REACTIONS OF 1-HALO-3-METHYL-2, 3-EPOXYBUTANE WITH ALCOHOLS

UDC 547.717

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The reaction of 1-bromo(or chloro)-3-methyl-2, 3-epoxybutane with alcohols in the presence of the alkali metal alkoxides leads to the formation of epoxy ethers by direct replacement of the halogen atoms without participation of the epoxide ring.

It is known that the reactions of  $\alpha$ -epihalohydrins with nucleophilic agents leads to halogen-substitution products. Most of these reactions are represented as proceeding through addition with the generation of halohydrins and subsequent cleavage and the formation of an epoxide group [1]. Direct replacement of halogen atoms is observed in rare cases [2].

The data obtained during a study of the reaction of 1-bromo(or chloro)-3-methyl-2,3epoxybutane with alcohols are of definite interest in this respect. Epoxy ethers I are

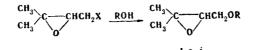
Com- pound	bp, °C (mm) [mp, °C] ,	n <sub>D</sub> <sup>20</sup>	đ4 <sup>20</sup>				Calc., %		Yield, %
				с	н	formula	с		(from the chloride)
Ia Ib Ic Id Ie If If In Ii	$\begin{array}{c} 120 - 121  (652) \\ 147 - 149  (650) \\ 62 - 64  (10) \\ 51 - 53  (10) \\ 75  (11) \\ 84 - 86  (12) \\ 142 - 144  (14) \\ 92 - 93  (12) \\ 103 - 106  (2) \\ 1571 \end{array}$	1,4110 1,4120 1,4150 1,4158 1,4200 1,4230 1,5010 1,4398		64,6 66,4 66,5 68,1 69,5 75,2	10,7 11,0 12,3 11,7	$\begin{array}{c} C_6 H_{12} O_2 \\ C_7 H_{14} O_2 \\ C_8 H_{16} O_2 \\ C_8 H_{16} O_2 \\ C_9 H_{18} O_2 \\ C_1 0 H_{20} O_2 \\ C_{12} H_{16} O_2 \\ C_{10} H_{20} O_2 \\ C_{10} H_{18} O_2 \\ C_{11} H_{14} O_2 \end{array}$	62,1 64,6 66,7 68,4 69,8 75,0 70,6 74,2	10,3 10,8 11,1 11,1 11,4 11,6 8,3 10,5 7,9	58,661,559,748,659,5 (49,3)52,443,359,5 (48,4)76,4 (69,8)
Ij	[57] 113—114 (1,5)	1,4448	1,0211	62,4	9,4	$C_{12}C_{22}O_4$	62,6	9,6	40,6

TABLE 1. 2-Methyl-2, 3-epoxy-4-alkoxybutanes I

TABLE 2. PMR Spectra of I

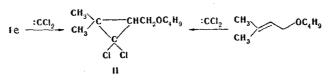
Com - pound	ð, ppm			J <sub>33</sub> , Hz	<b>δ, pp</b> m			
	(CH	(3)2	3-H	4-CH2	$(J/\nu_{ob})$	CH <sub>2</sub> OCH <sub>2</sub>	R	
Ia Ib Ic Id Id If	1,23 s 1,23 s 1,24 s	1,28s 1,28s 1,29s	2,76m 2,76m 2,77 t 2,76m	3,46m 	$\begin{array}{c} 6,3 & (0,16) \\ 5,8 & (0,14) \\ & \overline{5,5} \\ 5,2 & \overline{(0,13)} \end{array}$	3,40 m 	3,40 s (OCH <sub>3</sub> ) 1,18 t (CH <sub>3</sub> ); 3,49 q (CH <sub>2</sub> ) 0,93 t (CH <sub>3</sub> ); 1,51 q (CH <sub>2</sub> ) 1,13 d 1,15 d (CH <sub>3</sub> ) (6,4 Hz), 3,64 (CH) 0,97 m (CH <sub>3</sub> ); 1,55 m (CH <sub>2</sub> CH <sub>2</sub> ) 0,92 d (CH <sub>3</sub> ) <sub>2</sub> ; $J = 5.5$ Hz; 1,75 m (CH); 1,43 dt (2CH <sub>2</sub> ); $J_1 = J_2 = 6.5$ Hz; 3,45 td . (1CH <sub>2</sub> ); $J_1 = 6.5$ Hz; $J_2 = 1.3$ Hz	
I.g Ih	1,17 s 1,21 s	1,25s 1,26s		3,43d. —	-	4,4 s 3,46 m	J = 0.8 Hz; 3.51 m (OCH <sub>2</sub> );	
li Ij	1,32 s 1,25 s	1,36 s 1,30 s	3,02t 2,80t	4,07 m 3,54 m		-	2,25 t $(CH_2)$ 6,9—7,5 m $(C_6H_5)$ 3,6 s $(CH_2)$	

Institute of Organic Chemistry, Academy of Sciences of the Armenian SSR, Erevan 375094. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 878-880, July, 1981. Original article submitted November 26, 1980. obtained in good yields (Table 1) as a result of the reaction that takes place with alkali metal alkoxides. Bisepoxy compound Ij is formed in the reaction of ethylene glycol with two equivalents of the bromide.



X=CI, Br; I a R=CH<sub>3</sub>; b R=C<sub>2</sub>H<sub>5</sub>; c R=C<sub>3</sub>H<sub>7</sub>; d R=*i*-C<sub>3</sub>H<sub>7</sub>; e R=C<sub>4</sub>H<sub>9</sub>; f R=*i*-C<sub>5</sub>H<sub>11</sub>;

It is interesting to note that the epoxy ethers obtained do not react with alcoholic alkali even when they are refluxed [1]. As expected [3], 4-butoxy-2-methyl-2,3-epoxybutane reacts with dichlorocarbene under interphase-catalysis conditions to give 1,1-dichloro-2,2dimethyl-3-butoxymethylcyclopropane (II), which is identical [according to gas-liquid chromatography (GLC) and PMR spectroscopy] to the sample obtained from butyl prenyl ether:



In addition, the reduction of epoxide Ie with lithium aluminum hydride by the method in [2] gave 4-butoxy-2-methyl-2-butanol (III), which was identical to a genuine sample [4]. These data, together with the data from the PMR spectra of I (see Table 2), confirm the structure of the epoxy ethers obtained.

## EXPERIMENTAL

The PMR spectra of solutions of the compounds in CCl<sub>4</sub> were obtained with a Perkin-Elmer R-12B spectrometer (60 MHz) with tetramethylsilane as the internal standard. The purity and identity of the synthesized products were determined by GLC with an LKhM-8D chromatograph with a catharometer with a column (l = 2 m and 1 m) filled with 15% PEG-20M (15% APL) on Chromaton N-AW-HMDS; the carrier-gas (helium) flow rate was 40-60 ml/min, and the temperature was 120-180°C.

<u>4-Alkoxy-2-methyl-2,3-epoxybutanes (I)</u>. A solution of the alkoxide [from 1.15 g (50 mmole) of sodium and 25 ml of alcohol] was added dropwise at room temperature for 2-3 h to a mixture of 50 mmole of 1-bromo (or chloro)-3-methyl-2,3-epoxybutane and 10 ml of alcohol, and the mixture was stirred at 40-80°C for 8-10 h. The excess alcohol was removed by distillation, the residue was diluted with water, and the aqueous mixture was extracted with ether. The constants of the synthesized alkoxy ethers are presented in Table 1.

<u>1,1-Dichloro-2,2-dimethyl-3-butoxymethylcyclopropane (II)</u>. A) A 1.3-g (52.5%) sample of 1,1-dichloro-2,2-3-butoxymethylcyclopropane with mp 110-111°C (12.5 mm)  $n_D^{20}$  1.4572, and d<sub>4</sub><sup>20</sup> 1.0706 was obtained from 1.6 g (11 mmole) of butyl prenyl ether, 7.9 g (66 mmole) of chloroform, and 2.65 g (66 mmole) of 50% sodium hydroxide in the presence of catalytic amounts of triethylbenzylammonium chloride (TEBAC). PMR spectrum: 1.22 and 1.39 (s, 2-CH<sub>3</sub>); 0.92 (t, 3-CH<sub>3</sub>); 1.53 (m, 4H, 3-CH<sub>2</sub> from C<sub>4</sub>H<sub>9</sub>); 3.20-3.80 ppm (m, 5H, CH<sub>2</sub>OCH<sub>2</sub>, 3-H). Found: C 53.1; H 7.7; Cl 31.1%. C<sub>10</sub>H<sub>18</sub>Cl<sub>2</sub>O. Calculated: C 53.3; H 8.0; Cl 31.5%.

B) A 2.3-g (32.5%) sample of II, which was identical with respect to its constants and GLC data to the sample described above, was obtained from 5.0 g (32 mmole) of Ie, 22.6 g (189 mmole) of chloroform, 15.0 g (189 mmole) of 50% sodium hydroxide, and catalytic amounts of TEBAC in 15 ml of benzene.

<u>4-Butoxy-2-methyl-2-butanol (III)</u>. A mixture of 3.9 g (25 mmole) of 4-butoxy-2-methyl-2,3-epoxybutane (Ie) and 1.0 g (26 mmole) of lithium aluminum hydride in 30 ml of anhydrous ether was refluxed for 3 h, after which 5 ml of water was added, and the mixture was filtered, washed with ether, dried, and distilled to give 2.1 g (52.4%) of III with bp 83-84°C (10 mm),  $np^{2\circ}$  1.4293, and  $d_4^{2\circ}$  0.9601 {bp 82-85°C (10 mm),  $np^{2\circ}$  1.4297, and  $d_4^{2\circ}$  0.9603 [4]}.

## LITERATURE CITED

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MERCURATION OF  $\alpha$ - AND  $\gamma$ -METHYLPYRYLIUM SALTS WITH MERCURIC ACETATE AND TRIFLUOROACETATE

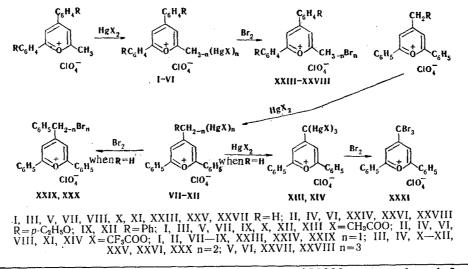
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UDC 547.813.254.9:542.957.1

Mercury-containing methylpyrylium perchlorates were synthesized by mercuration of  $\alpha$ - and  $\gamma$ -methylpyrylium perchlorates with mercuric acetate and trifluoroacetate. A mechanism is proposed for the mercuration reaction. The salts obtained undergo decomposition upon reaction with mineral acids to give the starting methyl-pyrylium salts, while bromomethylpyrylium perchlorates are formed upon reaction with bromine as a result of cleavage of the C-Hg bond.

The high lability of the hydrogen atoms of the methyl groups in  $\alpha$ - and  $\gamma$ -methylpyrylium salts is widely known. These salts readily undergo condensation with various aldehydes [1] to give styrylpyrylium salts, even with such inactive carbonyl-containing compounds as dimethylformamide (DMF) [2]; the hydrogen atoms of the methyl groups are rapidly exchanged by deuterium upon refluxing in D<sub>2</sub>O [3] and also react smoothly via the methyl group with diazonium salts [4].

One might have assumed that methylpyrylium salts would react with mercury salts, which are known [5] to be effective mercurating agents of compounds with labile hydrogen atoms. As we established for the first time in the present research, 2-methyl-4,6-diphenylpyrylium and 2-methyl-4,6-(p-ethoxyphenyl)pyrylium perchlorates are readily mercurated by mercuric acetate and trifluoroacetate to give products of replacement of the hydrogen atoms of the methyl group by HgX (X = CH<sub>3</sub>COO and CF<sub>3</sub>COO) in high yields. The reactions were carried out by brief refluxing of the substrates cited above in ethanol, and, depending on their ratio, products of mono- (I, II), di- (III, IV), and trimercuration (V, VI) were obtained, and the formation of acetic or trifluoroacetic acid, which we were able to isolate in the form of the ethyl ester, was also observed.



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