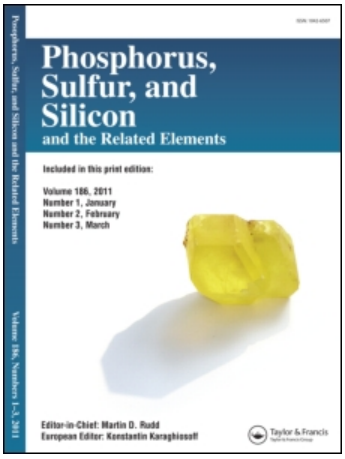

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REARRANGEMENT IN THE ACETYLENIC NUCLEOPHILIC SUBSTITUTION WITH THE *O*-ALKYL CARBONODITHIOATE ANIONS

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(Alkylthio)chloroacetylenes react with potassium *O*-alkyl carbonodithioates under mild conditions (25–30°C, DMSO) to form an approximately equimolar mixture of *O*-alkyl-*S*-[2-(alkylthio)ethynyl] carbonodithioates and *S*-alkyl-*S*-[2-(alkylthio)ethynyl] carbonodithioates in a total yield of up to 65%. The rearrangement is proved to occur in an anionic intermediate, probably, of the thiete structure.

Keywords: (Alkylthio)chloroacetylenes; *O*-alkyl carbonodithioates; *O*-alkyl-*S*-[2-(alkylthio) ethynyl] carbonodithioates; *S*-alkyl-*S*-[2-(alkylthio)ethynyl] carbonodithioates; rearrangement

INTRODUCTION

(Organylthio)chloroacetylenes are known to readily react with amines[1], pyrroles[2], alcohols[3], phosphines[4], sodium sulfide[5], thiols[6], mercaptoacetic acid[7] to afford both the products of substitution at the halogen atom[1,4,6,7] and adducts across the triple bond[2,3,5], depending on the nature of nucleophile used and reaction conditions. At the same time, in the literature there are no data concerning the interaction of haloacetylenes with alkali metal *O*-alkyl carbonodithioates (xanthates), although the reaction of the latter with alkyl halides is widely used in organic synthesis for the preparation of dithiocarbonic acid esters[8]. An addition reaction of alkali metal xanthates with acetylenes[9–11] and their functional derivatives[12], which, under certain conditions, leads to vinyl sulfides has also been reported.

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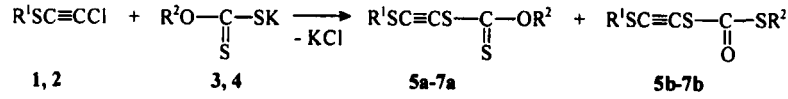
In the present work, the reaction of (alkylthio)chloroacetylenes with potassium *O*-alkyl carbonodithioates has been carried out and studied the first time with a goal of obtaining new information on the reactivity of haloacetylenes and xanthates and synthesizing their new derivatives.

RESULTS AND DISCUSSION

We have found that (alkylthio)chloroacetylenes **1, 2** react with equimolar quantities of potassium *O*-alkyl carbonodithioates **3, 4** in DMSO in a nucleophilic substitution mode to form not only the expected *O*-alkyl-*S*-[2-(alkylthio)ethynyl] carbonodithioates **5a-7a**, but also their structural isomers *S*-alkyl-*S*-[2-(alkylthio)ethynyl] carbonodithioates **5b-7b** (Scheme 1).



R^1 = Et (**1**, **5**, **6**), *n*-Pr (**2**, **7**); R^2 = Et (**3**, **5**), *n*-Bu (**4**, **6**, **7**)

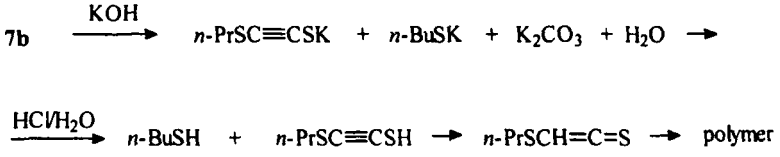
SCHEME 1

The reaction is exothermic (the reaction temperature was maintained within the 25–30°C range by means of external cooling) and leads to an approximately equimolar mixture of isomers **5a,b-7a,b** in a total yield of 53–65%. It should be noted that the ratio of isomers remains practically unchanged after storing the mixture for a long time (e. g., 4 months, room temperature). Apparently, the obtained ratio of isomers **5a,b-7a,b** is kinetically determined. Excess potassium *O*-alkyl carbonodithioate does not have any effect on the isomer ratio and their yield.

The IR spectrum of the obtained mixture of compounds **5a,b-7a,b** shows absorption bands of stretching vibrations of C≡C (2084 cm^{-1}), C=O (1728 cm^{-1}) and C=S (1250 cm^{-1}) bonds[13]. In the initial (alkylthio)chloroacetylenes **1, 2**, the triple bond absorption band is observed at a higher frequency region (2150–2160 cm^{-1}). The ^1H and ^{13}C NMR spectra for the mixture of isomers **5a,b-7a,b** are also in agreement with the proposed

structures[14,15]. In their ^1H NMR spectra, together with signals of aliphatic protons, one can see signals of the SCH_2 protons (at 2.70 ppm) in the alkylthio group at the acetylenic carbon atom as well as signals at the 3.06 and 4.57 ppm region related to the SCH_2 and OCH_2 protons, respectively, in alkyl carbonodithioatic moieties $R^2SC{=}O$ and $R^2OC{=}S$. In the ^{13}C NMR spectrum, recorded for the mixture of isomers **7a,b**, along with the signals of carbon atoms of the alkylthio and alkoxy groups, there are signals of acetylenic carbon atoms (74.0 and 89.1 ppm) as well as signals at 206.8 and 214.6 ppm corresponding to the carbon atoms of the C=O and C=S groups, respectively.

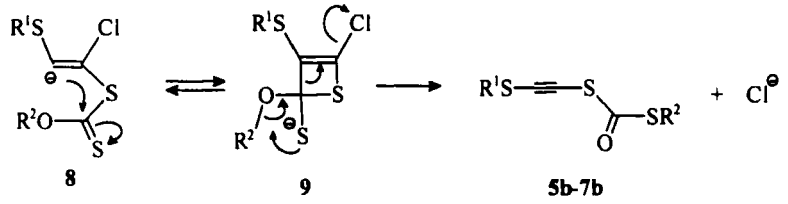
Additionally, formation of *S*-*n*-butyl-*S*-[2-(alkylthio)ethynyl] carbonodithioate **7b** has been also proved in a chemical way. Thus, *n*-butylmercaptan, evidently formed as a result of alkaline hydrolysis of the dithioether **7b** was identified (GLC) in the reaction mixture resulting from the consecutive treatment of the net product **(7a+7b)** with KOH-DMSO-EtOH system and 3% aqueous HCl (Scheme 2).



SCHEME 2

As inferred above, the formation of *S*-alkyl-*S*-ethynylcarbonodithioates **5b-7b** along with *O*-alkyl-*S*-ethynyl carbonodithioates **5a-7a** probably occurs during the reaction and is not a result of rearrangement of the final products (**5a-7a ≠> 5b-7b**). This is in keeping with the fact that isomerization of this kind in xanthates is readily accomplished only for *O*-allyl carbonodithioates and followed, as a rule, by allyl shift in the migrating group[16], whereas *O,S*-dialkyl and *O,S*-diaryl carbonodithioates are prone to isomerization to the corresponding *S,S*-dialkyl and *S,S*-diaryl carbonodithioates either in the presence of equimolar quantities of $AlCl_3$[17]or at a high temperature (200–300°C)[18].

A conceivable anionic rearrangement during the acetylenic nucleophilic substitution of the chlorine atom by the xanthate anion may look as follows (Scheme 3):



SCHEME 3

The driving force of the rearrangement is assumed to be the stabilization of the intermediate anion **8** by the intramolecular interaction of the developing negative charge with the electron-deficient thiocarbonyl center. This leads to the charge transfer to the thionic sulfur with the closing of the thiete ring to form intermediate **9**, which finally decomposes as shown in Scheme 3. The normal products **5a-7a** are originated through releasing chloride ions from the open intermediate **8**.

Similar kinetic rearrangements have been earlier observed in the reaction of xanthates with acetylenes under the action of the same KOH-DMSO system[19–21].

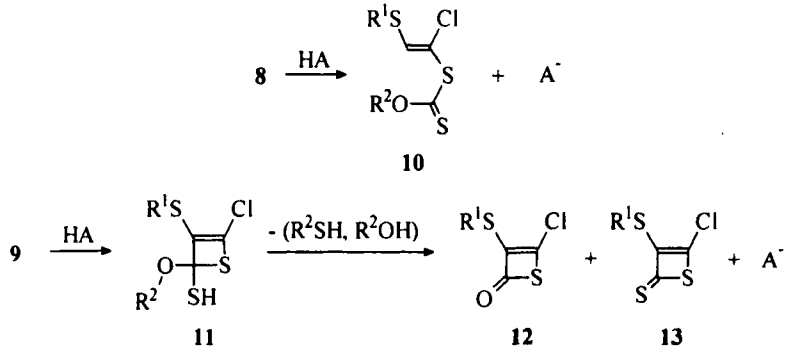
Replacement of DMSO by dioxane in the reaction of chloroacetylenes **1, 2** with carbonodithioates **3, 4** leads to an abrupt decrease in the reaction rate: some initial chloroacetylene remains unreacted even 17 h after the reaction start. In diethyl ether the reaction fails to occur.

Carbanions **8** and **9** may in a minor degree be quenched with protogenic impurities to give the addition products of the types **10–13** and their polymers (Scheme 4).

The contamination of the major products **5–7** with these minor ones and also those formed by the alternative addition to the carbon atom adjacent to the sulfur atom explains the presence of small quantities of chlorine in the net reaction products.

EXPERIMENTAL

IR spectra were recorded on a Specord IR-75 instrument in a microlayer for 400–4000 cm^{-1} range. ^1H and ^{13}C NMR spectra were taken on a Jeol FX-90Q spectrometer using $CDCl_3$ as solvent and HMDS as internal



SCHEME 4

standard. The reaction mixture analysis and purity control for the obtained compounds were performed using TLC (on plates with Al_2O_3 layer in hexane, I_2 as a developer) and GLC (gas-liquid chromatograph Chrom-4, steel columns (2.4 m), sorbents: NaCl + 1% PEG 20000 (0.16–0.25) and Inerton-AW-DMCS, 0.2–0.25 + 10% PEG 20000, gas carrier - helium).

Compounds **5–7** are likely to contain some impurities of the minor products **10–13**, which may account for the presence of chlorine (1–4% by elemental analysis data) in the isolated products.

Reaction of (ethylthio)chloroacetylene 1 with potassium *O*-ethyl carbonodithioate 3

A. To a suspension of 1.34 g (8.3 mmol) of salt **3** in 20 ml of DMSO, 1.00 g (8.3 mmol) of acetylene **1** was added dropwise upon stirring. Since the reaction was found to proceed exothermically, the temperature was kept in the range of 25–30°C using external cooling with a cold water bath. After addition of acetylene **1**, the reaction mixture was stirred for another 2 h at 20–25°C, poured into 40 ml of cold water (solution pH = 8–9) and extracted with ether (3 × 20 ml). The ether extract was washed with water (3 × 10 ml) and dried over $MgSO_4$, the ether was evaporated, and the residue was dried *in vacuo* to give 1.02 g (60%) of isomer **5a,b** mixture, viscous liquid of cherry color. IR: 2976, 2924, 2850 (ν, C-H), 2082 w (ν, C≡C), 1729 (ν, C=O), 1432, 1410,

1376 (δ, C-H), 1250 (ν, C=S), 1210, 1104 (ν, C-O-C), 1050, 1024, 954 (δ, C-H), 752, 690 (ν, C-S) cm^{-1}. ^1H NMR (ppm, $CDCl_3$): δ 1.27 (t, CH_3), 1.35 (t, CH_3), 2.79 (q, CH_2S), 3.09 (t, CH_2S), 4.58 (t, CH_2O). The isomer ratio is about 1:1 according to this spectrum. Anal. Calcd for $C_7H_{10}OS_3$: C, 40.74; H, 4.88; S, 46.62. Found: C, 39.85; H, 4.12; S, 47.52; Cl, 1.05 %.

B. Under analogous conditions, from 1.00 g (8.3 mmol) of acetylene **1** and 2.67 g (16.6 mmol) of salt **3** in 20 ml of DMSO, 0.90 g (53%) of an approximately equimolar mixture of isomers **5a,b** was prepared.

Reaction of (ethylthio)chloroacetylene 1 with potassium *O*-*n*-butyl carbonodithioate 4

A. To a suspension of 1.90 g (10.0 mmol) of salt **4** in 20 ml DMSO, 1.20 g (10.0 mmol) of acetylene **1** was added dropwise upon stirring. The temperature of the reaction mixture was kept at 25–30°C using a cold water bath. After addition of acetylene **1**, the mixture was stirred for 2 h at 20–25°C, poured into 40 ml of cold water (solution pH 8–9) and extracted with ether (3 × 20 ml). The ether extract was washed with water (3 × 10 ml) and dried over $MgSO_4$. The ether was evacuated, the residue was dried *in vacuo* to afford 1.52 g (65%) of isomer **6a,b** mixture. IR: 2956, 2928, 2884 (ν, C-H), 2084 (ν, C≡C), 1728 (ν, C=O), 1500, 1456, 1384 (δ, C-H), 1256 (ν, C=S), 1200, 1142 (two intense bands, ν, C-O-C), 1042, 970, 914 (δ, C-H), 814, 770, 670 (ν, C-S) cm^{-1}. ^1H NMR (ppm, $CDCl_3$): δ 0.94 (t, CH_3), 1.37 (m, CH_3), 1.78 (m, CH_2), 2.71 (q, CH_2S), 3.06 (t, CH_2S), 4.57 (t, CH_2O). Judging from the spectrum, the isomer ratio is nearly 1:1. Anal. Calcd for $C_9H_{14}OS_3$: C, 46.12; H, 6.02; S, 41.04. Found: C, 47.37; H, 6.26; S, 40.74; Cl, 3.91 %.

B. To a suspension of 1.90 g (10.0 mmol) of salt **4** in 20 ml of dioxane, 1.20 g (10.0 mmol) of acetylene **1** was introduced dropwise upon stirring at 20–22°C. The reaction mixture was stirred at 20–22°C during 17 h, then 40 ml of water was added (solution pH = 8–9) and the solution was extracted with ether (3 × 20 ml). The ether extract was washed with water and dried over $MgSO_4$. The solvent was removed, and the residue was dried *in vacuo* to give 1.00 g (42.9%) of yellow liquid containing initial chloroacetylene and the products of its polymerization (^1H NMR, GLC and elemental analysis data). IR: 2970, 2942, 2884 (ν,

C-H), 2156 (ν, C≡C, corresponds to initial chloroacetylene **1**), 1728 (ν, C=O), 1456, 1384 (δ, C-H), 1256 (ν, C=S), 1214, 1114 (ν, C-O-C), 1070, 1056, 956, 914 (δ, C-H), 800, 790 (ν, C-S) cm^{-1}. NMR ^1H (ppm, $CDCl_3$): δ 0.92 (t, CH_3), 1.37 (t, CH_3), 1.70 (m, CH_2), 2.73 (q, CH_2S), 3.05 (t, CH_2S), 4.57 (t, CH_2O). Anal. Calcd for $C_9H_{14}OS_3$: C, 46.12; H, 6.02; S, 41.04. Found: C, 43.59; H, 5.35; S, 34.17; Cl, 13.01 %.

Reaction of (*n*-propylthio)chloroacetylene 2 with potassium *O*-*n*-butyl carbonodithioate 4

To a suspension of 4.06 g (21.48 mmol) of salt **4** in 20 ml of DMSO, 2.86 g (21.48 mmol) of acetylene **2** was added dropwise with stirring. A cold water bath was used to maintain the reaction temperature at 25–30°C. After addition of acetylene **2**, the mixture was stirred for 2 h at 20–25°C, poured into 40 ml of cold water (solution pH = 8–9) and extracted with ether (3 × 20 ml). The ether extract was washed with water (3 × 20 ml) and dried over $MgSO_4$. The solvent was removed, and the residue was dried *in vacuo*. A total of 3.30 g (62%) of isomer **7a,b** mixture was isolated. IR: 2970, 2942, 2884 (ν, C-H), 2084 (ν, C≡C), 1728 (ν, C=O), 1456, 1370 (δ, C-H), 1228 (ν, C=S), 1200, 1114 (two intense bands, ν, C-O-C), 1042, 900 (δ, C-H), 800, 742 (ν, C-S) cm^{-1}. ^1H NMR (ppm, $CDCl_3$): δ 0.97 (m, CH_3), 1.31–1.71 (m, CH_3, CH_2), 2.70 (m, CH_2S), 3.10 (t, CH_2S), 4.57 (t, CH_2O) (the isomer ratio ~ 1:1). ^{13}C NMR (δ, ppm, $CDCl_3$): Structure **7a**: *n*-BuO - 12.92 (CH_3), 18.96, 30.28 (CH_2), 73.20 (CH_2O); *n*-PrS – 13.94 (CH_3), 21.82 (CH_2), 35.29 (CH_2S), 74.04, 89.13 (≡C), 214.57 (C=S). Structure **7b**: **n**-BuS - 12.59 (CH_3), 29.95, 30.08 (CH_2), 30.02 (CH_2S); *n*-PrS – 13.37 (CH_3), 22.34 (CH_2), 35.74 (CH_2S), 74.04, 89.13 (≡C), 206.77 (C=O). Anal. Calcd for $C_{10}H_{16}OS_3$: C, 48.35; H, 6.49; S, 38.72. Found: C, 48.16; H, 6.81; S, 38.27; Cl, 1.74 %.

Solvolysis of the product 7b

To a solution of 0.84 g (3.38 mmol) of product **7** dissolved in a mixture of 5 ml of DMSO and 5 ml of ethanol, 0.9 g (13.52 mmol plus excess calculated for 15% H_2O content) of KOH was added and the solution was stirred for 3 h at 20–22°C. Then 3 ml of cold 3% HCl was added, the solution was stirred another at the same temperature and extracted with ether

(3 × 10 ml). The ether extract was washed with water (3 × 10 ml) and dried over $MgSO_4$. The GLC analysis revealed the presence of *n*-butylmercaptan in the reaction mixture (comparison with the authentic sample through two different columns). The solvent was removed and after drying *in vacuo*, 0.10 g of a dark-brown tarlike product was isolated. IR: 2956, 2928, 2870 (ν, C-H), 1728 w (ν, C=O), 1500, 1456, 1414, 1370, 1298, 1288, 1042, 1026, 898, 798, 728 cm^{-1}. ^1H NMR (ppm, $CDCl_3$): δ 0.98 (t, 3H, CH_3), 1.24 (t, 3H, CH_3), 1.55 (m, 2H, CH_2), 2.69 (m, 2H, CH_2S), 6.22, 6.69 (s, 1H, =CH). Anal. Calcd for $C_5H_8S_2$: C, 45.41; H, 6.10; S, 48.49. Anal. Calcd for $C_7H_{12}S_2$: C, 52.45; H, 7.54; S, 40.01. Found: C, 50.57; H, 7.39; S, 37.54 %.

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