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REACTION OF THE OXIDES OF SULFOLENE AND 1-METHYLCYCLOPENTENE WITH SODIUM AZIDE

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The oxides of sulfolene and 1-methylcyclopentene form the corresponding azidoalcohols with sodium azide. In the case of the methylcyclopentene oxide, the attack takes place primarily at the tertiary carbon atom.

It is known that the azide ion adds rather readily to either aliphatic or cyclic epoxides to form azidoalcohols [1-3]. There is no information in the literature concerning the reaction of oxides of the heterocyclic series with sodium azide. We showed previously that with all of the nucleophilic reactants studied, the structure and nature of the products of epoxide ring scission in epoxysulfolanes are determined by the α- or β-position of the sufonyl group with respect to the oxide ring [4, 5, 10]. It was of interest, therefore, to investigate the behavior of the epoxides of sulfolene and its methyl derivatives, I-III, in the reaction with sodium azide.

As the investigations showed, unsubstituted 3,4-epoxysulfolane (I) reacts with sodium azide in aqueous alcoholic solution in the presence of ammonium chloride to form addition product IV. In the IR spectrum of IV there is an absorption band 2125 cm^{-1} corresponding to the azido group and a hydroxyl group absorption band at 3415 cm^{-1}. The PMR spectrum of IV (DMSO-d_6) is analogous to that found in [4, 6], having lines in the 2.93-3.66 ppm region (two methylene groups), two proton multiplets at 4.33 ppm (3-H and 4-H), and also a doublet at 6.07 ppm (OH, J = 4 Hz) that disappears in dueteromethanol. This confirms that the structure of IV is 3-azido-4-hydroxysulfolane.

The action of sodium azide under analogous conditions and in the presence of mineral acids (H_2SO_4, H_3BO_3, $HClO_4$) on methyl substituted 3,4-epoxysulfolane (II) and 3-methyl-2,3-epoxysulfolane (III) did not lead to the formation of addition products. On brief heating, the initial epoxides escape and an increase in the reaction time leads to intense tar formation in the reaction mixture. A similar inertness toward azide ion was noted in the aliphatic, α,β-epoxysulfone series [7].

At the same time, the oxide of methylcyclopentene, V, which differs from oxide II by the absence of an SO_2 group in the ring, forms addition product VI when acted upon by sodium azide in aqueous solution in the presence of NH_4Cl. It is known that when sodium azide acts on saturated monoalkylepoxides, the azide ion attack is directed primarily, if not wholly,

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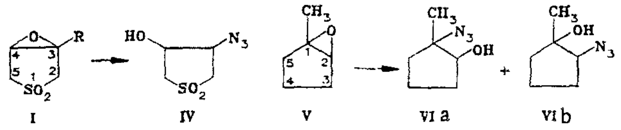
at the less-substituted carbon atom of the epoxide ring [1]: for cyclic epoxides the data is ambiguous [2, 3]. Therefore, the formation of structural isomers might be expected in the case of epoxycyclopentene, V. The PMR spectrum (DMSO-d_6) of the resultant compound has a doublet at 4.93 ppm (secondary OH, J = 4 Hz) along with a proton singlet at 4.67 ppm that we assign to a proton of a tertiary OH group. Both lines disappear when the DMSO is replaced with dueteromethanol. The presence of two hydroxylic proton lines and also of two methyl proton lines at 1.23 and 1.60 ppm in reaction product VI suggests the formation of structural isomers in ~63:37 ratio with the secondary OH group – 1-methyl-1-azido-2-hydroxycyclopentane (VIa) – predominating. This agrees with the GLC data (the VIa:VIb ratio equals ~64:36) and is in accord with our data [3].



EXPERIMENTAL

IR spectra were taken on an UR-20 instrument in petroleum jelly and in a film between KBr plates. The PMR spectra were recorded on a Varian T-60 instrument; DMSO-d_6 and CD_3OD solvents, TMS internal standard. The purity of the compounds obtained was checked by TLC on Silufol plates in a 12:1 benzene/ethanol system with development by iodine vapor and with an ethanolic solution of sulfuric acid with anisaldehyde, 1:1. The GLC analysis was done on a Khrom-5 instrument, 250 × 0.3 cm column, 15% poly(phenylmethylsiloxane) on Chromatone N-AW-DMCS, 130°C, ionization flame detector.

3,5-Epoxy- and 3-methyl-3,4-epoxysulfolane (I and II), T_{mp} 159-160°C and 89-90°C, respectively, were obtained by the procedure in [9]; 3-methyl-2,3-epoxysulfolane (III), T_{mp} 77-78°C, was synthesized by the procedure in [10]; and 1-methyl-1,2-epoxycyclopentene (V), T_{mp} 109-110°C (758 mm Hg), was obtained by the procedure in [8].

3-Azido-4-hydroxysulfolane (IV). A mixture of 3 g (20 mmole) of epoxide I in 40 ml of ethanol, 1.74 g (20 mmole) of NaN_3, and 1.44 g (20 mmole) of NH_4Cl in 10 ml of water was stirred for 16 h at 80°C. After separation of the precipitated NaCl, distilling off the excess ethanol with water, and cooling, 1.8 g (55%) of substance IV, T_{mp} 102-104°C (from ethanol), is isolated. IR spectrum: 1110, 1295 (SO_2), 2125 ($N_{(3)}$), 3410 cm^{-1} (OH). Found, %: C 27.4, H 4.1, N 24.2, S 17.5%. $C_4H_7N_3O_3S$. Calculated, %: C 27.1, H 4.0, N 23.7, S 18.1%.

1-Azido-1-methyl-2-hydroxycyclopentane (VIa) and 2-Azido-1-methyl-1-hydroxycyclopentane (VIb). A solution of 2 g (30 mmole) of NaN_3 and 1.6 g (30 mmole) of NH_4Cl in 25 ml of water was added to 2 g (20 mmole) of the oxide. The mixture was stirred for 8 h at 100°C and then extracted with ether. The ethereal extract was washed with water until the reaction was neutral and dried over calcined $MgSO_4$. After removal of the drying agent and distilling off the solvent, 1.4 g (50%) of substance VI, T_{bp} 86°C (12 mm Hg) and n_D^{20} 1.4870, was separated by vacuum distillation. IR spectrum: 2100 ($N_{(3)}$), 3100-3600 cm^{-1} (OH). Found, %: C 51.0, H 7.6, N 30.0%. $C_6H_{11}N_3O$. Calculated, %: C 51.1, H 7.9, N 29.8%.

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