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α,β-Acetylenic Acids and Their Derivatives in Reactions with Hydrogen Sulfide and Thiols

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Abstract — Results of the research into reactions of α,β-acetylenic acids and their derivatives with hydrogen sulfide and thiols are summarized. The addition direction and stereochemistry depend on whether there is an activating group at the triple bond, as well as on the structure of the thiol. The reactions not infrequently provide not only monothiylation products, but complete with intramolecular cyclization yielding polyfunctional heterocyclic compounds.

I. INTRODUCTION

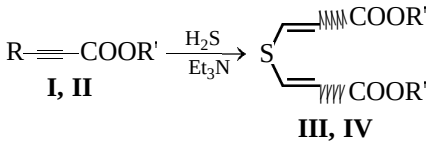
α,β-Acetylenic acids and their derivatives are typical representatives of activated acetylenes which serve as synthetic precursors of a great number of biologically important compounds, such as leucotrienes, eicosanoids and their antagonists, ascorbic, penicillic, lenicillic, and tetrolic acids, etc.). The carboxy group at the triple bonds much enhances the electrophilicity of the latter, thus favoring facile nucleophilic addition, as well as [4*p* + 2*p*]-cycloaddition reactions [1–3].

General synthetic approaches to acetylenic acids and their derivatives have presently rather well developed [4], which allows much room for progress in this field of fine organic synthesis. The accessibility of α,β-acetylenic acids makes them convenient starting materials for synthesis of new types of organic sulfur compounds.

Reactivity studies on acetylenes [5, 6] and sulfur compounds [7–10] have been systematized and summarized in the monographs [11–13] and reviews [14–16]. However, no comprehensive reviews concerning reactions of α,β-acetylenic acids and their derivatives with hydrogen sulfide and thiols have so far been available.

II. REACTIONS WITH HYDROGEN SULFIDE

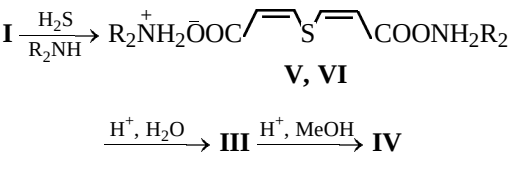
Hydrogen sulfide underoges a fairly facile nucleophilic addition to the unsaturated bonds C≡C, C=C, and C=O [7, 10]. The reactivity of acetylenes depends on the donor power of the reagent and on the nature of the substituent at the triple bond [2]. Haefliger and Peterzilka showed [17] that propiolic acid (**I**) and its esters **II** [R' = Me (**a**), Et (**b**)] regioselectively react with H_2S under nucleophilic addition conditions (ether, Et_3N, 0°C, 3 h) to give (*E*,*E*)-divinyl sulfides **III**, **IV** in yields of up to 53%.



I, II **III, IV**

R = H; R' = H (**I, III**), Me (**II, IV**).

However, more recenty Dallas *et al.* [18] established that the stereochemical result of base-catalyzed additions of H_2S to ester **IIa** at 20°C can be varied by varying solvent polarity. As a rule, increasing solvent polarity increased reaction yield (MeOH, >90%) and fraction of *Z*,*Z* isomers (~34%). The reactions in CCl_4 or benzene in the presence of *N*-methylmorpholine (~1%) gave a mixture of *E*,*E*, *E*,*Z*, and *Z*,*Z* isomers (68 : 23 : 9), implying violation of the *trans*-addition rule. At the same time, isomerization was not excluded. By contrast, acid **I** (R = H) reacted with H_2S in liquid ammonia or secondary amine media, forming ammonium salts of (*Z*,*Z*)-bis(2-carboxyvinyl) sulfide (**V**, **VI**) in 81% yield [19]. Salts **V**, **VI** are readily hydrolyzed to give acid **III** whose treatment with MeO_2C results in formation of ester **IV** with retention of the *Z*,*Z* configuration.



V, VI

R = H (**V**), Et (**VI**).

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Salts **V**, **IV** were also obtained from acid **I** (R = H) and CS_2 in liquid ammonia by the following scheme.

$$CS_2 + NH_3 \longrightarrow H_4\overset{+}{N}\overset{-}{S}(S)NH_2 \xrightarrow[-(H_2N)_2CS]{NH_3} (H_4N)_2S,$$

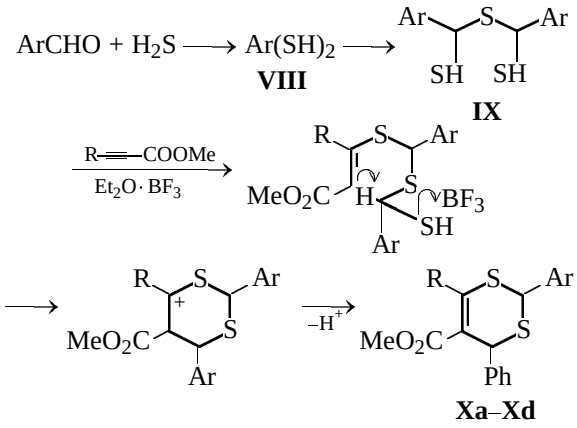
$$\mathbf{I} + \bar{S}C(S)NH_2 \longrightarrow \bar{O}_2C\diagup\!\!=\!\!\diagdown SC(S)NH_2$$

$$\xrightarrow[-(H_2N)_2CS]{NH_3} \bar{O}_2C\diagup\!\!=\!\!\diagdown S \xrightarrow{\mathbf{I}} \mathbf{V},$$

$$\mathbf{I} + (H_2N)_2S \xrightarrow{NH_3} \mathbf{V}.$$

Both procedures provide good yields of salts **V**, **VI**, which allows the latter to be used in various syntheses and polymerization.

By varying conditions of H_2S addition to ester **IIa** one can radically vary the reaction direction. For example, Eisner and Krishnarmuthy [20] observed an unusual cyclization in reactions of H_2S with ester **IIa** and dimethyl acetylenedicarboxylate (**VIIa**) in the presence of aromatic aldehydes and BF_3 etherate. The referees proposed a mechanism of these reactions, involving formation of dithiol **VIII** and its self-cyclization into dithiol **IX**. The subsequent addition of the latter to ester **IX** or **VIIa** followed by cyclization into 1,3-dithiines **Xa**–**Xd** in nearly quantitative isolable yields [19].

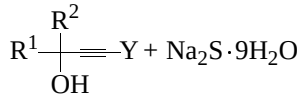


Xa–**Xd**

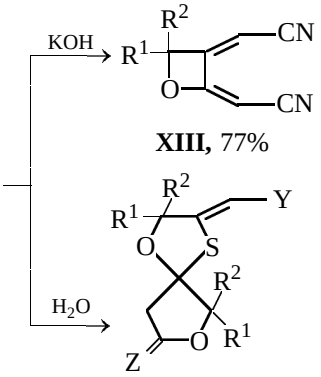
R = H, COOMe; Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4.

An alternative scheme of formation of 1,3-dithiine **Xa** (R = H, Ar = Ph) can be proposed, involving H_2S addition to ester **IIa** to form (*E*,*E*)-divinyl disulfide (**IV**), in view of the fact that sulfide **IV** reacts with benzaldehyde in benzene ($BF_3 \cdot Et_2O$, ~80°C, 24 h), affording 1,3-dithiine **Xa** in 35% yield. Heating (185°C) of 1,3-dithiine **Xb** (R = COOMe, Ar = Ph) induces its isomerization into dimethyl 3,4-dihydro-3,4-diphenyl-1,2-dithiine-5,6-dicarboxylate.

Skvortsov *et al.* [21] reported an unexpected cyclization of nitriles of acetylenic α-hydroxy acids **XI**



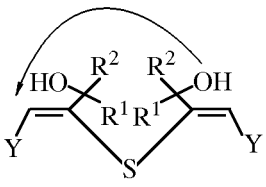
XI, XII



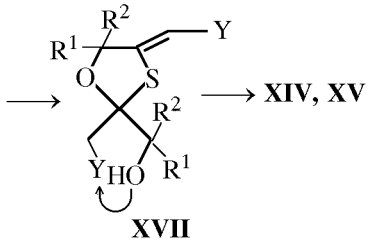
XIVa–**XIVd, XVa, XVb**

R^1 = R^2 = Me (**a**); R^1 = Me, R^2 = Et (**b**); R^1 = Me, R^2 = *t*-Bu (**c**); R^1, R^2 = $(CH_2)_5$ (**d**). Y = CN (**XI**); Y = CN, Z = NH (**XIV**); Y = Ar = COOMe (**XII**); Y = COOMe, Z = O (**XV**).

into 2,3-bis(cyanomethylene)oxetanes **XIII** under the action of sodium sulfide (dioxane, KOH). In the absence of alkali (H_2O, 20°C), nitriles **XI** and esters **XII** form spirocyclic lactones, 1,7-dioxa-8-imino-2,2,6,6-tetraalkyl-3-cyanomethylene-4-thiaspiro[4.4]-nonanes **XIVa**–**XIVd** and 1,7-dioxa-3-methoxycarbonylmethylene-2,2,6,6-tetraalkyl-4-thiaspiro[4.4]-nonan-8-ones **XVa** and **XVb**, respectively, in yields of up to 92% [22–27]. Presumably, the reactions involve formation of (*Z*,*Z*)-divinyl sulfide **XVI** whose one hydroxy group adds across the remote double bond to form oxathiolane **XVII**, whereas the second reacts with the carboxy or cyano group, closing the spirocyclic system.



XVI



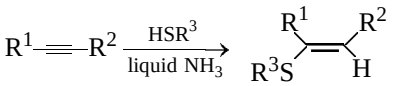
XVII

This cyclization opens up a facile route to pre-

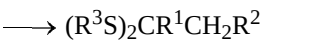
viously unknown functionally substituted spirocycliic compounds [28].

III. ADDITION OF ALKANE- AND ARENETHIOLS

Truce [9] thoroughly examined reactions of thiols with acetylenes under nucleophilic addition condition. They are most frequently catalyzed by bases and adhere to the *trans*-addition rule. The results of these reactions were theoretically substantiated [5] and generalized in the monograph [2, 7]. Acid **I** (R = H) was initially proposed to undergo *cis*-addition [29]. However, more recently it was established that the addition is largely *trans* and forms *Z* isomers but they can convert into *E* isomers under the reaction conditions [30]. Under mild nucleophilic addition conditions (liquid ammonia, –33°C) activated acetylenes readily react with thiols and take up one or two thiol molecules, depending on the nature of the activating group [31, 32].



II, XI, XII, XVIII–XX → **XXI, XXIII, XXV, XXVI**



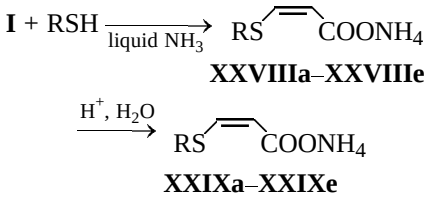
XXII, XXIV, XXVII

R^1 = H, R^2 = COOMe (**IIa**); R^1 = $(Me)_2COH$, R^2 = CN (**XI**); R^1 = $(Me)_2COH$, R^2 = COOMe (**XII**); R^1 = H, R^2 = CN (**XVIII**); R^1 = Ph, R^2 = CN (**XIX**); R^1 = R^2 = NH_2CO (**XX**); R^1 = H, R^2 = COOMe, R^3 = Et (**XXI, XXII**); R^1 = $(Me)_2COH$, R^2 = COOMe, R^3 = Alk (**XXIII**); R^1 = H, R^2 = CN, R^3 = Et (**XXIV**); R^1 = $(Me)_2COH$, R^2 = CN, R^3 = Pr (**XXV**); R^1 = Ph, R^2 = CN, R^3 = Pr (**XXVI**); R^1 = R^2 = NH_2CO, R^3 = Et (**XXVII**).

The carboxy group (ester **IIa**), being a strong electron acceptor, activates the triple bond and leads to formation of (*Z*)-vinyl sulfide **XXI**, as well as diadduct **XXII**. By varying the reagent ratio, one can encourage the reaction to form compoud **XXI** or compound **XXII** (yields 99 and 93%, respectively. Methyl 3-hydroxy-3-methyl-2-pentynoate (**XIIa**) in liquid NH_3 regio- and stereospecifically reacts with thiols (R^3 = Alk), affording (*Z*)-3-alkylsulfanyl-2-pentenoates **XXIII** [32]. The cyano group in cyanoacetylene **XVIII** even stronger enhances the electrophilicity of the triple bond, thus favoring addition of two thiol molecules to form thioacetal **XXIV**. The activating effect of the cyano group in substituted cyanoacetylenes **XI** [R^1 = $(Me)_2COH$] and **XIX** (R^1 = Ph) is attenuated, which results in formation of vinyl sulfides **XXV**, **XXVI** in high yields. Unlike substituted acetylenes **XI**, **XIX**, acetylenedicarboxamide **XX** under the same conditions takes up 2 mol of thiol and converts into 2,2-bis(ethylsulfanyl)succinamide (**XXVII**) in 81% yield [31].

Thiylation of acid **I** (R = H) in liquid NH_3 is a preparative method of synthesis of ammonium 3-(alkylsulfanyl)-2-propenoic acids **XXVIII** [33].

The basicity of ammonia not only favor dissolution of proton-donor compounds but also formation of ammonium salts with both acid **I** (R = H) and thiols. Such salts in ammonia solutions apparently exist as tight ion pairs and free ions. Therewith, the thiolate ion acquires enhanced reactivity, since it is only weakly solvated by ammonia molecules, and it attacks the β-carbon atom of the triple bond, forming salts **XXVIIIa**–**XXVIIIe** of *Z* configuration. The salts were neutralized with 40% HCl to obtain (*Z*)-3-alkylsulfanyl-2-propenoic acids **XXIX**.



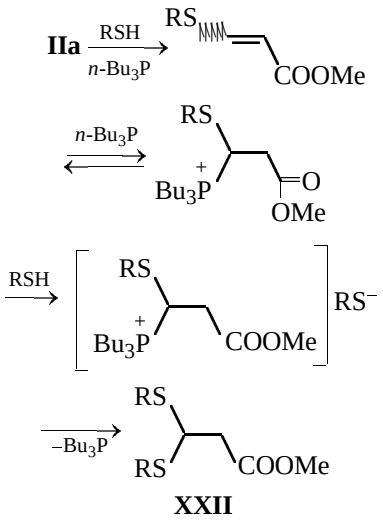
XXVIIIa–**XXVIIIe** → **XXIXa**–**XXIXe**

R = Et (**a**), Bu (**b**), C_6H_{13} (**c**), C_8H_{17} (**d**), $C_{12}H_{25}$ (**e**).

The patents [34–36] reported the preparation of alkali and alkaline-earth metal salts of 3-alkyl(aryl)sulfanyl2-propenoic acids **XXVIII** is aqueous-alkaline medium in yields of up to 93%. The interest in such salts, as well as their oxidation products (sulfones and sulfoxides) is explained by the fact that many of them exhibit surfactant properties [33, 36, 37], biological activity [38, 39], and can find application in perfumery [40].

Recently Trofimov and Shainyan [41] synthesized dithioacetals **XXII** by adding of 2 mol of thiols to ester **IIa** in the presence of tributylphosphine (THF, 20°C, 24 h), yield ~79%. Therewith, it was noted that dithioacetals **XXII** are important intermediates in organic synthesis.

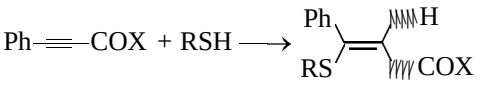
As far back as 1959, Truce *et al.* [29] obtained from sodium phenylpropiolate **I** (R = Ph) and *p*-toluenethiol a mixture of (*Z*)- and (*E*)-3-phenyl-3-(*p*-tolylsulfanyl)-2-propenoic acids (**XXIX**). However, later Raistekene *et al.* [42] showed that the ionic addition of thiophenol to acid **I** (R = Ph) and its methyl ester and anilide (MeOH, Na, N_2, 20°C) results in regioselective formation of (*Z*)-3-phenyl-3-



XXII

R = Ph, CH_2Ph, $(CH_2)_3$.

phenylsulfanyl-2-propenoic acod and its derivatives **XXX** in 65–70% yields [42]. Under the same conditions, phenylmethanethiol forms a mixture of the *Z* and *E* isomers of 3-benzylsulfanyl-3-phenyl-2-propenoic acid derivatives **XXXI** in a total yield of 85–90% (*Z*:*E* ratios 65:35 and 75:25 for ester and anilide, respectively).

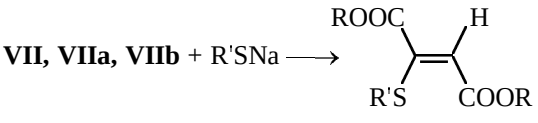


XXXa–**XXXc, XXXIb, XXXIc**

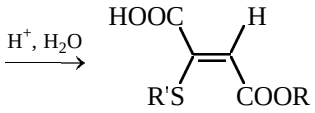
R = Ph (**XXX**), CH_2Ph (**XXXI**); X = OH (**a**), OMe (**b**), NHPh (**c**).

Spectral [43] and kinetic [44] monitoring of additions of substituted thiophenols and thionaphthols to various propiolic acid esters (NaOEt–EtOH, –30 to 35°C) gave evidence for the nucleophilic nature of these reactions and their high regio- and stereoselectivity. Certain of them afforded 5:1 to 10:1 *Z/E* mixtures. It was noted that electron-acceptor substituents on the benzene ring of the thiol make it less reactive. Acid **I** (R = H), too, readily takes up phenylmethanethiol in methanol (MeONa, 0°C, N_2, 30 min) to give (*Z*)-3-benzylsulfanyl-2-propenoic acid in 88% yield [17]. The same acid and its esters as *Z/E* mixtures were also obtained by the action of NaHS or Na_2S (H_2O, 0°C, N_2, 5 h) on acid **I** (R = H) and esters **II** followed by treatment with benzyl bromide.

Acid **VII** and its esters **VIIa**, **VIIb** take up sodium salts of thiols in aqueous alcoholic media by the *trans*-scheme to form sulfanylfumarates **XXXII** whose hydrolysis gives fumaric acids **XXXIII** [45, 46].



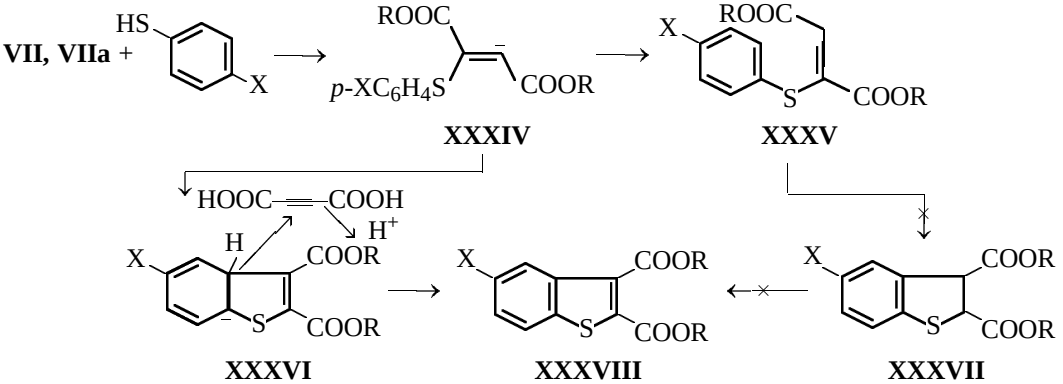
XXXII, 80–85%



XXXIII

R = Me, Et; R' = Alk, Ar.

Reactions of *para*-substituted thiophenols (X = Me, Cl, NO_2) with acid **VII** and ester **VIIa** provide evidence for a mechanism involving formation of anion **XXXIV** which, depending on the substituent in the thiophenol, temperature, and solvent, converts either into vinyl sulfides **XXXV** or, via intermediate **XXXVI**, to benzo[*b*]thiophenes **XXXVIII** [47]. The yield of thiophene **XXXVIII** (X = H, R = Me) in the same conditions (35°C, 14 days) varies with solvent (29, 14, 18, and 36% in ethyl acetate, dioxane, toluene, and acetic acid, respectively).

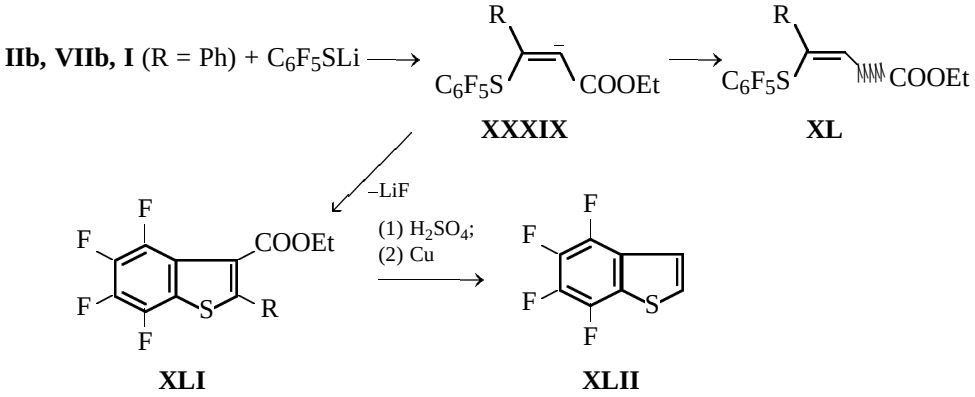


XXXIV **XXXV** **XXXVI** **XXXVIII** **XXXVII**

X = H, Me, Cl, NO_2; R = H, Me.

The mechanism is initially ionic, as judged from the fact that in ethyl acetate in the presence of benzoyl peroxide or hydroquinone the rates and yields are almost the same. The intermediacy of 1,2-dihydrobenzo[*b*]thiophene **XXXVII** is absolutely excluded, since heating of vinyl sulfide **XXXV** (X = H, R = Me) in ethyl acetate in the presence of ester **VIIa** produces no cyclization products. It was also noted that the reaction in ethyl acetate (20°C, 5 days) results in exclusive formation of thiophenes **XXXVIII** (yield 16%), but with *p*-nitrothiophenol no thiophene formation is observed. In other conditions (MeOH, ~65°C), a mixture of (*E*)-vinyl sulfides **XXXV** and thiophenes **XXXVIII** was obtained.

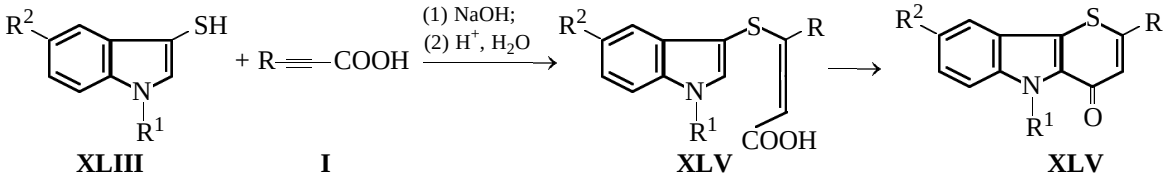
Brooke [48] has studied nucleophilic additions (THF, –70 to –65°C) to lithium pentaflurophenolate to esters **IIb** and **VIIb** and ethyl ester of acid **I** (R = Ph). The reactions might be expected to involve an (*E*)-carbanion as a common intermediate, which, depending on the starting acetylene and conditions, converts either into (*Z*)- and (*E*)-vinyl sulfides **XL** or into tetrafluorobenzo[*b*]thiophenes **XLI**.



R = H, COOEt, Ph.

With ester **IIb** in THF (–70 to –25°C), a mixture of the *Z* and *E* isomers of vinyl sulfide **XL** was obtained (yields 69 and 10%, respectively). By contrast, the reaction of ether **VIIb** with C_6F_5SLi affords thiophene **XLI** (R = COOEt) exclusively (yield 74%). (*E*)-Carbanion **XXXIX** is considered to convert into the *Z* isomer which cyclizes into the corresponding benzo[*b*]thiophene via nucleophilic substitution of fluorine. The reaction of ethyl ester of acid **I** (R = Ph) with C_6F_5SLi in THF at 65°C provides both thiophene **XLI** (R = Ph) in 72% yield and a mixture (~5%) of (*Z*)- and (*E*)-vinyl sulfides **XL** (R = Ph). Hydrolysis and decarboxylation of thiophene **XLI** (R = COOEt) gives 4,5,6,7-tetrafluorobenzo[*b*]thiophene (**XLII**).

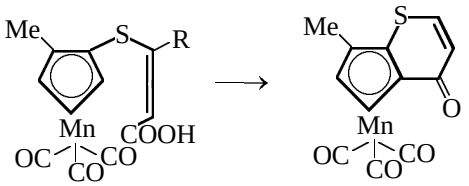
3-Sulfanylindoles **XLIII** react with 3-alkyl(aryl)-propynoic acids **I** (R = Alk, Ar) in 1 N NaOH (95°C, 1 h) to form 3-(3-indolylsulfanyl)-2-propenoic acids **XLIV**. Under the action of 10% polyphosphoric acid in AcOH (20°C, 65 h) the latter convert into thiopyrano[3,2-*b*]indol-4(5*H*)-ones **XLV** which are applied in treatment of stenocardia [49].



R = H, Me, Ph; $R^1 = R^2$ = Alk.

The addition of tricarbonyl[3-methyl-4(5)-sulfanylcyclopentadiene]manganese to acid **I** (R = H) in basic medium (0.2 N Na_2CO_3) results in formation of compound **XLVI** whose treatment with oxalyl chloride (~20°C, 3 h) followed by heating with polyphosphoric acid provides compound **XLVII** [50].

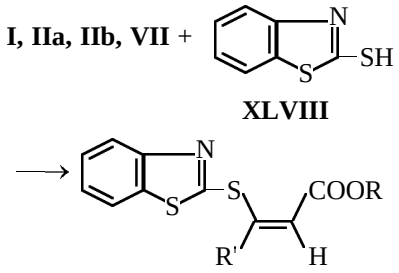
Acid **I** (R = H), esters **IIa** and **IIb**, and diacid **VII**



XLVI **XLVII**

in neutral medium (alcohol, 75–80°C, 2–5 h) react with 2-sulfanylbenzothiazole (**XLVIII**), yielding corresponding derivatives of 3-(2-benzothiazolylsulfanyl)-2-propenoic **XLIX** and 3-(2-benzothiazolylsulfanyl)fumaric (**L**) acids (R' = COOH) [51].

As shown by Mal'kina *et al.* [32], cyanoacetylene **XVIII** readily takes up alkanethiols in liquid ammonia. Nitrile **XVIII** could be reacted with thiophenol in methanol (NaOH, 10°C) to obtain 3-phenylsulfanyl-2-propenenitrile in 75% yield. Murahashi *et al.* [52]

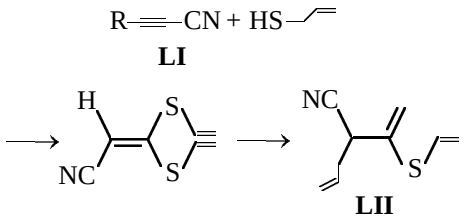


XLVIII

XLIX, L

R = H, Me, Et; R' = H, COOH.

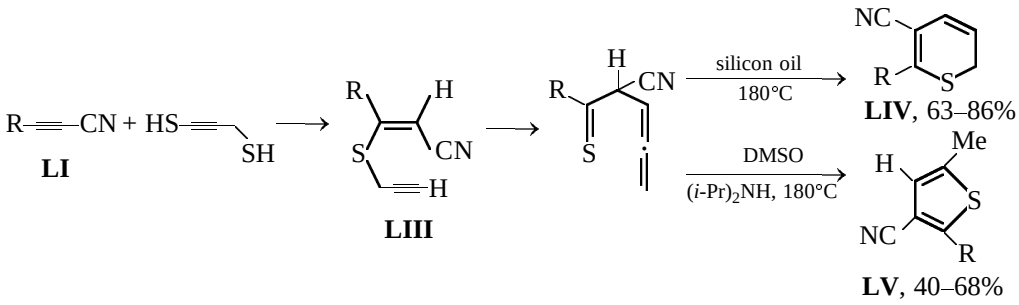
prepared 3,3-bis(phenylsulfanyl)propionitrile under the same conditions with excess thiophenol. In the presence of sodium *p*-toluenethiolate, nitrile **XVIII** forms (*Z*)-3-*p*-tolylsulfanyl-2-propenenitrile exclusively (yield ~100%) [53, 54], whereas with *tert*-bytanethiol (Et_2O, Et_3N, –15°C), the *Z* isomer is a major product [55]. 2-Propenethiol very slowly adds to nitrile **XVIII** in the absence of catalysts, whereas in the presence of sodium methylate the reaction is accelerated and gives a mixture of (*Z*)- and (*E*)-3-allylsulfanyl-2-propenenitriles in 46% yield [56]. Under the same conditions, 2-propenethiol reacts with nitrile **LI** (R = Cl, Et_2N), giving Claisen rearrangement products, such as **LII**.



LI **LII**

R = Cl, Et_2N.

Welle and Brandsma [57] found that 2-propynethiol adds to cyanoacetylenes **LI** (R = Alk) in HMPT. The reaction occurs exothermally in the absence of catalysts and produces (*Z*)-3-alkyl-3-(2-propynylsulfanyl)-2-propenenitriles **LIII** in 86–93% yields. When heated, these nitriles undergo sigmatropic rearrangement to form 2*H*-thiopyranes **LIV** or cyanothiophenes **LV**.



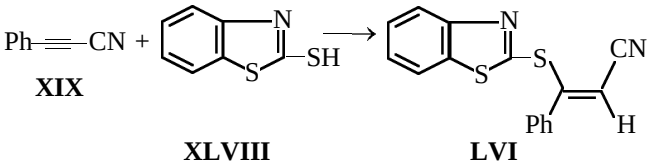
LI **LIII** **LIV**, 63–86% **LV**, 40–68%

R = H, Me, Et, *n*-Pr, *n*-Bu.

Nitrile **LI** (R = Me) with EtSH or PhSH forms (*Z*)-3-ethylsulfanyl- or (*Z*)-3-phenylsulfanyl-2-butenenitriles like **LIII** (yield 95–98%) under nucleophilic addition conditions [58].

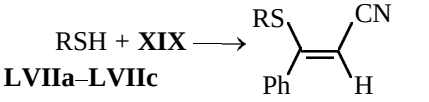
Nosyreva *et al.* [59] showed that thiazole **XLVIII** regio- and stereospecifically reacts with 3-phenylcyanoacetylene (**XIX**) (dioxane, 7 wt% KOH, 20–25°C, 9 h), affording (*Z*)-3-(2-benzothiazolylsulfanyl)-3-phenyl-2-propenenitrile (**LVI**) (yield 88%).

2-, 5-, and 8-Sulfanylquinolines (**LVIIa**–**LVIIc**) regio- and stereospecifically react with nitrile **XIX** in the presence of KOH (10 wt%) to form (*Z*)-3-phenyl-

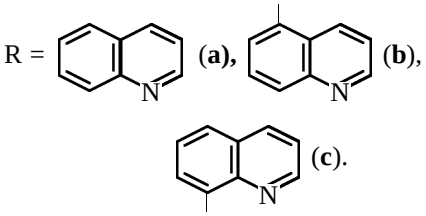


XIX **XLVIII** **LVI**

3-[2(5,8)-quinolylsulfanyl]-2-propenenitriles (**LVIIIa**–**LVIIIc**) in 79, 47, and 75% yields, respectively [60].

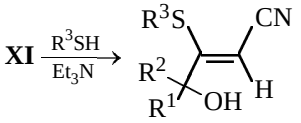


LVIIa–**LVIIc** **LVIIIa**–**LVIIIc**

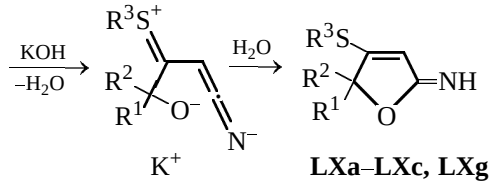


Andriyankova *et al.* [61] found that 2- and 4-sulfanylpyridines, too, regio- and stereospecifically react with nitrile **XIX** in the presence of KOH (10 wt%) in dioxane, providing (*Z*)-3-phenyl-3-[2(4)-pyridylsulfanyl]-2-propenenitriles in 64 and 34% yields, respectively.

Recently Trofimov *et al.* [25, 26] have studied reactions of hydroxyacetylenic nitriles **XI** and acids **XII** with thiols. The reactions of nitriles **XI** with thiols in the presence of Et_3N occur in regio- and stereospecific fashions in protic (alcohols) and aprotic (dioxane) solvents (20–25°C, Et_3N, 1–2 h), resulting in quantitative formation of (*Z*)-3-(organylsulfanyl)-2-alkenenitriles **LIX** [62, 63].



XI **LIXa**–**LIXn**



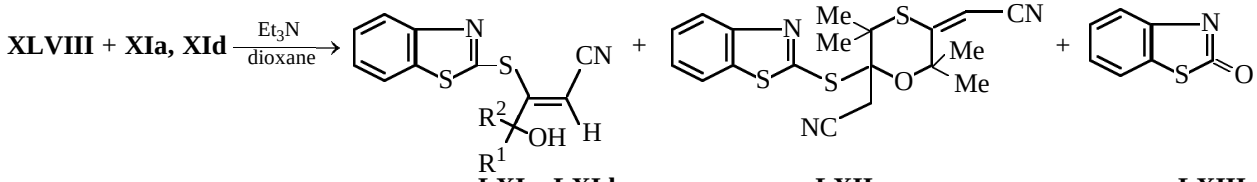
LXa–**LXc, LXg**

$R^1 = R^2 = Me$, $R^3 = Et$ (**a**), *i*-Pr (**b**), *n*-Bu (**c**), *n*-C_5H_{11} (**d**), C_6H_{13} (**e**), *n*-$C_{12}H_{25}$ (**f**), Ph (**g**), CH_2Ph (**h**); $R^1 = Me$, $R^2 = Et$, $R^3 = Et$ (**i**), *i*-Pr (**j**), *n*-Bu (**k**), C_6H_{13} (**l**), Ph (**m**); $R^1 = Me$, R^2 = *i*-Bu, R^3 = *i*-Pr (**n**).

Nitriles **LIX** in the presence of large quantities (30 wt%) of KOH in absolute dioxane undergo isometrization into the *E* isomers and cyclize to form 2,5-dihydro-2-iminofurans **LX**. On treatment with conc. HNO_3 or HCl (EtOH, 20–50°C, 3–5 h) the latter quantitatively convert into the corresponding salts [64].

Dihydroiminofurans **LX** present interest for pharmacology and also can be used to form a chain comprising dihydroiminofuran units [26].

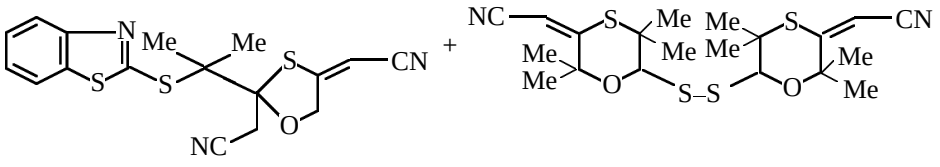
The reaction direction of thiazole **XLVIII** with nitriles **XIa**, **XId** depends strongly on the catalyst (Et_3N, 1,4-diazabicyclo[2.2.2]octane, LiOH), solvent (dioxane, ethanol, acetonitrile), and starting reactant ratio. The reaction fails in the absence of catalysts. In the presence of Et_3N (4–6 wt%, dioxane, 20–25°C, 15 h), thiazole **XLVIII** regio- and stereospecifically reacts with nitriles **XIa**, **XId** (reagent molar ratio 1 : 1), giving (*Z*)-4-alkyl-3-(2-benzothiazolylsulfanyl)-4-hydroxy-2-alkenenitriles **LXIa**, **LXId** in 40 and 51% yields, respectively [59].



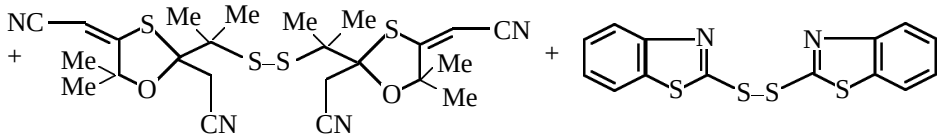
LXIa, LXId **LXIIa** **LXIII**

$R^1 = R^2 = Me$ (**a**), $R^1, R^2 = (CH_2)_5$ (**d**).

In the presence of 1,4-diazabicyclo[2.2.2]octane (**LXIIa**) (1.3 wt%, dioxane, 20–25°C, 17 h), the reaction of nitrile **XIa** with compound **XLVIII** produces a mixture of nitrile **LXIa** and 2-(2-cyanomethyl-5-cyanomethylene-3,3,6,6-tetramethyl-1,4-oxathian-2-yl)sulfanylbenzothiazole (**LXIIa**) in a 1 : 6 ratio (^1H NMR data). Furthermore, benzothiazol-2-one (**LXIII**) was isolated. In the presence of LiOH (6 wt%,



LXIVa **LXVa**

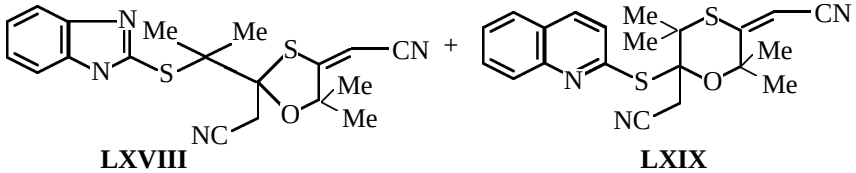


LXVIa **LXVII**

dioxane or acetonitrile, 20–25°C, 4–10 h), the reaction mixture, by ^{1}H NMR data, contained, along with oxathiane **LXIIa**, 1,3-oxathiolane **LXIVa**, bis(6-cyanomethyl-3-cyanomethylene-2,2,5,5-tetramethyl-1,4-oxathian-6-yl) disulfide (**LXVa**), bis[1-(2-cyanomethyl-4-cyanomethylene-5,5-dimethyl-1,3-oxathiolan-2-yl)-1-methylethyl] disulfide (**LXVIa**), di(benzothiazol-2-yl) disulfide (**LXVII**), and thiazolone **LXVIII**.

Quinoline **LVIIa** react with nitrile **XIa** in an unexpected fashion, yielding 1,3-oxathiolane **LXVIII** [65]. In addition, the reaction mixture contains an isomer of the latter, oxathiane **LXIX**, as well as 2-hydroxyquinoline [66].

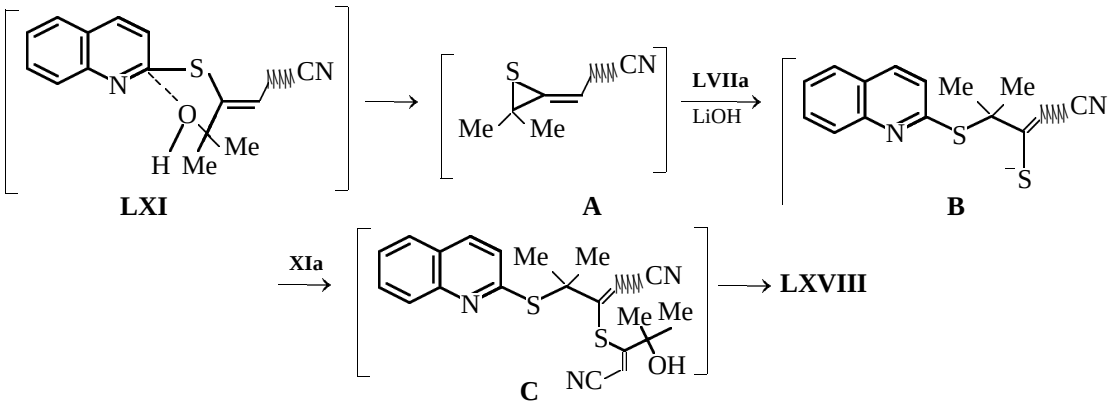
LVIIa + **IXa** ⟶



LXVIII **LXIX**

In the presence of LiOH (5 wt%, dioxane, ethanol, 20–25°C, ~30 h), the reaction products are thiolane **LXVIII** and oxathiane **LXIX** (total yield 72%). These structures could only be distinguished by spectral methods (COSY, HMBC).

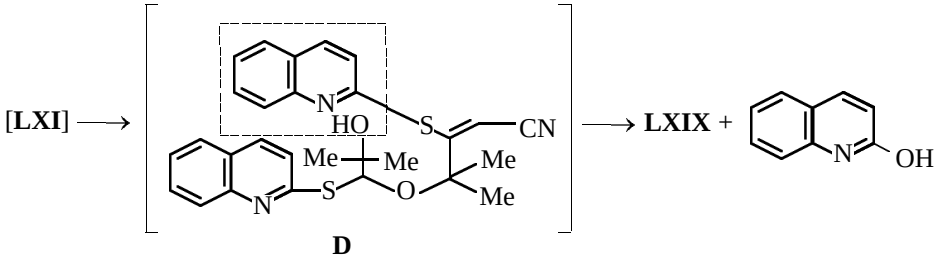
Compounds **LXVIII** and **LXIX** are presumably formed via addition of the thiol to the β-carbon atom of the triple bond in **XIa** to give an adduct like **LXI** and its subsequent transformations.



LXI **A** **B** **C**

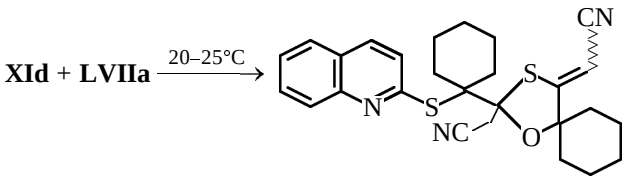
Intermediate **LXI** cleaves to form thiirane **A** whose reaction with the second quinoline **LVIIa** molecule affords compound **B**. The latter adds to the second nitrile **XIa** molecule, leading to intermediate **C** which undergoes intramolecular cyclization and converts into oxathiolane **LXVIII**. Oxathiane **LXIX**, too, is

formed via adduct **LXI** whose subsequent isomerization gives rise to compound **D**. Intramolecular processes in the latter result in cleavage of 2-hydroxyquinoline to produce oxathiane **LXIX**.



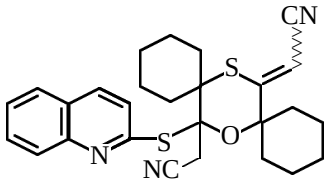
D

The reaction direction is also much affected by the structure of nitrile **XI** and temperature. For example, the reaction of 3-(1-hydroxycyclohexyl)-2-propynenitrile (**XId**) with quinoline **LVIIa** in the presence of LiOH (5–10 wt%, 20–25°C, 30 h) selectively provides 2-cyanomethyl-4-cyanomethylene-2-[1-(2-quinolylsulfanyl)cyclohexyl]-1-oxa-3-thia-spiro[4.5]decane (**LXX**), yield 36% [67].



LXX

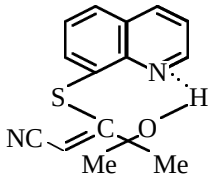
The same reaction at a higher temperature (5–10 wt% LiOH, 50–60°C, 20 h) results in selective assembling of another structural isomer, 8-cyanomethyl-16-cyanomethylene-7-oxa-15-thia-8-(2-quinolylsulfanyl)dispiro[5.2.5.2]hexadecane (**LXXI**), yield 25%.



LXXI

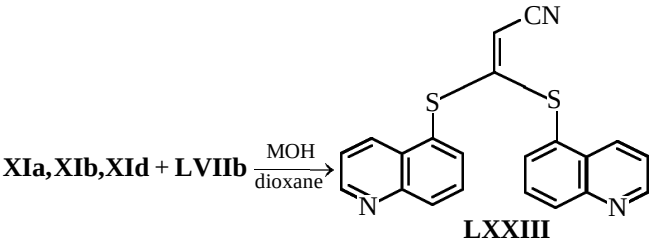
The probable mechanisms of formation of **LXX** and **LXXI** are described in the review [26].

The reactions of sodium salt of quinoline **LVIIc** with nitriles **XIa**, **XIb**, and **XId** are completed in the stage of thiol addition to the triple bond of compound **XI**, affording 4-hydroxy-3-(8-quinolylsulfanyl)-2-alkenenitriles **LXXIIa**, **LXXIIb**, and **LXXIId**, respectively, which do not further cyclize [60]. In aqueous dioxane, the same salt reacts without catalysts (20–25°C, 30 h), providing adducts **LXXIIa**, **LXXIIb**, and **LXXIId** in low yields (9, 32, and 33%, respectively). In the presence of LiOH (10 wt%), the yields of adducts are better (23, 40, and 43%). However, the best yields (62, 70, and 80%) were obtained in water (LiOH, 20–25°C, 10 h). According to spectral data, alkenenitrile **LXXIIa** contains an intramolecular hydrogen bond.



LXXIIa

Quinoline **LVIIb** quite differently behaves in reactions with nitriles **XIa**, **XIb**, and **XIc** [68]. In the presence of alkali (MOH, M = Li, Na, K) in dioxane (20–25°C, 30 h), these reactions unexpectedly provide 3,3-di(5-quinolylsulfanyl)-2-propenenitrile (**LXXIII**), yield 60%.

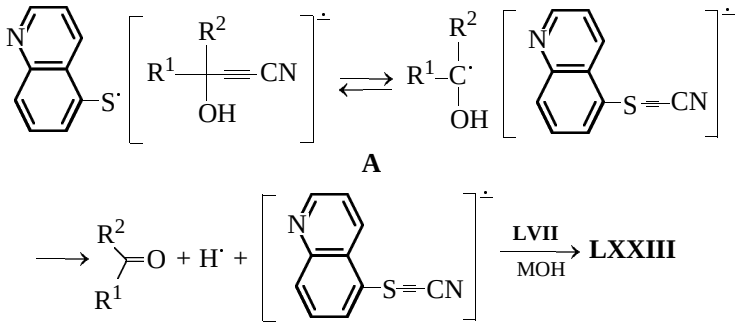


LXXIII

$R^1 = R^2 =$ Me (**a**), $R^1 =$ Me, $R^2 =$ Et (**b**), $R^1, R^2 = (CH_2)_5$ (**d**); M = Li, Na, K.

By following the reaction progress by ESR [68] Trofimov *et al.* obtained evidence to state that addi-

tion of the bulky sulfanylquinolyl anion anion to the triple bond in nitriles **XIa**, **XIb**, **XId**, rather than giving an adduct carbocation, stops on the electron-transfer stage giving radical anion **A**. Consecutive recombinations of the latter lead finally to compound **LXXIII**.



A

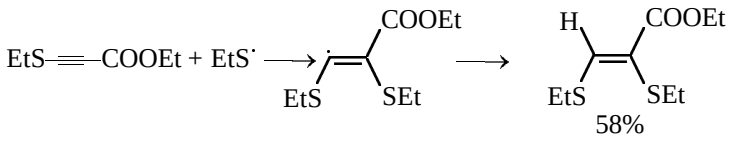
Thus, reactions of quinolines **LVIIa**–**LVIIc** with nitriles **XI** open up new possibilities for synthesis of functionally substituted compounds of the quinoline series. Nitriles **XIa**, **XIb**, **XId** can take up 2- and 4-sulfanylpyridines in mild conditions (20–25°C, triethylamine, 8–20 h) to form hydroxy-3-[2(4)-pyridylsulfanyl]-2-alkenenitriles of *Z* configuration in 77–96% yields [61]. Therewith, unlike (*Z*)-3-organylsulfanyl-2-alkenenitriles **LIX**, the S-adducts show no tendency for isomerization (30 wt% KOH, dioxane, 20–25°C, 20 h) and cyclization into 2,5-dihydroiminofurans **LX**.

Generally, the final products and stereochemistry of thiol addition to α,β-acetylenic acids and their derivatives depend on whether there are activating groups at the triple bond, on the nature of the thiol and solvent, as well as on reaction conditions.

Acid **I** (R = H) reacts with phenylmethanethiol [69] in the presence of benzoyl peroxide (3%, 80°C, 0.75 h), with ethanethiol [70] (UV irradiation, 2 weeks), and with cyclohexanethiol [71] (70–100°C, 1 h), forming sulfides **XXIX** in 47, 28, and 48% yields, respectively.

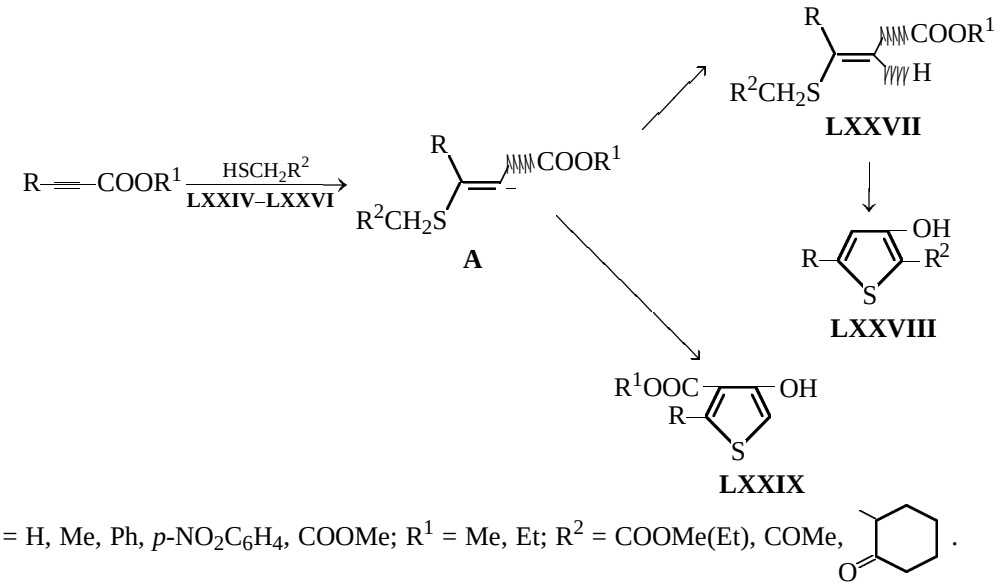
Volkova *et al.* [72] have studied the behavior of acid **I** (R = H) mixed with thiols in the light and in the dark, as well as in the presence of hydroquinone and azodiisobutyronitrile (AIBN). To bring reaction to completion, the mixture was left to stand at 20°C for 20 days and more. Mixtures of (*Z*)- and (*E*)-sulfides **XXVI** (R = Et, Pr, Bu, C_6H_{13}, C_8H_{17}, $C_{12}H_{25}$) were always obtained in 82–94% yields. Hydroquinone was insufficiently effective to suppress formation of thiyl radicals, since reaction took place. By contrast, AIBN accelerated reaction and increased the fraction of the *E* isomer. In the absence of hydroquinone and AIBN, a radical reaction took place, resulting in preferential formation of the *Z* isomer. With time, however, dynamic equilibrium with a 1 : 1 ratio of the *Z* and *E* isomers was attained. The initial prevalence of the *Z* isomer can be explained by the fact that a radical of *Z* configuration faster abstract hydrogen from thiols [2]. The phenylthiyl radical similarly adds to acids **I** (R = H, Me) and ester **IIa** [73] in the presence of benzoyl peroxide. With acid **I** (R = Ph) and its ethyl ester, the phenylthiyl radical in the presence of benzoyl peroxide attacks the β-carbon atom of the triple bond to form 3-phenyl-2-phenylsulfanyl-2-propenoic acid and its ester. Rasteikene *et al.* obtained the same *Z*-sulfides in yields of 65–90% (MeOH, O_2, 20°C) [42]. The above observation suggests that the direction of addition of the phenylthiyl radical is determined by the stability of the intermediate radical, which decreases in the following order R = Ph > COOH ≈ COOEt > Me, Et , where R is substituent at the triple bond [73].

Bonnema and Arens [74] proposed a scheme of the reaction of ethyl 3-(ethylsulfanyl)propiolate with ethanethiol in the presence of AIBN (benzene, 50°C, UV, 15 h).



IV. REACTIONS WITH SULFANYLKETONES AND THIOACIDS

Many addition reactions of thiols containing functional groups are of preparative value, since their subsequent cyclization gives rise to heterocyclic compounds. Thus, esters **IIa**, **VIIa** readily react (benzene, MeONa, N_2) with thioglycolic esters. The subsequent Dickmann cyclization opens up the way to 3-hydroxythiophenes **LXXVIII** (R = H, R^2 = COOMe (**a**); R = R^2 = COOMe (**b**)] [75]; yield ~30%.



R = H, Me, Ph, *p*-$NO_2C_6H_4$, COOMe; R^1 = Me, Et; R^2 = COOMe(Et), COMe, .

Under the same conditions, linear products **LXXVII** might have been formed but could not be isolated. In the presence of piperidine, the reaction is completed by the addition of two thioacid molecules to esters **IIa**, **VIIa**. Bohlmann and Bresinsky [76] found that, depending on conditions, either protonation of intermediate anion **A** to form adduct **LXXVII**, followed by cyclization into thiophene **LXXVIII** or direct attack of the enolate ion by the carbonyl group to form thiohene **LXXIX** occur. Thus, in mild conditions, from ester **IIb** and thioester **LXXIV** (R^2 = COOMe) in the presence of *t*-BuOK, a mixture of the *E* and *Z* isomers of **LXXVII** (R = H) is formed in 50 and 33% yields, respectively, as well as thiophene **LXXIX** (R = H) in 8% yield. In the presence of mole quantities of *t*-BuOK, thiophene **LXXVIII** (R = H, R^2 = COOMe) rather than thiophene **LXXIX** was isolated. Esters of substituted acids **I** (R = Me, Ph, *p*-$NO_2C_6H_4$) behave in a similar way. It was also shown [76] that the addition of sulfanylketones **LXXV**, **LXXVI** to esters of acids **I** (R = H, Me, Ph) under the action of proton donors can occur both by the *cis*- and *trans*-scheme, forming thioesters **LXXVII** whose cyclization gives rise to thiophenes **LXXVIII** and **LXXIX**.

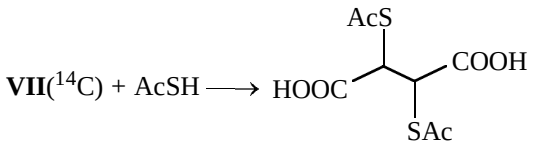
Acid **VII** takes up aliphatic thioacids in aqueous-alcoholic medium in the presence of alkali metals, providing (*E*)-thioesters **LXXVII** in 78–85% yields [45]. From ester **IIa** and thioglycolamide, too, a linear product, (*E*)-1-(carbamoylmethylsulfanyl)-2-methoxycarbonylethene (acetonitrile, 60°C, yield 85%) [77]. In the presence of Et_3N and AcOH, a 1 : 2 *Z*/*E* mixture was obtained (yield 95%).

Thioesters **LXXVII** were obtained in high yields by prolonged heating (20°C, 2–5 days) of mixtures of acid **I** (R = H) with thioglycolic, thiolactic, or *o*-sulfanylbenzoic acids [78]. According to ^{1}H NMR data, the fraction of the *E* isomer in thioester **LXXVII** (R = H, R^1 = Me, R^2 = COOMe) is 92%, whereas thioesters of lactic and *o*-benzoic acid are largely *Z* isomers.

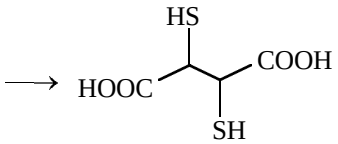
The reaction of ester **VIIa** with *o*-sulfanylbenzoic acid in alcohol gives rise to an S-monoadduct like **LXXVII** with a fumaric acid configuration (yield 58%) [79, 80].

Owen and Sultanova [69] have described the reactions of acid **I** (R = H) and ester **IIa** with thioacetic acid, yielding a mixture of (*Z*)- and (*E*)-3-acetylsul-

fanyl-2-propenoic acids and their esters, as well as a diadduct. The addition of AcSH to acid **VII** (^{14}C) in ethyl acetate gave diadduct **LXXX** whose successive treatment with NaOH and HCl resulted in preparation of 2,3-disulfanylsuccinic (^{14}C) acid (**LXXXI**) [81].



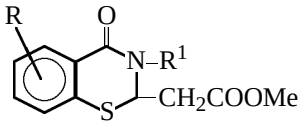
LXXX, 81%



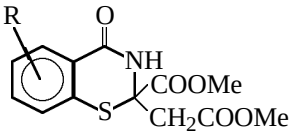
LXXXI, 90%

Guy *et al*. reacted acid **VII** with thiols $HSCH_2 \cdot CH2R$ (R = $^{+}NHMeCl^{-}$, SO_3Na, COOH) to obtain a diastereomeric mixture of compounds **LXXX** [82].

Substituted *o*-sulfanylbenzamides react with esters **IIa**, **VIIa** in solvents in the presence of basic catalysts, affording substituted benzo-1,3-thiazin-4-ones **LXXXII**, **LXXXIII** [79, 80]. These compounds are interesting in that they are capable to affect the central nervous system.



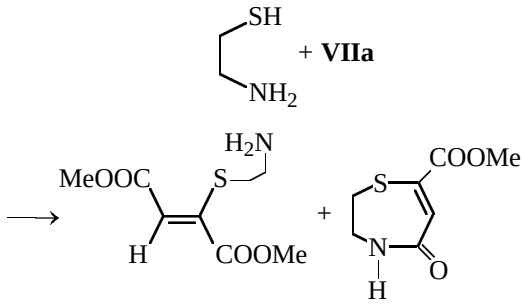
LXXXII



LXXXIII

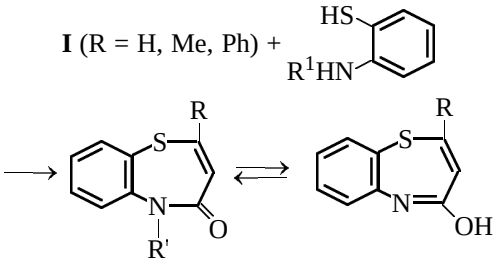
V. REACTIONS WITH BINUCLEOPHILES

Reactions with β-aminothiols. Aminothiols, being S,N-difunctional nucleophiles, can enter chemical reactions involving both the NH_2 and SH groups and thus are perspective starting materials for heterocyclic synthesis. Combining acidic and basic properties in one molecule, these compounds can exist as internal salts (zwitter ions). By varying the pH of the medium one can make the ammonium salt $HSCH_2CH_2{}^{+}NH_3$ to convert via $^{-}SCH_2CH_2{}^{+}NH_3$ into the free base $^{-}SCH_2 \cdot CH_2NH_2$ [83]. The results of Mushkalo [84, 85], Calbag [86], and Ried [87] establish that the HS group of aliphatic and aromatic *o*-aminothiols is more active in nucleophilic addition to activated triple bonds. These results are nicely consistent with the relative acidities of the HS and NH_2 groups in aminothiols [83]. Thus, Friedman *et al.* [88] showed that the HS^{-} anion is 280 times more active that R^2N^{-}. Therefore, proton abstraction in β-sulfanylethylamine occurs exclusively from the HS group. For example, β-aminothiols [NH_2, NEt_2, $N(CH_2CH_2)_2O$] readily react with acid **I** (R = H) in mild conditions (liquid NH_3, –33°C), forming a mixture of (*E*)- and (*Z*)-3-alkylsulfanyl-2-propenoic acids **XXVI** (~1 : 1) in 91–99% yields [89]. With β-sulfanylethylamine, cyclization products would be expected, but they were not found. Apparently, zwitter ion formation prevents cyclization. The reaction of β-sulfanylethylamine with ester **VIIa** (ether, 10–20°C) produces a mixture of vinyl sulfide **XXXII** and heterocycle **LXXXIV** [84].



XXXII, 21% **LXXXIV**, 21%

o-Aminothiophenol with *N*-methyl-*o*-aminothiophenol more readily condense with acids **I** (R = H, Me, Ph) in ether to give benzohepta-1,5-thiazine derivatives **LXXVa**, **LXXVb**. Thiazine **LXXXVa** undergoes isomerization into an unstable hydroxy derivative **LXXXVI** during experiment or on handling [84, 90, 91].



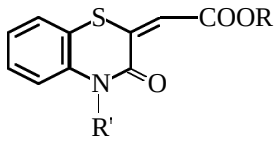
LXXXVa, LXXXVb **LXXXVI**

R = H (yield 33%), Me (yield 44%), Ph (yield 29%); R' = H (**a**), Me (**b**).

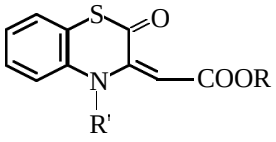
The structure of 1,5-thiazine **LXXXVa** was confirmed by spectral data [92]. Thiazines **LXXXV** were found to act as antidepressants [90].

Aminothiophenols also readily react with acid **VII**

and its ester, providing benzo-1,4-thiazin-3-one derivatives **LXXXVII** in high yields (91–98%) [93].



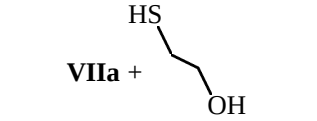
LXXXVII



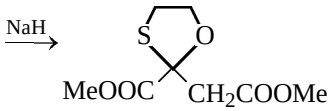
LXXXVIII

However, Iwanami [94] contends that in alcoholic medium at 20°C *o*-aminophenol with ester **VIIa** forms not only thiazinone **LXXXVII** but also its isomer benzo-1,4-thiazin-2-one **LXXXVIII**. More recently Kalbag *et al.* [86] gave convincing evidence to show that the major reaction product between *o*-aminothiophenol with ester **VIIa** is benzo-1,4-thiazinone **LXXXVII** rather than **LXXXVIII**. Further evidence for structure **LXXXVII** is provided by its reactions (hydrogenation, reactions with P_2S_5, primary amines, and ammonia) [95].

Reactions with S,O- and S,S-nucleophiles. 2-Sulfanylethanol was reacted with equimolar amount of ester **VIIa** with ice cooling to obtain (2-dimethyl 2-(hydroxyethylsulfanyl)fumarate (**LXXXIX**). Cyclization of the latter under the action of sodium hydride in absolute toluene (46°C, 0.75 h) gave 1,3-oxathiolane **XC** [96].



LXXXIX

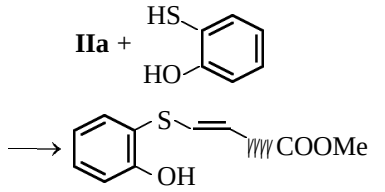


XC, 66%

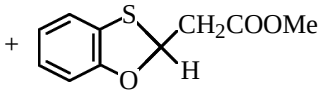
Vinyl sulfide **LXXXIX** was oxidized (50% H_2O_2) into the corresponding sulfone.

o-Sulfanylphenol racts with ester **IIa** (DMSO, *t*-BuOK, 80–100°C), giving a mixture of (*Z*)- and (*E*)-vinyl sulfides **XCI** (1:4) and 2-(methoxycarbonylmethyl)-1,3-benzoxathiolane (**XCII**) [76].

Esters **IIa**, **IIb** react with equimolar amount of 2-sulfanylethanol ($CHCl_3$, K_2CO_3, 60°C) to form

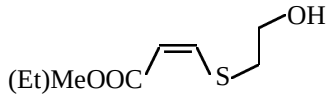


XCI, 44% (*E*), 11% (*Z*)

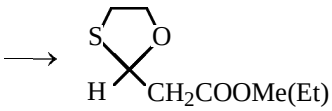


XCII, 40%

vinyl sulfide **XCIII** which is presumably partially cyclizes into 1,3-oxathiolane **XCIV** [97].

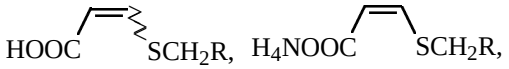


XCIII, 59%



XCIV, 12%

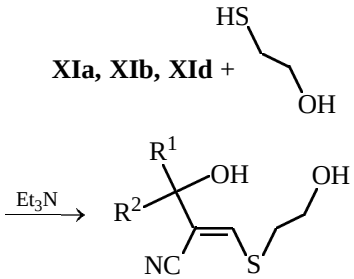
Acid **I** (R = H) regioselectively reacts by the HS group with 2-sulfanylethanol and 2-sulfanylpropane-2,3-diol in the absence of solvents at 20°C, affording a 1:1 mixture of the *Z* and *E* isomers of sulfides **XCVa**, **XCVb** (yield 97%) [98]. The reactions with the same thiols in liquid NH_3 produce ammonium salts **XCVIa**, **XCVIb** as *Z* isomers.



XCVa, XCVb **XCVIa, XCVIb**

R = CH_2OH (**a**), $CH(OH)CH_2OH$ (**b**).

Cyanoacetylenic alcohols **XIa**, **XIb**, **XId** with 2-sulfanylethanol (1:1) react under mild conditions

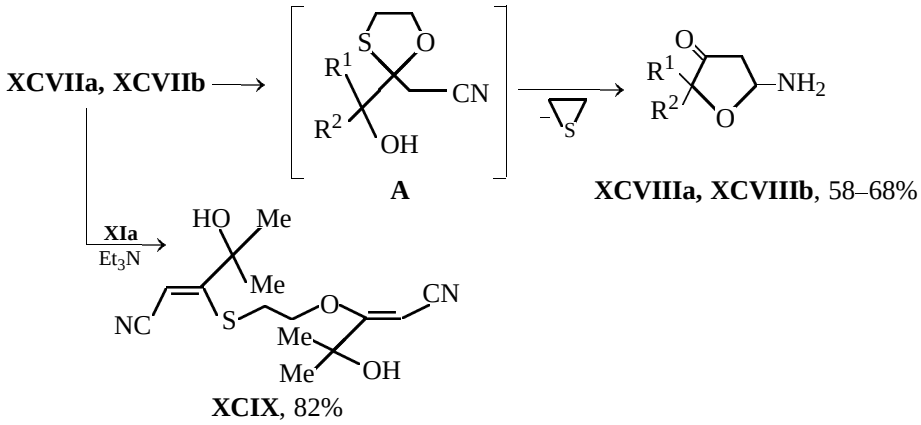


XCVIIa, XCVIIb, XCVIId

R^1 = R^2 = Me (**a**); R^1 = Me, R^2 = Et (**b**); R^1, R^2 = $(CH_2)_5$ (**d**).

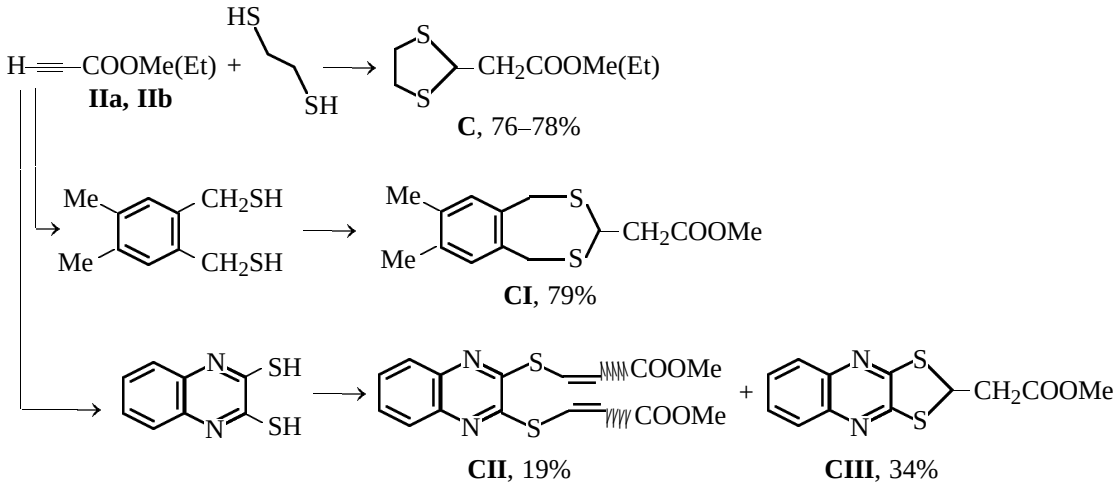
in protic (alcohol) and aprotic (dioxane) solvents to form 3-hydroxy-2-(2-hydroxyethylsulfanyl)-3,3-dialkyl-1-alkene-1-carbonitriles **XCVIIa**, **XCVIIb**, **XCVIId** in yields of up to 93% [99].

Nitriles **XCVIIa**, **XCVIIb** exhibhit a peculiar behavior in the presence of bases. They readily cleave thiirane (apparently, from intermediate 1,3-oxathiolane **A**) and cyclize into 2-amino-4,5-dihydrofuran-4-ones **XCVIII** [99, 100].

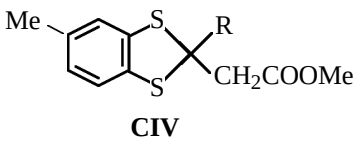


It was also shown that monoadduct **XCVIIa** can add (Et_3N, 45°C, 20 h) by its primary OH group to the second nitrile **XIa** molecule to form bis(alkenenitrile) **XCIX**.

The reactions ($CHCl_3$, 60°C, $_{¤2}CO_3$) of ethane-1,2-dithiol, 1,2-dimethyl-4,5-di(sulfanylmethyl)benzene or 2,3-disulfanylquinoline with equimolar amounts of esters **IIa**, **IIb** do not stop on monothiylation and are completed by cyclization into 1,3-dithiolanes **C**, **CI**, and **CIII** [97]. Intermediate bis(vinyl sulfide) **CII** was isolated only in the case of 2,3-disulfanylquinoxaline (DMSO, 80–90°C).



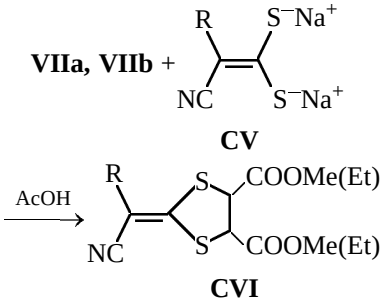
Esters of acids **I** (R = Ph, 4-ClC_6H_4) react with 3,4-disulfanyltoluene (AcOH, 120°C, 4 h) to give 2-R-2-(methoxycarbonylmethyl)-5-methyl-1,3-benzodithiolanes **CIV**, yield 40–45% [101].



Salts **CV** react with esters **VIIa**, **VIIb** in the pre-

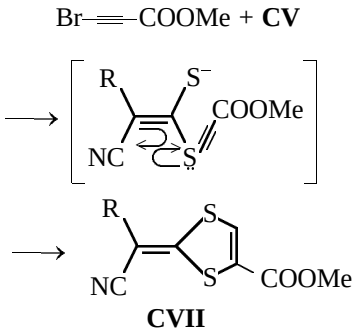
R = Ph, 4-Cl_6H_4.

sence of glacial AcOH in ethanol at 20°C, providing (*E*)-4,5-disubstituted 2-alkylidene-1,3-dithiolanes **CVI** [102, 103]; yield up to 90%.



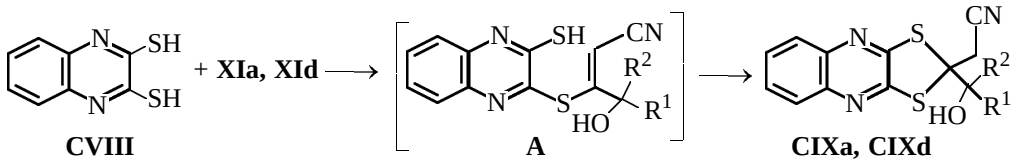
R = CN, $CONH_2$, COOMe(Et).

The same salts **CV** react with methyl bromopropiolate in MeOH in the presence of glacial AcOH, giving rise to methyl 2-(R,CN-methylene)-1,3-dithiol-4-carboxylates **CVII** [104].

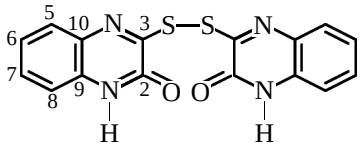


R = CN, COOEt.

The nucleophilic addition of 2,3-disulfanylquinoxaline **CVIII** to nitrile **XIX** resulted in isolation of 2,3-bis[(1-phenyl-2-cyanoethyl)sulfanyl]quinoxaline in 80% yield [KOH (10 wt%), water–dioxane (4 : 1), 20°C] [105]. The reaction route of quinoxaline **CVIII** with nitriles **XIa**, **XId** is not so unambiguous and strongly depends on the starting reagent ratio and solvent. At equimolar quinoxaline **CVIII**/nitrile **XIa**, **XId** ratio, the reaction does not stop on the addition stage (monoadduct **A**) and is completed by cyclization into 1,3-dithiolanes **CIXa**, **CIXd**.



The reaction of a double excess of nitrile **XIa** with disodium salt of quinoxalinedithiol **CVIII** unexpectedly provides 3-cyanomethylene-8-imino-2,2,6,6-tetramethyl-1,7-dioxa-4-thiaspiro[4.4]nonane (**XIVa**) (yield 64–66 %) and 2,2'-dioxodi(quinoxaline-3-yl)-disulfide (**CX**) (yield 11%) [105].



The synthesis of spirocycle **XIVa** is consistent with the scheme of its formation from nitrile **XIa** and sodium sulfide [25].

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