Chemistry of Heterocyclic Compounds, Vol. 43, No. 2, 2007

SYNTHESIS AND CHARACTERISTICS OF THE MASS SPECTRA OF 2,5-DIMERCAPTO-2,5-DIMETHYLTETRAHYDROTHIOPHENE

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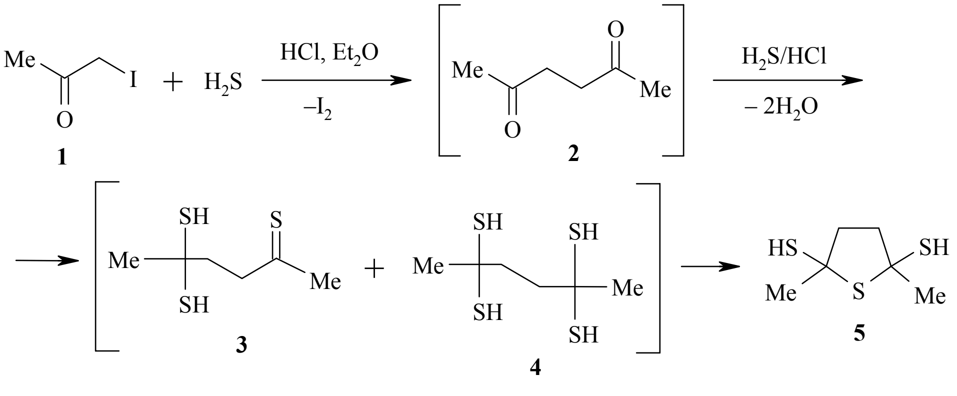
2,5-Dimercapto-2,5-dimethyltetrahyrothiophene was synthesized by the reaction of 1-iodopropan-2-one with hydrogen sulfide in an ether solution of hydrogen chloride at -70˚C. Its structure was established by mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy.

Keywords: 2,5-hexanedione, 2,2,5,5-hexanetetrathiol, 2,5-dimercapto-2,5-dimethyltetrahydrothiophene, 1-iodopropan-2-one, intramolecular cyclization, mass spectra.

Reaction of 2,5-hexanedione with hydrogen sulfide in an ethanol solution of hydrogen chloride at -35°C gave a mixture of three compounds: 2,5-dimethylthiophene, 2-mercapto-2,5-dimethyl-2,3-dihydrothiophene, and 2,5-dimercapto-2,5-dimethyltetrahydrothiophene in yields of 33, 3, and 15% respectively [1]. According to [2] the intermediate in the formation of 2,5-dimethylthiophene is 2,5-hexanedithione, while the intermediate for the formation of 2,5-dimercapto-2,5-dimethyl-2,3-tetrahydrothiophene is 2,2,5,5-hexanetetrathiol. That 2,5-dimercapto-2,5-dimethyl-2,3-tetrahydrothiophene may be a product of intramolecular cyclization of 5,5-dimercaptohexan-2-thione was not excluded. The synthesis and possible conversions of 2,5-hexanedithione and 2,2,5,5-hexanetetrathiol have been discussed previously [3,4].

In a study of the reaction of 1-iodopropan-2-one (**1**) with hydrogen sulfide in an ether solution of hydrogen chloride at -70°C, we established that the reaction began with the separation of iodine and the formation of 2,5-hexanedione (**2**), the hydrothiolysis might lead to the formation 5,5-dimercaptohexane-2-thione (**3**) and 2,2,5,5-hexanetetrathiol (**4**). 2,3-Dimercapto-2,5-dimethyltetrahydrothiophene (**5**) is formed in 75% yield by intramolecular cyclization of the thione (**3**) and tetrathiol (**4**) intermediates.



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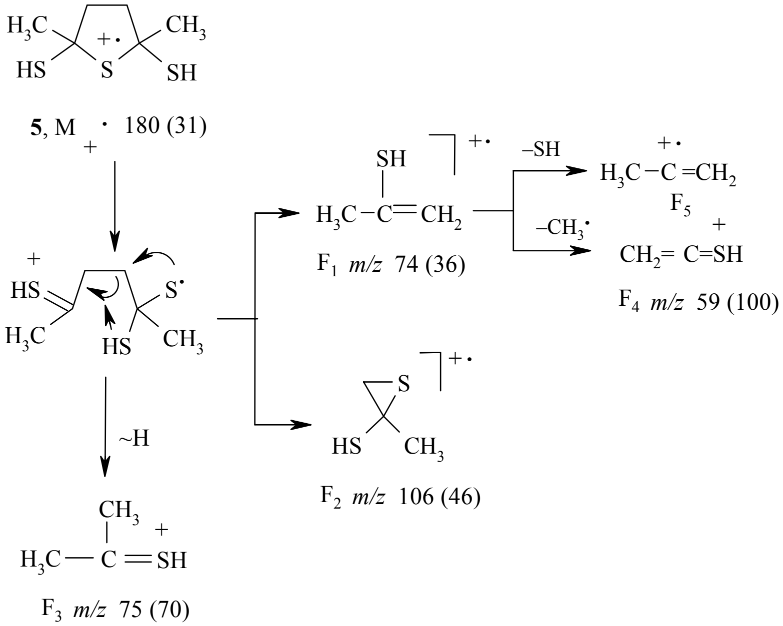
The absence of 2,5-dimethylthiophene among the reaction products of this reaction shows that 2,5-hexanedithione is not formed. We observed formation of the latter in the hydrothiolysis of iodoacetone in the absence of a solvent [5]. The most probable intermediate of the reaction of iodoacetone with hydrogen sulfide is the tetrathiol **4**. An additional argument in favor of this suggestion may be the formation of geminal dithiones in quantitative yield on the interaction of ether solutions of α-haloketones with ether solutions of hydrogen sulfide at low temperatures [6-8].

The initial formation of 2,5-hexanedione **2** when iodoacetone reacted with hydrogen sulfide was confirmed by ^1H and ^{13}C NMR spectroscopy. Along with resonances of iodoacetone **1** at 2.39 (s, $C\underline{H}_3$), 3.77 (s, $C\underline{H}_2I$), 26.37 ($\underline{C}H_3$), 48.69 ($\underline{C}H_2I$), and 200.65 ($\underline{C}{=}O$), signals of compound **2** were observed at 2.25 (s, 2 $C\underline{H}_3$), 3.42 (q, 2 $C\underline{H}_2$), 30.91 (2 $\underline{C}H_3$), 65.82 (2 $\underline{C}H_2$), and 206.99 ppm (2 $\underline{C}{=}O$).

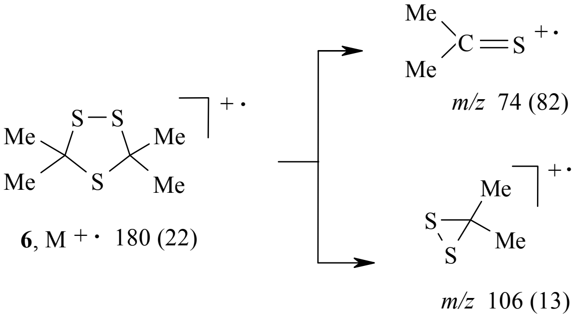
The ^1H NMR and IR spectra (ν_{SH} 2524 cm^{-1}) of compound **5** correspond to the literature data [1]. The ^{13}C NMR spectrum of tetrahydrothiophene **5** contains signals at 31.24 ($\underline{C}H_3$), 34.82 ($\underline{C}H_2$), and 53.40 ppm ($>\underline{C}(SH)(CH_3)$).

In the mass spectrum of compound **5** a moderately strong molecular ion peak was observed, decomposition of which was connected with scission of a heterocyclic C-S bond with further decomposition of the structure into two odd-electron ions, 2-mercaptopropene (F_1) and thiooxide (F_2).

In addition decomposition of the molecular ion was accompanied to a considerable extent by migration of a hydrogen atom to the methylene group with the formation of the high intensity even-electron ion F_3. The ion F_1 underwent further elimination of a methyl or mercapto group to form the secondary even-electron ions F_4 and F_5.



Comparison of the mass spectrum of compound **5** with that previously reported [9] of the isomer, 3,3,5,5-tetramethyltrithiolan (**6**) showed considerable similarities. However they differ sharply in the intensities of ions F_1 and F_3. In the spectrum of tetrahydrothiophene **5** $IF_1/IF_3 = 1.95$, whereas in the spectrum of **6** this ratio is equal to 0.5. This permits the suggestion that in the process of formation of the ion F_3 a hydrogen atom migrates predominantly from the mercapto group and not from the methyl radical.



EXPERIMENTAL

^{1}H and ^{13}C NMR Spectra of $CDCl_3$ solutions with HMDS as internal standard were recorded on a DPX-400 instrument (400 and 100 MHz respectively). IR spectra of KBr disks were recorded on a Bruker IFS-25 spectrometer. Mass spectra were recorded with a Shimadzu GCMS-QP5050A quadrupole chromato-mass spectrometer (ionization energy 70 eV).

Progress of reactions was monitored by TLC on Silufol UV-254 strips with $CHCl_3$ as eluant.

2,5-Dimercapto-2,5-dimethyltetrahydrothiophene (5). Hydrogen sulfide at -70˚C was passed through a solution of 1-iodopropan-2-one **1** (1 g, 5.4 mmol) in absolute ether (10 ml) (saturated with dry hydrogen chloride at -20°C) for 4 h until the ketone starting material had disappeared. Argon was passed through the mixture for 2 h to remove the HCl and H_2S, cold ether (15 ml) was added, and portions of powdered sodium thiosulfate (~2 g) were added at -70°C until the solution was decolorized. The ether solution was decanted, dried over $CaCl_2$, and the ether was evaporated in vacuum to give practically pure tetrahydrothiophene **5** (0.36 g, 75%) as a colorless oil, bp 72°C (1 mmHg), n_D^{20} 1.5700. ^{1}H NMR Spectrum, δ, ppm: 1.72 (6H, s, CH_3), 1.79 (2H, s CH), 1.89 (4H, s, CH_2). ^{13}C NMR Spectrum, δ, ppm: 31.24 ($\underline{C}H_3$), 34.82 ($\underline{C}H_2$), 53.40 ($>\underline{C}(SH)(CH_3)$). IR Spectrum, ν, cm^{-1}: 2525 (SH). Found, %: C 39.35, H 6.19, S 53.84. Calculated for $C_6H_{12}S_3$, %: C 40.00, H 6.71, S 53.29.

This work was carried out with financial support of the Russian Foundation for Basic Research (RFFI), grant 05-0303041a.

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