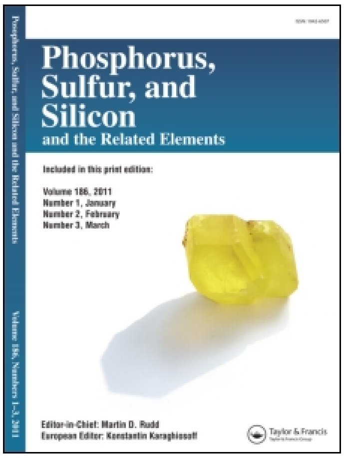

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Thiazolidin-5-Ones: Synthesis and Reactions

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Thiazolidin-5-Ones: Synthesis and Reactions

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Thiazolidin-5-ones and their derivatives have been long used as precursors for the synthesis of biologically active molecules. The general methods of preparations of thiazolidinones have been mentioned. The reactions of the title compounds are subdivided into groups that cover reactions to yield monoheterocycles.

Keywords Biological activity of thiazolidinones; general and physical properties; reactions; synthetic utility; thiazolidin-5-ones

INTRODUCTION

Thiazolidinones are the derivatives of thiazolidine, which belong to an important group of heterocyclic compounds. Thiazolidinones, with a carbonyl group at position 2, 4, or 5, have been the subject of extensive study in the recent past. Numerous reports have appeared in the literature, which highlights their chemistry and use. A comprehensive review[1] has been written on thiazolidin-4-ones in 1961. Later, a review article[2] appeared that dealt with the use of thiazolidinone derivatives as stabilizers for polymeric materials. Recently two reviews[3,4] have been presented; one relates to the preparation of rhodanines (2-thioxothiazolidin-4-ones), and the other describes their uses as intermediates in organic synthesis.

Divers biological activities such as bactericidal, pesticidal, fungicidal, insecticidal, anticonvulsant, tuberculostatic, antithyroidal, and the potential of pentobarbital induced sleeping time, etc., have been found to be associated with thiazolidinone derivatives. In recent years, several new methods for the preparation of thiazolidinone derivatives and reactions have been reported in the literature. Thiazolidinones,

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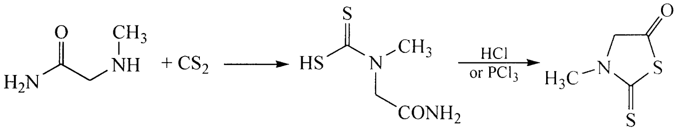
in the presence of various reagents, undergo different types of reactions to yield other heterocyclic compounds, e.g., thiazole, benzimidazole, thiopyrano-thiazolone, benzodiazepine, triazoles, benzothiophenes, triazinones, etc. These advances warrant reviewing the chemistry and biological properties of various 2-, 4-, and 5-thiazolidinones.

SYNTHESIS AND PROPERTIES OF THIAZOLIDIN-5-ONE DERIVATIVES

Synthesis of 2-Thioxo-5-Thiazolidinones from Glycinamides

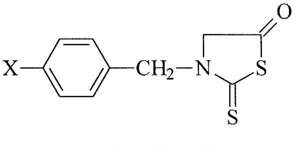
N-methylglycinamide reacts with carbon disulfide in the presence of methanol and gives *N*-methyl-*N*-(carbamoylmethyl)ammonium *N*-methyl-*N*-(carbamoylmethyl)-dithiocarbamate **1**. This dithiocarbamate on acidification[5,6] with concentrated hydrochloric acid or phosphorus trichloride gives 2-thioxo-3-methyl-5-thiazolidinone **2**.



1 **2**

SCHEME 1

Also several 2-thioxothiazolidin-5-one derivatives **3** substituted by a benzyl or chlorobenzyl group were prepared.[7] Compounds (**3**)[7] proved inferior to the rhodanine analogs in activity toward *B. subtilis* and *E. coli*, while toward *Aspergillus niger* **3a** was significantly inferior and **3b** superior in activity.



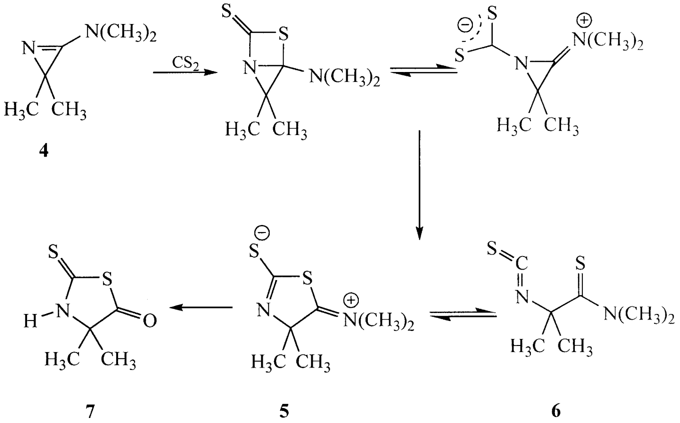
3a, X = H
3b, X = Cl

SCHEME 2

Synthesis of 2-Thioxothiazolidin-5-Ones from Azirines

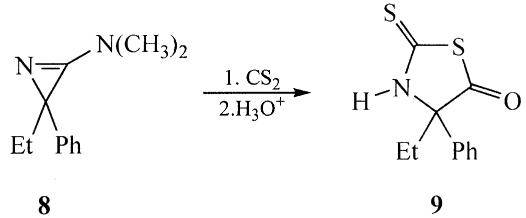
3-(dimethylamino)-2,2-dimethyl-2*H*-azirine **4** reacts with carbon disulfide to give a crystalline product that has the dipolar structure [4,4-dimethyl-5-(dimethyliminium)-2-thiazoline-2-thiolate] **5**.

In solution, nondipolar (charge-free) isomeric form (1-dimethylthiocarbamoyl)-1-methylethyl isothiocyanate) **6** is almost exclusively populated. The hydrolysis of the dipolar structure of 3-(dimethylamino)-2,2-dimethyl-2*H*-azirine **5** with 3 N hydrochloric acid results in the formation of 4,4-dimethyl-2-thiono-5-thiazolidinone **7** in an 84% yield. The structure of this compound is confirmed on the basis of IR, NMR, and mass spectral data analysis.[8]



SCHEME 3

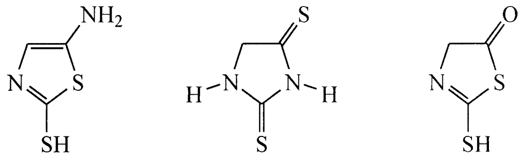
Similarly, Schaumann and colleagues.[9,10] reported the synthesis of 4-ethyl-4-phenyl-2-thionothiazolidin-5-one **9** starting with 3-(dimethylamino)-2-ethyl-2-phenyl-2*H*-azirine **8**.



SCHEME 4

Synthesis of 2-Thioxothiazolidin-5-One from 5-Amino-2-Mercaptothiazole

The reaction between amino acetonitrile and carbon disulfide led to the formation of 5-amino-2-mercaptothiazole **10**, which was converted by alkali into 2,4-dithiohydantoin **11** and by acid[5] into 2-mercapto-4H-thiazol-5-one **12**.

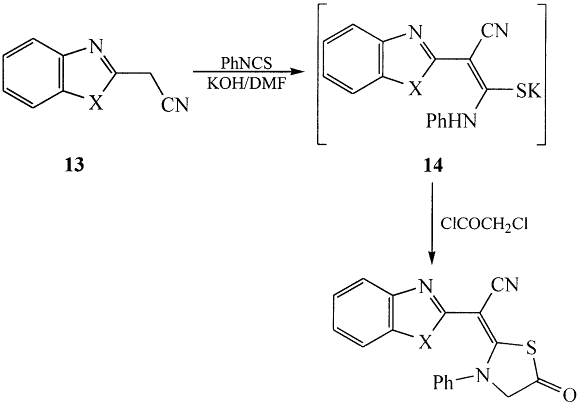


10 **11** **12**

SCHEME 5

Synthesis of Thiazolidin-5-Ones from Active Methylene Compounds

The reaction of 2-cyanomethylimidazo[4,5-b]pyridine **13** (X = NH) with phenyl isothiocyanate in the presence of potassium hydroxide gave the non-isolated adduct **14**, which reacted[11] with chloroacetyl chloride to give 2-[3-phenyl-5-oxothiazolidin-2-ylidene)cyanomethyl]-1H-imidazo[4,5-b]-pyridine **15** (X = NH).



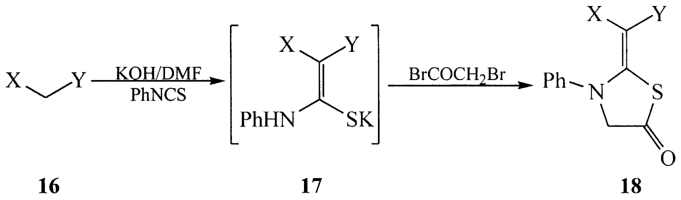
13 **14** **15**

SCHEME 6

It is known that a great variety of reactants bearing the N=C=S fragment undergo cyclization by treatment with α-halocarbonyl compounds to afford thiazolidines.

The reaction of the nonisolable **17** prepared in situ from the base-promoted nucleophilic addition of phenyl isothiocyanate to acidic cyanomethylenes **16** at r.t. with bromoacetyl bromide afforded the thiazolidin-5-ones **18** by KBr and HBr elimination.[12,13]

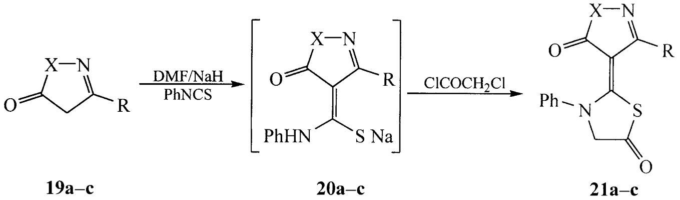
El-Desoky and colleagues[14] reported the reaction of the active methylene heterocyclic compounds, namely 1-phenyl-3-methyl-2-pyrazolin-5-one **19a**, 1-(3′-chlorophenyl)-3-methyl-2-pyrazolin-5-one **19b**, and



X = CN; Y = CN, COOEt, PhCO
X = CH_3CO; Y = COOEt, $COCH_3$

SCHEME 7

3-phenylisoxazol-5-one **19c** with phenyl isothiocyanate in DMF/NaH to give the nonisolable sodium salts **20a–c**, which subsequently react with chloroacetyl chloride at r.t[14] to give the corresponding thiazolidin-5-ones **21a–c**.



a; X = N-Ph, R = Me

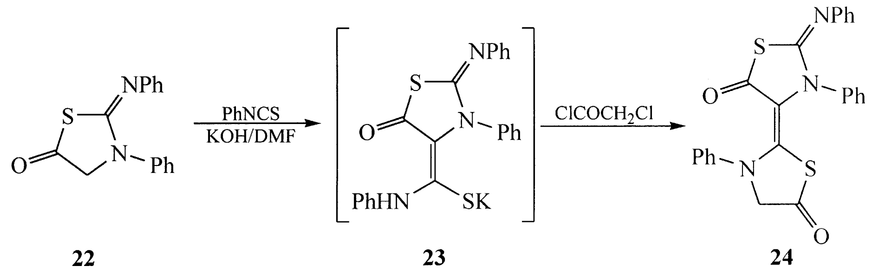
b; X = N-C_6H_4Cl-3, R = Me

c; X = O, R = Ph

SCHEME 8

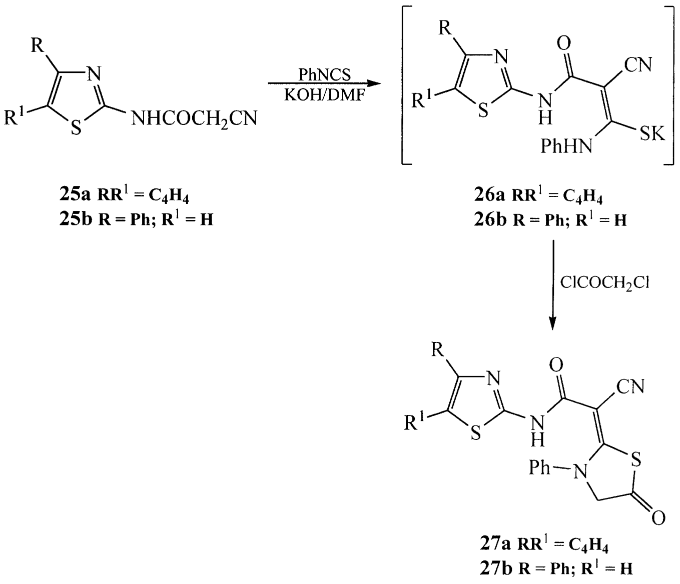
3-phenyl-2-phenyliminothiazolidin-5-one **22**[15] was prepared by the reaction of diphenylthiourea and chloroacetyl chloride in DMF containing a quantitative amount of KOH. The base-promoted nucleophilic addition of 3-phenyl-2-phenylimino-thiazolidin-5-one **22** to an equimolar amount of phenyl isothiocyanate in DMF containing potassium hydroxide afforded the corresponding, nonisolable intermediate potassium sulphide salt **23**. In situ heterocyclization of **23** was achieved by the reaction with chloroacetyl chloride to furnish the corresponding 3,3′-diphenyl-2′-phenylimino[2,4′]bisthiazolidin- ylidene-5,5′-dione **24**.[16]

Furthermore, The base-promoted nucleophilic addition of cyanoacetamide derivatives **25a**,**b** to an equimolar amount of phenyl isothiocyanate in DMF containing potassium hydroxide afforded the corresponding nonisolable intermediate potassium sulphide salts **26a**,**b**.



SCHEME 9

Heterocyclization of the intermediate **26a,b** with chloroacetyl chloride gave the corresponding 2-cyano-2-(5-oxo-3-phenylthiazolidin-2-ylidene)-acetamide derivatives **27a,b**.[17]

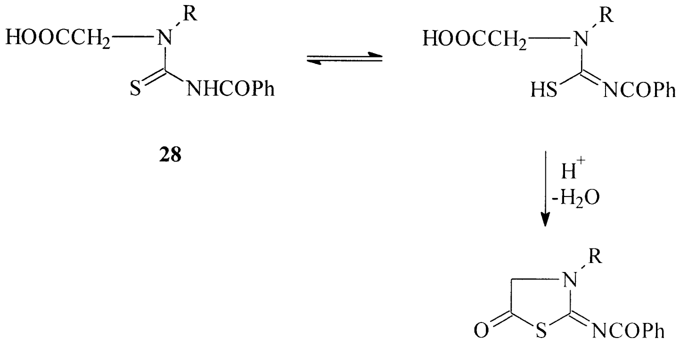


SCHEME 10

Synthesis of Thiazolidin-5-Ones from Thiocarbamoyl Derivatives

N-benzoylthiocarbamoyl *N*-substituted glycines **28** undergo acid-catalyzed[18,19] cyclization to give 3-substituted thiazolidin-5-ones **29**.

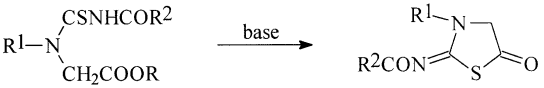
Thiocarbamoyl derivatives **30** (R = CH_3, C_2H_5, $C(CH_3)_3$; R^1 = 2,6-$(CH_3)_2C_6H_3$, Ph, CH_3; R^2 = Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$, CH_3) were



28

29

SCHEME 11

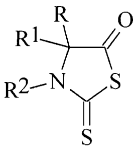


30 **31**

SCHEME 12

cyclized with a base to give the corresponding thiazolidin-5-one derivatives **31**.[20]

The title compounds **32** (R^1 = H, monovalent organic group; R, R^2 = H, monovalent organic group or RR^2 together with adjacent C and N from a fused ring) were prepared by the cyclization[21] of a salt $MS_2CNR^2CRR^1CO_2M$ (M = cation). Similar compounds **32** (R^2 = H; $RR^1 = CR^4R^5$; R^5, R^6 = H, or monovalent organic group) were prepared by the cyclization of $MS_2CNHCH_2CO_2M$ (M = cation) with Ac_2O in the presence of R^4COR^5 (R^4, R^5 as before). For example, **32** (R, R^1–R^4 = H) was prepared by treating a solution of glycine in aq. NaOH with methanolic CS_2 and a subsequent treatment with aq. H_2SO_4.

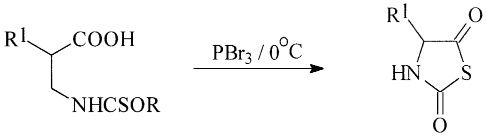


32

SCHEME 13

Synthesis of Thiazolidin-2,5-Diones

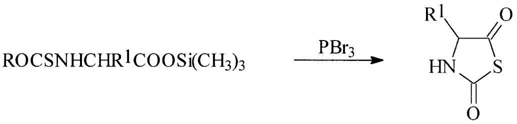
The cyclization of an α-(N-alkoxythiocarbonylamino) acid **33** with acid, or under conditions where acid is liberated by the interaction of the reagent with the carboxy group of the substrate, leads to the thiazolidin-2,5-dione **34** by cleavage of the alkoxy group in the initially-formed 2-alkoxythiazolin-5-one. Phosphorus tribromide is the recommended reagent for the cyclization reaction,[22] leading to crystalline, optically-pure thiazolidin-2,5-diones from L-aminoacids; thionyl chloride is also effective but leads to oils as reaction products.[22] The preparation can be conducted in separate steps, employing dicyclohexylcarbodiimide or acetic anhydride for the cyclization and using hydrogen chloride in benzene for alkyl-oxygen fission.[23] Racemization occurs during the 2-alkoxythiazolidin-5-one isolation procedure in the two-step route, rather than at the alkyl-oxygen fission stage, because representative thiazolidin-2,5-diones are not racemized in contact with HCl.[21]



33 **34**

SCHEME 14

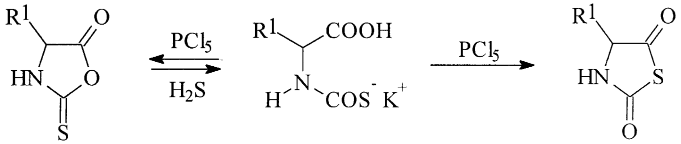
The use of alkoxythiocarbonylamino acid trimethylsilyl esters **35** has been advocated for the synthesis of thiazolidin-2,5-diones **34** under anhydrous conditions using phosphorus tribromide.[24]



35 **34**

SCHEME 15

α-isothiocyanato-alkanoic acids **36** exist in equilibrium with 2-thiono-oxazolidin-5-ones **37**, which do not show through their reactions any tendency to isomerize into thiazolidin-2,5-diones **34**.[25]

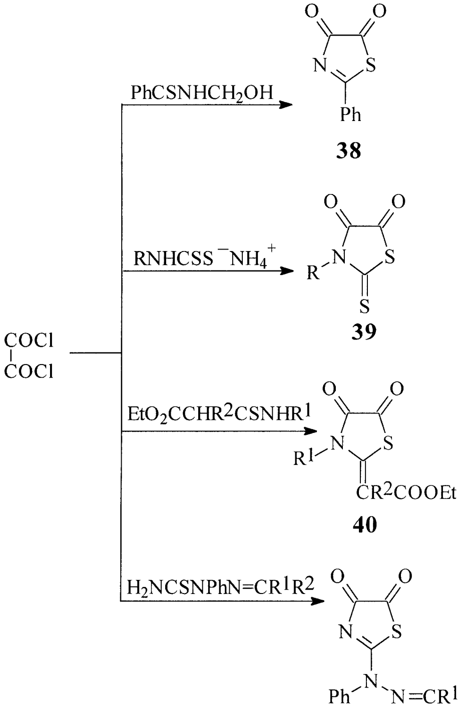


37 **36** **34**

SCHEME 16

Synthesis of Thiazolidin-4,5-Diones

The use of oxalyl chloride opened the way for the synthesis of thiazolidin-4,5-diones **38–41** from a variety of thiocarbamoyl derivatives.[26–28]



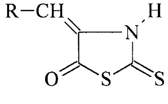
38 **39** **40** **41**

SCHEME 17

REACTIONS OF THIAZOLIDIN-5-ONES

Knoevenagel Condensation with Aldehydes

Phenylacrolein, furylacrolein, benzaldehyde, and furfural undergo a condensation reaction with 2-thioxo-5-thiazolidinone to give the corresponding condensation products **42**,[6,29,30] (R = PhCH=CH, 2-furyl-CH=CH, Ph, 2-furyl).

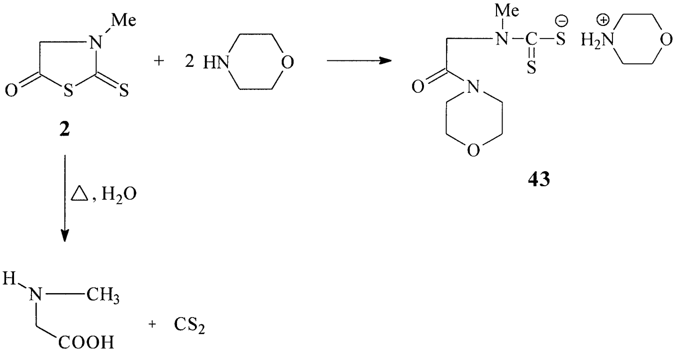


42

SCHEME 18

Ring Cleavage Reactions

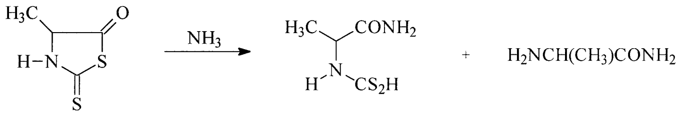
2-thioxo-3-methylthiazolidin-5-one **2** on treatment with two equivalents of morpholine in acetone leads to the formation of the morpholinium salt **43**. The 5-thiazolidinone on boiling in water undergoes ring cleavage, giving sarcosine **44** and carbon disulfide.[5]



SCHEME 19

Ammonium α-carbonyl methyl dithiocarbamate (**46**)[31] was obtained in a 90% yield by the treatment of (±) 2-thioxo-4-methylthiazolidine-5-one **45** with ammonia in ethanol.

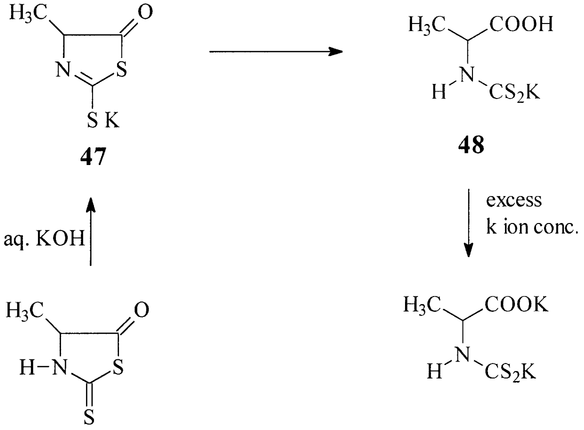
When thioxothiazolidinone **45** was dissolved in one equivalent of aqueous barium hydroxide or potassium hydroxide, a slow ring opening



45 **46**

SCHEME 20

takes place giving the carboxylic acid **48**.[31] Increasing the alkali concentration leads to the formation of **49**.



45 **49**

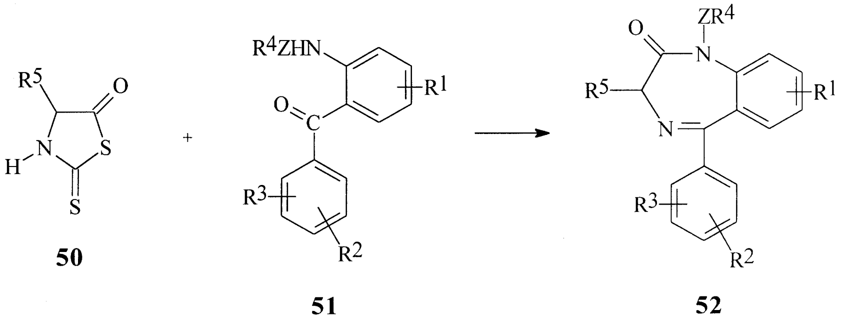
SCHEME 21

Ring Expansion Reactions

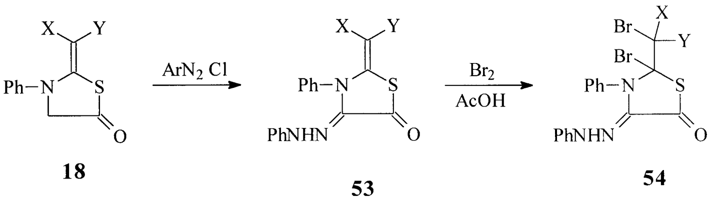
The reaction[32] of 2-thionothiazolidin-5-one **50** with amino ketones **51** in dichloromethane in the presence of ethereal HCl gives an excellent route for the preparation of various substituted benzodiazepines **52**, which belong to an important group of psychopharmacological agents.

Electrophilic Coupling Reactions

Metwally and colleagues[33,34] reported the formation of 4-arylazo-3-phenyl-2-substituted-1,3-thiazolidin-5-ones **53** by treatment of the corresponding 3-phenyl-2-substituted-1,3-thiazolidin-5-one derivatives **18** with aryl diazonium salts. Bromination of the thiazolidin-5-one derivatives **53** with bromine proceeded in glacial acetic acid to give the corresponding dibromo derivatives **54**. The synthesized 1,3-thiazolidin-5-one



SCHEME 22



X = CN, Y = COOEt

X = COMe, Y = COOEt

X = Y = CN

SCHEME 23

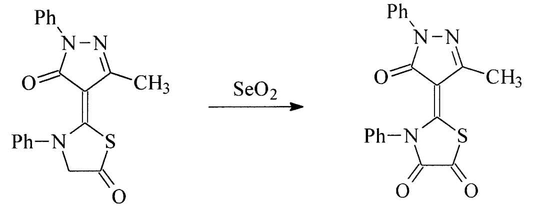
azo dyes[33,34] were applied on polyester fabrics, and their fastness properties were evaluated.

Oxidation

El-Desoky and colleagues[35] reported the oxidation of 2-(3-methyl-5-oxo-1-phenyl-1,5-dihydropyrazol-4-ylidene)-3-phenylthiazolidin-4-one **21a** with selenium oxide to afford the corresponding thiazolidin-4,5-diones **55**.

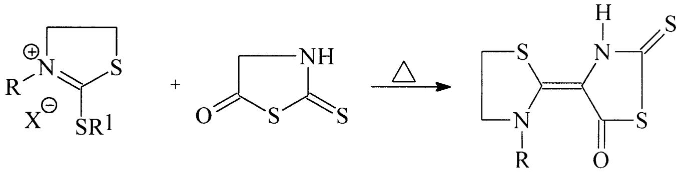
Miscellaneous Reactions

Thiazolidines **57** were prepared by the thermal condensation[36] of 2-(alkylthio)thiazoline quaternary salts **56** (R^1 = alkyl, halo) with 2-thionothiazolidin-5-one in organic solvents in the presence of pyridine or triethylamine as catalyst.



21a **55**

SCHEME 24



56 **57**

SCHEME 25

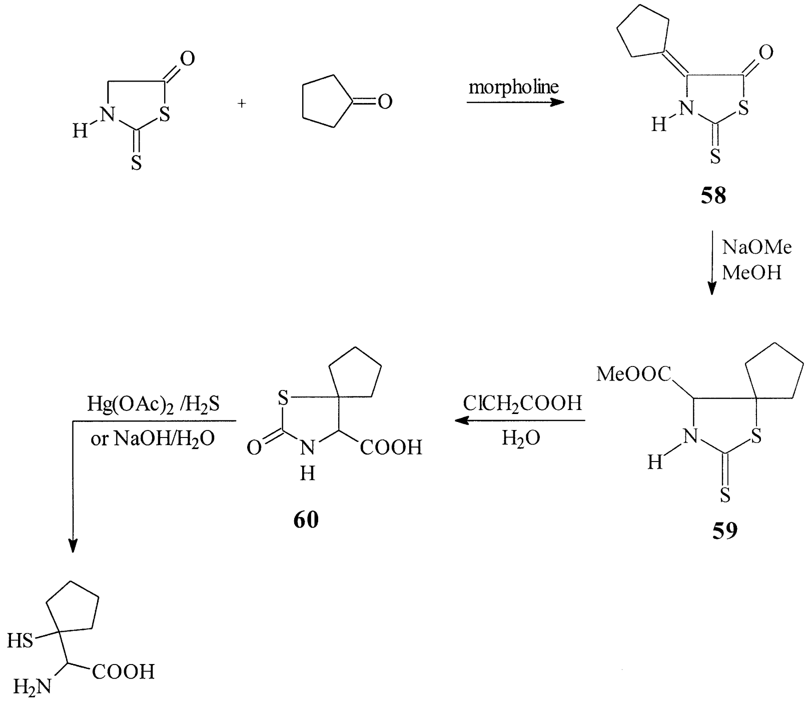
The condensation of cyclopentanone with 2-thionothiazolidin-5-one gave 2-thioxo-4-cyclopentylidene-thiazolidin-5-one **58**[37] in the presence of morpholine as a base catalyst.

The treatment of **58** with sodium methoxide in methanol gave the methyl 2-thioxo-5,5-tetramethylene-thiazolidine-4-carboxylate **59**. The conversion to the corresponding 2-oxo-5,5-tetramethylene thiazolidine-4-carboxylic acid **60** proceeded smoothly with aqueous chloroacetic acid.

Because the mercuric acetate catalyzed solvolysis of the 2-oxo derivatives **60** gave a poor yield of the desired product β,β-tetramethylene DL-cysteine **61**. Alkaline hydrolysis of **60** was affected to give **61** in a 54% yield. β,β-tetramethylene-DL-cysteine **61**[37] is good sequestering agent for blood AcH and was equally effective as D-(−) pencillamine.

The title compounds **63** [R^1 = C_{1-7} alkyl, (C_{1-4} alkyl-substituted) cycloalkyl or cycloalkenyl, at least one halo-, CF_3, OH, NO_2, COOH, (C_{1-4} alkyl-substituted) amino-, C_{1-4} alkoxy, C_{1-4} alkylthio, naphthyl, anthryl, mono- or bicyclic heterocyclyl; R^2 = C_{1-7} alkyl, $PhCH_2$; n = 0–4], which are useful for the treatment of diabetes complications, were prepared by condensation[38] of 2-thioxothiazolidin-5-one with aldehydes R^1CHO and enol thioetherification of the resulting 4-methylenethiazolidine derivatives **62** with $X(CH_2)_nCOOR^2$ (X = halo).

Cyclic sarcosine derivative **64** condensed with $MeO_2CCH_2COCH_2CONH_2$ in THF containing NaH to give benzothiazole **65** instead of an expected cyclohexenone compound.[39]



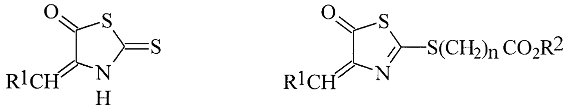
58

59

60

61

SCHEME 26



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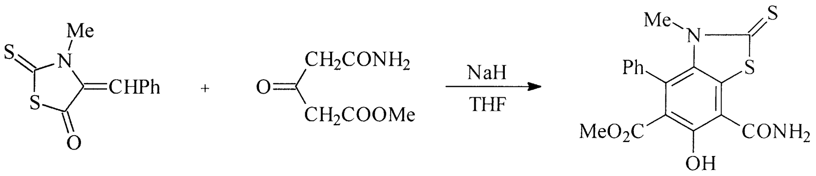
SCHEME 27

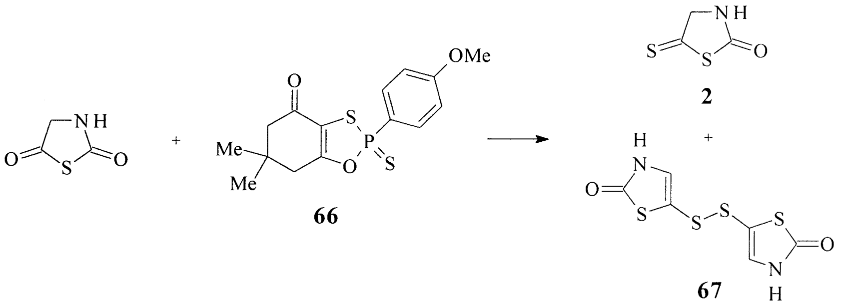


64

65

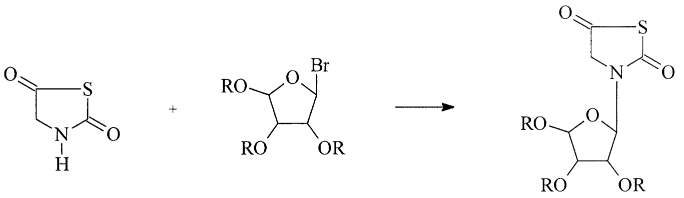
SCHEME 28

Thiazolidin-2,5-dione reacted[40] with Lawesson's reagent **66** to give 5-thioxo-2-thiazolidinone and bis(2,3-dihydro-2-oxo-5-thiazolyl) disulfide **67**.



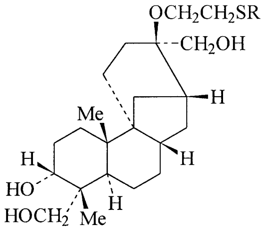
SCHEME 29

2,5-thiazolidinedione was condensed with tri-O-acyl-D-ribofuranosyl bromides **68** to give **69** (R = Ac, Bz).[41]



SCHEME 30

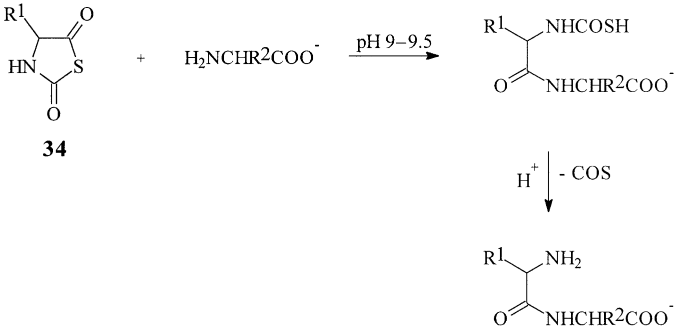
Aphidicolanes **70** (R = 2-thiazolin-2-yl),[41] which inhibit the mouse tumor cell YAC-1 at 0.1–1.6 μg/mL, was prepared by treating 16β-(2-halogenoethoxy)-2α,17,18-trihydroxyaphidicolanes with 2-mercapto-2-thiazoline.



SCHEME 31

Reactions of Thiazolidin-2,5-Diones

Ring cleavage by nucleophiles and condensation reactions involving the "active methylene group" in the 4-unsubstituted thiazolidin-2,5-diones are the main reactions of these compounds. The particular nucleophilic cleavage reaction with considerable value in synthesis is aminolysis by an amino acid or a peptied.[42] The net result of the aminolysis of a thiazolidin-2,5-dione by a peptide is the addition of an amino-acid residue to the N-terminus of the peptide. Thus, a "one-pot" stepwise peptide synthesis involving the sequential addition of amino-acids as the appropriately 4-substituted thiazolidin-2,5-diones is feasible and has been investigated as a possible improvement over the analogous use of oxazolidin-2,5-diones.[43]



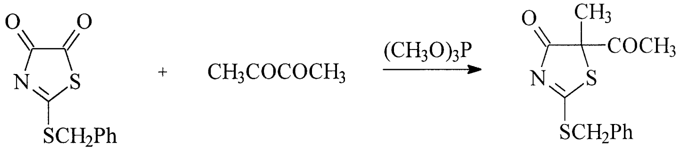
SCHEME 32

The use of thiazolidin-2,5-diones in peptide synthesis shows some equality with, or advantages over, the use of oxazolidin-2,5-diones in the cases of glycine and alanine derivatives, where aminolysis proceeds without significant racemization, and in the case of histidine, where a troublesome side-reaction in the oxazolidin-2,5-dione series is not a problem with the thiazolidin-2,5-dione analogues because intermediate thiolcarbamates formed from these compounds on aminolysis do not rearrange readily.[22]

Optically-pure thiazolidin-2,5-diones are not racemized in contact with HCl, but the mildly basic conditions accompanying aminolysis lead to unacceptably high proportions of unwanted diastereoisomers during peptide synthesis in nearly all cases.[22] An explanation for the higher acidity at C-4 in this series, relative to corresponding oxazolidin-2,5-diones, has been found[22] in the higher resonance energy of hydroxythiazole anions relative to their oxazole analogues. A further relevant factor[22] may be the smaller bond angle strain at the sp^2 C-4 center resulting from the different geometry of the two ring systems (C—S bonds are longer than C—O bonds). The factor controlling racemization in the thiazolin-5-one series is the nature of the 2-substituent, and the lower bond order of the carbonyl groups in thiazolin-5-ones and thiazolidin-2,5-diones shown by IR spectroscopic studies[44] indicates the greater contribution of canonical forms with high electron density in the ring, compared with oxazolinones.

Reactions of Thiazolidin-4,5-Diones

The reaction of a thiazolidin-4,5-dione[45] is a superficial analogy to the reversal of this synthesis.



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SCHEME 33

BIOLOGICAL ACTIVITY OF THIAZOLIDINONES

Hypnotic Activity

All thiazolidinones were found to potentiate pentobarbital sleeping time. The increase in the duration of sleep ranged from 10 ± 3 min in untreated control to 98.6 ± 10 min in mice pretreated with substituted thiazolidinones.

Respiratory Activity

All thiazolidinones selectivity inhibited the NAD-dependent in vitro oxidation of various substrates, whereas the NAD-independent oxidation of succinate remained unaltered. The presence of added NAD not only increased the cellular respiratory activity of rat brain homogenates during oxidation of pyruvate but also decreased the inhibitory effectiveness of substituted thiazolidinones.[46,47]

Antitubercular Activity

Several other derivatives of thiazolidinones have also been found[48,49] to inhibit the growth of the *Myobacterium* tuberculosis H37Rv strain.

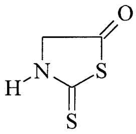
Cardiovascular Effects

All substituted thiazolidinones induced hypotension of varying degree. The duration of hypotensive activity observed with most of these compounds with less than 15 min.

Insecticidal Activity

Several other derivatives of thiazolidinones are also reported to be insecticides.[50–53]

Preliminary studies of several classes of organic sulphide compounds such as 2-thiazolidinethiones **72** and **73**[54] lead to possible chemotherapeutic agents for the inhibition of histoplasma capsulatum.



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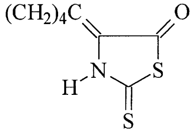

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SCHEME 34

GENERAL AND PHYSICAL PROPERTIES

Tautomerism of Thiazolidin-2,5-Diones and 2-Thionothiazolidin-5-Ones

The optical stability thiazolidin-2,5-diones in solution is less that of corresponding oxazolidin-2,5-diones,[22] but nevertheless is sufficiently high that their use in peptide synthesis can lead to optically-pure products when aminolyzed in aqueous reaction media at pH 10.[22] The tendency towards enolization shown by certain thiazolin-5-ones is therefore almost extinguished in these compounds, which extend the trend towards the predominance of the keto-tautomeric form that is initiated by replacing a 2-alkyl or phenyl substituent by an alkoxy-substituent. A 2-hydroxy group would be expected to have a similar influence to an alkoxy-group if the inductive effect of the 2-substituent controls the keto-enol equilibrium,[23] but infrared spectroscopic data[23] indicate the presence of a 2-keto-substituent in this series both for solid samples and for solutions in polar solvents.

2-thionothiazolin-5-ones are commonly depicted but more correctly as 2-mercaptothiazolin-5-ones when drawn to illustrate their applications in synthesis.[55] The greater propensity towards the thiolimidate form, which contrasts with the behavior of the thiazolidin-2,5-diones, may account for the greater tendency of 2-mercaptothiazolin-5-ones to undergo racemization. Optically active 4-(phydroxybenzyl)-2-mercaptothiazolin-5-one is completely racemized after 2–3 h in a solution in methanol. An identical solution containing 0.1 equivalents of hydrogen chloride shows a much slower racemization rate, and surprisingly, racemization was extremely slow in ethyl acetate as a solvent.[56]

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