

Reactions of 1-chloro-2,3-epoxy-2-methylpropane with lower aliphatic alcohols. I. Reaction products

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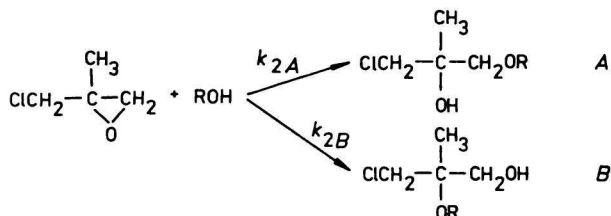
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It has been found that in the presence of a catalytic amount of $F_3B \cdot O(C_2H_5)_2$ the reaction of 1-chloro-2,3-epoxy-2-methylpropane with lower aliphatic alcohols gives, besides the known 1-alkoxy-3-chloro-2-methyl-2-propanols, also the not described 2-alkoxy-3-chloro-2-methyl-1-propanols.

Было обнаружено, что продуктами реакции 1-хлор-2,3-эпоксид-2-метилпропана с низшими алифатическими спиртами при каталитическом действии $F_3B \cdot O(C_2H_5)_2$, кроме известных 1-алкокси-3-хлор-2-метил-2-пропанолов, являются и до сих пор в литературе не описанные 2-алкокси-3-хлор-2-метил-1-пропанола.

By the acid-catalyzed reaction of epoxides with alcohols the oxiran ring is opened to form the corresponding alkoxy alcohols. 1-Chloro-2,3-epoxy-2-methylpropane (β -methylepichlorohydrine) (MECH) can react in the first stage to give rise to 1-alkoxy-3-chloro-2-methyl-2-propanols (A) and/or 2-alkoxy-3-chloro-2-methyl-1-propanols (B)



The A and B type substances derived from nonsymmetrically substituted α epoxides are sometimes termed "normal" (or C_α ethers) and "abnormal" (or C_β ethers) products, respectively.

Despite voluminous literature on the acid-catalyzed reaction of various epoxides with alcohols [1, 2], this reaction of MECH is described only scarcely. The authors in [3, 4] record compounds only of A type and their incomplete characteristics

(boiling points and densities). The compounds of *B* type have not been prepared even by other methods.

Therefore in this work catalytic effect of boron trifluoride etherate $F_3B \cdot O(C_2H_5)_2$ upon the reactions of methanol, ethanol, 1-propanol, 2-propanol, and 2-methyl-2-propanol with MECH has been studied.

Experimental

Chemicals

1-Chloro-2,3-epoxy-2-methylpropane was prepared from 2-methyl-1-propene via methallylchloride and 1,3-dichloro-2-methyl-2-propanol [5]. It was purified by three rectifications on a laboratory column with the efficiency of 15 TP at the reflux ratio 10:1; fraction having b.p. 120.7–121.2°C/99.9 kPa contained 0.066 wt. % of water and max. 0.4 wt. % of other impurities (g.l.c. method); $n_D^{20} = 1.4340$ and $\rho_{20^\circ C} = 1103.2 \text{ kg m}^{-3}$.

Alcohols, reagent grade, after drying with molecular sieve Calsit 5A (product of J. Dimitrov Chemical Works, Bratislava) and distillation had physical properties corresponding to the known data [6] and contained 0.025–0.05 wt. % of water.

Boron trifluoride etherate, "pure", was distilled under nitrogen and fraction having b.p. 124.5–125.0°C/98.5 kPa was collected.

Other chemicals were of reagent grade purity.

Preparation of reaction products of MECH with alcohols

The products were obtained from combined reaction mixtures used for kinetic study of the reaction of MECH with individual alcohols run at the initial molar ratios 1:3—1:30 at 15–35°C and at the concentration of $F_3B \cdot O(C_2H_5)_2$ ranging from 0.897×10^{-2} to $14.531 \times 10^{-2} \text{ mol dm}^{-3}$. Experimental details and the results of reaction kinetics study were published elsewhere [7]. After the neutralization of the catalyst by shaking with powdered $NaHCO_3$, the unreacted alcohol was distilled off and the reaction products were isolated and purified by a repeated rectification.

Analytical methods

Water content was determined by the *Fischer* method [8].

The purity of reaction products and the relative elution times were determined with chromatograph Mikrochrom 03 (Research Institute for Petrochemistry, Nováky) equipped with a thermal conductivity detector on three s.s. columns, $l = 100 \text{ cm}$, inner diameter 3 mm, packed with 10 wt. % of stationary phase on Chromaton NAW 0.16 to 0.2 mm at 80 to 120°C. Hydrogen at a flow rate of $40 \text{ cm}^3 \text{ min}^{-1}$ was used as the carrier gas.

The reaction mixture was analyzed, after neutralization of the catalyst with powdered $NaHCO_3$, with a chromatograph equipped with a flame ionization detector using s.s. column,

$l = 100$ cm, inner diameter 3 mm, containing Chromosorb (0.16 to 0.20 mm) and 10 wt. % of di-2-ethylhexylsebacate as a stationary phase. When estimating the MECH content the column temperature was 120°C and when analyzing the composition of the reaction products the temperature was 130°C . Flow rates: hydrogen $60\text{ cm}^3\text{ min}^{-1}$, air $350\text{ cm}^3\text{ min}^{-1}$, and nitrogen $30\text{ cm}^3\text{ min}^{-1}$. The evaluation was done by known [9] methods.

In the case of the reaction of *tert*-butyl alcohol with MECH the product was analyzed on a Perkin—Elmer 900 chromatograph equipped with a flame ionization detector and an s.s. column, $l = 200$ cm, inner diameter 3 mm. The column was packed with 3 wt. % of polyethylene glycol adipate on Chromaton NAW DMCS (0.16 to 0.2 mm). The column temperature was programmed from 60 to 170°C ($10^{\circ}\text{C min}^{-1}$); inject port temperature 160°C . Flow rates: hydrogen $40\text{ cm}^3\text{ min}^{-1}$, oxygen $150\text{ cm}^3\text{ min}^{-1}$, nitrogen $35\text{ cm}^3\text{ min}^{-1}$.

Molecular weights of the products were determined by an osmometric method with a Vapor Pressure Osmometer 302 B (Hewlett—Packard), a Vapor Pressure Osmometer constructed at the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, and by p.m.r. spectroscopy. The CH_3 proton signals from the epoxide residue were compared with those of chloroform used as the internal standard.

Infrared absorption spectra were measured at $25 \pm 2^{\circ}\text{C}$ with a UR-10 instrument (Zeiss, Jena) using neat samples and KBr cell. The measurements were recorded from 650 to 3900 cm^{-1} and, after dilution with CCl_4 to 0.03 molar concentration, in the range of 3100 to 3900 cm^{-1} in NaCl cell of 1.48 mm thickness. The position of absorption bands is given for their peaks in wavenumbers after the calibration of the instrument with a polystyrene foil and acetamide.

P.m.r. spectra (80 MHz) for 5—15 volume % solutions in CCl_4 were obtained in a frequency sweep mode with a BS 487 C (Tesla, Brno) spectrometer at -60 to 60°C . The measurements in DMSO-d_6 were run at 20 — 150°C . Hexamethyldisiloxane was used as the internal and external standard.

Results and discussion

We have found by g.l.c. that the products of the reaction of MECH with aliphatic alcohols consist invariably of two compounds, of which one predominates. We were not successful in isolating the by-product only from the reaction involving *tert*-butyl alcohol, because the content of the substance in the reaction mixture was very low.

The estimated molecular weights of the resulting compounds and by-products were equal to the sum of the mol. wt. of MECH and that of the alcohol used. The boiling points, densities, and refractive indices (Table 1) of the main products were always lower than those of the by-products. This fact, taking into account similar properties of analogous compounds based on 1,2-epoxypropane [10, 11], 1,2-epoxy-2-methylpropane [12, 13], and 1-chloro-2,3-epoxypropane [14—16] indicated that the main products of the studied reaction were 1-alkoxy-3-chloro-2-methyl-2-propanols (A) and that the by-products were the corresponding 2-alkoxy-3-chloro-2-methyl-1-propanols (B).

Table 1
Specifications of the prepared compounds

Compound	R	Calculated/found			B.p. interval of fractions, °C/kPa	Density $\rho_{20^\circ\text{C}}$ kg m ⁻³	
		% C	% H	% Cl			
IA	CH ₃	43.33	8.00	25.58	89.5— 91.0/9.3	1100.8	1.4418
		43.45	8.18	25.82			
IB		43.33	8.00	25.58	123.0—125.0/9.3	1151.1	1.4593
		43.42	8.31	25.40			
IIA	C ₂ H ₅	47.22	8.59	23.23	78.0— 79.0/4.0	1054.0	1.4370
		47.23	8.78	23.56			
IIB		47.22	8.59	23.23	110.0—111.0/3.6	1105.1	1.4549
		46.98	8.65	23.48			
IIIA	<i>n</i> -C ₃ H ₇	50.45	9.07	21.27	92.0— 95.0/4.0	1025.8	1.4378
		50.40	9.28	21.50			
IIIB		50.45	9.07	21.27	119.0—120.0/3.6	1070.1	1.4532
		50.52	9.21	21.45			
IVA	<i>i</i> -C ₃ H ₇	50.45	9.07	21.27	84.0— 85.5/4.0	1016.7	1.4335
		50.20	9.15	21.10			
IVB		50.45	9.07	21.27	114.0—115.0/3.6	1089.4	1.4532
		50.35	9.22	21.35			
VA	<i>tert</i> -C ₄ H ₉	53.18	9.49	19.62	90.0— 90.3/4.0	1005.7	1.4352
		53.30	9.62	19.83			

It has been shown by g.l.c. analysis that the isolated fractions from *A* and *B* contain up to 2 and 5 wt. % of impurities, respectively, consisting mostly of related isomers. By using three chromatographic columns of substantially different polarity of stationary phase we confirmed the purity of the studied fractions. The chromatographic data (Table 2) indicate that the major products contain an OH group at the tertiary and the by-products at the primary positions, respectively.

The basic i.r. and p.m.r. data for MECH and its reaction products have been published [18]. The i.r. spectra of the products show no bands at 822, 900, and 1262 cm⁻¹ characteristic of the oxiran ring ([19] p. 283) in MECH. In the region of the expected stretching vibrations of C—OH bonds a very strong absorption band corresponding to ([19] p. 282) $\nu_{\text{as}}(\text{C—O—C})$ is present. This band is located at 1110—1114 cm⁻¹ and 1087 cm⁻¹ with compounds *A* containing nonbranched and branched alkyls, respectively, possibly overlapped with $\nu(\text{C—OH})$. There is a similar band in the case of *B* compounds at 1057—1068 cm⁻¹ together with less intensive band at 1106—1114 cm⁻¹.

The i.r. spectra of 0.03 molar solutions of the products in CCl₄ do not contain broad bands of intermolecularly associated OH groups. The by-products show two absorption bands around 3600 cm⁻¹. The band at 3641—3646 cm⁻¹ with

Table 2

Relative g.l.c. elution times (corrected) of products as a function of column temperature

Compound	Stationary phase					
	Apiezon M		Carbowax 20 M		1,2,3-Tris-(2-cyanoethoxy)propane	
	Polarity [17]					
	44		1052		1885	
	80°C	100°C	80°C	100°C	80°C	100°C
MECH	1.00	1.00	1.00	1.00	1.00	1.00
IA	3.26	2.88	3.83	3.41	3.09	2.80
IIA	5.32	4.50	4.33	3.78	3.14	2.76
IIIA	11.08	8.95	6.76	5.72	4.26	3.65
IVA	7.32	6.13	4.21	3.70	2.82	2.45
VA	11.23	8.94	4.67	4.11	3.05	2.63
IB	9.41	8.27	22.67	17.62	19.51	15.61
IIB		10.00		15.82		11.51
IIIB		18.20		22.47		14.54
IVB		12.47		14.73		9.82

a half-width of 24 to 28 cm^{-1} is associated with $\nu(\text{OH})$ on a primary carbon and that at 3593 to 3596 cm^{-1} , with a half-width of 29 to 34 cm^{-1} , with $\nu(\text{OH})$ involved in intramolecular hydrogen bridges. This type of absorption is common in the case of diolmonoethers having an OH group on a primary carbon [20]. Under the same condition of the measurements only one absorption band at 3572 to 3577 cm^{-1} with a half-width of 35 to 39 cm^{-1} can be assigned to the main products, which probably contains unresolved absorptions of both free and intramolecular hydrogen-bonded OH groups on a tertiary carbon atom.

In p.m.r. spectra of the products in DMSO- d_6 , and especially in CCl_4 , with decreasing temperature the signal of the OH group proton is shifted to higher δ values [21]. The singlet present in the spectra of the main products is somewhat broadened, but not split. On the contrary, in the spectra of by-products taken in DMSO- d_6 a triplet of this proton and a doublet corresponding to $\text{CH}_2\text{—O}$ protons (in IVB only indication) was observed, attributed to the interaction of the hydroxyl proton with the heteroatom [22] as a result of braking the proton exchange with the solvent. A similar effect, described [22] for neat substances or occurring in nonpolar solvents at lower temperature has not been observed in our case in CCl_4 even at -50 to -60°C .

Both i.r. and p.m.r. spectra confirmed that the reaction of MECH with lower aliphatic alcohols catalyzed with $F_3B \cdot O(C_2H_5)_2$ yields, besides 1-alkoxy-3-chloro-2-methyl-2-propanols which are the major products, also the isomeric 2-alkoxy-3-chloro-2-methyl-1-propanols.

More extensive formation of 2-alkoxy-3-chloro-2-methyl-1-propanols (*B*) in addition to the main products (Table 3) is not surprising when analogous reactions

Table 3

Effect of alcohol used on the composition of products in the reaction with MECH

Alcohol	Reaction time min	Products ratio <i>A/B</i>	Conversion MECH %
CH_3OH	60	3.15	86.0
C_2H_5OH	105	4.35	86.6
<i>n</i> - C_3H_7OH	105	5.00	89.7
<i>i</i> - C_3H_7OH	180	6.15	82.1
<i>tert</i> - C_4H_9OH	180	7.7	77.6

Conditions: temperature 30°C; initial molar ratio of alcohol to MECH 10:1; conc. $F_3B \cdot O(C_2H_5)_2$ 9.744×10^{-2} mol dm⁻³ (for CH_3OH 4.901×10^{-2} mol dm⁻³).

of structurally related epoxides are considered. In this way, 1,2-epoxy-2-methylpropane yields under similar conditions almost exclusively C_β ethers, C_α ethers being formed up to max. about 4% [12]. On the contrary, from reaction mixtures of 1-chloro-2,3-epoxypropane with alcohols under similar conditions C_β ethers have not been isolated because these are formed only in a negligible quantity [23]. However, at substantially higher temperatures (120 to 125°C) the reaction product of 1-butanol and 1-chloro-2,3-epoxypropane with $HClO_4$ as a catalyst, contains besides 86.2% of C_α ether 13.8% of its C_β isomer [24].

The achieved results suggest further, technically utilizable [25] possibilities of analogous reactions of 1-chloro-2,3-epoxy-2-methylpropane e.g. with higher or unsaturated alcohols.

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