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VICINAL HETEROAROMATIC HYDROXY, MERCAPTO AND HYDROSELENO ALDIMINES. SYNTHESIS, STRUCTURE, PROPERTIES

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This review is devoted to the latest achievements in the chemistry of vicinal heteroaromatic hydroxy, mercapto and hydroseleno aldimines. The synthesis, structure and reactivity of the above compounds are presented and discussed.

Key words: Hydroxy, mercapto, hydroseleno aldimines; alkylation, oxidation, condensation, cycloaddition.

CONTENTS

I. INTRODUCTION

Vicinal heteroaromatic hydroxy, mercapto and hydroseleno aldimines have attracted attention for approximately 30 years. This is due to a number of factors. First the aldimines in question are convenient models for the study of prototropic tautomerism (and the electron tautomerism connected with it) and are therefore of interest as potential thermo- and solvatochromes. On the other hand, the presence of adjacent proton donating and proton accepting functions in these compounds allows the formation of an intramolecular hydrogen bond (H-bond) the study of which is of great theoretical significance. The investigation of the chemical transformations of hydroxy, mercapto, and hydroseleno aldimines has established their high reactivity and, consequently, future promise for their application in organic synthesis. The ability of these aldimines to form chelates, to inhibit hydrocarbon oxidation, to act as thermo- and

light stabilizers of polymers,[1] and as electron donating components in charge-transfer complexes,[2] gives them special importance.

The above statements explain the great number of papers devoted to the study of hydroxy, mercapto, and hydroseleno aldimines. However, the literature lacks a comprehensive review interpreting all the experimental material accumulated so far (the available reviews only reflect the advances of particular scientific schools in the field discussed).[3,4] Therefore, an attempt has been made in the present review to generalize and classify the published data on the synthesis, structure and chemical properties of vicinal heteroaromatic hydroxy, mercapto, and hydroseleno aldimines.

II. SYNTHESIS

The majority of the methods for the synthesis of hydroxy, mercapto, and hydroseleno aldimines are based on reactions leading to the formation of a hydroxy (mercapto, hydroseleno) aldimine function on a heterocycle. The oxo derivatives of heteroaromatic systems, vicinal halo aldehydes, and dialkyl acetals of vicinal alkylthio aldehydes serve most commonly as starting materials, while hydroxy, mercapto, and hydroseleno aldehydes, β-enamino ketones and β-keto enol ethers are intermediates in these reactions.

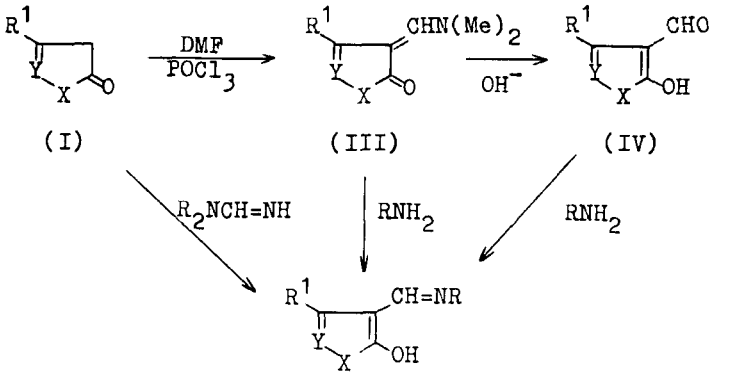
Aldimines of this type are brightly colored crystalline substances melting within a wide temperature range. They are stable in the solid state and, in most cases, in organic solvents.

Hydroxy Aldimines

When heteroaromatic oxo derivatives **I** react with *N,N*-diarylformamidines, the hydroxy aldimines **II** derived from pyrrole, furan and thiophene, respectively, are formed in 20–80% yield.[5] The interaction of the same ketones with DMF in the presence of phosphorus oxychloride results in the heteroaromatic β-enamino ketones **III** which upon reaction with primary amines (or ammonia), convert to pyrazole-,[6,7] pyrrole-,[5,8] furan- and thiophenecarboxaldimines[5] **II** in 60–80% yield.

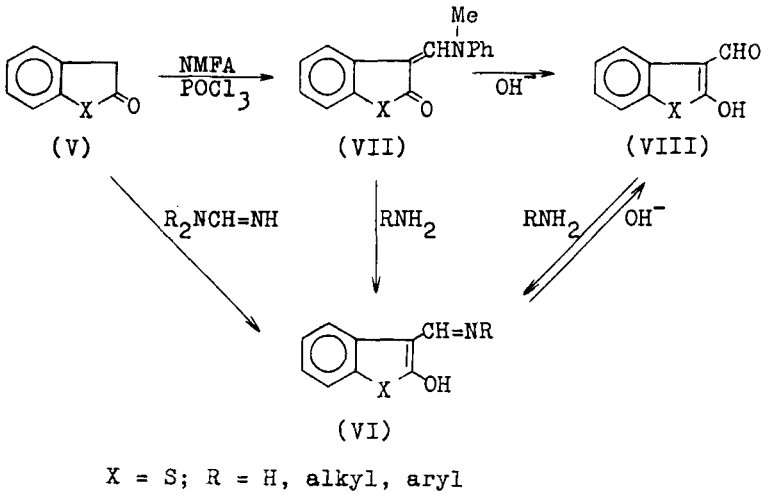
In the synthesis of hydroxy aldimines on the basis of heteroaromatic oxo derives the heteroaromatic hydroxy aldehydes may act as intermediates along with the enamino ketones **III**. Thus, in the basic hydrolysis of the enamines **III** the hydroxy aldehydes **IV** are subsequently formed and condensed subsequently with primary amines to pyrazole-,[7,9-12] pyrrole-, furan- and thiophenecarboxaldimines[5] **II** in 65–90% yield.

Similarly to oxo derivatives of five-membered heterocycles **I** used as starting materials for the synthesis of the hydroxy aldimines **II**, the oxo derivatives **V** have been used in the synthesis of aldimines of five-membered benzo[*b*]annelated heterocycles. Thus their reaction with *N,N*-diarylformamidines gives the hydroxy aldimines **VI** derived from benzo[*b*]thiophene (R = Ph)[13-15] and indole,[16] in 50–70% yield. 2(3*H*)-Benzo[*b*]thienone **V** (X = S) with *N*-methylformanilide (NMFA) in the presence of phosphorus oxychloride forms the enamine **VII** which, upon reaction with primary amines, gives hydroxybenzo[*b*]thiophenecarboxyaldimines **VI** in 70–90% yield. The hydroxyaldimine **VI** (X = S, R = Ph) has been transformed to the hydroxy aldehyde **VIII** (X = S) by reaction with alkali and then, after treatment with primary amines, to the hydroxy-



X = NMe, Y = CPh, R^1 = H; X = S, Y = CPh, R^1 = H;
X = O, Y = CPh, R^1 = H; X = NPh, Y = N, R^1 = Me;
R = H, alkyl, aryl

Scheme 1.



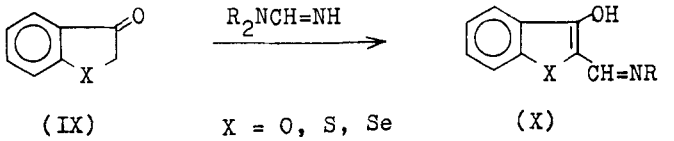
X = S; R = H, alkyl, aryl

Scheme 2.

benzo[*b*]thiophenecarboxaldimines **VI**.[13-15] The aldehyde **VIII** (X = S) has also been obtained by basic hydrolysis of the enamine **VII**.[13]

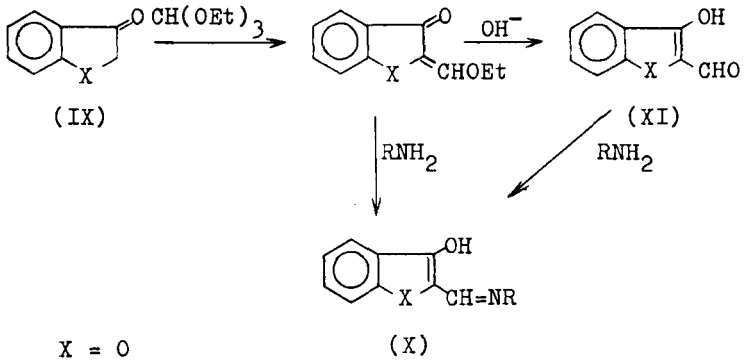
Similar to the enamine **VII**, 1-methyl-3-(ethoxyethylene)-2-indolone, formed by interaction of compound **V** (X = NMe) with ethyl formate,[17] converts, when treated with alkali, to the hydroxy aldehyde **VIII** (X = NMe) producing, upon treatment with primary amines, the hydroxy aldimines **VI** (X = NMe) in quantitative yield.[16]

The reaction of the oxo derivatives **IX** (isomers of **V**) with *N*,*N*-diarylformamidines results in the formation of the hydroxy aldimines **X**, derived from benzo[*b*]thiophene (X = S),[18] benzo[*b*]furan (X = O)[19] and benzo[*b*]selenophene (X = Se),[20] in 40–87% yield. The aldimine **X** (X = S, R = H) was obtained by gradual action of a mixture of HCN/HCl and aqueous ammonia[21,22] on the ketone **IX** (X = S), and compound **X** (X = Se, R = Ph) by reaction of ketone **IX** (X = Se) with *N*-(ethoxymethylene)-aniline.



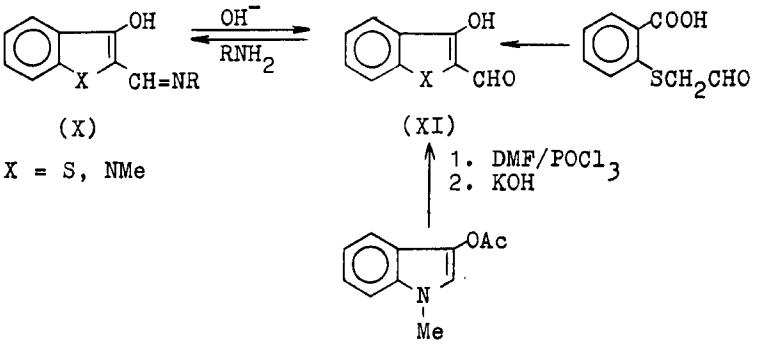
Scheme 3.

In the interaction of ketone **IX** (X = O) with triethyl orthoformate 2-(ethoxymethylene)benzo[*b*]furan-3-one is formed which, upon reaction with primary amines, forms the hydroxybenzo[*b*]furancarboxaldimines **X** (X = O) in 50–80% yield.[19]



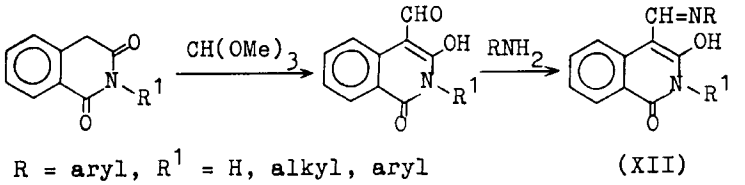
Scheme 4.

In the basic hydrolysis of 2-(ethoxymethylene)benzo[*b*]furanone the hydroxy aldehyde **XI** (X = O) is formed which, upon treatment with primary amines, forms the hydroxy aldimines **X** (X = O) in 80–90% yield. The aldimines of the indole series **X** (X = NMe) have been obtained from the corresponding hydroxy aldehyde **XI** (X = NMe), formed by gradual action of the Vilsmeier reagent and potassium hydroxide on 1-methyl-3-acetoxyindole;[23] the hydroxybenzo[*b*]thiophenecarboxaldimines **X** have also been obtained from the aldehyde **XI** (X = S), synthesized either from *S*-(formylmethyl)-thiosalicyclic acid,[21,24] or by alkaline hydrolysis of the aldimines **X** (X = S, R = Ph)[25] or **X** (X = S, R = H).[21,22] The yields of the aldimines **X** (X = NMe) amount to 70–100%.[23,25]



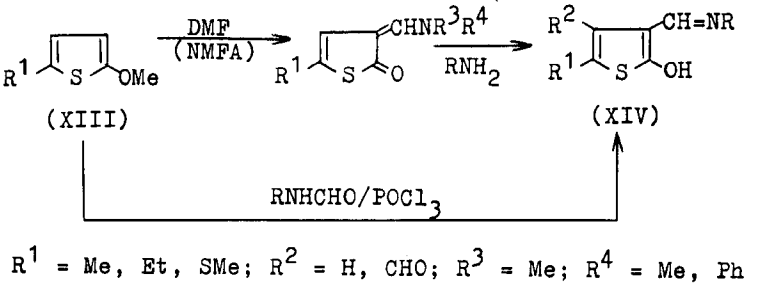
Scheme 5.

Hydroxyisoquinolinecarboxaldimines **XII** have been synthesized by reaction of primary amines with 1,2-dihydro-3-hydroxy-4-formylisoquinolin-2-ones, obtained by interaction of 1,2,3,4-tetrahydroisoquinoline-1,3-diones with trimethyl orthoformate.[26]



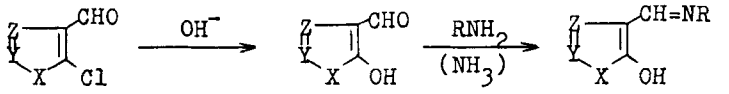
Scheme 6.

2-Methoxy-5-methyl(ethyl-, methylthio)thiophenes **XIII** are useful starting materials for the synthesis of hydroxythiophenealdimines.[27,28] When they interact with DMF or NMFA in the presence of phosphorus oxychloride demethylation of the methoxy group takes place and 5-methyl(ethyl-, methylthio)-3-[*N*,*N*-dimethyl(*N*,*N*-methylphenyl)-aminomethylene]thiolen-2-ones are formed which transform to 2-hydroxy-5-methyl(ethyl-, methylthio)-3-thenylidenearyl(alkyl)amines **XIV**[27,28] by reaction with primary amines. When the methoxythiophenes **XIII** react with a Vilsmeier reagent obtained from monosubstituted formamides, the aldimines **XIV** are formed in one step. When the compounds **XIII** react with the Vilsmeier reagent obtained from formamide the aldimines **XIV** with the aldehyde group in position 4 of the thiophene ring are also obtained in one step.



Scheme 7.

Another general method for obtaining hydroxy aldimines is based on the use of vicinal heteroaromatic halo aldehydes as starting compounds. Thus, in the reaction of aldehydes **XV** with alkali the hydroxy aldehydes **XVI** are formed. Condensation of **XVI** with primary amines yields hydroxy aldimines **XVII**, derived from pyrrole,[30,31] imidazole[32] and triazole.[33]



(XV) (XVI) (XVII)

X = NMe, Y = CCl, Z = CCHO; X = NPh, Y = CH, Z = N;

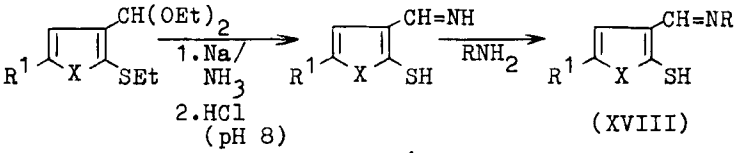
X = NBz, Y = N, Z = N; R = alkyl, aryl

Scheme 8.

Also transamination can be regarded as suitable for the synthesis of hydroxy aldimines. Aldimines of the pyrrole, furan, thiophene **II**[5] and imidazole **XVII**[34] series have been obtained in this way. It has also been demonstrated that hydroxy aldimines (the thiophene derivates **XIV** in particular) can be obtained by interaction of the corresponding mercapto aldimines with nitrile oxides.[35] When *N*-glycylaniline reacts with an orthoformate, a hydroxyimidazolecarboxaldimine **XVII** (X = NPh, Y = CH, Z = N, R = $CH_2CONHPh$) is formed.[34]

Mercapto Aldimines

The first heteroaromatic mercapto aldimines were mercaptothiophenecarboxaldimines formed by action of sodium in liquid ammonia on diethyl acetals of vicinal alkylthio aldehydes and subsequent acidification of the reaction mixture. Thus, for example from the diethyl acetal of 2-(ethylthio)-5-ethyl-3-thiophenecarboxyaldehyde the mercapto aldimine **XVIII** (X = S, R = H, R^1 = Et) was obtained which is easily transaminated to form mercaptothiophenealdimines **XVIII** with different substituents on the nitrogen atom.[36] By this method different mercaptothiophenecarboxaldimines **XVIII** (X = S),[36-44] 2,2-bis[5-mercapto-4-(iminomethyl)-2-thienyl]butanes,[37,45] 2,5-dimercapto-3,4-bis(iminomethyl)thiophenes,[46] mercaptofurancarboxaldimines **XVIII** (X = O),[47-49] 2-mercapto-3-benzo[*b*]thenylidenamines **XIV** and 2-mercapto-3-thieno[3,2-*b*]thenylideneamines[50] have been obtained. The yields of aldimines unsubstituted at the nitrogen atom amount, on the average, to 60–90%, while those of homologs substituted at the nitrogen atom amount to 70–100%.



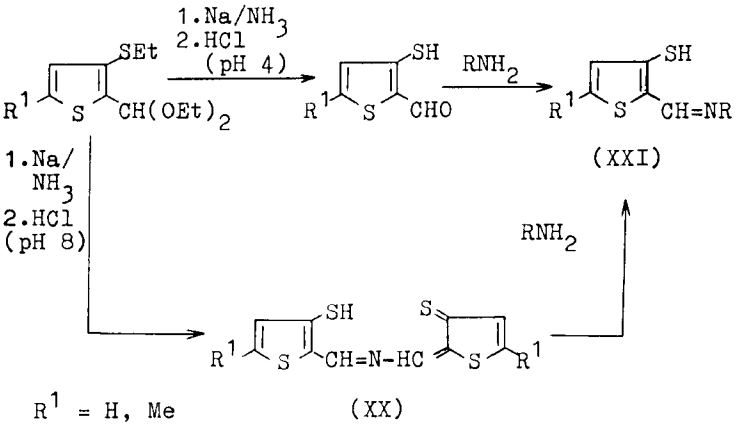
(XVIII)

X = O, S; R = alkyl, aryl; R^1 = H, Me, Et, OMe

Scheme 9.

It should be noted that no formation of mercapto aldimines is observed when sodium in liquid ammonia is allowed to act on the diethyl acetals of 2-(ethylthio)-5-ethyl-3-thieno-[2,3-*b*]thiophenecarboxaldehyde[50] and 4-(methylthio)-3-thiophenecarboxaldehyde.[51] When sodium in liquid ammonia acts on the diethyl acetal of 3-(ethylthio)-2-thiophenecarboxaldehyde with subsequent adjustment of the reaction mixture to pH 8 (the conditions of the synthesis of the aldimines **XVIII**), 3-mercapto-2-thenylidene(3-thiono-2-thienylidene)methylamine **XX**[51] is obtained, while upon dealkylation of this acetal and its 5-ethyl substituted homolog and acidification of the reaction mixture to pH 4 3-mercapto-2-thiophene- and 3-mercapto-5-methyl-2-thiophenecarboxaldehyde were isolated which form the mercaptoaldimines **XXI**[51] upon reaction with primary amines.

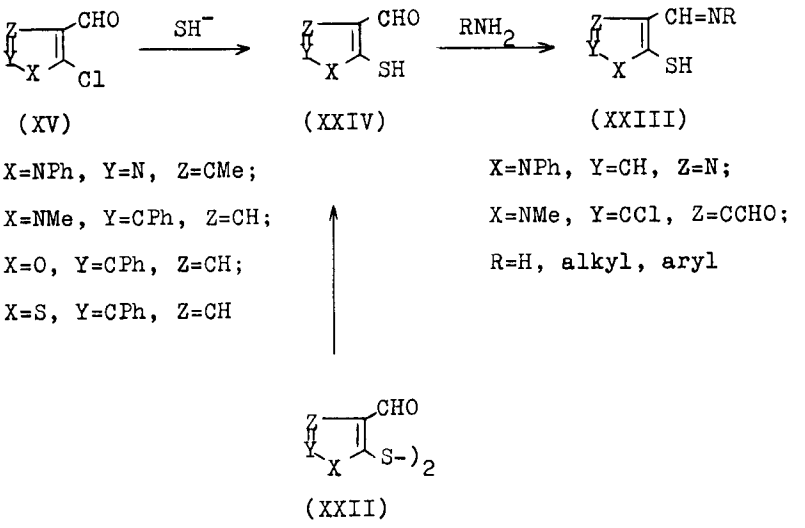
Mercapto aldimines can also be obtained by interaction of heteroaromatic β-enaminothiones with primary amines. Thus, 5-ethyl-3-(*N*,*N*-dimethylaminomethylene)thiolene-2-thione has been transformed to aldimine **XVIII** (X = S, R = cyclohexyl)[52] and compound **XX** to the aldimines **XXI** in 70–85% yield.[53]



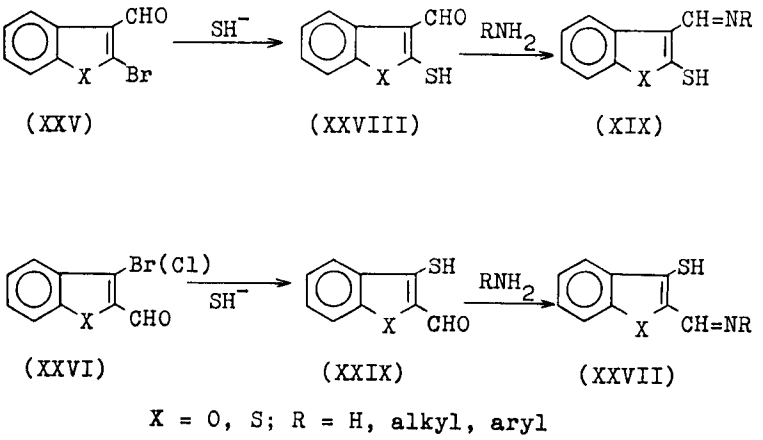
Scheme 10.

In the interaction of ammonia with vicinal formylhetaryl disulfides **XXII** the mercapto aldimines **XXIII**, unsubstituted at the nitrogen atom, are obtained in 41–46% yield.[54] According to the authors' opinion,[54] when the disulfide bond cleavage occurs, the mercapto aldehydes **XXIV** are formed; these mercapto aldehydes form with excess ammonia pyrazole-, pyrrole-, furan- and thiophenecarboxaldimines **XXIII**.

When heteroaromatic *vic*-halo aldehydes react with alkali metal hydrosulfides, followed by acidification of the reaction mixture, the corresponding mercapto aldehydes are formed which transform into mercapto aldimines after treatment with primary amines (or ammonia). Similar results are obtained when salts of primary amines act on salts of mercapto aldehydes without isolation of the latter from the reaction mixture. Thus, starting from the aldehydes **XV**, this method was used to synthesize the mercapto aldimines **XXIII** derived from pyrazole,[7,11,12,55] pyrrole,[5,8,31] furan,[5,56] thiophene,[5] and imidazole,[32] as well as *N*-methyl-2,5-dimercapto-3,4-bis(iminomethyl)pyrroles,[31] while the aldehydes **XXV** and **XXVI** formed the benzo[*b*]thiophene derivatives **XIX** (X = S)[57,58] and **XXVII** (X = S)[57–59] and the benzo[*b*]furan derivatives **XIX** (X = O)[60,61] and **XXVII** (X = O) in 60–90% yield via the corresponding mercapto aldehydes **XXIV**,



Scheme 11.



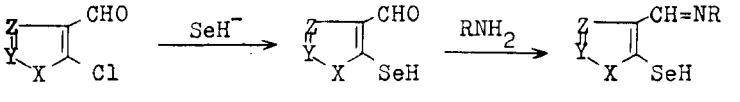
Scheme 12.

N-methyl-2,5-dimercapto-3,4-pyrroledicarboxaldehyde, **XVIII**, and **XXIX** (X = O, S) as intermediates.

A synthesis of mercapto aldehydes based on the application of organolithium reagents is also known. Thus, when *n*-butyllithium, DMF, a second equivalent of *n*-butyllithium and elemental sulfur act successively on 3-bromobenzo[*b*]thiophene with subsequent acidification of the reaction mixture, the mercapto aldehyde **XXVIII** (X = S) is obtained in 80% yield; this mercapto aldehyde reacts with primary amines or ammonia to form the aldimines **XIX** (X = S).[62]

Hydroseleno Aldimines

When heteroaromatic *vic*-halo aldehydes interact with alkali metal hydroselenides with subsequent acidification of the reaction mixture, the corresponding hydroseleno aldehydes, forming the corresponding hydroseleno aldimines with primary amines, are formed. A similar result is obtained with salts of primary amines and salts of hydroseleno aldehydes without isolation of the latter in the free state. Thus, the hydroseleno aldimines **XXX** derived from pyrazole,[7,11,12,63] pyrrole,[5,31,64] furan,[5,56] and thiophene[5] have been synthesized from the halo aldehydes **XV**, while hydroseleno aldimines derived from benzo[*b*]thiophene [**XXXI** and **XXXII** (X = S)][57,58] and benzo[*b*]furan [**XXXI** and **XXXII** (X = O)][61,65] have been prepared from the halo aldehydes **XXV** and **XXVI** via the hydroseleno aldehydes **XXXIII–XXXV**. They were isolated, in a number of cases, in the free state and characterized. The yields of the hydroseleno aldimines are 45–80%.



(XV) (XXXIII) (XXX)

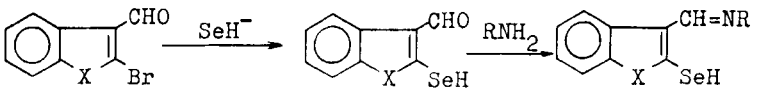
X = NPh, Y = N, Z = CMe; X = O, Y = CPh, Z = CH;

X = NMe, Y = CPh, Z = CH; X = S, Y = CPh, Z = CH;

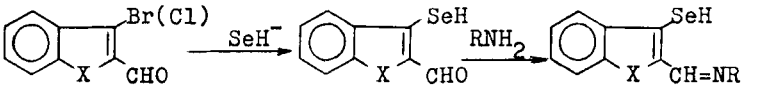
X = NMe, Y = CCl, Z = CCHO R = H, alkyl, aryl

Scheme 13.

In paper,[57] selenourea was used as a reagent for introducing selenium in the synthesis of the hydroseleno aldehydes **XXXIV** and **XXXV** (X = S). In this case, the hydroseleno aldehydes were obtained in lower yields and were contaminated with by-products. The organolithium synthesis of these hydroseleno aldimines has also been discussed.[66] However, this method has found limited application due to the lower yields (no more than 25%).



(XXV) (XXXIV) (XXXI)



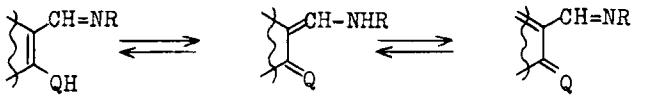
(XXVI) (XXXV) (XXXII)

X = O, S; R = H, alkyl, aryl

Scheme 14.

III. STRUCTURE

In the study of the structures of heteroaromatic hydroxy, mercapto and hydroseleno aldimines, which can potentially exist in one of several possible tautomeric forms, for example, **A–C** or their equilibrium mixtures, NMR, IR and electron absorption spectroscopy, X-ray crystallography, as well as the quantum chemical methods[67–69] have been used.



A B C

Q = O, S, Se

Scheme 15.

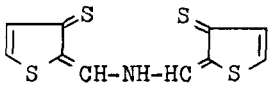
In contrast to similar arenecarboxaldimines, for which an equilibrium of the type **A** ⇄ **B** is typical,[70] heteroaromatic hydroxy, mercapto, and hydroseleno aldimines suffer, in most cases, no such changes.

NMR Spectroscopy

^{1}H NMR spectroscopy has been used to study the structure of hydroxy aldimines derived from pyrazole,[7,11,12] pyrrole,[5,31] furan,[5] thiophene,[5,67,71] imidazole,[32,34,72] triazole,[33] benzo[*b*]thiophene,[15,18,73] benzo[*b*]furan,[19] indole,[16,23] and benzo[*b*]selenophene[20]; of mercapto aldimines derived from pyrazole,[7,11,12] pyrrole,[5,31] furan,[5,74,75] thiophene,[5,46,53,74,76] imidazole,[32] benzo[*b*]thiophene,[59,73] and benzo[*b*]furan,[59,60] and of hydroseleno aldimines derived from pyrazole,[7,11,12] pyrrole,[5,31] furan,[5] thiophene,[5] benzo[*b*]thiophene,[77] and benzo[*b*]furan.[65,77]

In the ^{1}H NMR spectra of the above-mentioned aldimines with aryl substituents at the nitrogen atom the signals of two protons lie in the downfield ranges at 8–9 and 10–16 ppm. These signals manifest themselves as doublets with coupling constants J = 12–15 Hz. Such spectra correspond to the *cis*-keto(thione, selenone)enamine tautomeric form **B** and the signals in question are due to the CH- and NH-protons, respectively (the presence of a *cis*-structure is favored by the possibility of an intramolecular hydrogen bond (H-bond), evidence of which is given below). This conclusion is also confirmed by a number of other factors. Thus, for example, in the case of replacement of the aryl substituent at the nitrogen atom by benzyl,[16,59] butyl, or cyclohexyl,[76] the signal of the NH-proton appears as a multiplet, while the signal of the methylene group of the benzyl moiety appears as a doublet with J = 4–6 Hz.[16,59] The substitution of the NH-proton of an aldimine by deuterium results in the disappearance of the NH signal and the transformation of the CH-doublet into a singlet, for example.[15,23,59,76] In the ^{1}H NMR spectra of ^{15}N-aldimines $J_{^{15}N-H}$ = 82–95 Hz is observed.[5,11,15,67,76] In any series of aldimines, when a change Q = O → S → Se takes place, an increase of the NH-proton chemical shift (δ NH) is observed.

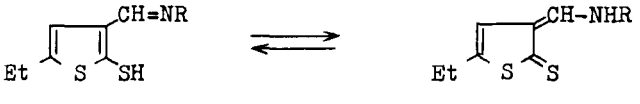
The mercapto aldimine **XX** described in paper[53] also has, according to ^{1}H NMR, the thionoenamine structure **XX–B**; however, in contrast to the aldimines discussed above, the δNH value is 3.7 ppm in this case.



(XX)-B

Scheme 16.

Variation of concentration and temperature usually has no effect on the ^{1}H NMR spectra of aldimines, which testifies to the stability of tautomeric form **B** and the absence, in the majority of cases, of tautomerism.[12,76] However, in the spectra of the mercaptothiophenecarboxaldimines **XVIII** (X = S), broadening of the signals of the CH- and NH-protons, followed by disappearance of the NH-proton signal, and transformation of the CH-doublet into a distinct singlet is observed in DMSO upon heating.[76] The ^{1}H NMR spectrum of molten **XVIII** (X = S, R = cyclohexyl, R^1 = Et) at 170 °C contains distinct and broadened singlets in the downfield range.[77] These facts in the opinion of the authors[76] show the occurrence in the solution and melt of the listed aldimines of a benzoid-quinoid equilibrium **A** ⇄ **B** shifting, upon heating, towards the tautomeric form **A** (though the disappearance of the NH-signal and the transformation of the CH-doublet into a singlet could also be explained by enhancement of proton exchange connected with increasing temperature, rather than with an **A** ⇄ **B** tautomeric equilibrium).

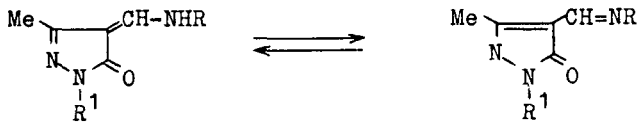


(XVIII)-A (XVIII)-B

X = O, S; R = cyclohexyl

Scheme 17.

A prototropic equilibrium is also observed in a number of hydroxypyrazolecarboxaldimines **II**. The ^{1}H NMR spectra indicate that these aldimines exist as enaminoketones **II-B** at low temperatures, while at room temperature and above as the pyrine structures **II-C**.[11]



(II)-B (II)-C

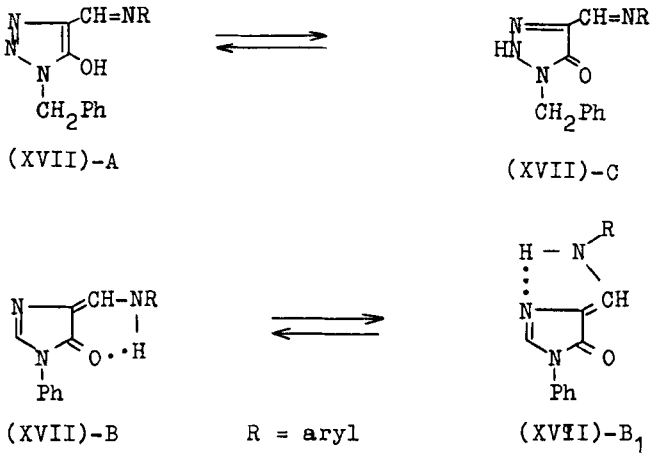
R = R^1 = Me, Ph

Scheme 18.

A hydroxy aldimine structure **XVII-A** is attributed to the 1,2,3-triazole derived hydroxy aldimines **XVII** (X = NR, Y = Z = N) on the basis of ^{1}H NMR spectra (the signals attributed by the authors[33] to CH- and OH-protons are present). However, the corresponding structure **XVII-C** can give the same picture in the ^{1}H NMR spectra. The

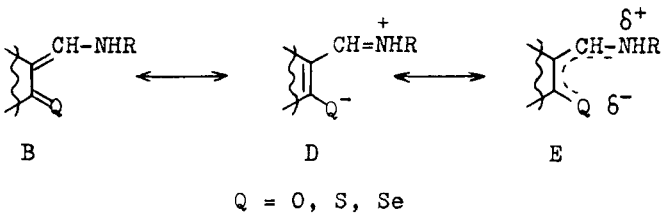
data given in paper[33] on the IR spectra of these compounds make the structure **XVII–C** most likely.

Thus, ^{1}H NMR spectra showed that practically all heteroaromatic hydroxy, mercapto and hydroseleno aldimines exist as *cis*-keto (thiono, selenono) enamines (tautomeric form **B**), except for the hydroxyimidazolealdimines **XVII** (X = NPh, Y = CH, Z = N) existing, at the moment of dissolution, as an equilibrium mixture of the *cis*- and *trans*-isomers **XVII-B** and **XVII-B$_1$**; the equilibrium shifts in time towards **XVII-B**.[72]

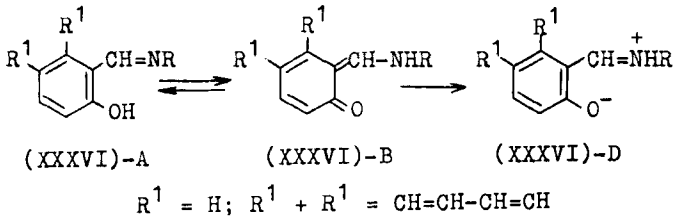


Scheme 19.

However, upon examination of the ^{13}CNMR spectra of the hydroxy **II**, mercapto, **XXIII** and hydroseleno aldimines **XXX** derived from pyrazole and pyrrole,[78] specifically when comparing the chemical shifts of the carbon atoms bonded to the exocyclic heteroatom Q (Q = O, S, Se), the conclusion can be made of little double-bond character of the C=Q bonds in the tautomeric form **B** and, consequently, of increased multiple-bond character of the bonds in the heterocycle and the C–N bond in the enamine moiety, which allows the conclusion of a significant contribution of form **D** to the tautomeric form **B**. The simultaneous impact of the forms **D** and **B** corresponds to the mesomeric form **E** with a general "uniformity" of bonds in the chelate ring implying that the polarization of the aldimines in the chelate ring increases with a change of Q (Q = O, S, Se). Least polarized are the hydroxy aldimines characterized by the greatest degree of double bonding in the C–Q (Q = O) bonds.[78]



Scheme 20.

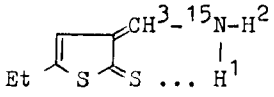


Scheme 21.

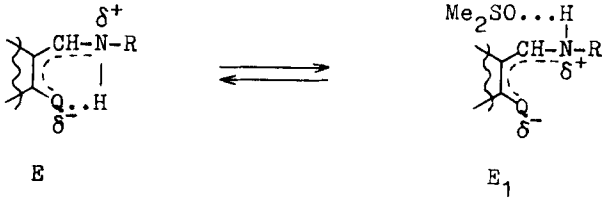
Somewhat later, with the use of ^1H and ^{13}C NMR spectroscopy, it could be demonstrated that the hydroxy aldimines derived from benzene and naphthalene **XXXVI** undergoing tautomeric **A** ⇄ **B** transformation upon solvent and temperature change exist as dipolar **XXXVI-D(E)**, not as keto enamine **XXXVI-B** structures[79] in polar solvents at low temperatures.

Thus, based on the ^1H NMR spectra, the location of the "bridge" proton in heteroaromatic hydroxy, mercapto and hydroseleno aldimines has been established, while on the basis of the ^{13}C NMR spectra a conclusion was made about the delocalization of the multiple bonds and the polarization of their chelate rings, i.e. structure **E**.

The structure **E** (as, for example, does structure **B**) of the aldimines in question infers the presence of a hydrogen bond of the type NH. . .Q (Q = O, S, Se). Indeed, this assumption is confirmed by the independence of the ^1H NMR spectra of these aldimines of concentration changes in solvents such as chloroform, carbon tetrachloride, and benzene[12,76] and by the different behavior of the NH-protons in the ^1H NMR spectrum of the ^{15}N-mercaptothiophenecarboxaldimine **XVIII** (R = H, R' = Et), in which the signal of the proton H^1 appears as a distinct quartet (doublet of doublets) ($J_{H^1-H^3}$ = 13 Hz, $J_{^{15}N-H^1}$ = 85 Hz) (absence of intermolecular proton exchange of H^1, participating in a hydrogen bond), while the signal of the proton H^2 appears as a broad singlet (participation of H^2 in intermolecular proton exchange).[76] In addition, the presence of a hydrogen bond is confirmed by the change, in a number of cases, of ^1H NMR spectra of aldimines upon change of the solvent from chloroform to a basic solvent, say, DMSO.



(XVIII)



E E_1

Scheme 22.

These changes are connected with the fact that some aldimines in DMSO solution interact with the solvent forming associates of the putative structure $\mathbf{E}_1$ which are in equilibrium with the initial structure **E**.[5,73–75,77] Thus, in the ^{1}H NMR spectrum of 3-mercapto-2-benzo[*b*]furylidene-*p*-methoxyphenylamine **XXVII** (X = O) in DMSO-d_6, the doublets at δ 14.65 (NH–E) and 9.11 (CH–E) and the broad singlets at 11.57 (NH–E_1) and 8.19 (CH–E_1) ppm lie in the downfield region,[77] whereas the ^{1}H NMR spectrum of this compound in $CDCl_3$ contains two doublets at δ 14.58 and 8.19 ppm.[60]

The study of the hydrogen bonds in heteroaromatic hydroxy, mercapto and hydroseleno aldimines has been carried out in terms of their keto (thiono, selenono) enamine (structure **B**) composition. The data obtained from ^{1}H NMR spectra of aldimines[5,11,31,67,71,74–76,80] led the authors to the wrong conclusion that the large δ_{NH} values (10–16 ppm) are due to the participation of the NH-proton in a hydrogen bond, the relative strength of which can be estimated from δ_{NH}; the larger δ_{NH} for structurally similar compounds, the stronger the hydrogen bond. The same conclusion was also used in the form of a "rule" for the evaluation of the relative strength of the hydrogen bond even after the dipolar nature of the aldimines had been established.[78] The invalidity of this conclusion follows from the mesomeric dipolar structure **E** of the aldimines: the large δ_{NH} values are due to an "acidic" character of the NH-proton, as well as to its presence in the plane of the conjugated π-system of the chelate part of the aldimines, while the change of δ_{NH} of aldimines upon the change Q = O, S, Se is connected with a changing degree of dipolar character in this series (but not with increasing overlap of the orbitals of the NH-proton and the heteroatoms O, S, Se, which would have led to a decrease of δ_{NH}).[77]

Thus, NMR spectroscopy indicates that heteroaromatic hydroxy, mercapto, and hydroseleno aldimines exist as polarized mesomeric structures **E** with a hydrogen bond NH . . . Q (Q = O, S, Se).

Electron Absorption Spectroscopy

Electron absorption spectroscopy has been used for the study of the structure of hydroxy aldimines derived from pyrazole,[12] pyrrole,[5,31] furan,[5] thiophene,[5] imidazole,[32] benzo[*b*]thiophene,[15,18] benzo[*b*]furan,[19] indole,[16,23] and benzo[*b*]selenophene[20]; of mercapto aldimines derived from pyrazole,[12] pyrrole,[5,31] furan,[5] thiophene,[5,53] imidazole,[32] benzo[*b*]thiophene,[58,59] and benzo[*b*]furan[59,60] and of hydroseleno aldimines derived from pyrazole,[12] pyrrole,[5,31] furan,[5] thiophene,[5] benzo[*b*]thiophene,[58] and benzo[*b*]furan.[65]

The electron absorption spectra of the mentioned aldimines contain an intensive long-wave band in the region 370–560 nm the position of which, in an overwhelming number of cases, practically does not depend on the temperature and the polarity of the medium (in contrast, for example, to mercaptobenzaldimines[70]), which shows the stability of one of the theoretically possible tautomeric forms **A–C**.

The choice of a probable tautomeric form is carried out by comparing the electron absorption spectra of the aldimines with those of compounds simulating the single tautomeric forms, for example, **A–a** or **B–b**, as well as by correlation with the ^{1}H NMR data.

Thus, based on the fact that the electron absorption spectra of the hydroxy, mercapto, and hydroseleno aldimines differ from the spectra of the compounds "**a**" simulating the

imino tautomeric form **A**, but are similar to the spectra of the compounds "**b**", simulating the keto (thiono, selenono) enamino tautomeric form **B**, this tautomeric form **B** has been attributed to them.

It is necessary to point out that in the electron absorption spectrum of the mercapto aldimine **XX**,[53] to which the thiono enamine structure was attributed on the basis of a ^{1}H NMR spectrum, an absorption band in the visible region is lacking, which shows that this aldimine differs from the remaining compounds.

A-a B-b

R = aryl; R^1, R^2, R^3 = alkyl

Scheme 23.

In a study of the electron absorption spectra of photo- and solvatochromic hydroxy aldimines derived from benzene and naphthalene absorbing in the visible region and by comparison with the spectra of compounds simulating the keto enamino-quinoid structure, but not absorbing in this part of the spectrum (1,2,5-thiadiazoles, 1,2,3-triazoles), the conclusion was drawn that the presence of a long-wave absorption band of aldimines has no connection with the presence of a quinoid structure **B**, but can be explained by the dipolar structure **D(E)**.[81] This conclusion can also be extended to the analogous heteroaromatic aldimines with similar electron absorption spectra which was confirmed in a study of the protonation of hydroxy aldimines derived from benzo[*b*]furan, benzo[*b*]thiophene, and benzo[*b*]selenophene **X** (X = O, S, Se),[82] as well as by analysis of changes in the electron absorption spectra of the hydroselenobenzo[*b*]furancarboxaldimines **XXXI** and **XXXII** (X = O) upon a change of pH.[65]

Thus, on the basis of electron absorption spectroscopy, the similarity of hydroxy, mercapto, and hydroseleno) aldimines with keto (thiono, selenono) enamines "**b**" and, consequently, the occurrence of a "bridge" hydrogen atom at the nitrogen atom have been determined; it has also been indicated that the color of the aldimines in question is determined by their dipolarity. The combination of these data permits to describe the aldimines under discussion in terms of structures **D(E)**, which is in good agreement with the NMR data.

Now it is of interest to refer again to the aldimine **XX** with a clear-cut thiono enamine structure, but not absorbing in the visible region.[53] The last detail shows the absence of polarization (see Section "NMR spectroscopy").

IR Spectroscopy

IR spectroscopy has been used in the study of hydroxy aldimines derived from pyrazole,[12] pyrrole,[5,31] thiophene,[5] imidazole,[32] furan,[5] triazole[33] (see Section "NMR spectroscopy"), benzo[*b*]thiophene,[15,18] benzo[*b*]furan,[19] indole,[16,23] and benzo[*b*]-selenophene[20], of mercapto aldimines derived from thiophene,[5,36,38,45,46,53,76] pyrazole,[12] pyrrole,[5,31] furan,[5] imidazole,[32] benzo[*b*]thiophene,[50,58,59] thieno[3,2-*b*] thiophene,[50] and

benzo[*b*]furan,[59,60] and of hydroseleno aldimines derived from pyrazole,[12] pyrrole,[5,31] furan,[5] thiophene,[5] benzo[*b*]thiophene,[58] and benzo[*b*]furan.[65]

In the study of the structure of heteroaromatic hydroxy, mercapto, and hydroseleno aldimines IR spectroscopy has been used as an additional method along with electron absorption and NMR spectroscopy, while the assignment of the bands in the IR spectra of aldimines was carried out on the basis of their keto (thiono, selenono) enamine structure.

Two specific bands are present, usually in the region of 1650–1680 and 1600–1630 cm^{-1}, in the IR spectra of hydroxy aldimines. These bands have been attributed either to the vibrations of the C=O and the exocyclic C=C bond, for example,[5,16,18,19,31] or to the vibrations of the conjugated vinylogous amide moiety CH=C–C=O, for example,[5,12,31] or to the deformation vibrations of NH bonds.[31] Lines due to amino groups do not always appear; the wide bands of NH-bonds of aldimines have been studied in Refs.[5,15,16,31,46,59] These facts indicate the presence of hydrogen bonds in aldimines.

In the IR spectra of mercapto and hydroseleno aldimines a specific band in the region 1630–1660 cm^{-1} is present which has been attributed to the vibrations of the exocyclic C=C bond in the thionoenamine tautomeric form[59], or, more frequently, to the vibrations of the vinylogous amide moiety CH=C–C=X (X = S, Se).[5,12,31,75] In Refs.[36,45,50] this band has been classified as the vibrations of a C=N bond.

Upon comparison of the IR spectra of the hydroselenobenzo[*b*]thiophenealdimines **XXXI** and **XXXII** (X = S) with the spectra of the corresponding hydroseleno aldehydes **XXXIV** and **XXXV** (X = S), it was demonstrated that the band in the region 1630–1660 cm^{-1} can be attributed to the vibrations of a $C=N^+$ bond in the structure **D(E)**,[58] which is in good agreement with the NMR data[78,79] and the electron absorption[81] spectra.

It is of interest to note that in the IR spectrum of the mercapto aldimine **XX** with, according to its UV and ^1H NMR spectra, a thionoenamine structure without any dipolar contribution, a band in the region 1630–1660 cm^{-1} is absent, while bands at 3300 and 1140 cm^{-1} were attributed by the authors[53] to the vibrations of respectively, -NH- and S=C–C=C.

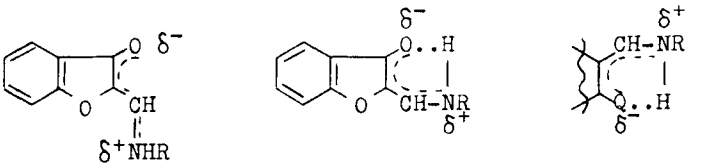
Thus, the absorption bands of hydroxy aldimines in the range 1650–1680 cm^{-1} can be attributed to the vibrations of C=O and exocyclic C=C, while the bands of mercapto and hydroseleno aldimines in the range 1630–1660 cm^{-1} belong to the vibrations of $C=N^+$. However, this conclusion cannot be regarded as final because additional lines, the nature of which is still to be determined, are present in the region being discussed.

X-Ray Analysis

The literature contains several X-ray studies of aldimines of the relevant type: 3-hydroxy-2-benzo[*b*]furylidenephenylamine **X** (X = O, R = Ph),[83] 3-hydroxy-2-benzo[*b*]thenylidene-*m*-nitrophenylamine **X** (X = S, R = *m*-nitrophenyl),[4] *N*-methyl-3-hydroxy-2-indolidenephenylamine **X** (X = NMe, R = Ph),[4] 2-mercapto-3-thenylidenecyclohexylamine **XVIII** (R = cyclohexyl, R^1 = H),[84] and 3-mercapto-2-benzo[*b*]furylidene-*p*-methylphenylamine **XXVII** (X = O, R = *p*-tolyl).[85]

All these compounds exist in the crystalline state in the tautomeric form **B** (*cis*-**B**) with the exception of 3-hydroxy-2-benzo[*b*]furylidenephenylamine which exists in the *trans*-**B**

form.[83] The bond lengths in the chelate regions OCCCN or SCCCN have mean values between the standard double and single bonds which permits to specify the structure of these compounds as *cis*-**E**, not *cis*-**B** (for 3-hydroxy-2-benzo[*b*]furylidenephenylamine it is *trans*-**E**).



trans-(X)-E cis-(X)-E E

Q = O, S, Se

Scheme 24.

In paper,[84] the position of the chelated NH-proton was not determined; the mean bond lengths of the fragment SCCCN in the mercapto aldimines **XVIII** were explained by the authors[84] by the presence of a prototropic equilibrium **A** ⇄ **B**.

In papers,[4,85] on the basis of a decrease of the bond length $X-C^5$ (X = O, S, NMe) in comparison with standard values, the conclusion was made that a lone electron pair of the heteroatom X participates in conjugation with the chelate fragments SCCCN and OCCCN, while, on the basis of the distances between atom Q (Q = O, S) and the hydrogen atom the conclusion was drawn that an H–H . . . Q hydrogen bond is present in these aldimines.

Thus, on the basis of spectral and X-ray data, one can see that practically all heteroaromatic hydroxy, mercapto, and hydroseleno aldimines exist as polarized mesomeric structures with an N–H . . . Q hydrogen bond (Q = O, S, Se) **E**.

IV. CHEMICAL PROPERTIES

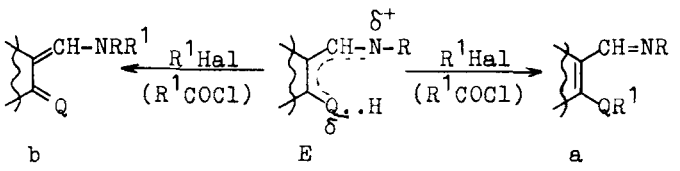
The chemical properties of heteroaromatic hydroxy, mercapto, and hydroseleno aldimines are typically reactions resulting either in ortho-bifunctional derivatives or in annelated heterocycles. This situation permits such aldimines to function as convenient synthetic intermediates.

The ability of aldimines to form complexes of the chelate type with transition metals is one of their most important characteristics.[1,61,66,86–92] However, this problem is of special interest and, therefore, not covered in the present review.

To simplify the representation and to avoid confusion in nomenclature, the hydroxy, mercapto, and hydroseleno aldimines are presented most commonly as aldimine rather than enamine or dipolar structures.

Alkylations and Acylations

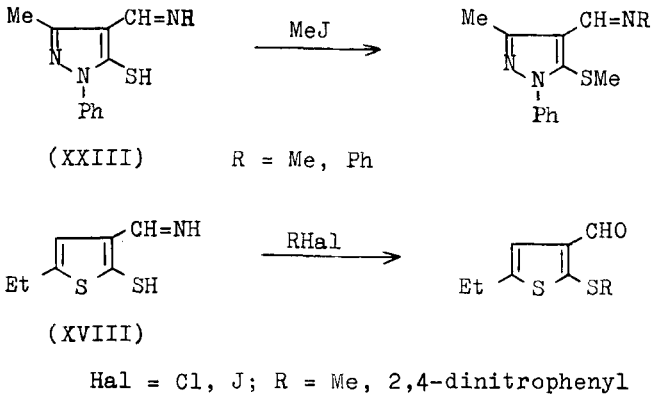
Proceeding from the structure of hydroxy, mercapto, and hydroseleno aldimines given as the structure **E**, a dual reactivity of these compounds in alkylations and acylations should be expected: the formation either of the product of *Q*-alkylation (acylation) –



Scheme 25.

compounds "**a**", or of products of *N*-alkylation (acylation) – compounds "**b**", or of mixtures of products "**a**" and "**b**".

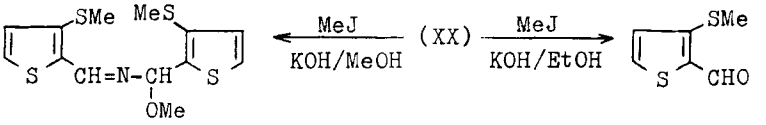
Examples of alkylations of hydroxy aldimines are lacking in the literature. The mercapto and hydroseleno aldimines are alkylated with alkyl (aryl) halides in the presence of bases to give *S*(*Se*)-alkylation products "**a**". For example, upon alkylation of the mercaptopyrazolecarboxaldimines **XXIII** (X = NPh, Y = N, Z = CMe, R = Ph, Me) with methyl iodide 2-methylthio-1-phenyl-5-methyl-3-pyrazolidenephenyl(methyl)amines are obtained.[93] Similar derivatives are formed in the alkylation of *N*,*N*-bis(2-mercapto-5-ethyl-3-thenylidene)benzidine with benzyl chloride,[36] of 2,2-bis[5-mercapto-4-(iminomethyl)-2-thienyl]butanes with 2,4-dinitrochlorobenzene,[45] or of 2-mercapto-3-benzo[*b*]furylidenephenylamine **XIX** (X = O, R = Ph) with methyl iodide.[60] By alkylation of 1-methyl-2,5-dimercapto-3,4-bis(iminomethyl)pyrrole with methyl chloroacetate,[94] of the mercapto aldimines **XXIII** with chloroacetic acid,[56,95] or of the hydroseleno aldimines **XXX** with chloroacetic acid,[56,63,64,95] the corresponding carbomethoxymethylthio- and carboxymethylthio(seleno) derivatives have been obtained, which have been used in the synthesis of bisthienopyrrole,[95] thienopyrrole,[95] selenolopyrrole,[56,64] thieno- and selenolofurans,[56,95] thieno- and selenolothiophenes,[56,95] and selenolopyrazoles.[63]



Scheme 26.

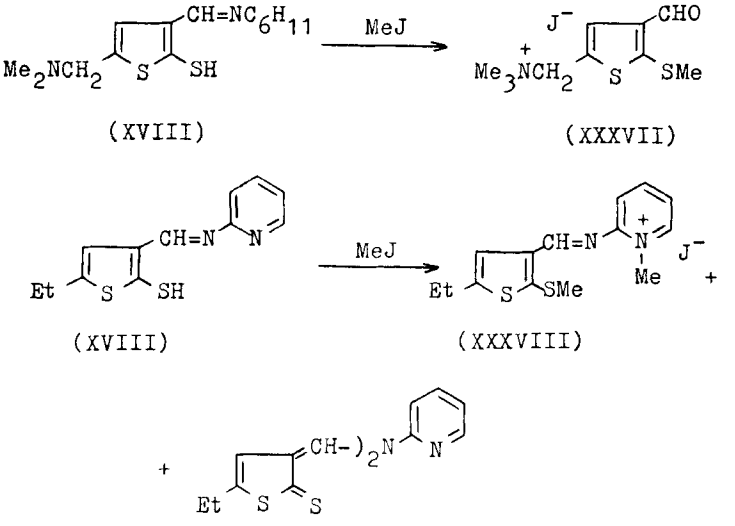
When mercapto aldimines unsubstituted at the nitrogen atom interact with alkylating agents in the presence of aqueous bases, hydrolysis of the azomethine group goes parallel with the alkylation of the mercapto group and *o*-alkylthio aldehydes are isolated as reaction products. Thus, for example, 2-mercapto-5-ethyl-3-thenylideneamine **XVIII** (X = S, R = H) upon reaction with methyl iodide or 2,4-dinitrochlorobenzene forms

2-methylthio(2,4-dinitrophenylthio)-5-ethyl-3-thiophenecarboxaldehydes.[36,52] In alkylation reactions, 2-mercapto-3-benzo[*b*]thenylideneamine **XIX** (X = S, R = H) and 2-mercapto-5-ethyl-3-thieno[3,2-*b*]thenylideneamine[50] behave in a similar manner. The alkylation of **XX** (R^1 = H) with methyl iodide in the presence of KOH/MeOH results in the formation of (3-methylthio-2-thenylidene)[(α-methoxy)-3-methylthio-2-thenyl]-amine (55%), while alkylation of the same compound with methyl iodide in the presence of KOH/EtOH gives 3-methylthio-2-thiophenecarboxaldehyde (83%).[53]



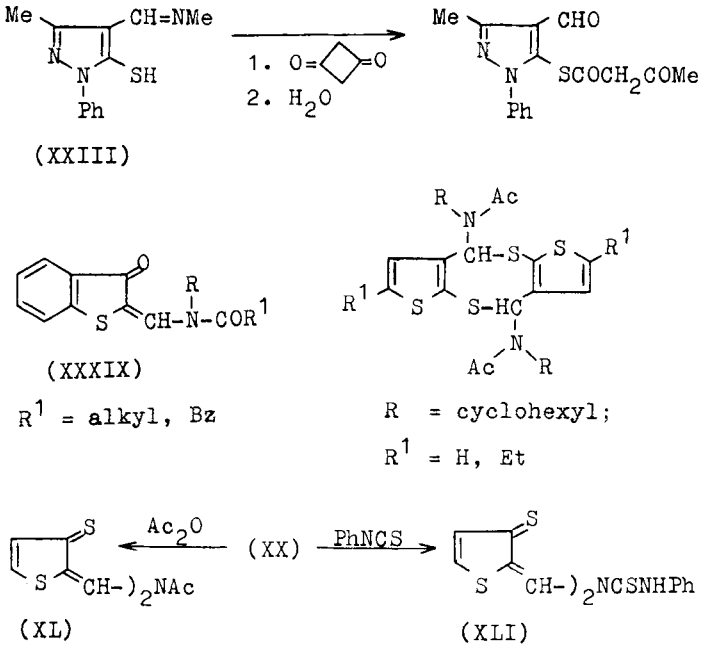
Scheme 27.

The alkylation of 2-mercapto-5-(*N*,*N*-dimethylaminomethyl)-3-thenylidenecyclohexylamine **XVIII** with methyl iodide is accompanied by hydrolysis of the azomethine group and quaternization of the side chain nitrogen atom with formation of **XXXVII**,[41] while the alkylation of the mercapto aldimine **XVIII** (X = S, R = 2-pyridyl) results in the formation of a mixture of the salt **XXXVIII** and *N*,*N*-bis(5-ethyl-2-thiono-3-thienylidenemethyl)-2-aminopyridine.[39] The treatment of 1-phenyl-3-methyl-5-hydroxy-4-pyrazolidene-*N*-alkylamines **II** with methyl iodide also results in the formation of quaternization products.[9] In this case no *O*-alkylation occurs.



Scheme 28.

Compared to alkylation, the acylation of hydroxy, mercapto, and hydroseleno aldimines has been studied to a lesser degree. As an example of *S*-acylation, the interaction of 5-mercapto-1-phenyl-3-methyl-4-pyrazolidene-*N*-methylamine **XXIII** with diketene and water, resulting in 5-acetonylcarbonylthio-1-phenyl-3-methyl-4-pyrazolecarbox-

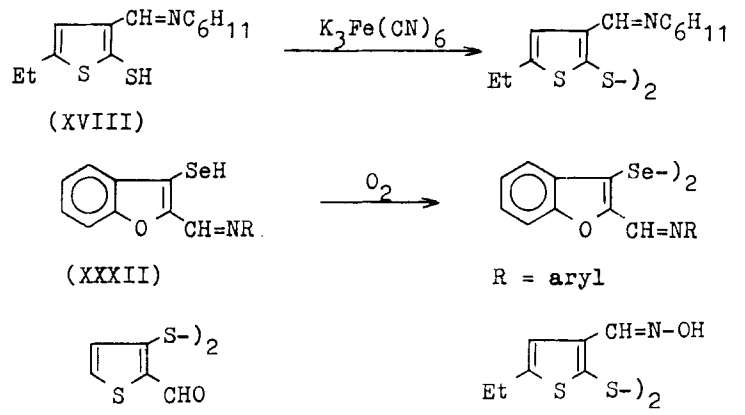


Scheme 29.

aldehyde can be given.[55] Examples of *N*-acylation are the successive interaction of 3-hydroxy-2-benzo[*b*]thenylideneamines **X** (X = S) with potassium isopropoxide and acyl chlorides with formation of the *N*-acyl derivates **XXXIX** (X = S, R^1 = alkyl, Bz),[93] as well as the interaction of the hydroxy aldimines **X** (X = S, NMe) with acetyl chloride with formation of homologs of **XXXIX** (X = S, NMe; R = alkyl, R^1 = Me)[96] and the synthesis of 4,9-bis(*N*-acetyl-*N*-cyclohexylamino)-4*H*,9*H*-dithieno[2,3-*b*;2,3-*f*]-5,10-dithiocenes (R^1 = H, Et) from the mercapto aldimines **XVIII** (X = S; R = cyclohexyl, R^1 = H, Et) and acetic anhydride.[38] The interactions of **XX** with phenyl isothiocyanate and acetic anhydride with formation of the corresponding *N*-derivatives **XL** and **XLI**[53] can be regarded as processes of the same type.

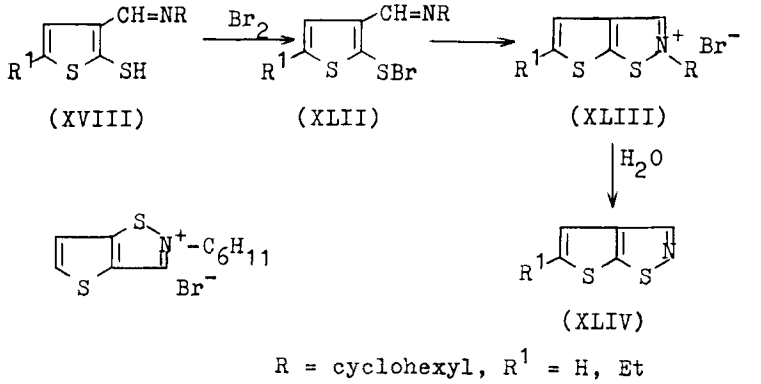
Oxidations and Reductions

The presence of SH and SeH groups in mercapto and hydroseleno aldimines allows oxidation to the corresponding disulfides and diselenides. Thus, for example, 2-mercapto-5-ethyl-3-thenylidene-*N*-cyclohexylamine **XVIII** (X = S; R = cyclohexyl), when treated with potassium ferricyanide in the presence of base, forms bis(5-ethyl-3-thenylidene-*N*-cyclohexylamino-2) disulfide,[97] while the 3-hydroseleno-2-benzo[*b*]furylideneamines **XXXII** (X = O; R = aryl) are oxidized to bis(2-benzo[*b*]furylideneamino-3) diselenides by atmospheric oxygen upon short time storage in solution.[65] Compound **XX**, when treated with iodine in acetic acid, forms bis[(2-formylthienyl)-3] disulfide[53] while the mercapto aldimine **XVIII** (X = S; R = H; R^1 = Et), interacting with hydroxylamine and, probably, atmospheric oxygen is converted to 2,2′-dithiobis[5-ethyl-3-thiophenecarboxaldehyde] dioxime.[36]



Scheme 30.

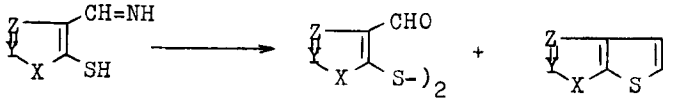
For synthetic purposes the oxidation of mercapto and hydroseleno aldimines with elemental bromine and concomitant formation of N–Q bonds deserves greater interest. Thus, interaction of the mercapto aldimines **XVIII** (X = S; R = H, cyclohexyl; R^1 = H, Et) with bromine results, via the sulfenyl bromides **XLII**, in the formation of the isothiazolium bromides **XLIII**[38,97] which easily exchange the bromide ion forming iodides, picrates, and perbromides.[97] The hydrolysis of **XLIII** (R = H, R^1 = Et) gives 5-ethylthieno[3,2-*d*]isothiazole **XLIV** (R^1 = Et).[97] The bromination of 2-mercapto-5-phenyl-3-thenylidenamine **XXIII** (X = S; Y = CPh; Z = CH) also gives the thieno-isothiazole **XLIV** (R^1 = Ph) in 90% yield[87] while the bromination of 3-mercapto-2-thenylidene-*N*-cyclohexylamine **XXI** (R = cyclohexyl, R^1 = H) leads to 2-cyclohexyl-thieno[2,3-*d*]isothiazolium bromide (74%), also easily transforming to the corresponding iodide, picrate or perbromide.[98]



Scheme 31.

The bromination of mercapto aldimines derived from pyrazole, furan, and pyrrole **XXIII** (R = H) proceeds in a somewhat different way. Thus, for the aldimines derived from pyrazole and furan the major reaction products, along with the annelated isothia-

zoles **XLV** (X = NPh, Y = N, Z = CPh; X = O, Y = CPh, Z = CH) are bis(1-phenyl-3-methyl-4-formyl-5-pyrazolyl) and bis(2-phenyl-4-formyl-5-furanyl) disulfide **XXII** in 87 and 70% yield, respectively. When the mercaptopyrrolecarboxaldimine **XXIII** (X = NMe, Y = CPh, Z = CH) was treated with bromine, only disulfides **XXII** (X = NMe, Y = CPh, Z = CH) were isolated.[87]

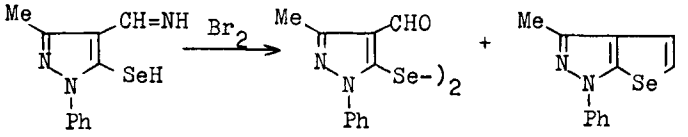


(XXIII) (XXII) (XLV)

X = NPh, Y = N, Z = CMe; X = NPh, Y = N, Z = CMe;
X = O, Y = CPh, Z = CH; X = O, Y = CPh, Z = CH
X = NMe, Y = CPh, Z = CH

Scheme 32.

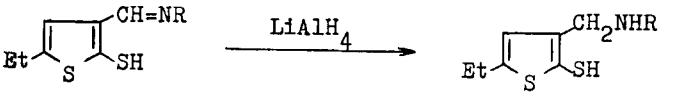
The bromination of 5-hydroseleno-1-phenyl-3-methyl-4-pyrazolylidenamine **XXX** gave a mixture of two products: bis(1-phenyl-3-methyl-4-formyl-5-pyrazolyl) diselenide **XLVI** (28%) and 1-phenyl-3-methylpyrazolo[4,5-*d*]isoselenazole **XLVII** (60%).[99]



(XXX) (XLVI) (XLVII)

Scheme 33.

It should be noted that the bromination of the hydroxypyrazolecarboxaldimine **II** (X = NPh, Y = N; R = H, R^1 = Me) does not lead to the corresponding pyrazolo-isoxazole: 1-phenyl-3-methyl-4,4-dibromo-5-pyrazolone (90%)[87] is the reaction product.



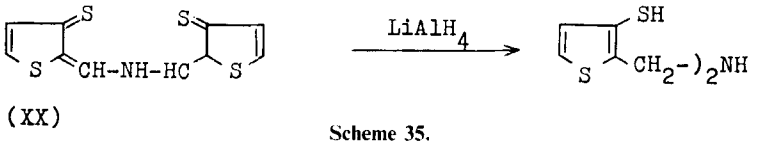
(XVIII)

R = H, cyclohexyl

Scheme 34.

Reductions of hydroxy, mercapto, and hydroseleno aldimines have been presented in the literature in a lesser degree. Thus, the mercapto aldimines **XVIII** (X = S, R = H, cyclohexyl), when treated with lithium aluminum hydride form 2-mercapto-5-ethyl-3-thenylamines isolated as hydrochlorides, useful in the synthesis of dihydrothieno[3,2-

e]thienothiazines and thienothiazole **XLIV** (R^1 = H).[97,100] Similarly, by reduction of **XX**, bis(3-mercapto-2-thenyl)amine was obtained, also isolated as the corresponding hydrochloride.[53]

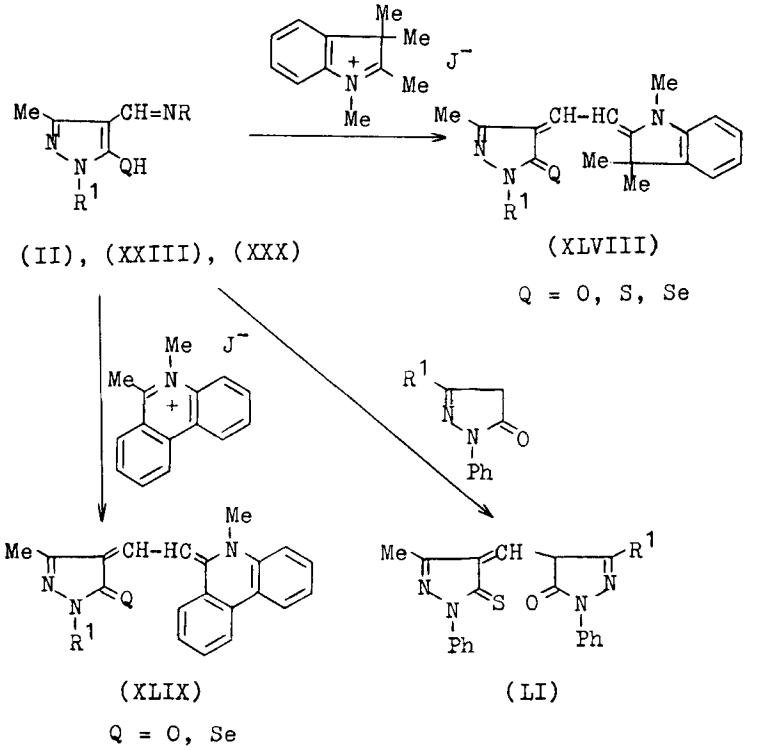


(XX)

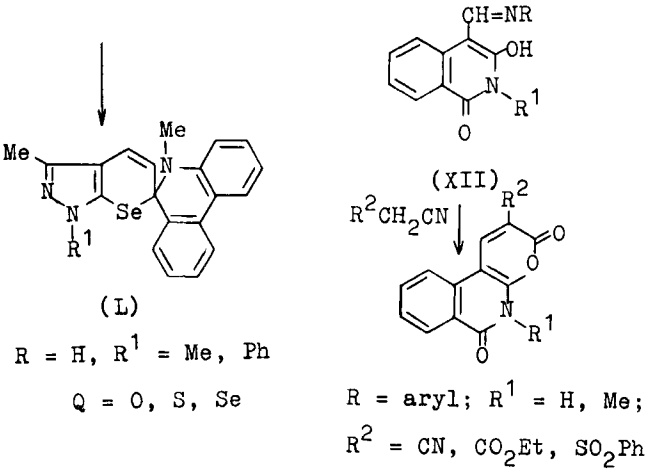
Scheme 35.

Condensations

Condensations with different CH-acids represent an important part of the reaction possibilities of the aldimines considered here. Relevant examples are the reactions of hydroxy, mercapto, and hydroseleno aldimines derived from pyrazole **II**, **XXIII**, and **XXX** with 1,2,3,3-tetramethylindoleninium and 5,6-dimethylphenanthridinium iodide, resulting in the formation of the merocyanine dyes **XLVIII** and **XLIX**.[55,101] It should be noted here that during interaction of the hydroseleno aldimines **XXX** with 5,6-dimethylphenanthridinium iodide the spiro compounds **L** are formed along with the dyes **XLIX**.[101]



Scheme 36.



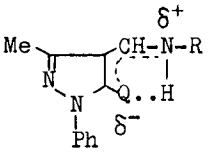
Scheme 36. (Cont.).

Dyes similar to **XLVIII** and **XLIX** have also been obtained from reactions of hydroxy aldimines derived from isoquinoline with 1,2- and 1,4-dimethylpyridinium, 1,2-dimethylquinolinium, and 1,2-dimethylbenzothiazolium iodide in 46–70% yields.[26] In addition, the same aldimines when interacting with nitriles of the type $CH_2(CN)_2$, $NCCH_2COOEt$, $PhCH_2CN$, etc. in the presence of bases were transformed to 5,6-dihydro-3*H*-pyrano[2,3-*c*]isoquinoline-3,6-diones in 51–74% yields.[26]

By boiling the mercaptopyrazolecarboxaldimines **XXX** (X = NPh, Y = N, Z = CMe; R = H) with 1-phenyl-3-R-5-pyrazolones (R = Ph, Me) the condensation products **LI** have been obtained.[55]

Cycloadditions

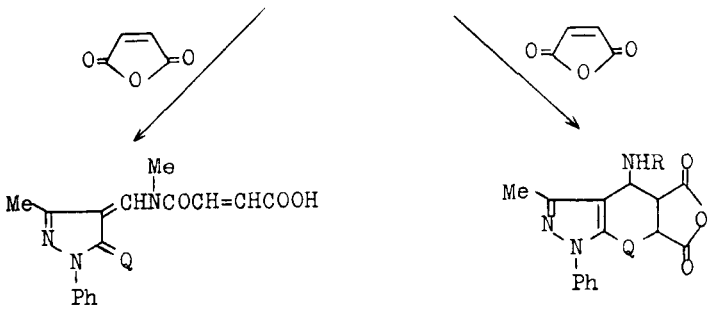
The chemical nature of heteroaromatic hydroxy, mercapto and hydroseleno aldimines manifests itself more clearly in their reactions with compounds containing an activated double bond. Examples of such reactions are few. Nevertheless, they permit to establish a clear interconnection between the structure and reactivity of aldimines. Thus, the 1-phenyl-3-methyl-5-mercapto(hydroseleno)-4-pyrazolidenamines **XXIII** and **XXX** upon interaction with maleic anhydride give the products of 1,4-dipolar cycloaddition, i.e. 1-phenyl-3-methyl-4-(R-amino)-4,5,6-tetrahydrothio(seleno)-pyrano[2,3-*d*]pyrazole-5,6-dicarboxylic acid anhydrides.[102] It has been shown that the reaction is first order with respect to both reagents and proceeds by a concerted mechanism.[103]



(II), (XXIII), (XXX)

Q = O, S, Se

Scheme 37.



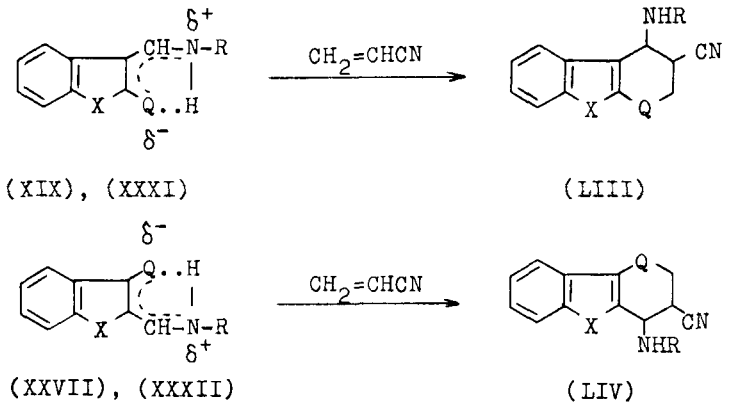
(LII) Q = O

Q = S, Se

Scheme 37 Continued.

It is interesting to note that the oxygen analogs of the mercapto and hydroseleno aldimines **XXIII** and **XXX**, the hydroxy aldimines **II**, when reacting with maleic anhydride do not form cycloadducts but give the *N*-acyl derivates **LII**[102] which has been explained by the insufficient polarity of the chelate system in **II** required for a dipolar cycloaddition. This fact, as well as the increase of the reaction rate with maleic anhydride upon transition from the mercapto **XXIII** to the hydroseleno aldimines **XXX** confirms the conclusion that the polarity of the chelate system in the aldimines increases upon change of Q in the order O, S, Se (see Section "NMR spectroscopy").

The interaction of mercapto and hydroseleno aldimines derived from benzo[*b*]furan and benzo[*b*]thiophene **XIX**, **XXVII**, **XXXI**, and **XXXII** (X = O, S) with acrylonitrile with formation of the annelated thio- and selenopyrans **LIII** and **LIV** was studied in paper.[77] It was demonstrated that the reaction rate depends not only on the polarity of the chelate system of the aldimines (*Se*-derivatives react faster than *S*-analogs), but also on the strength of the H-bond: the compounds **XXVII** and **XXXII** with an H-bond of lesser strength react faster than the isomers **XIX** and **XXXI** with a stronger H-bond.[77]



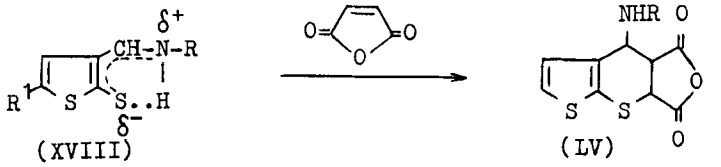
(XIX), (XXXI) (LIII)

(XXVII), (XXXII) (LIV)

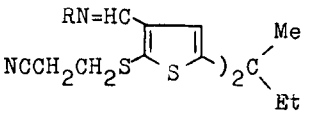
X = O, S; Q = S, Se

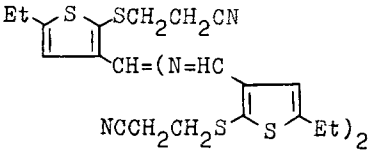
Scheme 38.

Reactions of mercaptothiophenecarboxaldimines with maleic anhydride and acrylonitrile have also beeen described. Thus, the aldimines **XVIII** (R = cyclohexyl; R^1 = Et, OMe) interact with maleic anhydride to form the cycloadducts **LV**[104] while 2,2-bis[(5-mercapto-4-(*N*-cyclohexyliminomethyl)-2-thienyl]butane with acrylonitrile forms 2,2-bis-[5-(β-cyanoethylthio)-4-(*N*-cyclohexyliminomethyl)-2-thienyl] butane[45] and the aldimine **XVIII** (R = H) in a similar reaction gives the hydramide of 2-(2-cyanoethylthio)-5-ethyl-3-thiophenecarboxaldehyde (47%).[36]



R = cyclohexyl, R^1 = Et, OMe





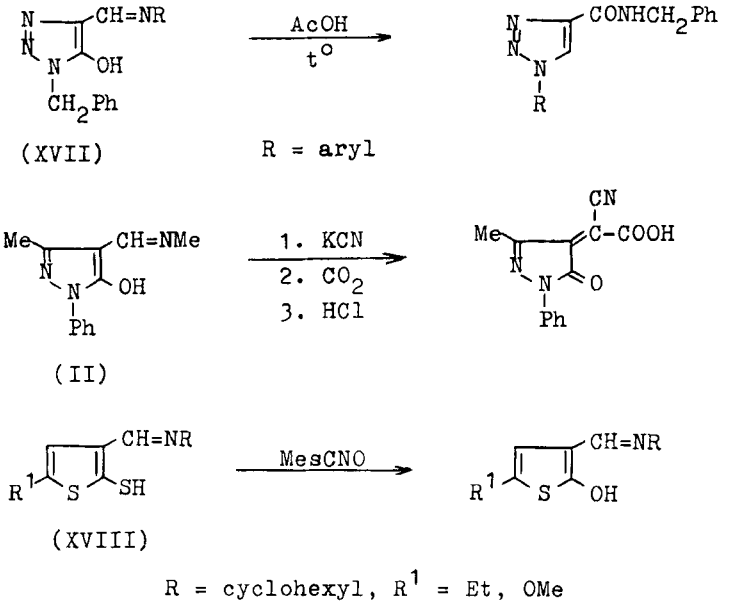
Scheme 39.

Miscellaneous Reactions

The literature contains data concerning photochemical transformations of mercapto and hydroseleno aldimines. Thus, the mercapto aldimine **XXIII** (X = NPh, Y = N, Z = CMe; R = H) being exposed to ultraviolet light or light in the violet region forms a mixture of four products: the isothiazole **XLV**, the mercapto aldehyde **XXIV**, the disulfide **XXII** (X = NPh, Y = N, Z = CMe), and 1-phenyl-3-methyl-4-pyrazolecarboxaldehyde **LVI** in 24, 36, 12 and 16% yield, respectively,[105] while the hydroseleno aldimine **XXX** (X = NPh, Y = N, Z = CMe; R = H) gives the isoselenazole **XLVII**, the diselenide **XLVI** and the aldehyde **LVI** in 40, 40, and 10% yield, respectively.[99]

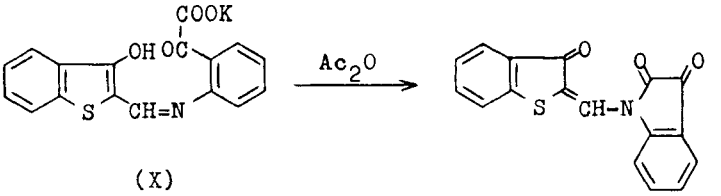
The rearrangement of the hydroxy-1,2,3-triazolecarboxaldimine **XVII** (R = Ar), heated or boiled in acetic acid, to 1-aryl-1,2,3-triazole-4-carboxylic acid *N*-benzylamides,[33] the synthesis of 1-phenyl-3-methyl-5-oxopyrazolidene-4-malonic acid from the hydroxy aldimine **II** (X = NPh, Y = N; R = Me) by successive interaction with KCN, CO_2, and HCl,[106] and the reaction of the mercaptothiophenecarboxaldimines

XVIII (R = cyclohexyl, R^1 = Et, OMe) with mesitonitrile *N*-oxide, resulting in the formation of the corresponding hydroxythiophenecarboxaldimines **XIV**[35] are also known.



Scheme 40.

When the hydroxybenzo[*b*]thiophenecarboxaldimine **X** (X = S, R = 2-KOOCCOC$_6$H$_4$) reacts with acetic anhydride, 2-(*N*-isatinomethylene)-3(2*H*)-benzo[*b*]thienone is obtained (95%).[107] Besides, the hydrolysis of aldimines with formation of the corresponding aldehydes belongs also to the chemical properties of aldimines (see Section "Synthesis").



Scheme 41.

These are the chemical properties of heteroaromatic hydroxy, mercapto, and hydroseleno aldimines known at present. They cover a wide range of reactions by which derivatives of different types can be obtained. These derivatives are bifunctional compounds capable, in turn, of undergoing further chemical transformations,[56,64,97] and of forming annelated heterocyclic systems,[77,97,102,104] substances with a "long" chain of conjugation which absorb in the visible region of the spectrum and, therefore, represent

potential dyes,[26,55,101] as well as new tautomeric systems exhibiting photo- and solvatochromism.[93,96,107]

All the aforesaid permits the conclusion that it is promising to study the present aldimines as convenient intermediates for organic synthesis and to search for substances with practically useful properties among their transformation products.

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