SYNTHESIS OF HETEROCYCLIC COMPOUNDS FROM CYCLOHEXANE-1,3-DIONES (REVIEW)

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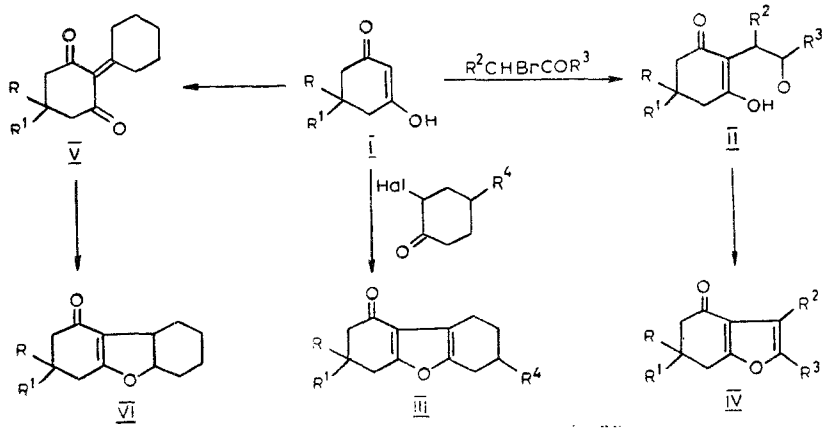
The literature data on the synthesis of partially hydrogenated heterocyclic compounds containing a 3-oxocyclohexene structural fragment condensed with five-, six-, or seven-membered oxygen-, nitrogen-, and sulfur-containing heterorings from cyclohexane-1,3-diones and their derivatives are examined in this review.

The well-known trend of intensive development of the chemistry of heterocyclic compounds is also finding lively expression in the publication of an ever increasing number of studies devoted to the synthesis of heterocycles from cyclohexane-1,3-diones (I) and their simplest derivatives. Only the general schemes for the synthesis of heterocyclic compounds containing, as a rule, a common structural fragment – 3-oxocyclohexene – are examined in the present review, in which the literature up to January 1, 1973, is included. All of the material in this review has been systematized with respect to the classes of heterocycles.

Benzofurans and Dibenzofurans

The most universal and convenient method for the synthesis of benzofurans (III, IV) from cyclohexane-1,3-diones (I) is reaction of the latter with α-halo ketones [1-10]. In the case of α-bromoethyl ketones, the first step is alkylation in the 2-position to give III, while aldol condensation is the first step in the case of α-halocyclohexanones [4], α-keto-β-bromobutyric acid, and α-chloroacetoacetic ester [3]. However, 2-bromocyclobutanone reacts with dimedone (Ib) to give cyclopropyl 5,5-dimethyl-1,3-dioxo-2-cyclohexyl ketone [11]. 2-Propargylcyclohexane-1,3-dione, obtained from cyclohexane-1,3-dione (Ia) and propargyl bromide by the action of zinc carbonate, was converted [12] to 2-methyl-4-oxo-4,5,6,7-tetrahydrobenzofuran (IV, $R^2=R^3=H$).



Here and subsequently, a $R=R^1=H$; b $R=R^1=CH_3$; c $R=H$, $R^1=C_6H_5$; d $R=H$, $R^1=CH_3$

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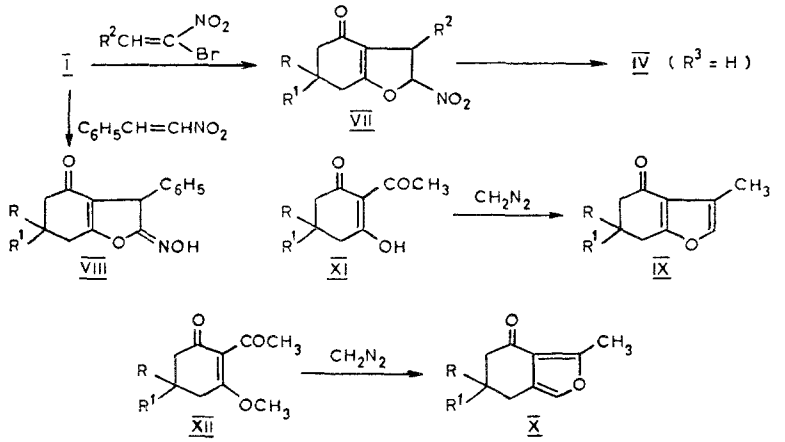
The products (V) of the crotonic condensation of diketones I with cyclohexanone give decahydrodibenzofurans (VI) when they are heated with phosphoric acid [13].

Perekalin and co-workers [14-17] have shown that cyclohexane-1,3-diones (I) react with 1-bromo-1-nitroalkenes in the presence of basic agents to give 2-nitro-4-oxo-2,3,4,5,6,7-hexahydrobenzofurans (VII), whereas, as a result of denitration, they react with excess base to give 4,5,6,7-tetrahydrobenzofurans IV (R^3=H). Reaction of dimedone (Ib) with ω-nitrostyrene gives 2-isonitroso-3-phenyl-4-oxo-4,5,6,7-tetrahydrobenzofuran (VIII) [18], which refutes the structures proposed earlier in [19-21].

Benzofuran derivatives (IX, X) were obtained as a result of reactions of 2-acetylcyclohexane-1,3-diones (XI) [22, 23] and their enol ethers (XIIa) [24] with diazomethane:

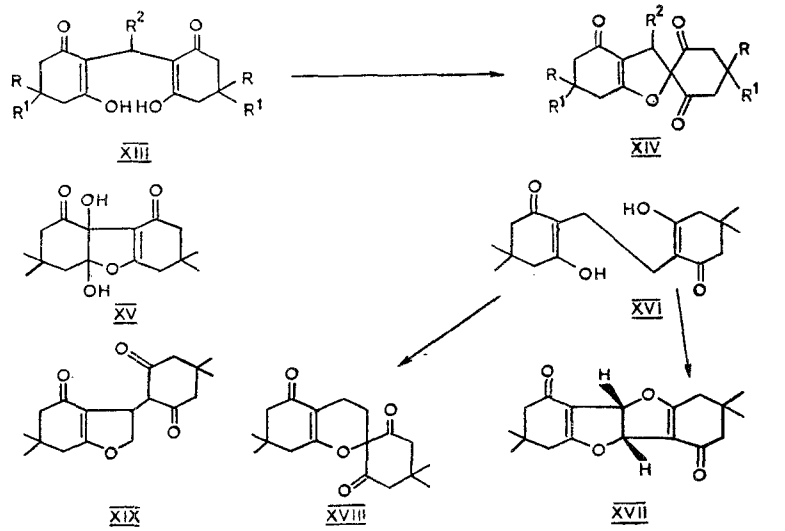


The possibilities of the preparation of spirans XIV – griseofulvin analogs – from bis(1,3-dioxo-2-cyclohexyl)methanes XIII have been studied in detail. Spirans XIV were obtained from the disodium salt of tetraketone XIII and iodine [25] and also by bromination of ketone XIII in chloroform [26] or in acetic acid [27]. The latter method is the most universal and convenient method. Spirans XIV are also formed by oxidation of ketones XIII with iron (III) hexacyanoferrate [28, 29] or by anodic oxidation of dimedone [30].

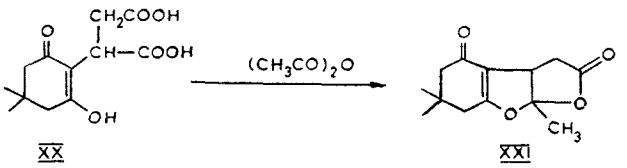
It has been shown [31] that the oxidation of dimedone (Ib) with hydrogen peroxide in alkaline media gives the diol three-ring form of 2-hydroxybisdimedone (XV).

Oxidation of 1,2-bis(1,3-dioxo-5,5-dimethyl-2-cyclohexyl)ethane (XVI) with oxygen gives XVII, while oxidation with iron (III) hexacyanoferrate gives spiran XVIII [32].

Glycolaldehyde [33] and monochloroacetaldehyde [34] react with dimedone (Ib) to give 3-(1,3-dioxo-5,5-dimethyl-2-cyclohexyl)-4-oxo-6,6-dimethyl-2,3,4,5,6,7-hexahydrobenzofuran (XIX).



Less common methods for the synthesis of benzofuran derivatives from diketones I are also known. Thus, 2-phenyl-4-oxo-6,6-dimethyl-4,5,6,7-tetrahydrobenzofuran was obtained by treatment of 2-bromodimedone with copper phenylacetylide in dimethylformamide (DMF) [35]. Alkaline hydrolysis of the product of condensation of cyclohexane-1,3-dione (Ia) with tetracyanoethylene gives 2-carbamido-3-cyano-4-oxo-4,5,6,7-tetrahydrobenzofuran [36]. Three-ring system XXI was obtained by the action of acetic anhydride on substituted succinic acid XX [37].

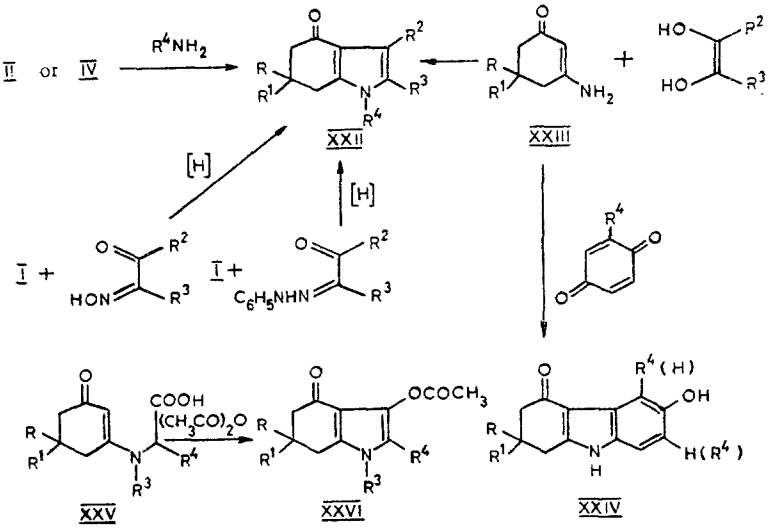


XX XXI

Indoles and Carbazoles

The most general and universal method for the synthesis of 4-oxo-4,5,6,7-tetrahydroindoles (XXII) from I is C-alkylation of the latter with α-bromo ketones and subsequent treatment of 1,4-diketones II or their cyclization products – benzofurans IV – with ammonia or primary amines [1, 10, 12, 38]. Dibenzofurans III are similarly converted to carbazole derivatives [38]. 3-Unsubstituted 2-methyl-4-oxo-4,5,6,7-tetrahydroindoles are conveniently obtained by the action of amines on 2-propargylcyclohexane-1,3-dione in the presence of copper (I) chloride [12].

Cyclohexane-1,3-diones are extensively used as the ketone component for the Knorr synthesis of pyrroles. α-Isonitroso ketones are most often used for the generation of the α-amino ketone component in the reduction process [20, 39-41], but it has recently been shown [42] that better results are achieved when α-diketone monophenylhydrazones are used. The possibility of the direct use of N-monosubstituted α-amino ketones was demonstrated by the preparation of indole XXII ($R^2=R^3=R^4=C_6H_5$) from diketones I and α-phenylaminobenzyl phenyl ketone [43]. Indoles XXII can also be obtained with equal success from 3-amino-2-cyclohexen-1-ones (XXIII) and α-hydroxy ketones [44, 45].



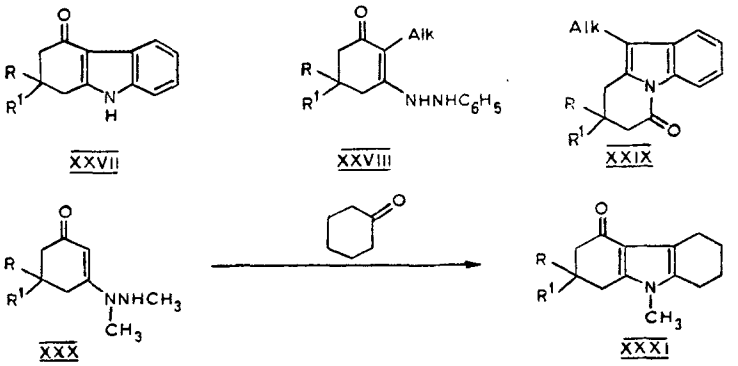
1,2,3,4-Tetrahydro-4-oxo-6-hydroxycarbazoles (XXIV) were obtained as a result of the addition of enamines XXIII to p-quinones [46].

Enamines XXV, obtained from diketones I and α-amino acids, including N-monosubstituted acids, are readily cyclized [47] under the influence of acetic anhydride to 3-acetoxy-4-oxo-4,5,6,7-tetrahydroindoles (XXVI).

2,3-Unsubstituted 4-oxo-4,5,6,7-tetrahydroindoles were obtained [48] in reactions of diketones I with acetals of N-monosubstituted aminoacetaldehydes.

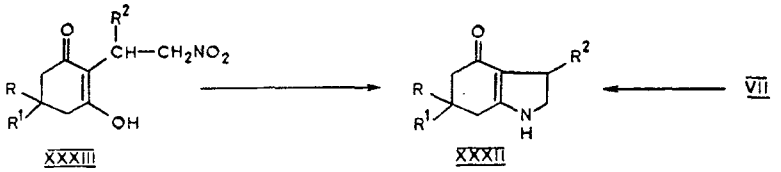
Cyclohexane-1,3-dione monophenylhydrazones undergo the Fischer reaction to give 4-oxo-1,2,3,4-tetrahydrocarbazoles (XXVII) [50-52]. Benzo[b]pyrrocoline derivatives (XXIX) are obtained from 2-alkylcyclohexanedione monophenylhydrazone XXVIII in this case [51]. Enehydrazines XXX, obtained from cyclohexane-1,3-diones and N,N'-dimethylhydrazine, react with cyclohexanones, including 3-ketosteroids, in the presence of acids to give octahydrocarbazoles XXXI [53].

9-Methyl-4-oxo-1,2,3,4-tetrahydrocarbazoles are the main products of the photochemical transformation of 3-(N-methylanilino)-2-cyclohexen-1-ones, while the N-phenyl derivatives give 5-hydroxy-3,4-hydrobenzazocines [49].



XXVII XXVIII XXIX XXX XXXI

4-Oxo-2,3,4,5,6,7-hexahydroindoles (XXXII) are obtained [19, 54, 55] by reduction of 2-(β-nitroethyl)-cyclohexane-1,2-diones (XXXIII). Transheterocyclization to give hexahydroindoles XXXII occurs during the hydrogenation of nitrobenzofurans VII in methanol on Raney nickel [16, 17, 56]. However, when nitro derivatives VII are refluxed in the presence of a Raney nickel catalyst in ethanol, XXXII are dehydrogenated to tetrahydroindoles XXII ($R^3=R^4=H$) [17].

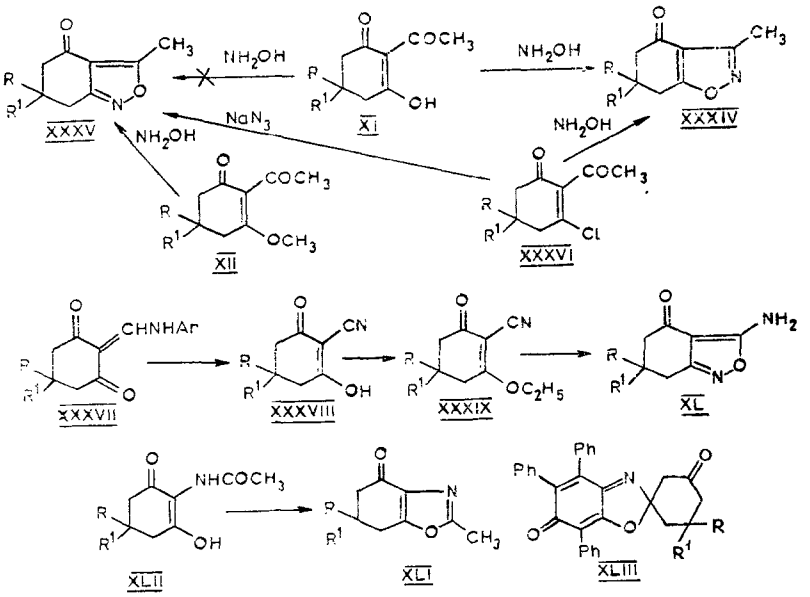


XXXIII XXXII VII

4-Oxo-7-amino-1,2,3-4-tetrahydrocarbazole was obtained by hydrogenation of 2-(2,4-dinitrophenyl)-cyclohexane-1,3-dione [52].

Benzisoxazoles and Benzoxazoles

2-Acetylcyclohexane-1,3-diones (XI) have been used for the preparation of 4-oxo-4,5,6,7-tetrahydrobenzisoxazoles. One might expect the formation of two isomers – indoxazene derivatives (XXXIV) and anthranil derivatives (XXXV) – in the reaction of hydroxylamine with triketones XI and with any unsymmetrical cis-fixed enol form of a β-diketone. It has been shown [57-59] that the reaction proceeds structurally selectively to give exclusively isomer XXXIV. The electrophilic center in the ethers of enol forms XII is in the 3-position, and only 4-oxo-4,5,6,7-tetrahydroanthranil derivatives (XXXV) are formed by the action of hydroxylamine, while 3-chloro-2-acetyl-2-cyclohexen-1-ones (XXXVI) give 4-oxo-4,5,6,7-tetrahydro-



XXXV XI XXXIV XII XXXVI XXXVII XXXVIII XXXIX XL XLII XLI XLIII

indoxazene (XXXIV) [59-61]. Tetrahydroanthranil XXXV is also obtained by reaction of chloro ketone XXXVI with sodium azide [62].

The reaction of 2-anilinomethylenecyclohexane-1,3-diones (XXXVII) with hydroxylamine gives [63, 64] 2-cyanocyclohexane-1,3-diones (XXXVIII), the ethers of the enols (XXXIX) of which react with hydroxylamine to give 3-aminoanthranils (XL). The preparation of 4-oxo-4,5,6,7-tetrahydroindoxazene in the reaction of 2-(m-anisidinomethylene)cyclohexane-1,3-dione with hydroxylamine was noted in [65].

The formation of benzoxazole derivatives (XLI) was observed [66] only when 2-acetamidocyclohexane-1,3-diones (XLII) were refluxed in acetic anhydride.

Enamines obtained from cyclohexane-1,3-diones and 2,4,5-triphenyl-6-aminoresorcinol are cyclized during oxidation [67] to 6,3'-dioxo-4,5,6-triphenyl-6H-spiro(benzoxazole-2,1'-cyclohexanes) (XLIII).

Indazoles

A large number of 4-oxo-4,5,6,7-tetrahydroindazoles have been obtained in the reaction of 2-acylcyclohexane-1,3-diones and their enol ethers and enamines with hydrazines [57, 58, 60, 62, 65, 68-76]. The reaction was first realized in [68] and was subsequently studied in greatest detail in the cases of the readily accessible 2-acetylcyclohexanediones (XI) and their fixed derivatives (XII, XXXVII, etc.) It has been proved [58, 59, 74] that of the two possible structurally isomeric indazoles, XLV and XLVI, in reactions with monoarylhydrazines, triketones XI give precisely 1-aryl-3-methyl-4-oxo-4,5,6,7-tetrahydroindazoles (XLV, $R^2 = CH_3$), and intermediate arylhydrazones XLIV have been isolated and characterized [74]. 2-Aryl-4-oxo-4,5,6,7-tetrahydroindazoles XLVI were obtained from ethers XII and arylhydrazines [59, 60, 76], while arylindazoles XLV were obtained from XXXVI [62]. A mixture of isomeric tetrahydroindazoles is formed in the reactions of XI with alkylhydrazines [75, 77].

3-Unsubstituted tetrahydroindazoles (XLV, $R^2 = H$) are primarily obtained [65, 70, 72, 78] by trans amination of 2-arylaminomethylenecyclohexanediones (XXXVII) – the products of the reaction of I with the ethyl esters of N-arylformimidic acid or with N,N'-diarylformamidines [70, 79-81] – with arylhydrazines and subsequent cyclization of the intermediate 2-hydrazinomethylenecyclohexanediones (XLIV, $R^2 = H$).

2-Cyano-3-ethoxy-5,5-dimethyl-2-cyclohexen-1-one (XXXIXb) reacts with hydrazine and phenylhydrazine to give the corresponding 3-amino-4-oxo-6,6-dimethyl-4,5,6,7-tetrahydroindazoles (XLVII) [64].

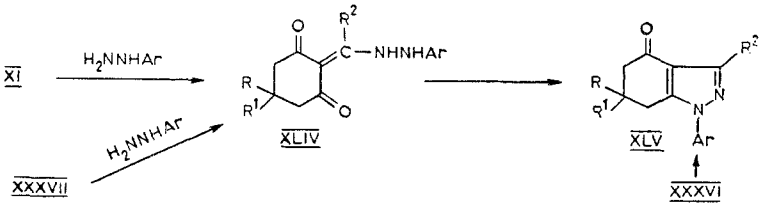
1-Amino-3-methyl-4-oxo-4,5,6,7-tetrahydroindazoles (XLVIII) are formed instead of the expected N-unsubstituted indazoles in the reaction of indoxazenes XXXIV with hydrazine. Nitrosation of XLVIII gives 1,1-bis(3,6,6-trimethyl-4-oxo-4,5,6,7-tetrahydroindazole) [82, 83].

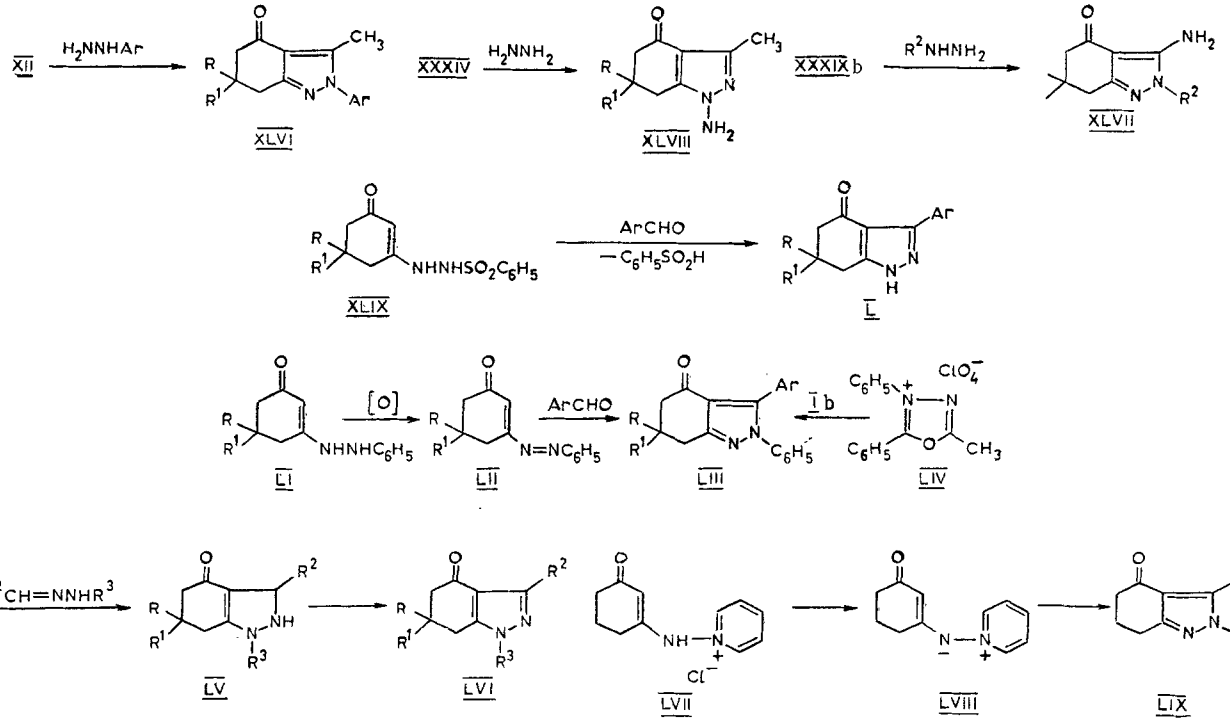
General methods for the preparation of 3-aryl-4-oxo-4,5,6,7-tetrahydroindazoles, the synthesis of which from 2-aroylcyclohexane-1,3-dione is markedly hampered in veiw of the limited accessibility of the latter, have been proposed [84, 85]. N-Unsubstituted 3-aryl-4-oxo-4,5,6,7-tetrahydroindazoles (L) have been obtained [84] from aromatic aldehydes and 3-phenylsulfonylhydrazino-2-cyclohexen-1-ones (XLIX). Phenylazocyclohexenones LII, obtained by oxidation of 3-phenylhydrazino-2-cyclohexen-1-ones (LI), react with benzaldehyde and furfural to give the corresponding 2,3-diaryl-4-oxo-4,5,6,7-tetrahydroindazoles (LIII).

2,3-Diphenyl derivative LIII ($Ar = C_6H_5$) has also been obtained [86] directly from dimedone (Ib) and 1,3,4-oxadiazolium perchlorate (LIV) by refluxing in acetonitrile in the presence of triethylamine for 3 h.

A general method for the synthesis of 1,3-disubstituted (including 3-aryl-) 4-oxo-4,5,6,7-tetrahydroindazoles (LVI) by the action of N-monosubstituted aldehyde hydrazones on cyclohexane-1,3-diones in refluxing benzene has been proposed [77]. Air oxygen is sufficient for the oxidation of the intermediate pyrazolines (LV → LVI).

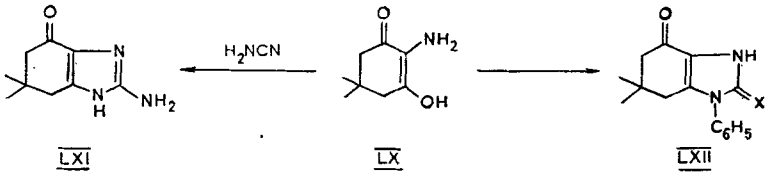
Reaction of 3-chloro-2-cyclohexen-1-one with N-aminopyridine hydrochloride gave enamine LVII, which is converted to ylid LVIII in aqueous potassium carbonate solution; LVII is converted to 10-oxo-7,8,9,10-tetrahydropyrido[1,2-b]indazole (LIX) on heating in toluene [87].



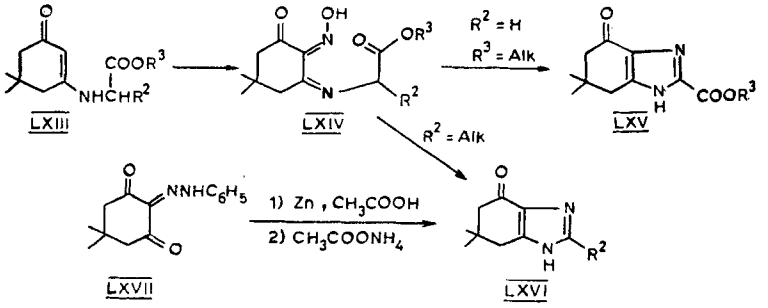


Benzimidazoles

2-Aminodimedone (LX), which reacts with cyanamide [88] to give 2-amino-4-oxo-4,5,6,7-tetrahydrobenzimidazole (LXI) and with phenyl isothiocyanate [89] and phenyl isocyanate [90] to give 2-thio-4-oxo- and 2,4-dioxo-1-phenyl-6,6-dimethyl-2,3,4,5,6,7-hexahydrobenzimidazoles (LXII), respectively, has been used for the synthesis of 4-oxo-4,5,6,7-tetrahydrobenzimidazoles. 1-Phenyl-4-oxo-6,6-dimethyl-4,5,6,7-tetrahydrobenzimidazole [89] was obtained by catalytic hydrogenation of thio derivative LXII (X=S) in the presence of Raney nickel.



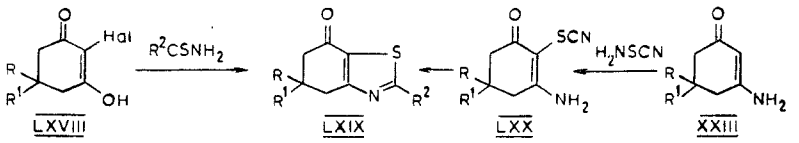
Nitrosation of derivatives of α-amino acids and their esters (LXIII) gives oximes LXIV, which, when R^2=H, are cyclized by refluxing in ethanol to benzimidazoles LXV, but, when R^2=alkyl and aralkyl, are decarboxylated to give alkylbenzimidazoles LXVI [91]. Reductive acylation of 5,5-dimethylcyclohexane-1,2,3-trione monophenylhydrazone (LXVII) and subsequent treatment of the reaction product with ammonium acetate gives benzimidazole LXVI (R^2=CH_3) [92].



Benzothiazoles

2-Amino-, 2-alkyl-, and 2-aryl-6-oxo-4,5,6,7-tetrahydrobenzothiazoles (LXIX) are obtained by reaction of 2-halocyclohexane-1,3-diones (LXVIII) with thioureas [93-96] and thioamides [93-98]. Amines LXIX

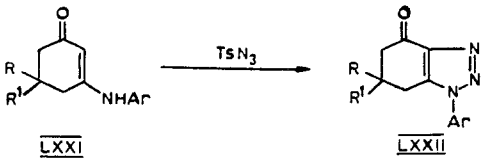
($R^2=NH_2$) can be synthesized directly from diketones I and thiourea in the presence of free halogen [93]. Amine LXIX ($R^2=NH_2$) was also obtained from 3-amino-2-cyclohexen-1-one (XXIII) and H_2NSCN through 2-thiocyanato derivative LXX [99].



LXVIII LXIX LXX XXIII

Benzotriazoles

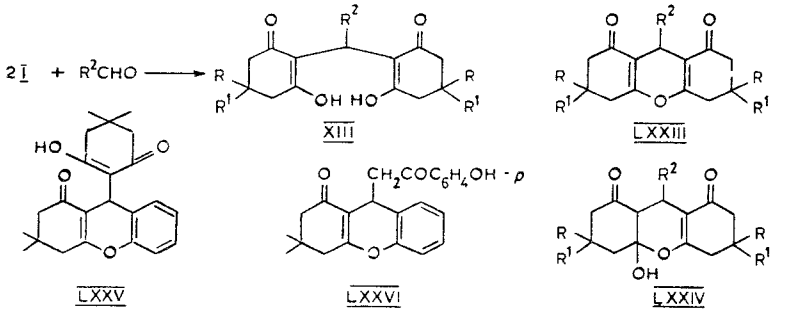
A convenient method for the synthesis of 1-aryl-4-oxo-4,5,6,7-tetrahydrobenzotriazoles (LXXII) consists in treatment of 3-arylamino-2-cyclohexen-1-ones (LXXI) with tosyl azide in the presence of p-toluene-sulfonic acid [100].



LXXI LXXII

Xanthenes and Benzopyrans

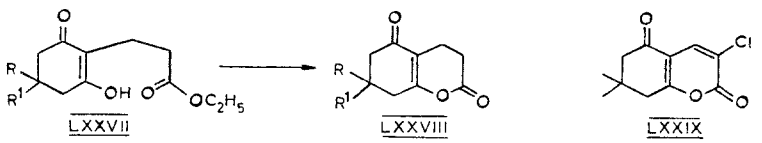
With respect to the number of compounds that exist, the most prolific class of heterocycles obtained from cyclohexane-1,3-diones are 1,8-dioxo-1,2,3,4,5,6,7,8-octahydroxanthenes (LXXIII). Reaction of diketones I with aldehydes in neutral media gives, as a rule, bis(1,3-dioxo-2-cyclohexyl)methanes (XIII), which are dehydrated to octahydroxanthenes LXXIII by means of acids. Some condensation products previously determined to be XIII are actually hydroxydecahydroxanthenes LXXIV [101, 102].



XIII LXXIII LXXV LXXVI LXXIV

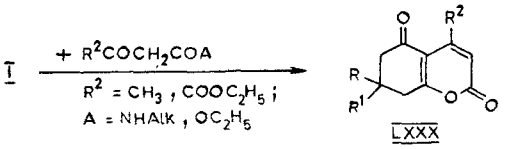
Dimedone [103-109] has been used most extensively in these reactions. The references presented at at the end of this paper include only the principal studies. It has been proposed that the xanthenes obtained from Ia [110], 5-phenyl- and 5-(p-hydroxyphenyl)cyclohexane-1,3-diones [111, 112], and 4,6-dibromodimedone [113] be used for analytical purposes. Acetals may be used in place of aldehydes [114, 115]. 3,3,6,6-Tetramethyl-9-(3-hydroxy-5,5-dimethyl-1-oxo-2-cyclohexenyl)-1,2,3,4,5,6,7,8-octahydroxanthene-1,8-dione was obtained by reaction of dimedone with formic acid derivatives [116, 117]. In the condensation of dimedone with salicylaldehyde, the intermediate bis product forms 5,6,7,8-tetrahydro-8-xanthenone LXXV as a result of further dehydration [118, 119]. The co-condensation of salicylaldehyde, Ib, and 4-hydroxyacetophenone gives diketone LXXVI [118]. 1-Oxo-1,2,3,4-tetrahydrobxanthene was obtained from Ia and salicyl alcohol in hexametapol [120].

The synthesis of hydrogenated benzopyran and, particularly, coumarin derivatives has been described in many papers. 5-Oxo-3,4,5,6,7,8-hexahydrocoumarin LXXVIII is formed by refluxing 2-(β-carbethoxyethyl)dimedone (LXXVII) with acetic anhydride [37]. 3-Chloro-5-oxo-5,6,7,8-tetrahydrocoumarin (LXXIX) was obtained by heating dimedone with trichloroacrolein in methanol for 3 h [121].

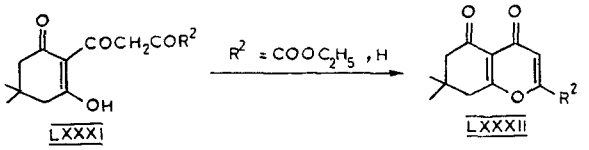


LXXVII LXXVIII LXXIX

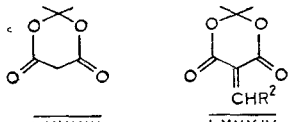
Cyclohexane-1,3-diones react with the amide and N-alkylamides of acetoacetic acid in refluxing toluene in the presence of pyridine [122] and also with its ethyl ester in diethylaniline [122] or trifluoroacetic acid [123] to give 5-oxo-5,6,7,8-tetrahydrocoumarins LXXX ($R^2=CH_3$). Chromones LXXXII were obtained [123] from the products of ω-acylation of 2-acetyldimedone (LXXXI), while isomeric coumarins LXXX ($R^2=COOC_2H_5$) were obtained from dimedone and oxalacetic ester.



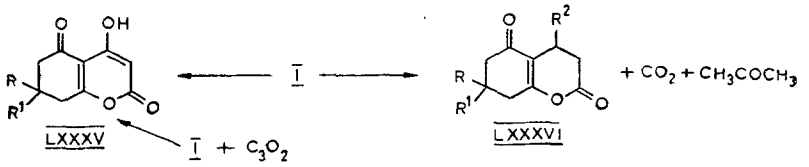
LXXX



LXXXI LXXXII



LXXXIII LXXXIV



LXXXV LXXXVI

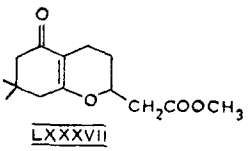
The reactions of cyclohexane-1,3-diones with isopropylidene malonate (LXXXIII) [124] and its derivatives (LXXXIV) [125] have also been used for the synthesis of coumarin derivatives LXXXV and LXXXVI. 4-Hydroxy-5-oxo-5,6,7,8-tetrahydrocoumarins (LXXXV) have also been obtained [126] from I and carbon suboxide.

Hexahydrobenzopyran derivatives have been obtained from cyclohexane-1,3-diones by several methods. 3,4,5,6,7,8-Hexahydro-2H-benzopyran LXXXVII was obtained from methyl vinylacrylate and the potassium salt of dimedone [127].

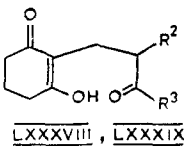
1,5-Diketones LXXXVIII [128] and LXXXIX [129] were converted to benzopyran (XC) and xanthene (XCI) derivatives, respectively, by hydrogenation by means of Raney nickel [128] and by reduction with sodium borohydride [129].

2-Amino-3,4,4-tricyano-5-oxo-5,6,7,8-tetrahydro-γ-chromene was obtained by the action of tetracyanoethylene on I [36]. Chromanone XCII was obtained by refluxing 2-(γ-ketobutyl)cyclohexane-1,3-dione in acetic anhydride [130].

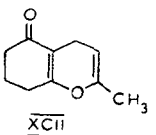
9-Oxaphenanthrene derivatives (XCIII) are formed from I and o-bromobenzoic acids in the presence of copper salts [131, 132].



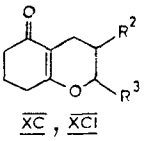
LXXXVII



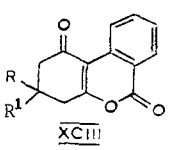
LXXXVIII , LXXXIX



XCII



XC , XCI



XCIII

LXXXVIII , XC $R^2 = H$, $R^3 = CH_3$

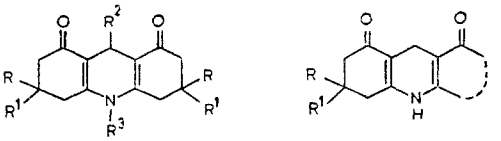
LXXXIX , XCI $R^2 - R^3 = (CH_2)_4$

Condensed Heterocyclic Compounds Containing a Pyridine Ring

One should first of all note a number of variations of the Hantzsch method involving the use of diketones I and their simplest derivatives, which lead to condensed heterocycles containing 1,4-dihydropyridine fragments – mainly decahydroacridine-1,8-diones XCIV and 1,4,5,6,7,8-hexahydro-5-quinolones. Decahydroacridines XCIV were obtained by the action of ammonium acetate or amines on bis(1,3-dioxo-2-cyclohexyl)methanes (XIII) [133-135] or on octahydroxanthenes LXXIII [119, 136, 137], or directly from cyclohexane-1,3-diones, aromatic aldehydes, and ammonium acetate [138], from cyclohexane-1,3-diones and urotropin [139], and from 3-amino-2-cyclohexen-1-one and aldehydes [140].

In condensations involving the participation of diketones I, an aldehyde, and an enamine, 4-aminouracils [143, 144] have been used as enamines in addition to β-aminocrotantes [138, 141, 142].

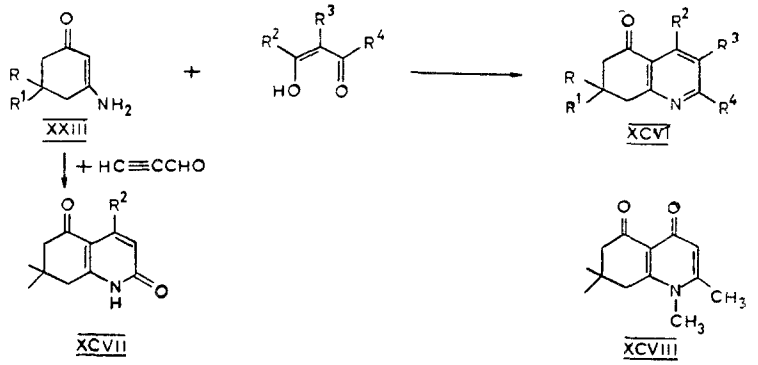
Polycondensed systems XCV, which include 1,4-dihydropyridine, were also obtained by the action of cyclohexanedione imines (XXIII) on 2-arylidenecycloalkane-1,3-diones [145, 146] and also on mixtures of the corresponding aldehydes and diketones [144, 147] or 5-arylidenebarbituric acids [144].



XCIV XCV

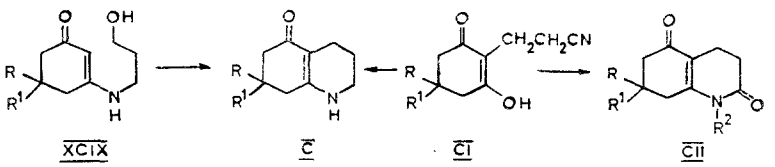
All of the N-unsubstituted 1,4-dihydropyridines mentioned above are readily oxidized to the corresponding pyridines [148].

Enamines XXIII react with the cis-fixed enol forms of β-dicarbonyl compounds to give [149] the corresponding 5-oxo-5,6,7,8-tetrahydroquinolines XCVI (R^2 and R^4=Alk, Ar; R^3=H), 1-oxo-1,2,3,4,5,6,7,8-octahydroacridine XCVI [R^2=H, R^3=R^4=$(CH_2)_4$], and 5-oxo-1,2,3,4,5,6,7,8-octahydrophenanthridine XCVI [R^2 R^3=$(CH_2)_4$]. Enamine XXIII reacts with acetoacetic ester to give quinolone XCVII (R^2=CH_3 [149]. The reaction of enamine XXIII with propargylaldehyde [150] and methyl propiolate [151-153] has also been used for the direct synthesis of 5-oxo-5,6,7,8-tetrahydroquinolines of the XCVI and XCVII types.



XXIII XCVI XCVII XCVIII

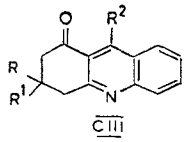
3-Methylamino-5,5-dimethyl-2-cyclohexen-1-one reacts with diketene to give [154] 4,5-dioxo-1,4,5,6,7,8-hexahydroquinoline XCVIII. 2,5-Dioxo-1,2,3,4,5,6,7,8-octahydroquinoline CII (R^2=$CH_2C_6H_5$) was obtained [155] from 3-(N-benzylamino)-2-cyclohexen-1-ones and acryloyl chloride. Octahydroquinoline CII (R^2=H) is formed [156] by hydrolysis of 2-(β-cyanoethyl)cyclohexane-1,3-dione (CI), while hydrogenation of the latter on a nickel catalyst gives [157] 5-oxo-1,2,3,4,5,6,7,8-octahydroquinolines C. The latter were also obtained [158] by heating 3-(γ-hydroxypropylamino)-2-cyclohexen-1-one (XCIX) with pyridine hydriodide.



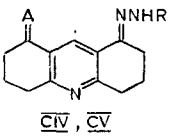
XCIX C CI CII

The synthesis of cyano derivatives of quinoline from diketones I and tetracyanoethylene [36] and also from 2-acetylcyclohexane-1,3-diones and malononitrile in the presence of a base [159] should be noted.

The synthesis of a number of acridine derivatives, quite apart from different variants of the Hantzsch reaction, is known. 1-Oxo-1,2,3,4-tetrahydroacridines CIII were obtained from cyclohexane-1,3-diones and aromatic o-aminocarbonyl compounds [160-162]. The reaction of methylenebisdihydroresorcinol with phenylsulfonylhydrazine gives dihydrazone CIV [84], while refluxing methylenebisdihydroresorcinol di(phenylhydrazone) in acetic acid gives monophenylhydrazone CV [85].



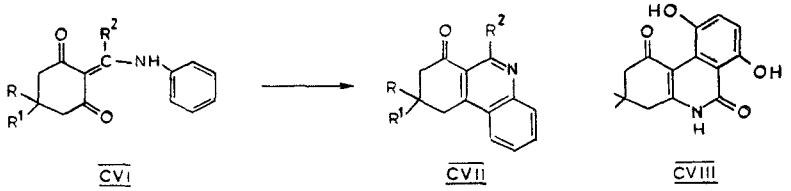
CIII



CIV, CV

CIV A = $NNHSO_2C_6H_5$, R = $SO_2C_6H_5$; CV A = O, R = C_6H_5

Enamines CVI, obtained from 2-acylcyclohexane-1,3-diones and primary aromatic amines, give the corresponding 7-oxo-7,8,9,10-tetrahydrophenanthridines (CVII) when they are heated with polyphosphoric [58, 65, 163] or sulfuric acid [164]. Phenanthridone CVIII was obtained [46] from 2-carbomethoxyquinone and enamine XXIIIb. Schiff bases from β- and α-naphthylamines readily add cyclohexane-1,3-diones to give 7-oxo-5,6,7,8,9,10-hexahydrobenzo[a]- (CIX) and -benzo[c]phenanthridines (CX), respectively [165-168]. Benzophenanthridines CIX can also be obtained from β-naphthlamine and bis(1,3-dioxo-2-cyclohexyl)-methanes [169] or by cocondensation of the aldehyde, β-naphthylamine, and I. Hexahydrobenzophenanthridines CIX and CX are readily oxidized to the corresponding 7,8,9,10-tetrahydro derivatives, CXI and CXII [167, 168].

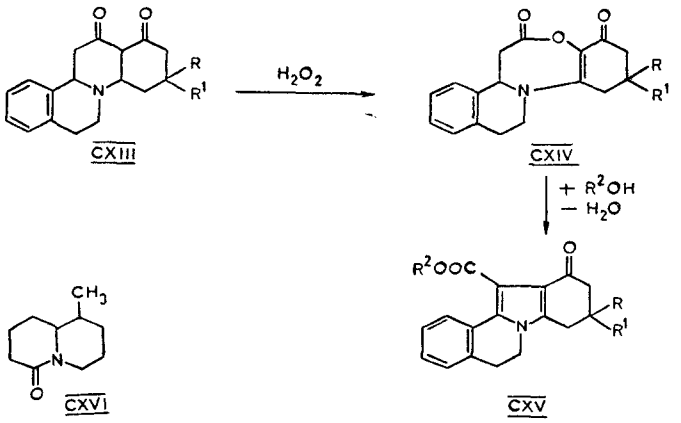


CVI CVII CVIII

CIX, CX CXI, CXII

CIX, CXI R^2 = 1,2-benzo; CX, CXII R^2 = 3,4-benzo

The condensation of 2-acetylcyclohexane-1,3-diones (XI) with 3,4-dihydroisoquinoline makes it possible to arrive at azasteroid analogs – dibenzo[a,f]quinolizines (CXIII) [170, 171]. The corresponding dibenzopyrrocolines (CXV) [172] were obtained as a result of Baeyer–Villiger oxidation of the latter, subsequent alcoholysis of lactone CXIV, and condensation.

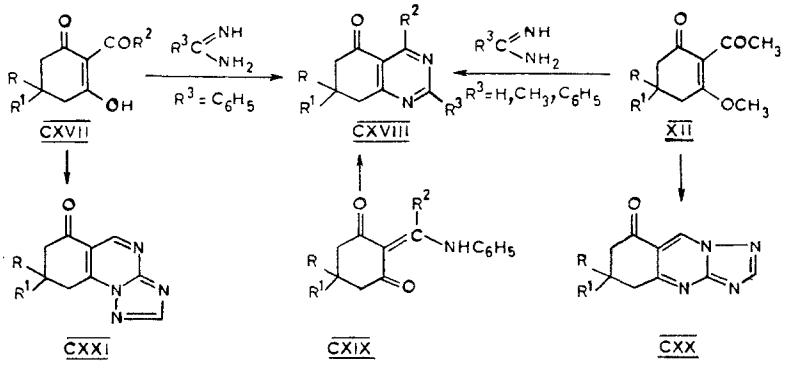


CXIII CXIV CXV CXVI

1-Methyl-6-oxoquinolizidine (CXVI) is formed [173] by hydrogenation of 2-methyl-2-(β-cyanoethyl)-cyclohexane-1,3-dione over a Raney nickel catalyst in the presence of alkali.

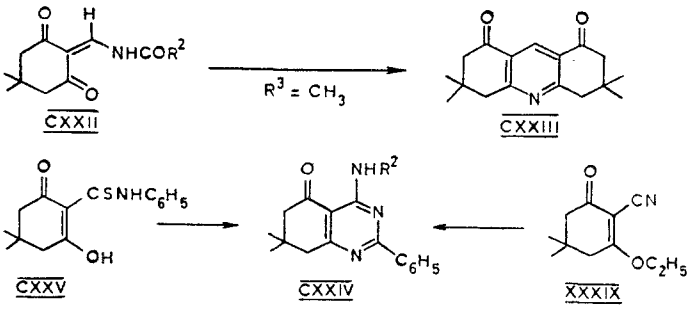
Quinazolines

2-Phenyl-5-oxo-5,6,7,8-tetrahydroquinazolines (CXVIII) are obtained by reaction of 2-formyl- and 2-acetylcyclohexane-1,3-diones (CXVII) with benzamidine [174-176]. The use of anilides CXIX in place of their 2-acyl derivatives increases the yields of quinazolines CXVIII [176, 177]. Acetamidine and formamidine display only an iminating effect with respect to CXVII, but form the corresponding quinazoline in reactions with enol ethers XII. An unsymmetrical amidine – 3-amino-sym-triazole – reacts with ethers XII and triketones CXVII to give quinazoline derivatives CXX and CXXI, respectively [178].



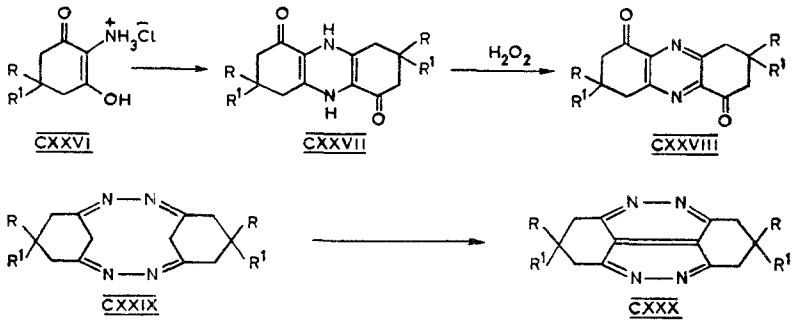
The imination of 2-benzamidomethylene-5,5-dimethylcyclohexane-1,3-dione (CXXII, $R^2=C_6H_5$) also gives CXVIII ($R^2=H$, $R^3=C_6H_5$), while 2-acetamidomethylene derivative CXXII ($R^2=CH_3$) gives CXXIII [117].

4-Anilino- (CXXIV, $R^2=C_6H_5$) and 4-amino-2-phenyl-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydroquinazline (CXXIV, $R^2=H$) have also been synthesized; the former was prepared from 5,5-dimethylcyclohexane-1,3-dione-2-thiocarboxylic acid anilide (CXXV) and benzamidine [179], while the latter was obtained from 2-cyano-3-ethoxy-5,5-dimethyl-2-cyclohexen-1-one (XXXIXb) and benzamidine [64].



Condensed Systems Containing Pyrazine and Pyridazine

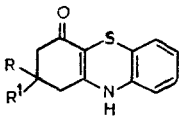
The self-condensation of 2-aminocyclohexane-1,3-diones (CXXVI) to 1,5-dioxodecahydrophenazines (CXXVII) was carried out in [66, 180] in the presence of acids. Decahydrophenazines are readily oxidized by hydrogen peroxide to octahydrophenazines CXXVIII.



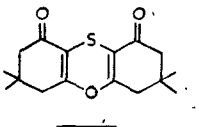
3,4,5,8,9,10-Hexahydro-1,2,6,7-tetraazapyrenes CXXX were obtained [181] by oxygen oxidation of diazines CXXIX, synthesized both directly from I and hydrazine and also from cyclohexane-1,3-dione mono- and dihydrazones.

Other Six-Membered Heterocycles with Two and Three Heteroatoms

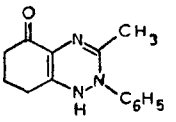
Sulfides, which are converted to 4-oxo-1,2,3,4-tetrahydrophenothiazines (CXXXI) by reduction with zinc in acetic acid, were obtained [182] from diketones I and o-nitroarenesulfenyl chlorides. A dibenzo-[b,e]oxatine derivative (CXXXII) is formed in 80% yield [183] by refluxing bisdimedonyl sulfide in acetic anhydride.



CXXXI



CXXXII

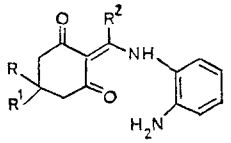


CXXXIII

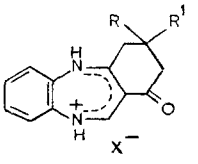
The only example of the synthesis of a triazine derivative is [85] cyclization of 2-acetamidocyclohexane-1,3-dione phenylhydrazone to 5-oxo-1,2,5,6,7,8-hexahydrobenzo-1,2,4-triazine CXXXIII in acetic acid.

Condensed Systems Including Azepine and 1,4-Diazepine

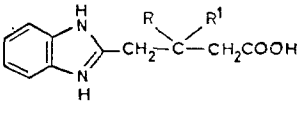
Schiff bases from 2-acylcyclohexane-1,3-diones and o-phenylenediamine (CXXXIV) are cyclized [184, 185] to 1,2,3,4-tetrahydro-11H-dibenzo(b,e)-1,4-diazepin-4-one salts (CXXXV) by the action of acids. The corresponding bases have also been isolated and the pathways for their conversion to benzimidazole derivatives CXXXVI [186] have been demonstrated. 5-Substituted 2,2-dimethyl-1,2,3,4,5,6-hexahydro-11H-dibenzo(b,e)-1,4-diazepin-4-ones were obtained [187] in reactions of 3-(o-aminoanilino)-5,5-dimethyl-2-cyclohexen-1-one with aliphatic and aromatic aldehydes.



CXXXIV



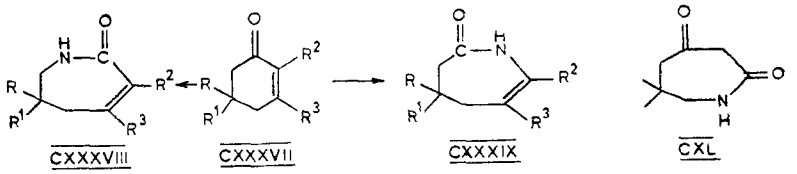
CXXXV



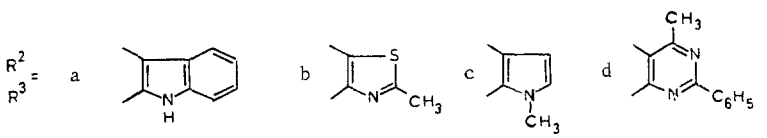
CXXXVI

Ketones of the CXXXVII type have been used to obtain condensed systems including azepine. Two methods have been used for this: the Beckmann rearrangement of their oximes and the Schmidt reaction. Both possible isomers (CXXXVIIIc and CXXXIXc) were isolated [188] only from the products of the Beckmann rearrangement in polyphosphoric acid of 1-methyl-4-oxo-4,5,6,7-tetrahydroindole oxime. 4-Oxo-1,2,3,4-tetrahydrocarbazole oxime was converted [51] to CXXXVIIIa, 2-methyl-7-oxo-4,5,6,7-tetrahydrobenzothiazole oxime was converted to CXXXIXb [189], and 2-phenyl-4,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydroquinazoline oxime was converted to CXXXIXd [190].

The Schmidt reaction (the action of hydrazoic acid in polyphosphoric acid) is suitable only for CXXXVIId and gives the same CXXXIXd [190].



CXXXVIII CXXXVII CXXXIX CXL



2,4-Dioxo-1,2,3,4,5,6-hexahydroazepine CXL was obtained by photochemical decomposition of 3-azido-5,5-dimethyl-2-cyclohexenone in tetrahydrofuran [191, 192].

Of other general pathways for the subsequent construction of polycondensed heterocyclic systems by means of ketones CXXXVII, one should note reactions involving their α-formylation with subsequent synthesis of the heterocycle from an α-formyl ketone structural fragment [193-195].

Two-ring systems of the CXXXVII type (4-oxo-4,5,6,7-tetrahydroindazoles [71, 72], 7-oxo-4,5,6,7-tetrahydrobenzothiazoles [98], 5-oxo-5,6,7,8-tetrahydroquinolines [152], and 4-oxo-4,5,6,7-tetrahydrobenzofurans [196]) have also been used in place of 6-methoxytetralone for the synthesis, via the Torgov scheme, of heterocyclic analogs of estrone with a modified A ring.

LITERATURE CITED

1. H. Stetter and E. Siehnhold, Ber., 88, 271 (1955).
2. J. N. Chatterjea and R. R. Ray, Ber., 92, 998 (1959).
3. H. Stetter and R. Lauterbach, Ber., 93, 603 (1960).
4. H. Stetter and R. Lauterbach, Ann., 652, 40 (1962).
5. E. B. McCall, A. J. Neale, and T. J. Rawlings, J. Chem. Soc., 4900 (1962).
6. E. B. McCall, A. J. Neale, and T. J. Rawlings, J. Chem. Soc., 5291 (1962).
7. J. N. Chatterjea and V. N. Mehrotra, J. Indian Chem. Soc., 39, 599 (1962).
8. V. A. Barkhash, V. S. Velezheva, and I. V. Machinskaya, Zh. Organ. Khim., 2, 1083 (1966).
9. K. Takagi and T. Ueda, Chem. Pharm. Bull. (Tokyo), 19, 1218 (1971).
10. R. Nagarajan and R. Shah, Tetrahedron Lett., 1467 (1972).
11. V. S. Velezheva, I. V. Machinskaya, and V. A. Barkhash, Zh. Vsesoyuzn. Khim. Obshchestva, 14, 467 (1969).
12. U. E. Schulte, J. Reisch, and H. Lang, Ber., 96, 1470 (1963).
13. S. I. Zav'yalov, G. V. Kondrat'eva, and D. F. Kundryavtseva, Zh. Obshch. Khim., 31, 3695 (1961).
14. A. S. Sopova, V. V. Perekalin, and V. M. Lebedneva, Zh. Obshch. Khim., 33, 2143 (1963).
15. A. S. Sopova, V. V. Perekalin, and V. M. Lebedneva, Zh. Obshch. Khim., 34, 2638 (1964).
16. O. I. Yurchenko, A. S. Sopova, V. V. Perekalin, V. M. Berestovitskaya, A. S. Polyanskaya, and N. I. Aboskalova, Dokl. Akad. Nauk SSSR, 171, 1123 (1966).
17. V. M. Berestovitskaya, A. S. Sopova, and V. V. Perekalin, Khim. Geterotsikl. Soedin., 396 (1967).
18. S. J. Dominianni, M. O. Chaney, and N. D. Jones, Tetrahedron Lett., 4735 (1970).
19. H. Stetter and K. Koehne, Ber., 91, 1344 (1958).
20. H. O. Larson, T. C. Ooi, A. K. Siu, K. H. Hollenbeak, and F. L. Cue, Tetrahedron, 25, 4005 (1969).
21. A. T. Nielsen and T. G. Archibald, Tetrahedron, 25, 2393 (1969).
22. G. Nowy, W. Riedl, and H. Simon, Ber., 99, 2075 (1966).
23. A. A. Akhrem, A. M. Moiseenkov, and F. A. Lakhvich, Dokl. Akad. Nauk SSSR, 193, 1053 (1970).
24. A. A. Akhrem, A. M. Moiseenkov, F. A. Lakhvich, and A. I. Poselenov, Izv. Akad. Nauk SSSR, Ser. Khim., 143 (1972).
25. F. H. Greenberg, J. Org. Chem., 30, 1251 (1965).
26. G. B. Kondrat'eva, G. A. Kogan, and S. I. Zav'yalov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1441 (1962).
27. I. É. Lielbriedis and É. Yu. Gudrinietse, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 192 (1968).
28. O. Mattsson and C. Wachtmeister, Acta Chem. Scand., 22, 49 (1968).
29. O. Mattsson, B. Sjöquist, and S. Wachmeister, Acta Chem. Scand., 24, 3326 (1970).
30. R. Brette and D. Seddon, J. Chem. Soc., 2174 (1970).
31. S. I. Zav'yalov, A. F. Vasil'ev, and L. P. Vinogradova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 850 (1961).
32. O. Mattsson, Tetrahedron Lett., 2489 (1969).
33. D. C. Smith, J. Chem. Soc., 1244 (1956).
34. E. Kopp and J. Smith, Ann., 693, 117 (1966).
35. K. Gump, S. Moje, and C. Castro, J. Amer. Chem. Soc., 89, 6770 (1967).
36. H. Junek and H. Aigner, Z. Naturforsch., 25b, 1423 (1970).
37. H. J. Schaeffer and R. Vince, J. Org. Chem., 27, 4502 (1962).
38. H. Stetter and R. Lauterbach, Ann., 655, 20 (1962).
39. C. D. Nenitzescu (Nenitzesky), Bull. Soc. Chim. Romania, 10, 134 (1928).
40. S. Hauptmann, H. Blume, G. Hartmann, D. Haendel, and P. Franke, Z. Chem., 6, 107 (1966).

41. A. N. Kost, L. G. Ovseneva, and T. V. Shuvaeva, Khim. Geterotsikl. Soedin., 717 (1966).
42. V. I. Shvedov, L. B. Altukhova, and A. N. Grinev, Khim. Geterotsikl. Soedin., 342 (1972).
43. H. J. Roth and H. E. Hagen, Arch. Pharm., 304, 70 (1971).
44. H. J. Roth and P. Lepke, Arch. Pharm., 305, 159 (1972).
45. H. J. Roth and H. E. Hagen, Arch. Pharm., 304, 159 (1971).
46. R. Littel, G. Morton, and G. Allen, J. Amer. Chem. Soc., 92, 3740 (1970).
47. R. Friary, R. France, and J. Tobin, Chem. Commun., 283 (1970).
48. J. M. Bobbit and C. P. Dutta, Chem. Commun., 1429 (1968).
49. H. Yamada, T. Konakhara, S. Ishihara, H. Kahamori, T. Itoh, K. Kimura, and H. Iida, Tetrahedron Lett., 2513 (1972).
50. G. R. Clemo and D. G. I. Felton, J. Chem. Soc., 700 (1951).
51. H. J. Teuber, D. Cornelius, and E. Worbs, Tetrahedron Lett., 331 (1964).
52. H. J. Teuber, D. Cornelius, and U. Wolcke, Ann., 696, 116 (1966).
53. W. Sucrow and E. Wiese, Ber., 103, 1767 (1970).
54. V. V. Perekalin and K. S. Parfenova, Zh. Obshch. Khim., 30, 388 (1960).
55. E. M. Danilova and V. V. Perekalin, Zh. Organ. Khim., 1, 1708 (1965).
56. E. M. Danilova, V. V. Perekalin, and T. Ya. Paperno, Zh. Organ. Khim., 3, 1860 (1967).
57. A. W. Crossley and N. Renouf, J. Chem. Soc., 1524 (1912).
58. H. Smith, J. Chem. Soc., 803 (1953).
59. A. A. Akhrem, A. M. Moiseenkov, and M. B. Andaburskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 2846 (1969).
60. A. A. Akhrem, A. M. Moiseenkov, M. B. Andaburskaya, and A. V. Mkhitaryan, Izv. Akad. Nauk SSSR, Ser. Khim., 1196 (1969).
61. A. A. Akhrem, A. M. Moiseenkov, F. A. Lakhvich, and S. P. Smul'skii, Izv. Akad. Nauk SSSR, Ser. Khim., 1089 (1971).
62. A. A. Akhrem, A. M. Moiseenkov, and F. A. Lakhvich, Izv. Akad. Nauk SSSR, Ser. Khim., 2786 (1971).
63. A. A. Akhrem, A. M. Moiseenkov, A. Ya. Strakov, and M. B. Andaburskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 836 (1973).
64. A. Ya. Strakov, M. B. Andaburskaya, A. M. Moiseenkov, and A. A. Akhrem, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 330 (1973).
65. G. Lehmann, Angew. Chem., 77, 383 (1965).
66. A. K. Aren and D. V. Bite, Khim. Geterotsikl. Soedin., 1283 (1971).
67. W. Ried and A. Strätz, Ann., 764, 11 (1972).
68. W. Diekcmann and R. Stein, Ber., 37, 3370 (1904).
69. É. Yu. Gudrinietse and I. A. Strakova, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 128 (1963).
70. I. A. Strakova and É. Yu. Gudrinietse, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 680 (1966).
71. G. Lehmann, H. Wehlan, and G. Hilgetag, Ber., 100, 2967 (1967).
72. G. Lehmann, H. Wehlan, and G. Hilgetag, Tetrahedron Lett., 123 (1967).
73. I. A. Strakova, Ya. Ya. Linaberg, and É. Yu. Gudrinietse, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 188 (1968).
74. I. A. Strakova, A. Ya. Strakov, M. T. Strautzele, and É. Yu. Gudrinietse, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 597 (1968).
75. I. A. Strakova, É. Yu. Gudrinietse, Ya. Ya. Linaberg, A. Ya. Strakov, and D. R. Kreitsberga, Khim. Geterotsikl. Soedin., 520 (1970).
76. A. A. Akhrem, A. M. Moiseenkov, F. A. Lakhvich, M. B. Andaburskaya, A. V. Mkhitaryan, G. N. Sedletskaya, and V. A. Petukhov, Izv. Akad. Nauk SSSR, Ser. Khim., 594 (1971).
77. W. Sucrow, M. Slopianka, and A. Neophyton, Ber., 105, 2143 (1972).
78. I. A. Strakova, A. Ya. Strakov, and É. Yu. Gudrinietse, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 593 (1973).
79. N. Rogers and H. Smith, J. Chem. Soc., 341 (1955).
80. S. Forsen and M. Nilson, Arkiv Kemi, 19, 569 (1962),
81. D. V. Brutane, A. Ya. Strakov, and I. A. Strakova, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 485 (1970).
82. A. A. Akhrem, A. M. Moiseenkov, M. B. Andaburskaya, and A. Ya. Strakov, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 740 (1970).
83. A. A. Akhrem (Achrem), A. M. Moiseenkov, M. B. Andaburskaya (Andaburskaja), and A. Ya. (J.) Strakov, J. prakt. Chem., 314, 31 (1972).
84. H. J. Teuber and R. Braun, Ber., 100, 1353 (1967).
85. H. J. Teuber, E. Worbs, and D. Cornelius, Ber., 101, 3918 (1968).
86. G. V. Boyd and S. R. Dando, J. Chem. Soc., C, 225 (1971).

87. Y. Tamura, N. Tsujimoto, Y. Sumida, and N. Ikeda, Tetrahedron, 28, 21 (1972).
88. É. V. Vanag, V. Ya. Grinshtein, and A. É. Sausin', Izv. Akad. Nauk Latv. SSR, Ser. Khim., 215 (1964).
89. A. K. Aren and D. V. Bite, Zh. Vsesoyuzn. Khim. Obshchestva, 12, 708 (1967).
90. F. A. Grunsberg, Author's Abstract of Dissertation, Riga (1970).
91. A. Cross and A. Deer, Chem. Ind., 18, 731 (1966).
92. V. I. Shvedov, L. B. Altukhova, and A. N. Grinev, Khim. Geterotsikl. Soedin., 131 (1972).
93. I. K. Gaile, É. Yu. Gudrinietse, and G. Ya. Vanag, Dokl. Akad. Nauk SSSR, 146, 817 (1962).
94. I. K. Gaile, É. Yu. Gudrinietse, and G. Ya. Vanag, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 523 (1962).
95. H. Albers and W. Mohler, Ber., 96, 357 (1963).
96. G. Lehmann, B. Lücke, H. Schick, and G. Hilgetag, Z. Chem., 11, 422 (1967).
97. M. Mühlstadt and E. Bordes, J. prakt. Chem., 20, 285, (1963).
98. G. Lehmann, H. Schick, B. Lücke, and G. Hilgetag, Ber., 101, 787 (1968).
99. E. Schmitz and H. Stiegler, J. prakt. Chem., 313, 1125 (1971).
100. M. Regitz and H. Schwall, Ann., 728, 99 (1969).
101. I. É. Lielbriedis and É. Yu. Gudrinietse, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 684 (1966).
102. Ya. Ya. Lemba and I. É. Lielbriedis, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 598 (1973).
103. D. Vorlander, Z. anal. Chem., 77, 241 (1929).
104. G. Klein and H. Linser, Mikrochemie Pregl-Festschrift (Vienna), 204 (1929); Chem. Zentrallblat, 1, 2085 (1930).
105. E. Hornig and M. Hornig, J. Org. Chem., 11, 95 (1946).
106. D. Spencer and T. Henshall, J. Amer. Chem. Soc., 77, 1943 (1955).
107. C. Duval and Nguen Dat Kuong, Anal. Chim. Acta (Amsterdam), 10, 47 (1955); Chem. Zentrallblat, 9870 (1958).
108. J. Thomas, E. Sanborn, M. Mukai, and B. Tebbens, Ind. Eng. Chem., 51, 774 (1959).
109. E. Padilla, An. Fac. Farmac. Bioquim., 7, 598 (1956); Chem. Zentrallblat, 3924 (1962).
110. F. King and D. Felton, J. Chem. Soc., 1371 (1948).
111. Desai and M. Wali, J. Indian Chem. Soc., 13, 735 (1936).
112. P. E. Papadakis, J. Org. Chem., 19, 51 (1954).
113. T. Voitila, Suomen Kemistilehti, 10, (14), 25 (1937).
114. Zh. A. Krasnaya, S. S. Yufit, and V. F. Kucherov, Izv. Akad. Nauk SSR, Otd. Khim. Nauk, 1104 (1967).
115. W. Back and E. Mutschler, Arch. Pharm., 300, 955 (1967).
116. B. Akehurst and J. Bartels-Keith, J. Chem. Soc., 4798 (1957).
117. A. Ya. Strakov, D. V. Brutane, S. P. Valter, and M. T. Shultsa, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 141 (1971).
118. L. Jurd, J. Org. Chem., 31 1639 (1966).
119. J. Baldas and Q. Porter, Tetrahedron Lett., 1351 (1968).
120. P. Yates, D. Bichan, and J. McCloskey, Chem. Commun., 839 (1972).
121. A. Roedig and S. Schodel, Ber., 91, 330 (1958).
122. G. V. Kondrat'eva, V. I. Gunar, L. F. Ovechkina, S. I. Zav'yalov, and A. I. Krotov, Izv. Akad. Nauk SSR, Ser. Khim., 633 (1967).
123. J. H. Sellstedt, J. Org. Chem., 37, 1337 (1972).
124. E. Ziegler, H. Junek, and U. Herzog, Monatsh., 102, 1616 (1971).
125. P. Margaretha, Tetrahedron Lett., 1449 (1970).
126. A. Omori, N. Sonoda, Y. Uchida, and S. Tsusumi, Bull. Chem. Soc. Japan, 42, 3233 (1969).
127. S. Danishefsky, G. Koppel, and R. Lewine, Tetrahedron, 24, 2257 (1968).
128. G. Sauer, U. Eder, and G. Hoyer, Ber., 105, 2358 (1972).
129. V. I. Gunar, L. F. Ovechkina, S. I. Zav'yalov, G. N. Pershin, and S. N. Milovanova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1827 (1964).
130. S. I. Zav'yalov, G. V. Kondrat'eva, and L. F. Kudryavtseva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 529 (1961).
131. H. Fales, E. Warnhoff, and H. Wildman, J. Amer. Chem. Soc., 77, 5885 (1955).
132. H. Stetter and E. Sienhold, Ber., 88, 1223 (1955).
133. G. Ya. Vanag and É. I. Stankevich, Zh. Obshch. Khim., 30, 3287 (1960).
134. É. I. Stankevich and G. Ya. Vanag, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 223 (1961).
135. I. É. Lielbriedis and É. Yu. Gudrinietse, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 318 (1967).
136. H. Antaki, J. Chem. Soc., 2263 (1965).
137. D. Vorländer and F. Kalkow, Ber., 30, 1801 (1897).

138. H. Antaki, J. Chem. Soc., 4877 (1963).
139. M. V. Ionescu and V. N. Georgescu, Bull. Soc. Chim. France, 41, 692 (1926).
140. D. V. Shveits, É. I. Stankevich, and O. Ya. Neiland, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 213 (1968).
141. É. I. Stankevich, É. É. Grinshtein, and G. Ya. Vanag, Khim. Geterotsikl. Soedin., 583 (1966).
142. É. É. Grinshtein, É. I. Stankevich, and G. Ya. Dubur, Khim. Geterotsikl. Soedin., 1118 (1967).
143. É. É. Grinshtein, É. I. Stankevich, and G. Ya. Dubur, Khim. Geterotsikl. Soedin., No. 1, 395 (1967).
144. Yu. É. Pelcher, É. É. Grinshtein, É. I. Stankevich, and G. Ya. Vanag, Khim. Geterotsikl. Soedin., No. 1, 406 (1967).
145. É. I. Stankevich and G. Ya. Vanag, Zh. Obshch. Khim., 32, 1146 (1962).
146. A. Ya. Ozola, É. I. Stankevich, and G. Ya. Dubur, Khim. Geterotsikl. Soedin., 632 (1971).
147. É. I. Stankevich and G. Ya. Vanag, Dokl. Akad. Nauk SSSR, 140, 607 (1961).
148. U. Eisner and K. Kuthan, Chem. Rev., 72, 1 (1972).
149. C. Ruanopiyanand, H. J. Rimek, and F. Zymalkowski, Ber., 103, 2043 (1970).
150. F. Bohlmann and R. Mayer-Mader, Tetrahedron Lett., 171 (1965).
151. M. Sluyter, U. Pandit, W. Speckamp, and H. Huisman, Tetrahedron Lett., 87 (1966).
152. N. Finch and C. W. Gemender, J. Org. Chem., 35, 3114 (1970).
153. M. A. T. Dubas-Sluyter, W. N. Speckamp, and H. Huisman, Rec. Trav. Chim., 91, 157 (1972).
154. S. I. Zav'yalov, I. A. Mikhailopulo, V. I. Gunar, and L. F. Ovechkina, Izv. Akad. Nauk SSSR, Ser. Khim., 859 (1967).
155. P. W. Hickmott and G. Sheppard, J. Chem. Soc., C, 2112 (1971).
156. H. Dugas, M. E. Hazenberg, Z. Valenta, and K. Wiesner, Tetrahedron Lett., 4931 (1967).
157. C. A. Grob and H. R. Kiefer, Helv. Chim. Acta, 48, 799 (1965).
158. H. Dugas, R. A. Ellison, Z. Valenta, K. Wiesner, and C. M. Wong, Tetrahedron Lett., 1279 (1965).
159. É. Yu. Gudrinietse and A. D. Yukhnevich, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 622 (1972).
160. B. H. Iyer and G. C. Chakravarti, J. Indian Inst. Sci., A14, 157 (1932); Chem. Zentrallblat, 1, 2953 (1932).
161. G. Kempter and G. Mobiuss, J. prakt. Chem., 306, 298 (1966).
162. G. Kempter and P. Klug, Z. Chem., 11, 61 (1971).
163. W. Kirkor and J. Baranowicz, Acta Chim., 8, 69 (1962).
164. G. M. Chopra and B. H. Iyer, Current Sci. (India), 22, 210 (1953); Chem. Abstr., 49, 887 (1955).
165. I. É. Lielbriedis, V. V. Chirkova, and É. Yu. Gudrinietse, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 251 (1968).
166. I. É. Lielbriedis, V. V. Chirkova, and É. Yu. Gudrinietse, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 197 (1969).
167. I. É. Lielbriedis and N. I. Veretennikova, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 453 (1971).
168. I. É. Lielbriedis, S. R. Trusov, and É. Yu. Gudrinietse, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 39 (1971).
169. I. É. Lielbriedis and É. Yu. Gudrinietse, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 193 (1969).
170. A. A. Akhrem, A. M. Moiseenkov, and A. I. Poselenov, Dokl. Akad. Nauk SSSR, 203, 95 (1972).
171. A. A. Akhrem, A. M. Moiseenkov, V. A. Krivoruchko, F. A. Lakhvich, and A. I. Poselenov, Izv. Akad. Nauk SSSR, Ser. Khim., 2078 (1972).
172. A. A. Akhrem, A. M. Moiseenkov, and A. I. Poselenov, Izv. Akad. Nauk SSSR, Ser. Khim., 2579 (1972).
173. V. I. Gunar and S. I. Zav'yalov, Dokl. Akad. Nauk SSSR, 139, 367 (1961).
174. G. Lehmann, B. Lücke, H. Wehlan, and G. Hilgetag, West German Patent No. 62,062 (1967); Ref. Zh. Khim., 20N428 (1969).
175. D. V. Brutane and A. Ya. Strakov, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 248 (1969).
176. D. V. Brutane and A. Ya. Strakov, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 202 (1970).
177. D. V. Brutane, A. Ya. Strakov, and I. A. Strakova, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 485 (1970).
178. D. V. Brutane, A. Ya. Strakov, A. M. Moiseenkov, and A. A. Akhrem, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 610 (1970).
179. A. Ya. Strakov, D. V. Brutane, and V. V. Leich, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 248 (1970).
180. A. K. Aren, and D. V. Bite, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 246 (1971).
181. J. K. Stille, J. M. Unglaube, and M. E. Freeburger, J. Amer. Chem. Soc., 90, 7076 (1968).
182. V. I. Shvedov, L. B. Altukhova, V. M. Lyubchanskaya, and A. N. Grinev, Khim. Geterotsikl. Soedin., 1509 (1972).

183. R. Gompper, H. Euchner, and H. Kast, Ann., 675, 151 (1964).
184. A. Ya. Strakov, Ya. Ya. Linaberg, M. T. Strautzele, and D. A. Lautsenietse, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 722 (1968).
185. M. T. Shultsa and A. Ya. Strakov, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 329 (1971).
186. A. Ya. Strakov and M. T. Shultsa, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 355 (1972).
187. S. Miyand and N. Abe, Chem. Pharm. Bull. (Tokyo), 20, 1588 (1972).
188. A. Stoll and F. Troxler, Helv. Chim. Acta, 51, 1864 (1968).
189. N. Buu-Hoi, A. Crossy, P. Jacquignon, and A. Martani, J. Chem. Soc., C, 1109 (1971).
190. D. V. Brutane and A. Ya. Strakov, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 225 (1973).
191. S. Sato, Bull. Chem. Soc. Japan, 41, 2524 (1968).
192. Y. Tamura, Y. Yoshimura, T. Nishimura, S. Kato, and Y. Kita, Tetrahedron Lett., 35 (1973).
193. W. Kemers, R. Roth, G. Gibs, and M. Weiss, J. Org. Chem. 36, 1232 (1971).
194. W. Remers and M. Seiss, J. Org. Chem., 36, 1241 (1971).
195. I. A. Strakova, A. Ya. Strakov, and É. Yu. Gudrinietse, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 627 (1972).
196. G. Lehmann and B. Lücke, Ann., 727, 88 (1969).