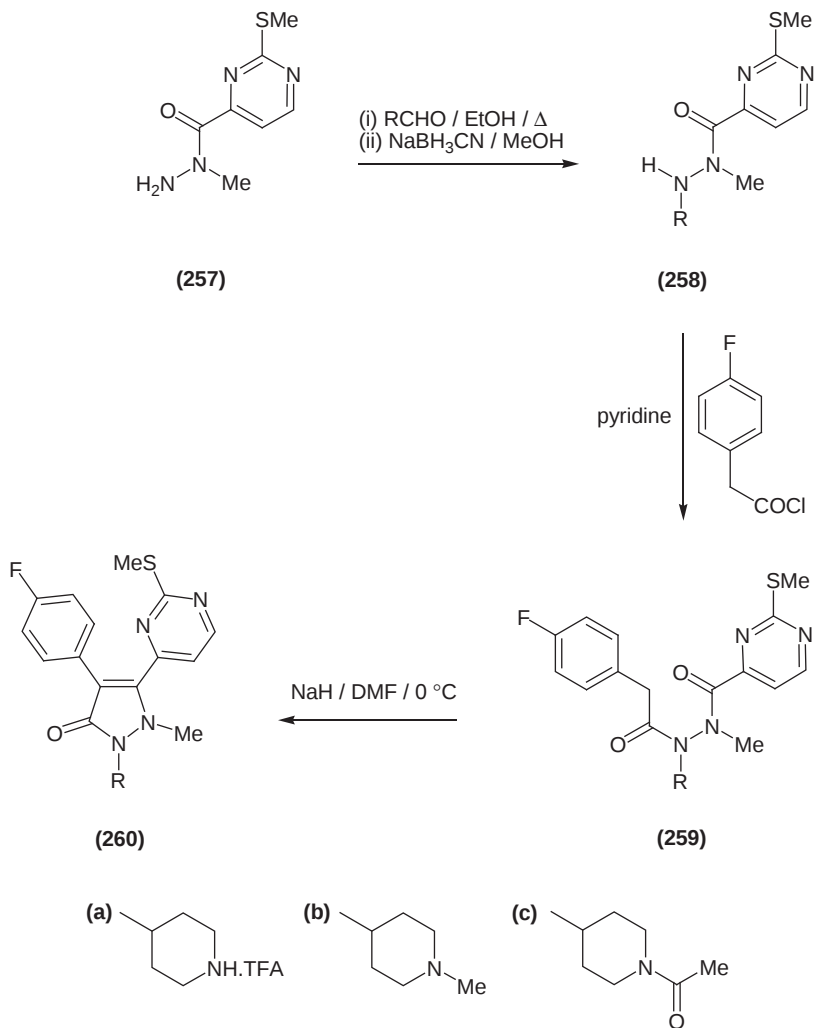


Scheme 57

cyclization with sodium hydride to pyrazol-3-ones **256a,b**. 2-(4-Fluorophenyl)-*N*-methylacetohydrazide **252** was condensed with carbonyl compounds **253a,b** in refluxing ethanol and the resulting imines reduced with sodium cyanoborohydride in methanol to the 2-(4-fluorophenyl)-*N*-methylacetohydrazides **254a,b**. Acylation of the latter with 2-methylsulfanylpuridine-4-carbonyl chloride afforded *N'*-(4-fluorophenyl)acetyl-*N'*-methyl-2-(methylthio)pyrimidine-4-carbohydrazides **255a,b**. Sodium hydride-mediated cyclization of hydrazides **255a,b** in DMF at low temperature led to the pyrazol-3-ones **256a,b** in good yields.

A complementary regioisomeric synthesis starts with *N*-methyl-2-(methylthio)pyrimidine-4-carbohydrazide **257** and in an analogous sequence it was transformed into pyrazolones **260a–c** (05BMCL2285) (Scheme 58).

A similar cyclization leading to pyrazol-3-one **266** was described by Brugel et al. (06TL3195) (Scheme 59). Beginning with 4-fluorophenylacetyl chloride **261**, reaction with methylhydrazine at -78°C led to the selective formation of 2-(4-fluorophenyl)-*N*-methylacetohydrazide **262** in 61% yield. Reductive amination with piperidone **263** afforded **264** in excellent yield. A second acylation with 2-methylsulfanylpuridine-4-carbonyl chloride **265** in pyridine gave the *bis*-acylated precyclization intermediate **266** that was cyclized with sodium hydride

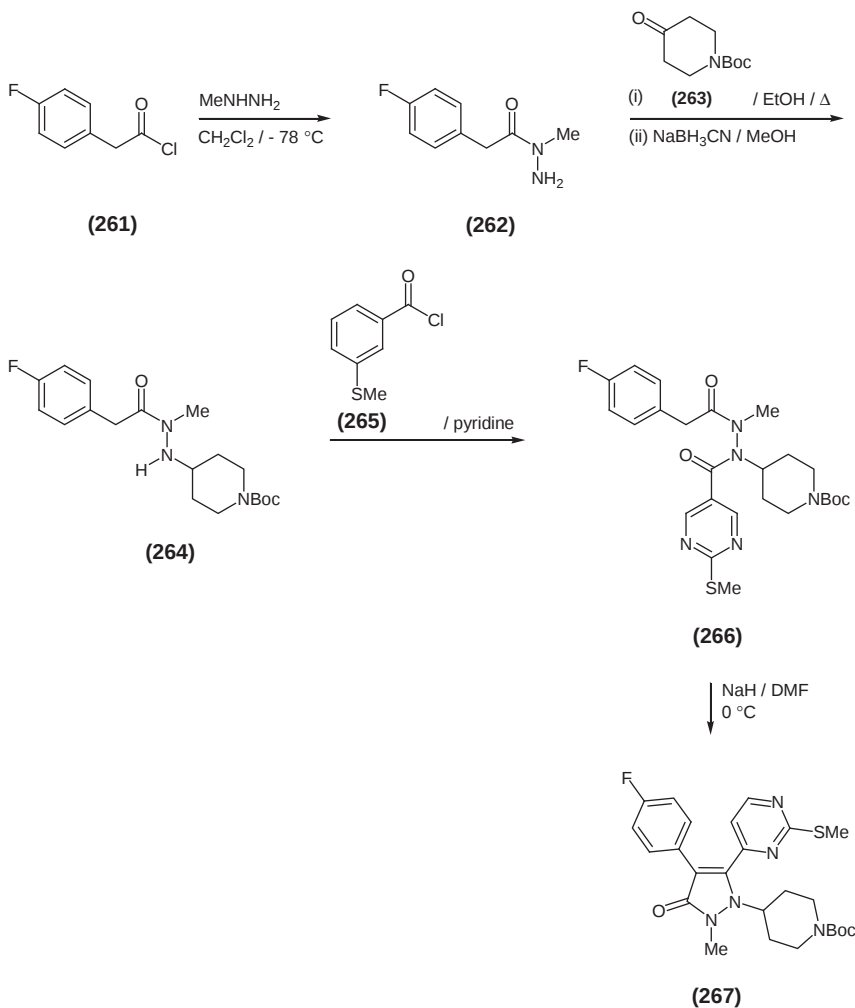


Scheme 58

to the asymmetrically substituted monocyclic pyrazol-3-one **267**, in 73% yield.

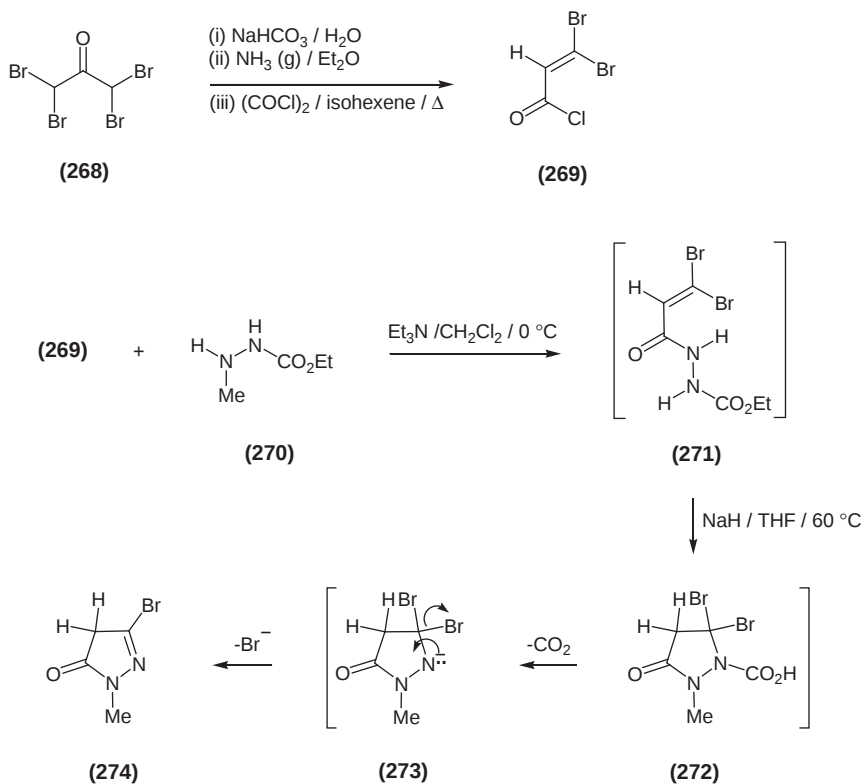
2.1.11 From α,β -unsaturated hydrazides

2.1.11.1 From in situ generated *N'*-(3,3-dibromoacryloyl)hydrazinecarboxylic acid ethyl ester. The previously unreported 5-bromopyrazol-3-one **274** was prepared on a multigram scale by adaptation of standard literature procedures (04SL795) (Scheme 60). Thus, 1,1,3,3-tetrabromopropan-2-one **268** underwent a Favorski rearrangement to 3,3-dibromopropanoic



Scheme 59

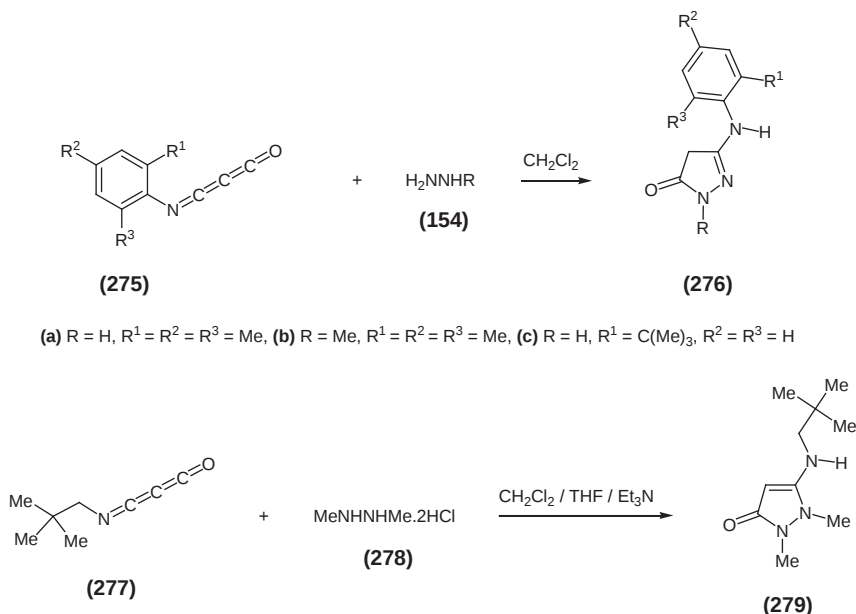
acid which was then converted to the acid chloride **269** *via* formation of the ammonium salt and chlorination with oxalyl chloride. Acid chloride **269** was condensed with ethyl 3-methylhydrazinecarboxylate **270** in dichloromethane containing triethylamine to give hydrazide **271** that was then cyclized in tetrahydrofuran with sodium hydroxide at 60 °C. Intermediate **271** may cyclize by an intramolecular Michael addition after hydrolysis of the ester group to give pyrazolidinone **272**. The latter decarboxylated to pyrazolidinone anion **273** which then converted to pyrazol-3-one **274** by loss of bromine ion. The regiochemistry of **274** was identified by NMR spectroscopy.



Scheme 60

2.1.12 From iminopropanediones

2.1.12.1 From 3-[(2,2-dimethylpropyl)imino]allen-1-one or 4-[(4-methylphenyl)imino]buta-1,2,3-trien-1-one. Alkyliminopropanediones, $\text{RN}=\text{C}=\text{C}=\text{C}=\text{O}$, are notoriously unstable compounds which can be isolated and characterized in low-temperature matrixes; the aryl derivatives are more stable and undergo reactions at about -100 to -50°C . Wentrup and co-workers (02JOC2619) (Scheme 61) prepared several iminopropanediones that are stable at room temperature and react with hydrazines to give pyrazol-3-ones. Thus, aromatic 3-(phenylimino)propa-1,2-dien-1-ones **275a–c** with the corresponding hydrazines **154a–c** in dichloromethane afforded pyrazol-3-ones **276a–c** in 72%, 70% and 55% yield, respectively. Similarly, aliphatic derivative 3-(2,2-dimethyl-propylimino)-propa-1,2-dien-1-one **277** and N,N' -dimethylhydrazine hydrochloride **278** in a mixture of dichloromethane and tetrahydrofuran containing triethylamine yielded 5-(2,2-dimethylpropylamino)pyrazol-3-one **279** in a much lower yield, 37% as expected.



Scheme 61

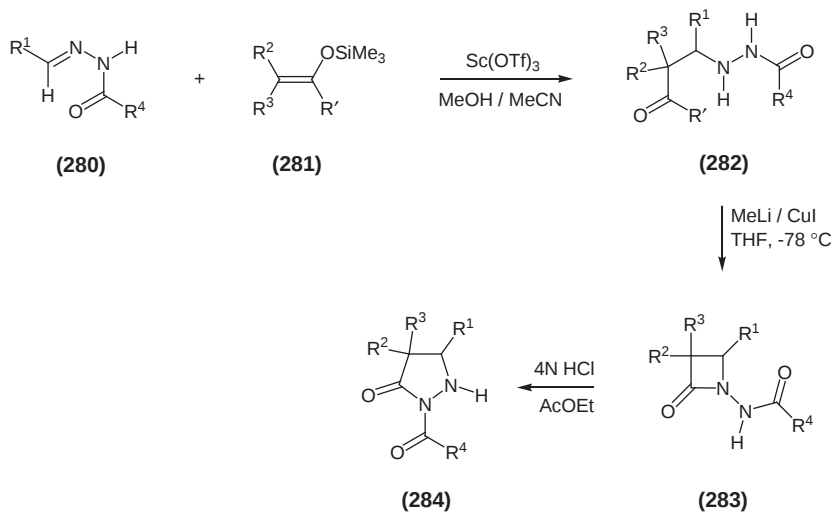
2.2 Synthesis from four-membered rings

2.2.1 From lactams

2.2.1.1 From *N*-(2-oxoazetidin-1-yl)-4-arylamides. 2-Aroyl-4,5-di(or tri)-substituted pyrazol-3-ones **284** have been prepared in high yields from β -lactams (00H1143) (Scheme 62). The overall synthesis from aliphatic or aromatic aldehydes and benzoylhydrazine or 4-trifluoromethylbenzoylhydrazine is a four-step sequence. The acylhydrazones **280a–e** thus obtained react with silyl enolates **281a–e** in the presence of scandium triflate to afford β -*N*-acylhydrazinocarbonyl compound **282a–e**. Treatment of **282a–e** with methyl lithium–cuprous iodide yielded β -lactams **283a–e** in excellent yields. The latter undergo ring opening–ring closure in the presence of acid to afford pyrazol-3-ones **284a–e**. Furthermore, pyrazol-3-ones **284a,b,d** were prepared in not less than 90% yield from hydrazine esters **282a,b,d** on dissolving in methanolic sodium methoxide.

2.3 Synthesis from five-membered rings

Several syntheses of pyrazol-3-ones from five-membered rings omitted in Part 1 are presented here.



(a) $\text{R}' = \text{OMe}$, $\text{R}^1 = \text{Ph}(\text{OCH}_2)_2$, $\text{R}^2 = \text{R}^3 = \text{Me}$, $\text{R}^4 = \text{Ph}$, (b) $\text{R}' = \text{OMe}$, $\text{R}^1 = \text{R}^4 = \text{Ph}$, $\text{R}^2 = \text{R}^3 = \text{Me}$,
 (c) $\text{R}' = \text{OMe}$, $\text{R}^1 = \text{PhCH=CH}$, $\text{R}^2 = \text{R}^3 = \text{Me}$, $\text{R}^4 = \text{Ph}$, (d) $\text{R}' = \text{OPh}$, $\text{R}^1 = \text{Ph}(\text{CH}_2)_2$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{H}$,
 $\text{R}^4 = 4\text{-CF}_3\text{C}_6\text{H}_4$, (e) $\text{R}' = \text{S}(t\text{-Bu})$, $\text{R}^1 = \text{Ph}(\text{CH}_2)_2$, $\text{R}^2 = \text{R}^3 = \text{H}$, $\text{R}^4 = 4\text{-CF}_3\text{C}_6\text{H}_4$

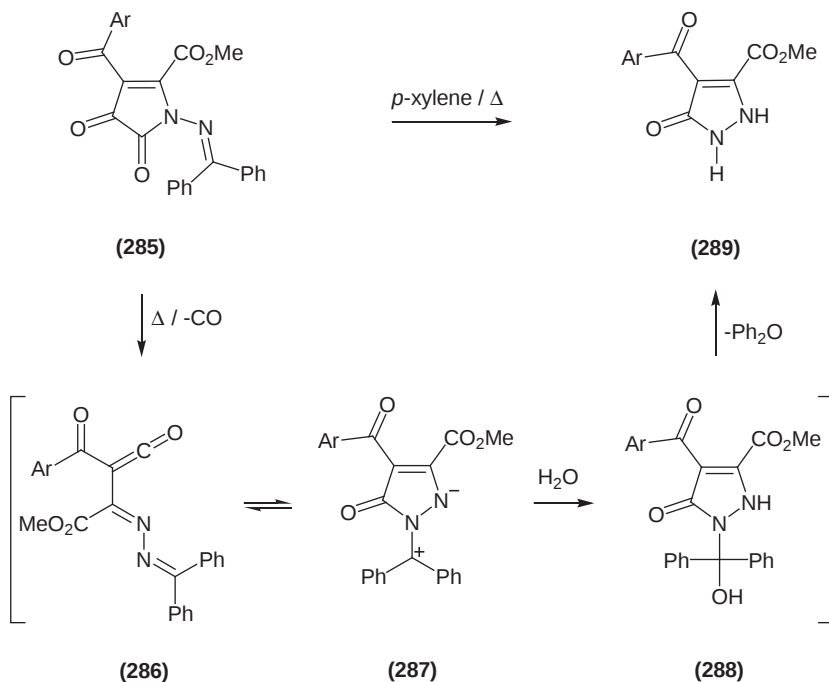
Scheme 62

2.3.1 From pyrrolediones

2.3.1.1 From pyrrole-2,3-diones. Thermolysis of 1-(benzhydrylideneamino)-3-aryl-4,5-dioxypyrrole-2-carboxylic acid methyl esters **285a,b** in *p*-xylene at $138\text{--}140^\circ\text{C}$ resulted in the isolation of pyrazol-3-ones **289a,b** (01CHC777) (Scheme 63). In a plausible mechanism, ketenes **286** formed by thermal decarboxylation of pyrrole-2,3-diones **285a,b** may undergo intramolecular cyclization to 3-oxopyrazolides **287**, which are hydrolyzed to **288** on exposure to traces of water followed by cleavage of benzophenone.

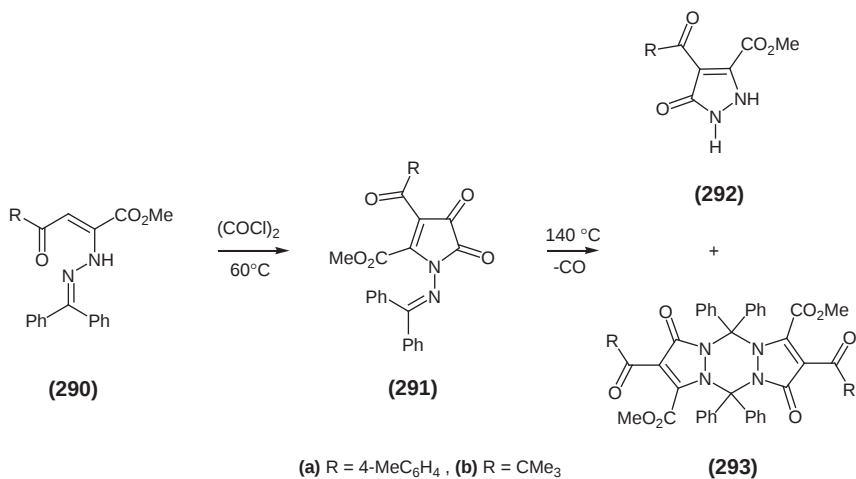
Lisowskaya et al. (04T5319) (Scheme 64) obtained the corresponding 1-(benzhydrylideneamino)-3-acyl-4,5-dioxypyrrole-2-carboxylic acid methyl esters **291a,b** from methyl ethers of butanoic acids **290a,b** and oxalyl chloride in 80% and 60% yield, respectively. The thermal cheletropic extrusion of CO from **291a,b** afforded dimethyl dipyrazolo-tetrazinedicarboxylates **293a,b** and in a parallel hydrolysis by traces of solvent water and loss of benzophenone also produced pyrazol-3-ones **292a,b** obtained in 15% and 25% yield, respectively. The proposed mechanism is analogous to the mechanism shown in Scheme 63, suggesting that compounds **293a,b** arise from a head to tail dimerization of intermediates analogous to **287** in Scheme 63.

Flash vacuum thermolysis (FVT) of 1-(dimethylamino)pyrrole-2,3-dione **294** at 400°C resulted in a mixture which was separated by dry



(a) Ar = 4-MeC₆H₄, (b) Ar = 4-FC₆H₄

Scheme 63



(a) R = 4-MeC₆H₄, (b) R = CMe₃

Scheme 64

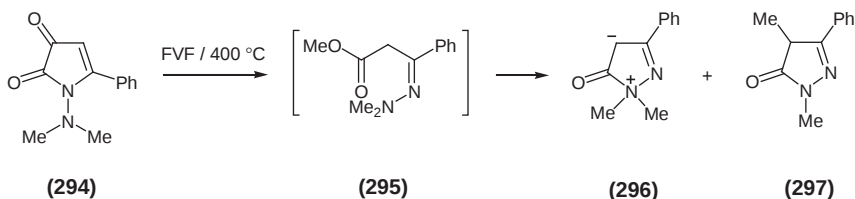
column chromatography into the orange pyrazolium oxide **296** and its rearranged 2,4-dimethyl-5-phenylpyrazol-3-one **297** in a 1:4 ratio (03OBC2550) (Scheme 65). The reaction occurs *via* extrusion of CO with the formation of hydrazoneketene intermediate **295**, observed as a weak band at 2130 cm^{-1} in an argon matrix IR spectrum resulting from FVT of **294**. IR and NMR spectra demonstrated that only traces of the known antipyrine-type isomer **297** were formed. A plausible reason can be found in thermochemistry; the calculated energy of **297** is *ca.* 12 kcal/mol above that of **296** at the B3LYP/6-31+G* level of theory.

2.3.2 From furanones

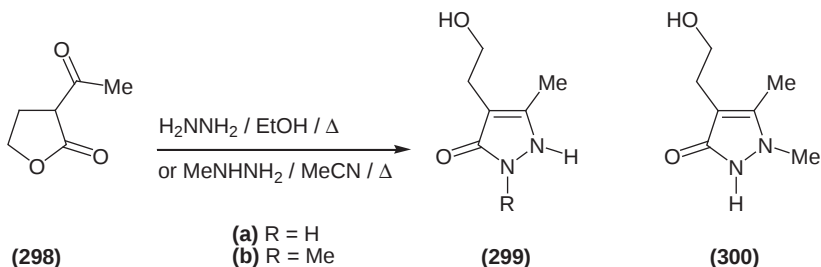
2.3.2.1 From 3-acetyldihydrofuran-2(3H)-one. The condensation of 3-acetyldihydrofuran-2-one **298** with hydrazine in water or methylhydrazine in acetonitrile gave pyrazol-3-ones **299a** and **299b** in 65% and 75% yield, respectively. Compound **299b** was isolated together with 3% of *N*-1-methyl isomer **300** (99EJMC967) (Scheme 66).

2.3.3 From pyrazoles

2.3.3.1 Oxidation of 5-(fluoro-dimethylsilanyl)-3-methyl-1-phenyl-1H-pyrazole. Oxidative desilylation of 5-(fluoro-dimethylsilanyl)pyrazole **301** with 3-chloroperbenzoic acid and potassium fluoride in *N,N*-dimethylformamide at -100°C afforded pyrazol-3-one **302**, in 58% yield (01S1949) (Scheme 67).



Scheme 65

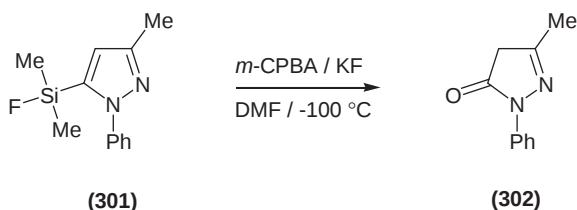


Scheme 66

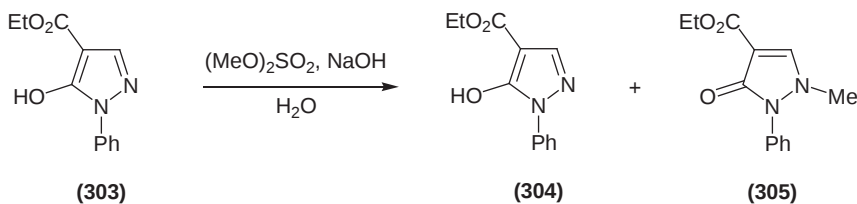
2.3.3.2 From 3(5)-hydroxypyrazoles. 5-Hydroxy-1-phenyl-1*H*-pyrazole-4-carboxylic acid ethyl ester **303**, derived from diethyl (ethoxymethylene)-malonate and phenylhydrazine hydrochloride, when methylated with dimethyl sulfate in aqueous sodium hydroxide solution afforded pyrazole **304** together with pyrazol-3-one **305** in 16% and 33% yield, respectively (95JHC1341) (Scheme 68).

3-Hydroxy-5-methyl-2-phenyl-4-(2-nitrophenyl)thiopyrazole **306** reacted nucleophilically at its sulfur atom at position 4 toward 2-nitrobenzenesulfonyl chloride **307** to give 4,4-di(2-nitrophenyl)thiopyrazol-3-one **308**, in 74% yield (99RJOC281) (Scheme 69).

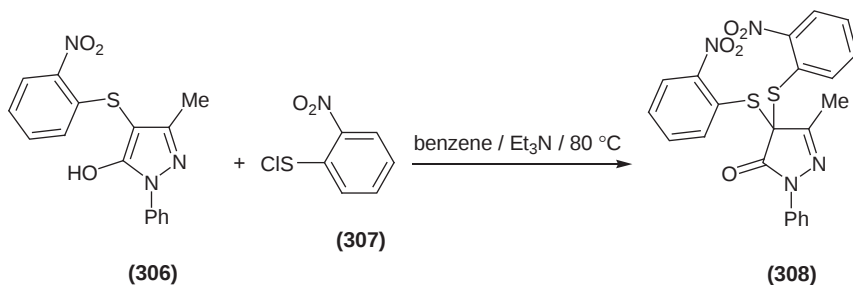
Dehydration of octafluorobutylpyrazol-3-ol **309** with morpholinotriethylamine trifluoride **310** in dichloromethane gave pyrazol-3-one **311**. The process is stereospecific. A single set of signals in the ^{19}F NMR spectrum



Scheme 67



Scheme 68

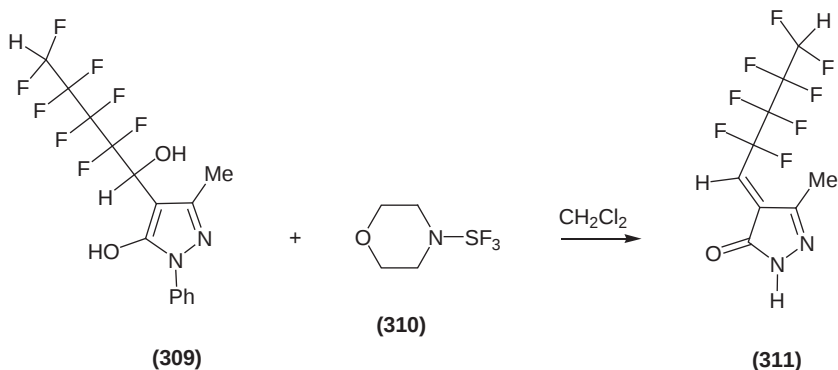


Scheme 69

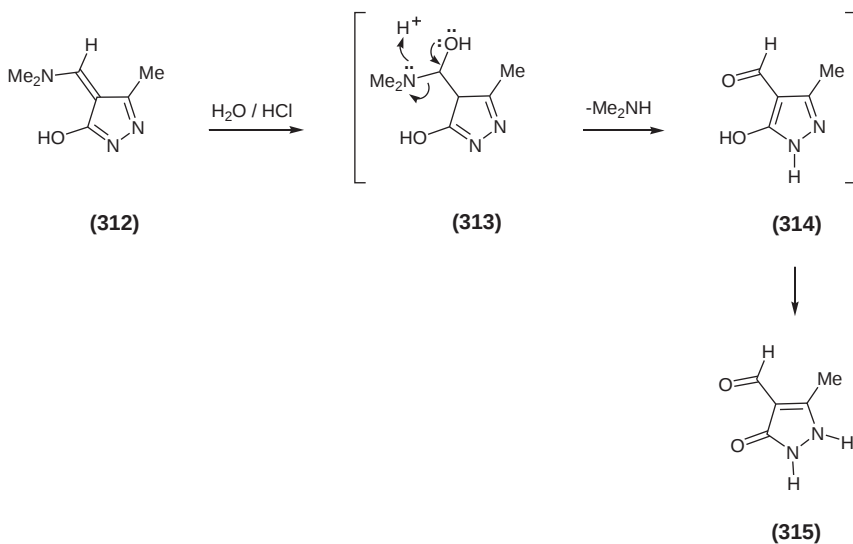
of the mixture indicates that only one of the two possible geometrical isomers of compound **311** was formed (00JFC111) (Scheme 70).

Michael addition of water to 4-methylenepyrazol-3-ol **312**, derived from 5-methyl-1,2-dihydro-3*H*-pyrazol-3-one and neat *N,N*-dimethylformamide dimethylacetal in the presence of acid, gave 4-formylpyrazol-3-one **315** *via* intermediate **313** which loses dimethylamine to form, after tautomerization, aldehyde **314** (02EJOC1763) (Scheme 71). The slow reaction is complete in 2 days.

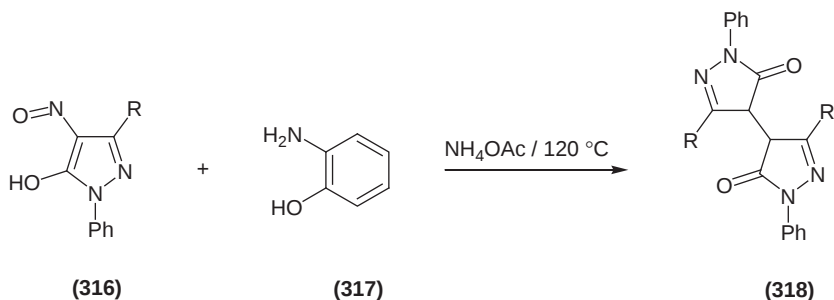
El-Rady (04JCCS859) (Scheme 72) reported that fusion of 4-nitroso-2-phenylpyrazol-3-ols **316a,b** with either 2-aminophenol **317** (X = OH) or



Scheme 70

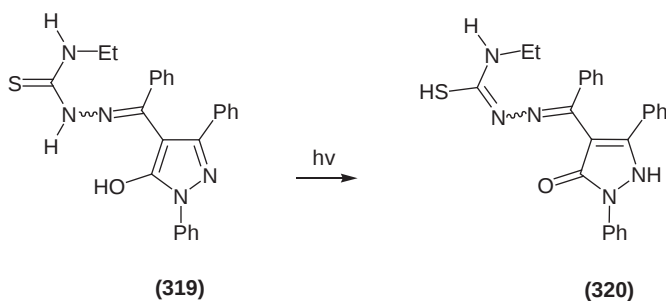


Scheme 71



X = O or S, (a) R = Me, (b) R = Ph

Scheme 72



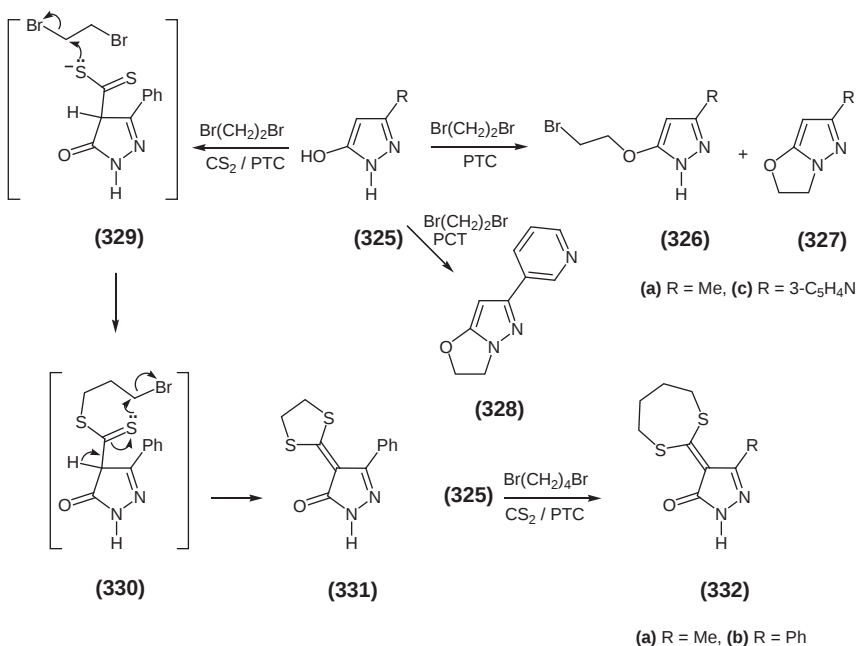
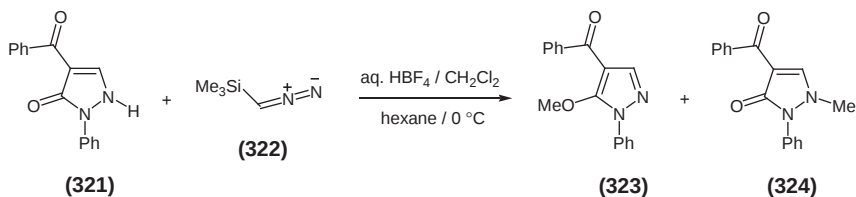
Scheme 73

2-aminobenzenethiol **317** (X = SH) and ammonium acetate at 120°C gave the 2,2'-diphenyl-2,2',4,4'-tetrahydro-3H,3'H-4,4'-bipyrazolyl-3,3'-diones **318a,b** in 50% yields.

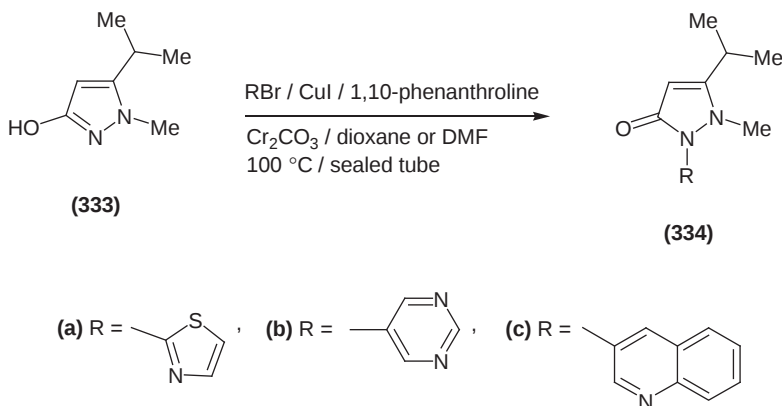
Peng et al. (04JMS217) (Scheme 73) reported that irradiation of (*E/Z*)-pyrazol-3-ol **319** with ultraviolet light caused conversion of the thiourea group into an isothiurea with concomitant formation of the corresponding pyrazol-3-one tautomer **320**.

(5-Hydroxypyrazol-4-yl)phenylmethanone **321** with trimethylsilyldiazomethane **322** in hexane and dichloromethane containing aqueous tetrafluoroboric acid afforded (5-methoxy-pyrazol-4-yl)phenylmethanone **323** and pyrazol-3-one **324**. The mixture was not separated (04T6791) (Scheme 74).

Khalil et al. (05PS479) reacted hydrazine hydrate with ethyl acetoacetate, ethyl benzoylacetate or ethyl nicotinoylacetate in boiling ethanol and obtained 5-substituted pyrazol-3-ols **1a-c** (Scheme 75). The existence of pyrazoles **325a-c** predominantly in their enol tautomeric form was confirmed by spectroscopic data as well as by phase-transfer catalysis (PTC) alkylations, affording *O*-monoalkylated or *O*- and



N-dialkylated or cycloalkylated products. For example, 5-hydroxy-3-methyl-1*H*-pyrazole **325a** and 1,2-dibromoethane in acetonitrile containing anhydrous potassium carbonate as liquid–solid phases and in the presence of tetrabutylammonium bromide (TBAB) catalyst yielded 5-(2-bromoethoxy)-3-methyl-1*H*-pyrazole **326a** and 6-methyl-2,3-dihydropyrazolo[5,1-*b*]oxazole **327a**. Under the same PTC conditions, 5-hydroxy-3-phenyl-1*H*-pyrazole **325b** yielded only 6-phenyl-2,3-dihydropyrazolo[5,1-*b*]oxazole **328b** while 5-hydroxy-3-(pyrid-3-yl)-1*H*-pyrazole **325c** gave a mixture of 5-(2-bromoethoxy)-3-(pyrid-3-yl)-1*H*-pyrazole **326c** and 6-(pyrid-3-yl)-2,3-dihydropyrazolo[5,1-*b*]oxazole **327c**. The addition of carbon disulfide changed their course and led to pyrazol-3-ones. Thus, pyrazole **325b** with 1,2-dibromoethane and carbon disulfide



Scheme 76

in acetonitrile and anhydrous potassium carbonate as liquid–solid phases and TBAB catalyst afforded 4-(1,3-dithiolan-2-ylidene)-5-phenyl-2,4-dihydro-3*H*-pyrazol-3-one **331**. This reaction probably proceeds *via* nucleophilic addition of C4 of pyrazole **325b** to CS₂ to give the intermediate carbodithioate anion **329b** which then is alkylated intermolecularly to intermediate sulfide anion **330b** that undergoes alkylation to **331**. Under similar conditions, pyrazoles **325a,b** and 1,4-dibromobutane gave pyrazol-3-ones **332a** and **332b**, respectively.

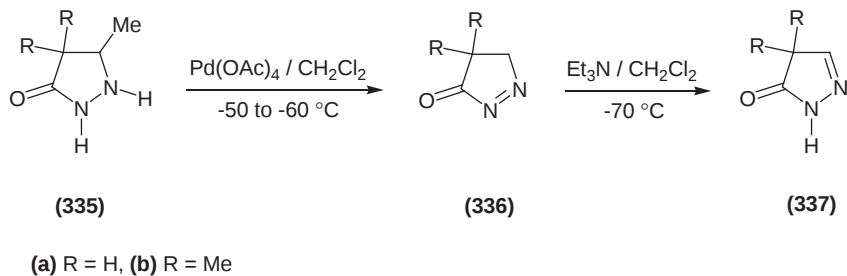
Coupling 5-isopropyl-1-methylpyrazol-3-ol **333** with 2-bromothiazole, 5-bromo-pyrimidine and 3-bromoquinoline under Buchwald-type amidation gave pyrazolones **334a–c**, in modest yields (06BMCL3713) (Scheme 76).

2.3.4 From pyrazolidinones

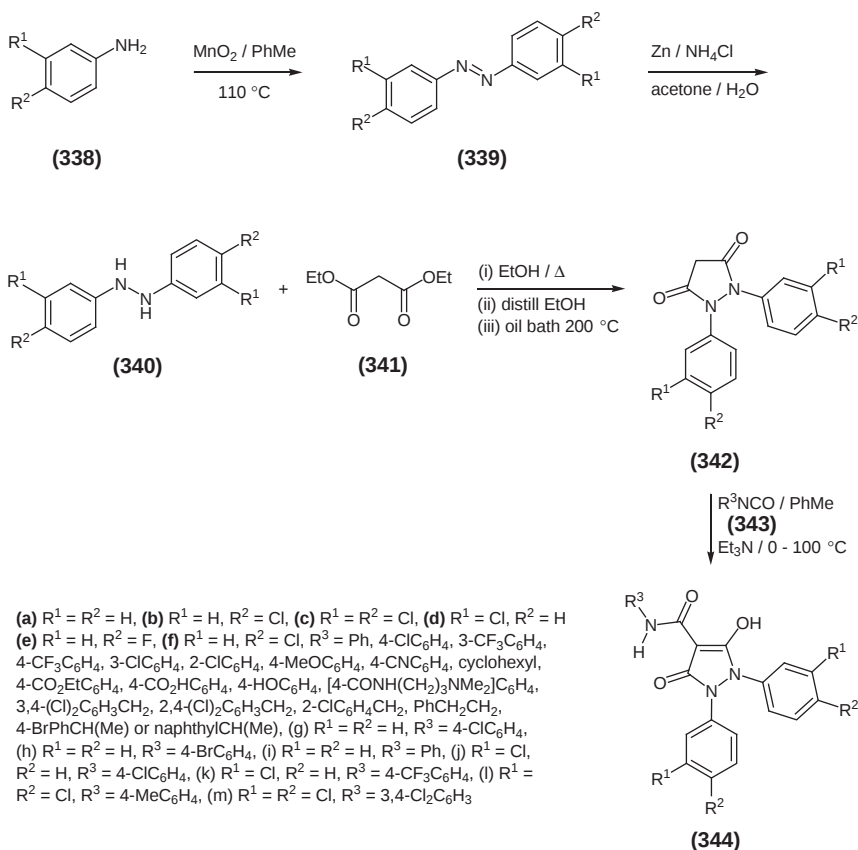
2.3.4.1 From unsubstituted or 4,4-dimethylpyrazolidin-3-ones. Pyrazolidin-3-ones **335a,b** were oxidized to 4,5-dihydropyrazol-3-ones **336a,b** with lead(IV) acetate at low temperature; **336a** isomerizes readily to 2,4-dihydropyrazol-3-one **337** by triethylamine in methylene chloride at –70 °C (70JCS(C)540) (Scheme 77).

2.3.5 From pyrazolidinediones

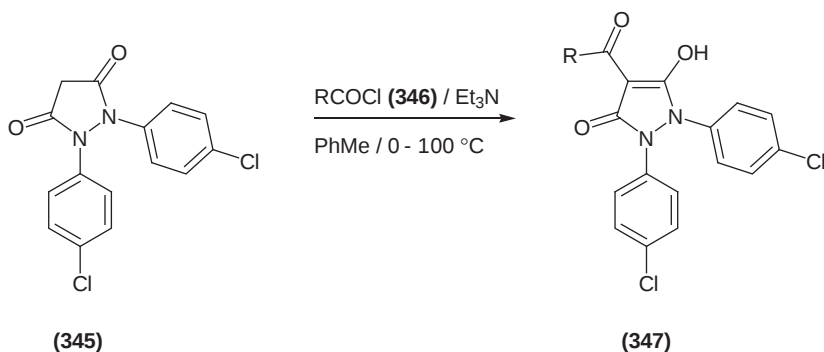
2.3.5.1 From 1,2-diarylpyrazolidine-3,5-diones. A new method for the synthesis of 4-amido(or 4-keto)-1,2-diaryl-5-hydroxy-1*H*-pyrazol-3-ones **344f–m** has been developed by Gilbert et al. (06JMC6027) (Scheme 78). The synthesis involves the dimerization of anilines **338b–e** to diazo compounds **339b–e** *via* oxidation with manganese dioxide, reduction to the corresponding hydrazines **340a–e** by zinc dust and ammonium



Scheme 77



Scheme 78



- (a) R = Ph, (b) R = 4-ClC₆H₄, (c) R = 3-CF₃C₆H₄, (d) R = 4-CF₃C₆H₄,
 (e) R = 3-ClC₆H₄, (f) R = 2-ClC₆H₄, (g) R = 4-MeOC₆H₄, (h) R = 4-CNC₆H₄,
 (i) R = cyclohexyl, (j) R = 4-CO₂EtC₆H₄, (k) R = 4-CO₂HC₆H₄, (l) R =
 4-HOC₆H₄, (m) R = [4-CONH(CH₂)₃NMe₂]C₆H₄, (n) R = 3,4-(Cl)₂C₆H₃CH₂,
 (o) R = 2,4-(Cl)₂C₆H₃CH₂, (p) R = 2-ClC₆H₄CH₂, (q) R = PhCH₂CH₂, (r) R =
 4-BrPhCH(Me), (s) R = naphthylCH(Me)

Scheme 79

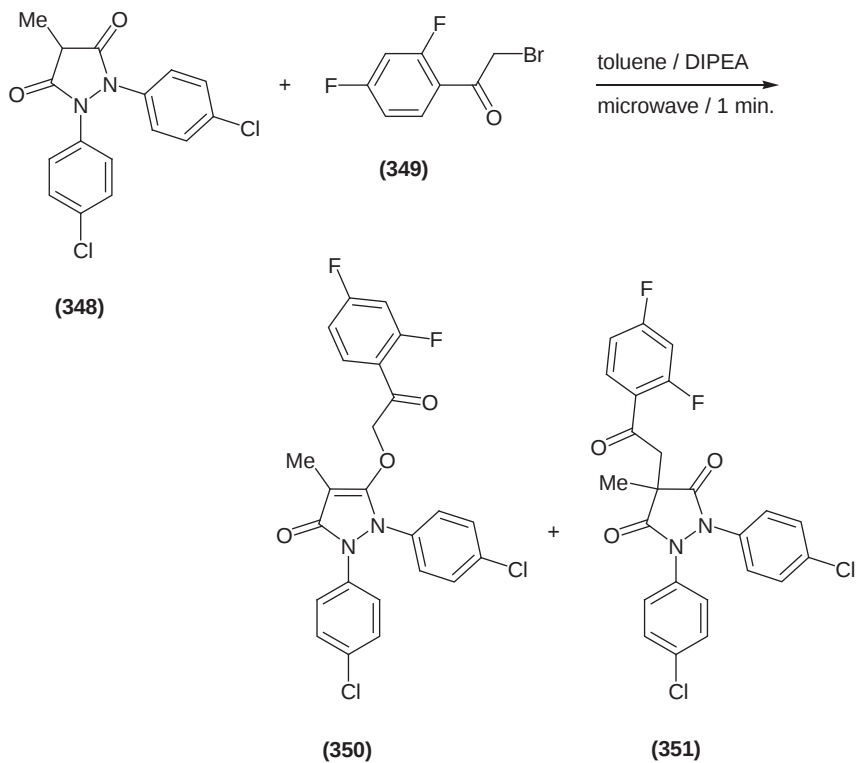
chloride in aqueous acetone, followed by heating with diethyl malonate **341** in ethanol to give the pyrazolidine-3,5-diones **342a–e** which were then treated with isocyanates **343** in toluene in the presence of triethylamine to yield 4-amidopyrazol-3-ones **344f–m**.

The corresponding 4-ketopyrazol-3-ones **347a–s** (Scheme 79) were prepared from pyrazolidine-3,5-dione **345b** under the conditions described in Scheme 78 except that acid chlorides **346a–s** were used in place of isocyanates.

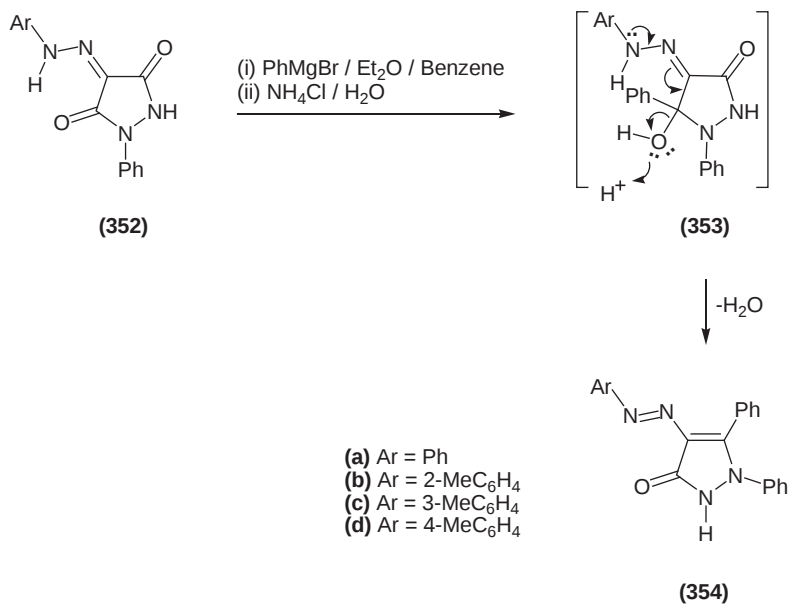
Earlier, Kutterer et al. (05BMCL2527) (Scheme 80) reported that 4-methyl-1,2-bis(4-chlorophenyl)pyrazolidine-3,5-dione **348** with 2-bromo-1-(2,4-difluorophenyl)ethanone **349** in toluene containing DIPEA under MW heating (900 W) for 1 min gave 4'-alkyl-4-methylpyrazolidine-3,5-dione **350** and 4-methyl-5-alkyloxy-pyrazol-3-one **351**. Although compound **351** was evaluated as new inhibitor of bacterial cell wall biosynthesis, no separation and yields of **350** and **351** were reported.

Pyrazole-3,5-diones **352a–d** and phenylmagnesium bromide yielded pyrazol-3-one **354a–d** in 70–75% yield (73IJC219) (Scheme 81) probably by addition product **353** which undergoes dehydration.

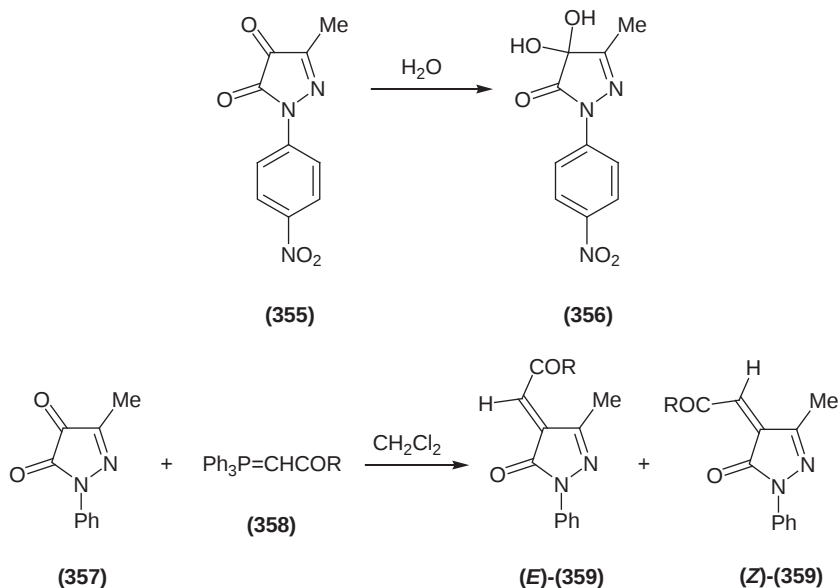
The keto group of pyrazol-4,5-diones is susceptible to nucleophilic addition that leads to pyrazol-3-ones. Thus, 3-methyl-1H-1-(4-nitrophenyl)pyrazole-4,5-dione **355** readily hydrated to 4,4-dihydroxypyrazol-3-one **356** (99T10447) (Scheme 82). The keto group of pyrazole-4,5-dione **357** undergoes a Wittig reaction as demonstrated by Tacconi et al.



Scheme 80



Scheme 81



(a) R = Ph, (b) R = OMe

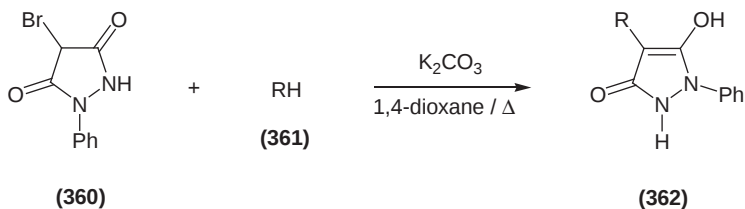
Scheme 82

(80JPR711). Therefore, **357** with methyl(triphenylphosphoranylidenes)-acetate **358a** or 1-phenyl-2-(triphenylphosphoranylidenes)ethanone **358b** in methylene chloride afforded pyrazol-3-ones **359a** and **359b**, each as mixtures of *E/Z* isomers in a ratio of 25:75.

Nucleophilic substitution of the bromine atom of 4-bromo-1-phenylpyrazolidine-3,5-dione **360** by 2-aminoethanethiole hydrochloride **361a**, guanidine hydrochloride **361b**, glycine ethyl ester hydrochloride **361c**, 4-aminobenzoic acid **361d**, benzene-1,2-diamine **361e**, 2-aminobenzenethiol **361f** or benzene-1,4-diol **361g** in refluxing 1,4-dioxane containing potassium carbonate yielded 4-substituted 5-hydroxypyrazol-3-ones **362a–g** (04JCCS103) (Scheme 83).

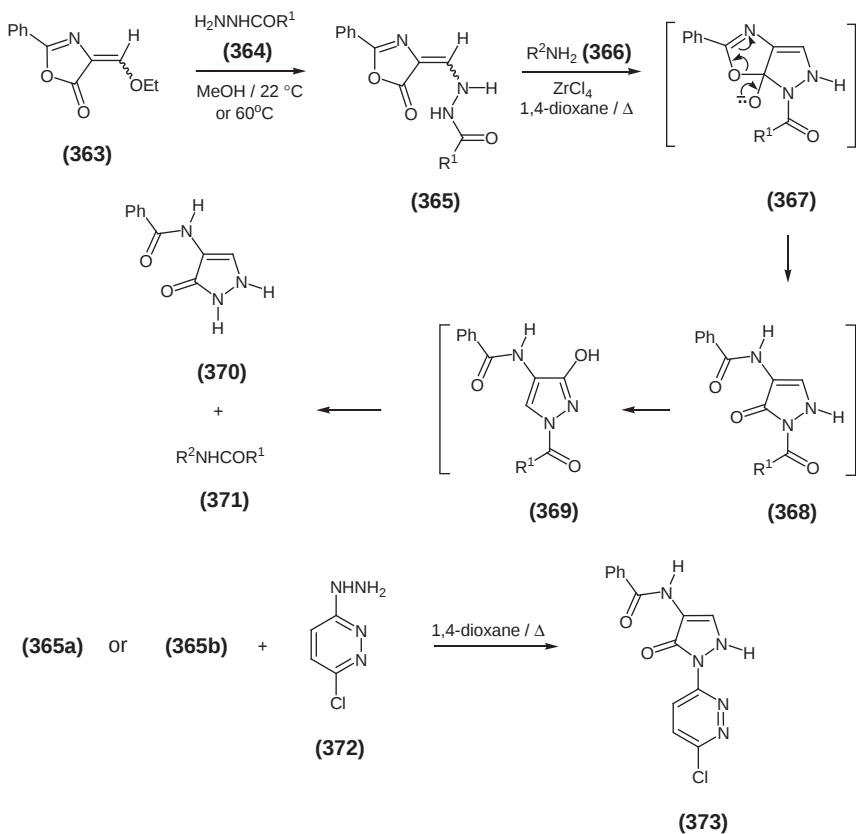
2.3.6 From oxazolones

2.3.6.1 From 4-ethoxymethylene-2-phenyl-4H-oxazol-5-one. During the transformation of hydrazides **364a–c** into acylhydrazinomethylene derivatives **365a–c** with oxazolone **363**, and then further reaction of **365a–c** with amines **336a–h** in the presence of zirconium(IV) chloride catalyst, amides **371a–h** were obtained together with pyrazol-3-one **370** side-product (Scheme 84). Kočevár and co-workers (01H1011) explained the formation of pyrazol-3-one **373** from 4-acylhydrazinomethylene-2-phenyloxazol-5-(4*H*)-ones **365a,h** and 3-chloro-6-hydrazinopyridazine



(a) $R = S(CH_2)_2NH_2$, (b) $R = NH(C=NH)NH_2$, (c) $NHCH_2CO_2Et$,
 (d) $NHC_6H_4CO_2H-4$, (e) $NHC_6H_4NH_2-4$, (f) NHC_6H_4SH-4 , (g) OC_6H_4OH-4

Scheme 83



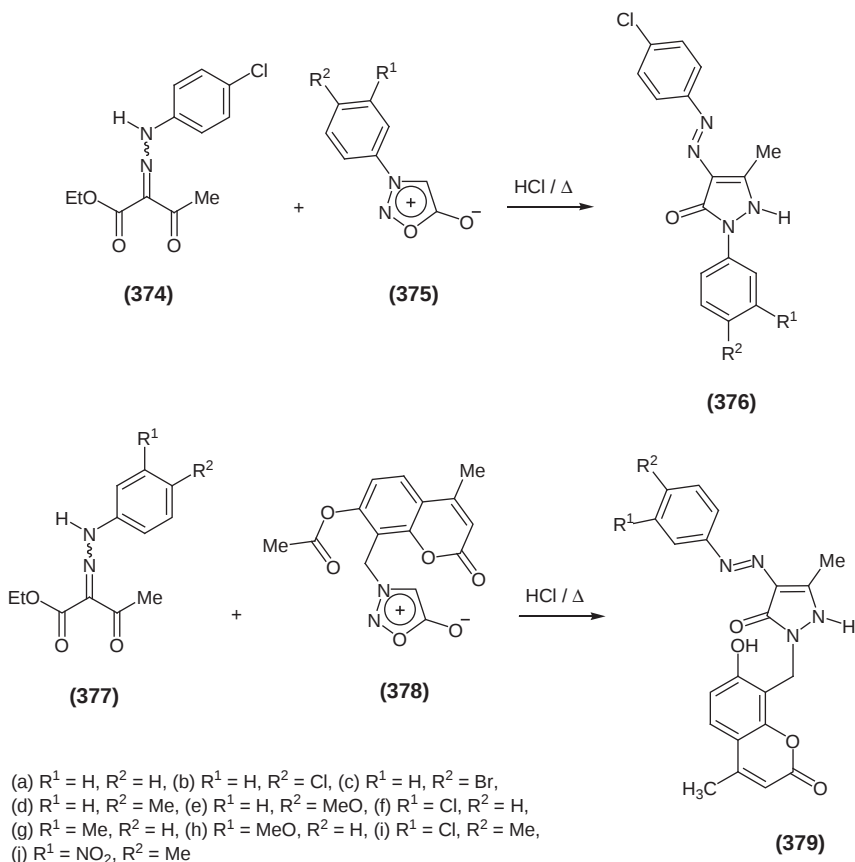
(a) $R^1 = Me$, $R^2 = H$, (b) $R^1 = Ph$, $R^2 = H$, (c) $R^1 = 4-HOC_6H_4$, $R^2 = H$, (d) $R^1 = R^2 = Me$, (e) $R^1 = Ph$, $R^2 = Me$
 (f) $R^1 = 4-HOC_6H_4$, $R^2 = Me$

Scheme 84

372 as follows. Substitution of the acylhydrazino moiety in **365a,b** with the nucleophilic nitrogen of **372** followed by the nucleophilic attack of the second nitrogen of the hydrazine group at position 5 of oxazolone ring yields pyrazol-3-one **373**.

2.3.7 From sydnes

2.3.7.1 From 3-arylsydnes. Sydnes undergo hydrolysis with hydrochloric acid to give hydrazines. The use of sydnes as masked hydrazines was exploited by Singe et al. (05SC2169) who synthesized 4-(4-chlorophenylazo)-5-methyl-2-aryl-1,2-dihydropyrazol-3-ones **376a-j** by a one-pot reaction of 3-arylsydnes **375a-j** with 2-(4-chlorophenyl)hydrazono-3-oxo-butyric acid ethyl ester **374** in boiling concentrated hydrochloric acid. In a similar way, β -keto esters **377a-j** reacted with sydnes **378** to give 4-arylazo-2-(7-hydroxy-4-methyl-2-oxo-2*H*-chromen-8-ylmethyl)-5-methyl-1,2-dihydropyrazol-3-ones **379a-j** (05SC2169) (Scheme 85).



Scheme 85

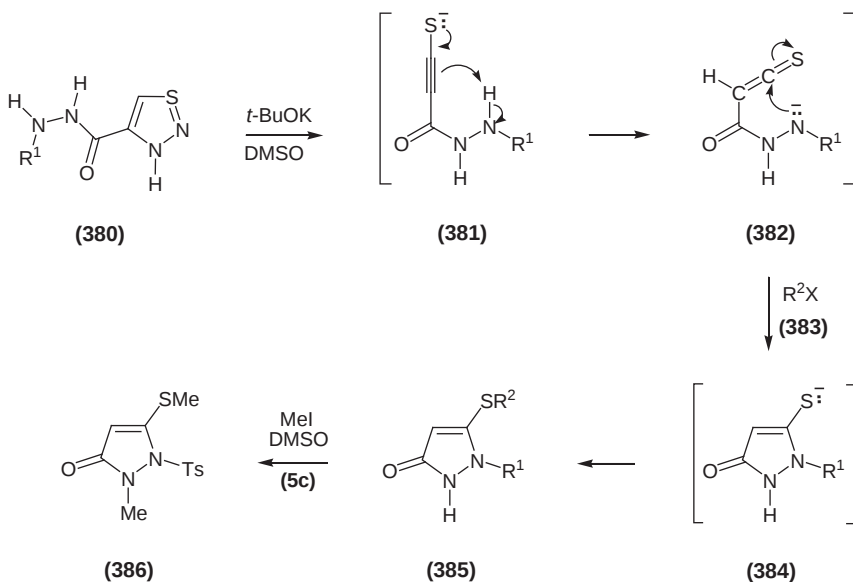
2.3.8 From thiadiazoles

2.3.8.1 From 1,2,3-thiadiazole-4-carbohydrazides. Base-catalyzed ring cleavage of 1,2,3-thiadiazole-4-carbohydrazides **380a,b** by one equivalent of potassium *tert*-butoxide in dimethylsulfoxide followed by alkylation with one equivalent of methyl iodide, 1-bromohexadecane or benzyl chloride **383a,b,e** afforded 5-alkylthiopyrazol-3-ones **385a–e** in yields ranging from 20 to 35% (02TL1015) (Scheme 86). The pyrazol-3-ones **385a–e** apparently result from cleavage of the thiadiazole ring of **380** with formation of the alkynethiolate **381**, fast intramolecular proton shift to the reactive thioketene **382**, intramolecular nucleophilic cyclization to pyrazol-3-one-5-thiolate anion **384** and finally alkylation. Further reaction of **385c** with an equivalent of methyl iodide in dimethylsulfoxide afforded dimethylated pyrazol-3-one **386**.

2.4 Synthesis from bicyclic 6,6-membered fused rings

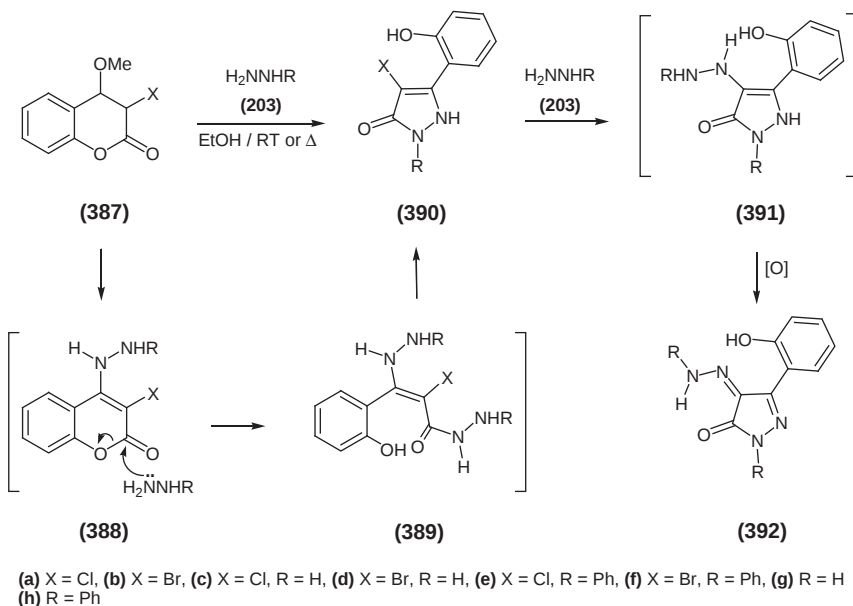
2.4.1 From chromenones

2.4.1.1 From 3-bromo(or chloro)-4-methoxychromen-2-one. Okamoto and co-workers (99JHC767) (Scheme 87) described an efficient method of converting chromen-3-ones **387a,b** into 4-bromo(or chloro)-1,2-dihydro-5-(2-hydroxyphenyl)pyrazol-3-ones **390a,b** and 4-hydrazono(or



(a) $\text{R}^1 = \text{COPh}$, $\text{R}^2 = \text{Me}$, (b) $\text{R}^1 = \text{COPh}$, $\text{R}^2 = \text{C}_{16}\text{H}_{33}$, (c) $\text{R}^1 = \text{Ts}$, $\text{R}^2 = \text{Me}$ (d) $\text{R}^1 = \text{Ts}$, $\text{R}^2 = \text{C}_{16}\text{H}_{33}$, (e) $\text{R}^1 = \text{Ts}$, $\text{R}^2 = \text{Bn}$, $\text{X} = \text{Cl}$, Br , or I

Scheme 86



Scheme 87

phenylhydrazono)-2,4-dihydro-5-(2-hydroxyphenyl)pyrazol-3-ones **392g,h**. Reaction of chromen-2-ones **387a,b** with hydrazine hydrate in ethanol occurs at room temperature and gives pyrazol-3-ones **390a,b** in 71% and 73% yield, respectively. Further reaction of **390c,d** with hydrazine hydrate in refluxing ethanol afforded 4-hydrazonopyrazol-3-ones **392g,h** in 81% and 65% yield, respectively. Phenylhydrazine did not react with chromen-2-ones **387a,b** under similar conditions. However, heating with an excess of phenylhydrazine in ethanol, **387a,b** led to 4-phenylhydrazonopyrazol-3-one **392** in 29% and 33% yield, respectively. A possible mechanism involves initial attack of the hydrazine on C4 of **387**, subsequent substitution to give intermediate **388** and another attack by the hydrazine on C2 of **388** resulting in ring opened adduct **389**, which then cyclizes to pyrazol-3-one **390**. Bromine substitution in **390** by the hydrazine leads to **391** that is oxidized to pyrazol-3-one **392**.

2.5 Synthesis from tricyclic 5,5,6-membered fused rings

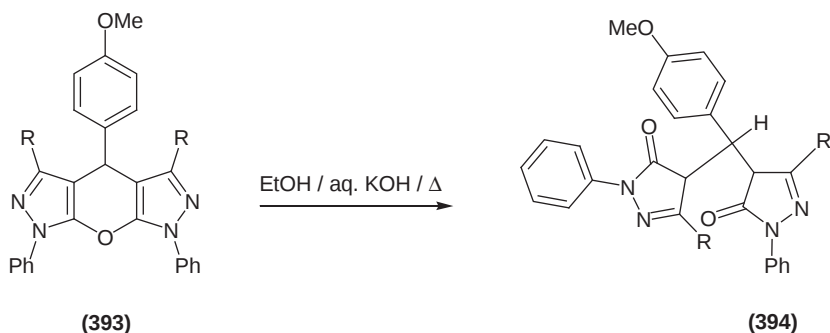
2.5.1 From pyranodipyrzoles

2.5.1.1 From 4-(4-methoxyphenyl)-3,5-disubstituted-1,7-diphenylpyrano[2,3-c;6,5-c']dipyrzole. Heating pyranodipyrzoles **393a,b** in aqueous potassium hydroxide gave bis-pyrazol-3-ones **394a,b** in 82% yield, respectively (04PS61) (Scheme 88).

2.6 Synthesis from tricyclic 5,6,7-membered fused rings

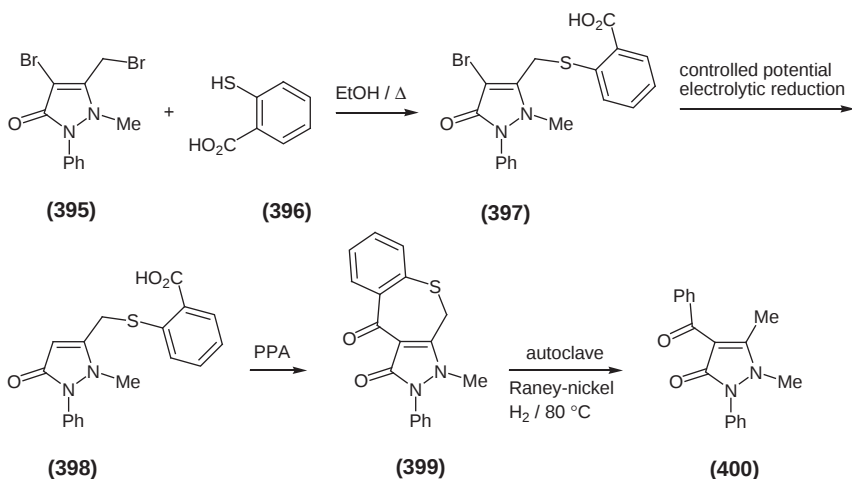
2.6.1 From diazabenzof[*f*]azulenes

2.6.1.1 From 9-thia-2,3-diazabenzof[*f*]azulene-1,4-dione. Ito and Ueda (70CPB1994) (Scheme 89) converted 4-bromo-5-bromomethylpyrazol-3-one **395** into 4-benzoyl-5-methylpyrazol-3-one **400** by a four-step sequence that involved nucleophilic substitution, dehalogenation, ring closure and ring opening. Thus, S_N2 substitution of the bromine in **395** by 2-mercaptobenzoic acid **396** gave 2-(4-bromo-5-oxopyrazol-3-ylmethylsulfanyl)benzoic acid **397** that was dehalogenated by controlled potential electrolytic reduction to derivative **398**. The latter was cyclized into 9-thia-2,3-diazabenzof[*f*]azulene-1,4-dione **399** by heating in PPA. Ring

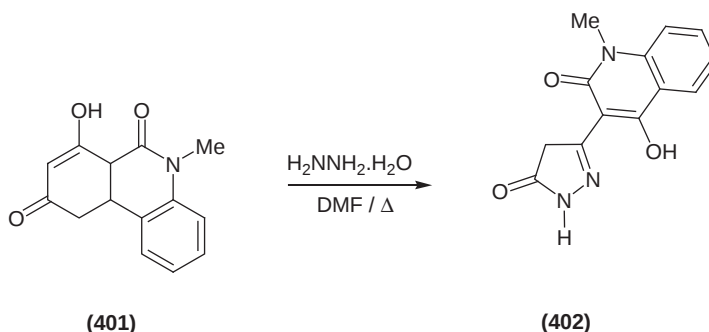


(a) R = Me, (b) R = Ph

Scheme 88



Scheme 89



Scheme 90

opening of the seven-membered ring of **399** and desulfuration by heating at 80 °C in an autoclave under hydrogen and with Raney-nickel catalyst led to pyrazol-3-one **400**.

2.7 Synthesis from tricyclic 6,6,6-membered fused rings

2.7.1 From phenanthridines

2.7.1.1 From 7-hydroxy-5-methyl-10,10a-dihydro-5H,6aH-phenanthridine-6,9-dione. Abass and Othman (01SC3361) heated phenanthridine-6,9-dione **401** with hydrazine hydrate in *N,N*-dimethylformamide to afford 3-(3-oxopyrazol-3-yl)quinolin-2-one **402**, in 92% yield (Scheme 90).

3. APPLICATIONS

Pyrazol-3-ones published after 1999 are very versatile compounds and are important as products and intermediates in analytical, dye, biological and pharmaceutical chemistry and as chemicals in photography.

3.1 Analytical uses

The use of pyrazol-3-ones as analytical reagents has been published in numerous articles and patents. For example, derivatives are useful for the extraction and separation of various metal ions (88JIC661), for the determination of phenol (87CJC2082), cyanides and ammonia (78ZN450), and as photographic sensitizers (71USP3615608).

Trofimov et al. summarized the uses of pyrazol-3-one dyes as analytical reagents (82MI1).

3.2 Agrochemical uses

Pyrazol-3-ones have been tested and found useful as fungicides (99MI1), herbicides (96JAP(K)217777) and insecticides (99MI2).

3.3 Dye chemistry uses

The applications of pyrazol-3-ones as dyes have been mentioned in a major work (84MI2). Pyrazol-3-ones proved to be good disperse dyes for cotton, wool, silk and polyester fabrics (07DP387), and as coloring agents for keratin fibers (06PCT12934).

3.4 Pharmaceutical uses

Pyrazol-3-ones exhibit a wide range of biological properties: analgesic, antibacterial and antifungal (04JIC(I)32, 04PS61, 05ARK98(xiii)), anti-inflammatory (06BMCL3713), CCR3 antagonists (07BMCL4228), anti-inflammatory and antimicrobial (05AP167), antimicrobial (05SC2169, 04APH143), antitumor (06PCT116713, 07APC591, 08PCT86014), antidiabetic (05USP272794), antihyperglycemic (96JMC3920) and anxiolytic (04BMC6559).

Pyrazol-3-ones were found to be inhibitors of CD80 useful in immunomodulation therapy (05PCT46679), to have potent activity in inhibiting protease-resistant prion protein accumulation (07JMC5053), cytokine synthesis inhibitors (05BMCL2285), orally bioavailable inhibitors of p38 kinase (98BMCL2689), inhibitors of UDP-*N*-acetylenolpyruvyl glucosamine reductase (06JMC6027), inhibitors of bacterial cell wall biosynthesis (05BMCL2527) and cholecystokinin antagonists (05AF251).

Pyrazol-3-ones have also been studied as multidrug resistance modulators (06BMC5061), cardiovascular agents (06PCT114213), protein kinase inhibitors for treating hepatocyte growth factor-related diseases (06PCT116713) and antagonists of CGRP receptors useful in the treatment or prevention of headache, migraine and cluster headache (06PCT78554).

3.5 Photographic uses

(5-Methyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)(phenyl)methanone thiosemicarbazone and (5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(phenyl)methanone thiosemicarbazone showed a photochromic phenomenon that was due to the photoisomerization from the enol to the keto form (00JPH23).

3.6 Miscellaneous uses

The oxidation potentials as well as the hydroxyl radical scavenging activities for some pyrazol-3-ones have been detected and compared with edavarone's. 5-Methyl-2-pyridin-2-yl-2,4-dihydro-3H-pyrazol-3-one was found to be more effective in a hydroxyl radical scavenging assay than edaravone, with an IC₅₀ value of 0.018 mM as compared to edavarone's IC₅₀ value of 0.25 mM (06BMCL5939).

The Schiff base 4-[(4-hydroxy-3-hydroxymethylbenzylidene)amino]-1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one retards the corrosion of steel (06CS797). Certain azopyrazol-3-ones may prove useful as labels for chromatographic analysis of carbohydrates (00CAR169).

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CHAPTER 3

Organometallic Complexes of Polypyridine Ligands V: Their Analogues, and N,O(S)-Chelating Pyridines

Alexander P. Sadimenko

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1. INTRODUCTION

This chapter concludes a series on the organometallic chemistry of polypyridine ligands (07AHC(93)185, 07AHC(94)109, 08AHC(95)221, 08AHC(97)45) and covers some illustrations mainly on organocopper and organogold compounds, complexes of the rare earth elements and organometallic chemistry of pyridylphosphinines and biphosphinines. Owing to the scarcity of these compounds, we also included organometallic derivatives of the N,O(S)-chelating pyridines. This opens the series on the pyridine chelates and reviews hydroxy- and mercaptopyridines, pyridyl alcohols and ketones, pyridine carboxylates, and some specific related classes of ligands. They offer a wide variety of coordination modes, but in line with the style of the whole series, after an overview of coordination situations, material will be grouped by metals, starting from nontransition metal derivatives, and then sequentially across the groups of transition metals. Further chapters will be devoted to the organometallic chemistry of amino-, phosphino-, azomethine, and azopyridines as well as mixed pyridine-containing heterocycles.

2. POLYPYRIDINES, PYRIDYLPHOSPHININES, AND BIPHOSPHININES

2.1 Late transition metal organometallic complexes

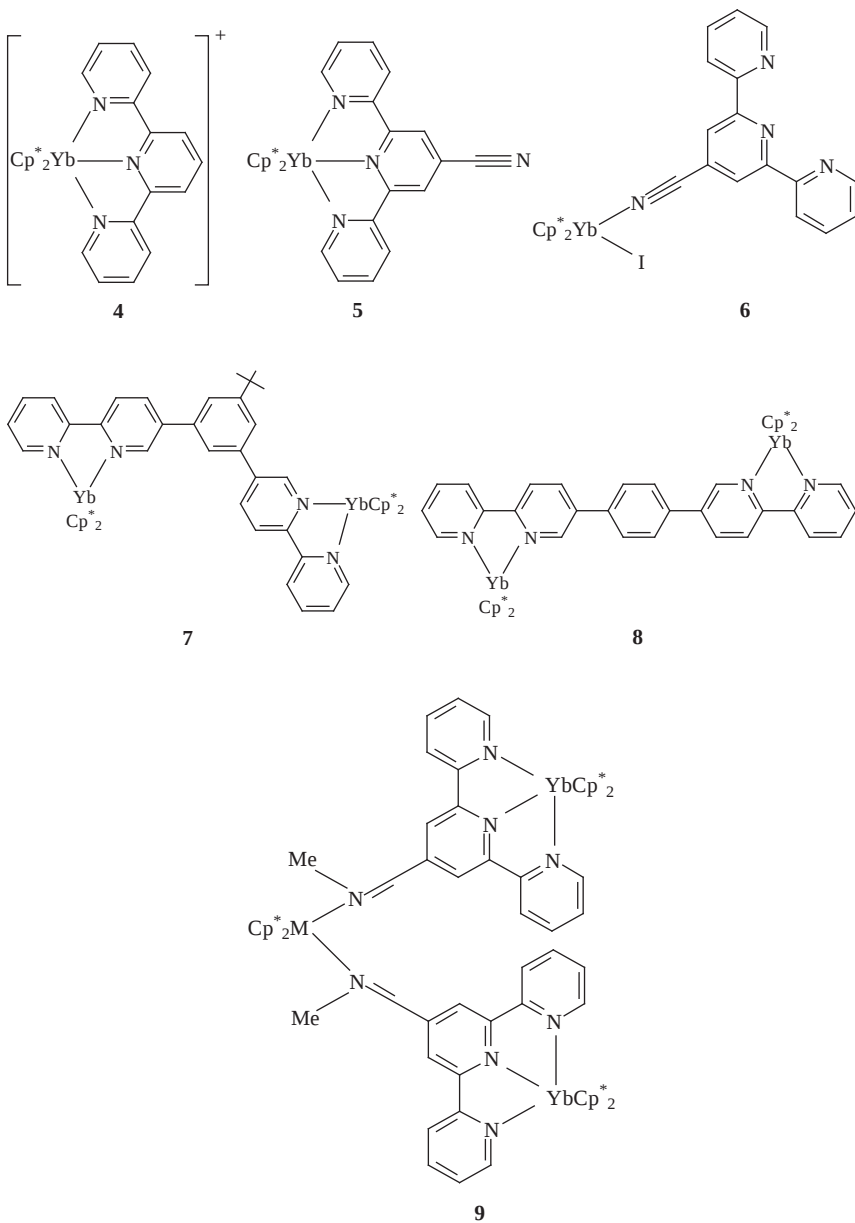
2,2'-Bipyridine and 1,5-cyclooctadiene react with $[\text{Cu}(\text{AN})_4](\text{PF}_6)$ in ethanol to yield $[(\eta^4\text{-cod})\text{Cu}(\text{bipy})](\text{PF}_6)$ (91IC2610). The structures of this complex, $[(\eta^2\text{-C}_2\text{H}_4)\text{Cu}(\text{bipy})](\text{ClO}_4)$, and $[(\eta^2\text{-C}_2\text{H}_4)\text{Cu}(\text{phen})](\text{ClO}_4)$ (87JOM121) have been determined from X-ray diffraction studies. Reduction of copper(II) perchlorate hexahydrate with copper wire in the presence of styrene and 2,2'-bipyridine in methanol gives the copper(I) $[\text{Cu}(\text{bipy})(\eta^2\text{-CH}_2=\text{CHPh})(\text{ClO}_4)]$ (88JCS(D)1907). The copper(I) solvate $[\text{Cu}(\text{OTf})_2 \cdot \text{PhMe}]$ with 2,2'-bipyridine and ethyl acrylate yields copper(I) $[\text{Cu}(\text{bipy})(\eta^2\text{-CH}_2=\text{CHCOOMe})(\text{OTf})]$ (06JOM3948). When the reaction starts with $[\text{Cu}(\text{AN})_4](\text{ClO}_4)$ or $[\text{Cu}(\text{AN})_4](\text{PF}_6)$, the corresponding perchlorate or hexafluorophosphate monocationic derivatives are prepared.

Dinuclear complexes with the bridging oxo-groups, $[(6\text{-R-bipy})\text{Au}(\mu\text{-O})_2\text{Au}(6\text{-R-bipy})](\text{PF}_6)_2$ ($\text{R} = \text{Me}$, *i*-Pr, neopentyl, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$) react with norbornene in acetonitrile–water to give the η^2 -alkene derivatives **1** and auraoxetanes **2** (05AGE6892, 05AGE6990). The reaction of 6-R-substituted-2,2'-bipyridines (HL) ($\text{R} = \text{CH}_2\text{Ph}$, CHMePh, CMe₂Ph, CH₂Me, *t*-Bu, or CH₂Bu-*t*) with HAuCl_4 or NaAuCl_4 leads to cyclometalated derivatives $[\text{Au}(\text{L})\text{Cl}](\text{X})$ ($\text{X} = \text{AuCl}_4$, BF_4 or PF_6) (96JCS(D)4217, 01JOM47). The cyclometalated species are the result of

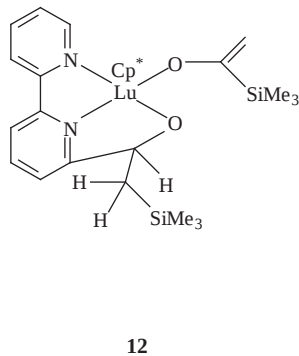
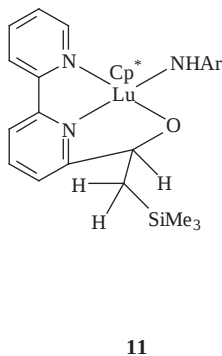
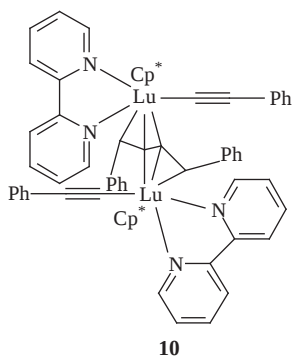
2,2'-Bipyridine with $[\text{CdFe}(\text{CO})_4]_4$ gives trimeric $[(\text{bipy})\text{CdFe}(\text{CO})_4]_3$ (77JA2098). In the same way monomeric $[(\text{NH}_3)(\text{bipy})\text{ZnFe}(\text{CO})_4]$, $[(\text{terpy})\text{CdFe}(\text{CO})_4]$, $[(\text{bipy})\text{ZnFe}(\text{CO})_4]$, and oligomeric $[(4,4'\text{-bipy})\text{CdFe}(\text{CO})_4]$ can be prepared (78IC1477, 80IC2375).

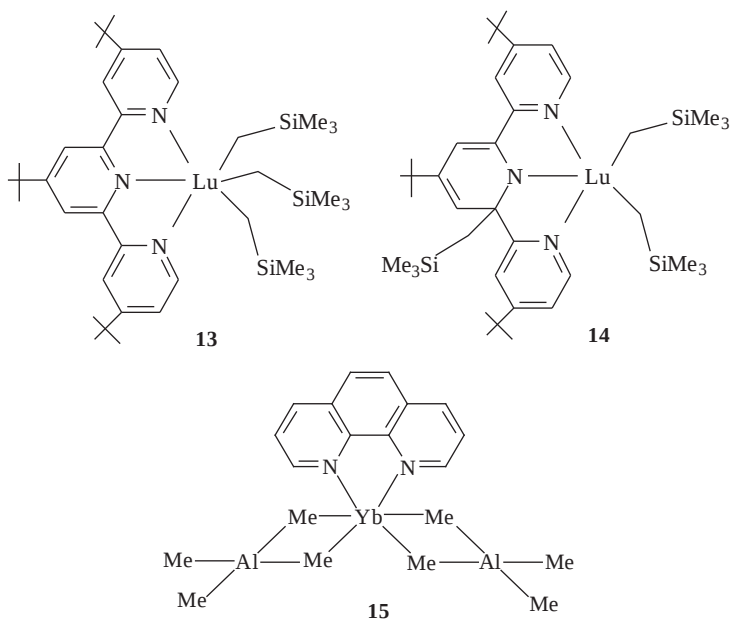
2.2 Complexes of polypyridines with the rare earth metals

2,2'-Bipyridine or 1,10-phenanthroline with $[(\eta^5\text{-Cp}^*)_2\text{Yb}(\text{OEt}_2)]$ give adducts $[(\eta^5\text{-Cp}^*)_2\text{Yb}(\text{LL})]$ (LL = bipy, phen), which contain a polypyridyl radical-anion (02OM460, 05PRL267202). A similar trend is observed for substituted 2,2'-bipyridine complexes (06NJC238). Species $[(\eta^5\text{-Cp}^*)_2\text{Yb}(\text{LL})]$ (LL = bipy, phen) possess interesting photochemical properties (03IC5551). $[(\eta^5\text{-Cp}^*)_2\text{Yb}(\text{OEt}_2)]$ and 4,4'-disubstituted 2,2'-bipyridines give $[(\eta^5\text{-Cp}^*)_2\text{Yb}(4,4'\text{-X}_2\text{bipy})]$ (X = COOMe, COOEt, Ph, H, Me, *t*-Bu, OMe) (06OM3228). Neutral complexes with silver iodide give cation-anions $[(\eta^5\text{-Cp}^*)_2\text{Yb}(4,4'\text{-X}_2\text{bipy})][(\eta^5\text{-Cp}^*)_2\text{YbI}_2]$. Similar adducts are formed with 4,4'-bipyridine (02OM4622). 2,2':6',2''-Terpyridine is known to be terdentately coordinated to the ytterbocene(III) unit, 4. Addition of 4'-cyano-2,2':6',2''-terpyridine (LL) to $[(\eta^5\text{-Cp}^*)_2\text{Yb}(\text{OEt}_2)]$ in toluene gives ytterbium(II) $[(\eta^5\text{-Cp}^*)_2\text{Yb}(\eta^3\text{-LL})]$, 5 (05IC5911). Ytterbium(III) complex 6, however, is coordinated *via* the nitrogen atom of the cyano-group. Similar trends are observed in the allyl complexes $[(\eta^3\text{-1,3-(SiMe}_3)_2\text{C}_3\text{H}_3)_2\text{Yb(terpy-CN)}]$, $[(\eta^3\text{-1-(SiMe}_3)_3\text{C}_3\text{H}_4)_2\text{Yb(terpy-CN)}]$, $[(\eta^3\text{-1-(SiPh}_3)_3\text{-3-(SiMe}_3)_3\text{C}_3\text{H}_3)_2\text{Yb(terpy-CN)}]$, and $[(\eta^3\text{-1,3-(SiMe}_3)_2\text{C}_3\text{H}_3)_2\text{Yb(terpy)}]$ (06IC7004). Samarium(III) analogue has the composition $[(\eta^5\text{-Cp}^*)_2\text{Sm}(\eta^3\text{-terpy})]$, and $[(\eta^5\text{-Cp}^*)_2\text{Sm}(\eta^3\text{-terpy})](\text{PF}_6)$ is the product of one-electron oxidation (08IC5841). 2:1 Metal-to-ligand adducts of the type $[(\eta^5\text{-Cp}^*)_2\text{Yb}(\text{LL})\text{Yb}(\eta^5\text{-Cp}^*)_2]$ (LL = tetra(2-pyridyl)pyrazine, 6',6''-bis(2-pyridyl)-2,2':4',4'':2'',2'''-quaterpyridine, 1,4-di(2,2':6',2''-terpyridyl)-benzene, 1-methyl-3,5-bis(2,2':6',2''-terpyridin-4'-yl)benzene) have interesting magnetic and electronic properties (06JA7230, 07IC5013). 1,3-(2,2'-Bipyridyl)-5-*t*-butylbenzene and 1,4-(2,2'-bipyridyl)benzene with $[(\eta^5\text{-Cp}^*)_2\text{Yb}(\text{OEt}_2)]$ form similar dinuclear complexes with a bridging ligand, 7 and 8 (07OM4234). 2,2':6',2''-Terpyridine and tetrapyridinylpyrazine react with $[(\eta^5\text{-Cp}^*)_2\text{Yb}(\text{OEt}_2)]$ to afford mixed-valent systems (03CC2336). Using a terpyridyl-functionalized ketimide linking group, heterotrimetallic 4f-5f complexes of uranium(IV) and thorium(IV) with ytterbium being in the mixed valence equilibria of II and III, can be prepared, 9 (M = U, Th) (06JA2198, 08CEJ422).



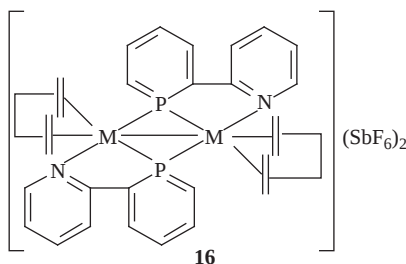
2,2'-Bipyridine with $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)_2\text{Nd}(\mu_2\text{-}\eta^2\text{-OTf})(\mu_3\text{-}\eta^3\text{-OTf})\text{Li}(\text{THF})_2]$ in ether gives $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)_2\text{Nd}(\text{bipy})(\text{OTf})]$ (06ICA2998). 2,2'-Bipyridine with $[(\eta^5\text{-Cp}^*)\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$ in toluene gives $[(\eta^5\text{-Cp}^*)\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(\text{bipy})]$ (04OM2995). The product reacts with 2,6-di-*i*-propylaniline (NH_2Ar) to yield first $[(\eta^5\text{-Cp}^*)\text{Lu}(\text{CH}_2\text{SiMe}_3)(\text{NHAr})(\text{bipy})]$ and then $[(\eta^5\text{-Cp}^*)\text{Lu}(\text{NHAr})_2(\text{bipy})]$. With phenylacetylene, dimer **10** follows. On dissolution in THF, it forms $[(\eta^5\text{-Cp}^*)\text{Lu}(\text{-CC}\equiv\text{CPh})_2(\text{THF})]$, which in pyridine turns into $[(\eta^5\text{-Cp}^*)\text{Lu}(\text{-CC}\equiv\text{CPh})_2(\text{py})]$. Carbon monoxide activates $[(\eta^5\text{-Cp}^*)\text{Lu}(\text{bipy})(\text{NHAr})(\text{CH}_2\text{SiMe}_3)]$ and $[(\eta^5\text{-Cp}^*)\text{Lu}(\text{bipy})(\text{CH}_2\text{SiMe}_3)_2]$ to yield **11** and **12**, respectively (04CC1398). Lutetium(III)-bis(alkyl) and -tris(alkyl) derivatives form η^3 -coordinated chelates with 2,2':6',2''-terpyridine or 4,4',4''-tri-*t*-butyl-2,2':6',2''-terpyridine, for example, **13** (06JA6322). The products undergo 1,3-alkyl migration, which results in dearomatization and *ortho*-functionalization of the terpyridyl ligand, for example, **14**. Complex **13** reacts with 2,4,6-triphenylaniline to yield the mono- and bis-amides $[\text{Lu}(\eta^3\text{-LL})(\text{CH}_2\text{SiMe}_3)(\text{NHC}_6\text{H}_2\text{Ph-2,4,6})]$ and $[\text{Lu}(\eta^3\text{-LL})(\text{NHC}_6\text{H}_2\text{Ph-2,4,6})_2]$ (08OM803). Species of type **14**, where one of the CH_2SiMe_3 moieties is replaced with the pentamethylcyclopentadienyl ligand, is also capable of substituting the CH_2SiMe_3 groups bound to the lutetium site by $\text{NHC}_6\text{H}_2\text{Ph-2,4,6}$. 2,2'-Bipyridine is reduced by $[(\eta^5\text{-Cp}^*)_2\text{Sm}(\text{THF})_2]$ to yield the samarium(III) complex $[(\eta^5\text{-Cp}^*)_2\text{Sm}(\text{LL})]$ (89JA3329). Reduction of 2,2'-bipyridine with $[(\text{C}_{10}\text{H}_8)\text{Yb}(\text{THF})_2]$ in THF is more profound and gives species with the bridging 2,2'-bipyridine dianion, $[\text{Yb}(\mu_2\text{-bipy})(\text{THF})_2]_3$ (99AGE2262). 1,10-Phenanthroline reacts with the polymer $[\text{Yb}(\text{AlMe}_4)_2]_n$ to afford the heterotrinnuclear complex **15** with bridging methyl groups (08JCS(D)1899).



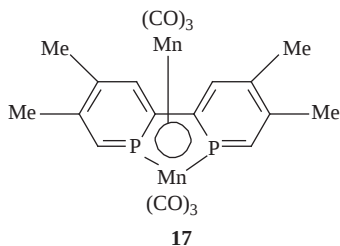


2.3 Complexes of pyridylphosphanines and biphosphanines

4,5-Dimethyl-2-(2-pyridyl)phosphinine reacts with $[\text{M}(\text{CO})_5(\text{THF})]$ ($\text{M} = \text{Cr}, \text{W}$) to yield at the first stage the pentacarbonyl P-coordinated complexes (84IC3463). Further, the thermal loss of carbon monoxide takes place and the N, P-coordinated complexes of composition $[\text{M}(\text{CO})_4(\text{LL})]$ result. $[\text{Mo}(\text{CO})_6]$ in this type of reaction straightforwardly affords the chelated product. 2-(2'-Pyridyl)-4,5-dimethylphosphinine reacts with the dimers $[(\eta^4\text{-nbd})\text{Rh}(\text{Cl})]_2$ and $[(\eta^4\text{-cod})\text{Ir}(\text{Cl})]_2$ in the presence of silver hexafluoroantimonate to yield the dinuclear species **16** ($\text{M} = \text{Rh}, \text{Ir}$) where the phosphorus atoms of each pyridylphosphinine ligand serve as bridges between the two metal atoms forming a bond between each other (92IC5117).

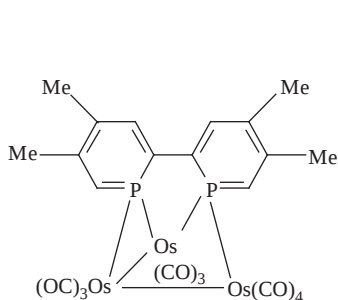


2,2'-Biphosphinines, phosphorus analogues of 2,2'-bipyridines reveal a more expressed π -back-bonding function (π -acceptor properties) and weaker σ -donor function in the complexation reactions to yield the $[M(CO)_4(LL)]$ ($M = Cr, Mo$) complexes ($LL = 4,4',5,5'$ -tetramethyl-2,2'-biphosphinine) (91JA667, 92AGE1343, 92OM2475, 98CCR771, 98JOC4826, 98SCI1587). It is noteworthy that 4,4',5,5'-tetramethyl-2,2'-biphosphinine completely displaces 4,4'-dimethyl-2,2'-bipyridine on reaction with the tetracarbonylchromium complex of the latter. They are more efficient than polypyridines in stabilizing the electron-excessive metal centers in their low oxidation states (95IC11). With $[Mn(CO)_5Br]$ in methylene chloride and $[Re(CO)_5Cl]$ in toluene the products are $[M(CO)_3X(LL)]$ ($M = Mn, X = Br$; $M = Re, X = Cl$) (96CB263). However, with $[Mn_2(CO)_{10}]$ a unique coordination situation is realized. In the product **17**, the aromatic metallacycle is formed and one of the $Mn(CO)_3$ groups is coordinated via the phosphorus heteroatoms, and another is coordinated in an η^5 fashion via the π -delocalized system of metallacycle (95IC5070).

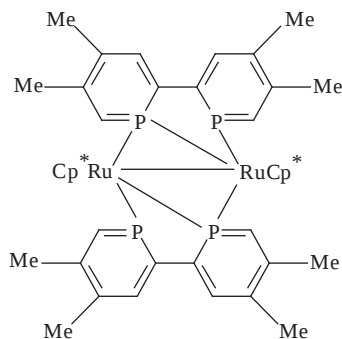


4,4',5,5'-Tetramethyl-2,2'-biphosphinine (LL) with $[(\eta^5-Cp^*)Ru(\eta^4-diene)Cl]$ in THF yields $[(\eta^5-Cp^*)Ru(\eta^2-LL)Cl]$ (96CB263). Further interaction with a series of ligands in the presence of ammonium hexafluorophosphate in methylene chloride gives $[(\eta^5-Cp^*)Ru(\eta^2-LL)L](PF_6)$ ($L = py, AN, (MeO)_3P, C_5H_2Me_2BrP, C_8H_{14}$). The lithium salt of 2,2'-biphosphinine dianion with $[(\eta^6-p-cymene)RuCl_2]_2$ gives $[(\eta^6-p-cymene)Ru(LL)]$ (99OM3348). 4,4',5,5'-Tetramethyl-2,2'-biphosphinine with $[Os_3(CO)_{10}(AN)_2]$ in THF gives cluster **18** (00EJI843). The ligand performs a rare double μ_2-P bridging function. The dianion of 4,4',5,5'-tetramethyl-2,2'-biphosphinine reacts with $[(\eta^5-Cp^*)Ru(\eta^4-C_6H_{10})Cl]$ to yield $[(\eta^5-Cp^*)Ru(LL)Cl]$ (96OM3267). The product can be reduced using sodium naphthalenide in DME to yield the dinuclear product **19** (00OM5247). One phosphorus atom of each heterocyclic ligand bridges two ruthenium sites, while the other is $\eta^1(P)$ -coordinated. In excess sodium naphthalenide, the product is $Na[(\eta^5-Cp^*)Ru(LL)]$. Further

interaction of the latter with electrophiles (methyl iodide, triphenyltin chloride, trimethyltin chloride) in DME gives the series $[(\eta^5\text{-Cp}^*)\text{-Ru}(\text{LL})\text{R}]$ ($\text{R} = \text{Me}, \text{Ph}_3\text{Sn}, \text{Me}_3\text{Sn}$). Quenching with acetic acid produces the Ru-H compound $[(\eta^5\text{-Cp}^*)\text{Ru}(\text{LL})\text{H}]$.

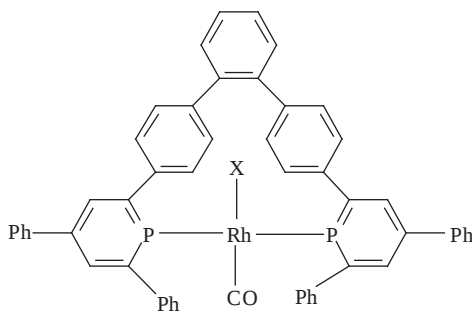


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2,2'-Biphosphinines tend to form homoleptic compounds in the reactions with organometallic precursors, for example Group 4 compounds (00AGE1823). The dianionic sodium salt 4,4',5,5'-tetramethyl-2,2'-biphosphinine with $[\text{M}(\text{acac})_3]$ ($\text{M} = \text{Co}, \text{Rh}$) yields anionic complexes $[\text{M}(\text{LL})_2]^-$, which with Ph_3SnCl form $[\text{M}(\text{LL})\text{SnPh}_3]$ (00OM2941). In a similar way, the lithium salt reacts with $[\text{FeCl}_2(\text{THF})_{1.5}]_n$ or $[(\eta^4\text{-cod})\text{Ru}(\text{acac})_2]$ in THF to yield the iron(-2) or ruthenium(-2) complexes $[\text{M}(\text{LL})_2(\text{Li}(\text{THF})_3)_2]$ (01AGE1251). With triphenyltin chloride in THF, $[\text{M}(\text{LL})_2(\text{SnPh}_3)_2]$ are formed. Terphenyl bis(phosphinine)ligand reacts with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ to yield **20** ($\text{X} = \text{Cl}$) (08OM834). With methyl iodide, **20** ($\text{X} = \text{I}$) results. 2,2'-Diborabiphenyl (04OM3085) may be an interesting ligand in the future.



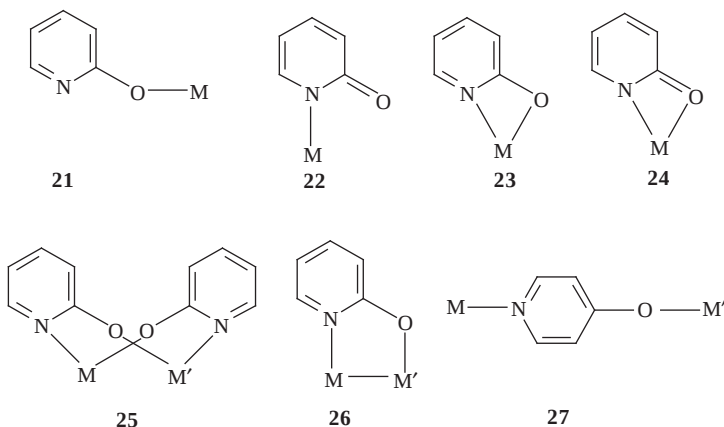
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3. N,O(S)-CHELATING PYRIDINES

3.1 Hydroxypyridines and –quinolines, pyridine alcohols and ketones

3.1.1 General remarks

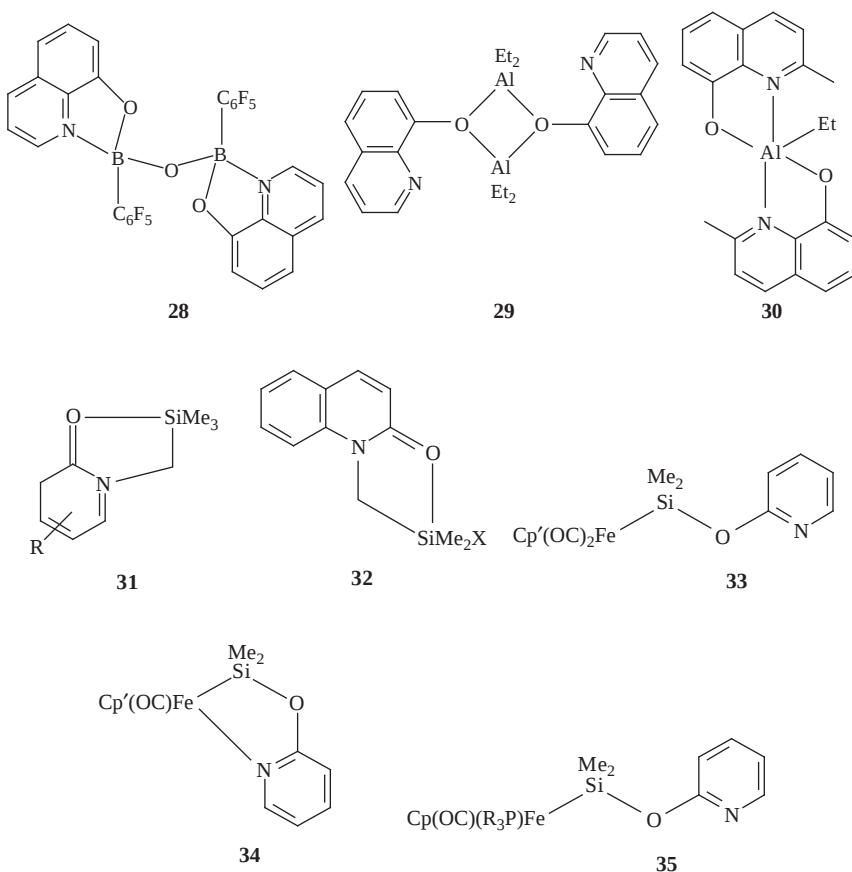
The monodentate function in 2-hydroxypyridines is commonly described by O-coordination in the pyridinol tautomeric form **21** or N-coordination in the pyridinone tautomer **22**. The N,O-chelation is observed in both pyridinol **23** and pyridinone **24**. Bridging function of 2-pyridones can be of two principal types **25** and **26** (95CCR313, 97ACR89). The bridging function **27** in 4-hydroxypyridine derivatives is quite common. A similar situation is observed in hydroxyquinoline analogues.



3.1.2 Nontransition metals

8-Hydroxyquinoline (HL) with $B(C_6F_5)_3$ forms the zwitterionic compound $[(C_6F_5)_3B(LH)]$ (07JCS(D)1425). Thermal reaction leads to $[(C_6F_5)_2B(\eta^2(O,N)-L)]$. 8-Hydroxyquinoline (HL) with $(C_6F_5)_2B(OC_6F_5)_2$ followed by hydrolysis generates diboron **28**. Tetrahedral 8-hydroxyquinolinato (L) complexes $[BPh_2(\eta^2(N,O)-L)]$, $[BPh_2(\eta^2(N,O)-5-(1-naphthyl)-L)]$, $[BPh_2(\eta^2(N,O)-5-(2-benzothienyl)-L)]$, $[B(2-benzothienyl)_2(\eta^2(N,O)-L)]$, and $[B(2-benzothienyl)_2(\eta^2(N,O)-2-Me-L)]$ are luminescent materials (05IC601). 8-Quinolinol (HL) with AlR_3 ($R = Alk$) gives $[AlL_3]$ and the dimer $[AlR_2L_2]$ (67IC1311). The ethyl derivative was proven to have structure **29** (02JOM(654)229, 04JOM2421, 06JOM5016). 2-Methyl-8-quinolinol with triethyl aluminum gives the mononuclear compound **30** containing two chelate units. 2-Pyridones with diethylaminotrimethylsilane give a series **31** ($R = 5-Cl, 6-Cl, H, 6-Me, 3-NO_2, 3-Ome$) (91CC1499, 91CC1501). 2-Quinolinone in this reaction gives the trimethyl derivative **32**

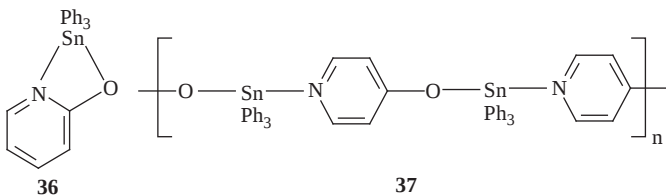
(X = Me) (03JOM(667)66), and with chloro(chloromethyl)dimethylsilane **32** (X = Cl), similarly (bromomethyl)(chloro)dimethylsilane **32** (X = Br). Complex **32** (X = Cl) with antimony trifluoride gives **32** (X = F) and with trimethylsilyl triflate **32** (X = OTf). Sodium 2-hydroxypyridinate reacts with $[(\eta^5\text{-Cp}')(\text{OC})_2\text{FeSiMe}_2\text{Cl}]$ ($\text{Cp}' = \text{Cp}$, $\text{C}_5\text{H}_4\text{Me}$) in acetonitrile to yield the $\eta^1(\text{O})$ -coordinated species **33** where the ligand is in its enol form (03JOM(669)189). The products under photolysis decarbonylate, rearrange, and form chelates **34**. Complex **34** ($\text{Cp}' = \text{Cp}$) with trimethyl- and triphenylphosphine is converted to the $\eta^1(\text{O})$ -species **35**.

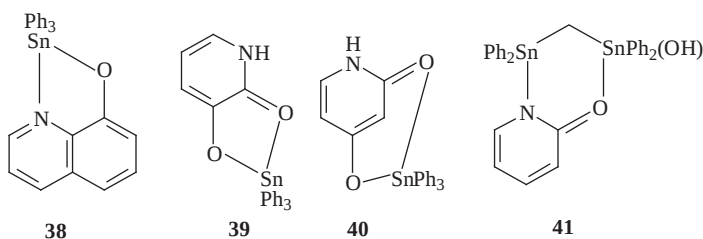


Tin 8-hydroxyquinolinato (L) complexes include $[\text{R}_2\text{SnL}_2]$, $[\text{R}_2\text{SnX(L)}]$, $[\text{RSn(X)L}_2]$, $[\text{RSn(L)}_3]$, and $[\text{R}_3\text{Sn(L)}]$ (R = Alk, Ar; X = halogen or isothiocyanate) (69JCS(A)2273), $[(p\text{-ClC}_6\text{H}_4)\text{SnL}_3]$ (99JOM(584)103), $[\text{R}_2\text{SnX(L)}]$, $[\text{RSnClL}_2]$ (R = Me, Et, *n*-Pr, *n*-Bu, Ph; X = Cl, NCS) (66JOM249, 67BCJ2693, 67IC2012, 73JINC306, 95JOM(493)13), $[\text{Sn}(p\text{-ClC}_6\text{H}_4)(p\text{-Tol})(\text{L})]$ (89AX(C)861), $[\text{Ph}_3\text{SnL}]$ (71JCS(A)1940, 72JOM121).

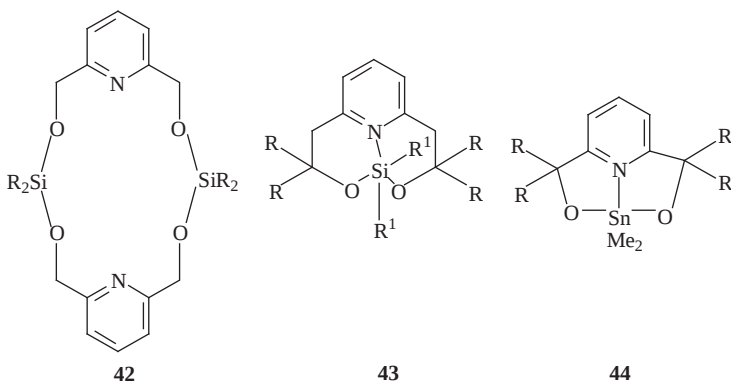
The ligand in these complexes performs the $\eta^2(\text{N,O})$ -chelating function. The complex of 8-quinolinolate (L), $[\text{Sn}(\text{Me})((\text{Me}_3\text{Si})_3\text{C})(\eta^2(\text{N,O})\text{-L})_2]$ in ethanol forms $[\text{Sn}(\text{Me})((\text{Me}_3\text{Si})_2\text{CH})(\eta^2(\text{N,O})\text{-L})_2]$ (81JCS(D)1101). Complexes of alkyl-substituted 8-quinolinolates (L), $[\text{Me}_2\text{M}(\eta^2(\text{N,O})\text{-L})_2]$ ($\text{M} = \text{Sn}, \text{Pb}$) are stable (74JOM(81)363). 8-Hydroxyquinoline (HL) and $[\text{PbCl}_2\text{Me}(\text{C}(\text{SiMe}_3)_3)]$ in an ethanolic medium yield first $[\text{Pb}(\text{Me})(\text{CH}(\text{SiMe}_3)_2)(\eta^2(\text{N,O})\text{-L})_2]$ and further $[\text{Pb}(\text{Me})(\text{CH}_2\text{SiMe}_3)(\eta^2(\text{N,O})\text{-L})_2]$ and $[\text{PbMe}_2(\eta^2(\text{N,O})\text{-L})_2]$ (82JCS(D)2191). In $[\text{Ph}_2\text{Sn}(\eta^2(\text{N,O})\text{-L})_2]$, the 8-quinolinol ligand L is classically chelated (05AX(E)27). Tri(*t*-butyl)tin(IV) and triphenyltin(IV) 8-quinolinolates also form chelates (85JOM323). Six-coordinate 8-quinolinolate complexes prepared from *n*-Bu₂SnCl₂ and *t*-Bu₂SnCl₂ and having composition $[\text{R}_2\text{Sn}(\eta^2(\text{N,O})\text{-L})_2]$ follow the same structural pattern (05JOM2243). In bis(2-carbomethoxyethyl)chloro(quinoline-8-olato)tin(IV), the carbonyl oxygen of one of the 2-carbomethoxyethyl groups, the nitrogen and oxygen atoms of the chelating quinoline-8-olato ligand form the coordination unit (89JOM(364)343). Sodium salts of 5-[(E)-2-(aryl)-1-diazenyl]quinoline-8-ol (NaL; aryl = 4-MeOC₆H₄, 4-ClC₆H₄, 4-MeC₆H₄, 4-BrC₆H₄) react with $[(\text{PhCH}_2)_2\text{SnCl}_2]$ to yield $[(\text{PhCH}_2)_2\text{Sn}(\eta^2(\text{N,O})\text{-L})_2]$ where only the N,O-atoms of the 8-quinolinol moiety comprise the coordination unit (06JOM2605). A similar coordination is observed for the diphenyltin complexes of this group of ligands (06JOM3416). 5-[(E)-2-(aryl)-1-diazenyl]quinoline-8-ol ligands (HL, aryl = Ph, 2-Tol, 3-Tol, 4-Tol, 4-MeOC₆H₄, 4-EtOC₆H₄) with Ph₃SnCl in the presence of sodium methoxide yield $[\text{Ph}_3\text{Sn}(\eta^2(\text{N,O})\text{-L})]$, where chelation occurs only *via* the 8-hydroxyquinolinolate unit (08JOM1751).

2-, 3-, and 4-Hydroxy-, 2,3-dihydroxypyridine, 2,4-quinolinediol, and 8-hydroxyquinoline (HL) react with Ph₃SnOH in methanol to yield polymeric complexes of general composition $[(\text{Ph}_3\text{Sn})_n\text{L}]$ with exceptions (06JOM1622). For the chelate based on 2-hydroxypyridine, the structure with $\eta^2(\text{N,O})$ -coordination **36** is realized. For 4-hydroxypyridine, the classical polymeric structure **37** with the bridging function of the ligand is observed. 8-Hydroxyquinoline forms the mononuclear chelate **38**. 2,3-Dihydroxypyridine and 2,4-quinolinediol form the monomeric chelates **39** and **40**, respectively, where one oxygen atom is of the phenolic type and another of the ketonic type. 2-Hydroxypyridine with Ph₂ClSnCH₂SnClPh₂ gives the dinuclear complex **41** in which the N,O-bridging ligand is in its thione form (06JOM1637).





2,6-Pyridinedimethanol with dimethyldichlorosilane forms dimer **42** ($R = \text{Me}, \text{Ph}$) (96IC4342, 98OM2656, 99JOM(581)70). Other pyridine alcohols with chlorosilanes give monomeric compounds **43** ($R = \text{Ad}, R^1 = \text{Me}, \text{Ph}; R = R^1 = \text{Ph}$) (94JOM(464)127). Compounds **36** ($R = p\text{-BrC}_6\text{H}_4, p\text{-t-BuC}_6\text{H}_4; R^1 = \text{Me}$) can be prepared from the corresponding pyridinediol and $\text{Me}_2\text{Si}(\text{NMe}_2)_2$ in toluene (01JOM54). 1,3-(2',6'-Pyridinebis(methyleneoxy))-1,3-bis(diphenyl)cyclodisiloxane and 2,6-pyridinebis(1,1-diphenylethoxy)diphenylsilane can be prepared from 2,6-pyridinediols and dichlorodiphenylsilane, dichloromethylphenylsilane and bis(dimethylamino)dimethylsilane (99JOM(590)237, 02JOM(648)280). Diols 2,6- $R_2(\text{OH})\text{CC}_5\text{H}_3\text{N}$ ($R = \text{Me}, \text{Ph}, p\text{-t-BuC}_6\text{H}_4$) react with Me_2SnCl_2 to yield chelates **44** (03JOM(672)115). Bis(alkoxy)tin(IV) derivatives of pyridine-2,6-dimethanol ($R = n\text{-Bu}, \text{Ph}$) are monomeric (86JOM(315)277, 92H549).

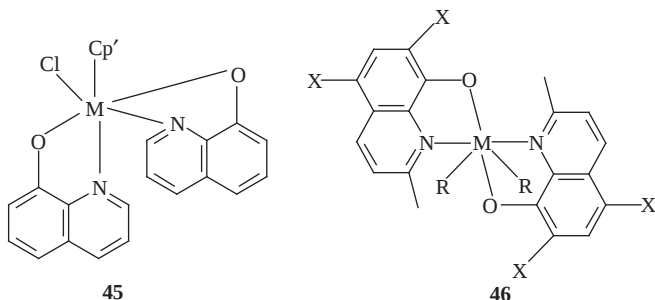


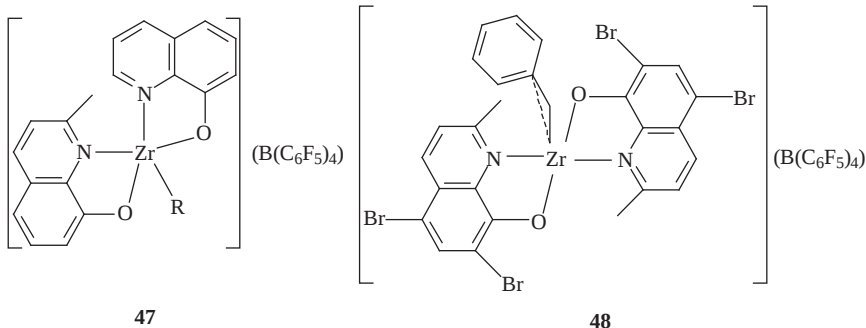
Pyridoxine, 3-hydroxy-4,5-bis(hydroxymethyl)-2-methylpyridine (L), with dimethyltin(IV) cation in ethanol–water containing NO_3^- and Cl^- , NO_3^- and MeCOO^- , or Cl^- and MeCOO^- ions gives $[\text{SnMe}_2(\text{LH})]\cdot\text{NO}_3\cdot 2\text{H}_2\text{O}$, $[\text{SnMe}_2(\text{H}_2\text{O})(\text{LH})]\text{Cl}\cdot\text{H}_2\text{O}$, and $[\text{SnMe}_2(\text{H}_2\text{O})(\text{LH}_2)]\cdot 0.5\text{H}_2\text{O}$ (97JCS(D)4421). In each dimeric unit the tin atom is coordinated to two methyl groups, the phenolic O atom, the O atoms of two deprotonated CH_2OH groups, and the O atom of a non-deprotonated CH_2OH group. Pyridoxine (L) with the diethyltin(IV) cation in ethanol–water containing NO_3^- and Cl^- , NO_3^- and MeCOO^- , or Cl^- and MeCOO^- ions gives $[\text{SnEt}_2(\text{LH})]\text{Cl}$, $[\text{SnEt}_2(\text{LH})](\text{NO}_3)\cdot 2\text{H}_2\text{O}$, and $[\text{SnEt}_2(\text{LH}_2)]$ (00POL813).

The structure consists of dimeric $[\text{SnEt}_2(\text{LH})]_2^{2+}$ units in which two bridging-chelating hydrogen pyridoxinate anions link tin atoms with coordination number five. Dimethyl-, diethyl-, di-*n*-butyl-, and diphenyltin(IV) complexes of N-methylpyridoxine (L), $[\text{SnMe}_2(\text{LH})]\text{I}$, $[\text{SnEt}_2(\text{LH})]\text{I}$, $[\text{Sn}(n\text{-Bu})_2(\text{LH})]\text{I}$, and $[\text{SnPh}_2(\text{LH})]\text{I} \cdot \text{H}_2\text{O}$ have a similar structure (03EJ12790). Pyridoxine (L) also reacts with dimethyl-, diethyl-, and di-*n*-butyl tin(IV) oxide in toluene-ethanol to yield $[\text{SnR}_2(\text{LH}_2)]$ (R = Me, Et, *n*-Bu), where the structure is based on a dimeric unit $[\text{SnR}_2(\text{LH}_2)]_2$ and two pyridoxinate units bridge two tin atoms via oxygen donor sites (04JOM620). 2-(Hydroxymethyl)-3-hydroxy-6-methylpyridine (H_2L) reacts with dimethyl-, diethyl-, and di-*n*-butyltin oxides to yield chelates $[\text{SnR}_2(\text{H}_2\text{O})(\eta^2(\text{O}, \text{O})\text{-L})]$ (07JOM3547).

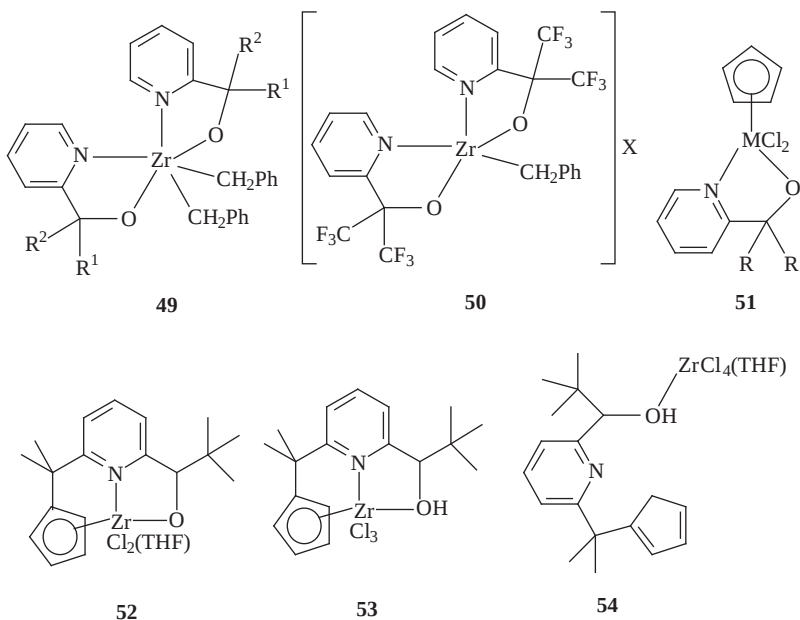
3.1.3 Early transition metals

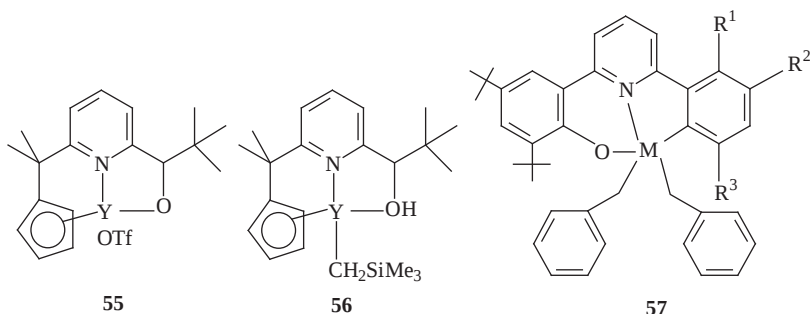
Reaction of $[(\eta^5\text{-Cp})\text{Ti}(\text{OEt})(\text{LH})_2]$ (LH = 8-hydroxyoxyquinoline) with acetyl chloride gives $[(\eta^5\text{-Cp})\text{Ti}(\text{Cl})(\text{LH})_2]$ (63IZV751). Similar compounds are described (69JCS358). $[(\eta^5\text{-Cp})_2\text{MX}_2]$ (M = Ti, Zr, Hf; X = Cl, Br) with 8-hydroxyquinoline gives $[(\eta^5\text{-Cp})\text{MX}(\text{LH})_2]$ (71JCS(A)2487), in particular $[(\eta^5\text{-Cp})\text{Ti}(\text{Cl})(\text{LH})_2]$ (70JCS(A)2545). 8-hydroxyquinoline with $[(\eta^5\text{-Cp})\text{TiCl}_3]$ gives $[(\eta^5\text{-Cp})\text{Ti}(\text{Cl})(\text{LH})_2]$ (95ZAAC1761). 5-Chloro-8-hydroxyquinoline with $[(\eta^5\text{-Cp})\text{TiCl}_3]$ in acetonitrile gives $[(\eta^5\text{-Cp})\text{Ti}(\text{Cl})(\text{L})]$. Other complexes $[(\eta^5\text{-Cp}')\text{M}(\text{Cl})(\text{L})]$ were prepared from 8-hydroxyquinoline or 5-chloro-8-hydroxyquinoline in methylene chloride and $[(\eta^5\text{-Cp}')\text{MCl}_3]$ (M = Zr, Hf; Cp' = Cp, $\text{C}_5\text{H}_4\text{Me}$, $\text{C}_5\text{H}_4\text{SiMe}_3$). The representative scheme is illustrated as 45. By alkane elimination and halide displacement, complexes 46 (M = Zr, R = CH_2Ph , $\text{CH}_2\text{Bu-}t$, CH_2SiMe_3 , X = H, Br; M = Hf, R = CH_2Ph , X = H, Br) can be prepared (97OM3282). Complexes 46 (M = Zr, R = CH_2Ph , $\text{CH}_2\text{Bu-}t$; X = H) with $(\text{HNMe}_2\text{Ph})(\text{B}(\text{C}_6\text{F}_5)_4)$ give cations 47 (R = CH_2Ph , CH_2CMe_3), while the similar reaction of derivative 46 (M = Zr, R = CH_2Ph , X = Br) gives an isomeric form 48. Other complexes of this group are $[\text{W}(\text{CO})_2(\eta^2(\text{N}, \text{O})\text{-L})(\text{PPh}_3)\text{Cl}]$, $[\text{W}(\text{CO})_2(\eta^2(\text{N}, \text{O})\text{-L})(\text{PPh}_3)_2\text{Cl}]$, and $[\text{W}(\text{CO})_3(\eta^2(\text{N}, \text{O})\text{-L})_2(\text{PPh}_3)] \cdot \text{CH}_2\text{Cl}_2$ (79IC48, 80IC2113). 8-Hydroxyquinoline (HL) with $[\text{Re}(\text{CO})_5\text{Cl}]$ in toluene forms the chelate $[\text{Re}(\text{CO})_4(\eta^2(\text{N}, \text{O})\text{-L})]$ (98ICC398). The product with pyridine gives $[\text{Re}(\text{CO})_3(\text{L})(\text{py})]$ (01JCS(D)2756).



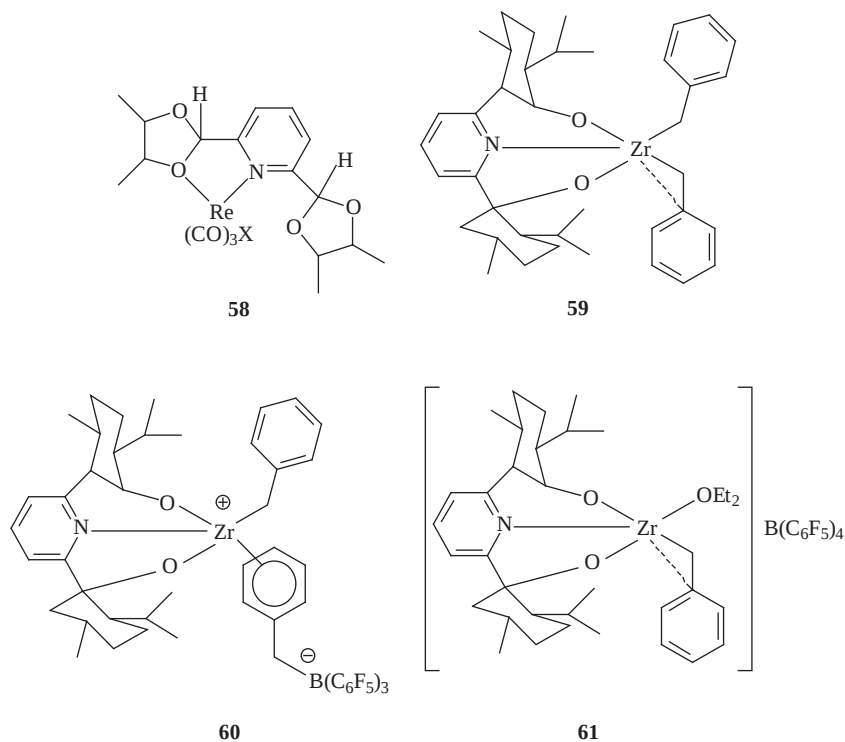


Pyridine alcohols $C_5H_4NC(OH)R^1R^2$ ($R^1 = R^2 = CF_3$, Me; $R^1 = H$, $R^2 = CF_3$) react with $[Zr(CH_2Ph)_4]$ in toluene to yield **49** (97OM3303). The product **49** ($R^1 = R^2 = CF_3$) reacts with $B(C_6F_5)_3$ in benzene to yield the cationic **50** ($X = B(C_6F_5)_3(CH_2Ph)$). Similarly, with $(HNMe_2Ph)(B(C_6F_5)_4)$, species **50** ($X = B(C_6F_5)_4$) results. Lithium salts of di-2-pyridyl alcohols $Li(NC_5H_4(CR_2O)-2)$ ($R = i\text{-Pr}$, Ph) react with $[(\eta^5\text{-Cp})MCl_3]$ ($M = Ti$, Zr) to yield $\eta^2(N,O)$ -pyridylalkoxide chelates **51** (98OM3408). Dilithium 2-(1'-hydroxy-2,2'-diethylpropyl)-6-(1'',1'-dimethylcyclopentadienylmethyl)-pyridine reacts with zirconium(IV) chloride in THF to yield a mixture of products **52–54** (03JOM(687)161). With $[Y(OTf)_3]$, the product is **55**, which when reacted with $LiCH_2SiMe_3$, transforms into **56**. 2-(2'-Phenol)-6-arylpyridine ligands with $[M(CH_2Ph)_4]$ ($M = Ti$, Zr, Hf) in pentane-ether produce chelate complexes **57** ($R^1 = R^2 = Br$, $R^3 = H$; $R^1 = R^3 = Cl$, Me, $R^2 = H$) (07JOM4750).

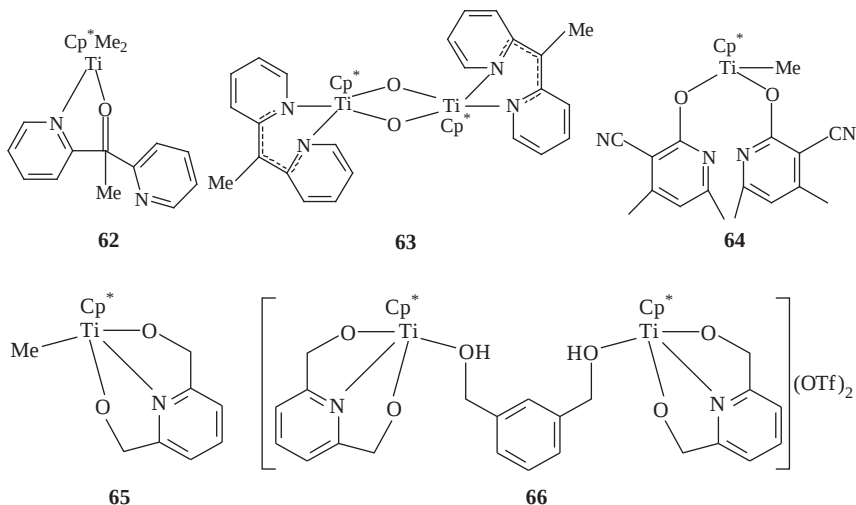


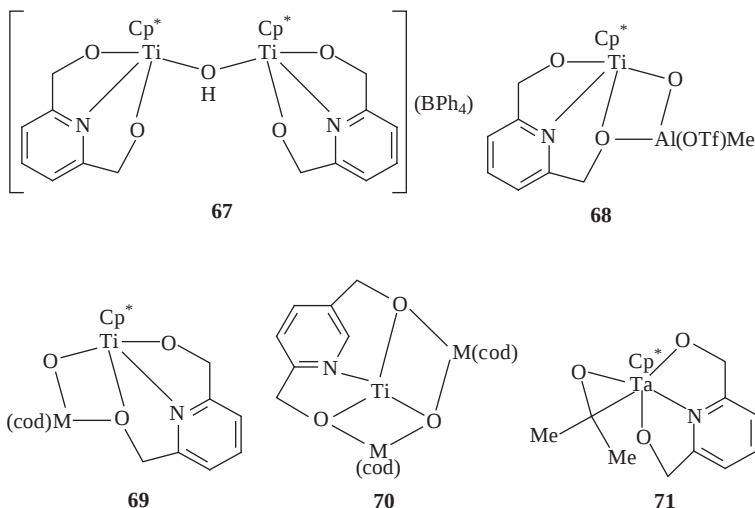


2,6-Bis[(4R,5R)-dimethyl-1,3-dioxan-2-yl]pyridine reacts with $[\text{Re}(\text{CO})_5\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in benzene to yield **58** characterized by solution stereodynamics (99JCS(D)4495). In a similar way, the $\text{Re}(\text{CO})_3\text{X}$ complexes of 2-[(4R,6R)-4,6-dimethyl-1,3-dioxan-2-yl]pyridine and 2,6-bis[(4R,6R)-4,6-dimethyl-1,3-dioxan-2-yl]pyridine were prepared (00JCS(D)1769). 2,6-Bis[1S,2S,5R)-(-)-menthoxy]pyridine with $[\text{Zr}(\text{CH}_2\text{Ph})_4]$ gives chelate **59** where one of the benzyl ligands coordinates in an η^2 fashion (00OM2944). The product interacts with $\text{B}(\text{C}_6\text{F}_5)_3$ to give zwitterionic species **60** where the benzylborate is coordinated in an η^0 -mode. Complex **60** with $(\text{CPh}_3)^+(\text{B}(\text{C}_6\text{F}_5)_4)^-$ and diethyl ether gives **61**.

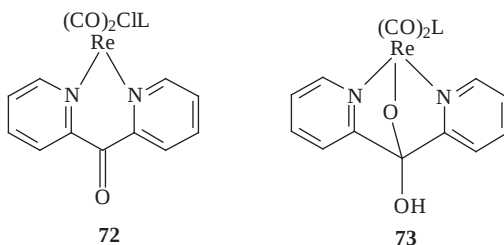


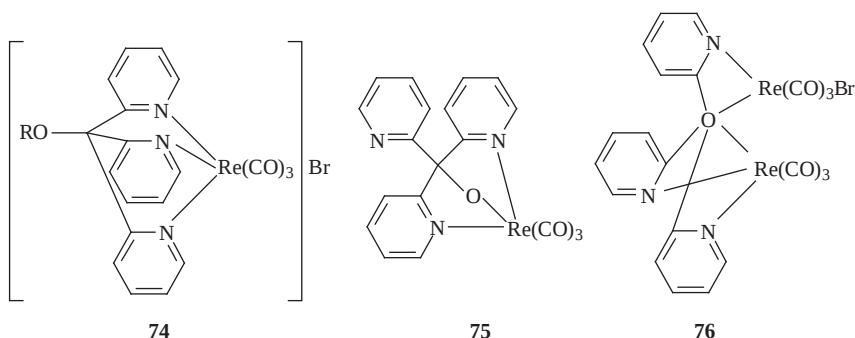
Di-2-pyridyl ketone reacts with $[(\eta^5\text{-Cp}^*)\text{TiMe}_3]$ in THF to yield the product of insertion into the titanium–methyl bond, **62** (00JCS(D)2990), which reacts with 2,6-dimethylphenylisocyanide in toluene to yield the bis(2-pyridyl)carbyl **63** (02JCS(D)11). In contrast, 3-cyano-2-hydroxy-4,6-dimethylpyridine with $[(\eta^5\text{-Cp}^*)\text{TiMe}_3]$ in toluene gives the $\eta^1(\text{O})$ -coordinated **64** (03EJI493). A pathway based on insertion of the isocyanide yielding the η^2 -iminoacyl mononuclear complex was proposed. An identical complex is formed from $[(\eta^5\text{-Cp}^*)\text{TaMe}_4]$ and has composition $[(\eta^5\text{-Cp}^*)\text{TaMe}_3(\eta^2(\text{O},\text{N})\text{-OCMePy}_2)]$. 3-Cyano-2-hydroxy-4,6-dimethylpyridine with $[(\eta^5\text{-Cp}^*)\text{TaMe}_4]$ in the presence of triethylamine in toluene results in a similar product. 2,6-Pyridinedimethanol with $[(\eta^5\text{-Cp}^*)\text{TiMe}_3]$ gives **65** (03CEJ671). The product with triflic acid in the presence of a base ($\text{L}^1 = \text{H}_2\text{O}$, py, 4-*t*-Bupy) yields cationic complex $[(\eta^5\text{-Cp}^*)\text{Ti}(\eta^3(\text{O},\text{N},\text{N})\text{-L})(\text{L}^1)](\text{OTf})$ (07OM2896). When 2,6-pyridinedimethanol is used as a base, the dicationic dinuclear species **66** follows, where the dimethanol ligand serves as the O,O-bridge. 2-Pyridinemethanol (L^1) forms the monocationic complex $[(\eta^5\text{-Cp}^*)\text{Ti}(\eta^3(\text{O},\text{N},\text{N})\text{-L})(\eta^1(\text{O})\text{-L}^1)](\text{OTf})$ with O-coordination of the entering base. $[(\eta^5\text{-Cp}^*)\text{Ti}(\eta^3(\text{O},\text{N},\text{N})\text{-L})(\text{H}_2\text{O})](\text{OTf})$ with sodium tetraphenylborate gives μ -hydroxo-dinuclear complex **67**. With triethylaluminum the product is heterodinuclear **68**. Complex **69** reacts with $[(\eta^4\text{-cod})\text{M}(\mu\text{-OH})_2]$ ($\text{M} = \text{Rh}, \text{Ir}$) to yield heterobimetallic **70** ($\text{M} = \text{Rh}, \text{Ir}$), where the protonolysis of the Ti–Me bond occurs (03CEJ671). The latter react with $[(\eta^4\text{-cod})\text{M}(\text{THF})_2](\text{OTf})$ ($\text{M} = \text{Rh}, \text{Ir}$) to yield cations **70** ($\text{M} = \text{Rh}, \text{Ir}$) (04JOM2641). Tantalum dialkoxide complexes of 2,6-pyridinedimethoxide include $[(\eta^5\text{-Cp}^*)\text{TaCl}_2(\eta^3(\text{O},\text{O},\text{N})\text{-(OCH}_2)_2\text{py})]$ and $[(\eta^5\text{-Cp}^*)\text{TaMe}_2(\eta^3(\text{O},\text{O},\text{N})\text{-(OCH}_2)_2\text{py})]$ (04OM5030). The latter with carbon monoxide renders unusual product **71**, and with 2,6-dimethylphenyl- and *t*-butylisocyanide it yields azatantalacyclopropanes $[(\eta^5\text{-Cp}^*)\text{Ta}(\eta^2\text{-Me}_2\text{CNR})(\eta^3(\text{O},\text{O},\text{N})\text{-(OCH}_2)_2\text{py})]$ ($\text{R} = 2,5\text{-Me}_2\text{C}_6\text{H}_3$, *t*-Bu).





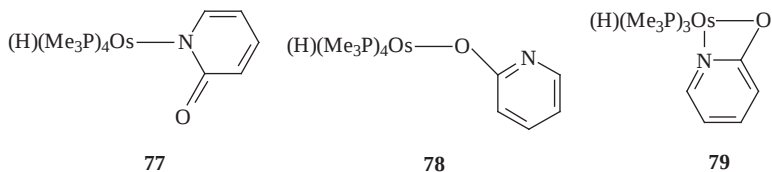
$[\text{Re}(\text{CO})_3(\eta^2\text{-LL})\text{Cl}]$ (LL = di-2-pyridylketone) electrochemically reacts with carbon dioxide to yield $[\text{Re}\{(\text{C}_5\text{H}_4\text{N})_2\text{C}(\text{O})^-\bullet\}(\text{CO})_3]$ and the product of binding of CO_2 , $[\text{Re}\{(\text{C}_5\text{H}_4\text{N})_2\text{C}(\text{O})^-\bullet\}(\text{CO})_3(\text{CO}_2)]$ (97JEAC621). The starting complex follows from dipyridylketone and $[\text{Re}(\text{CO})_5\text{Cl}]$ in refluxing toluene. $[\text{Re}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}]$ gives $[\text{Re}(\text{CO})_2(\text{PPh}_3)(\eta^2(\text{N},\text{N})\text{-LL})\text{Cl}]$ (97JCS(D)3571). Both $\eta^2(\text{N},\text{N})$ -complexes, **72** (L = CO, PPh_3) in water-alcoholic mixture give $\eta^3(\text{N},\text{N},\text{O})$ -species **73** (L = CO, PPh_3). Identical transformations occur with $[\text{Mn}(\text{CO})_5\text{Br}]$ in dry ether and ether containing several drops of water, respectively (03JMS75). Tris(2-pyridyl)methanol with $[\text{Re}(\text{CO})_5\text{Br}]$ gives three products, one with N,N,N-coordination, **74** (R = H), another with N,N,O-mode, **75**, and the third is dinuclear species **76** where the ligand plays the N,N,N,O-bridging function (08JCS(D)3605). Tris(2-pyridyl)methoxymethane gives only **74** (R = Me).

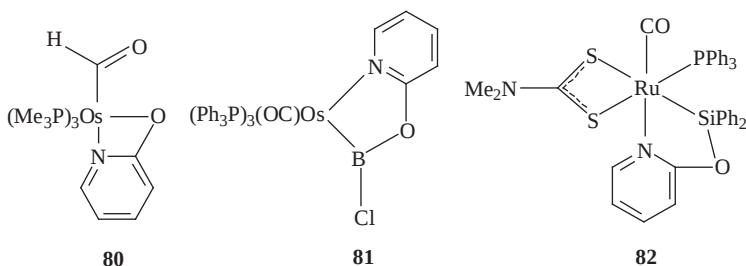




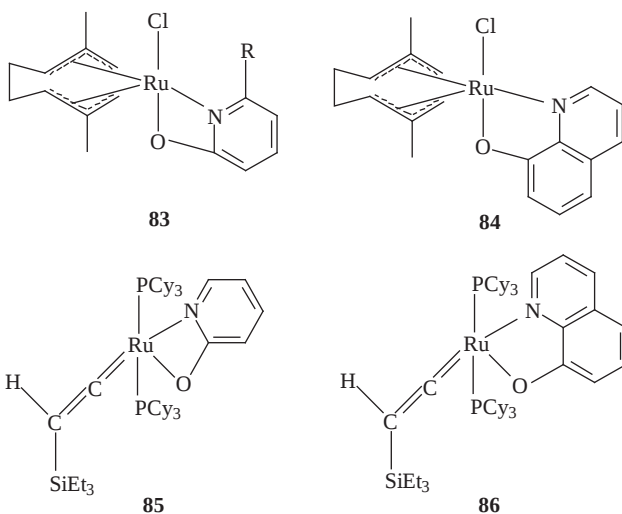
3.1.4 Iron group

2-Hydroxy- and 2-mercaptopyridine react with $[\text{Os}(\text{PMe}_3)_2(\text{H})(\eta^2\text{-CH}_2\text{PMe}_2)]$ to yield $[\text{Os}(\text{PMe}_3)_4(\text{H})(\text{NC}_5\text{H}_4\text{X})]$ ($\text{X} = \text{O}, \text{S}$); the pyridone complex was studied more carefully (00OM2310). Among the expected tautomers, **77** and **78**, the one with N-coordination, **77**, predominates in solution and exists in the solid state. Sublimation of the product yields the chelate **79**. With carbon dioxide the chelated product forms **80**. 2-Hydroxypyridine with $[\text{Os}(\text{BCl}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ forms six-coordinate **81** ($\text{X} = \text{Cl}$) by the route of nucleophilic substitution of the B–Cl bond, which with anhydrous hydrogen iodide gives **81** ($\text{X} = \text{I}$), with ethanol **81** ($\text{X} = \text{OEt}$), *n*-butylamine **81** ($\text{X} = \text{NHNBu-}n$), $\text{Et}_3\text{N} \cdot 3\text{HF}$ **81** ($\text{X} = \text{F}$) (02OM1714). Complex $[\text{Ru}(\text{SiClPh}_2)(\eta^2\text{-S}_2\text{CNMe}_2)(\text{CO})(\text{PPh}_3)_2]$ enters nucleophilic substitution at the Si–Cl bond with 2-hydroxypyridine to afford **82** (04JOM2979). 8-Hydroxyquinoline (HL) with $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$ gives the homoleptic chelate $[\text{Ru}(\eta^2(\text{N},\text{O})\text{-L})_3]$ (05POL3012). 8-Hydroxyquinoline (HL) with $[\text{Ru}(\text{H})\text{Cl}(\text{CO})(\text{PPh}_3)_3]$ in DME gives chelate $[\text{Ru}(\text{Cl})(\text{CO})(\text{PPh}_3)(\eta^2(\text{N},\text{O})\text{-L})]$ (07POL4201). 8-Hydroxy-2-methylquinoline-7-carboxylic acid (HL) also forms the $\eta^2(\text{N},\text{O})$ -coordinated complex $[\text{Ru}(\text{H})(\text{CO})(\text{PPh}_3)(\eta^2(\text{N},\text{O})\text{-L})]$, where the coordination is *via* the hydroxylic oxygen, and the carboxylic oxygen remains intact (07POL5120).

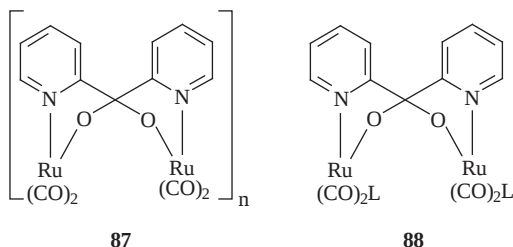




6-Methyl- or 6-chloro-2-hydroxypyridine with $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{Cl})(\text{OOCCH}_3)_3]$ give $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{Cl})(\eta^2(\text{N},\text{O})\text{-6-R-C}_5\text{H}_3\text{NO-2})]$ (88JOM105). The parent 2-hydroxypyridine, in contrast, initially gives the O-coordinated $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2(\text{C}_5\text{H}_4\text{NHO-2})]$, which transforms into the chelate only after a long reflux. The reaction of sodium 2-hydroxypyridinate (NaL) with $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$ in THF yields $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{Cl}(\eta^2(\text{N},\text{O})\text{-L})]$ (88POL1311) and with the silver salt AgL gives $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\eta^2\text{-L})(\eta^1\text{-L})]$. Bis(allyl)chloro-bridged dimer $[(\eta^3, \eta^3\text{-C}_{10}\text{H}_6)\text{Ru}(\text{Cl})(\mu\text{-Cl})_2]$ with 2-hydroxypyridines in CH_2Cl_2 gives **83** ($\text{R} = \text{H}, \text{Cl}, \text{Me}$) (92JCS(D)2765). With 8-hydroxyquinoline, the product is **84**. Mononuclear complexes of similar composition are also formed from quinoline-2-thiol and 6-methylpyridine-2-thiol or their sodium salts. $[\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2]$ reacts with 2-hydroxypyridine and quinoline to yield $[\text{Ru}(\text{H})(\text{H}_2)(\text{L})(\text{PCy}_3)_2]$, which on further interaction with $\text{CH}_2=\text{CH}(\text{SiEt}_3)$ gives organometallic derivatives **85** and **86** (96OM3471). $\eta^2(\text{N},\text{O})$ -Coordinated complexes of 6-chloro- and 6-bromo-2-hydroxypyridine (HL) $[\text{Ru}_2\text{L}_4\text{Cl}]$ react with $\text{Me}_3\text{SnC}\equiv\text{CPh}$ to yield the organometallic derivatives $[\text{Ru}_2\text{L}_4(\text{C}\equiv\text{CPh})]$ (00JOM(595)300).

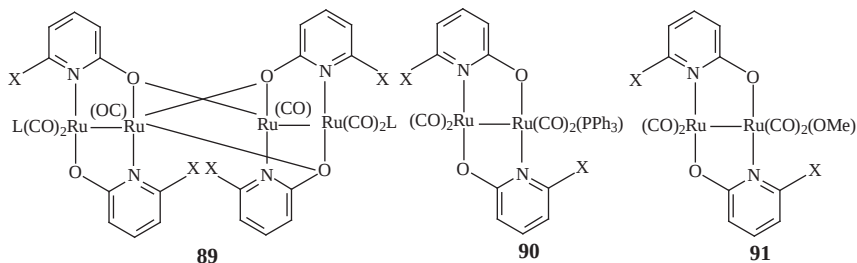


2-Pyridone under reflux in toluene with $[\text{Ru}_3(\text{CO})_{12}]$ forms polymer **87** with the dinuclear unit (90JCS(D)2201, 91JOM305), which reacts with a variety of ligands to give dinuclear neutral complexes **88** ($\text{L} = \text{CO}$, AN, PPh_3 , $\text{P}(\text{OPh})_3$, HOpy N-coordinated). Complex **88** ($\text{L} = \text{PPh}_3$) also follows from 2-pyridone and $[\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3]$ (89JOM(372)C15). An alternative synthesis is based on sodium pyridonate and $[\text{Ru}_2(\mu\text{-OOCR})\text{-}(\text{CO})_4](\text{PPh}_3)_2]$ (89JOM(361)353). In contrast, 2-pyridone with $[\text{Os}_3(\text{CO})_{12}]$ gives $[\text{Os}_3(\mu\text{-H})(\mu\text{-Opy})(\text{CO})_{10}]$ at elevated temperatures in toluene, $[\text{Os}_3(\mu\text{-H})(\mu_3\text{-Opy})(\text{CO})_9]$ in refluxing toluene, or $[\text{Os}_2(\mu\text{-Opy})_2(\text{CO})_6]$ at elevated temperatures in nonane (82JCS(D)1205, 83IC3637, 85IC258, 86IC763, 89JOM(366)377). 2-Pyridone with $[\text{Os}_3(\text{CO})_{10}(\text{COE})_2]$ gives $[\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\mu\text{-Opy})]$ (82JCS(D)1205). 6-Halogeno-2-hydroxypyridines (F, Cl, Br) react with $[\text{Ru}_3(\text{CO})_{12}]$ to yield $[\text{Ru}_2(\mu\text{-XpyO})_2(\text{CO})_4]_2$ for $\text{X} = \text{Cl}$ and Br, and $[\text{Ru}_2(\mu\text{-FpyO})_2(\text{CO})_6]_2$ (08ICA109). The dimeric units can be readily cleaved by Lewis bases. Thus, chloro- and bromo-complexes react with triphenylphosphine in methylene chloride to yield dinuclear compounds $[\text{Ru}_2(\mu\text{-XpyO})_2(\text{CO})_4(\text{PPh}_3)_2]$ ($\text{X} = \text{Cl}$, Br). Benzonitrile leads to $[\text{Ru}_2(\mu\text{-ClpyO})_2(\text{CO})_4(\text{PhCN})_2]$.

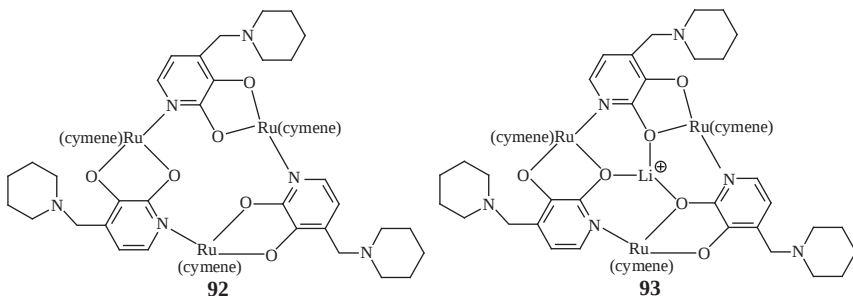


2-Hydroxy-6-methylpyridine (L) in toluene with $[\text{Ru}_3(\text{CO})_{12}]$ forms tetranuclear complex $[\text{Ru}(\eta^2, \mu\text{-L})(\text{CO})_2(\mu_3\text{-L})\text{Ru}(\text{CO})_2]_2$ (05ICA3152). Reaction of 2-hydroxy-4,6-diphenylpyridine with $[\text{Ru}_3(\text{CO})_{12}]$ in methanol proceeds differently and includes orthometalation at the phenyl ring, furnishing the dinuclear $[\text{Ru}(\eta^2(\text{N,C})\text{-L})(\text{CO})_2(\mu\text{-OMe})_2\text{Ru}(\text{CO})_2(\eta^2(\text{N,C})\text{-L})]$, where $\text{L} = (2\text{-}(6\text{-hydroxy-4-phenylpyridin-2-yl})\text{phenyl})$. 2-Hydroxy-6-X-pyridine ($\text{X} = \text{F}$, Cl, Br) in toluene gives tetranuclear **89** (06ICA970). In the case of $\text{X} = \text{Cl}$, Br, cluster **89** reacts with triphenylphosphine in methylene chloride to yield the cleavage product of partial ligand substitution **90**. 2-Hydroxy-6-chloro- and 6-bromopyridine react with $[\text{Ru}_3(\text{CO})_{12}]$ in methanol differently, yielding dinuclear **91**. Dinuclear 2-pyridonate $[\text{Ru}_2(\text{CO})_4(\mu\text{-2-pyridonate})_2]_n$ as well as $[\text{Ru}_2(\text{CO})_4(\mu\text{-6-chloro- or 6-bromopyridonate})_2]_2$, $[\text{Ru}_2(\text{CO})_4(\mu\text{-6-chloro- or 6-bromopyridonate})_2\text{L}]$ ($\text{L} = \text{MeOH}$, PPh_3) and $[\text{Ru}_2(\text{CO})_4(\text{AN})_2(\mu\text{-6-chloro- or 6-bromopyridonate})_2]$ catalyze efficiently cyclopropanation of alkenes with methyl diazoacetate (05JOM5562) and intramolecular carbenoid

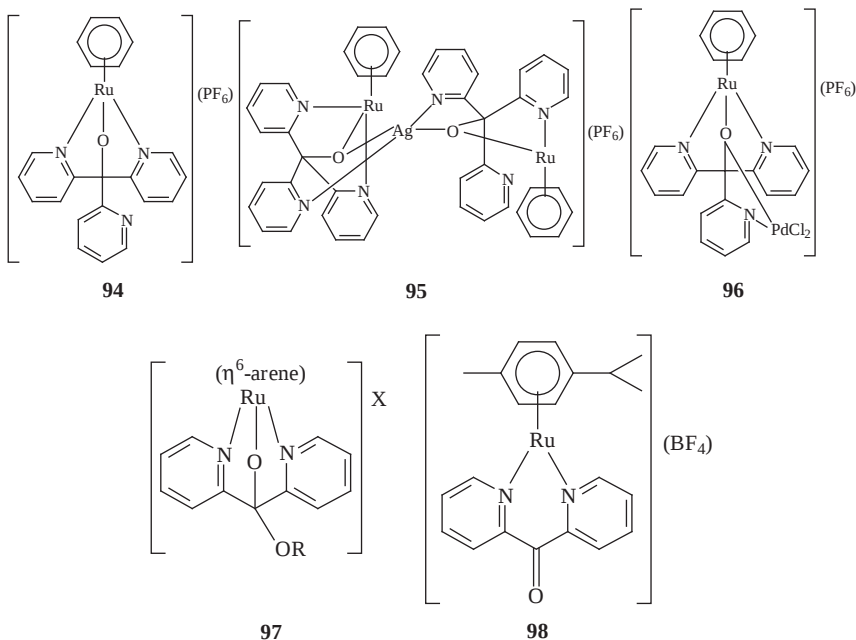
C-H insertion of diazoacetamides (06ASC(348)2203).



The hydroxypyridone ligand with $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$ forms the trinuclear macrocycle **92**, which further forms the crown-type compound **93** with lithium cation (02AGE1419, 03CCR3, 03JA13638). Lithium cation is remarkably selective in the presence of Na^+ , K^+ , Cs^+ , Ca^{2+} , and Mg^{2+} cations (02PNA4997). Another agent is Na_2SiF_6 (02CC2766). 2-Hydroxynicotinic acid and 2-aminonicotinic acid form dinuclear complexes with $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$ and $[(\eta^5\text{-Cp}^*)\text{RhCl}_2]_2$, whereas 2,3-dihydroxyquinoline gives rise to the trimeric assembly (04IC1609). The same type of assembly is realized in the 12-metallacrown-3 complex $[(\eta^6\text{-cymene})\text{Ru}(\text{C}_5\text{H}_2\text{ClNO}_2)]_3$ with the chloro-substituent in position 5 of the pyridonate ligand (03IC3576). Complexes of molecular lithium fluoride and $\text{LiF}\cdot\text{HF}$ are based on the metallamacrocycles $[(\eta^6\text{-cymene})\text{Ru}(\text{C}_5\text{H}_3\text{NO}_2)]_3$, $[(\eta^5\text{-Cp}^*)\text{Rh}(\text{C}_5\text{H}_3\text{NO}_2)]_3$, and $[(\eta^5\text{-Cp}^*)\text{Ir}(\text{C}_5\text{H}_3\text{NO}_2)]_3$ (02IC5466). 3-Hydroxy-2-pyridone with $[(\eta^6\text{-arene})\text{RuCl}_2]_2$ (arene = C_6H_6 , cymene, C_6Me_6) or $[(\eta^5\text{-Cp}^*)\text{RhCl}_2]_2$ in the presence of cesium carbonate gives trinuclear macrocycles (01CEJ3196, 01JA2699). In some cases, the existence of mononuclear intermediates $[(\eta^6\text{-arene})\text{Ru}(\text{Cl})(\text{C}_5\text{H}_4\text{NO}_2)]$ (arene = cymene, C_6Me_6) has been proven. Similarly, a trimer follows from 3-acetamido-2-pyridone and $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$. The macrocycles have affinities for Na^+ and/or Li^+ cations. Thus $(\eta^6\text{-C}_6\text{H}_6)\text{Ru}$ - and $(\eta^6\text{-cymene})\text{Ru}$ -complexes bind both Li^+ and Na^+ , while the $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}$ - and $(\eta^5\text{-Cp}^*)\text{Rh}$ complexes bind exclusively Li^+ . A very much enhanced scope of hydroxypyridone ligands and ruthenium, rhodium, and iridium precursors was also considered (04JA16959).



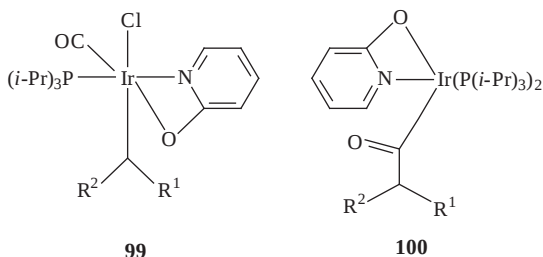
Tris(2-pyridyl)methanol (HL) reacts with $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$ in ethanol in the presence of ammonium hexafluorophosphate to yield cationic $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\eta^3(\text{N},\text{N},\text{O})\text{-L})](\text{PF}_6)$, **94** (99POL2981). This complex serves as a ligand with respect to silver hexafluorophosphate to yield heterotrinnuclear species **95**. With $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$, the product is heterodinuclear **96**. 2,2'-Dipyridylketone reacts with $[(\eta^6\text{-arene})\text{Ru}(\text{Cl})(\mu\text{-Cl})_2]$ in the presence of sodium tetraphenylborate or ammonium hexafluorophosphate in a protic solvent ROH to yield the N,O,N chelates **97** ($\text{R} = \text{H}$, arene = *p*-cymene; $\text{R} = \text{Me}$, arene = *p*-cymene, C_6Me_6 ; $\text{R} = \text{CH}_2\text{OH}$, Et, *i*-Bu, arene = *p*-cymene; $\text{X} = \text{BPh}_4$, PF_6) (07OM6099). The same reaction in the presence of silver tetrafluoroborate in methylene chloride gives the N,O-chelate **98**, which under ROH gives a series of **97** ($\text{R} = \text{H}$, Me, CH_2OH , Et, *i*-Bu; $\text{X} = \text{BF}_4$).



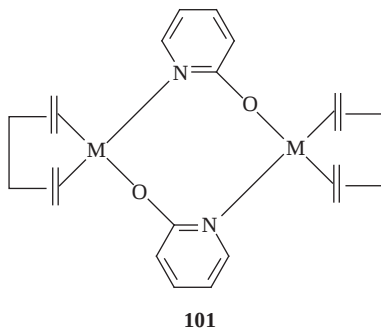
3.1.5 Cobalt group

2-Pyridylformate on interaction with rhodium(I) complexes decarbonylates and releases the CO ligand (80TL3853). Among the products of 2-pyridylesters $\text{C}_5\text{H}_4\text{NOC}(\text{O})\text{CH}(\text{R}^1)(\text{R}^2)$ ($\text{R}^1 = \text{R}^2 = \text{Ph}$; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = 4\text{-MeOC}_6\text{H}_4$; $\text{R}^1 = 4\text{-MeOC}_6\text{H}_4$, $\text{R}^2 = \text{Ph}$; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$) with $[\text{Ir}(\text{Cl})(\text{P}(i\text{-Pr})_3)]$ are also decarbonylation products **99** and **100** (95OM5463). 8-Hydroxyquinoline (HL) reacts with $[\text{Rh}(\text{acac})(\text{CO})_2]$ in benzene to yield $[\text{Rh}(\eta^2(\text{N},\text{O})\text{-L})(\text{CO})_2]$ (07JOM5788). Addition to the product of trimethylnitroxide in acetonitrile gives $[\text{Rh}(\eta^2(\text{N},\text{O})\text{-L})(\text{CO})(\text{AN})]$ and $[\text{Rh}(\eta^2(\text{N},\text{O})\text{-L})(\text{CO})(\text{Me}_3\text{N})]$. Bubbling

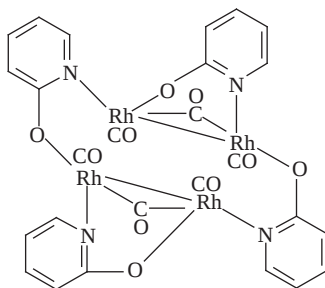
ammonia through the mixture of products leads to $[\text{Rh}(\eta^2(\text{N},\text{O})\text{-L})(\text{CO})(\text{NH}_3)]$. Ammonia may be replaced with trimethylamine, tri-*n*-butylamine, pyridine, tri-*n*-butylphosphine, triphenylphosphine, triphenoxyphosphine, and cyclooctene. 2-Pyridinemethanol, 2-pyridine-*n*-propanol, and 8-hydroxyquinoline (HL) react with $[(\eta^4\text{-cod})\text{Ir}(\text{Cl})_2]$ in the presence of sodium hydride in THF to yield $[(\eta^4\text{-cod})\text{Ir}(\eta^2(\text{N},\text{O})\text{-L})]$, the active catalysts of dehydrogenation of cyclooctane (08JOM1808).



The hydroxypyridinate complexes $[(\eta^4\text{-cod})\text{M}(\mu\text{-L})_2]$ ($\text{M} = \text{Rh}, \text{Ir}$; $\text{L} = 2\text{-hydroxypyridinate}, 6\text{-methyl-2-hydroxypyridinate}$; $\text{M} = \text{Ir}$, $\text{L} = 6\text{-chlorohydroxypyridinate}, 2\text{-hydroxyquinolate}$) contain the N,O-bridging heterocyclic ligand and have structural pattern **101** (85IC3507, 88IC3347). Sodium 6-methyl-2-hydroxypyridinate reacts with $[(\eta^4\text{-cod})\text{Ir}(\mu\text{-Cl})_2]$ in THF to yield $[(\eta^4\text{-cod})\text{Ir}(\mu\text{-6-Me-2-Opy})_2]$ (88IC3338). Similarly, with sodium 6-chloro-2-hydroxypyridinate and sodium-2-hydroxyquinolate (NaL) with $[(\eta^4\text{-cod})\text{Ir}(\mu\text{-Cl})_2]$ they give the mononuclear $[(\eta^4\text{-cod})\text{Ir}(\text{L})]$, known earlier (81JOM(205)259). Sodium 2-hydroxypyridinate or sodium 6-methyl-2-hydroxypyridinate (NaL) with $[(\eta^4\text{-cod})\text{Rh}(\text{AN})_2](\text{BF}_4)$ gives $[(\eta^4\text{-cod})\text{Rh}(\mu\text{-L})_2]$, while sodium 8-hydroxyquinolate gives the previously known (68JOM159) $[(\eta^4\text{-cod})\text{Rh}(\text{L})]$ (88IC3338). $[\text{Rh}(\text{CO})_2(\eta^2(\text{N},\text{O})\text{-L})]$ (L is quinoline-8-olate) (67ZKN1709) enters ligand substitution reactions with $\text{P}(\text{OPh})_3$ to yield first $[\text{Rh}(\text{CO})(\text{P}(\text{OPh})_3)(\eta^2(\text{N},\text{O})\text{-L})]$ and then $[\text{Rh}(\text{P}(\text{OPh})_3)_2(\eta^2(\text{N},\text{O})\text{-L})]$ (00JOM(602)59). $[(\eta^4\text{-cod})\text{Ir}(\mu\text{-Opy})_2]$ under carbon monoxide in toluene gives the dinuclear $[\text{Ir}(\text{CO})_2(\mu\text{-Opy})_2]$ (01AGE4084, 05IC6536). Oxidation by molecular iodine gives the mixed-valence tetrametallic cluster $[\text{Ir}_4(\text{CO})_4(\mu\text{-Opy})_2\text{I}]_2$.

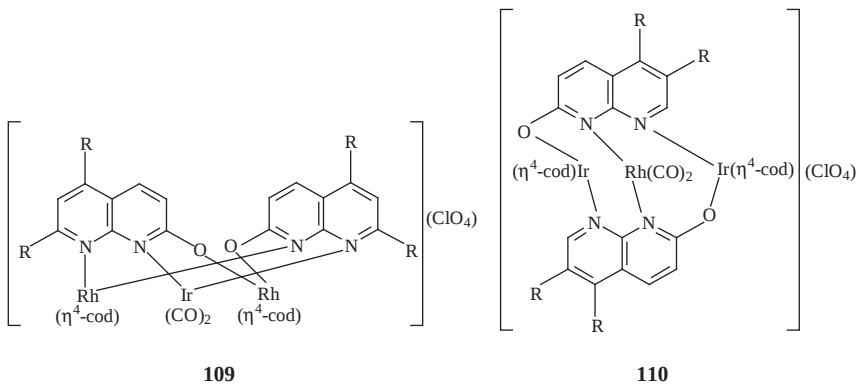
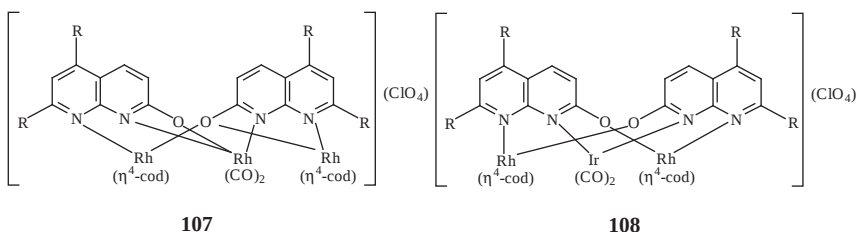
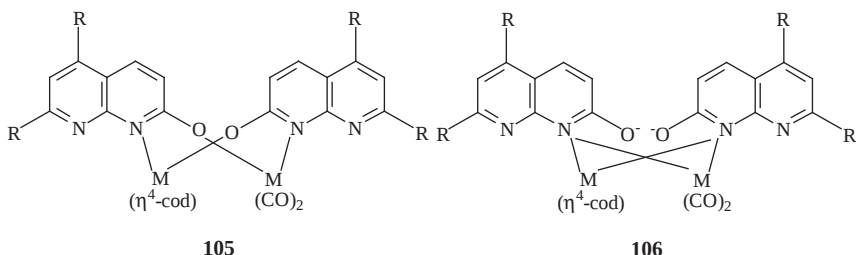
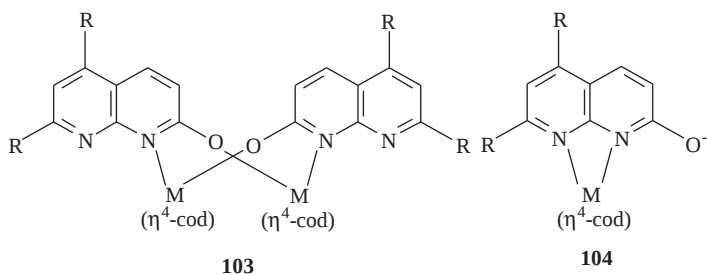


Rhodium carbonyl complexes of 2-hydroxypyridine catalyze the conversion CO and H₂ to HO(CH₂)₂OH (80MI1). 2-Hydroxypyridine in the presence of potassium hydroxide in methanol reacts with the dimer [Rh(μ -Cl)(CO)₂]₂ to yield tetranuclear species **102** (87JCS(D)981). The same reaction but performed in methanol/methylene chloride under carbon monoxide affords binuclear complex [Rh₂(μ -Opy)₂(CO)₄]. A related complex is [Rh₂(1,8-naphthyridine-2-one)(CO)₄] (84ICAL9). [Rh₂(μ -Opy)₂(CO)₄] reacts with bis(diphenylphosphino)methane and perchloric acid in methylene chloride to give [Rh₂(μ -Opy)(μ -dppm)₂(CO)₂](ClO₄). Alternatively, this product follows from potassium 2-pyridonate and [Rh₂(μ -dppm)(CO)₂(Me₂CO)₂](ClO₄)₂ (85JCS(D)1487). The ligand substitution reaction of [Ir₂(μ -OOCMe)₂Cl₂(CO)₂] with 1-hydroxyisoquinoline (HL) gives [Ir₂(μ -L)₂(CO)₂Cl₂], which can form adducts of composition [Ir₂(μ -L)₂(CO)₂Cl₂(L¹)₂] (L¹ = 4-Mepy, PPh₃) with 4-methylpyridine or triphenylphosphine (05ICA2174). The starting complex also reacts with 2-hydroxy-4-methylpyridine (HL) to give the triply-bridged complex [Ir₂(μ -L)₃(CO)₂Cl(HL)], where HL is η^1 (N)-coordinated and is in the pyridinone form.

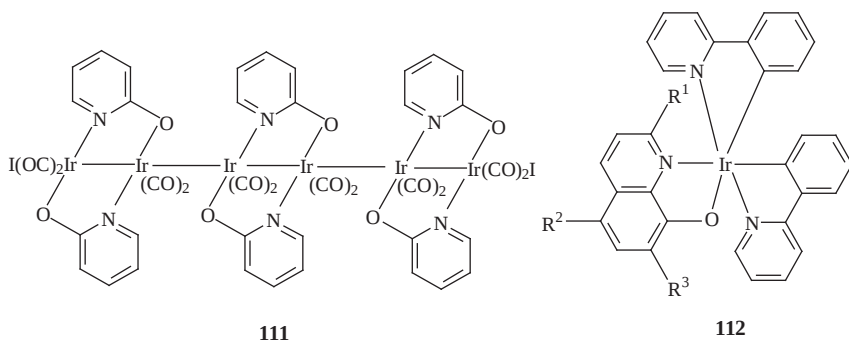
**102**

1,8-Naphthyridine-2-onate and 5,7-dimethyl-1,8-naphthyridine-2-onate are capable of forming η^3 (N,N,O)-rhodium complexes of composition [Rh₃(μ_3 -L)₂(CO)₂(η^4 -cod)₂](ClO₄) · 1.5C₂H₄Cl₂ (84JCS(D)125, 86ICA(111)L1). These ligands with [η^4 -cod]Ir(μ -OMe)]₂ gives **103** (M = Ir; R = H, Me) (86ICA(120)43, 96ICA(250)241). The products in solution are in equilibrium with monomeric η^2 (N,N)-coordinated **104** (M = Ir, R = H, Me). Under carbon monoxide, **103** (M = Ir, R = H, Me) are transformed to the equilibrium mixture of isomers **105** and **106** (M = Ir, R = H, Me), the products of incomplete substitution of the cod-ligand by the η^2 (N,O) and mixed η^2 (N,O) : η^2 (N,N)-coordination mode. Complete substitution gives the tetracarbonyl species. In a similar way, rhodium species were prepared. Reaction of [(η^4 -cod)M(μ -L)]_n (M = Rh, Ir) with [Ir(Cl)(CO)₂(NH₂-*p*-Tol)] or [Rh(μ -Cl)(CO)₂]₂ allowed the preparation of heterometallic dinuclear complexes [Rh(Ir)(μ -L)₂(CO)₂(η^4 -cod)] where the

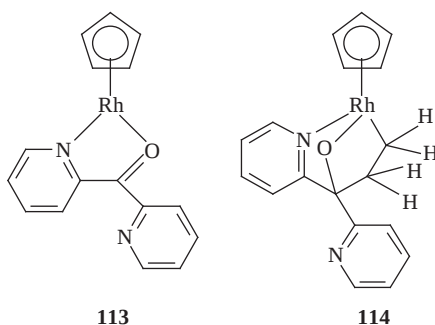
ligands are $\eta^2(\text{N},\text{O})$ -coordinated as in **105**. $[(\eta^4\text{-cod})\text{Rh}(\eta^2(\text{N},\text{N})\text{-L})]$ with $[\text{Rh}(\text{CO})_2(\text{acetone})_2](\text{ClO}_4)$ give the trinuclear cationic **107**, characterized by $\eta^3(\text{N},\text{N},\text{O})$ -coordination. $[\text{Rh}_2(\mu\text{-L})_2(\text{CO})_4]$ and $[(\eta^4\text{-cod})\text{Ir}(\text{solvent})_x](\text{ClO}_4)$ give a mixture of trinuclear isomers **108** and **109**. Compounds containing an RhIr_2 -core, **110**, can be prepared from $[\text{Rh}(\text{CO})_2(\text{solvent})_x](\text{ClO}_4)$ and $[(\eta^4\text{-cod})\text{Ir}(\mu\text{-L})]_n$. Complexes $[(\eta^4\text{-cod})\text{Ir}(\mu\text{-Opy})]_2$ (95CCR313), $[(\eta^4\text{-nbd})\text{Rh}(\mu\text{-6-Cl-2-Opy})]_2$ (89OM790) were described.



A metallic chain made of six iridium atoms is observed in **111** connecting dinuclear Ir(I) and Ir(II) moieties (03AGE529). A special class of organoiridium(III) quinolinolate compounds, **112** ($R^1 = R^2 = R^3 = H$; $R^1 = H, R^2 = R^3 = Cl, Br, I, Me, Ph$; $R^1 = Me, CN, R^2 = R^3 = H$; $R^1 = H, R^2 = CHO, NO_2, R^3 = H$) follows from 8-hydroxyquinoline derivatives with $[(2-Phpy)Ir(\mu-Cl)Ir(2-Phpy)]$ in methylene chloride-ethanol in the presence triethylamine (07EJ14207). These and other similar complexes (06JMC4389, 07CM1209) are remarkable for their photochemical properties. The $\eta^1(N)$ -coordinated half-sandwich $[(\eta^5-Cp^*)IrCl_2(\eta^1(N)-C_5H_4NOH-2)]$ is an effective catalyst of oxidation for secondary alcohols (07OL109, 08CCR782).



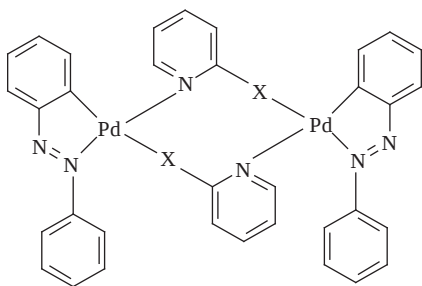
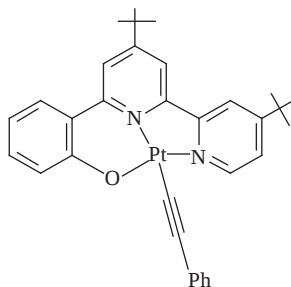
2,2'-Dipyridylketone and $[(\eta^5-Cp)Rh(\eta^2-C_2H_4)_2]$ under UV irradiation yield **113**, which reversibly further inserts a molecule of ethylene to afford oxametallacyclopentane **114** (03CC2332).



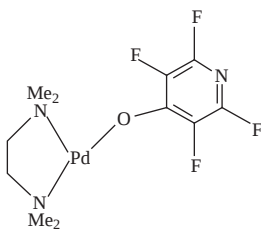
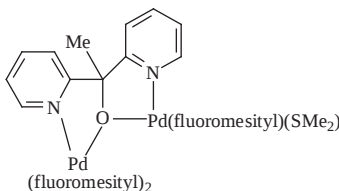
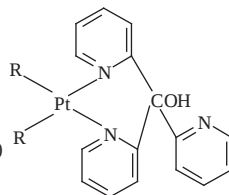
3.1.6 Nickel group

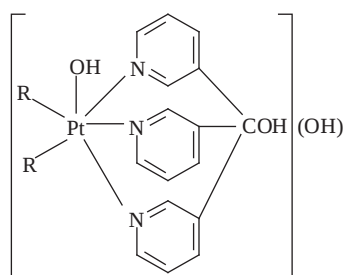
8-Hydroxyquinoline (HL) with $(NBu-n_4)[Pt_2(\mu-C_6F_5)_2(C_6F_5)_4]$ in methylene chloride gives $(NBu-n_4)[Pt(C_6F_5)_3(\eta^1(N)-HL)]$ with substantial $Pt \cdots H$ interaction (96IC6009). The same product can be prepared from $(NBu-n_4)[Pt(C_6F_5)_3Cl]$ and silver perchlorate in THF. Refluxing of it in chloroform gives $(NBu-n_4)[Pt(C_6F_5)_2(L)]$ where the ligand is coordinated

in the $\eta^2(\text{N},\text{O})$ -chelating mode. The cyclometalated derivative $[\text{Pd}((\text{C},\text{N})\text{-azobenzene})(\mu\text{-Cl})_2]$ reacts with 8-quinolinol (LH) in the presence of silver nitrate to produce the mixed chelate $[\text{Pd}((\text{C},\text{N})\text{-azobenzene})(\eta^2(\text{N},\text{O})\text{-L})]$ (98POL4109). $[\text{Pd}((\text{C},\text{N})\text{-azobenzene})(\mu\text{-Cl})_2]$ reacts with 2-hydroxypyridine or 2-mercaptopyridine in the presence of sodium methoxide in methylene chloride or with silver nitrate and subsequently with the same ligands in the presence of triethylamine in acetone gives dinuclear **115** ($\text{X} = \text{O}, \text{S}$) with bridging heterocyclic ligands (02JOM(650)202). The derivative of 6-(2-hydroxyphenyl)-2,2'-bipyridine **116** has interesting photochemical properties (05IC4442).

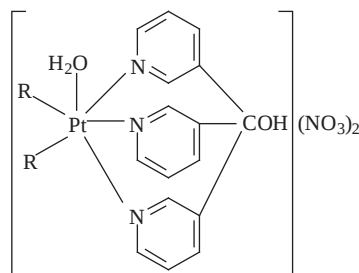
**115****116**

Pentafluoropyridine reacts with $[\text{PdMe}_2(\text{TMEDA})]$ in the presence of water and triethylamine to give $\eta^1(\text{O})$ -coordinated aryloxy-species **117** by nucleophilic substitution of one of the fluorine groups by a hydroxyl-moiety (03ICC752). Bis(2-pyridyl)ketone with $[\text{Pd}(\text{fluoromesityl})_2(\text{SMe}_2)_2]$ yields chelate $[\text{Pd}(\text{fluoromesityl})_2(\eta^2(\text{N},\text{N})\text{-OCpy}_2)]$ (04EJI2326). Bis(2-pyridyl)ethanol in the same reaction yields binuclear **118** where the heterocyclic ligand performs the bridging function. Di-2-pyridyl ketone (LL) forms $[\text{PtMe}_2(\eta^2(\text{N},\text{N})\text{-LL})]$ with a six-membered chelate ring, which is protonated by hydrochloric acid (06OM1583). It is readily protonated by hydrochloric acid to yield $[\text{PtMe}_2(\text{H})(\text{Cl})(\eta^2(\text{N},\text{N})\text{-LL})]$. Tris(pyridine-2-yl)methanol reacts with $[\text{PtR}_2(\text{SEt}_2)_2]$ ($\text{R} = \text{Me}, \text{Ph}$) to yield **119** ($\text{R} = \text{Me}, \text{Ph}$) (94JOM(471)C8, 96JOM(510)281). In wet acetone, these are converted to cationic **120** ($\text{R} = \text{Me}, \text{Ph}$), and the phenyl complex with dilute nitric acid yields aqueous dicationic **121**.

**117****118****119**



120

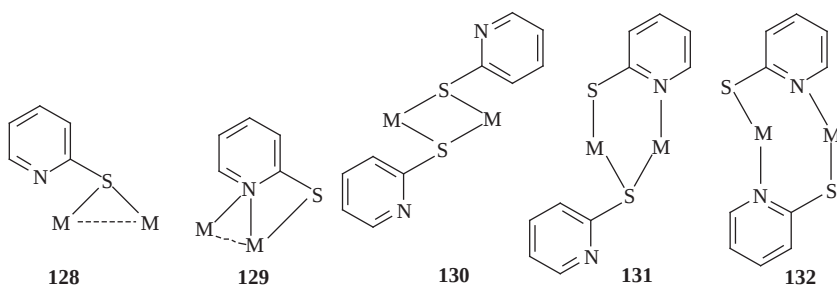
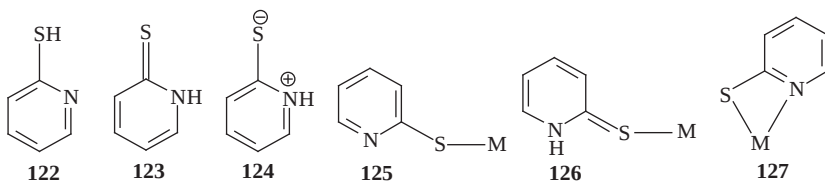


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3.2 Mercaptopyridines and other N,S-ligands

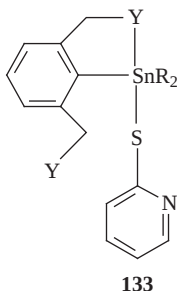
3.2.1 General remarks

Pyridine-2-thiol is presented by forms **122**–**124**, thiol tautomer **122**, thione tautomer **123**, and pyridinium form **124**, the thione tautomer generally predominating. Pyridine-2-thionate provides a variety of coordination modes in its complexes (85CCR115, 96CCR199, 97CCR475, 99CCR941, 01CCR181): S-monodentate (one-electron donor, MS) **125** and **126**, S,N-chelating (three-electron donor, NMS) **127** (78IC3254, 83CL141), M₂S bridging function (three-electron donor) **128**, S,N-bridging, and S-monodentate with a weak metal-nitrogen interaction, NM₂S-bridging (three- or four-electron donor) **129** (83ICA(80)L13, 89JCS(D)815), NM₃S (five-electron donor) (88JCS(D)2193). This mode termed as μ_3 -mode is not a limit, and further functioning of a lone pair on the sulfur atom is possible to realize the seven-electron donor function in tetranuclear metal complexes. Cleavage of the pyridine-2-thiolate ligand into μ -2-pyridyl and μ_4 -S counterparts leads to the three-electron situation. Some of the coordination modes of pyridine-2-thiolates can be illustrated as **130** (μ - η^2 (S)), **131** (μ - η^1 (S): η^2 (N): μ - η^2 (S)), and **132** (μ - η^1 (S): η^2 (N)).



3.2.2 Nontransition metals

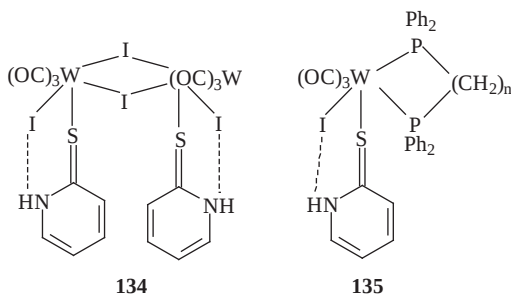
Triphenyltinquinoline-8-thiolate (80JSC766), [*n*-Bu₂Sn(SC₅H₃N-2,NO₂-5)₂] (79JINC1555), [*p*-MeC₆H₄)₃Sn(SC₅H₄N-2)] (81JSC569), [Ph₃Sn(SC₅H₄N-4)] (73JSC458), dicyclohexyltin(IV) bis(2-pyridylthiolate) (92ICA249), triorganotin(IV) 8-quinolinethiolates and diorganotin(IV) di(8-quinolinethiolates) (R = *n*-Bu, PhCH₂, Ph, CH₂=CH) (89JOM(372)327) contain the N,S-chelates. Bis(2-pyridylthio)methane (L) reacts with R_nSnCl_{4-n} (R = Me, n = 1; R = Me, *n*-Bu, Ph, n = 2; R = Me, *n*-Bu, Ph, Cy, n = 3) to yield [LSnR_nCl_{4-n}] where the sulfur atoms do not participate in coordination and the more likely coordination mode is $\eta^2(\text{N,N})$ (06JOM1615). The same situation is realized in the products of interaction of tris(2-pyridylthio)methane and R_nSnCl_{4-n} (n = Me, n = 2; R = Ph, Cy, n = 3). 2-Mercaptopyridine (LH) reacts with Ph₂SnCl₂ in methanol water to yield [Ph₂Sn($\eta^2(\text{N,S})$ -L)Cl] where the carboxylic group does not participate in coordination (03BCA227, 03JIB425, 06JOM1780). Sodium pyridine-2-thiolate (NaL) reacts with [Me₂Sn(C₆H₃(CH₂NMe₂)₂-2,6)]Cl or [Ph₂Sn(C₆H₃(CH₂OBu-*t*)₂-2,6)](OTf) to yield the $\eta^1(\text{S})$ -coordinated species **133** (Y = NMe₂, OBu-*t*; R = Me, Ph) (07JOM3415).



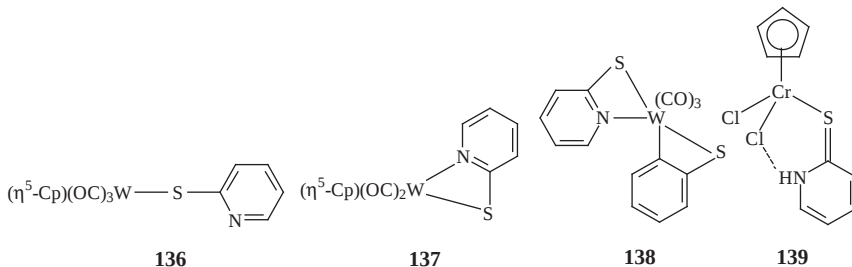
3.2.3 Vanadium and chromium group

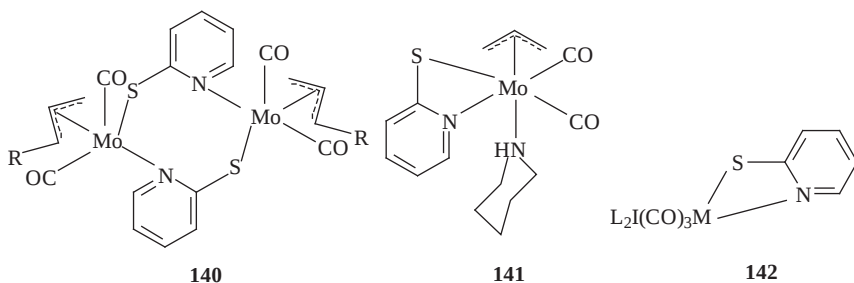
4,6-Dimethyl-2-mercaptopyridine (HL) with [$(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Nb}(\text{H})_3$] in hexane gives [$(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Nb}(\eta^2(\text{N,S})\text{-L})$] (00ICA(300)131). Pyridine 2-thiol (LH) reacts [M(CO)₆], [M(CO)₅(2-Rpy)], [M(CO)₄(2-Rpy)₂] (M = Mo, W, R = Me, H) to give two types of anionic complexes: [M(LH)(CO)₅][−] and [M(L)(CO)₄][−] as tetraphenylphosphonium or triethylammonium salts (90JOM79, 98POL1267). Pyridine-2-thione with an equimolar amount of [Wl₂(CO)₃(AN)₂] forms dimer **134** (95JCC1) with S-coordination of the ligand in the thione form and hydrogen-bond stabilization between the NH-group of the heterocyclic ligand and the iodide ligand. Pyridine-2-thione and [Ml₂(CO)₃(AN)₂] (M = Mo, W) in 2:1 ratio give the ligand substitution products [Ml₂(CO)₃($\eta^1(\text{S})$ -LH)₂] where the ligand (LH) is again in its thione form and S-coordinated. [Wl₂(CO)₃(AN)₂] with PPh₃ or Ph₂P(CH₂)_nPPh₂ (n = 1–6) and pyridine

2-thione give $[\text{WI}(\text{CO})_3(\text{PPh}_3)_2(\text{LH})]\text{I}$ or $[\text{W}(\text{CO})_3(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)(\text{LH})]\text{I}$, whose proposed structural motif is illustrated as **135**.

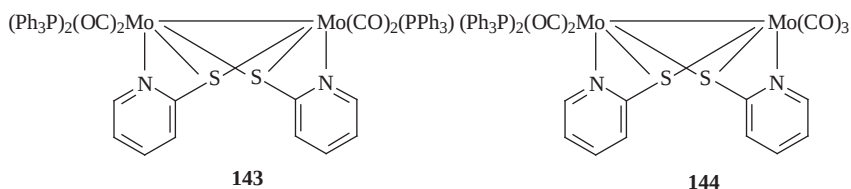


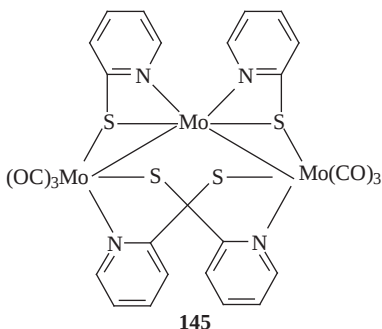
The photochemical reaction of bis(2-pyridyl)disulfide with $[(\eta^5\text{-Cp})_2\text{W}_2(\text{CO})_6]$ gives mononuclear **136** (87IC1064). Further ultraviolet irradiation causes chelation to yield **137**. Chelation can also proceed under thermal conditions. Dipyridyl-2,2'-disulfide with $[(\eta^3\text{-cycloheptatriene})\text{W}(\text{CO})_3]$ or $[\text{W}(\text{py})_3(\text{CO})_3]$ forms double chelate **138** (01IC2402). The reaction between complex **136** and *m*-chloroperoxybenzoic acid leads to the sulfinato-S (-S(O),R) compound (87IC3034). 2,2'-Dithiodipyridine with $[(\eta^5\text{-Cp})\text{Cr}(\text{CO})_3]_2$ gives the chromium analogue of **137** (04JOM3210). The latter reacts with hydrogen chloride to give $\eta^1(\text{S})$ -coordinated **139** where the ligand is protonated and is in its thione form. Potassium pyridine-2-thionate with $[(\eta^3\text{-C}_3\text{H}_4\text{R})\text{Mo}(\text{CO})_2(\text{AN})_2\text{Br}]$ (R = H, Me) in methylene chloride gives the dinuclear **140** where the ligand performs its doubly bridging $\eta^1, \eta^2\text{-}\mu$ function (03ICC213). Further interaction with $\text{C}_5\text{H}_{10}\text{NH}$ gives monomeric **141**. Pyridine-2-thiol (LH) reacts with $[\text{M}(\text{CO})_3(\text{AN})_3]$ (M = Mo, W) in acetonitrile to yield seven-coordinate M(II) complexes $[\text{M}(\text{CO})_3(\eta^2(\text{N},\text{S})\text{-L})_2]$ containing the S,N-chelating unit and six-coordinate complexes $[\text{M}(\text{CO})_5(\text{LH})]$ (90JCS(D)2321). 6-Methylpyridine-2-thiol (LH) gives only $[\text{W}(\text{CO})_5(\eta^1(\text{S})\text{-LH})]$. From the seven-coordinate derivatives, the ligand-substitution products $[\text{M}(\text{CO})_2(\text{PMe}_2\text{Ph})(\eta^2(\text{N},\text{S})\text{-L})_2]$ (M = Mo, W) can be prepared. $[\text{Ml}_2(\text{CO})_3(\text{AN})_2]$ (M = Mo, W) react with a phosphine ligand L (M = Mo, L = PPh_3 ; M = W, L = PPh_3 , PPh_2Cy , PPh_2Nap) and potassium pyridine-2-thionate to yield **142** (95JOM(498)257).





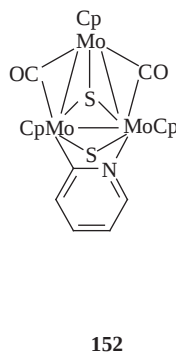
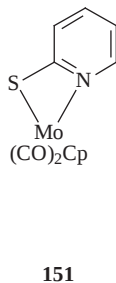
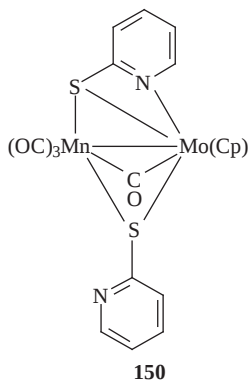
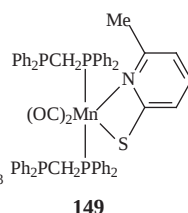
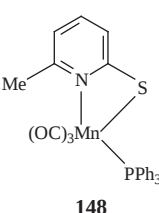
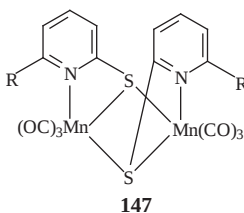
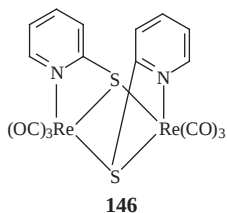
Potassium pyridine-2-thionate with $[\text{Wl}_2(\text{CO})(\text{AN})(\eta^2\text{-MeC}\equiv\text{CMe})_2]$ gives $[\text{Wl}(\text{CO})(\eta^2(\text{N,S})\text{-SC}_5\text{H}_4\text{N})(\eta^2\text{-MeC}\equiv\text{CMe})_2]$ in methylene chloride (94JCS(D)37). In excess potassium pyridine-2-thionate, $[\text{W}(\text{CO})(\eta^2(\text{N,S})\text{-SC}_5\text{H}_4\text{N})_2(\eta^2\text{-MeC}\equiv\text{CMe})]$ results. $[\text{Wl}(\text{CO})(\eta^2(\text{N,S})\text{-SC}_5\text{H}_4\text{N})(\eta^2\text{-MeC}\equiv\text{CMe})_2]$ with sodium tetraphenylborate in acetonitrile leads to the cationic species $[\text{W}(\text{CO})(\text{AN})(\eta^2(\text{N,S})\text{-SC}_5\text{H}_4\text{N})(\eta^2\text{-MeC}\equiv\text{CMe})_2](\text{BPh}_4)$, which on interaction with triphenylphosphine in methylene chloride forms ligand-substitution product $[\text{W}(\text{CO})(\text{PPh}_3)_2(\eta^2(\text{N,S})\text{-SC}_5\text{H}_4\text{N})(\eta^2\text{-MeC}\equiv\text{CMe})_2](\text{BPh}_4)$. Other ligand substitutions were run with 2,2'-bipyridine, 1,10-phenanthroline, 4,7- and 5,6-dimethyl-1,10-phenanthroline (LL), the products being $[\text{W}(\text{CO})(\text{LL})(\eta^2(\text{N,S})\text{-SC}_5\text{H}_4\text{N})(\eta^2\text{-MeC}\equiv\text{CMe})_2](\text{BPh}_4)$. The related complex is $[\text{W}(\text{CO})(\eta^2(\text{N,S})\text{-SC}_5\text{H}_4\text{N})_2(\eta^2\text{-PhC}\equiv\text{CPh})_2]$ (88JCS(D)2071). 2,2'-Dipyridyl disulfide and 8,8'-diquinolyl disulfide with $[(\eta^5\text{-Cp})_2\text{Mo}_2(\text{CO})_4]$ in toluene results in the cleavage of the $\text{Mo}\equiv\text{Mo}$ bond to yield $[(\eta^5\text{-Cp})\text{Mo}(\text{CO})_2(\eta^2(\text{N,S})\text{-C}_5\text{H}_4\text{NS})]$ and $[(\eta^5\text{-Cp})\text{Mo}(\text{CO})_2(\eta^2(\text{N,S})\text{-C}_9\text{H}_6\text{NS})]$ (93JOM115, 94AX(C)1191). Pyridine-2-thione with $[\text{Mo}(\text{CO})_3(\text{AN})_3]$ and triphenylphosphine in THF gives 143–145, where the trinuclear complex, $[\text{Mo}_3(\mu\text{-pyS})_2(\mu_3\text{-pyS})_2(\text{CO})_6]$, 145, is formed in minor amount (96JOM(514)183). 2,2'-Bis(pyridyl)diselenide with norbornadiene carbonyl complexes of molybdenum and tungsten involves reductive cleavage of the selenium–selenium bond, oxidation of the metal center and chelation of pyridine-2-selenolate to the metal carbonyl fragment (96IC3990). The products are the seven-coordinate complexes $[\text{M}(\eta^2(\text{Se,N})\text{-Sepy})_2(\text{CO})_3]$ ($\text{M} = \text{Mo}, \text{W}$).



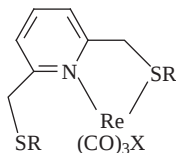


3.2.4 Manganese group

Pyridine-2-thione (LH) with $[\text{Re}_2(\text{CO})_{10}]$ in refluxing xylene gives dinuclear $[\text{Re}_2(\text{L})_2(\text{CO})_6]$ **146** where pyridine-2-thionate fulfills the role of a five-electron donating bridge (88POL1401). A similar coordination is realized in the products from pyridine-2-thiolate or 6-methylpyridine-2-thiolate with $[\text{Mn}_2(\text{CO})_{10}]$ in refluxing hexane, **147** ($\text{R} = \text{H}$, Me) (96JOM(517)155). Complex **147** ($\text{R} = \text{Me}$) with triphenylphosphine in cyclohexane yields mononuclear **148** and with bis(diphenylphosphino)-methane to give **149**. Complex **148** with $[(\eta^5\text{-Cp})\text{Mo}(\text{CO})_3]_2$ in toluene under reflux yields heterodinuclear **150**, the mononuclear **151**, and the homotrimeric molybdenum cluster **152** (05OM266).



Selenoether and thioether ligands, 2-MeSeC(R)(R¹)C₅H₄N (R = SiMe₃, R¹ = H; R = R¹ = H; R = R¹ = SiMe₃) and 2-RSCH₂C₅H₄N (R = Me, Ph) (L) react with [Mn(CO)₅Br] in chloroform to yield ordinary η^2 (N,E)-chelates (N = S, Se) [Mn(CO)₃(Br)L] (03JOM(674)38). 2,6-Bis(thioalkyl)- and -(thioaryl)pyridines react with [Re(CO)₅X] (X = Cl, Br, I) in THF to yield **153** (R = C₆H₄Me-*p*, Me; X = Cl, Br, I) (92JCS(D)2243). In solution, they possess dynamic character on switching sulfur atoms in the N,S-coordination mode.

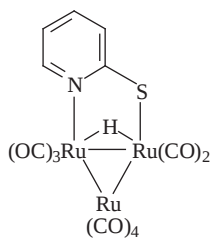
**153**

3.2.5 Iron group

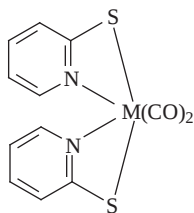
Pyridine-2-thiol, quinoline-8-thiol (LH) or dipyridyl-2,2'-disulfide (LL) react with [MH(Cl)(CO)(PPh₃)₃], [MH₂(CO)(PPh₃)₃] (M = Ru, Os), [Ru(CO)₃(PPh₃)₂], [OsH₂(CO)₂(PPh₃)₂] under reflux in benzene or toluene to afford [M(Cl)(L)(CO)(PPh₃)₂], [M(L)₂(CO)₂(PPh₃)], [M(L)₂(CO)(PPh₃)], and [M(L)₂(PPh₃)₂] in which the pyridine-2-thiolate ligands are coordinated in an η^1 (S) monodentate or η^2 (N,S) bidentate fashion (85ICA(98)L21, 85ICA(104)L5, 85JCS(D)2101, 95CC625, 96OM4423). Their protonation of the products using HBF₄·Et₂O in methylene chloride gives the tautomeric forms, [M(η^2 -H₂)(CO)(L)(PPh₃)₂](BF₄) and [M(H)(CO)(LH)(PPh₃)₂](BF₄), in which the sulfur atoms are protonated, but the η^2 (N,S)-chelating mode is retained. [Os(η^2 -H₂)(CO)(L)(PPh₃)₂](BF₄) (L = pyridine-2-thiolate) is one of the most acidic complexes (93OM3808). Similar products follow from pyridine-2-thiol and [RuCl₂(CO)₂(PPh₃)₂] in the presence of triethylamine, where [Ru(L)₂(CO)₂(PPh₃)] contains both monodentate and bidentate pyridine-2-thiolate ligands. [Ru(L)₂(CO)(PPh₃)] involves a pair of bidentate heterocyclic ligands. The reaction of bis(2-pyridyl) disulfide with [HFe(CO)₄]⁻ affords [Fe(CO)₄(η^1 (S)-SC₅H₄N)]⁻ (98OM2370). Bis(2-pyridyl) disulfide adds to the product followed by displacement of the pyridine-2-thionate and formation of neutral monomeric [Fe(CO)₂(η^2 (N,S)-SC₅H₄N)₂]. The η^2 (N,Se)-coordination pattern is observed in the product from bis(2-pyridyl) diselenide with [Fe₂(CO)₉], [Fe(η^2 (N,Se)Sepy)₂(CO)₂] (96IC3990).

Pyridine-2-thiol (LH) reacts with [Ru₃(CO)₁₂] to yield minor amounts of [RuL₂(CO)₂] and predominantly [Ru₃(μ -H)(μ_3 -L)(CO)₉], **154**, where the pyridine-2-thiolato-unit bridges two ruthenium atoms (92IC4792).

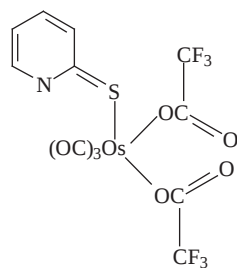
Heating the cluster product gives a trimeric cluster of composition $[\text{Ru}_3(\mu_3\text{-H})(\mu_4\text{-L})(\text{CO})_7]_3$. Three Ru_3 -clusters are linked by a Ru_3S_3 -ring. Pyridine-2-thiol with $[\text{Ru}_3(\text{CO})_{12}]$ in refluxing toluene yields polymeric $[\text{Ru}(\mu_3\text{-pyS})(\text{CO})_2]_n$ through the stage of the μ_3 -bridged complex **154**, but each ruthenium atom carries three CO ligands in minor amounts, which can be increased when reflux is carried out in THF (90JCS(D)2927). Polymer with additional pyridine-2-thiol gives mononuclear **155** ($\text{M} = \text{Ru}$). Complex **154** with triphenylphosphine and bis(diphenylphosphino)methane gives the ligand-substitution products $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-pyS})(\text{CO})_8(\text{PPh}_3)]$ and $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-pyS})(\text{CO})_7(\mu\text{-dppm})]$ while **155** ($\text{M} = \text{Ru}$) with phosphine in refluxing toluene gives $[\text{Ru}(\text{pyS})_2(\text{CO})(\text{L})]$ ($\text{L} = \text{PPh}_3$, $\text{P}(\text{OEt})_3$). Potassium pyridine-2-thionate (NaL) with $[\text{Ru}_3(\text{CO})_{12}]$ or $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in DMF gives monomeric **155** ($\text{M} = \text{Ru}$) (91POL837). Pyridine-2-thiol reacts with $[\text{Os}(\text{CF}_3\text{COO})_2(\text{CO})_4]$ in refluxing chloroform to give monodentately coordinated **156**, where the heterocyclic ligand is in its thione tautomeric form, which is further transformed into the $\eta^2(\text{N},\text{S})$ -chelate **157** (89JCS(D)2211). When the reaction was carried out for a longer time and at higher temperatures, **158** followed. The latter in the presence of $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ in methylene chloride yields **155** ($\text{M} = \text{Os}$). Pyridine-2-thiol with $[\text{Os}_3(\text{CO})_{12}]$ in refluxing toluene yields $[\text{Os}_3(\mu\text{-H})(\mu_2\text{-pyS})(\text{CO})_{10}]$, $[\text{Os}_3(\mu\text{-H})(\mu_3\text{-pyS})(\text{CO})_9]$, and $[\text{Os}(\text{pyS})_2(\text{CO})_2]$ (82JOM(233)C55).



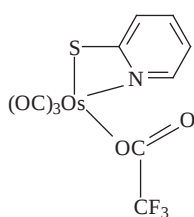
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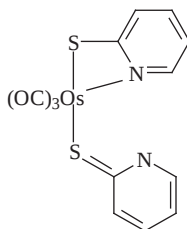
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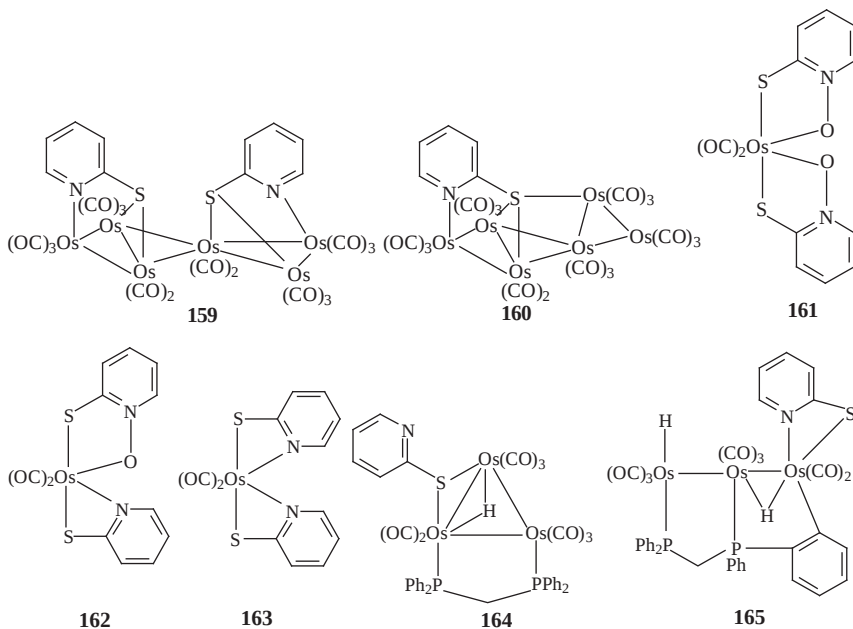


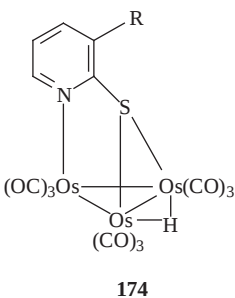
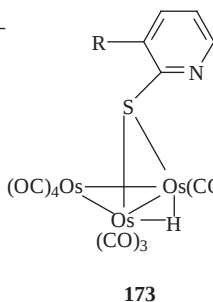
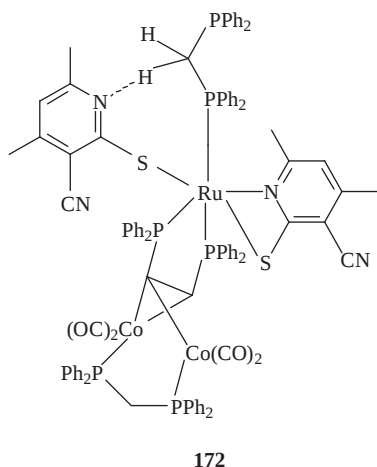
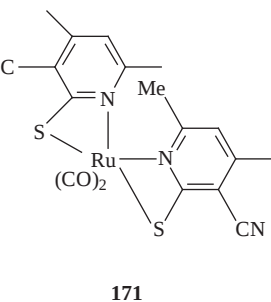
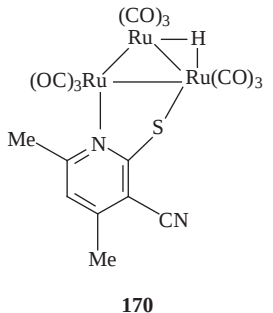
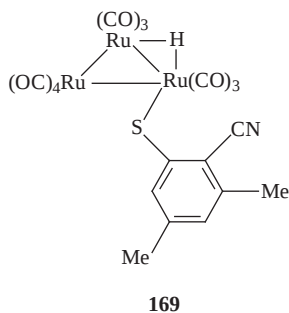
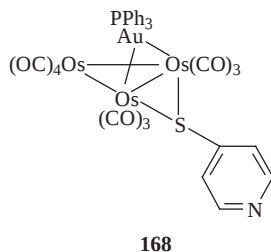
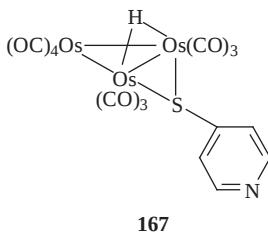
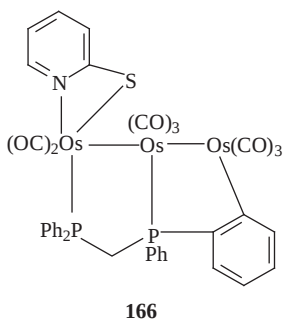
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158

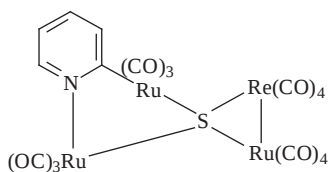
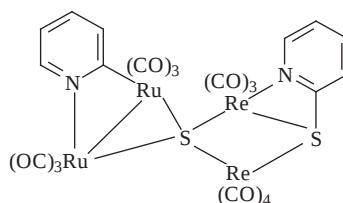
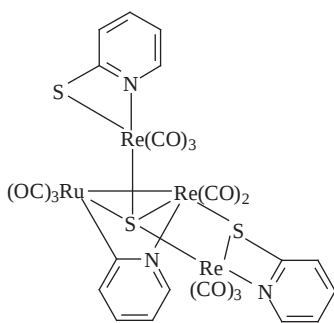
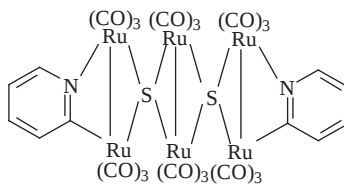
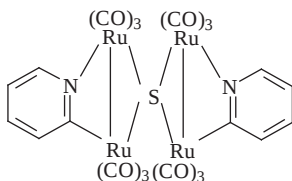
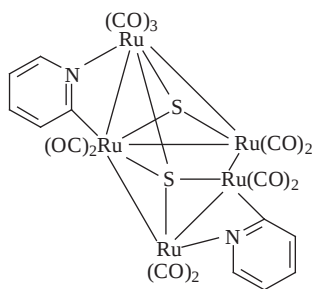
Di-2-pyridylsulfide with $[\text{Os}_6(\text{CO})_{16}(\text{AN})_2]$ in methylene chloride gives clusters **159** with the $\mu_3\text{-}\eta^2\text{-}$ and **160** with the $\mu_4\text{-}\eta^2\text{-}$ pyridine-2-thionate ligand (99JCS(D)2521). 2,2'-Dipyridyl disulfide with $[\text{Os}_3(\text{CO})_{10}(\text{AN})_2]$ gives a range of oxidative addition products: $[\text{Os}_3(\text{pyS})_2(\text{CO})_{10}]$, $[\text{Os}_3(\text{pyS})_2(\text{CO})_9]$, $[\text{Os}_2(\text{pyS})_2(\text{CO})_6]$, $[\text{Os}(\text{pyS})_2(\text{CO})_2]$, and $[\text{Os}_3\text{H}(\text{pyS})(\text{CO})_9]$. The products contain chelating, $\mu_2\text{-}\mu_3\text{-}$ bridging pyridine-thionate ligands (94POL3285). 1-Hydroxypyridine-2-thione with $[\text{Os}_3(\text{CO})_{12}]$ in the presence of Me_3NO gives three mononuclear osmium complexes **161**–**163** (05JOM441). The intermediates in this transformation are the triosmium complexes $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})(\mu\text{-}\eta^1\text{-S-C}_5\text{H}_4\text{N(O)})]$ and $[\text{Os}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-}\eta^1\text{-}\eta^2\text{-SC}_5\text{H}_4\text{N(O)})]$. Pyridine-2-thiol reacts with $[\text{Os}_3(\text{CO})_8(\text{Ph}_2\text{PCH}_2\text{P(Ph)C}_6\text{H}_4)]$ in methylene chloride at room temperature to yield clusters **164** and **165** (00JOM(616)157). When the same reaction is conducted in benzene at elevated temperatures, the sole product is cluster **166**. 4-Mercaptopyridine with $[\text{Os}_3(\text{CO})_{10}(\text{AN})_2]$ gives a mixture of products, of which only cluster **167** could be characterized (07JOM2138). Similar **168** follows from $[\text{Os}_3(\text{CO})_{10}(\mu\text{-Cl})(\mu\text{-AuPPh}_3)]$. 3-Cyano-4,6-dimethyl-2-mercaptopyridine with $[\text{Ru}_3(\text{CO})_{12}]$ in toluene gives two clusters, **169** and **170**, and one chelate, **171** (04BCJ103). The latter reacts with $[\text{Co}_2(\text{CO})_4(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)(\mu\text{-Ph}_2\text{PC}\equiv\text{CPh}_2)]$ to yield **172**, in which one of the chelate rings is opened. 2-Mercaptopyridine, 3-carboxy-2-mercaptopyridine, and 3-hydroxy-2-mercaptopyridine react with $[\text{Os}_3(\text{CO})_{10}(\text{AN})_2]$ to yield the $\mu(\text{S})$ -bridging clusters **173** ($\text{R} = \text{H}, \text{COO}, \text{OH}$), which on photochemical decarbonylation give N,S-bridging species **174** ($\text{R} = \text{H}, \text{COO}, \text{OH}$) (96JOM(517)173).





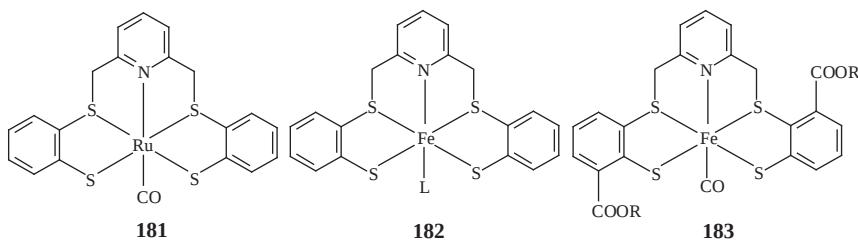
$[\text{Re}_2(\eta^2(\text{N,S})\text{-L})_2(\text{CO})_6]$ with $[\text{Ru}_3(\text{CO})_{12}]$ gives tetranuclear products $[\text{ReRu}_3(\mu_4\text{-S})(\mu\text{-C}_5\text{H}_4\text{N})(\text{CO})_{14}]$ **175**, $[\text{Re}_2\text{Ru}_2(\mu_4\text{-S})(\mu\text{-C}_5\text{H}_4\text{N})(\mu_2\text{-L})(\text{CO})_{13}]$ **176**, and $[\text{Re}_3\text{Ru}(\mu_4\text{-S})(\mu\text{-C}_5\text{H}_4\text{N})(\mu_2\text{-L})(\mu_3\text{-L})(\text{CO})_{11}]$ (90POL623). $[\text{Re}_2(\eta^2(\text{N,S})\text{-L})_2(\text{CO})_6]$ with $[\text{Ru}_3(\text{CO})_{12}]$, results in splitting of the pyridine-2-thionate ligand, followed by $[\text{Ru}_6(\mu_4\text{-S}_4)(\mu\text{-C}_5\text{H}_5\text{N})_2(\text{CO})_{18}]$ formation containing the bridging 2-thiopyridyl ligand, **177** (91JCS(D)431).

Complex **155** ($M = \text{Ru}$) reacts with $[\text{Ru}_3(\text{CO})_{12}]$ in light petroleum to yield a mixture **178** and **179** (92JCS(D)1607). In xylene under reflux **180** follows.

**175****176****177****178****179****180**

Dilithium 2,6-bis(2-mercaptophenylthio)dimethylpyridine reacts with $[\text{RuCl}_2(\text{DMSO})_4]$ in methanol and further with carbon monoxide in THF to yield **181** (00EJI423). In a similar way, an iron(II) analogue can be obtained (99IC5314). The ligand 2,6-bis(phenylthio)dimethylpyridine readily forms mononuclear **182** ($L = \text{PMe}_3$, $\text{P}(n\text{-Pr}_3)$, N_2H_4 , py) (01ZN(B)581). Ligands L exchange for CO to give **182** ($L = \text{CO}$). 2,6-Bis(2-mercapto-3-(methoxycarbonyl)phenylthio)dimethylpyridine and the

ethoxycarbonyl-analogue react with lithium methylate, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and excess carbon monoxide in methanol to give **183** ($\text{R} = \text{Me}, \text{Et}$) (04EJI581).



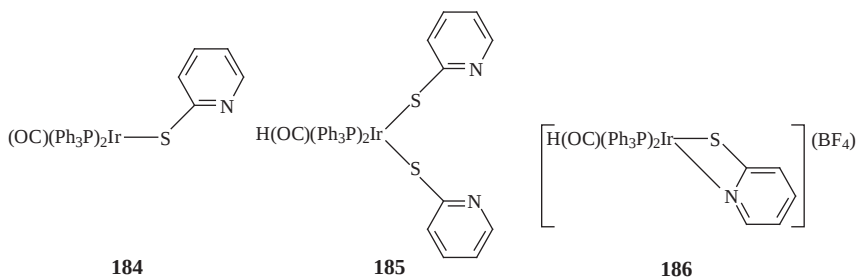
Pyridine-2-thiol with $[(\eta^3, \eta^3\text{-C}_{10}\text{H}_6)\text{Ru}(\text{Cl})(\mu\text{-Cl})_2]$ initially gives $[(\eta^3, \eta^3\text{-C}_{10}\text{H}_6)\text{Ru}(\text{NC}_5\text{H}_5\text{SH-2})\text{Cl}]$, which further eliminates hydrogen chloride to yield monomeric $[(\eta^3, \eta^3\text{-C}_{10}\text{H}_6)\text{Ru}(\text{NC}_5\text{H}_5\text{S-2})\text{Cl}]$ (91JCS(D)1563). In acetonitrile with silver tetrafluoroborate, $[(\eta^3, \eta^3\text{-C}_{10}\text{H}_6)\text{Ru}(\text{NC}_5\text{H}_5\text{S-2})(\text{AN})](\text{BF}_4)$ results. A chelate form is established for the pyridine-2-thionato (L) complex $[(\eta^4\text{-nbd})\text{Ru}(\eta^2(\text{N,S})\text{-L}_2)]$ (91ICA(183)21). Sodium pyridine-2-thiolate with the aryl complexes $[\text{Ru}(\eta^2\text{-Ar})(\text{PPh}_3)_2(\text{CO})\text{Cl}]$ affords $[\text{Ru}(\eta^1\text{-RL})(\text{PPh}_3)_2(\text{CO})(\eta^2(\text{N,S})\text{-L})]$ ($\eta^2\text{-Ar} = \text{C}_6\text{H}_2\text{O-2-CHNC}_6\text{H}_4\text{R}$ (*p*)-3-Me-5, $\eta^1\text{-RL}$ is $\text{C}_6\text{H}_2\text{OH-2-CHNC}_6\text{H}_4\text{R}$ (*p*)-3-Me-5; $\text{R} = \text{Me}, \text{OMe}, \text{Cl}$) (02POL899). 2-Mercaptopyridine and 8-hydroxyquinoline (LH) react with $[(\eta^4\text{-cod})\text{Ru}(\mu\text{-X})_2]_n$ ($\text{X} = \text{Cl}, \text{Br}$) in dimethylformamide and sodium carbonate to give complexes $[(\eta^4\text{-cod})\text{Ru}(\eta^2(\text{N,O(S)})\text{-L}_2)]$ (74JOM(65)89). A pyridine-2-thiol derivative with methyl iodide gives the iodide-bridged dimer $[(\eta^4\text{-cod})\text{Ru}(\text{L})(\mu\text{-I})_2]$ and the S-methylated derivative MeL (83JOM(254)105). New mononuclear complexes of osmium with sulfur-containing ligands have been prepared. Pyridine-2-thiol reacts with osmium-nitride complex $(\text{NBu-}n)_4[\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2\text{Cl}_2]$ containing triethylamine to yield a dinuclear complex with bridging and chelating heterocyclic ligand $[\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\text{SC}_5\text{H}_4\text{N})_2]$ (88OM1126).

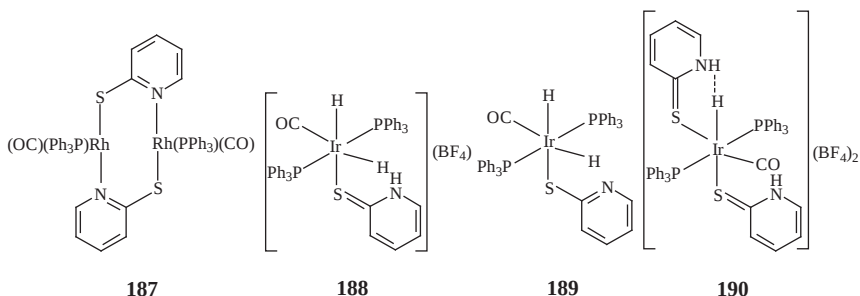
2-Mercaptopyridine (HL) with $[(\eta^5\text{-Cp})\text{Ru}(\text{Cl})(\text{PEt}_3)_2]$, $[(\eta^5\text{-Cp})\text{Ru}(\text{Cl})(\text{PMe}(i\text{-Pr})_2)(\text{PPh}_3)]$, and $[(\eta^5\text{-Cp}^*)\text{Ru}(\text{Cl})(\text{PEt}_3)_2]$ in ethanol yielded cationic complexes in which the ligand is in the 1 H-pyridine thione form (98OM4392, 99JCS(D)4309). $[(\eta^5\text{-Cp})\text{Ru}(\text{dppf})\text{Cl}]$ reacts with 2-mercaptopyridine (HL) in the presence of sodium tetraphenylborate to yield $[(\eta^5\text{-Cp})\text{Ru}(\text{dppf})(\eta^1(\text{S})\text{-HL})\text{BF}_4]$ (04JOM1444). Pyridine-2-thiol (HL) reacts with methyl lithium and $[(\eta^5\text{-Cp})\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ in THF to yield $[(\eta^5\text{-Cp})\text{Ru}(\text{PPh}_3)(\eta^2(\text{N,S})\text{-L})]$ (07JOM2227). The product reacts with NOBF_4 to yield dicationic complex $[(\eta^5\text{-Cp})\text{Ru}(\text{PPh}_3)(\text{NO})(\eta^2(\text{S})\text{-LH})]$ where the heterocyclic ligand is $\eta^2(\text{S})$ -coordinated and the ligand is transformed to the thione form. Under carbon monoxide, the product now is $[(\eta^5\text{-Cp})\text{Ru}(\text{PPh}_3)(\text{CO})(\eta^1(\text{S})\text{-L})]$. Pyridine-2-thiol (HL) with

methyl lithium and $[(\eta^5\text{-Cp})\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ in THF but in the presence of bis(diphenylphosphino)ethane leads to the $\eta^1(\text{S})$ -coordinated neutral complex $[(\eta^5\text{-Cp})\text{Ru}(\eta^2(\text{P}, \text{P})\text{-dppe})(\eta^1(\text{S})\text{-L})]$. Pyridine-2-thiol (HL) with $[(\eta^5\text{-Cp})\text{Ru}(\text{PPh}_3)_2\text{Cl}]$ and sodium tetraphenylborate in THF gives cationic complex $[(\eta^5\text{-Cp})\text{Ru}(\text{PPh}_3)_2(\eta^2(\text{S})\text{-LH})](\text{BPh}_4)$ where the ligand is in its thione form. Bis(2-pyridyl) disulfide (HLLH) with $[(\eta^5\text{-Cp})\text{Ru}(\text{AN})_3](\text{PF}_6)$, depending on the conditions, may form either mononuclear $[(\eta^5\text{-Cp})\text{Ru}(\eta^2(\text{N}, \text{S})\text{-L}_2)](\text{PF}_6)$ or dinuclear $[(\eta^5\text{-Cp})\text{Ru}(\mu\text{-L})_2\text{RuCp}](\text{PF}_6)_2$ with S-coordination of the bridging ligand (04OM2876).

3.2.6 Cobalt group

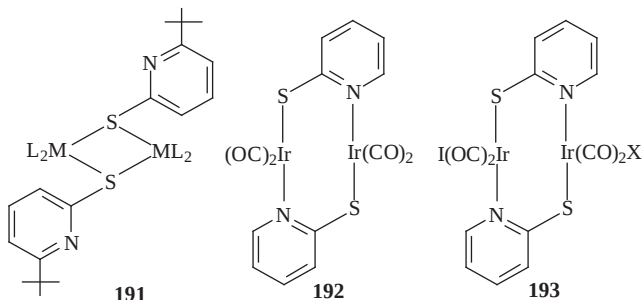
A mixed coordination mode is realized in the oxidized product from pyridine-2-thiol (LH) with $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ having composition $[\text{Rh}(\text{L})_2(\text{LH})_2]\text{Cl}$, where LH is $\eta^1(\text{S})$ -coordinated and L is $\eta^2(\text{N}, \text{S})$ chelated (88JCS(D)227). 2-Pyridone, 2-thiopyridone, 6-methyl-2-thiopyridone, 2-methylmercaptopyridine, and *N*-methyl-2-thiopyridone react with $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ to give bridged $[\text{Rh}(\text{Cl})(\text{CO})_2(\eta^2\text{-L})]$ (88ICA(142)37). The product from pyridine-2-thiol and dimer $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ in chloroform is dinuclear rhodium(II) $[\text{Rh}_2\text{Cl}_2(\mu\text{-NC}_5\text{H}_4\text{S})_2(\eta^1(\text{S})\text{-NHC}_5\text{H}_4\text{S})_2(\text{CO})_2] \cdot 2\text{CHCl}_3$, which can further be oxidized to rhodium(III) derivative $[\text{Rh}(\text{NC}_5\text{H}_4\text{S})_3]$ (86JOM(299)C25). Sodium pyridine-2-thiolate with $[\text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2]$ in THF gives the S-coordinated complex **184** (00EJI2117). The product oxidatively adds pyridine-2-thiol to yield **185**. The latter interacts with HBF_4 in chloroform forming the ionic chelate **186**. The rhodium analogue under these conditions gives dinuclear **187** with the bridging pyridine-2-thionate ligand. Pyridine-2-thione (LH) reacts with $[\text{IrH}_3(\text{CO})(\text{PPh}_3)_2]$ and HBF_4 in chloroform to yield the $\eta^1(\text{S})$ -species **188** and **189** (00JOM(609)110). After crystallization **190** was isolated.





6-*t*-Butylpyridine-2-thiol with $[(\eta^4\text{-cod})\text{M}(\mu\text{-OMe})_2]$ ($\text{M} = \text{Rh}, \text{Ir}$) in methylene chloride gives dinuclear **191** ($\text{M} = \text{Rh}, \text{Ir}$; $\text{L}_2 = \text{cod}$) (06OM4374). With $[\text{M}(\text{acac})(\text{CO})_2]$, the products are **191** ($\text{M} = \text{Rh}, \text{Ir}$; $\text{L}_2 = (\text{CO})_2$). Rhodium species **191** [$\text{L}_2 = (\text{CO})_2$] with triphenylphosphine gives **191** ($\text{M} = \text{Rh}$, $\text{L}_2 = (\text{CO})(\text{PPh}_3)$). Reaction of 2-hydroxypyridinate and 2-mercaptopyridinate (L) with $[(\eta^4\text{-cod})\text{M}(\mu\text{-Cl})_2]$ ($\text{M} = \text{Rh}, \text{Ir}$) yields binuclear $[(\eta^4\text{-cod})\text{M}(\mu\text{-L})_2]$ (88OM707). Oxidative addition of methyl iodide or methylene iodide to the iridium complex **192** in the presence of tetra-*n*-butyl bromide in methylene chloride gives stable iridium(II) **193** ($\text{R} = \text{Me}, \text{Me}_2\text{I}$) (87AGE444). The binuclear $[(\eta^4\text{-diene})\text{Rh}(\mu\text{-pyS})_2]$ (diene = cod, nbd, tfb), as well as $[\text{Rh}(\text{CO})_2(\mu\text{-pyS})_2]$ and $[\text{Rh}(\text{CO})(\text{PPh}_3)(\mu\text{-pyS})_2]$ react with $[(\eta^4\text{-diene})\text{Rh}(\text{Me}_2\text{CO})_x](\text{ClO}_4)$, $[\text{Rh}(\text{CO})_2(\text{Me}_2\text{CO})_x](\text{ClO}_4)$, or $[\text{Rh}(\text{CO})(\text{PPh}_3)(\text{Me}_2\text{CO})_x](\text{ClO}_4)$ to give trinuclear clusters $[(\eta^4\text{-diene})_3\text{Rh}_3(\mu_3\text{-pyS})_2](\text{ClO}_4)$, $[\text{Rh}_3(\text{CO})_6(\mu_3\text{-pyS})_2](\text{ClO}_4)$, or $[\text{Rh}_3(\text{CO})_3(\text{PPh}_3)_3(\mu_3\text{-pyS})_2](\text{ClO}_4)$, in which the pyridine-2-thiolate ligands act as triple bridges through the nitrogen and one sulfur atom with respect to all three metal atoms (90JCS(D)1493). The μ_3 -bridging function is also realized in $[\text{Rh}_3(\mu_3\text{-pyS})_2(\text{CO})_6]^+$ (86NJC75) where a ligand is bonded to one metal center via a nitrogen atom and to two others via sulfur. Lithium pyridine-2-thionate with $[(\eta^4\text{-diolefin})\text{Rh}(\mu\text{-Cl})_2]$ gives binuclear $[(\eta^4\text{-diolefin})\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})_2]$ (diolefin = cod, nbd, tfb) where the ligand bridges two rhodium atoms via the sulfur atom (89JCS(D)25). Carbonylation gives $[\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{CO})_2]_2$, where bridging occurs via both N- and S-centers. Methyl iodide on addition affords diacetyl derivative $[\text{Rh}(\mu\text{-SC}_5\text{H}_4\text{N})(\text{COMe})\text{I}(\text{CO})_2]$. Lithium pyridine-2-thiolate (LiL) with $[(\eta^2\text{-C}_2\text{H}_4)\text{Ir}(\text{Cl})(\text{PPh}_3)_2]$ gives $[\text{Ir}(\eta^2(\text{N},\text{S})\text{-L})(\text{PPh}_3)_2]$, which oxidatively adds methyl diphenylsilane to yield $[\text{Ir}(\eta^2(\text{N},\text{S})\text{-L})(\text{PPh}_3)_2(\text{SiPh}_2\text{Me})(\text{H})]$ and *p*-tolylacetylene to afford

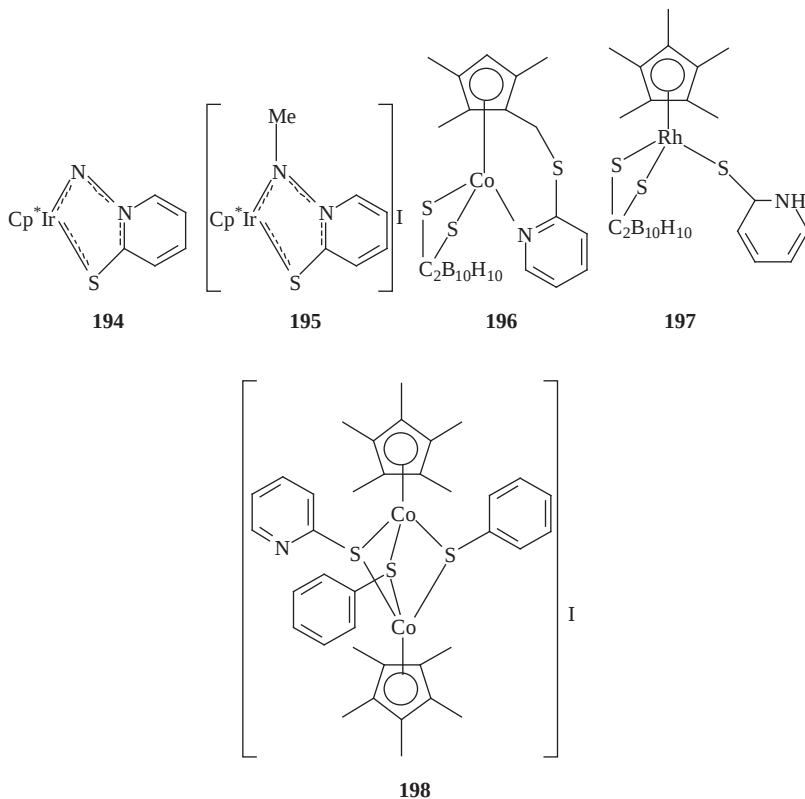
$[\text{Ir}(\eta^2(\text{N},\text{S})\text{-L})(\text{PPh}_3)_2(p\text{-TolC}\equiv\text{C})(\text{H})]$ (07JOM4139).



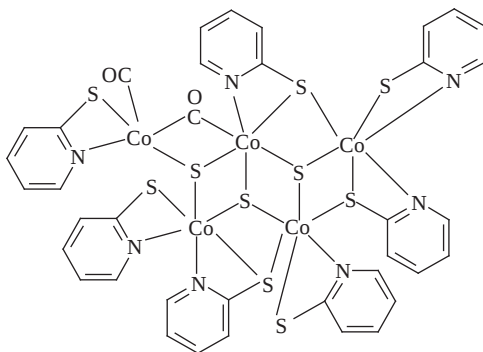
2,6-Dimercaptopyridine (H_2L) with $[(\eta^4\text{-diolefin})\text{Rh}(\mu\text{-OMe})_2]$ (diolefin = cod, nbd, tfb) gives tetranuclear $[(\eta^4\text{-diolefin})_4\text{Rh}_4(\mu\text{-L})_2]$ with doubly deprotonated bridging ligands (96IC1782). The dilithium salt of 2,6-dimercaptopyridine with $[\text{M}(\mu\text{-Cl})\text{L}_2]_2$ ($\text{M} = \text{Ir}$, $\text{L}_2 = \text{cod}$; $\text{M} = \text{Pd}$, $\text{L}_2 = \text{allyl}$) also leads to the tetranuclear species $[(\eta^4\text{-cod})_4\text{Ir}_4(\mu\text{-L})_2]$ and $[(\eta^3\text{-allyl})_4\text{Pd}_4(\mu\text{-L})_2]$. Carbonylation of $[(\eta^4\text{-cod})_4\text{Rh}_4(\mu\text{-L})_2]$ gives $[\text{Rh}_4(\text{CO})_8(\mu\text{-L})_2]$, and ligand substitution with triphenylphosphine gives $[\text{Rh}_4(\text{CO})_4(\text{PPh}_3)_4(\mu\text{-L})_2]$. $[(\eta^4\text{-cod})\text{Rh}(\text{acac})]$ with an equimolar amount of the starting ligand gives dinuclear $[(\eta^4\text{-cod})_2\text{Rh}_2(\mu\text{-L})_2]$. Similar procedures served for the synthesis of tetranuclear complex $[(\eta^4\text{-tfb})_4\text{Ir}_4(\mu\text{-L})_2]$ (01IC4785). Complexes $[(\eta^4\text{-diolefin})_4\text{Rh}_4(\mu\text{-L})_2]$ (diolefin = cod, tfb) can be oxidized by $[(\eta^5\text{-Cp})_2\text{Fe}](\text{PF}_6)$ to yield cationic $[(\eta^4\text{-diolefin})_4\text{Rh}_4(\mu\text{-L})_2]^+$ (PF_6^-). $[(\eta^4\text{-cod})_4\text{Ir}_4(\mu\text{-L})_2]$ is oxidized by silver tetrafluoroborate in methylene chloride to give $[(\eta^4\text{-cod})_4\text{Ir}_4(\mu\text{-L})_2](\text{BF}_4)$, however, in excess AgBF_4 transformation to the trinuclear cluster $[(\eta^4\text{-cod})_3\text{Ir}_3(\mu\text{-L})_2](\text{BF}_4)$ occurs. The tfb-analogue produces the trinuclear cluster in any ratio of reagents.

3-Trimethylsilylpyridine-2-thiol with methyltrioxorhenium in toluene affords $[\text{Re}(\text{Me})\text{O}(\eta^2\text{-2-SC}_5\text{H}_3\text{N-3-SiMe}_3)_2]$ and $[(\eta^5\text{-Cp}^*)\text{RhCl}_2]_2$ in THF yields $[(\eta^5\text{-Cp}^*)\text{Rh}(\eta^2(\text{N},\text{S})\text{-2-SC}_5\text{H}_3\text{N-3-SiMe}_3)(\eta^1(\text{S})\text{-2-SC}_5\text{H}_3\text{N-3-SiMe}_3)]$ (96ICA(244)199). Potassium pyridine-2-thionate (KL) with $[(\eta^5\text{-Cp}^*)\text{RhCl}_2]_2$ in methanol gives the rhodium(III) derivative $[(\eta^5\text{-Cp}^*)\text{Rh}(\eta^2(\text{N},\text{S})\text{-L})(\eta^1(\text{S})\text{-L})]$ (00ICA(299)100). The products from 2-pyridinethione with $[(\eta^5\text{-Cp}^*)\text{M}(\text{Cl})(\mu\text{-Cl})_2]$ ($\text{M} = \text{Rh}$, Ir) are the $\eta^1(\text{S})$ -coordinated species $[(\eta^5\text{-Cp}^*)\text{M}(\text{LH})\text{Cl}_2]$ where the heterocyclic ligand is in its thione form (08OM961). Photolysis of the (azido)(pyridine-2-thiolato)iridium(III) complex $[(\eta^5\text{-Cp}^*)\text{Ir}(\eta^2\text{-Spy})(\text{N}_3)]$ causes insertion of one of the azide nitrogen atoms into the Ir-N(py) bond **194** (05IC8173). Further reaction with methyl iodide gives N-methylated **195**. Lithium pyridine-2-thionate with $[(\eta^5\text{-Cp}^*)\text{Co}(\text{CO})\text{I}_2]$ and $[(\eta^5\text{-Cp}^*)\text{RhCl}_2]_2$ gives half-sandwich complexes $[(\eta^5\text{-Cp}^*)\text{M}(\eta^2(\text{N},\text{S})\text{-L})\text{X}]$ ($\text{M} = \text{Co}$, $\text{X} = \text{I}$; $\text{M} = \text{Rh}$, $\text{X} = \text{Cl}$) (08OM713). The products with $\text{LiSC}_2(\text{H})\text{B}_{10}\text{H}_{10}$ in THF

give the S-coordinated adducts $[(\eta^5\text{-Cp}^*)\text{M}(\eta^2(\text{N,S})\text{-L})(\text{SC}_2(\text{H})\text{B}_{10}\text{H}_{10})]$ ($\text{M} = \text{Co}, \text{Rh}$). The bidentate ligand $\text{Li}_2\text{C}_2\text{B}_{10}\text{H}_{10}$, with cobalt and rhodium behaves differently. The cobalt precursor experiences C-H activation of the Cp^* -ligand to yield **196**, while of the rhodium precursor, transforms the pyridine-2-thione ligand into the thione form and $\eta^1(\text{S})$ -coordination results in **197**. 2-Mercaptoquinoline and 8-mercaptoquinoline also react with $[(\eta^5\text{-Cp}^*)\text{Ir}(\text{N}_3)_2]_2$ in the presence of sodium methoxide in methanol to yield a similar chelate (08ICA1479). Half-sandwich compound $[(\eta^5\text{-Cp}^*)\text{Co}(\eta^2(\text{N,S})\text{-L})\text{I}]$ reacts with lithium pyridine-2-thiolate in THF to give first the product with mixed coordination mode of the heterocyclic ligand $[(\eta^5\text{-Cp}^*)\text{Co}(\eta^2(\text{N,S})\text{-L})(\eta^1(\text{S})\text{-L})]$ and then the homoleptic $[\text{Co}(\eta^2(\text{N,S})\text{-L})_3]$ (08JOM2903). A structure similar to that in the mixed-coordination mode species was established for $[(\eta^5\text{-Cp}^*)\text{Rh}(\eta^2(\text{N,S})\text{-L})(\eta^1(\text{S})\text{-L})]$ where L is 2- $\text{SC}_5\text{H}_3\text{N}$ -3- SiMe_3 (91ICA(190)97). The cobalt iodide precursor with lithium 4-pyridinethiolate (LiL^1) also gives the mixed-coordination mode and mixed-ligand product $[(\eta^5\text{-Cp}^*)\text{Co}(\eta^2(\text{N,S})\text{-L})(\eta^1(\text{S})\text{-L}^1)]$ (08JOM2903). The reaction with lithium benzene thiolate is interesting because the chelate unit in the precursor is opened and $\mu_3(\text{S})$ -bridging derivative **198** is formed.



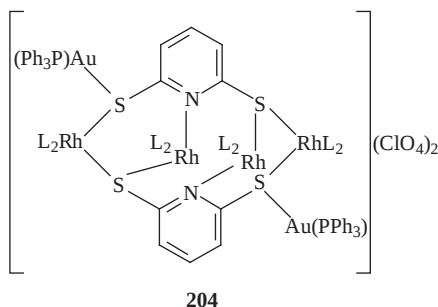
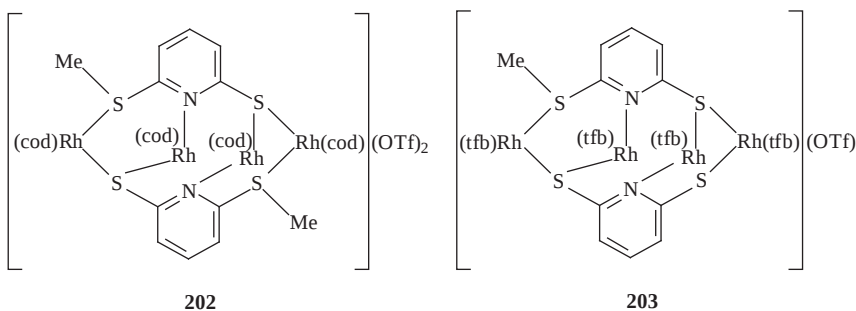
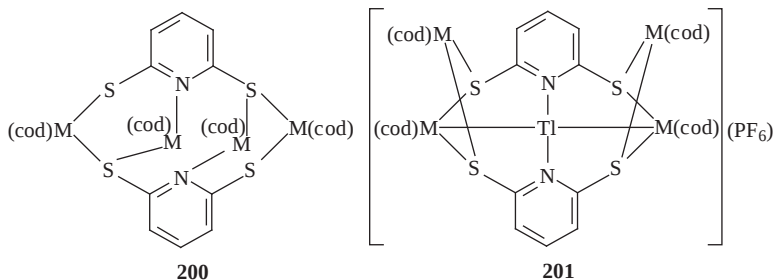
Pyridine-2-thiol with $[\text{Co}_2(\text{CO})_8]$, sodium hydroxide, and tetraethylammonium chloride yields cluster $[\text{Co}_5(\text{CO})_2(\mu_3\text{-S})_3(\text{SC}_5\text{H}_4\text{N})_7]$, **199** (97POL1425). There are four bridging five-electron donor and three terminal three-electron donor pyridine-2-thionate ligands. 2-Mercaptopyridine with $[\text{Co}_2(\text{CO})_8]$ in THF gives a sulfido-tricobalt cluster $[(\mu_3\text{-S})\text{Co}_3(\text{CO})_7(\mu(\text{C,N})\text{-C}_5\text{H}_4\text{N})]$ (02JOM(655)172). A similar reaction occurs between 2-quinolinethiol and $[\text{Co}_2(\text{CO})_8]$.

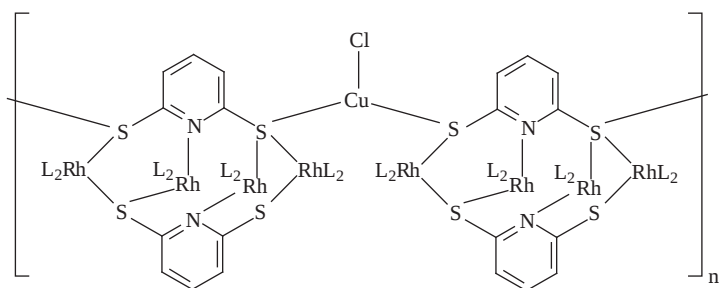


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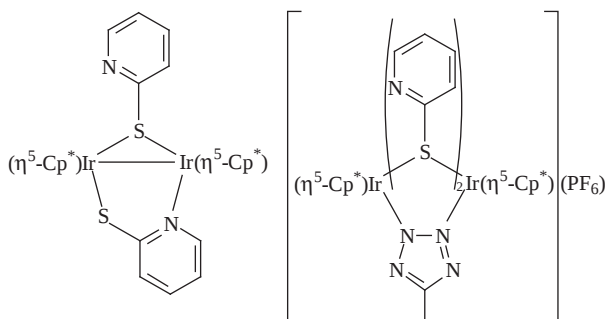
The rhodium(III) complex based on pyridine-2-thione (LH), $[\text{Rh}(\eta^2(\text{N,S})\text{-L})_3(\eta^1(\text{S})\text{-LH})]$, with $[\text{Pd}(\eta^3\text{-C}_4\text{H}_7)\text{S}_2](\text{BF}_4)$ ($\text{S} = \text{H}_2\text{O}$, acetone) and triethylamine yields the trinuclear rhodium(III)-palladium(II) species $[\text{Rh}(\eta^2(\text{N,S})\text{-L})_2(\mu_3\text{-L})_2\{\text{Pd}(\eta^3\text{-C}_4\text{H}_7)\}_2](\text{BF}_4)$. Two of the ligands bridge all three metal atoms in such a way that they are chelated to a palladium framework and bridged to the rhodium moiety via two sulfur atoms (88JCS(D)235). Reactions of $[(\eta^4\text{-cod})_4\text{M}_4(\mu\text{-pyS}_2)_2]$ ($\text{M} = \text{Rh}$, Ir), **200**, with thallium hexafluorophosphate give the heteropolymetallic complexes $[\text{Tl}(\eta^4\text{-cod})_4\text{M}_4(\mu\text{-pyS}_2)_2](\text{PF}_6)$, **201** (99IC2482). The products contain two Tl–Rh bonds and the thallium atom is coordinated to two pyridine nitrogen atoms, while rhodium and iridium atoms are bridged exclusively by the sulfur sites. Complex **200** ($\text{M} = \text{Rh}$) with methyl triflate gives the product of attack of the Me^+ groups onto one of the sulfur atoms of each bridging ligand to convert them to 6-(thiomethyl)pyridine-2-thiolate bridges in the product **202** (04IC1558). The tfb-analogue under similar conditions gives mixed-ligand monocationic **203**. Tetranuclear complexes $[(\eta^4\text{-L}_2)_4\text{Rh}_4(\mu\text{-pyS}_2)_2]$ ($\text{L}_2 = \text{cod}$, tfb) serve as the bidentate ligands in their reactions with $[\text{Au}(\text{PPh}_3)(\text{Me}_2\text{CO})](\text{ClO}_4)$ yielding the heteropolynuclear species **204** ($\text{L}_2 = \text{cod}$, tfb). $[(\eta^4\text{-cod})_4\text{Rh}_4(\mu\text{-pyS}_2)_2]$ with $[\text{Ag}(\text{PPh}_3)](\text{ClO}_4)$ gives a coordination polymer of

composition $[\text{Ag}(\eta^4\text{-cod})_4\text{Rh}_4(\mu\text{-pyS}_2)_2\text{I}_n(\text{ClO}_4)_n]$. A coordination polymer is also formed with copper(I) chloride and its structure can be illustrated in scheme 205 (00CEC125, 04IC1558). Similar polymers can be obtained with $[\text{Au}(\text{Cl})(\text{THT})]$. Cationic polymers are prepared with silver tetrafluoroborate. 2-Pyridinethiolate and 8-quinolinethiolate perform a mixed bridging function in the pentamethylcyclopentadienyl iridium(II) complexes termed as $\mu_3(\eta^2(\text{N},\text{S}):\eta^1(\text{S}))$ 206 (8-quinolinethiolate complex is similar) (08IC3948). The pyridine derivative further reacts with 5-methyltetrazole to yield iridium(III) 207 where $\eta^2(\text{N},\text{S})$ is replaced by $\eta^1(\text{S})$ and an additional tetrazolate N^2,N^3 -bridge is formed.

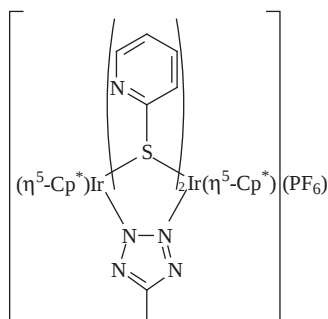




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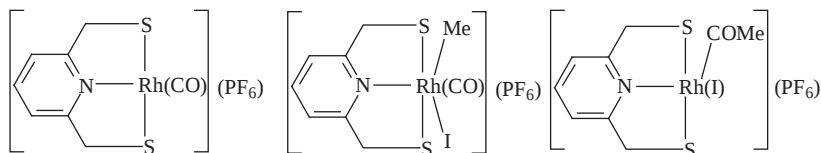


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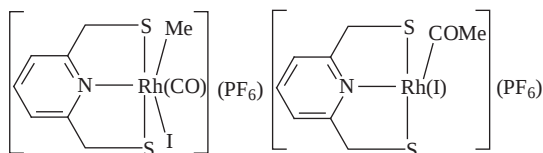


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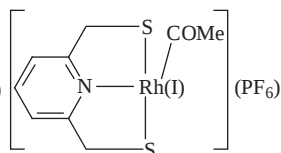
2,6-Bis(benzylthiomethyl)pyridine with dimer $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ in methanol followed by ammonium hexafluorophosphate gives **208** (03OM2535). The product oxidatively adds methyl iodide to yield rhodium(III) **209** in which the methyl group gradually migrates to the carbonyl ligand to afford the acetyl **210**. Cationic **211** ($\text{M} = \text{Rh}, \text{Ir}$; $\text{L} = \eta^2\text{-COE}$) react with carbon monoxide to yield carbonyls **211** ($\text{M} = \text{Rh}, \text{Ir}$; $\text{L} = \text{CO}$) (08JCS(D)3226). Only iridium **211** ($\text{M} = \text{Ir}$, $\text{L} = \eta^2\text{-COE}$) reacts with molecular hydrogen to yield dinuclear **212** with two S-bridging heterocyclic ligands.



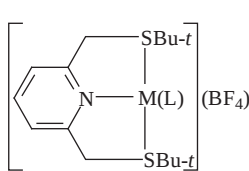
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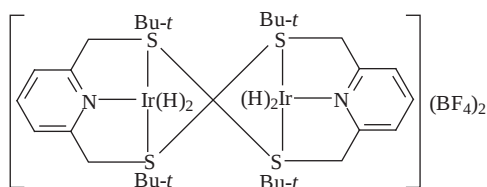
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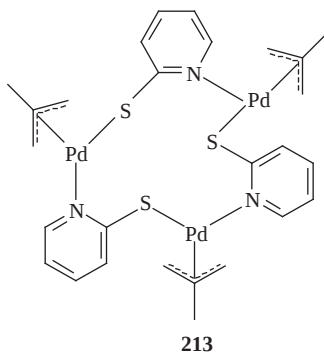
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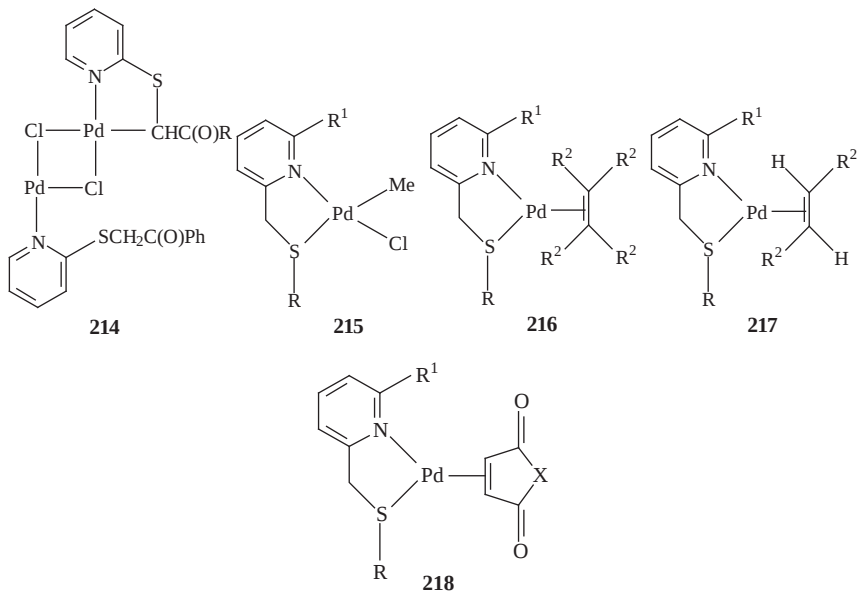
3.2.7 Nickel group

Pyridine-2-thionate with $[(\eta^3\text{-C}_4\text{H}_7)\text{Pd}](\text{OTf})$ gives complex **213** (99JOM(579)321). Pyridine-2-thione (HL) reacts with $[\text{Me}_3\text{Pt}(\text{OAc})(\text{bipy})]$ to yield the S-coordinated product $[\text{Me}_3\text{Pt}(\text{OAc})(\text{bipy})(\eta^1(\text{S})\text{-L})]$ (06ICA4326). With $[\text{PtMe}_3(\text{OAc})(\text{Me}_2\text{CO})_x]$ ($x = 1, 2$), the dinuclear complex with the bridging pyridine-2-thionate ligands is formed, $[\text{Me}_3\text{Pt}(\mu\text{-L})_2\text{PtMe}_3]$.

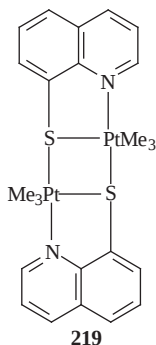


Phenylcarbonylmethylenethiopyridine reacts with $[\text{PdCl}_2(\text{NCPh})_2]$ in acetone to yield dinuclear **214** where one of the palladium units is cyclometalated (99OM2750). Pyridine thioether ligands react with $[(\eta^4\text{-cod})\text{Pd}(\text{Cl})(\text{Me})]$ in toluene to yield **215** ($\text{R}^1 = \text{H}, \text{Me}$; $\text{R} = t\text{-Bu}, \text{Ph}$) (00OM1461). Related complexes are $[(\eta^3\text{-C}_3\text{H}_5)\text{Pd}(\text{C}_5\text{H}_4\text{-N-2-CH}_2\text{SR})]$ ($\text{R} = \text{Ph}, \text{Et}$) (98ICA385, 98JOM61, 01ICA172). Pyridine thioether ligands also react with $[\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3]$ and naphthoquinone, maleic anhydride, fumaronitrile, tetramethylethylenetetra-carboxylate, tetracyanoethylene to yield **216** ($\text{R}^1 = \text{H}, \text{R} = \text{Me}, \text{Et}, i\text{-Pr}, t\text{-Bu}, \text{Ph}, \text{R}^2 = \text{COOMe}, \text{CN}$; $\text{R}^1 = \text{Me}, \text{R} = \text{Ph}, \text{R}^2 = \text{COOMe}, \text{CN}$), **217** ($\text{R}^1 = \text{H}, \text{R} = \text{Me}, \text{Et}, i\text{-Pr}, t\text{-Bu}, \text{Ph}, \text{R}^2 = \text{CN}$; $\text{R}^1 = \text{Me}, \text{R} = \text{Ph}, \text{R}^2 = \text{CN}$), and **218** ($\text{R}^1 = \text{H}, \text{R} = \text{Me}, \text{Et}, i\text{-Pr}, t\text{-Bu}, \text{Ph}, \text{X} = \text{O}, \text{C}_6\text{H}_4$; $\text{R}^1 = \text{Me}, \text{R} = \text{Ph}, \text{X} = \text{O}, \text{C}_6\text{H}_4$) (00JOM(601)1, 02JCS(D)3696, 02JOM(642)58). This technique was applied to 2-((2-pyridylmethylthio)methyl)pyridine and 2,6-bis(methylthiomethyl)pyridine (99ICA(293)44). Reaction of **215** ($\text{R}^1 = \text{H}, \text{R} = \text{Me}, \text{Et}, i\text{-Pr}, t\text{-Bu}, \text{Ph}$; $\text{R} = \text{Me}, \text{R}^1 = t\text{-Bu}, \text{Ph}$; $\text{R}^1 = \text{Cl}, \text{R} = \text{Me}, t\text{-Bu}, \text{Ph}$) with carbon monoxide results in an insertion into the palladium-carbon bond yielding an acyl species (02JOM(650)43). 2,6-Bis(phenylthiomethyl)pyridine (L) with $[(\eta^3\text{-C}_3\text{H}_5)\text{Pd}(\mu\text{-Cl})_2]$ or $[(\eta^3\text{-1,1-Me}_2\text{C}_3\text{H}_3)\text{Pd}(\mu\text{-Cl})]_2$ and silver triflate in methylene chloride gives $[(\eta^3\text{-allyl})\text{Pd}(\eta^2(\text{N,S})\text{-L})](\text{OTf})$ where one of the sulfur centers remains uncoordinated (02OM4342). Such complexes reveal fluxionality in solution. Palladium(II) pyridyl thioether complexes $[\text{Pd}(\text{Me})\text{Cl}(\eta^2(\text{N,S})\text{-2-RSCH}_2\text{-6-R}^1\text{-C}_5\text{H}_3\text{N})]$ ($\text{R} = \text{Me}, t\text{-Bu}, \text{Ph}$; $\text{R}^1 = \text{H}, \text{Me}, \text{Cl}$) with alkynes $\text{ZC}\equiv\text{CZ}$ ($\text{Z} = \text{COOMe}, \text{COOEt}, \text{COOBu-}t$) provides an

insertion into the palladium-methyl bond and the products are $[\text{Pd}(\text{C}(\text{Z})=\text{C}(\text{Z})\text{Me})\text{Cl}(\eta^2(\text{N},\text{S})\text{-}2\text{-RSCH}_2\text{-}6\text{-R}^1\text{-C}_5\text{H}_3\text{N})]$ (05OM3297). The second alkyne inserts into the C-Me bond to afford $[\text{Pd}(\text{C}(\text{Z})=\text{C}(\text{Z})\text{C}(\text{Z})=\text{C}(\text{Z})\text{Me})\text{Cl}(\eta^2(\text{N},\text{S})\text{-}2\text{-RSCH}_2\text{-}6\text{-R}^1\text{-C}_5\text{H}_3\text{N})]$.

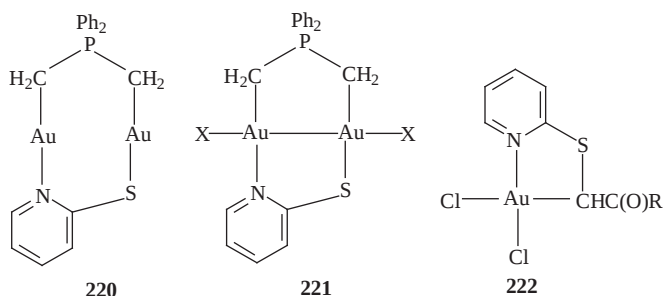


2,6-Bis(*p*-tolylthiomethyl)pyridine (L) reacts with platinum(IV) derivatives $[\text{PtMe}_3\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}$) to afford $[\text{PtXMe}_3(\eta^2(\text{N},\text{S})\text{-L})]$ ($\text{X} = \text{Cl}$ or Br) (93JCS(D)3795). 2,6-Bis(*t*-butylthiomethyl)pyridine with $[(\eta^3\text{-C}_3\text{H}_5)\text{Pd}(\text{Cl})]_2$ and silver triflate in chloroform gives $[(\eta^3\text{-C}_3\text{H}_5)\text{Pd}(\eta^3(\text{S},\text{N},\text{S})\text{-L})](\text{OTf})$ (01JOM155). 8-Methylthioquinoline (L) forms $\eta^2(\text{N},\text{S})$ -chelates containing moieties $\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}$, $[(\eta^5\text{-Cp}^*)\text{M}^{\text{III}}\text{Cl}]^+$ ($\text{M} = \text{Rh}, \text{Ir}$), and $\text{Pt}^{\text{IV}}\text{Me}_4$ (04ICA3325). With $[\text{PtMe}_2(\mu\text{-SMe}_2)]_2$ in THF the chelate $[\text{PtMe}_2(\eta^2(\text{N},\text{S})\text{-L})]$ follows (05OM794). Under prolonged heating in THF the dimeric rearrangement product **219** results, where the ligand methyl group migrated to the platinum center. This is an intramolecular redox process in which a platinum(IV) species is formed.



3.2.8 Late transition metals

2-Mercaptopyridine with [dichloro(2-dimethylaminomethyl)phenyl- C^1,N] gold(III) gives an $\eta^1(S)$ -coordinated complex with the heterocyclic ligand in its thione form (98JCS(D)1011). $[Au(\mu-C_5H_4NS)]_n$ reacts with $[Au_2\{\mu-(CH_2)_2PPh_2\}_2]$ to yield **220** (95JCS(D)2245). Under $[NEt_3(CH_2Ph)]Cl$, $\{N(n-Bu)_4\}Br$, $(PPh_3Me)I$, or $KSCN$ and $[(\eta^6-Cp)_2Fe](PF_6)$, gold(I) complexes **221** ($X = Cl, Br, I, SCN$) were generated. 2,2'-Bis(pyridyl)diselenide is characterized by the $\eta^2(Se,Se)$ -coordination in the adduct with bis(pentafluorophenyl)mercury(II) (96IC3990). Acylthiopyridine ligands $C_5H_4NSCH_2C(O)R$ ($R = Ph, Me, OMe$) and $Na[AuCl_4]$ in acetone yield cyclometalated **222** (98EJI511, 99OM753).



Pyridine-2-thiol (HL) reacts with methyl mercury(II) hydroxide or phenyl mercury(II) acetate to give $[Hg(R)(\eta^1(S)-L)]$ ($R = Me, Ph$) where an intramolecular mercury $\cdots$ nitrogen interaction is observed (86JCS(D)1945). Similar techniques based on dimethyl thallium hydroxide (88OM1897) allowed the preparation of $[TlMe_2(\eta^2(N,S)-L)]$ (90JCS(D)1001). Pyridine-2-thiol and $[SnMe_2Cl_2]$ in methanol with sodium hydroxide gives $[SnMe_2(\eta^2(N,S)-L)_2]$. Bis(trichlorovinyl)mercury with pyridine-3-thiol (HL) forms $\eta^1(S)$ -coordinated $[(C_2Cl_3)Hg(L)]$ where the nonbonding $Hg \cdots N$ interaction plays a role (00POL2539). 2,2'-Dipyridylsulfide with $[(C_2Cl_3)Hg(Br)]$ forms polymeric complex $[HgBr_2(L)]_n$, where $\eta^1(N)$ -coordination prevails and $Hg-S$ interaction is absent.

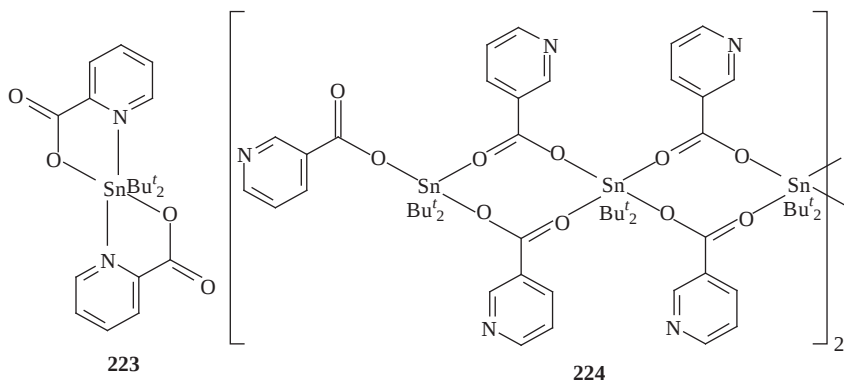
3.3 Pyridine carboxylates

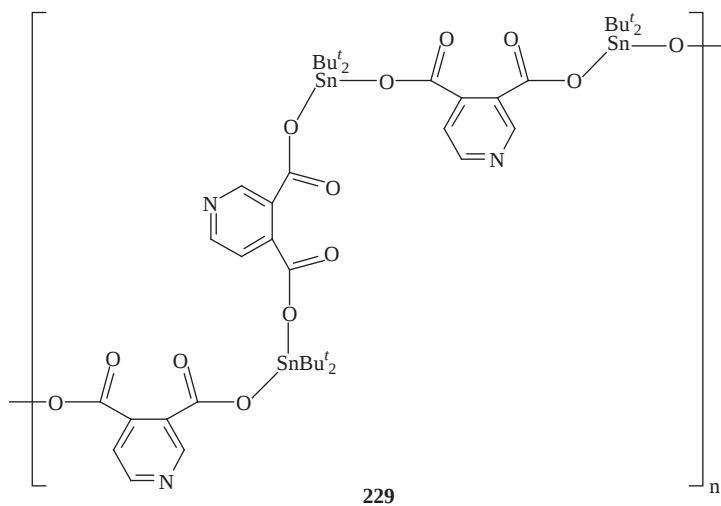
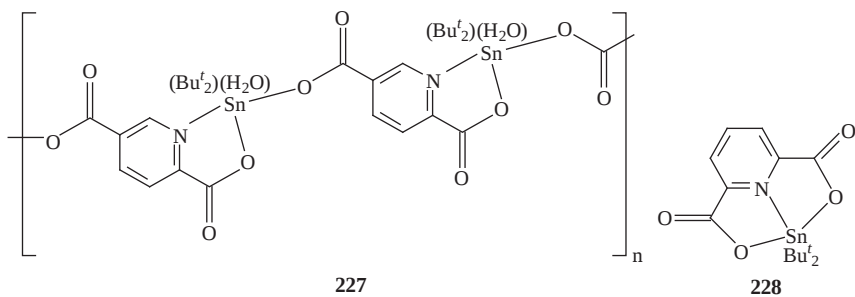
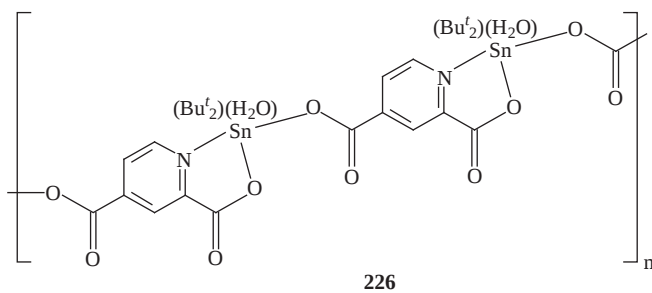
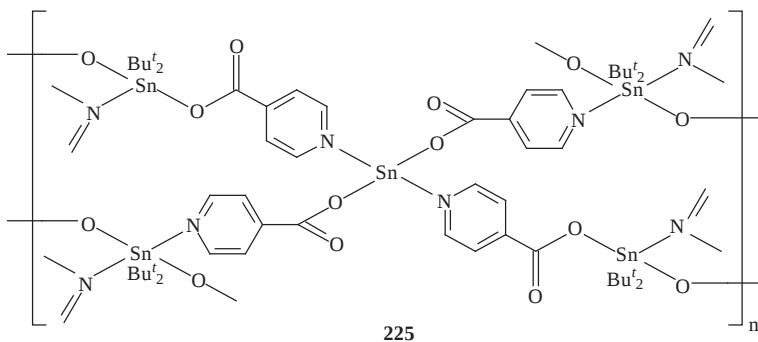
3.3.1 Tin

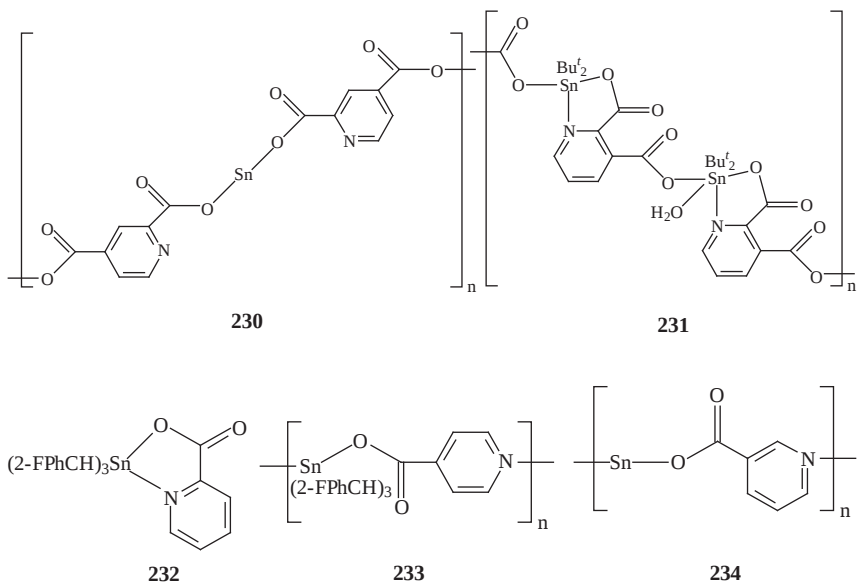
Dimethylchloro- and diphenylchlorotin 2-pyridinecarboxylate are characterized with a *trans*-octahedral R_2SnX_4 geometry (81JOM(204)47, 83JOM(244)119). An $Sn-N$ interaction is absent in trimethyltin-2-pyridinecarboxylate monohydrate (79JOM(182)37) and chlorotriphenyltin-2-pyridiniumcarboxylate (82AX(B)1325). In diethyltin bis(2-methylthio-3-pyridinecarboxylate), there is a six-coordinate tin atom and two equivalent

carboxylate groups chelating the tin atom (92POL1861). Bis(aquadi-methyl(2,6-pyridinedicarboxylato))tin(IV) hydrate and bis(aquadi-*n*-butyl(2,6-pyridinedicarboxylato))tin(IV) have similar structures (89AX(C)51). Bis(dicyclohexylammonium) bis(2,6-pyridinedicarboxylato)di-*n*-butylstannate is a seven-coordinate compound having a C_2SnNO_4 pentagonal bipyramidal structure (87MG147, 91MG73, 93MG367, 97AOC39). Tetraethylammonium (diorgano)halogeno(2,6-pyridinedicarboxylato)stannates are described (92AOC197, 93AOC311). Di-*n*-butyltin pyridine-2-phosphonate-6-carboxylate contains the μ_2 -tetradentate phosphonate carboxylate dianion, coordinating one tin atom via one of the phosphonate oxygen atoms, the pyridine nitrogen atom, and one of the carboxylate oxygen atoms; the latter atom also coordinates the second tin atom of the dimer in the seven-coordinate, pentagonal bipyramidal geometry (98OM4259). Pyridine-2-carboxylic acid (L) with $(ArCH_2)_2SnO$ ($Ar = Ph, 2-Cl-, 2-CN, 4-Cl, 4-CN, 2-FC_6H_4$) gives $[Ar(CH_2)_2Sn(\eta^2(N,O)-L)_2]$ (06JOM3331).

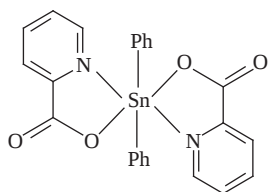
Sodium salts of 2-picolinic, nicotinic, *iso*-nicotinic, pyridine-2,4-, pyridine-2,5-, pyridine-2,6-, pyridine-3,4-, pyridine-3,5- and pyridine-2,3-dicarboxylic acids with $t-Bu_2SnCl_2$ in methanol give a series of complexes **223–234** manifesting a variety of coordination modes as a function of the ligand (04JOM1145, 04JOM2762). In species **223** there is the expected $\eta^2(N,O)$ -chelating mode. Compound **224** contains two types of modes-monodentate $\eta^1(O)$ - and bridging $\eta^2:\eta^1-\mu(O,O)$ -. In polymer **225**, the ligand performs the N,O-bridging function. Polymeric structures **226** and **227** contain ligands performing both N,O-chelating O-bridging functions. Complex **228** is a classical O_2N -chelate. Polymers **229** and **230** have O-bridges. In polymeric structure **231**, each ligand simultaneously fulfils the role of the O-bridge and O,N-chelating moiety. Sodium salts of pyridine-2-, -3, and 4-carboxylic acid react with tri(o-fluorobenzyl)tin chloride in benzene to yield simple chelate **232** in the first case, and polymers with the O,N-bridging ligands (04JOM246).



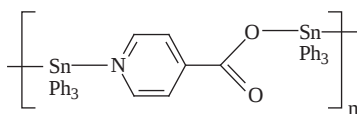




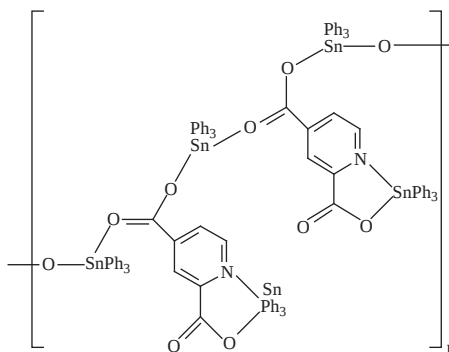
2-Picolinic, nicotinic, *iso*-nicotinic, pyridine-2,3-, 2,4-, 2,5-, 2,6-, 2,4-, and 3,5-dicarboxylic acid (HL) react with Ph_3SnOH in methanol to yield either mononuclear chelates or polymeric complexes of composition $[(\text{Ph}_3\text{Sn})_n\text{L}]$ (06JOM1622). Thus, 2-picolinic acid forms chelate **235** and *iso*-nicotinic acid gives polymer **236** with N,O-bridging of the ligand. 2,4- and 3,5-pyridinedicarboxylic acids give polymers **237** and **238**, respectively with O,O-bridges. N,O-bridges similar to that for *iso*-nicotinic acid are also realized in the complex of nicotinic and 2,6-dicarboxylic acid. The O,O-bridging structure is proposed for the derivatives of 3,4- and 3,5-pyridinedicarboxylic acids. 2,6-Pyridinedicarboxylic acid with R_3SnCl ($\text{R} = \text{Me}, \text{Ph}, \text{PhCH}_2$) in the presence of triethylamine produces trimeric complex **239** where the heterocyclic ligand plays the role of the O,O-bridge (06JOM1713). 3,5-Pyridinedicarboxylic acid similarly forms N-bridged polymer **240**, while 2,5-pyridinedicarboxylic acid reveals the O,O-bridging function, **241**. 2,6-Pyridinedicarboxylic acid (H_2L) with dimethyltin(IV) dichloride in methanol at elevated temperature gives cyclic trimer $[\text{Me}_2\text{Sn}(2,6\text{-L})]_3$ or at room temperature-a ladder complex $[\text{Me}_2\text{Sn}(2,6\text{-L})]_2(\text{MeOH})_2$ (05ICA4575). With 2,6-pyridinedicarboxylate $[\text{Sn}(\text{n-Bu})_3(\text{OOC})_2\text{C}_5\text{H}_3\text{N}]_n$, $[\text{Sn}(\text{n-Bu})\text{Cl}(\text{OOC})_2\text{C}_5\text{H}_3\text{N}]$ and $[\text{Sn}(\text{CH}=\text{CH}_2)_2(\text{OOC})_2\text{C}_5\text{H}_3\text{N}]$ were prepared (05SA(A)1971, 06ASC(349)375, 06SSC376). The latter has a dimeric structure due to Sn-O intermolecular interactions. In the monomeric unit $\eta^2(\text{N,O})$ -coordination of the heterocyclic ligand occurs.



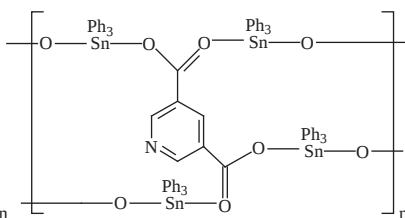
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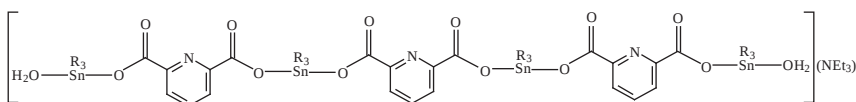
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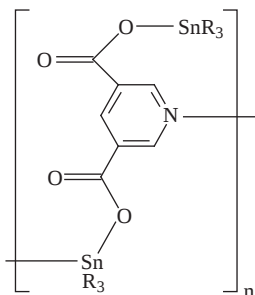
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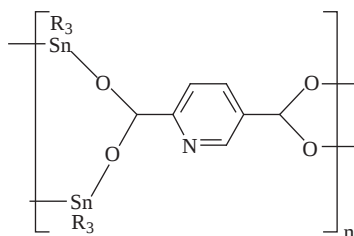
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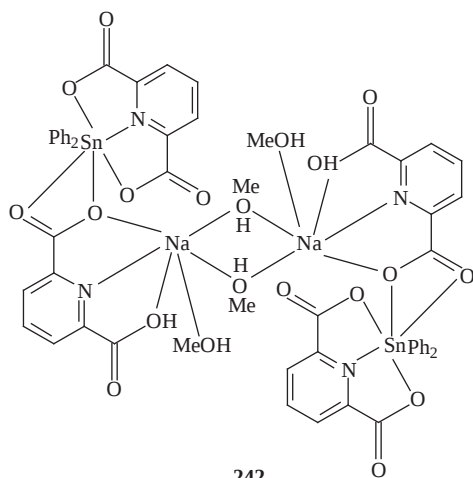
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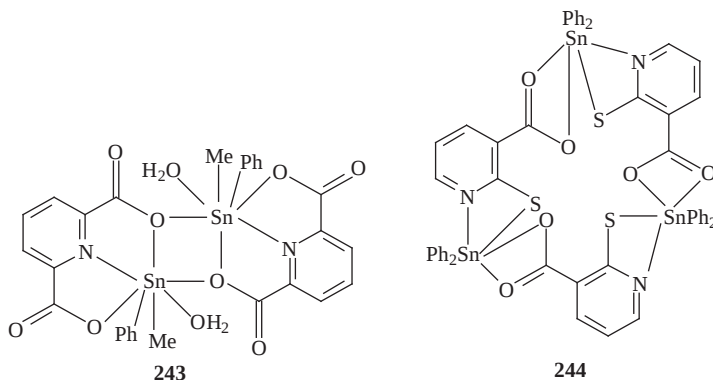


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2,6-Pyridinedicarboxylic acid (H_2L) reacts with triphenyltin chloride in the presence of sodium methoxide in methanol to yield

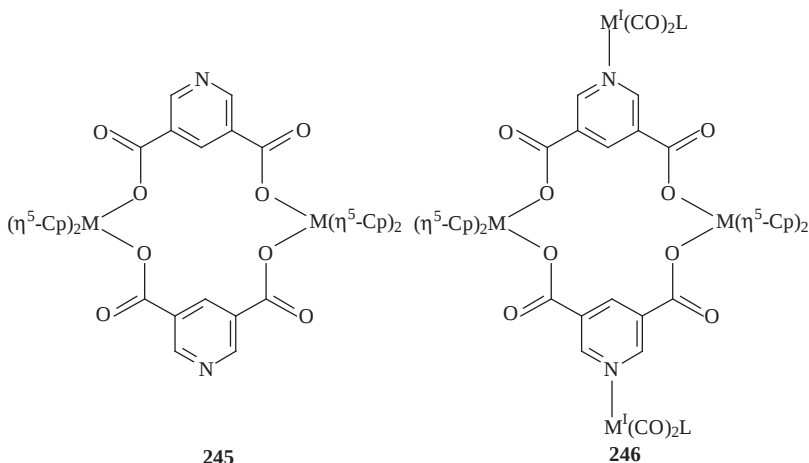
$[(\text{Ph}_2\text{Sn}(\text{L}))\text{Na}(\text{HL})(\text{MeOH})_2]_2$ **242** (08AOC19). With dimethylphenyltin iodide and potassium *i*-propoxide in *i*-propanol, the product is $[\text{Me}_2\text{Sn}(\eta^3(\text{N},\text{N},\text{O})\text{-L})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$. The dinuclear pyridine-2,6-dicarboxylato (L) complex $[\text{Sn}(\text{Me})(\text{Ph})(\text{L})(\text{H}_2\text{O})]_2 \cdot 2\text{CHCl}_3$ is seven-coordinate, **243**, with tetradentate coordination of the heterocyclic ligand performing a bridging function (07AX(E)810). 2-Mercaptopyridine reacts with diphenyltin dichloride and sodium ethoxide in methylene chloride to yield macrocyclic polychelate **244** (03JOM(678)148). Sodium bis(pyridylthio)acetate reacts with R_3SnCl ($\text{R} = \text{Me}, n\text{-Bu}, \text{Cy}, \text{Ph}$) to yield $[((\text{pyS})_2\text{CHCOO})\text{SnR}_3]_n$ with $\eta^1(\text{O})$ -coordination of the heterocyclic ligand (05POL995). Sodium bis(2-pyridylthio)acetate (NaL) enters a reaction with $\text{SnR}_n\text{Cl}_{4-n}$ ($\text{R} = \text{Me}, \text{Ph}$ and $n\text{-Bu}$, $n = 1-2$) to yield mononuclear complexes $[\text{R}_n\text{SnCl}_{4-n-1}\text{L}]$ where coordination occurs *via* the carboxylic moiety (05JOM1994). 2-(2-Pyridylmethylthio)benzoic acid (HL) reacts with R_2SnO ($\text{R} = \text{Et}, n\text{-Bu}$) in benzene to give dimers $[(\text{LSnR}_2)_2\text{O}]_2$ ($\text{R} = \text{Et}, n\text{-Bu}$) (07POL3743). Nitrogen and sulfur heteroatoms do not participate in coordination. One of the 2-pyridylcarboxylates serves as an $\eta^1(\text{O})$ -ligand, while the other bridges two tin sites by two oxygen atoms of the carboxyl group. 2-(4-Pyridylmethylthio)benzoic acid (HL) with Et_2SnO gives a dimer of the same composition but different structure with O,O-bridging and O,O-chelated carboxyl ligands, while $n\text{-Bu}_2\text{SnO}$ gives $[\text{SnL}_2(n\text{-Bu})]_2$ with two O,O-chelating carboxylate ligands. Both ligands also react with $(\text{Ph}_3\text{Sn})_2\text{O}$ to yield monomeric $[\text{Sn}(\text{L})\text{Ph}_3]$ with an $\eta^1(\text{O})$ -monodentate function of the carboxylate ligand for 2-(2-pyridylmethylthio)benzoic acid and a polymeric structure with N-bridging and simultaneous $\eta^1(\text{O})$ -coordination to the other tin center of 2-(4-pyridylmethylthio)benzoic acid.



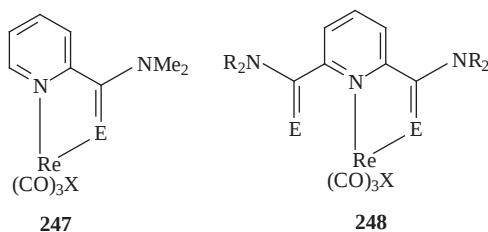


3.3.2 Titanium, zirconium, and rhenium

2-Pyridinecarboxylic acid and 6-methyl-2-pyridine carboxylic acid (HL) with $[(\eta^5\text{-Cp}^*)\text{TiCl}_3]$ in THF form chelates $[(\eta^5\text{-Cp}^*)\text{Ti}(\eta^2(\text{N,O})\text{-L})\text{Cl}]$ (07JOM1633). $[(\eta^5\text{-Cp}^*)\text{Ti}(\text{OMe})_3]$ with 2-picolinic acid in toluene they give chelates of different composition, $[(\eta^5\text{-Cp}^*)\text{Ti}(\eta^2(\text{N,O})\text{-L})_2(\text{OMe})]$, and both acids taken in excess give complexes where one of the heterocyclic ligands is $\eta^1(\text{O})$ -coordinated, $[(\eta^5\text{-Cp}^*)\text{Ti}(\eta^2(\text{N,O})\text{-L})_2(\eta^1(\text{O})\text{-L})]$. 2-Picolinic acid (HL) reacts with $[\text{Re}(\text{Cl})(\text{N}_2)(\text{CO})_2(\text{PPh}_3)_2]$ in methanol-benzene to yield $[\text{Re}(\eta^2(\text{N,O})\text{-L})(\text{N}_2)(\text{CO})(\text{PPh}_3)_2]$ (06JOM4153). Pyridine-3,5-dicarboxylic acid with $[(\eta^5\text{-Cp})\text{MCl}_2]$ ($\text{M} = \text{Ti, Zr}$) in the presence of triethylamine in THF gives dinuclear **245** (91JCS(D)1223). Products react with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ or $[\text{Ir}(\text{CO})_2(p\text{-MeC}_6\text{H}_4\text{NH}_2)\text{Cl}]$ in methylene chloride to give the heterotetranuclear **246** ($\text{M} = \text{Ti, Zr}$; $\text{M}^1 = \text{Rh, Ir}$). In contrast, pyridine-2,6-dicarboxylic acid with $[(\eta^5\text{-Cp})\text{MCl}_2]$ ($\text{M} = \text{Ti, Zr}$) in the presence of triethylamine gives mononuclear species $[(\eta^5\text{-Cp})\text{M}(2,6\text{-C}_5\text{H}_3\text{NCOO}(\text{COOH}))\text{Cl}]$ and $[(\eta^5\text{-Cp})\text{M}(2,6\text{-C}_5\text{H}_3\text{NCOO}(\text{COOH}))_2]$ ($\text{M} = \text{Ti, Zr}$), where chelation occurs via the carboxylate oxygen with retention of the hydrogen atom of the other carboxylic group (89ICA109). Pyridine-2,6-dicarboxylic acid with $[(\eta^5\text{-Cp})_2\text{TiMe}_2]$ gives the mononuclear five-coordinate complex $[(\eta^5\text{-Cp})_2\text{Ti}(\eta^2(\text{N,O})\text{-C}_5\text{H}_3\text{N}(\text{COO})_2)]$, where the coordination is *via* the carboxylic oxygen and pyridine nitrogen (86JOM(312)177). Complex $[(\eta^5\text{-Cp}^*)\text{Ti}(\text{Me})(\eta^3(\text{O,N,O})\text{-L})]$ ($\text{L} = 2,6\text{-pyridinedicarboxylate}$) reacts with water to yield $[(\eta^5\text{-Cp}^*)\text{Ti}(\eta^3(\text{O,N,O})\text{-L})_2\text{O}]$ and with isocyanides to yield iminoacyl derivatives $[(\eta^5\text{-Cp}^*)\text{Ti}(\eta^2\text{-MeCNR})(\eta^3(\text{O,N,O})\text{-L})]$ ($\text{R} = t\text{-Bu, } 2,6\text{-Me}_2\text{C}_6\text{H}_3$) (06JCS(D)2683). The starting compound is a building block for heterotetranuclear metallomacrocycles $[(\eta^5\text{-Cp}^*)\text{Ti}(\eta^3(\text{O,N,O})\text{-L})(\mu\text{-O})\text{M}(\eta^4\text{-cod})]_2$ ($\text{M} = \text{Rh, Ir}$) prepared $[\text{M}(\mu\text{-OH})(\eta^4\text{-cod})]_2$ ($\text{M} = \text{Rh, Ir}$). It also reacts with triflic acid in the presence of a base ($\text{L}^1 = \text{py, } 4\text{-}t\text{-Bupy}$) to yield cationic complexes $[(\eta^5\text{-Cp}^*)\text{Ti}(\eta^3(\text{O,N,O})\text{-L})(\text{L}^1)](\text{OTf})$ (07OM2896).



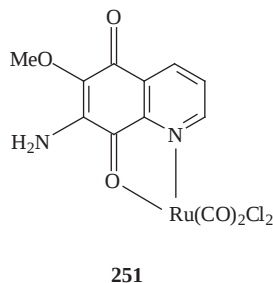
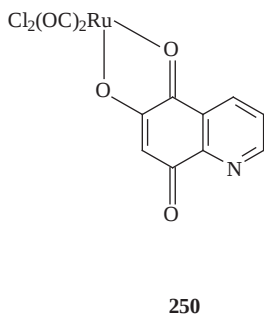
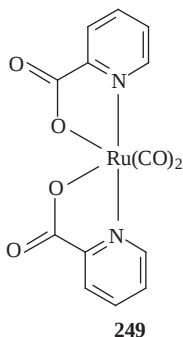
N,N-Dimethyl-2-pyridinecarboxamide, *N,N*-dimethyl-2-pyridinethioamide, *N,N,N',N'*-tetramethyl-2,6-pyridinedicarboxamide, *N,N,N',N'*-tetramethyl-2,6-pyridinedithioamide, *N,N,N',N'*-tetraethyl-2,6-pyridinedicarboxamide, and *N,N,N',N'*-tetraethyl-2,6-pyridinedithioamide react with $[\text{Re}(\text{CO})_5\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}$) in benzene to yield chelates **247** ($\text{E} = \text{O}, \text{S}$) and **248** ($\text{E} = \text{O}, \text{S}, \text{R} = \text{Me}, \text{Et}$) characterized by solution stereodynamics (00EJI383). *N*-Methyl-2-pyridinecarbothiamide (*L*) with $(\text{Et}_4\text{N})_2[\text{Re}(\text{CO})_3\text{Cl}_3]$ in methanol or with $[\text{Re}(\text{CO})_5\text{Cl}]$ in THF gives $[\text{Re}(\text{CO})_3(\eta^2(\text{N},\text{S})\text{-L})\text{Cl}]$ (04JOM4751).



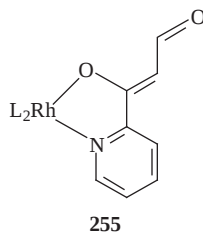
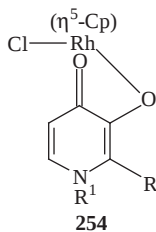
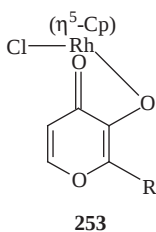
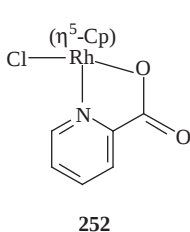
3.3.3 Ruthenium, rhodium, and iridium

2-Pyridinecarboxylic acid with $[\text{Ru}_3(\text{CO})_{12}]$ in toluene forms the chelate mononuclear complex **249** (99JOM(585)246). 2-Pyridinecarboxylic acid (*HL*) with $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ and further with tetraethylammonium perchlorate or tetra-*n*-butylammonium perchlorate yields $(\text{R}_4\text{N})[\text{Ru}(\eta^2(\text{N},\text{O})\text{-L})(\text{CO})_2\text{Cl}_2]$ ($\text{R} = \text{Et}, n\text{-Bu}$) (03JOM(665)107). The reaction of the same ligand with $[\text{Ru}(\text{bipy})(\text{CO})_2\text{Cl}_2]$ and silver nitrate in water and

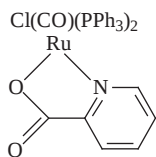
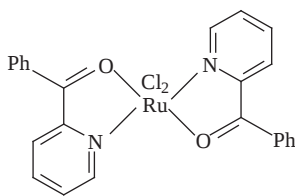
further with ammonium hexafluorophosphate leads to $[\text{Ru}(\text{bipy})(\eta^2(\text{N},\text{O})\text{-L})(\text{CO})_2](\text{PF}_6)$. 6-Methoxy-5,8-quinolinedione with $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ in THF forms $\eta^2(\text{O},\text{O})$ chelate **250**, whereas 7-amino-6-methoxy-5,8-quinolinedione gives $\eta^2(\text{N},\text{O})$ **251** (02IC1365). 4,6-Chloroquinoline-5,8-dione and 6-methoxybenzo[g]quinoline-5,10-dione (L) react with $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ in ethanol to yield $[\text{Ru}(\text{CO})_2\text{Cl}_2(\eta^2(\text{N},\text{O})\text{-L})]$ (07POL5527).



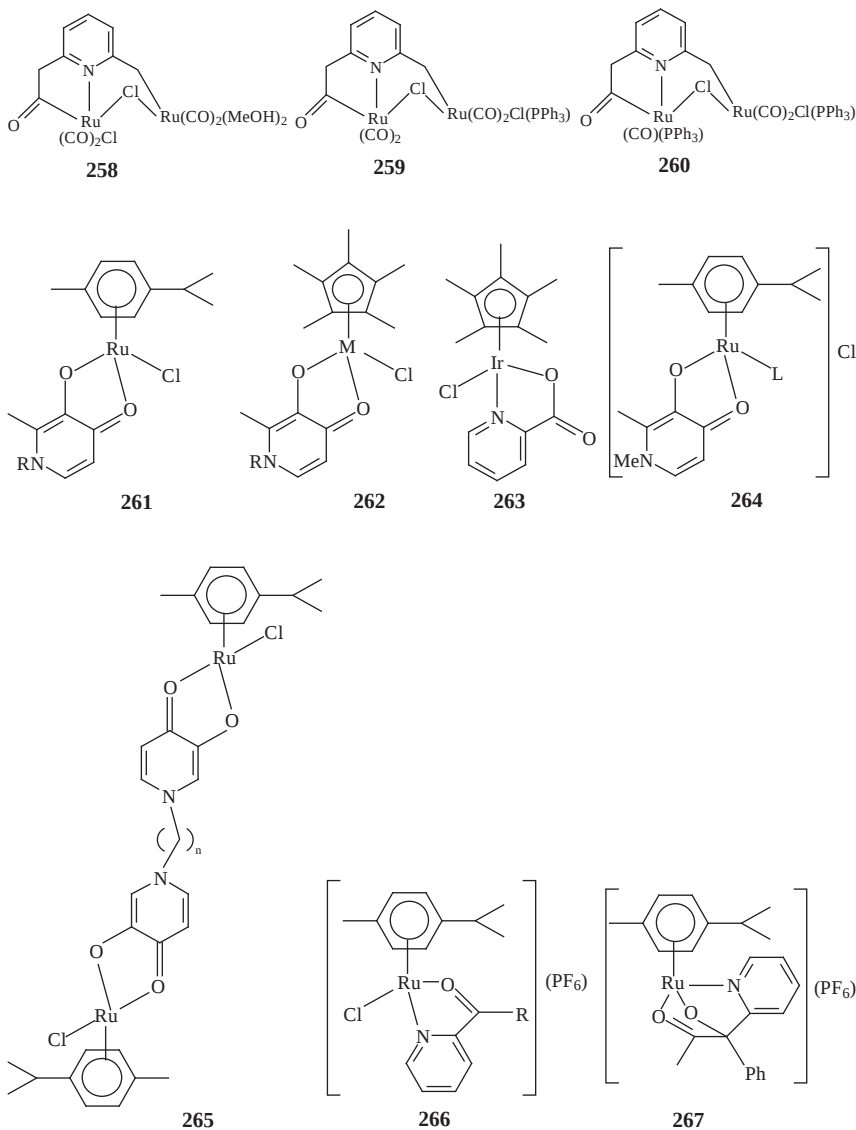
$[(\eta^6\text{-C}_6\text{H}_3\text{Me}_3\text{-1,3,5})\text{RuCl}_2]_2$ forms chelates with picolinic acid, pyrones, and pyridinones (93POL1599). Refluxing picolinic acid, pyrones, and pyridinones with $[(\eta^5\text{-Cp}^*)\text{RhCl}_2]_2$ in methanol gives **252**, **253** ($\text{R} = \text{Me}$, Et), and **254** ($\text{R} = \text{R}^1 = \text{Me}$, $\text{R} = \text{Et}$, H) (95JCS(D)3709). Pyridine-2-carboxylic acid, isoquinoline-1-carboxylic acid, and quinoline-2-carboxylic acid (LH) react with $[(\eta^4\text{-cod})\text{Ir}(\mu\text{-OMe})]_2$ to yield $[(\eta^4\text{-cod})\text{Ir}(\eta^2(\text{N},\text{O})\text{-L})]$ (00JOM(609)60). The products undergo oxidative addition with Ph_3SnH , Ph_3SiH , and $\text{C}_6\text{F}_5\text{SH}$. 1-(2'-Pyridyl)-(3-dimethylamine-1-propenone with $[(\eta^4\text{-cod})\text{Rh}(\mu\text{-OMe})]_2$ in the presence of traces of water forms **255** ($\text{L}_2 = \text{cod}$) containing the 1-(2'-pyridyl)-3-oxo-1-propenoxide ligand (02ICC245). Under carbon monoxide, **255** ($\text{L}_2 = (\text{CO})_2$) is formed. 2-Quinolinedicarboxylic acid (HL) and $[(\eta^5\text{-Cp})\text{Ru}(\text{AN})_3](\text{PF}_6)$ in the presence of 2-propen-1-ol in acetone give cationic $[(\eta^5\text{-Cp})\text{Ru}(\eta^2(\text{N},\text{O})\text{-L})]$ (06ASC(3439)375, 07JOM295) applied in numerous catalytic processes (04OL1873, 05AGE1730). Pyridine-2-acetic acid and 6-picolinic acid (HL) react with $[(\eta^4\text{-cod})\text{Ir}(\text{OMe})]_2$ in THF to yield $[(\eta^4\text{-cod})\text{Ir}(\eta^2(\text{N},\text{O})\text{-L})]$, the active catalysts for dehydrogenation of cyclooctane (08JOM1808).



The reaction of 2-benzoylpyridine with $[\text{Ru}(\text{H})(\text{Cl})(\text{CO})(\text{PPh}_3)_3]$ in DME is accompanied by the oxidation of the heterocyclic ligand to pyridine-2-carboxylate and the formation of chelate **256** (07POL2686). Quinoline-2-carboxylic acid forms $[\text{Ru}(\text{Cl})(\text{CO})(\text{PPh}_3)_2(\eta^2(\text{N},\text{O})-\text{L})]$ (07POL5120). With $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$, a simple chelation of 2-benzoylpyridine is observed to render **257**. $[(\eta^4\text{-cod})\text{Rh}(\text{L})]$ (HL = 1-phenyl-3-methyl-4-acetylpyrazol-5-one) interacts with 2-benzoylpyridine (L^1) yielding $[(\eta^4\text{-cod})\text{Rh}(\eta^1(\text{N})-\text{L}^1)(\text{Q}'')]$ in which the entering ligand acts as a N-monodentate donor (98JOM(566)187). 2-Acetylpyridine, 2-benzoylpyridine, and 2,2'-dipyridyl ketone (L) with *cis*- $[\text{M}(\text{PMe}_3)_2(\text{CO})_2(\text{Me})(\text{I})]$ (M = Fe, Ru) in the presence of sodium tetraphenylborate give $[\text{M}(\text{PMe}_3)_2(\text{CO})(\text{COMe})(\eta^2(\text{N},\text{O})-\text{L})](\text{BPh}_4)$ (98OM5025).

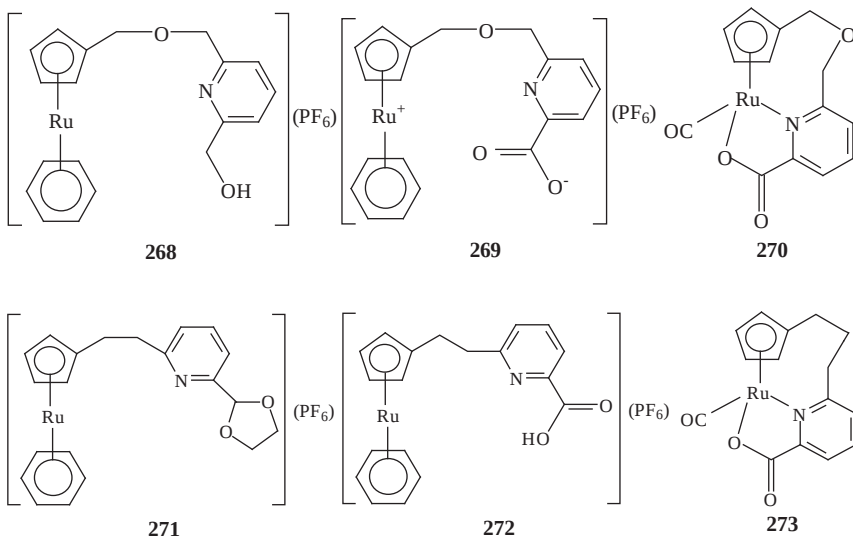
**256****257**

Pyridine-2,6-diyl-2-acetyl-6-methyl with C,N-coordination is created from 2,6-bis(chloromethyl)pyridine with $[\text{Ru}_3(\text{CO})_{12}]$ and further addition of methanol yields **258** and of triphenylphosphine to afford **259** (96CL773). Decarbonylation of **259** leads to **260**. Sodium salts of N-alkyl- and N-aryl-substituted 3-hydroxy-2-methyl-4-pyridones react with $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{Cl})]_2$ in methylene chloride to yield half-sandwich complexes **261** (R = Me, *n*-Pr, Ph, *o*-C₆H₄COOMe) (99ICA(294)62). Similarly, $[(\eta^5\text{-Cp}^*)\text{M}(\text{Cl})]_2$ yield **262** (M = Rh, Ir; R = Me, *n*-Pr, Ph, *o*-C₆H₄COOMe). Sodium pyridine-2-carboxylate forms the half-sandwich iridium(III) complex **263** (05EJI4840). Ruthenium **261** (R = Me) reacts with *n*-butylamine or triphenylphosphine to yield cationic **264** (L = *n*-BuNH₂, PPh₃). Similar are complexes $[(\eta^6\text{-C}_6\text{H}_3\text{Me}_3\text{-1,3,5})\text{Ru}(\text{Cl})(\text{L})]$ where HL is 2-methyl-3-hydroxypyran-4-one or pyridinone (96JCS(D)1399). Deprotonated bis(3-hydroxy-2-methyl-4-pyridinon-1-yl)alkanes (alkane = propane, hexane, dodecane) reacts with $[(\eta^6\text{-cymene})\text{RuRuCl}_2]_2$ to yield dinuclear complexes **265** (n = 3, 6, 12) (08OM2405). $[(\eta^6\text{-cymene})\text{Ru}(\eta^2\text{-N},\text{O}-\text{L})\text{Cl}](\text{PF}_6)$ **266** (R = Me, Ph) tend to π - π stacking in the crystalline phase. The derivative with R = Ph reacts with acetone in the presence of silver hexafluorophosphate by way of C-C coupling of the deprotonated methyl group of acetone and the ligand carbonyl group to yield **267** (06JCS(D)1963).

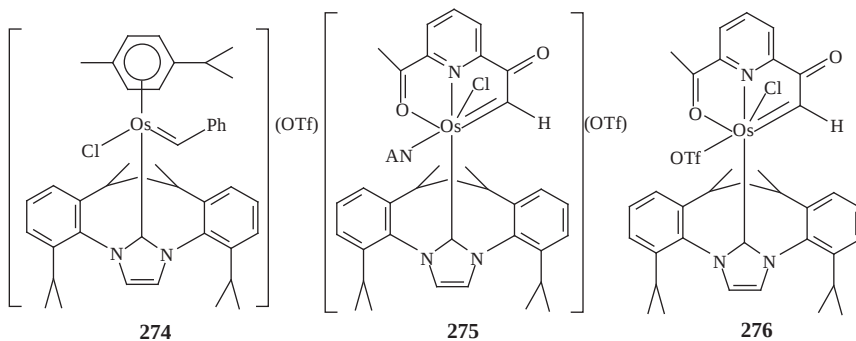


2,6-Pyridinedimethanol in the presence of sodium hydride reacts with $(\eta^5\text{-chloromethylcyclopentadienyl})(\eta^6\text{-benzene})\text{ruthenium(II)}$ hexafluorophosphate cation in DMF to yield the product of Cl-substitution **268** [08JOM551]. Oxidation of the OH-group using $\text{NaOCl}/\text{NaOCl}_2$ gives the carboxylate **269**. Under UV-light and carbon monoxide in acetonitrile

it gives **270**. A similar chain of transformations but with substitution of the chloride by the methylene carbon includes reaction of the 2-picoline derivative with the same ruthenium precursor in the presence of phenyl lithium in THF to yield cationic **271**. The acetal moiety can be cleaved using hydrochloric acid to carboxylic acid **272**. As before, carbonylation under UV-light in acetonitrile solution leads to the chelate-formation, **273**.

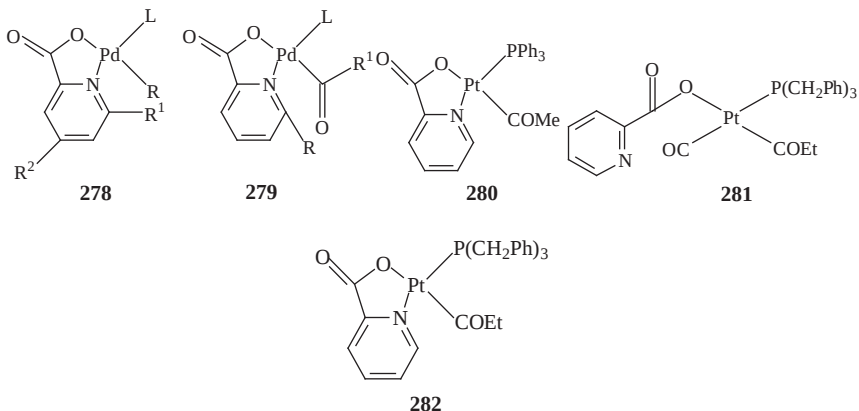


2,6-Diacetylpyridine reacts with half-sandwich **274** in acetonitrile by release of the arene moiety in the precursor, hydrogenation of the alkylidene ligand due to hydrogen migration from the methyl group in one of the acetyl substituents to yield cationic **275** (07OM3082). In methylene chloride, the process occurs in a similar way, although neutral **276** is formed.

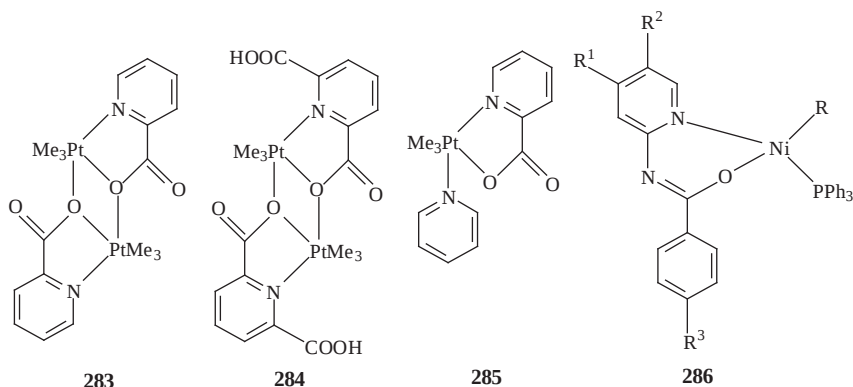


3.3.4 Nickel group

Thallium(I) pyridine-2-carboxylate reacts with $[\text{Pd}(\text{I})(\text{R})(\text{PPh}_3)_2]$ to give chelate complex **277** ($\text{R} = \text{Me}, \text{Ph}$; $\text{L} = \text{PPh}_3$, $\text{R}^1 = \text{R}^2 = \text{H}$) (95JCS(D)2159). A series **278** ($\text{R} = \text{Me}$, $\text{L} = \text{P}(\text{C}_6\text{H}_{11})_3$, PMePh_2 , PMe_2Ph , $\text{P}(i\text{-Pr})_3$, $\text{P}(\text{OMe})_3$, $\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3$, $\text{P}(\text{CH}_2\text{Ph})_3$, py , 4-Mepy, NMe_2Ph ; $\text{R}^1 = \text{R}^2 = \text{H}$) follows from thallium(I) pyridine-2-carboxylate, $[\text{Pd}(\text{Me})(\text{SMe}_2)(\mu\text{-I})_2]$, and the corresponding ligand L . Complexes **278** ($\text{R} = \text{Me}$; $\text{L} = \text{PPh}_3$, PMePh_2 , PMe_2Ph , $\text{P}(\text{CH}_2\text{Ph})_3$, py , 4-Mepy; $\text{R}^1 = \text{R}^2 = \text{H}$) can be carbonylated followed by insertion of carbon monoxide and formation of **279** ($\text{R} = \text{H}$, $\text{R}^1 = \text{Me}$) with the same set of ligands. A platinum(II) analogue with $\text{L} = \text{PPh}_3$ can be prepared similarly (94JCS(D)415). Thallium(I) pyridine carboxylates react with $[(\eta^4\text{-cod})\text{Pd}(\text{Me})\text{Cl}]$ or $[\text{Pd}(\text{Ph})(\text{I})(\text{tmen})]$ and a range of phosphine ligands (L) to yield chelates **278** ($\text{R} = \text{Me}$, $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$, NO_2 ; $\text{L} = \text{PPh}_3$, PMePh_2 , $\text{P}(\text{CH}_2\text{Ph})_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$; $\text{R} = \text{Ph}$, $\text{R}^1 = \text{H}$, Me , $\text{R}^2 = \text{H}$, NO_2 ; $\text{L} = \text{PPh}_3$, PMePh_2 , $\text{P}(\text{C}_6\text{H}_{11})_3$, PEt_3) (96JCS(D)2197). Under carbon monoxide complexes with the 6-methyl group in the pyridine ring undergo insertion to yield **279** ($\text{R} = \text{R}^1 = \text{Me}$, $\text{L} = \text{PPh}_3$, $\text{P}(\text{CH}_2\text{Ph})_3$; $\text{R} = \text{Me}$, $\text{R}^1 = \text{Ph}$, $\text{L} = \text{PPh}_3$). Sodium pyridine-2-carboxylate (NaL) or potassium 8-hydroxyquinolate (KL) with $[\text{Pt}(\text{Me})\text{I}(\text{PPh}_3)_2]$ and thallium hexafluorophosphate or silver tetrafluoroborate forms $[\text{Pt}(\text{Me})(\eta^2(\text{N},\text{O})\text{-L})(\text{PPh}_3)]$ (94JCS(D)415). Thallium(I) pyridine-2-carboxylate (TIL) with $[(\eta^4\text{-cod})\text{Pt}(\text{Me})\text{Cl}]$ and $\text{P}(\text{CH}_2\text{Ph})_3$ or $\text{P}(\text{C}_6\text{H}_{11})_3$ (L^1) in acetonitrile yields $[\text{Pt}(\text{Me})(\eta^2(\text{N},\text{O})\text{-L})(\text{L}^1)]$ ($\text{L}^1 = \text{P}(\text{CH}_2\text{Ph})_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$). $[\text{Pt}(\text{Me})(\eta^2(\text{N},\text{O})\text{-L})(\text{PPh}_3)]$ in the presence of pyridine or 4-methylpyridine (L^1) gives $[\text{Pt}(\text{Me})(\eta^2(\text{N},\text{O})\text{-L})(\text{L}^1)]$ ($\text{L}^1 = \text{py}$, 4-Mepy). $[\text{Pt}(\text{H})\text{Cl}(\text{PPh}_3)_2]$ reacts with silver tetrafluoroborate, then ethylene and sodium pyridine-2-carboxylate (NaL) to yield $[\text{Pt}(\text{Et})(\eta^2(\text{N},\text{O})\text{-L})(\text{PPh}_3)]$. $[(\eta^4\text{-cod})\text{Pt}(\text{Et})\text{I}]$ with thallium pyridine-2-carboxylate (TIL) and then $\text{P}(\text{CH}_2\text{Ph})_3$ affords $[\text{Pt}(\text{Et})(\eta^2(\text{N},\text{O})\text{-L})(\text{P}(\text{CH}_2\text{Ph})_3)]$. $[\text{Pt}(\text{R})(\eta^2(\text{N},\text{O})\text{-L})(\text{PPh}_3)]$ ($\text{R} = \text{Me}$, Et) under carbon monoxide provide insertion products **280**. Similarly, $[\text{Pt}(\text{Et})(\eta^2(\text{N},\text{O})\text{-L})(\text{P}(\text{CH}_2\text{Ph})_3)]$ give a mixture **281** and **282**.



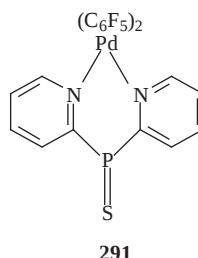
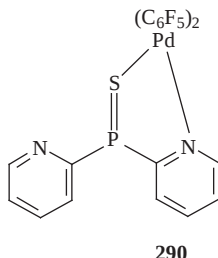
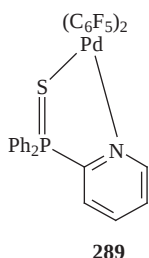
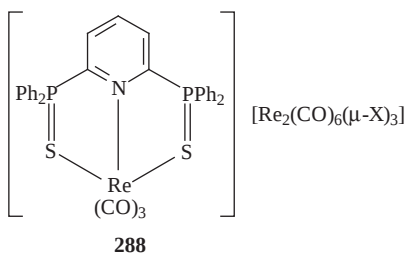
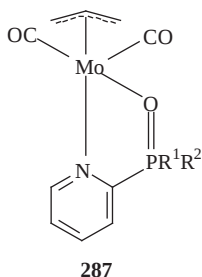
Pyridine-2-carboxylic acid reacts with trimethylplatinum(IV) sulfate to yield dinuclear **283** (98POL2543). Pyridine-2,6-dicarboxylic acid with (pentane-2,4-dionato)trimethylplatinum(IV) gives **284**. Complex **283** on heating with pyridine is converted to mononuclear **285**. Sodium salts of N-(2-pyridyl)benzamides react with $[\text{Ni}(\text{Cl})(\text{naphthyl})(\text{PPh}_3)_2]$ or $[\text{Ni}(\text{Cl})(\text{Ph})(\text{PPh}_3)_2]$ to yield the N,O-chelated **286** ($\text{R} = \text{naphthyl}$, $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$, $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{R}^3 = \text{H}$, $\text{R}^1 = \text{R}^3 = \text{H}$, $\text{R}^2 = \text{NO}_2$, $\text{R}^1 = \text{R}^2 = \text{H}$, $\text{R}^3 = \text{NO}_2$, $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{NO}_2$, $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{R}^3 = \text{NO}_2$; $\text{R} = \text{Ph}$, $\text{R}^1 = \text{R}^3 = \text{H}$, $\text{R}^2 = \text{NO}_2$, $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{R}^3 = \text{NO}_2$) (04JOM917).



3.4 Phosphine oxide and sulfide pyridines

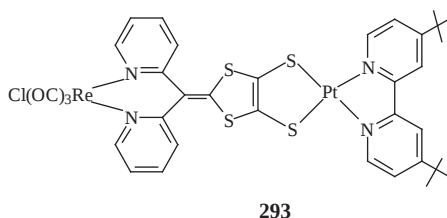
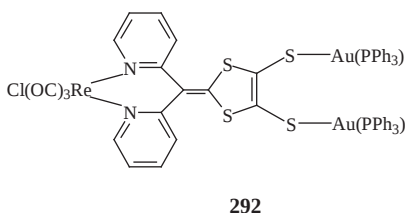
Bis(2-pyridyl) phenyl phosphine oxide and sulfide react with $[\text{Mo}(\text{CO})_6]$ or $[(\eta^4\text{-nbd})\text{Mo}(\text{CO})_4]$ to yield $\eta^3(\text{N},\text{N},\text{O}(\text{S}))$ chelates $[\text{Mo}(\text{CO})_3(\text{L})]$ (97IC44). 2-Pyridylphosphine oxides OPPyPh_2 , OPPy_2Ph , and OPPy_3 react with $[(\eta^3\text{-allyl})\text{Mo}(\text{Br})(\text{CO})_2(\text{AN})_2]$ to yield $\eta^2(\text{N},\text{O})$ -complexes **287** ($\text{R}^1 = \text{R}^2 = \text{Ph}$; $\text{R}^1 = \text{py}$, $\text{R}^2 = \text{Ph}$; $\text{R}^1 = \text{R}^2 = \text{py}$) (00EJI1031). 2,6-Bis(diphenylphosphinosulfide)pyridine with $[\text{Re}(\text{CO})_5\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) gives **288** where the ligand is terdentately coordinated (98POL3981). A pyridine ligand bearing a 2-diphenylphosphine sulfide group with $(n\text{-Bu}_4\text{N})_2[\text{Pd}_2(\mu\text{-Br})_2(\text{C}_6\text{F}_5)_4]$ in ethanol forms $\eta^2(\text{N},\text{S})$ -coordinated **289** (95OM3058, 97IC5428). When the phenyl ligand is substituted by a pyridyl moiety, the same reaction gives a mixture of the $\eta^2(\text{N},\text{S})$ - and $\eta^2(\text{N},\text{N})$ -coordinated isomers, **290** and **291**. The same situation is observed in the products of the reaction of the latter ligand with $[(\eta^4\text{-cod})\text{Pd}(\text{C}_6\text{F}_5)_2]$ in methylene chloride where the isomers have the composition $[\text{Pd}(\text{C}_6\text{F}_3\text{Cl}_2)_2(\text{SP}(\text{C}_5\text{H}_4\text{N})_2\text{Ph})]$. A mixture of isomers is also obtained when tris(2-pyridyl)phosphine sulfide reacts with

$(n\text{-Bu}_4\text{N})_2[\text{Pd}_2(\mu\text{-Br})_2(\text{C}_6\text{F}_5)_4]$ in ethanol. Similar complexes are formed by a series of phosphine oxide analogues (97OM770). 2-Pyridyldiphenylphosphine sulfide with $[\text{Pd}(\text{fluoromesityl})_2(\text{SMe}_2)_2]$ gives $[\text{Pd}(\text{fluoromesityl})_2(\eta^2(\text{S},\text{N})\text{-SPPH}_2\text{py})]$ (04EJ12326). Bis(2-pyridyl)phenylphosphine oxide also produces chelate $[\text{Pd}(\text{fluoromesityl})_2(\eta^2(\text{O},\text{N})\text{-OPPhpy}_2)]$.



3.5 Bis(2-pyridyl)-1,2-dithiolenes

4,5-Bis(2-cyanomethylthio)-2-bis(2-pyridyl)methylene-1,3-dithiole reacts with cesium hydroxide, further with $[\text{Au}(\text{PPh}_3)\text{Cl}]$ or $[\text{Pt}(4,4'\text{-t-Bu}_2\text{bi-py})\text{Cl}_2]$, and then with $[\text{Re}(\text{CO})_5\text{Cl}]$ in toluene to yield heterodinuclear **292** and **293** where rhenium is coordinated to the nitrogen and gold (platinum) to the sulfur counterpart of the ligand (08OM126).



4. CONCLUSION

1. Late transition metal complexes of polypyridines are rare; a number includes cyclometalated gold(III) compounds. Rare earth metals tend to transform polypyridines into radical-anion or dianion forms, or even structurally modify them by activation.
2. Pyridylphosphinines and biphosphinines reveal $\eta^1(\text{P})$ -chelating and bridging. The $\mu_2\text{-P}$ bridging function is rare. The case where the metal-chelate unit forms a fully π -delocalized aromatic system should be noted.
3. Hydroxypyridines are characterized by O- and N-monodentate coordination and N,O-chelation in both pyridinol and pyridinone tautomeric forms and bridging including one and two ligands, where in the latter case oxygen centers bridge different metal atoms. Pyridyl-2 alcohols are characterized mainly by N,O-chelation, and for pyridine-2,6-dialcohols O,O- and O,N,O-chelates are widespread. Dipyridyl ketones are characterized mainly by N,O-coordination where one of the pyridine rings is excluded, and N,N-coordination. For N,O,N-coordination, chemical modification of the ketone ligand is required.
4. Pyridine-2-thionates provide a much wider variety of coordination modes in complexes, including apart from routine monodentate, chelate, and bridging structures, complicated bridging species, including those with cleavage of the carbon – sulfur bond.
5. Pyridyl carboxylates tend to form oligomeric structures on coordination with organotin compounds. Generally, they show O-monodentate, N,O-chelate, O,O- and N,O-bridging.
6. Less common ligands include pyridyl phosphine oxides and sulfides, for which PE and PE₂ (E = O, S) chelates are typical, and bis(2-pyridyl)-1,2-dithiolenes, for which N- and S-donor functions are separated.

LIST OF ABBREVIATIONS

Ac	acetyl
acac	acetylacetonate
Ad	adamantyl
Alk	alkyl
AN	acetonitrile
Ar	aryl
bipy	2,2'-bipyridine

Bu	butyl
cod	1,5-cyclooctadiene
COE	cyclooctene
Cp	cyclopentadienyl
Cp'	variously substituted cyclopentadienyls
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
dba	dibenzoylacetonate
DME	dimethoxyethane
DMF	dimethylformamide
DMSO	dimethylsulfoxide
dppe	bis(diphenylphosphino)ethane
dppf	Bid(diphenylphosphino)ferrocene
dppm	bis(diphenylphosphino)methane
Et	ethyl
Me	methyl
Nap	naphthyl
nbd	norbornadiene
OTf	triflate
Ph	phenyl
Pr	propyl
phen	1,10-phenanthroline
py	pyridine
terpy	2,2':6',2''-terpyridine
tfb	tetrafluorobenzobarrelene
THF	tetrahydrofuran
THT	tetrahydrothiophene
TMEDA	tetramethylethylenediamine
tmen	$\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2$
Tol	tolyl

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