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REACTIONS OF SULFUR DICHLORIDE WITH ALLYLTHIENYL SULFIDES

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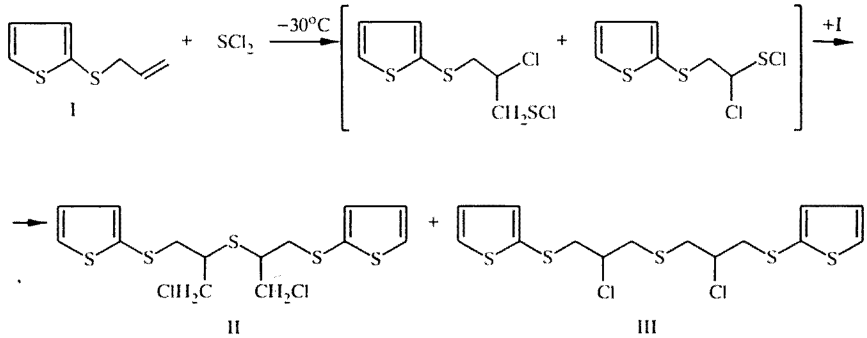
The reaction of allyl-2-thienyl sulfide with sulfur dichloride yields products of intermolecular addition of intermediately formed sulfenyl chloride to the starting sulfide, and in the case of allyl-3-thienyl sulfide, intramolecular cyclization also takes place with formation of a compound of the thienodithiin series.

The reaction of sulfur dichloride with diene systems, where one of the stages is intramolecular cyclization of the sulfenyl chloride formed, is a common method of synthesis of sulfur-containing heterocycles [1]. Reactions of SCl_2 with N-allylamines [2] and allyl phenyl ethers [3], which take place with the formation of six-member heterocyclic compounds with two heteroatoms containing chloromethylene groups on the periphery of the heterocycle, are special cases of such cyclization; the yields of these compounds were usually low.

Thermal rearrangements of allylthienyl sulfides and sulfoxides have been successfully used for constructing condensed heterocyclic systems containing a thiophene ring [4, 5]. Reacting these compounds with sulfur dichloride can reveal new ways of synthesizing heterocycles in which the thiophene ring would be condensed with other heterocyclic systems. The reaction of allyl-2- and allyl-3-thienyl sulfides with sulfur dichloride was investigated in the present study; one possible direction of this reaction could be formation of condensed heterocyclic compounds with three heteroatoms containing a halogen in the side chain.



In conducting the reaction of allyl-2-thienyl sulfide (I) with SCl_2, a mixture of two substances which could not be isolated by chromatographic methods was separated from the reaction mixture. According to chromatographic-mass spectrometric data, each of them has a molecular weight of 414. The presence of peaks of ions with *m/z* 416 and 418 in the mass spectra of these substances and their relative intensity suggest the presence of one sulfur atom and two chlorine atoms in these molecules; the PMR spectrum contains signals corresponding to protons of CH_2Cl, CHCl, CH_2S, and CHS groups and thiophene ring protons. These data suggest that the reaction takes place as "Markownikoff" and anti-"Markownikoff" addition of SCl_2 to the double bond of the allyl group with intermediate formation of two sulfenyl chlorides; they yield a mixture of two β,β'-dichlorosulfides II and III in reacting with a second molecule of sulfide I.

The chromatographic–mass-spectrometric analysis of the reaction mixture revealed the presence of another substance with a molecular weight of 446 in the amount of approximately 1%, and it could have been formed due to addition of sulfur monochloride, S_2Cl_2, always present as an impurity in commercial sulfur dichloride, at the allyl group.

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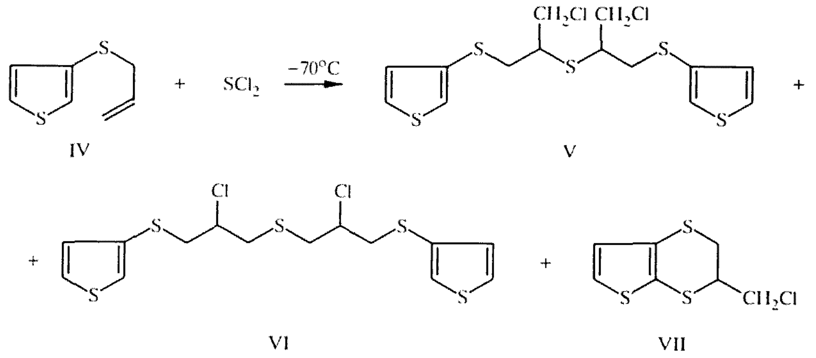
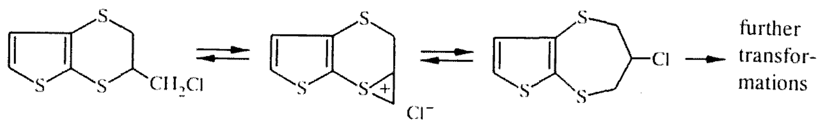
The nucleophilicity of position 2 in thiophenes substituted at position 3 is higher than the nucleophilicity of position 3 in thiophenes with a substituent in position 2 [6]. For this reason, for the reaction of allyl-3-thienyl sulfide (IV) with SCl_2, it should have been predicted that intramolecular cyclization of the intermediate sulfenyl chloride will be preferred to a greater degree than intermolecular reaction with the formation of β,β'-dichlorosulfide. In conducting the reaction of allyl-3-thienyl sulfide (IV) with SCl_2 with elevated dilution of the reagents at −70°C, a product of intramolecular cyclization of thienodithiin VII with a yield of 6% was separated together with products of intermolecular addition of intermediate sulfenyl chloride with dichlorosulfides V and VI:



Dithiin VII was a very unstable compound split by HCl and totally resinified in 2-3 h at 0°C. Two doublets of equal intensity with chemical shifts of 7.0 and 7.2 ppm and a spin-spin interaction constant of J_{HH} = 6.0 Hz are observed in the weak fields of the PMR spectrum; they can be identified as signals of protons in positions 2 and 3 of the thiophene ring, respectively. Aliphatic protons of the CH_2S, CHS, and CH_2Cl groups appear as two complex multiplets with centers at 3.2 and 3.9 ppm, respectively.

We will hypothesize that the instability of dithiin VII is due to the high mobility of the chlorine and the possibility of stabilization of the system due to formation of a thiiranium ion whose subsequent isomerization can yield an unstable derivative of thienodithiepine, which eliminates a molecule of HCl with subsequent polymerization of the unsaturated heterocyclic compound formed:



High enough yields of thienodithiin can probably be obtained in this reaction by nucleophilic substitution of the chlorine atom by another group which cannot be split as an anion (OR, NR_2, etc.) for this compound without its intermediate separation.

EXPERIMENTAL

The ^1H NMR spectra of 25% solutions of the samples in $CDCl_3$ were made on an AM-500 spectrometer with TMS as the internal standard and ±0.01 ppm precision of determination of the chemical shifts. The chromatographic−mass-spectrometric analysis was conducted on a Finnigan MAT-112S in the electron impact mode with 80 eV ionizing energy and a glass column with l = 50 m, d = 0.25 mm with OV-101 stationary phase and temperature programming from 100 to 300°C.

Allyl-2- and allyl-3-thienyl sulfides were prepared according to the methods reported in [7] by organolithium synthesis from thiophene and 3-bromothiophene, respectively.

Reaction of Allyl-2-thienyl Sulfide with SCl_2. While stirring vigorously at −40°C, solutions of 4.7 g (0.03 mole) of allyl-2-thienyl sulfide in 30 m of methylene chloride and 3.1 g (0.03 mole) of SCl_2 in 30 ml of methylene chloride were added at the same rate from two funnels to 200 ml of methylene chloride at such a rate that the temperature of the reaction mixture did not exceed −30°C. After the solutions were added, the reaction mixture was stirred for 1 h more at −30°C, then left overnight at 20°C. Methylene chloride was distilled off in a vacuum, and the viscous red residue was chromatographed on silica gel 40/100 with heptane—benzene, 10:1, as the eluent (an attempt to distill this residue led to its total resinification).

Then 0.87 g (14%) of a substance, homogeneous according to the TLC data, was obtained, a mixture of two β,β'-dichlorosulfides II and III. PMR spectrum ($CDCl_3$): 7.45 (1H, m, α-H thiophene), 7.25 (1H, m, β-H thiophene), 7.01 (1H, m, β-H thiophene), 3.82 (2H, m, CH_2Cl, CHCl), 3.00 ppm (3H, m, CH_2S, CHS). Mass spectrum: 418 (2), 416 (5), 414 (6), 227 (4), 225 (39), 223 (86), 191 (14), 156 (3), 155 (12), 149 (14), 148 (5), 147 (88), 117 (10), 116 (10), 115 (100), 103 (14), 73 (12), 71 (62).

Reaction of Allyl-3-thienyl Sulfide with SCl_2. The reaction of allyl-3-thienyl sulfide (4.7 g, 0.03 mmole) with SCl_2 (3.1 g, 0.03 mmole) was conducted similar to the reaction of sulfide I except that 500 ml of methylene chloride was used and the initial reaction temperature was −70°C. After the corresponding treatment, 0.92 g of a mixture of dichlorosulfides V and VI (yield of 15%) and 0.4 g of 2-chloromethylthieno-1,4-dithiin (VII) (yield of 6%) were separated from the reaction mixture.

Mixture of Dichlorosulfides V and VI. PMR spectrum (CDC_3): 7.39 (1H, m, α-H thiophene), 7.09 (1H, m, α-H thiophene), 6.92 (1H, m, β-H thiophene), 3.83 (2H, m, CH_2Cl, CHCl), 3.04 ppm (3H, m, CH_2S, CHS).

2-Chloromethylthieno-1,4-dithiin (VII). PMR spectrum ($CDCl_3$): 7.22 (1H, d, α-H thiophene), 7.01 (1H, d, β-H thiophene), 3.89 (2H, m, CH_2Cl), 3.21 ppm (3H, m, CH_2S, CHS).

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