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Organylthiochloroacetylenes: IX.[1] Reactions with Geminal and Vicinal Dithiols

M. G. Voronkov[b], S. G. D'yachkova[a], I. P. Lebedeva[a], A. V. Evart[a], and L. G. Shagun[b]

[a] *Irkutsk State Technical University, ul. Lermontova 83, Irkutsk, 664033 Russia e-mail: dsg@irk.ru*

[b] *Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, Russia*

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Abstract — Alkylthiochloroacetylenes react with geminal (in ether) and vicinal (in THF) dithiols to form, respectively, functional 1,3-dithiolenes (yield 43%) or 1,3-dithiolanes (yield 34%).
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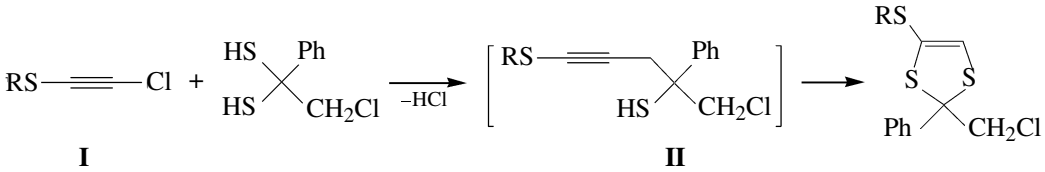
We found previously that the reactions of organylchloroacetylenes **I** with *S*-centered nucleophiles (thiols [2, 3] and sodium sulfide [4]) involve the C–Cl and C≡C bonds. These reactions open new possibilities for preparative synthesis of polyfunctional unsaturated compounds, including heterocyclic derivatives.

Among reactions of haloacetylenes with geminal dithiols, only reactions of 1,1-vinylidenedithiols with bromoethynyl organyl ketones and chloroethynylphosphonates have been studied [5]; these reactions yield the corresponding 1,3-dithiolene derivatives [5]. Reactions of acetylenes **I** with aliphatic geminal dithiols were not studied previously.

We found that compounds **I** react with 1,1-dimercapto-1-phenyl-2-chloroethane in ether at 0°C to form 2-chloromethyl-2-phenyl-4-organylthio-1,3-dithiolene (**II**) in 42% yield (Scheme 1).



(1)

I **II**

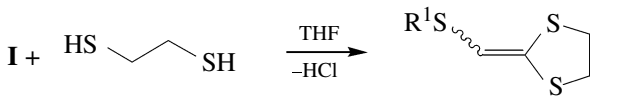
The ^{1}H and ^{13}C NMR spectra of dithiolene **II** show that reaction (1) is regiospecific. The ^{1}H NMR spectra of dithiolenes **II** contain, along with the signals of organylthio, chloromethyl, and phenyl groups, only one singlet of the heteroring proton at 7.32 ppm. The ^{13}C NMR spectra of these compounds contain signals of carbon atoms in the five-membered 1,3-dithiolene ring and its substituents [6–8]. The signal assignment is based on their splitting in the ^{13}C NMR spectra recorded without proton decoupling.

We have shown previously that the reaction of organylthiochloroacetylenes **I** with bifunctional nucleophiles proceeds as a double nucleophilic attack of haloacetylene **I** on the carbon atom atom bonded to chlorine and yields the heterocycles: 1,3-oxathiolanes [9], 1,3-oxazolidines [10], 1,3-oxazoles, 1,3-oxazines [11], and imidazoles [12]. The reaction of acetylenes **I** with geminal dithiols unexpectedly occurs as an attack of the nucleophilic centers on the both acetylenic carbon atoms, yielding 1,3-dithiolenes. A probable cause of this reaction pathway is formation of a five-membered ring which is energetically favorable as compared to the four-membered ring.

We have shown [13, 14] that the reaction of acetylenes **I** with 1,2-ethanedithiol and KOH in dimethyl sulfoxide (DMSO) yields 2-[(alkylthio)methylidene]-1,3-dithiolanes. In this study we found that 2-[(alkyl-

[1] For communication VIII, see [1].

thio)methylidene]-1,3-dithiolanes (**III**) are formed from acetylenes **I** and 1,2-ethanedithiol in THF without alkali in 34% yield. The absence of alkali and replacement of DMSO by THF as the reaction medium simplify the process and make it more feasible for commercial application.



III (2)

Thus, the reaction of organylchloroacetylenes **I** with geminal and vicinal dithiols is a new route to functional 1,3-dithiolanes and 1,3-dithiolenes which are of considerable practical interest. These structures are contained in effective radioprotectors [15], various cyanine dyes [16], antibacterial preparations [17], and electrochemically active polysulfide polymers, which are promising cathode materials [18–20].

EXPERIMENTAL

The IR spectra were recorded on an IR-75 spectrometer from thin films. The ^{1}H and ^{13}C NMR spectra were taken on a Bruker DPX-400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) in $CDCl_3$, internal reference TMS. The purity of the compounds prepared was monitored by GLC on a Tsvet-500 chromatograph (thermal conductivity detector, 3000 × 4-mm glass columns, Interon-Super 0.125–0.150 mm impregnated with 10% PSM-1000, carrier gas helium).

Acetylenes **I** were prepared according to [21], and 1,1-dimercapto-1-phenyl-2-chloroethane, according to [22].

2-Chloromethyl-2-phenyl-4-ethylthio-1,3-dithiolene (II). To a solution of 0.2 g of 1,1-dimercapto-1-phenyl-2-chloroethane in 5 ml of absolute diethyl ether, we added dropwise with stirring over a period of 30 min a solution of 0.1 g of acetylene **I** in 5 ml of absolute diethyl ether at 0°C. The reaction mixture was kept at this temperature for 30 days. The ether was removed, and the components of the reaction mixture were separated by preparative chromatography. Compound **II** was isolated in 42% yield. IR spectrum (thin film), cm^{-1}: 3074 (=C–H), 2968, 2912 (C–H), 1650 (C=C), 1596, 1572, 1526, 1492, (C=C_{arom}), 678 (C–Cl) [23, 24]. ^{1}H NMR spectrum, δ, ppm: 1.29 t (3H, CH_3), 2.76 q (2H, CH_2S), 4.66 s (2H, CH_2Cl), 7.32 s (1H, CH), 7.44, 7.56, 7.90 (=CH_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 15.66 (CH_3), 28.05 (CH_2), 46.01 (CH_2Cl), 65.84 (ring C^2), 127–129 (C of arom. ring), 134.52 (ring C^5), 190.10 (ring C^4). Found, %: C 48.49; H 4.12; Cl 13.85; S 32.99. $C_{12}H_{13}ClS_3$. Calculated, %: C 49.91; H 4.50; Cl 12.30; S 33.27.

2-[(Ethylthio)methylidene]-1,3-dithiolane (III). To a solution of 1.00 g of 1,2-ethanedithiol in 10 ml of THF at 20–22°C, we slowly added 1.28 g of acetylene **I**. The mixture was stirred for 7 days. The solvent was removed in a vacuum, and the residue was purified on a column with aluminum oxide. Compound **III** was isolated; yield 0.64 g (34%), light brown viscous substance. IR spectrum (thin film), cm^{-1}: 3110 (=C–H), 2970, 2920, 2873 (C–H), 1545 (C=C), 690, 532 (C–S) [23, 24]. ^{1}H NMR spectrum, δ, ppm: 1.26 t (3H, CH_3), 2.72 q (2H, SCH_2), 2.86–2.94 m (4H, ring SCH_2), 5.95 s (1H, =CH). ^{13}C NMR spectrum, δ_C, ppm: 16.42 (CH_3), 29.40 (SCH_2), 37.48 and 38.24 (ring SCH_2), 115.80 ($^3J_{CH}$ 4.0 Hz) and 140.24 (J_{CH} 168 Hz) (C_{sp^2}). Found, %: C 41.33; H 6.00; S 54.06. $C_6H_{10}S_3$. Calculated, %: C 40.41; H 5.65; S 53.94.

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