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LETTERS TO THE EDITOR

Synthesis of Thietane from Sulfur and 1-Bromo-3-Chloropropane in Hydrazine Hydrate–Alkali System

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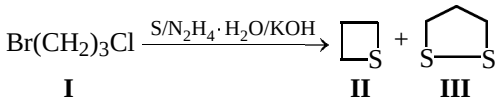
1-Bromo-3-chloropropane (**I**) reacts with solutions of sulfur in the water–hydrazine hydrate–alkali system to form polymeric products [1]. Our detailed gas chromatography–mass spectrometry analysis of chloroform extracts of the raw polymer and extracts of the aqueous layer after separation of the polymer showed that, together with the polymer, thietane (**II**) and 1,2-dithiolane (**III**) are formed in small amounts.

Unexpectedly, it was found that the reaction of dihalide **I** with sulfur in the hydrazine hydrate–KOH system without water takes another pathway, yielding heterocyclic compounds **II** and **III** as major products. Their yield depends on the KOH : sulfur ratio. When this ratio was 1 : 2, thietane **II** was isolated in 26% yield, and 1,2-dithiolane **III** is formed in 4% yield. Polymer **IV** is formed in 65% yield. At equimolar KOH : sulfur ratio, the yield of polymer **IV** is 50%, thietane **II** was obtained in 13% yield, and dithiolane **III**, in 23% yield. Besides, 1,3-propanethiol **V** is formed in 7% yield.

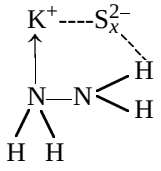


I **II** **III**

$+ \text{(–SCH}_2\text{CH}_2\text{CH}_2\text{S–)}_n + \text{HSCH}_2\text{CH}_2\text{CH}_2\text{SH}.$

IV **V**

The increased yield of the highly strained cyclic systems of thietane and 1,2-dithiolane [2, 3] in reaction (1) in the absence of water is caused by the different solvation of the sulfide and disulfide anions in water and hydrazine hydrate. Recently [4] we suggested formation in the hydrazine hydrate–alkali system of complex **VI**, which alters the reactivities of both polysulfide anions and hydrazine.



VI

x = 1–4.

Evidently, in the hydrazine hydrate–alkali system with an excess of hydrazine, the S_x^{2-} anions react with dielectrophile **I** mainly in the form of complex **VI**, which favors formation of kinetically controlled products **II** and **III**.

To a solution of 22.4 g of KOH in 60 ml of hydrazine hydrate, 6.4 g of powdered elemental sulfur was added in portions with vigorous stirring over the course of 1 h at 70–80°C. The reaction mixture was kept for 2 h at 80–85°C, cooled to 50°C, and addition of 1-bromo-3-chloropropane (**I**) was initiated at that temperature. The temperature of the exothermic reaction was maintained at 65–70°C. The organic layer that formed was removed, dried over calcium chloride, and distilled. The fraction with bp 96–100°C was almost pure thietane **II**, yield 3.5 g (26%). ^{1}H NMR

spectrum ($CDCl_3$), δ, ppm: 3.23 t (4H), 2.94 quintet (2H). Mass spectrum (*m/z*, *I*rel, %): M^+, 74, 50, $(CH_2S)^+$, 46, 100; $(CHS)^+$, 41, 10; $(C_3H_3)^+$, 39, 12 [5]. The yields of 1,2-dithiolane (**III**) and 1,3-propanedithiol (**V**) were evaluated by means of GLC and ^1H NMR spectroscopy.

The NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.1 MHz) against internal HMDS. The mass spectra were measured on a QP5050A GC–MS system, column 60 m × 0.25 mm, programmed temperature increase (15 deg min^{-1}), carrier gas helium, electron energy 70 eV.

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