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Anatoly Volkov[a]; Kaleria Volkova[a]
[a] Siberian Division Russian Academy of Sciences, A.E. Favorsky Irkutsk Institute of Chemistry, Irkutsk, Russia

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REVIEW

Substituted acetylenes in reactions with sulfide, thioacetate and thiocyanate anions

ANATOLY VOLKOV* and KALERIA VOLKOVA

A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Division Russian Academy of Sciences, 1, Favorsky Street, Irkutsk, 664033, Russia

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The interaction of substituted acetylenes with hydrogen disulfide and its salts, thioacetate and thiocyanate anions is considered.

Keywords: Phenylacetylene; Vinylacetylene; Esters of propiolic and acetylenedicarboxylic acids; Acetylenic ketones; Acetylenic nitriles; Hydrogen disulfides; Thioacetates; Thiocyanate

1. Introduction

The modern chemistry of organic compounds is closely connected with achievements in the chemistry of unsaturated and heterocyclic compounds [1, 2]. Therefore, the development of general approaches to the synthesis of new sulfur compounds on the basis of the reactions of sulfide anions with acetylenes presents a contemporary problem in the chemistry of sulfur and acetylenes. Special attention is given to the investigation of acetylenes containing withdrawing and donating substituents such as acids, nitriles, amides, ketones, halogens, alkylthio groups [3]. A strong electron acceptor at the triple bond sharply increases its electrophilicity, whereas an electron donor produces the same effect on nucleophilicity. This affect allows a compound to readily partake in nucleophilic, electrophilic, and radical additions as well as $[4\pi + 2\pi]$ cycloadditions.

The availability of activated acetylenes allows their use as the initial material in the synthesis and permits the study of new types of organic sulfur compounds [4–6]. Reactions of acetylene compounds with sulfide anions are of great importance in the synthesis of vinyl sulfides [7–9] and compounds of the thiophene series [10, 11]. Vinyl sulfides and other compounds of sulfur form the basis for the synthesis of drugs, highly active pesticides, thermally stable and electric conductive materials [12, 13].

This review aims to generalize the information and elucidate some features of the reactions of acetylene compounds with hydrogen sulfide, sodium sulfide, thioacetates and thiocyanates. The addition of sulfide anions to conjugated diacetylenes has been described in detail [14, 15] and, therefore, reactions of this type are not discussed in the present review.

* Corresponding author. E-mail: professor_volkov@mail.ru

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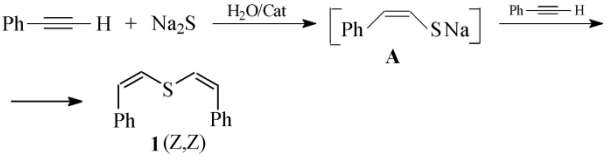
2. Reaction with hydrogen sulfide and its salts

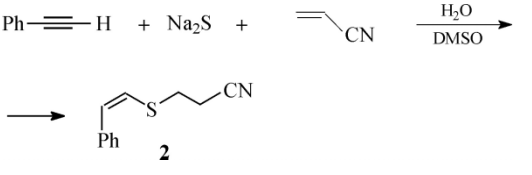
The addition of hydrogen sulfide to unsaturated C≡C, C=C, C=O bonds proceeds readily under both nucleophilic and radical conditions [9, 11]. When exposed to X-rays, H_2S adds to substituted acetylenes to form dithiols, along with other products [9]. In contrast to compounds with double bonds, those having triple bonds react preferably with nucleophilic reagents, the reactivity being dependent on the donating capability of the reagent and on the nature of substituent at the triple bond [1]. Trofimov and his team [6] have developed conditions for the activation of acetylenic compounds in dipolar aprotic solvents. Activation occurs at the expense of solvation of strong base cations. This greatly enhances the reactivity of conjugated anions and strengthens the triple bond polarization and ionization [6, 8, 16]. Phenylacetylene reacts with Na_2S to form bis(2-phenylethenyl) sulfide **1** (scheme 1) [1]. Crown ethers [6] and tetraalkylammonium salts [17, 18] can catalyze effectively the reaction of phenylacetylene with sodium sulfide in a two-phase system consisting of aqueous Na_2S and phenylacetylene.



SCHEME 1

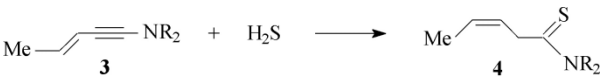
In triethylphosphine oxide (TEPO) in the presence of alkali and hydroquinone, hydrated sodium sulfide reacts with phenylacetylene to afford *Z,Z*-sulfide **1** in 90% yield [19, 20], whereas in DMSO–KOH–H_2O (30–35 °C) sulfide **1** is isolated as the *Z,E*-isomer [20]. Depending on the medium, the phenylacetylene/Na_2S reaction rate drops in the following order: HMPTA > DMSO > TEPO [20]. Kinetic studies using UV and NMR spectroscopy have shown that sulfide **1** formation from phenylacetylene and sodium hydrosulfide proceeds in a sequential–parallel manner *via* intermediate sodium (*Z*)-2-phenylethenethiolate **A** and involves two second-order reactions (first order with respect to phenylacetylene and sulfide anion) [21]. Intermediate **A** has not been isolated, but its presence is evidenced by the reaction with EtBr leading to (*Z*)-2-phenylvinyl ethyl sulfide (GLC, NMR) [21]. However, reference [21] gives no data on either conversion of the initial substances or the yield of sulfide **1**.

Upon the action of acrylonitrile on a mixture of sodium sulfide and phenylacetylene in DMSO in the presence of a small amount of water (30–35 °C), 2-phenylvinyl-1-ethylthiopropionitrile **2** is formed in ~30% yield (scheme 2) [22].



SCHEME 2

(3*E*)-1-Dialkylaminopent-3-en-1-ynes (**3**) react with hydrogen sulfide (ether, ~30 °C) in a preparative route to dialkylamides of 3-thioalkenic acids (**4**) in yields of up to 85% (scheme 3) [23].

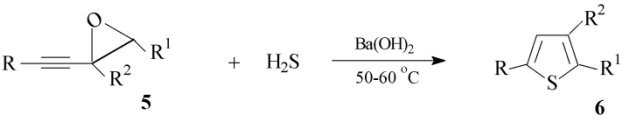


3 **4**

R = Et, Pr

SCHEME 3

The reactions of hydrogen sulfide with α-oxides and 2-alk-1-yn-1-yloxiranes of the acetylene and vinylacetylene series **5** have also been examined [24]. In the presence of $Ba(OH)_2$ the reaction proceeds in a rather complicated manner to give the corresponding thiophene homologs **6** in 30–80% yield [24] (scheme 4).



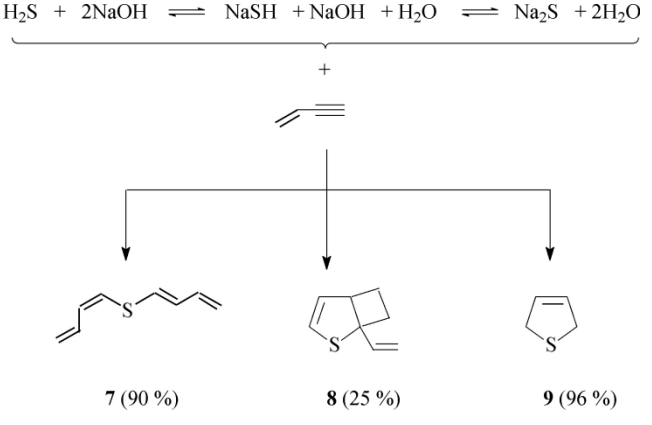
5 **6**

R = Me, CH_2 = CH-, Ph, $(Me)_2C(OH)$, Me(Et)C(OH)

R^1 = H, Me; R^2 =Me, Et.

SCHEME 4

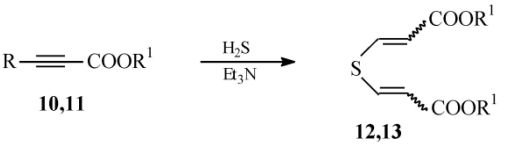
During the reaction with hydrated sodium sulfide in a caustic medium, vinylacetylene affords bis[(1*Z*)-buta-1,3-dien-1-yl] sulfide **7** in over 90% yield [18, 24, 25]. By varying the reaction conditions one may induce heterocyclization reactions [26, 27], leading either to 1-vinyl-2-thiabicyclo[3.2.0]hept-3-ene (**8**) or to dihydrothiophene (**9**) [28] (scheme 5). Thiophene **9** can be obtained in near quantitative yield [29].



7 (90 %) **8** (25 %) **9** (96 %)

SCHEME 5

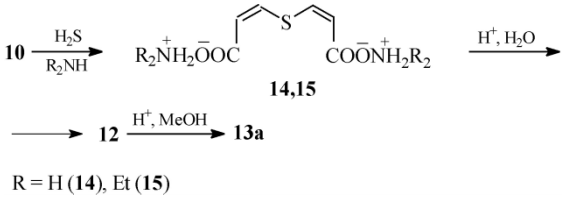
Propiolic acid **10** and its esters **11a**,**b** have been shown to regioselectively add H_2S (Et_3N, 0 °C) to form *E,E*-divinyl sulfides **12**, **13** in up to 53% yield (scheme 6) [11].



R = H; R^1 = H (**10,12**), R^1 = Me (**11a,13a**), Et (**11b,13b**)

SCHEME 6

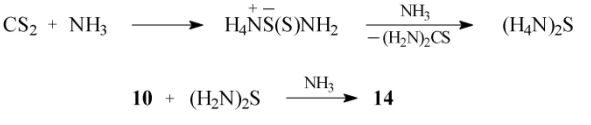
However, the stereochemical result of the above reaction of the ester **11a** with H_2S at 20 °C may be varied by changing the solvent polarity [30]. As a rule, an increase in the solvent polarity enhances the reaction product yield (MeOH, >90%) and increases the content of *Z,Z*-isomers (~34%). Whereas, when carried out in CCl_4 or benzene in the presence of methylmorpholine (~1%) the reaction affords a mixture of *E,E-, E,Z-* and *Z,Z*-isomers in a ratio of 68:23:9, indicating a violation of the *trans*-addition rule. Notably, isomerization is also possible. In contrast, in a medium of liquid ammonia or secondary amine the acid **10** reacts with H_2S and forms ammonium salts of *Z,Z*-di-(2-carboxyvinyl) sulfide (**14**, **15**) in 81% yield [31]. Salts **14** and **15** are readily hydrolyzed into the acid **12**, which is transformed into the ester **13a** with retention of the *Z,Z*-configuration (scheme 7).



R = H (**14**), Et (**15**)

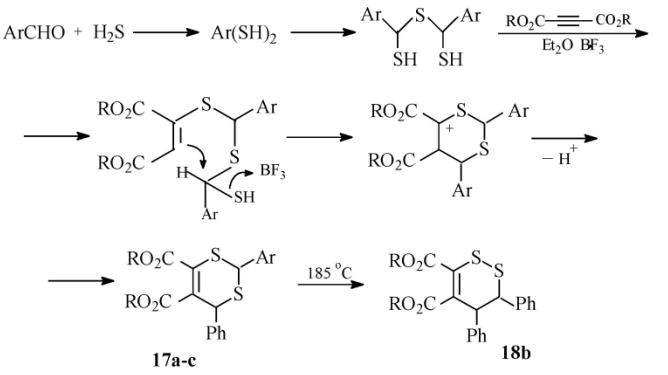
SCHEME 7

Salts **14** and **15** were also prepared from the acid **10** and CS_2 in liquid ammonia [31] (scheme 8).



SCHEME 8

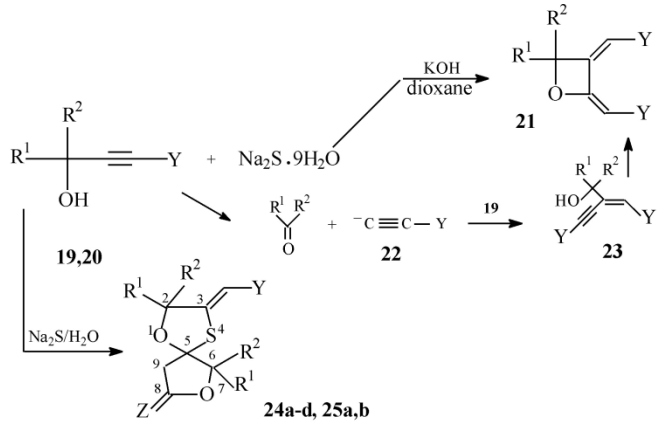
The two procedures provide good yields of the salts **14** and **15**, results that portend future usefulness in various syntheses and polymerization reactions. An unusual cyclization is observed in the reaction of H_2S with acetylenedicarboxylates (**16**) in the presence of aromatic aldehydes and BF_3·etherate [32]. A reaction mechanism involves the formation of dithiols [$Ar(SH)_2$ and Ar(SH)SAr(SH), see scheme 9]. Addition of the latter dithiol to **16** is followed by cyclization to 1,3-dithiins **17** (yield 95%). On heating, dithiin **17b** undergoes rearrangement to dimethyl-3,4-dihydro-3,4-diphenyl-1,2-dithiine-5,6-dicarboxylate **18b** [32] (scheme 9).



R = H (**16a**), Me (**16b**), Et (**16c**); Ar = Ph, *n*-MeC_6H_4, *n*-ClC_6H_4.

SCHEME 9

Another example of unexpected cyclization, of 4-hydroxyalk-2-ynenitriles **19** to 2,3-bis(cyanomethylene)oxetane **21** under the action of sulfide anion in dioxane in the presence of KOH, has been reported [33]. This is rationalized as follows: a retro-Favorsky reaction gives rise to the cyanoacetylene carbanion **22**, which is immediately captured by a second molecule of the nitrile **19** to form the vinylacetylene **23**, which undergoes final ring closure involving the remaining triple bond. Thus, no sulfur-containing products were detected in the reaction mixture. At the same time, in the absence of alkali (H_2O, 20 °C), nitriles **19** and methyl esters of methyl-4-hydroxyalk-2-ynoates **20** form spirocyclic lactones: 1,7-dioxa-8-imino-2,2,6,6-tetraalkyl-3-cyanomethylene-4-thiaspiro[4.4]-nonanes **24** and 1,7-dioxa-3-methoxycarbonylmethylene-2,2,6,6-tetraalkyl-4-thiaspiro[4.4]nonan-8-ones **25** in up to 92% yield [34–39] (scheme 10).

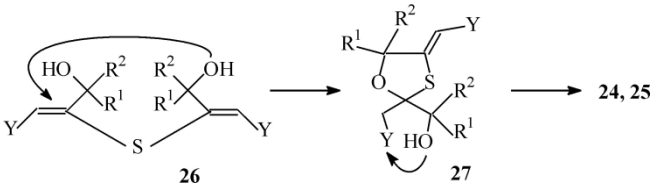


$R^1 = R^2$ = Me (a); R^1 = Me, R^2 = Et (b); R^1 = Me, R^2 = t-Bu (c), $R^1 - R^2 = (CH_2)_5$ (d);
Y = CN (**19, 21**), COOMe (**20**); Y = CN, Z = NH (**24**); Y = COOMe, Z = O (**25**).

SCHEME 10

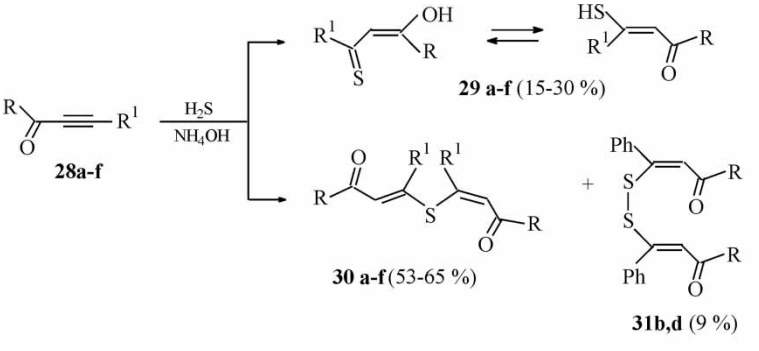
The reaction involves the formation of *Z,Z*-divinyl sulfides **26**, in which one hydroxylic group adds to the remote double bond, thus forming an oxathiolane ring (**27**, scheme 11), whilst the other interacts with the carboxylic or nitrile groups and closes the spirocyclic ring system.

Thus, these cyclizations open up a new way to previously unknown functionally substituted spirocyclic systems [40, 41].



SCHEME 11

In a 60% aqueous-dioxane solution aroylphenylacetylenes **28a–f** react with ammonium hydrosulfide at 15 °C to form β-oxy-α-thiobenzoylstyrenes **29** and (*Z,E*)-β,β-di-(α-aroyloxystyryl) sulfides **30** (scheme 12) [42].

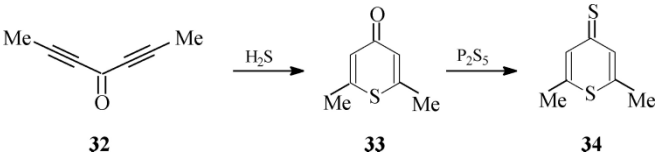


R = Ph (a), *p*-MeC_6H_4 (b), *m*-ClC_6H_4 (c), *p*-ClC_6H_4 (d), *p*-$MeOC_6H_4$ (e), 3,4-$(OCH_2O)C_6H_3$ (f); R^1 = H, Ph.

SCHEME 12

With ketones **28b,d** under the same conditions (H_2S, NH_4OH), apart from the adducts **29** and **30**, disulfides **31b,d** were also formed in low yield. Under analogous conditions (60% aqueous-dioxane) ketones **28** react with sodium sulfide to give styrenes **29** in high yields, which exist in an equilibrium mixture of enol–keto tautomers, with the enol form prevailing [42].

Hydrogen sulfide reacts with diyneketones **32** *via* conjugate addition across the ethynyl groups to form thiopyrones **33** in 90% yield (ampoule, alcohol, 100 °C, 1 h) [43, 44]. Heating **33** in benzene with P_2S_5 leads to the thione **34** (scheme 13).

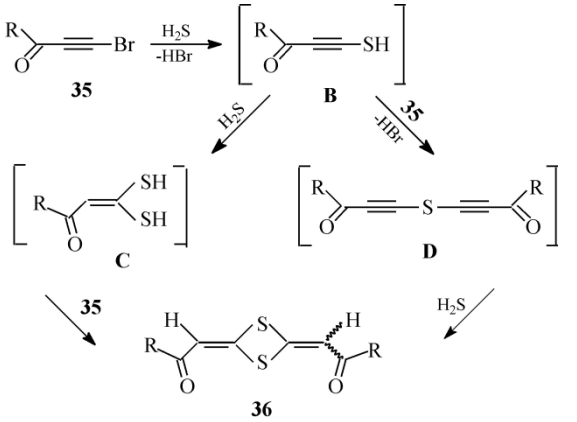


SCHEME 13

The addition of H_2S to α-acetylenic ketones in an alcohol medium (Et_3N, 0 °C) leads to the synthesis of bis(ketovinyl) sulfides **30** [45–47]. It was noted that the yield of sulfides **30**

containing the substituent R^1=aryl or hetaryl was 90–95%, whereas with R^1 = alkyl the yield was 68–72%.

Based on the reaction of 1-bromohex-1-yn-3-ones **35** with hydrogen sulfide in the presence of Et_3N a new route to the preparation of bis(acylvinylidene) sulfides (desaurines) **36** (yield 85–90%) was developed [48, 49]. The interaction of ketones **35** with hydrogen sulfide is likely to proceed as a nucleophilic substitution of the bromine atom to form compound **B** followed by the formation of the intermediate acylmethylenedisulfides **C**. Sulfide **C** then reacts with one more molecule of ketone **35** to form desaurines **36** (scheme 14).

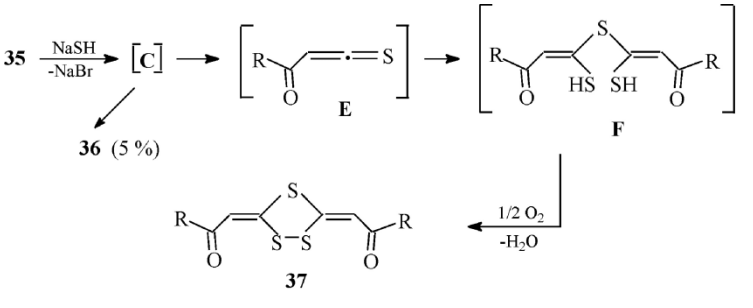


R = Ph, α-C_4H_3S, α-C_4H_2S-Et.

SCHEME 14

Furthermore, the thiol **B** can also react with the ketone **35** as a nucleophilic substitution of the bromine atom to form bisethynyl sulfide **D**. Desaurines **36** may be formed by the addition of dithiol **C** to the ketones **35** or the addition of H_2S to sulfide **D**.

During the reaction of ketones **35** with a two-fold excess of sodium hydrosulfide in dry alcohol, apart from a minor amount of desaurines **36**, 2,5-bis(β-acylmethylene)-1,3,4-trithiolanes **37** were obtained [48]. These substituted trithiolanes **37** probably form *via* dithiol **C,** which reacts with intermediate **E** to give dithiols **F**. When oxidized with air oxygen, dithiols **F** form the corresponding trithiolanes (**37**, scheme 15).

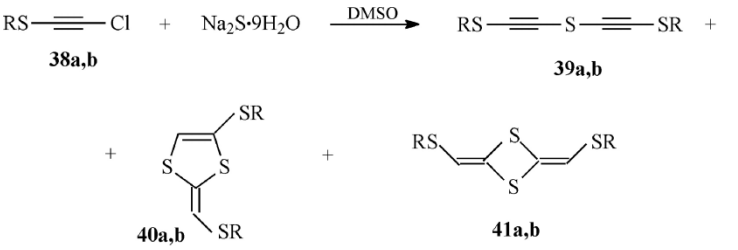


R = Ph, α-C_4H_3S, α-C_4H_2S-Et.

SCHEME 15

Halo(2-thienyl)acetylenes can react with sodium sulfide in alcohol to afford 2-thienylacetylenes [2]. Organylthiochloroacetylenes **38** react with sodium sulfide nonahydrate

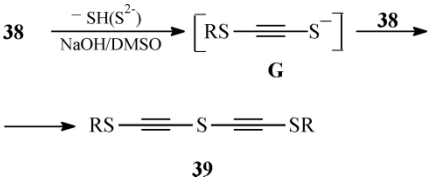
in DMSO in a quite different way. In this case, at equimolar ratio, three products: bis(alkylthioethynyl) sulfides **39a,b**, 4-(alkylthio)-2-[(alkylthio)methylene]-1,3-dithiols **40a,b** and 2,4-bis[(alkylthio)methylene]-1,3-dithiethanes **41a,b** are present in the reaction mixture (4:1:1, respectively, with a total yield of ∼77%) (scheme 16) [50].



R = Et (a), *n*-Pr (b).

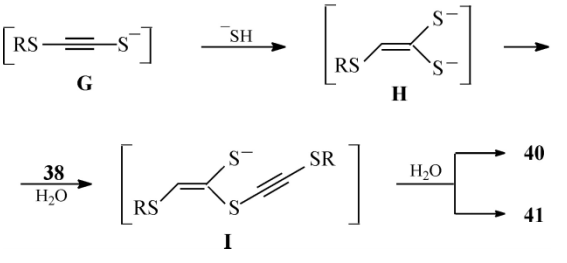
SCHEME 16

The reaction occurs *via* nucleophilic substitution of the chlorine atom by sulfide ions to form intermediate alkylthioethynylthiolate **G**, which further reacts with a second molecule of acetylene **38** to give bis(alkylthioethynyl) sulfide **39**. Acetylenes **38** react with sodium sulfide in a 2:1 ratio to give bis(alkylthioethynyl) sulfide **39** as the main reaction product (scheme 17).



SCHEME 17

Ethynethiolate **G** can react with sulfide ions to form vinylidenedithiolate **H**. Reaction of **H** with the initial acetylene **38** by nucleophilic substitution–addition along with intramolecular attack by the sulfide anion both at α- and β-carbon atoms of the acetylenic fragment in intermediate **I** lead to heterocycles **40** and **41**. Based on their spectral data, the products **40** and **41** were assigned a *syn*-configuration, which is consistent with the *trans*-addition of nucleophiles to acetylenes [50] (scheme 18).

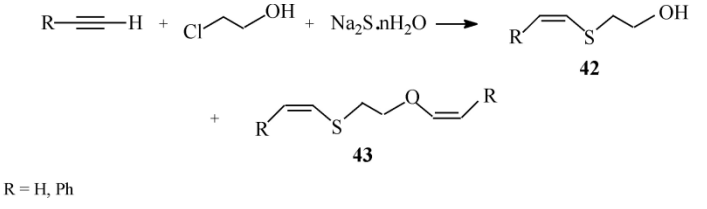


SCHEME 18

Furthermore, the suggested scheme 18 is in accord with other known data on the formation of substituted 1,3-dithiols and 2,4-bis(acylmethylene)-1,3-dithietanes in reactions of

1,1-ethenedithiols with activated acetylenes [51, 52]. Intermediate **I** can also be formed by addition of sulfide ions to adduct **39**. This direction looks more advantageous since the attack at the **G** anion by sulfide ions should be less favorable.

Interaction of acetylene and its derivatives with ethylenechlorohydrine and hydrated sodium sulfide leads to (2-hydroxyethyl)vinyl sulfides **42** (yield ∼50%) and (2-vinyloxyethyl)vinyl sulfides **43** (yield 14%) (scheme 19) [53].



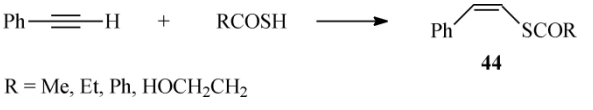
SCHEME 19

Some examples of the synthesis of vinyl sulfides have been presented in reviews [54, 55].

3. Reaction with thioacetate anions

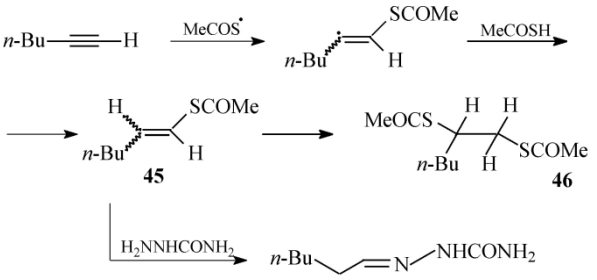
The addition of thioacetate anions to acetylenes provides a convenient route to diverse organic compounds, particularly vinylthioacetates [56]. In these reactions, thiolacetic acid acts as a very efficient addend for the creation of polyfunctional compounds having a thiolacetate group, which play an important part in biological processes [57]. Alcoholysis of β-thiolacetates in alkaline or acidic media are of interest as a synthetic route to substituted thiols [58]. In aqueous solutions thiocarboxylic acids undergo hydrolysis with elimination of hydrogen sulfide [59].

Thiolacetic acid is distinguished by high reactivity compared to thiols, which allows its wide application in the thiolation of multiple C−C bonds under both heterolytic and homolytic conditions [60, 61]. For example, thiolacetic acid reacts readily with substituted acetylenes under free-radical conditions to form thiolesters in 96% yield [62]. In the absence of an initiator the thiolesters **44** are formed in only 25% yield (scheme 20).



SCHEME 20

In general, electron-donating substituents at the triple bond accelerate the radical addition of thiolacetic acid. Thus, the free radical addition of thiolacetic acid to hex-1-yne (0 °C, 2:1 mole ratio, 1.5 h and 20 °C for 5 h) gives a mixture of (*E,Z*)-hex-1-enyl thiolacetates (**45**) in 55% yield (*E:Z* = 82:18). A mole ratio of 3:1 gave pure hexane-1,2-dithioldiacetate (**46**) in 33% yield [62] (scheme 21).



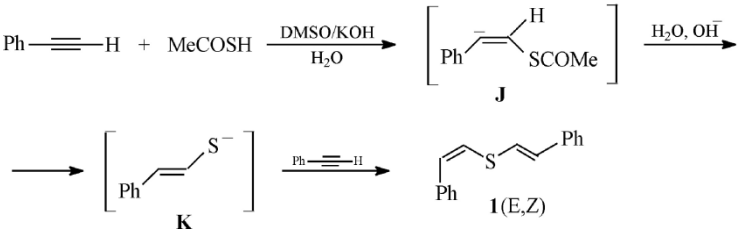
SCHEME 21

The gross anti-Markovnikoff structure of the monoadduct mixture **45** was confirmed by reaction of the mixture with 2,4-dinitrophenylhydrazine in ethanol containing sulfuric acid. These results on the stereochemistry of the addition of thiolacetic acid to hex-1-yne may be compared with data involving other acetylenes and addenda [1, 3]. The addition reaction presumably involves a vinyl radical intermediate (scheme 21).

This reaction makes it possible to transform terminal acetylenes into aldehydes [**45** reacts with $H_2NNHCONH_2$ to give 2-(hexylidene)-1-hydrazinecarboxamide, see scheme 21] and represents a key stage in the general synthesis of linolic acid [63]. Thus, for the preparation of linolic acid use is made of the reaction of deca-1,9-diyne with thiolacetic acid, which leads to the synthesis of 1-thiolacetodeca-1-en-9-yne (yield 60%) [63]. Consecutive treatment of the 1-thiolacetodeca-1-en-9-yne with NH_2OH, $HOCH_2CH_2OH$, $C_5H_{11}C{\equiv}CCH_2Br$, H^+, $AgNO_3$ and H_2/Ni gives linolic acid [63].

In a superbase medium (DMSO–KOH, 120–130 °C, 10 h) the addition of thioacetate anion to phenylacetylene results in the formation of sulfide **1** (yield 60%) with the *Z,E*-configuration [20].

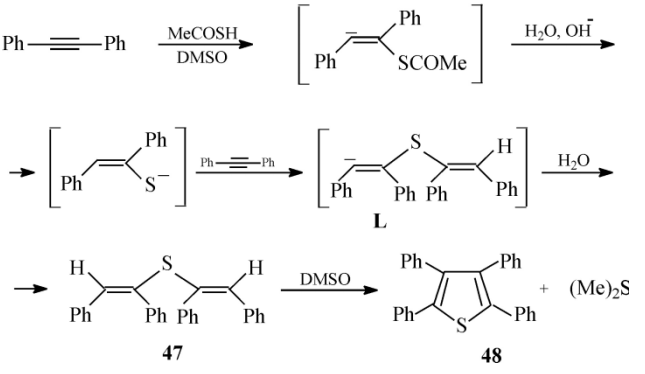
The formation of the *Z,E*-isomer is explained in terms of *trans*-nucleophilic addition of thioacetate anion to phenylacetylene followed by hydrolysis of acetate **J**, which leads to the formation of *trans*-vinylic fragment **K** (scheme 22). Intermediate **K** reacts with phenylacetylene to give the *Z,E*-isomer of sulfide **1**. This mechanism explains the absence of 2-phenylvinylthioacetate anions in the reaction mixture. The reaction of thioacetate with phenylacetylene in a TEPO medium (KOH, H_2O, 130 °C, 10 h) afforded a 90% yield of *Z,Z*-sulfide **1**. The *cis*-stereospecificity implies a *trans*-addition of both thioacetate and intermediate *cis*-2-phenylvinylthioacetate anions to the phenylacetylene triple bond [56, 64]. Phenylacetylene reacts with thioacetate anion in the presence of dibenzo-18-crown-6 at 70–80 °C in an aqueous-organic medium to furnish **1** in 78% yield as a 1:1 mixture of the two isomers.



SCHEME 22

The reaction of thioacetate anion with the ketone **28a** in an aqueous-etheral media (20 °C, 2 h) gives a mixture of *Z,Z*- and *Z,E*-isomers of the sulfide **30a** in 90% yield [56].

The reaction of thioacetate anion with diphenylacetylene (scheme 23, 150–160 °C, 8–10 h) proceeds in uncommon fashion. Instead of the expected tetraphenyldivinyl sulfide (**47**), tetraphenylthiophene (**48**) was obtained in 63% yield [65, 66] (scheme 23).



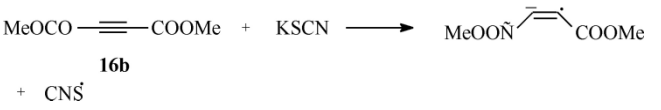
SCHEME 23

The structure of the thiophene **48** was determined by mass spectrometry, NMR, IR and UV spectroscopy. Interaction of MeCOSH with diphenylacetylene is suggested to involve the initial formation of sulfide **47** or anion **L**, which are further oxidized with DMSO or air-oxygen to thiophene **48**. Sulfide **47** has been prepared in aqueous DMSO in the presence of KOH (140–150 °C, 15 h, MeCOSH:PhC≡CPh:H_2O:KOH molar ratio 1:3:5:5) [66]. It transpired that sulfide **47** isolated without thermal treatment shows a geminal arrangement of phenyl groups, which was confirmed by NMR and ozonolysis data (CCl_4, O_3, 10 h, 58% yield). This points to possible migration of the phenyl group. When the sulfide with a geminal arrangement of phenyl groups is heated in air (200–220 °C, 45 min) the reverse 1,2-migration of phenyl group occurs, thus leading to the thiophene **48** in 92.5% yield [66].

Vinylacetylene actively reacts with thiolacetic acid in the presence of excess alkali (KOH, 90 °C, 6 h) with the isolation of three products: sulfide **7** (40%), thiabicycloheptene **8** (4%) and thiophene **9** (3%) [56]. With excess vinylacetylene and the contact time shortened to 2.5 h, the yield of sulfide **7** can be increased to 66%. Analysis of IR and NMR spectroscopic data asserts sulfide **7** to be a mixture of three isomers: *E,E, Z,Z* and *Z,E,* with a ratio of 1:1:5, respectively [28].

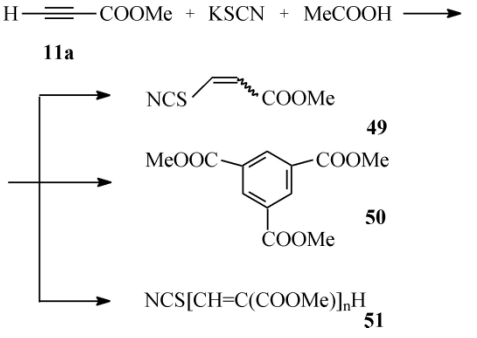
4. Reaction with thiocyanates

Activated acetylenes (acid **10**, esters **11** and **16**, propynal, among others) react with thiocyanate anion in the presence of acids to form the corresponding unsaturated thiocyanates [67–75]. According to a kinetic study, the addition of HSCN to the esters **11a**,**b** and **16b**,**c** in a solvent (methanol, acetonitrile, DMFA) in the presence of acetic acid seems to involve the formation of carbanions: $NCS^- + -C{\equiv}C- \rightarrow -C(SCN){=}C^-$ [68, 69]. Addition of the HSCN and KSCN mixture to ester **16b** under the same conditions proceeds very quickly without acetic acid, but the reaction does not come to the end [70]. Rather, depending upon the conditions, the addition of thiocyanates may lead to the formation of various intermediates such as π-complexes, σ-complexes, carbanions and radical anions [68]. For instance, on mixing KSCN solutions with the acid **10** or the ester **16b** in DMPA at 60–80 °C one may observe an EPR signal, the intensity of which rapidly increases [74]. This signal is caused by complete electron transfer from the salt atom onto the triple bond to form a radical anion (scheme 24). The reaction is inhibited by oxygen and proton donors.



SCHEME 24

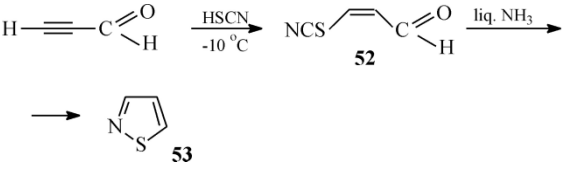
In the presence of carboxylic acids the reaction of KSCN with **11a** can proceed in three different directions (scheme 25) [75]. Depending on the reaction conditions, the reaction can be quantitatively directed to one or other pathway.



SCHEME 25

The reaction of **11a** with KSCN in the presence of a 2–3-fold excess of acetic acid in DMPA at 0–60 °C gives only the addition product **49**, β-thiocyanacrylate, whereas at 100 °C the main product is the trimesinic ester **50** (80%) [75]. With a decrease in acidity or increasing temperature the polymer **51** is observed in increasing yields [75]. This type of anion polymerization of acetylenes with electrophilic triple bonds affords, in reasonable yield, polyconjugated polymers with fairly high molecular mass [76]. In this case the rate of radical anion formation depends much on the electrophilicity of the triple bond and the nucleophilicity of the reacting anions. Thus, on going from the ester **11a** to the diester **16b** the rate of addition of HSCN across the triple bond in the presence of KSCN and acetic acid in DMPA at 81 °C increases 20-fold [74]. Dvorko's team has often used thiocyanates to study the theory of nucleophilic addition [68–70].

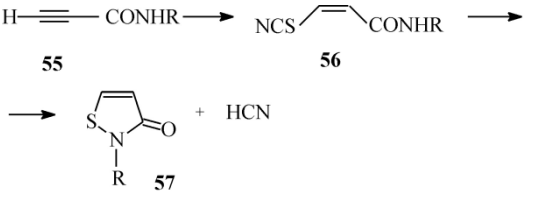
An aqueous HSCN solution with propynal in acetone gives, at −10 °C, presumably, (*Z*)-thiocyanopropynal **52** in 97% yield, whereas at 0 °C the *E*-isomer is formed. Aldehyde **52** in liquid ammonia affords isothiazole **53** (scheme 26) [71].



SCHEME 26

A study of the addition of aqueous HSCN to the acid **10** and ester **11a** has lead to the synthesis of 3-thiocyanacrylic acid (**54**) and its methyl ester (**54a**) up to 92% yield [77]. Treatment of **54a** with $AgNO_3$ in liquid ammonia in the presence of NaOH gives the salt *Z*-$MeO_2CCH{=}CHSAg$ (yield ~100%). The salt is transformed into (*Z*)-mercaptoacrylic acid

(CH_2Cl_2, HCl), which on storage (24 h) undergoes an 87% isomerization to the *E*-acid. Addition of thiocyanate anion to propiolic acid amides **55** in the presence of acids leads, reportedly, to the isolation of predominantly *cis*-3-thiocyanoacrylates **56** in 58–87% yield [78]. When heated in diluted acid (1–5 min), the *cis*/*trans* isomers **56** are cyclized to 2-alkylthiazol-3-ones **57** (63–88%) with the isolation of cyanohydric acid [78, 79]. Amide **56** can also be obtained by treating **55** with $Me_2S_2O_3$ in the presence of iodine. Unsaturated amide **56** can be further transformed into **57** in 64% yield (scheme 27) [78].

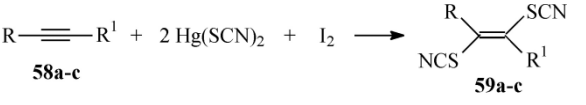


55 **56** **57**

R = H, Alk

SCHEME 27

Reasonable conditions for the addition of HSCN to inactivated acetylenes in the presence of mercury cyanate in two stages have been elaborated [72, 73]. The reaction probably involves the formation of intermediate $R^1C(SCN)=CR^2HgSCN$ followed by substitution of mercury by hydrogen. Substituted acetylenes **58** interact with mercury cyanate in the presence of iodine in dichloromethane to give the corresponding (*E*)-1,2-dithiocyanatoalkenes **59** in 70–90% yield [80] (scheme 28).

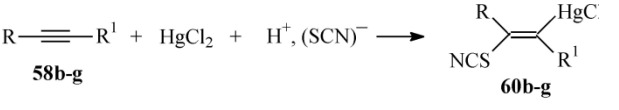


58a-c **59a-c**

R = R^1 = Et (a); R = n-Bu, R^1 = H (b); R = Ph, R^1 = H (c)

SCHEME 28

The reaction was carried out at 0 °C using a 1:2:1 molar ratio of alkynes:$Hg(SCN)_2$:I_2. This reaction can be used for a stereoselective preparation of (*E*)-1,2-dithiocyanatoalkenes **59a–c** [80]. With unsymmetrical alkynes **58b,c** the reaction took place regiospecifically according to the stability of the intermediate vinyl carbenium ion. An ionic mechanism has been proposed, based on the observed regio- and stereochemistry. Also, the thiocyanomercuration of acetylene **58** has been performed [81] (scheme 29).

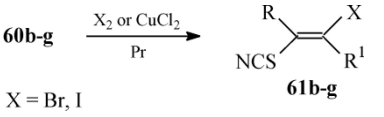


58b-g **60b-g**

R = Pr, R^1 = H (d); R = R^1 = Me (e); R = H, R^1 = CO_2Me (11a = f);
R = R^1 = CO_2Me (16b = g)

SCHEME 29

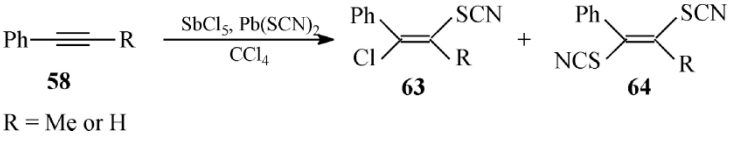
Using the interaction of **58b–g**, **11a** and **16b** with $HgCl_2$ in 3N aqueous HSCN the corresponding (*E*)-α-chloromercuro-β-thiocyanatoalkenes **60b–g** were synthesized in 50–60% yield (scheme 30) [81]. Treatment of **60** with halogens (Br_2, I_2) or $CuCl_2$ in pyridine leads to the synthesis of α-halo-β-thiocyanatoalkenes **61** in 40–70% yield [81].



SCHEME 30

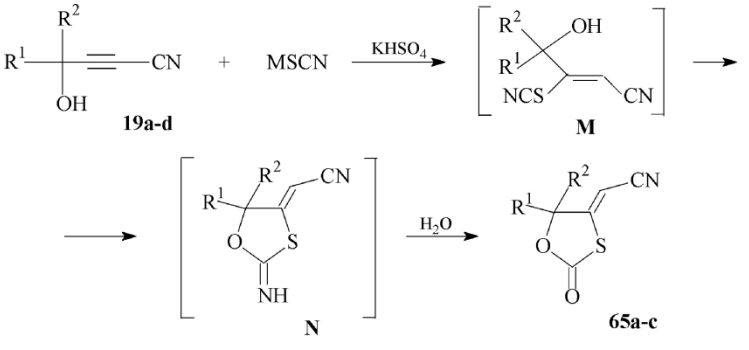
Consecutive treatment of **58b** with $HgCl_2$ and $(SCN)_2$ gives 1-thiocyanato-2-chlorohex-1-ene as an 8:2 mixture of *E,Z*-isomers. From **58b**,**c** with $HgCl_2$ in an alkaline KI solution it is possible to prepare acetylenides $[(RC{\equiv}C)_2Hg]$, which can give with $(SCN)_2$ the corresponding 1-thiocyanatoalk-1-ynes **62** [81]. Alkynes **62** have been prepared from acetylene iodides and NaSCN in 48–94% yield [82]. The presence of $Cu(SCN)_2$ favors the addition of two thiocyanate groups to acetylenedicarboxylates [83]. Thus, the interaction of NaSCN with ester **16b** in an $Cu(SCN)_2$ suspension in acetonitrile at 10 °C followed by heating to 25 °C for 15 min leads to the dimethyl ester of 1,2-dithiocyanofumaric acid in 85% yield. This ester can be used for the preparation of polymers possessing electron-conduction [82]. An efficient addition of two thiocyanate groups to various acetylenes **58** can be performed in the presence of dichloroiodobenzene and lead(II) dithiocyanate in dichloroethane at 0–5 °C [84].

Treatment of the acetylenes **58** (R = Me or H) in CCl_4 (76 °C, 2 h) with a mixture of antimony pentachloride and lead(II) thiocyanate gave, smoothly, the (*E,Z*)-chlorothiocyanatoalkenes **63** (*E:Z* = 1:4) in 39% yield [85]. The *E*-isomer was predominant except for **63** with R=H. The reactions were usually accompanied by formation of small amounts of the *bis*-thiocyanatoalkenes **64** (scheme 31).



SCHEME 31

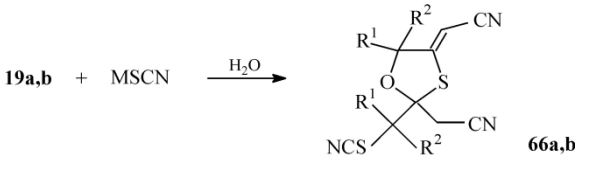
Trofimov *et al*. have found [39, 86–90] that α,β-acetylenic γ-hydroxynitriles **19** react readily with thiocyanic acid prepared *in situ* from MSCN (M=K, Na, NH_4) and $KHSO_4$ (20 °C, aqueous dioxane, 1 h) to give not the expected alkylthiocyanates **M**, but 1,3-oxathiolan-2-ones – the cyclic thiocarbonates **65** – in high yield (scheme 32).



$R^1 = R^2$ = 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)
M = NH_4, Na, K

SCHEME 32

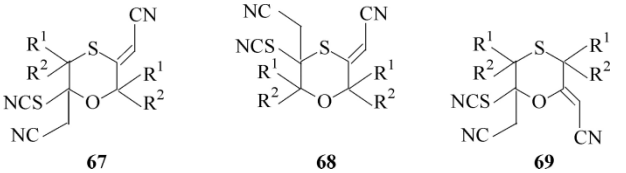
Thiocyanate **M** formed in the first stage undergoes intramolecular heterocyclization to form 2-imino-1,3-oxathiolanes **N**, which are further hydrolyzed to the corresponding thiolanones **65a–c**. In the absence of $KHSO_4$, 5,5-dialkyl-4-cyanomethylene-2-cyanomethyl-2-(1-thiocyano-1-methylalkyl)-1,3-oxathiolanes **66a**,**b** are formed in yields up to 93% rather than the expected cyanate **M** and subsequent cyanate **65** [89, 91–93] (scheme 33).



$R^1 = R^2$ = Me (a); R^1 = Me, R^2 = Et (b); M = NH_4, Na, K

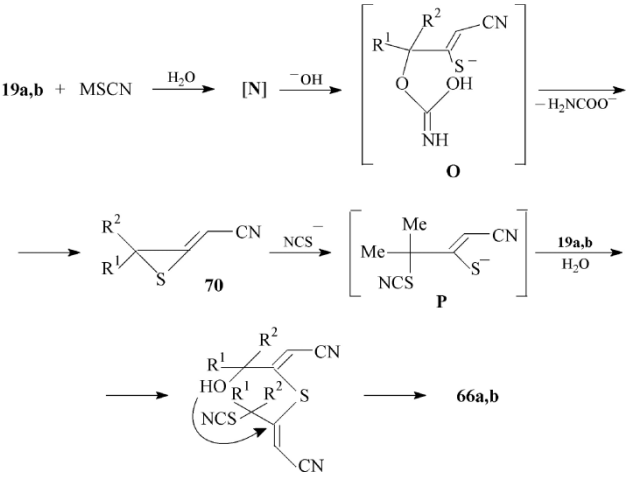
SCHEME 33

The yield of **66** depends on the nature of the cation of the thiocyanating agent. For example, on going from NH_4SCN to KSCN the yield of 1,3-oxathiothiolane **66** reduces from 90 to 51%. This yield drop is explained [87] by side processes, since in this case the formation of several alternative structures **67–69** is possible.



67 **68** **69**

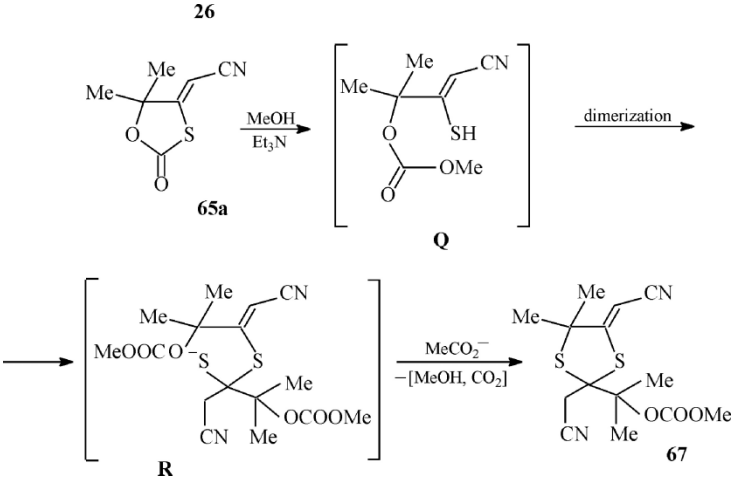
The structure of the 1,3-oxathiolane **66** was defined on the basis of X-ray diffraction data [89, 92]. The reaction mechanism seems to involve the formation of intermediate **N**, which undergoes nucleophilic cleavage by the released hydroxide anion, with elimination of the carbamic anion as a leaving group from intermediate **O** to extrude the cyanomethylene thiirane **70**. The latter reacts with the thiocyanate anion and another molecule of cyanoacetylene to give the intermediate **P**, hydroxy thiocyanates **71**, in which intermolecular Michael addition of hydroxyl to the double bond occurs to build up the 1,3-oxathiolane cycle **66a**,**b** (scheme 34) [39, 89, 92].



SCHEME 34

An interesting feature of this complicated reaction is the consistency and stereoselectivity observed in all its numerous stages: the formation of products of only one configuration in near quantitative yield.

The introduction into the nitriles **19c** or **19d** of bulky [R^1 = Me, R^2 = *t*-Bu (c)] or spirocyclic [R^1–R^2 = $(CH_2)_5$ (d)] substituents does not hinder the formation of hydroxythiocyanates **M** or 2-imino-1,3-oxathiolanes **N** (scheme 32) and, subsequently, **65**. Cyclization and subsequent hydrolysis of intermediates **M** and **N** proceeds more slowly (~15 h) with bulkier substituents and requires a 10-fold or greater molar excess of the hydrothiocyanating system (**19**:KSCN:$KHSO_4$ = 1:10:20). Under these conditions a quantitative yield of the thiolanes **65** is achieved [94] (scheme 32). In the presence of amines (primary, secondary, ammonia) the thiolane **65** (R^1 = R^2 = Me) stereoselectively reacts to form 5,5-dimethyl-4-cyanomethylene-2-cyanomethyl-[1-methyl-1-(carbamoyloxy)ethyl]-1,3-dithiolanes (20 °C, MeOH, 2–5 h) in quantitative yield [90, 95, 96]. The same thiolane **65** reacts with methanol in the presence of triethylamine (20 °C, 5 h) to give 5,5-dimethyl-2-[(1-methyl-1-methoxycarbonyloxyethyl)]-2-cyanomethyl-4-cyanomethylene-1,3-dithiolane (**67**) in 90% yield [94] (scheme 35).



SCHEME 35

Again, all these transformations are concerted, wonderfully clean, fast, facile and stereoselective, as followed from the single X-ray analysis [95] of dithiolanes **67**.

5. Conclusion

On the basis of substituted acetylenes in the reactions of hydrogen sulfide, its salts, thioacetate and thiocyanate anions, new approaches to the preparation of polyfunctional vinyl sulfides as well as five- and six-membered heterocyclic and spirocyclic systems are extensively elaborated. Consequently, the problem of synthetic application of these compounds becomes of primary importance. Preparative accessibility of vinyl sulfides, divinyl sulfides and 1,3-dithiolanes, along with high reactivity, makes them useful for the synthesis of various organic and heterocyclic compounds of great theoretical and practical interest.

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