RESEARCH ON POLYFUNCTIONAL OXIDES
VII.* STUDY OF THE REACTION OF SOME ESTERS OF 4,5-EPOXY-2-HEXENOIC ACID WITH ALCOHOLS

M. S. Malinovskii, L. P. Glushko,
and N. I. Pokhodenko

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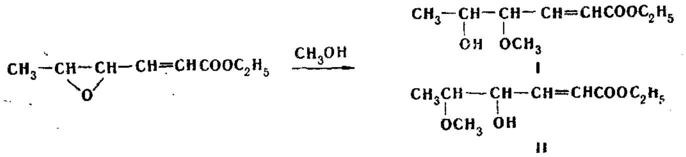
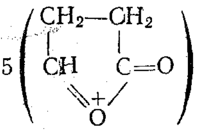
Esters of 5(4)-hydroxy-4(5)-alkoxy-2-hexenoic acid were obtained by reaction of esters of 4,5-epoxy-2-hexenoic acid with alcohols in the presence of acid catalysts. It was established that the reaction proceeds selectively in the presence of small amounts of BF_3 with predominant opening of the oxide ring on the side of the ester group.

We have previously studied the reaction of some esters of 4,5-epoxy-2-hexenoic acid with ketones [2] In the present communication we have studied the direction of opening of the epoxide ring in esters under the influence of alcohols in the presence of acid catalysts (H_2SO_4, KU-2, and BF_3). As in the case of other epoxides [3, 4], the reaction of the above oxides with alcohols may proceed with the formation of isomeric alkoxy alcohols with the following structures:



The reaction of the oxides with alcohols in the presence of BF_3 gives primarily isomer I (Table 1), and isomer II is formed in 1.5-2% amounts, according to the results of gas–liquid chromatography (GLC). In a detailed investigation of this reaction in the presence of other catalysts (H_2SO_4 and KU-2), it was shown that the reaction conditions have a great effect on the selectivity of the addition of the alcohols; depending on the reaction conditions, a second isomer is formed along with product I. The ratio of the isomeric esters was determined by GLC (Table 2).

The structure of the alkoxy alcohols obtained was proved on the basis of IR and mass spectroscopy. The IR spectra of the alkoxy alcohols contained absorption bands characteristic for the C=O group of esters (1723 cm^{-1}), C=C groups (1650 cm^{-1}), and OH groups (3450 cm^{-1}) linked by an intermolecular hydrogen bond. We established the type of hydrogen bond by IR spectroscopy. The presence of a hydroxyl group was also confirmed by acylation of ester IV with acetyl chloride in chloroform in the presence of pyridine.

The mass spectrum of ethyl 4-ethoxy-5-hydroxy-2-hexenoate (IV) contained intense peaks with m/e 45 ($CH_3CH=\overset{+}{O}H$), 85  and 159 ($H_2C_2{}^{+}{=}CH-CH_2COOC_2H_5$). The absence of ion peaks with m/e 73 ($CH_3CH=\overset{+}{C}_2H_5$) in the mass spectrum confirms that the hydroxyl group is attached to the carbon atom in the 5 position and that the ethoxy group is attached to C_4.

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*See [1] for communication VI.

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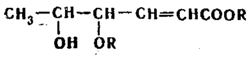
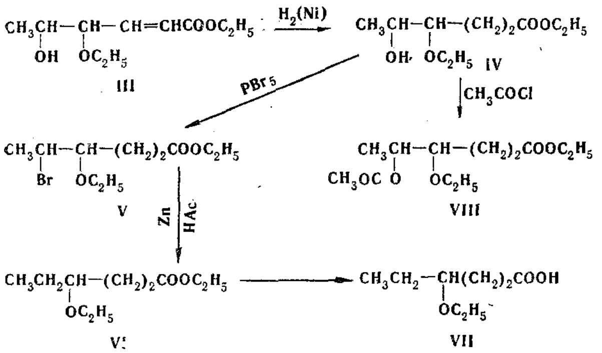
TABLE 1. Esters of 5-Hydroxy-4-alkoxy-2-hexanoic Acid  $CH_3-\underset{OH}{CH}-\underset{OR}{CH}-CH=CHCOOR$

Compound	R	R′	bp, deg °C (mm)	d_4^{20}	n_D^{20}	Empirical formula	Found			Calc.			Yield, %
							C, %	H, %	MR_D	C, %	H, %	MR_D	
I	C_2H_5	C_2H_5	120—121 (3)	1,0276	1,4575	$C_{10}H_{18}O_4$	59,8	9,1	52,90	59,4	8,9	52,8	50
II	C_2H_5	CH_3	96—97 (2)	1,0468	1,4590	$C_9H_{16}O_4$	57,2	8,7	49,10	57,4	8,5	48,9	51
III	n-C_3H_7	CH_3	102—103 (4)	1,0423	1,4595	$C_{10}H_{18}O_4$	59,6	8,8	53,01	59,4	8,9	52,8	53
IV	i-C_3H_7	CH_3	104—105 (1)	1,0244	1,4560	$C_{10}H_{18}O_4$	59,5	8,9	52,83	59,4	8,9	53,6	43
V	CH_3	C_2H_5	96—97 (3)	1,0249	1,4545	$C_9H_{16}O_4$	57,2	8,7	49,55	57,4	8,5	48,9	44
VI	C_2H_5	C_3H_7	107—109 (4)	1,0135	1,4535	$C_{11}H_{20}O_4$	61,4	9,4	57,48	61,1	9,2	57,5	35
VII	C_2H_5	$C(CH_3)_3$	112—113 (8)	1,0186	1,4590	$C_{12}H_{22}O_4$	62,4	9,3	61,73	62,6	9,6	63,9	35

TABLE 2. Products of the Reaction of Ethyl 4,5-Epoxy-2-hexenoate with Methanol

Exptl. conditions				bp, °C (mm)	d_4^{20}	n_D^{20}	Ratio of isomers I and II, %
catalyst	amount of oxide, mole	reaction temp., °C	reaction time, h				
KU-2 (1g)	0,015	20	20	114—116 (2)	1,0485	1,4585	59 : 41
		50—60	20				
H_2SO_4 (0,1 ml)	0,036	50—60	5	106 (3)	1,0688	1,4600	64 : 36
H_2SO_4 (0,1 ml)	0,02	50	5	119—122 (6)	1,0723	1,4600	67 : 33
BF_3 (0,1 ml)	0,07	60	15	115—116 (6)	1,0468	1,4590	98 : 2
BF_3 (0,2 ml)	0,2	25	20	110—112 (5)	1,0544	1,4580	95 : 5

The correctness of the proposed structure was also proved by a chemical method – by conversion of ester III to the known 4-ethoxyhexanoic acid [5].



Thus, openingup the epoxide ring in esters of 4,5-epoxy-2-hexanoic acid with alcohols in the presence of BF_3 occurs on the side of the ester group; this is in agreement with the influence of the inductive effect of the methyl group.

EXPERIMENTAL

The IR spectra of films of the substances were recorded with an IKS-14 spectrometer (NaCl and LiF prisms) at 700-3700 cm^{-1}. The mass spectra were recorded with an MKh-1303 spectrometer at 100° with an ionizing voltage of 30 eV. Chromatography was carried out with a UKh-1 chromatograph with a 3-m-long column with SE-301 on NaCl; the carrier gas was hydrogen, and the flow rate was 50 ml/min at 150°. The esters of 4,5-epoxy-2-hexenoic acid were obtained by the method in [6].

Ethyl 5-Hydroxy-4-ethoxy-2-hexenoate (III). The reaction of 9 g (0.059 mole) of ethyl 4,5-epoxy-2-hexenoate and 28 ml of ethanol in the presence of 0.2 ml of BF_3 etherate at 50-60° gave 4.6 g (50%) of a substance with bp 120-122° (2 mm), n_D^{20} 1.4575, d_4^{20} 1.0276, and R_f 0.28 [in ether–hexane (1 : 1)]. Found, %: C 59.8; H 8.9. $C_{10}H_{18}O_4$. Calculated, %: C 59.4; H 8.9. Compounds II-VII (Table 1) were similarly obtained.

Ethyl 5-Hydroxy-4-ethoxyhexanoate (IV). A 4.04 g (0.02 mole) sample of ethyl 5-hydroxy-4-ethoxy-2-hexenoate was hydrogenated with hydrogen over Raney nickel. The theoretically calculated amount of hydrogen (450 ml) was absorbed. Distillation of the reaction mixture gave 3.6 g (88%) of an ester with bp 105-107° (4 mm), n_D^{20} 1.4370 and d_4^{20} 1.0110. Found, %: C 58.9; H 10.01. $C_{10}H_{20}O_4$. Calculated, %: C 58.8; H 9.8.

Ethyl 5-Bromo-4-ethoxyhexanoate (V). A solution of 5.6 g of PBr_5 in 20 ml of $CHCl_3$ was added dropwise to a solution of 5.5 g (0.027 mole) of IV in 10 ml of chloroform, and the mixture was heated for 12 h and poured into water. Workup gave 3.2 g (45%) of a substance with bp 118-119° (5 mm), n_D^{20} 1.4630, d_4^{20} 1.2051, and R_f 0.68 [hexane–ether (1 : 1)]. Found, %: C 44.8; H 7.2. $C_{10}H_{19}BrO_3$. Calculated, %: C 44.9; H 7.1.

Ethyl 4-Ethoxyhexanoate (VI). A 2 g sample of zinc dust was added to a solution of 2.1 g (0.008 mole) of 5-bromo-4-ethoxyhexanoic acid in 10 ml of glacial acetic acid. Neutralization of the reaction mixture with NaOH gave 0.5 g (35%) of a substance with bp 97° (3 mm) and n_D^{20} 1.4470. Found, %: C 63.8; H 10.1. $C_{10}H_{20}O_3$. Calculated, %: C 63.5; H 10.0.

4-Ethoxyhexanoic Acid (VII). Ethyl 4-ethoxyhexanoate (VI) was heated with 10 ml of 0.5% alcoholic KOH, and the mixture was worked up to give VIII with bp 115° (2 mm) and n_D^{20} 1.4525. The physical constants of the product were in agreement with the literature data [5].

Ethyl 5-Acetoxy-4-ethoxyhexanoate (VIII). Acylation of 1.1 g (0.005 mole) of IV was carried out with 18 ml of CH_3COOCl in 15 ml of chloroform in the presence of 8 ml of pyridine. The mixture was worked up to give 1 g of VIII with bp 110° (3 mm), n_D^{20} 1.4360 and d_4^{20} 1.0061. Found, %: C 58.2; H 8.8; MR_D 63.69. $C_{12}H_{22}O_5$. Calculated, %: C 58.5; H 8.9; MR_D 62.34.

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