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The reaction of oxides of sulfolene and its methyl derivative with potassium and sodium thiocyanates was studied. It is shown that under the influence of potassium thiocyanate these oxides undergo isomerization to the corresponding unsaturated alcohols. In the presence of sulfuric acid, however, the oxides react with sodium thiocyanate to give addition products, viz., hydroxythiocyanatosulfolanes.

It is known that thiocyanates react with oxides of aliphatic and cycloaliphatic compounds to give thioxides (sulfides) [1, 2]. The data are contradictory only with respect to cyclopentene oxide [3, 4]. It therefore seemed of interest to investigate the behavior of sulfolene oxides, which have a polar SO_2 group in the ring, in the reaction with thiocyanates.

Our studies showed that sulfolene oxide (I) and 3-methylsulfolene oxide (II) under the influence of potassium thiocyanate undergo only isomerization to the corresponding hydroxy-sulfolenes, which are identical to the compounds previously described in [5-7]. The known dimer V [5] was also isolated in the case of oxide I.

The action of sodium thiocyanate in an acidic medium on oxides I and II leads to the formation of addition products. Analysis by thin-layer chromatography (TLC) confirmed the individuality of the compounds. A narrow intense band with a frequency of 2165 cm⁻¹ (SCN), as well as intense absorption at 3420 and 3450 cm⁻¹ (OH) in the spectra of VI and VII, respectively, is present in the IR spectra of both products. The PMR spectrum of VII in solution in d_c-DMSO contains a singlet at 1.67 ppm, which is related to the proton of a methyl group, and signals at 3.02-3.85 ppm, which correspond to the protons of two methylene groups. In addition, a multiplet signal at 4.43 ppm (J = 2.8, 3.6, and 5.5 Hz) and a doublet at 6.5 ppm (J = 5.5 Hz) are observed. A resonance signal similar to the latter is also noted in the spectrum of VI in the same solvent (6.45 ppm, J = 5.5 Hz). The signal at 6.5 ppm vanishes in the spectrum when DMSO is replaced by deuteromethanol, while the splitting of 5.5 Hz vanishes in the resonance signal at 4.43 ppm. The signal at 4.43 ppm is consequently related to the methylidyne proton, while the doublet signalat 6.5 ppm with ³J_{HCOH} = 5.5 Hz, correspondingly, is

related to the proton of the secondary hydroxy group. These data enabled us to assign a structure with a secondary OH group to the product of the reaction of unsymmetrical oxide II with thiocyanate. A similar assignment of the signals of the hydroxy groups for a number of compounds in solution in DMSO or acetone was made in [8]. To confirm the correctness of structure VII we carried out acetylation by the method in [9], in conformity with which the secondary hydro group is involved. As a result, we obtained 3-methyl-3-thiocyanato-4-acetoxysulfolane (VIII). Thus the reactions of oxides I and II with thiocyanate in an acidic medium can be represented by the scheme



A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR, Kazan 420083. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1333-1334, October, 1982. Original article submitted December 29, 1981. Cleavage of the C-O bond in the oxide ring and the formation of addition products, viz., hydroxythiocyanatosulfolanes VI and VII, occur under the influence of thiocyanate ion on the oxonium complex formed in the first step. Attack of the nucleophilic particle ("SCN) in unsymmetrical oxide II is realized at the more substituted carbon atom of the oxide ring; this is in agreement with our data, which was presented in [10].

EXPERIMENTAL

The IR spectra were recorded with a UR-20 spectrometer with KBr plates. The PMR spectra of solutions in d₆-DMSO and d₄-methanol were obtained with a Varian T-60 spectrometer with tetramethylsilane as the internal standard. The isomerization products obtained were identified by gas-liquid chromatography (GLC) with a Khrom-4 chromatograph with a 250 by 0.3 cm column filled with 15% PFMS on Chromaton N-AW-DMCS (0.200-0.250 mm) at 200°C with a flame-ionization detector. The purity of the compounds obtained was monitored by TLC on Silufol plates with development by means of iodine vapors. The starting oxides were obtained previously [6].

<u>Reaction of Oxides I and II with KSCN.</u> A 0.024-mole sample of oxide I and 0.034 mole of thiocyanate were heated at 80°C with stirring in 25 ml of ethanol for 5 h, after which the mixture was evaporated, and the precipitate was removed by filtration (mp 171-173°C; no melting-point depression was observed for a mixture of this product with KSCN). The filtrate was concentrated and distilled *in vacuo* to give 11% of 4-hydroxy-2-sulfolene (III) with bp 134-136°C (0.06 mm), $n_D^{2°}$ 1.5223, and $d_4^{2°}$ 1.4463. Found: C 35.8; H 4.7; S 23.7%; MR_D 28.3. C₄H₆O₃S. Calculated: 35.8; H 4.5; S 23.9%; MR_D 28.4. Workup of the residue gave dimer V (52%) with mp 260°C (no melting-point depression was observed for a mixture of this product with a genuine sample).

A mixture of 3-methyl-4-hydroxy-2-sulfolene (IVa) and 4-methyl-4-hydroxy-2-sulfolene (IVb) in a ratio (according to GLC data) of 1:(4-5) (50%), with bp 113.5-115°C (0.06 mm), $n_D^{2^\circ}$ 1.5072, and $d_4^{2^\circ}$ 1.3386, was similarly obtained from oxide II. Found: C 40.3; H 5.6; S 21.4%; MR_D 33.0. C₅H₈O₃S. Calculated: C 40.5; H 5.4; S 21.6%; MR_D 33.0.

<u>3-Thiocyanato-4-hydroxysulfolane (VI)</u>. A 0.05-mole sample of oxide I was added to a mixture of 0.06 mole of NaSCN and 0.03 mole of concentrated H_2SO_4 in 20 ml of water, and the mixture was heated at 80-90°C for 2 h. The precipitate that formed when the mixture was cooled was washed with water to give VI (67%) with mp 103.5-104.5°C [from methanol-chloroform (1:5)]. Found: C 31.3; H 3.6; N 7.1; S 33.0%. $C_5H_7NO_3S_2$. Calculated: C 31.1; H 3.6; N 7.2; S 33.2%. Compound VII (68%), with mp 149.5-150°C (from ethanol), was similarly obtained. Found: C 34.9; H 4.3; N 6.9; S 31.2%. $C_6H_9NO_3S_2$. Calculated: C 34.8; H 4.4; N 6.8; S 30.9%.

<u>3-Methyl-3-thiocyanato-4-acetoxysulfolane (VIII)</u>. A mixture of 0.002 mole of VII, 1 ml of acetic anhydride, and two drops of concentrated H_2SO_4 was refluxed for 1-1.5 min, after which the resulting solution was poured into water (\sim 3 ml). After a certain time, VIII (99%), with mp 141-142°C (from ethanol), precipitated. IR spectrum: 1740 (CO) and 2165 cm⁻¹ (SCN). Found: C 38.5; H 4.3; N 5.5; S 25.6%. C₈H₁₁NO₄S₂. Calculated: C 38.5; H 4.5; N 5.6; S 25.7%.

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