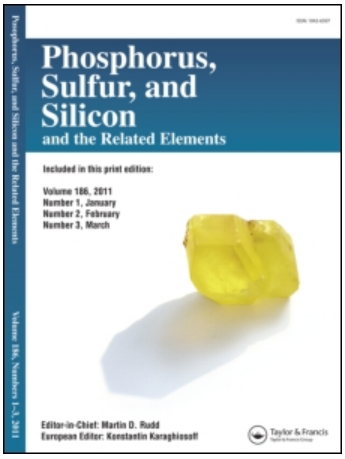

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REACTION OF (ORGANYLTHIO)CHLOROACETYLENES WITH ALIPHATIC 1,2-DITHIOLS: A ROUTE TO FUNCTIONALIZED 1,3-DITHIOLANES

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(Organylthio)chloroacetylenes react with aliphatic 1,2-dithiols in dimethyl sulfoxide at 20–25°C in the presence of a two-fold molar excess of alkali to form 2-[(alkylthio)methyliden]-1,3-dithiolanes in up to 66% yield.

Keywords: 1,2-Dithiols; 1,3-dithiolanes; (organylthio)chloroacetylenes

Earlier, we reported the reactions of (organylthio)chloroacetylenes **1** with *S*-centered nucleophiles (sodium sulfide,[1] thiols,[2] thioacetic acid[3]), which followed the addition and/or substitution schemes. (Organylthio)chloroacetylenes reacted with bidentate nucleophiles giving either functionally substituted acetylenic sulfides or organylthio substituted heterocyclic compounds.[2,4–6] Thus, 2-{[2-(alkylthio)ethynyl]thio}ethan-1-ammonium[5] and S-(alkylthioethynyl) isothiuronium[4] chlorides were prepared by the reaction of (alkylthio)-chloroacetylenes with 2-aminoethan-1-thiol and thiourea respectively. Under similar conditions, the reaction of (phenylthio)chloroacetylene with thiourea gave quantitatively 4-(phenylthio)-1,3-thiazol-2(3*H*)-imine hydrochloride.[4] (Organylthio)chloroacetylenes readily reacted with 2-mercaptoethan-1-ol (KOH-DMSO, 20–22°C) to afford

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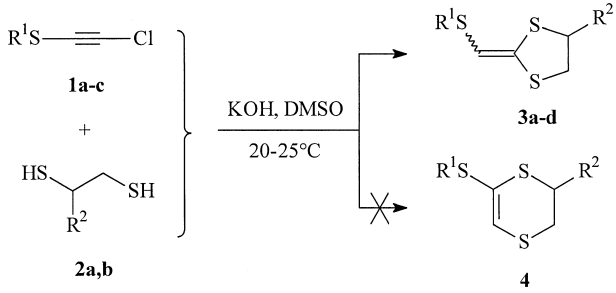
organylthioethynyl(2-hydroxyethyl)sulfides or 2-[(organylthio)methylene]-1,3-oxathiolanes,[6] depending on the reactant ratio and amount of KOH.

In order to obtain new information concerning the reactivity and synthetic potential of the available acetylenes **1**, which can be readily synthesized from trichloroethylene and thiols,[2] we have for the first time studied the reaction of (organylthio)chloroacetylenes with 1,2-ethanedithiols.

Taking into account the fact that (organylthio)chloroacetylenes may react differently with various bidentate nucleophiles, the pathway of the reaction under study could not be predicted a priori. At the same time, we hoped that under certain conditions this reaction might result in the targeted design of new heterocyclic systems, for example, polyfunctional 1,3-dithiolanes. The latter compounds attract much attention[7] owing to a variety of their application areas: they are used for the preparation of efficient radioprotectors,[8] antibacterial agents,[7] organic semiconductors,[9,10] and active cathode materials for rechargeable lithium batteries.[11]

RESULTS AND DISCUSSION

Chloroacetylenes **1a–c** react with dithiols **2a,b** in the presence of a two-fold molar excess of potassium hydroxide at a temperature of 20–25°C in dimethyl sulfoxide (DMSO) giving chemo- and regiospecifically 2-[(alkylthio)methyliden]-1,3-dithiolanes **3a–d** in 48–66% yield (Scheme 1). No reaction is observed without KOH or with catalytic amounts of the latter. The use of equimolar amounts of KOH results mainly in formation of unidentified polymeric products.

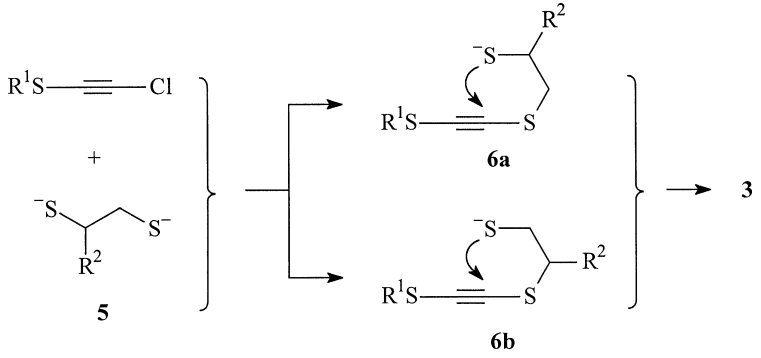


R^1 = Et (**1a**, **3a,b**), *n*-Pr (**1b**, **3c**), Ph (**1c**, **3d**)
R^2 = H (**2a**, **3a,d**), CH_2SO_3Na (**2b**, **3b,c**)

SCHEME 1

The structures of compounds obtained were confirmed by NMR data (^{1}H, ^{13}C). In the ^{1}H NMR spectra of dithiolanes **3a**,**d**, along with EtS or PhS protons' peaks, there is also a singlet of the vinyl proton. ^{13}C NMR spectra of dithiolanes **3a**,**d** show signals of organylthio group and dithiolane ring's carbon atoms, as well as two peaks located in the C_{sp} resonance region (~100 and 140 ppm). In the ^{13}C(H) NMR spectrum of compound **3d**, the C_{sp} 2 peak located in a stronger field is represented by a doublet with the coupling constant J_{CH}=179.1 Hz. In an analogous spectrum of dithiolane **3a**, the peak at 105.8 ppm is split into a doublet of triplets due to the coupling with the vinyl proton and α-protons of the ethyl group (J_{CH} = 178.2, $^3J_{CH}$ = 5.0 Hz). The peak at 139.7 ppm in the ^{13}C(H) NMR spectrum of this compound is also represented by a doublet of triplets with $^2J_{CH}$ = 3.9 and $^3J_{CH}$ = 3.0 Hz (the coupling with vinyl- and thiolane ring methylene protons). Each triplet component related to the exocyclic SCH_2 group coupling appears as a doublet of quartets. The coupling constant of 3.0 Hz between the latter group's carbon and olefinic proton indicates vicinal location of the above nuclei and allows to rule out the alternative, 5-(organylthio)-2,3-dihydro-1,4-dithiine structure **4** (Scheme 1).[12]

Apparently, the reaction represents a two-step process: first, a thiolate moiety of the ionized dithiol **5** attacks the triple bond with elimination of the chloride anion (simultaneously or as a successive addition-elimination) and then the second thiolate anion adds to the triple bond of thus formed intermediates **6a**,**b** (Scheme 2).



SCHEME 2

Obviously, a less sterically hindered thiolate moiety may be expected to participate mostly in the first step to form preferably the intermediate **6a**. Therefore, the final adducts **3** should have mainly *syn* configuration relative to the substituents R^1 and R^2, provided that the

second step ring-closing nucleophilic addition complies with the common *trans*-mechanism.[13]

In fact, as expected, according to NMR data, dithiolanes **3b**,**c** are formed as a mixture of *syn*- and *anti*-isomers, seemingly with the predominant formation of the *syn* isomer. The presence of two vinyl singlets (~1:2 ratio) and duplication of all proton groups' peaks in the ^{1}H NMR spectra and peaks of carbon atoms in ^{13}C NMR spectra are likely caused by the isomerism of these compounds, that is, different location of substituent R^1 relative to substituent R^2.

IR spectra of dithiolanes **3a–c** show absorption bands in the 1520–1550 cm^{-1} region attributable to stretching vibrations of the exocyclic double bond.[14,15] Elemental analyses of compounds **3a–d** are in agreement with the calculated values.

EXPERIMENTAL

^{1}H and ^{13}C spectra were taken on a Bruker DPX 400 (400 and 100 MHz, respectively) spectrometer in $DMSO_{d6}$ solutions and referenced to internal HMDS. IR spectra were run on a Bruker IFS 25 instrument in microlayer.

General Procedure

To a solution of 10.6 mmol of 1,2-alkanedithiol **2** in 10 mL of DMSO, 21.2 mmol of finely powdered KOH is added. The reaction mixture is stirred for 10 min at room temperature. Then, 10.6 mmol of acetylene **1** is slowly added dropwise over 20 min. The temperature of the reaction mixture (20–25°C) is kept by external cooling (a water bath). The mixture is stirred for 2 h at 20–22°C, poured into 10 mL of cold water and the oil formed is separated to give 2-[(organylthio)methyliden]-1,3-dithiolane **3**. Compounds **3a**,**d** were additionally purified using a column with Al_2O_3 (eluent: diethyl ether).

2-[(Ethylthio)methyliden]-1,3-dithiolane (3a): Oil, 59% yield. IR (cm^{-1}): 3100 (ν, =CH), 2963, 2914, 2863 (ν, CH), 1535 (ν, C=C), 1435, 1414, 1384, 1246, 1198, 1046, 970, 907, 835, 807, 770 (δ, C–C; δ, C–H; δ, C–C–S), 684, 528 (ν, C–S). ^{1}H NMR (δ, ppm): 1.20 t (CH_3), 2.68 q (SCH_2), 2.82 m, 2.91 m (SCH_2 cycle), 5.97 s (=CH). ^{13}C NMR (δ, ppm): 15.31 (CH_3), 28.33 (SCH_2), 37.67 and 38.07 (SCH_2 cycle), 105.83 [$J_{CH} = 178$ Hz] (C_{sp2}), 139.69 [$^2J_{CH} = 3.9$ Hz] (C_{sp2}).

2-[(Phenylthio)methyliden]-1,3-dithiolan (3d): Oil, 48% yield. IR (cm^{-1}): 3110, 3078, 3042, 3000 (ν, =CH), 2986, 2907 (ν, CH), 1630, 1584, 1530, 1507 (ν, C=C), 1428, 1407, 1270, 1200, 1114, 1084, 1014,

942, 900, 800, 728 (δ, C—C; δ, C—H; δ, C—C—S), 684, 548 (ν, C—S). ^{1}H NMR (δ, ppm): 2.99 m, 2.89 m (SCH_2 cycle), 5.56 s (=CH), 6.99–7.32 m (Ph). ^{13}C NMR (δ, ppm): 39.88, 40.37 (SCH_2cycle), 100.83 [J_{CH} = 179 Hz] (C_{sp2}), 138.77 (C_{sp2}), 126.55, 127.00, 129.56, 129.67, 129.82, 129.90 (Ph).

Sodium {2-[(Ethylthio)methyliden]-1,3-dithiolan-4-yl}methanesulfonate (3b): 59% yield. IR (cm^{-1}): 3105 (ν, =CH), 2970, 2928, 2870 (ν, CH), 1520 (ν, C=C), 1428, 1414, 1370, 1200 (δ, C—H), 1035, 950, 914, 786, 770 (δ, C—H), 700, 590, 528 (ν, C—S). ^{1}H NMR (δ, ppm): 1.16 t, 1.26 t (CH_3), 2.63–2.70 m (SCH_2), 2.80 d, 2.83 d (SCH_2 cycle), 2.97 m, 3.0 m (SCH cycle), 3.49 d, 3.53 d (CH_2SO_2), 5.92 s, 5.94 s (=CH). ^{13}C NMR (δ, ppm): 14.28, 15.43 (CH_3), 28.44, 30.0 (SCH_2), 41.98, 42.04 (SCH_2 cycle), 50.32, 51.03 (CH cycle), 54.52, 54.90 (CH_2SO_2), 106.33, 106.36 (H-C_{sp2}), 139.19, 139.75 (C_{sp2}).

Sodium {2-[(*n*-Propylthio)methyliden]-1,3-dithiolan-4-yl}methanesulfonate (3c): 66% yield. IR (cm^{-1}): 3058 (ν, =CH), 2970, 2928, 2870 (ν, CH), 1530 (ν, =CH), 1470, 1414, 1370, 1298, 1200 (δ, C—H), 1042 (ν, S=O), 950, 928, 884 (δ, C—H), 735, 598, 528 (ν, C—S). ^{1}H NMR (δ, ppm): 0.91 t, 0.94 t (CH_3), 1.54–1.60 m (CH_2), 2.61–2.68 m (SCH_2), 2.74 d, 2.77 d (SCH_2 cycle), 2.92 m, 2.94 m (SCH cycle), 3.52–3.56 m (CH_2SO_2), 5.92 s, 5.95 s (=CH). ^{13}C NMR (δ, ppm): 13.04, 13.59 (CH_3), 23.02, 23.20 (CH_2), 36.27, 37.00 (SCH_2), 42.0, 42.14 (SCH_2 cycle), 50.76, 50.84 (CH cycle), 54.40, 54.50 (CH_2SO_2), 106.26, 106.33 (H-C_{sp2}), 138.47, 138.86 (C_{sp2}).

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