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SHORT COMMUNICATIONS

Dedicated to Full Member of the Russian Academy of Sciences
M.G. Voronkov on his 90th anniversary

Reaction of Bis(prop-2-yn-1-yl) Sulfide with Sulfur Dichloride. First Example of Cyclization of Bis(prop-2-yn-1-yl) Chalcogenides by the Action of Chalcogen Halides

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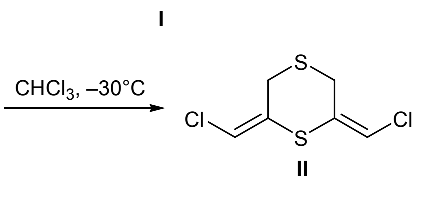
Electrophilic reactions of sulfur dichloride with various allyl and diallyl systems were reported [1–6]; however, among propargyl derivatives, data on reactions of sulfur dichloride only with propargyl alcohols are available [7–9]. These reactions lead to the formation of diallenic sulfones rather than addition products. We have found no published data on reactions of sulfur dihalides with compounds containing two propargyl fragments.

We have found that bis(prop-2-yn-1-yl) sulfide (**I**) reacts with sulfur dichloride in chloroform at –30°C in stereo- and regioselective fashion. The reaction follows anti-Markovnikov *anti* addition scheme at both triple bonds of compound **I** and yields previously unknown (*E*,*E*)-2,6-bis(chloromethylidene)-1,4-dithiane (**II**). The structure of heterocyclic compound **II** was confirmed by the ^{1}H and ^{13}C NMR spectra. The =CHCl group gave rise to a doublet of triplets at δ_C 115.56 ppm in the ^{13}C NMR spectrum ($^1J_{CH}$ = 200 Hz), indicating that the chlorine atom is attached to an sp^2-hybridized carbon atom [10]. The ^{1}H NMR spectrum of **II** contained a singlet at δ 6.29 ppm with satellites characterized by the same coupling constant. The *E* configuration of the exocyclic double bonds in molecule **II** follows from the coupling constant for the CH$_2$ carbon nuclei (t.d, $^3J_{CH}$ = 6.7 Hz [11]) in the ^{13}C NMR spectrum and from the absence of cross peaks for the vinylic and methylene protons in the 2D NOESY spectrum. The structure of compound **II** was also confirmed by elemental analysis and mass spectrum which contained a strong peak from the molecular ion, *m*/*z* 212 (^{35}Cl).



The observed regio- and stereoselectivity in the reaction of sulfur dichloride with bis(prop-2-yn-1-yl) sulfide (**I**) is consistent with the known preference of anti-Markovnikov *anti* addition over Markovnikov addition in electrophilic reactions of sulfenyl halides with terminal acetylenes [12]. However, it is interesting that reactions of propargyl alcohols with selenium dichloride lead to the formation of (*Z*,*Z*)-bis(2-chloro-1-hydroxymethylvinyl) selenides as a result of anomalous anti-Markovnikov *syn* addition [13].

The described reaction is the first example of cyclization of dipropargyl systems containing a bridging chalcogen atom by the action of chalcogen halides.

***(E,E)*-2,6-Bis(chloromethylidene)-1,4-dithiane (II).** A solution of 0.550 g (5 mmol) of bis(prop-2-yn-1-yl) sulfide (**I**) in 15 ml of anhydrous chloroform was cooled to –30 to –45°C, a solution of 0.514 g (5 mmol) of sulfur dichloride in 10 ml of chloroform was added over a period of 25 min under stirring in an argon atmosphere, and the mixture was allowed to warm up to room temperature and stirred for 5.5 h. The solvent was removed under reduced pressure, the residue was dissolved in methanol, and slow crystallization gave 0.690 g (65%) of compound **II** as white plates with mp 88°C. ^{1}H NMR spectrum, δ, ppm: 3.73 s (2H, CH_2, $^1J_{CH}$ = 142.0 Hz), 6.29 s (1H, =CHCl, $^1J_{CH}$ = 200.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.76 t.d (CH_2, $^1J_{CH}$ = 143, $^3J_{CH}$ = 6.7 Hz), 115.56 d.t (=CHCl, $^1J_{CH}$ = 200, $^3J_{CH}$ = 5 Hz), 131.78 s (C^2, C^6). Mass spectrum, *m*/*z* (^{35}Cl, I_{rel}, %): 212 (46) $[M]^+$, 177 (22) $[M - Cl]$, 141 (13), 138 (10), 106 (19), 103 (23), 92 (21), 71 (64), 45 (100), 39 (59). Found, %: C 33.42; H 2.75; Cl 33.10; S 29.62. $C_6H_6Cl_2S_2$. Calculated, %: C 33.81; H 2.84; Cl 33.27; S 30.09.

Bis(prop-2-yn-1-yl) sulfide (**I**) was synthesized from 3-bromopropyne and Na_2S in alcohol [14]. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.13 and 100.61 MHz, respectively, from 5–10% solutions in $CDCl_3$. The mass spectrum (electron impact, 70 eV) was obtained on a Shimadzu QP5050A GC–MS system (SPB-5 ms capillary column, 60 m; injector temperature 260°C, oven temperature 50–220°C).

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