REACTION OF 3-METHYL-2,3-EPOXYSULFOLANE WITH ALCOHOLS

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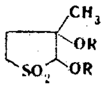
The corresponding dialkyl ethers of 3-methylsulfolane-2,3-diol are formed by the action of alcohols (methanol, ethanol, n-propyl alcohol, isopropyl alcohol, isobutyl alcohol, and n-octyl alcohol) on 3-methyl-2,3-epoxysulfolane in an acidic medium. The reaction proceeds through the intermediate formation of monoethers with subsequent etherification of the hydroxyl group by a second molecule of alcohol.

We have previously shown that products of the addition of alcohols to the oxide ring — sulfolane-3,4-diol monoethers — are formed by the action of alcohols in the presence of sulfuric acid on 3,4-epoxysulfolanes. [1]. It seemed of interest to investigate the behavior under similar conditions of 3-methyl-2,3-epoxysulfolane (I), in which the oxide ring is adjacent to a strong electron-acceptor group.

The studies showed that the corresponding 3-methylsulfolane-2,3-diol dialkyl ethers are formed by the action of alcohols on oxide I in the presence of sulfuric acid or boron trifluoride etherate. The constants of the compounds obtained are presented in Table 1. Their structures were established on the basis of the IR and PMR spectra. Bands at 1130 and 1310 cm^{-1}, which correspond to ν_{SO_2}, and an intense band at 1080 cm^{-1}, which is due to the vibrations of the C—O—C bond, are present in the IR spectra of the dialkyl ethers obtained. A characteristic feature of the spectra is the absence of the band of hydroxyl absorption. A solitary unresolved signal at 4 ppm, which corresponds to the proton attached to C_2, is observed in the PMR spectra. Thus a signal at 1.33 ppm (CH_3), multiplets at 2.13 and 3.06 ppm (β-CH_2 and α-CH_2), two signals at 3.30 and 3.73 ppm, which are related to the protons of the two methoxy groups, and a singlet at 4.06 ppm (C_2—H) are present in the PMR spectrum of III. The integral intensity ratio of these signals is 3:2:2:3:3:1, respectively. When the methyl group is replaced by other alkyl groups, the region of the PMR spectrum related to the sig-

TABLE 1. Characteristics of 3-Methylsulfolane-2,3-diol Dialkyl Ethers



Compound	R	bp, °C (mm)	d_4^{20}	n_D^{20}	Found, %			Empirical formula	Calc., %			MR_D		Yield, %
					C	H	S		C	H	S	found	calc.	
III	CH_3	86—88 (0,05)*	—	1,4795	43,4	7,3	16,7	$C_7H_{14}O_4S$	43,3	7,2	16,5	—	—	59
IV	C_2H_5	83—85 (0,04)	1,1386	1,4632	48,5	8,1	14,7	$C_9H_{18}O_4S$	48,6	8,1	14,9	53,75	53,72	40
V	C_3H_7	120—125 (0,01)	1,0908	1,4629	53,3	8,8	12,7	$C_{11}H_{22}O_4S$	52,8	8,8	12,8	63,17	62,95	48
VI	*i*-C_4H_9	120—126 (0,07)	1,0519	1,4595	55,7	9,2	—	$C_{13}H_{26}O_4S$	56,1	9,4	11,5	72,41	72,19	37
VII	C_8H_{17}	146—147 (0,05)	0,9830	1,4600	64,6	10,8	—	$C_{21}H_{42}O_4S$	64,5	10,8	8,2	108,84	109,13	59

*This compound has mp 76-78°C (from ethanol).

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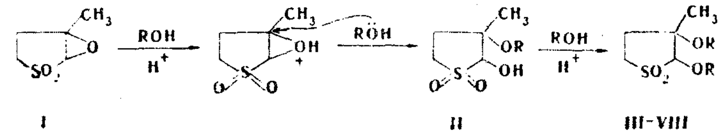
nals of the alkoxy protons becomes complicated, and the resonance signal of the methylidyne proton is shifted to 4.40 ppm.

A study of the reaction of oxide I with methanol by thermography showed the existence of one exothermic effect at 90-134°C (a maximum). Analysis of the reaction mixture by gas – liquid chromatography (GLC) confirmed the formation of a diether. Interruption of the recording of the thermograms at various points of the observed exothermic peak and subsequent analysis by GLC did not reveal the presence of a possible intermediate – 3-methylsulfolane-2,3-diol monomethyl ether. The formation of the diether evidently occurs immediately as the monosubstituted product is formed, which explains the presence of a broad but low exothermic peak.

The formation of the diether proceeds considerably more slowly in the case of the action of a secondary alcohol such as isopropyl alcohol on oxide I, evidently because of the lower tendency of the secondary alcohol to undergo etherification and because of steric hindrance. The intermediately formed monoether II (R = iso-C_3H_7) can be detected in the isolated fraction by means of GLC and the IR spectra. A broad band of hydroxyl absorption of weak intensity at 3200-3600 cm^{-1} appears in the IR spectra in these cases. A weak band of a free hydroxyl group at 3610 cm^{-1} can be observed in the case of recording of the spectra of solutions in $CHCl_3-CCl_4$ (1:1).

Thus it may be assumed that the reaction of alcohols with 3-methyl-2,3-epoxysulfolane to give the corresponding diethers proceeds via the scheme:



As a result of the concerted action of two factors (the +I effect of the methyl substituent and the considerable electron-acceptor effect of the SO_2 group), attack of the nucleophile in the resulting oxonium complex is directed to the ring C_3 atom, and the epoxide ring undergoes opening to give an intermediate monoether with structure II. The subsequent etherification by a second molecule of alcohol to give the final product – the diether – takes place readily because of the acid character of the proton of the hydroxyl group attached to C_2.

EXPERIMENTAL

The IR spectra of the compounds between KBr plates and in $CHCl_3-CCl_4$ (d 5 mm, c 0.01 mole) were obtained with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in chloroform were recorded with a Varian T-60 spectrometer with tetramethylsilane as the internal standard. Analysis by GLC was carried out with a Khrom-4 chromatograph with a 250 by 0.3 cm column filled with 15% PEMS (polyphenylmethylsilane) on Chromaton N-AW-DMCS (0.200-0.250 mm) at 180°C; the detector was a flame-ionization apparatus. Thermographic analysis was carried out with a PDS-021 two-coordinate potentiometer with Chromel – Alumel thermocouples under linear heating conditions at 2.5 deg/min.

Oxide I was obtained by the method in [2] and had mp 74-75°C.

3-Methylsulfolane-2,3-diol Dialkyl Ethers (III-VII). Oxide I (0.013 mole) was dissolved in 20 ml of absolute alcohol (methanol, ethanol, n-propyl, isobutyl, or n-octyl alcohol), two to three drops of concentrated H_2SO_4 or $BF_3 \cdot O(C_2H_5)_2$ were added, and the mixture was heated in sealed glass ampuls at 130-150°C for 7 h. The tubes were then cooled and opened, and the contents when H_2SO_4 was used were neutralized with the corresponding sodium alkoxide. The Na_2SO_4 was removed by filtration, and the residue was distilled in vacuo. The corresponding dialkyl ethers were obtained (Table 1).

Reaction of Oxide I with Isopropyl Alcohol. A 0.02-mole sample of the oxide was dissolved in 30 ml of absolute isopropyl alcohol, three drops of concentrated H_2SO_4 were added, and the mixture was heated in a sealed tube at 130-150°C for 9 h. The tube was then opened, and the contents were worked up as indicated above. The residue was distilled in vacuo with the collection of 2.06 g (40%) of a product with bp 77-78°C (0.06 mm), n_D^{20} 1.4680, and d_4^{20} 1.1345; according to the GLC data, this product contained 70% of the diether and 30% of the monoether. Found: C 50.7; H 8.8%. Calculated for a mixture of 70% $C_{11}H_{22}O_4S$ (VIII) and 30% $C_8H_{16}O_4S$ (II): C 50.8; H 8.5%.

LITERATURE CITED

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MECHANISM OF THE RING-CHAIN TAUTOMERISM OF 2,3,3-TRIMETHYL-2-HYDROXY-5-PYRROLIDONES

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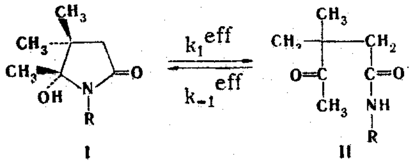
The mechanism of the prototropic equilibrium process of ring-chain tautomerization of 2,3,3-trimethyl-2-hydroxy-5-pyrrolidones is discussed on the basis of the results obtained by PMR spectroscopy. On the NMR time scale the reaction proceeds with the formation of a common intermediate anion, and the rate-determining step is the detachment of a proton.

In contrast to keto—enol tautomerism, the theory of which has been worked out in detail [1], there are an extremely limited number of studies (e.g., see [2]) devoted to the mechanism of ring-chain tautomerism.

In the present paper we examine a possible mechanism for prototropic ring-chain tautomerism and the rate-determining steps in the tautomerization on the basis of our new (and partially earlier [3, 4]) data on the tautomerism of 2,3,3-trimethyl-2-hydroxy-5-pyrrolidones.



I II

I, II R=H or 4-XC_6H_4; $X = N(C_2H_5)_2$, OCH_3, H, Cl, Br, COOH, $COOCH_3$, CN, NO_2

In addition to the available data on the thermodynamic and kinetic parameters of the tautomerism of pyrrolidones [3, 4], we investigated the effect of the acid—base properties of the medium on the rate of tautomerization of the unsubstituted compound (R = H). The rate constants were determined by PMR spectroscopy of solutions in 50% aqueous pyridine containing HCl or $KHCO_3$. The rate constant (k_1^{eff}) is directly proportional to the bicarbonate concentration (Fig. 1). This indicates the pseudo-monomolecular character of the reaction, i.e., the bicarbonate acts as a catalyst. The decrease in the k_1^{eff} constant when hydrochloric acid is added to pyridine (Fig. 2) up to 0.2 M (the medium loses its basic character upon further addition of acid) is in agreement with the decrease in the concentration of the basic catalyst. It should be noted that k_1^{eff} decreases considerably more markedly than the pyridine concentration: When the pyridine concentration changes from 6 to 5.8 M (which corresponds to the change in the hydrochloric acid concentration), the rate constant changes by a factor of approximately four. This is associated with the existence of a reverse reaction with the participation of pyridinium ion BH^+ (see the scheme given below); the addition of hydrochloric acid leads to a substantial increase in the BH^+ concentration.

The role of bases as catalysts of the process makes it possible to assert that the rate-determining step in the tautomerization in the forward (from the chain to the open tautometer) direction is detachment of a proton under the influence of the base to give an intermediate anion. Since the tautomerization is an equilibrium process and the equilibrium constant $K_T = k_1^{eff}/k_{-1}^{eff}$ in our experiments is independent of the basicity of the medium, detachment of a proton should also be the rate-determining step for the reverse direction. The transi-

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