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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 α -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-2,3-epoxybutane with alcohols are of definite interest in this respect. Epoxy ethers I are

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

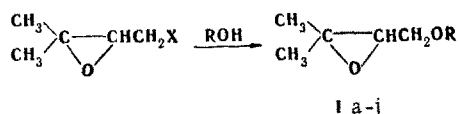
Compound	bp, °C (mm) [mp, °C]	n_D^{20}	d_4^{20}	Found, %		Empirical formula	Calc., %		Yield, % (from the chloride)
				C	H		C	H	
Ia	120—121 (652)	1,4110	0,9214	62,3	10,3	C ₆ H ₁₂ O ₂	62,1	10,3	58,6
Ib	147—149 (650)	1,4120	0,8978	64,6	10,7	C ₇ H ₁₄ O ₂	64,6	10,8	61,5
Ic	62—64 (10)	1,4150	0,8892	66,4	11,0	C ₈ H ₁₆ O ₂	66,7	11,1	59,7
Id	51—53 (10)	1,4158	0,8875	66,5	12,3	C ₈ H ₁₆ O ₂	66,7	11,1	48,6
Ie	75 (11)	1,4200	0,8871	68,1	11,7	C ₉ H ₁₈ O ₂	68,4	11,4	59,5 (49,3)
If	84—86 (12)	1,4230	0,8774	69,5	11,5	C ₁₀ H ₂₀ O ₂	69,8	11,6	52,4
Ig	142—144 (14)	1,5010	1,0196	75,2	8,0	C ₁₂ H ₁₆ O ₂	75,0	8,3	43,3
Ih	92—93 (12)	1,4398	0,9101	70,3	10,3	C ₁₀ H ₁₈ O ₂	70,6	10,5	59,5 (48,4)
Ii	103—106 (2)	—	—	74,4	7,8	C ₁₁ H ₁₄ O ₂	74,2	7,9	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 2. PMR Spectra of I

Compound	δ , ppm			J_{33} , Hz (J/ν_{ob})	δ , ppm		
	(CH ₃) ₂	3-H	4-CH ₂		CH ₂ OCH ₂	R	
Ia	1,28 s	1,34 s	2,28m	3,47m	6,3 (0,16)	—	3,40 s (OCH ₃)
Ib	1,23 s	1,28 s	2,76m	3,46m	5,8 (0,14)	—	1,18 t (CH ₃); 3,49 q (CH ₂)
Ic	1,23 s	1,28 s	2,76m	—	—	3,40 m	0,93 t (CH ₃); 1,51 q (CH ₂)
Id	1,24 s	1,29 s	2,77 t	3,48d	5,5	—	1,13 d 1,15 d (CH ₃) (6,4 Hz); 3,64 (CH)
Ie	1,26 s	1,32 s	2,76m	—	—	3,43 m	0,97 m (CH ₃); 1,55 m (CH ₂ CH ₂)
If	1,23 s	1,29 s	2,77 m	3,43m	5,2 (0,13)	—	0,92 d (CH ₃) ₂ ; $J=5,5$ Hz; 1,75 m (CH); 1,43 dt (2CH ₂); $J_1=$ $=J_2=6,5$ Hz; 3,45 td (1CH ₂); $J_1=6,5$ Hz; $J_2=1,3$ Hz
Ig	1,17 s	1,25 s	2,79t	3,43d	—	4,4 s	7,23 (C ₆ H ₅)
Ih	1,21 s	1,26 s	2,74m	—	—	3,46 m	4,70 m (=CH ₂); 1,73 t (CH ₃); $J=0,8$ Hz; 3,51 m (OCH ₂); 2,25 t (CH ₂)
Ii	1,32 s	1,36 s	3,02t	4,07m	5,3	—	6,9—7,5 m (C ₆ H ₅)
Ij	1,25 s	1,30 s	2,80t	3,54m	5,2	—	3,6 s (CH ₂)

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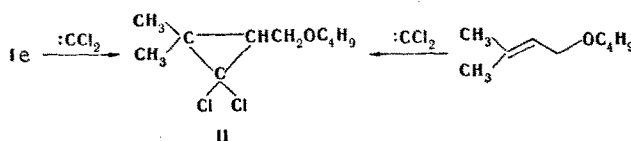
obtained in good yields (Table 1) as a result of the reaction that takes place with alkali metal alkoxides. Bisepoxy compound Ij is formed in the reaction of ethylene glycol with two equivalents of the bromide.



X=Cl, Br; I a R=CH₃; b R=C₂H₅; c R=C₃H₇; d R=*i*-C₃H₇; e R=C₄H₉; f R=*i*-C₅H₁₁;

g R=CH₂C₆H₅; h R=CH₂=C(CH₃)CH₂CH₂-; i R=C₆H₅; j R=(CH₂)₂OCH₂CH(CH₃)C(CH₃)₂O

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-2,2-dimethyl-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 CCl₄ 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.

4-Alkoxy-2-methyl-2,3-epoxybutanes (I). 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.

1,1-Dichloro-2,2-dimethyl-3-butoxymethylcyclopropane (II). 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_D²⁰ 1.4572, and d₄²⁰ 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-CH₃); 0.92 (t, 3-CH₃); 1.53 (m, 4H, 3-CH₂ from C₄H₉); 3.20-3.80 ppm (m, 5H, CH₂OCH₂, 3-H). Found: C 53.1; H 7.7; Cl 31.1%. C₁₀H₁₈Cl₂O. 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.

4-Butoxy-2-methyl-2-butanol (III). 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), n_D²⁰ 1.4293, and d₄²⁰ 0.9601 {bp 82-85°C (10 mm), n_D²⁰ 1.4297, and d₄²⁰ 0.9603 [4]}.

