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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Ionic Telomerization of 1-Chloro-2,3-epoxypropane with Allyl Alcohol and Properties of Products Obtained

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Abstract—Ionic telomerization of 1-chloro-2,3-epoxypropane with allyl alcohol in the presence of boron trifluoride etherate as a route to halogenated epoxy oligoethers was studied. Selective chlorination or bromination of the intermediate oligo(chlorohydrin), followed by dehydrochlorination (epoxidation) of the intermediate oligohalohydrins with NaOH, was performed. The synthesized products are efficient as active diluents for a compound based on ED-20 resin.

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The reaction of alkanols with 1-chloro-2,3-epoxypropane (1-Cl-2,3-EP) in the presence of aprotic acids, followed by epoxidation of the intermediate oligochlorohydrin with alkali, belongs to the well studied field of organic chemistry. Nevertheless, this reaction attracts steady researchers' attention, because many of its products have valuable technical properties and are used both themselves and as intermediates in organic synthesis [1, 2].

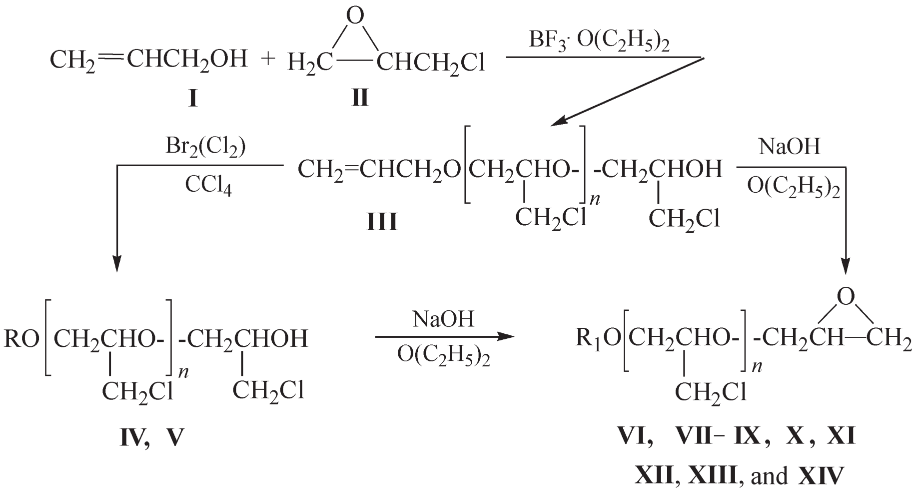
The reaction of alkenols, including allyl alcohol, with 1-Cl-2,3-EP has been studied insufficiently. Furthermore, available data on the order of the epoxy ring opening in 1-Cl-2,3-EP with allyl alcohol are contradictory [3–5]. Except a few papers [6, 7], the authors, as a rule, restrict themselves only to isolation of the primary reaction product [8, 9]. It is known, however, that the reaction, irrespective of the catalysis type (cationic or anionic), is accompanied by telomerization. Its restriction is difficult, because successive addition of ether alcohols formed in the course of the reaction to 1-Cl-2,3-EP leads to accumulation of the telomeric product in the system [2, 10, 11]. It should be noted that the lack of information on the composition of the telomeric product and on the effect of various factors on the telomerization complicate optimization of the reaction conditions.

This study deals with the reaction of allyl alcohol with 1-Cl-2,3-EP in the presence of boron trifluoride etherate, followed by dehydrochlorination (epoxidation) of the oligoether alcohol **III** obtained and of its bromination and chlorination products (**IV** and **V**, respectively) with NaOH in diethyl ether (Scheme 1).

We studied in detail the reaction of the starting alcohol **I** with 1-Cl-2,3-EP and developed a procedure for determining the composition of halogenated epoxy oligoethers **VI**, **X**, and **XIII** by vacuum fractionation and identification of separate components.

Previously we studied [2] the reaction of 1-Cl-2,3-EP with sterically hindered halohydrins and found that an increase in the process selectivity (restriction of telomerization) is possible only at five- to sixfold excess of the starting halohydrin, because the ether alcohols formed in the reaction compete with the starting halohydrin in the epoxy ring opening. However, as expected in accordance with [12], the chlorohydrins formed in the reaction of allyl alcohol with 1-Cl-2,3-EP are considerably less reactive than the starting alcohol in the epoxy ring opening in 1-Cl-2,3-EP, which somewhat simplifies the telomerization suppression.

In particular, we found that, at the **I** : **II** ratio of (3.5–4) : 1, the yield of **VII** (Scheme 1) is 72–75%, whereas at the ratio of (2.5–3) : 1, the chlorinated unsaturated epoxy oligoether (CUEOE, **VI**) formed is an oligomer of the following composition: $n = 0$ (**VII**) 53%, $n = 1$ (**VIII**) 27%, $n = 2$ (**IX**) 17%. Similar pattern is observed with the bromochlorinated unsaturated epoxy oligoether (BCUEOE, Scheme 1.



R = BrCH$_2$CH(Br)CH$_2$ (**IV**), ClCH$_2$CH(Cl)CH$_2$ (**V**); R$_1$ = CH$_2$=CHCH$_2$, *n* = 0, 1, 2 (**VI**), *n* = 0 (**VII**), *n* = 1 (**VIII**), *n* = 2 (**IX**); R$_1$ = CH$_2$=C(Br)CH$_2$, *n* = 0, 1 (**X**), *n* = 0 (**XI**), *n* = 1 (**XII**); R$_1$ = ClCH$_2$CH(Cl)CH$_2$ (**XIII**), *n* = 0 (**XIV**).

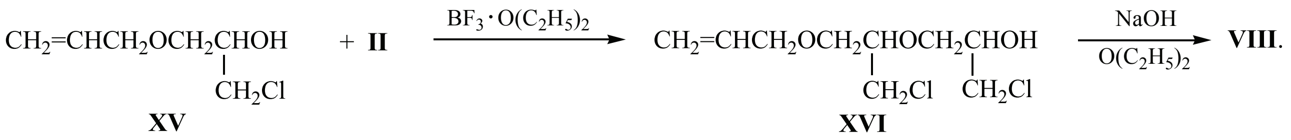
X) (Scheme 1), and from chlorinated epoxy oligoether (CEOE, **XIII**) we were able to isolate and identify only compound **XIV**. Analysis of the nondistillable fraction of CEOE (**XIII**) showed that it was a highly viscous oligomer. The compositions of individual compounds **XII–IX**, **XI**, and **XII**, isolated from CUEOE (**VI**) and BCUEOE (**X**), was confirmed by elemental analysis, and their structures were proved by MR$_D$ determination, by the IR and ^{1}H NMR data, and by independent synthesis of **VIII** by the reaction of ether alcohol **XV** with 1-Cl-2,3-EP (at 5 : 1 ratio), followed by dehydrochlorination with alkali (Scheme 2).

The properties of the samples of **VIII** prepared by Scheme 2 and isolated from CUEOE (**VI**) are identical. In the IR spectra of **VIII**, there are absorption bands at the following positions (cm^{-1}): 750 (C–Cl); 1030, 1120, and 1220 (C –O–C); 1645–1650 (C=C stretching); 660–670 (C=C bending); 881, 903, and 1250 (epoxy group) [13].

It should be noted that, in reactions of alcohols with 1-Cl-2,3-EP (and with unsymmetrically substituted α-oxides as a whole), the process selectivity should apparently be distinguished from the order of the epoxy ring opening (regioselectivity). These notions are identical only without telomerization, which inevitably contributes to the overall process. In particular, it was found that the reaction of allyl alcohol with 1-Cl-2,3-EP in the presence of boron trifluoride etherate under the conditions reducing to a minimum the contribution of successive reactions [at the ratio **I** : **II** = (3.5–4) : 1 and temperature not exceeding 20–25°C] yields products of normal (**XV**, 1-chloro-3-allyloxy-2-propanol) and abnormal (**XVII**, 3-chloro-2-allyloxy-1-propanol) opening of the epoxy ring in approximately 9 : 1 ratio [14]. Compounds **XV** and **XVII** were synthesized under the conditions of [14] and were identified by GLC. Hence, in catalysis of the reaction of allyl alcohol with 1-Cl-2,3-EP by aprotic acids [5], including anhydrous magnesium perchlorate [15], there are no deviations in the process regioselectivity compared to the reaction of alkanols with the same substrate.

Then we showed that intermediate adduct **III** under the conditions of [16] undergoes selective (without replacement of hydroxy group) bromination and chlorination [17] to form the corresponding dibromo (**IV**) and dichloro (**V**) derivatives.

Scheme 2.



$$\mathrm{CH_2{=}CHCH_2OCH_2CH(CH_2Cl)OH} + \mathbf{II} \xrightarrow{BF_3\cdot O(C_2H_5)_2} \mathrm{CH_2{=}CHCH_2OCH_2CH(CH_2Cl)OCH_2CH(CH_2Cl)OH} \xrightarrow[O(C_2H_5)_2]{NaOH} \mathbf{VIII}.$$

We found that the dehydrochlorination (epoxidation with alkali) of bromochlorinated oligoether alcohol **IV** is inevitably accompanied by dehydrobromination of its 2,3-dibromopropoxy moiety to form BCUEOE (**X**). This result is well consistent with the known ease of trans elimination [18]. Hence, the synthesis of BCUEOE (**X**) and of individual compounds **XI** and **XII** with preservation of the 2,3-dibromopropoxy moiety is practically impossible under these conditions (Scheme 1), because equal probability of these two reactions extremely complicates their separate analysis. However, dehydrochlorination of **V**, irrespective of the excess of the alkali, occurs selectively, with only the chlorohydrin moiety being involved, and yields chlorinated epoxy oligoether **XIII**, which was also confirmed by a model reaction (Scheme 3).

Hence, the dehydrochlorination selectivity in the case of oligoether alcohol **V** and compound **XIX** (Table 1) is apparently due, on the one hand, to less stereoselective arrangement of chlorine atoms in the 2,3-dichloropropoxy moiety [19] and, on the other hand, to higher strength of the C–Cl bond compared to the C–Br bond [19].

In the ^1H NMR spectrum of compound **XI** isolated from BCUEOE (**X**) and prepared by Scheme 3, the OCH_2 protons give a multiplet at 2.40–2.70 ppm. The methine proton in the epoxy group, $-\overline{\mathrm{CH{-}CH_2O}}$, gives a multiplet at 3.00–3.20 ppm, and the CH_2O protons give a multiplet at 3.15–3.80 ppm. The $=C(Br)CH_2O$ protons give a singlet at 4.05 ppm. The presence of a doublet at 5.50–5.90 ppm (2H, $CH_2=C$) in the ^1H NMR spectrum confirms the selectivity of dehydrobromination of the 2,3-dibromopropoxy moiety in **XVIII** with proton elimination from the secondary carbon atom.

The synthesized halogenated epoxy oligoethers **VI**, **X**, and **XIII** and individual compounds **VII–IX**, **XI**, **XII**, **XIV**, **XVI**, **XVIII**, and **XIX** are almost odorless transparent liquids insoluble in water and readily soluble in organic solvents (acetone, ether, ethanol, etc.). The physicochemical characteristics, analytical data, and molecular refractions of the individual compounds and some characteristics of the epoxy oligoethers are given in Tables 1 and 2.

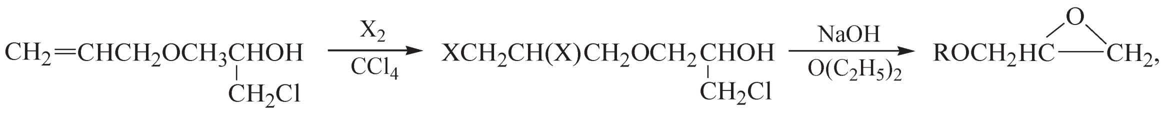
Because the development of high-performance composite materials based on commercial epoxy resins becomes more and more topical with the progress of engineering, some of the products that we prepared, in particular, oligoethers **VI** and **X** and compound **XIV**, were tested in a laboratory as plasticizers for a compound based on ED-20 epoxy–4,4'-isopropylidenediphenol resin cured with polyethylenepolyamine (PEPA).

The modification was performed as follows. With each product being tested, we prepared three formulations with the following proportions of the major components (parts): ED-20 resin, 90, 80, and 70; additive, 10, 20, and 30, respectively; PEPA, 20. Each formulation was cured separately in standard molds at room temperature for 24 h, after which the specimens were heat-treated for 2 h at 80°C and for 2 h at 120°C, and their physicomechanical characteristics were determined. The dielectric constant and the dielectric loss tangent were measured with a TR-9701 ac bridge. The electrical strength of the materials was determined with sphere–plane electrodes at a specimen thickness of 0.4 mm. The results of the tests (arithmetic mean of five determinations) are given in Table 3. The corresponding parameters for ED-20 resin cured with PEPA without modifier are given for comparison.

As seen from Table 3, on introducing 10–20 wt parts of each of the products being tested (**VI**, **X**, **XIV**), the ultimate strength of the compound increases relative to unmodified ED-20 compound by a factor of 2–2.5; the elasticity, by a factor of 10–14; the softening point, by a factor of 1.5; and the electrical strength, by a factor of 2–2.5. These data confirm that the additives used participate in the cross-linking in the course of curing of the compound with PEPA, which is apparently responsible for the enhancement of the main parameters of the compound.

Thus, the materials obtained have good physicomechanical and dielectric properties and can be used in

Scheme 3.



XV **XVIII** **XIX**

X = Br (**XVIII**), Cl (**XIX**); R = $CH_2=C(Br)CH_2$ (**XI**), $ClCH_2CH(Cl)CH_2$ (**XIV**).

Table 1. Physicochemical characteristics of the synthesized compounds and halogenated epoxy oligoethers

Compound or polyether	T_b, °C/P, mm Hg	n_D^{20}	d_4^{20}	Epoxy number, %		Yield, %
				found	calculated	
Chlorinated unsaturated epoxy oligoether (**VI**)	–	1.4700	1.1443	24.48	24.31	–
1,2-Epoxy-3-(allyloxy)propane (**VII**)	66–67/28	1.4343	0.9678	36.98	37.70	72.0
1,2-Epoxy-3-(1-chloromethyl-2-allyloxy)ethoxypropane (**VIII**)	107–108/1	1.4650	1.1247	20.65	20.83	79.0
1-Chloro-3-allyloxy-2-(2'-chloromethyl-2'-glycidyl) ethoxypropane (**IX**)	165–168/1	1.4748	1.1945	14.11	14.39	–
Bromochlorinated unsaturated epoxy oligoether (**X**)	–	1.5190	1.7189	18.19	18.68	–
1,2-Epoxy-3-(2-bromo-2-propenyloxy)propane (**XI**)	58–60/2	1.4860	1.4512	22.23	22.29	78.0
1-Chloro-2-glycidyl-3-(2'-bromo-2'-propenyloxy) propane (**XII**)	141–143/1	1.5100	1.4622	15.13	15.07	–
Chlorinated epoxy oligoether (**XIII**)	–	1.4682	1.1980	15.28	16.15	–
1,2-Epoxy-3-(2,3-dichloropropoxy)propane (**XIV**)	104–106/1	1.4730	1.2490	23.09	23.26	76.0
1-Chloro-3-allyloxy-2-propanol (**XV**)	73–74/1	1.4630	1.1120	–		86.0
1-Chloro-3-(1'-chloromethyl-2'-allyloxy)ethoxy-2-propanol (**XVI**)	135–137/1	1.4780	1.2025	–		68.0
3-Chloro-2-allyloxy-1-propanol (**XVII**)	90–91/1	1.4570	1.1149	–		64.0
1-Chloro-3-(2,3-dibromopropoxy)-2-propanol (**XVIII**)	146–148/1	1.5360	1.8299	–		91.0
1-Chloro-3-(2,3-dichloropropoxy)-2-propanol (**XIX**)	126–128/1	1.4950	1.3345	–		83.0

various fields, in particular, as high-performance casting formulations for sealing of electric units in electrical engineering.

EXPERIMENTAL

The IR spectra were recorded with a UR-20 device from thin films. The ^{1}H NMR spectra of the compounds synthesized (in particular, of XI) in CCl_4 were taken with a Tesla BS-487 B spectrometer (80 MHz, internal reference HMDS). The chromatograms of the glycidyl ethers were obtained with a Chrom-4 device (thermal conductivity detector, 2400 × 4-mm stainless steel column, on Chromaton N-AW-DMCS, carrier gas He, flow rate 30 ml min^{-1}, detector current 80 mA).

Chorinated unsaturated epoxy oligoether (VI*)*. To a stirred mixture of 58.1 g (1.0 mol) of allyl alcohol and 0.2 mL of $BF_3{\cdot}O(C_2H_5)_2$, 37 g (0.4 mol) of 1-chloro-2,3-epoxypropane was added over a period of 60 min at 30–35°C, after which the mixture was stirred for an additional 60 min. After cooling to room temperature, the catalyst was removed by washing with a 5% aqueous sodium carbonate solution, excess allyl alcohol was distilled off in a vacuum, and the residue was added from a dropping funnel into a three-necked flask charged with 20 g (0.5 mol) of NaOH and 80 mL of diethyl ether (with stirring). In the process, the mixture warmed up to 30–35°C. The suspension was stirred for an additional 40–60 min at 40–45°C. After cooling to room temperature, the organic phase was separated, and the salt precipitate was dissolved in water and extracted with ether. The combined extracts were washed with 5% aqueous acetic acid and water and dried over $MgSO_4$. The ether was distilled off, and the residue was kept in a vacuum to constant weight (65 g).

Table 2. Analytical and molecular refraction data for the compounds

Compound	MR_D		Found, %			Formula	Calculated, %		
	found	calculated	C	H	Cl		C	H	Cl
VIII	50.79	50.89	52.14	7.38	16.88	$C_9H_{15}ClO_3$	52.30	7.32	17.15
IX	70.50	71.25	48.04	6.68	23.48	$C_{12}H_{20}Cl_2O_4$	48.17	6.74	23.69
XI[a]	39.38	38.29	37.25	4.61		$C_6H_9BrO_2$	34.33	4.69	
XII[b]	58.41	58.66	37.79	4.90		$C_9H_{14}BrClO_3$	37.85	4.90	
XIV	40.73	41.56	38.87	5.35	38.46	$C_9H_{10}Cl_2O_2$	38.94	5.44	38.31
XVI	57.24	57.84	44.18	6.67	29.11	$C_9H_{16}Cl_2O_3$	44.46	6.63	29.16
XVIII	52.89	53.59	23.11	3.49		$C_6H_{11}Br_2ClO_2$	23.21	5.57	
XIX	48.40	47.68	32.49	4.94	48.16	$C_6H_{11}Cl_3O_2$	32.53	4.89	48.01

[a] Br. Found, %: 41.23. Calculated, %: 41.39.

[b] Br + Cl. Found, %: 40.12. Calculated, %: 40.39.

Table 3. Physicomechanical and dielectric properties of the epoxy compounds

Modifier	Content, wt parts	Ultimate tensile strength, MPa	Relative elongation at break, %	Vicat softening point, °C	Electrical strength, kV mm^{-1}	Dielectric loss tangent at 50 Hz	Dielectric permittivity at 50 Hz
VI	10	63.3	17	127	41.9	0.0169	4.13
	20	71.5	17	170	40.14	0.080	4.28
	30	76.4	19	175	43.30	0.0140	4.82
X	10	62.9	17	155	38.30	0.0168	4.19
	20	94.2	20	170	42.83	0.0210	4.76
	30	63.3	12	130	36.28	0.0186	4.84
XIV	10	68.1	20	160	39.15	0.0210	4.70
	20	71.4	20	170	40.33	0.0270	4.90
	30	82.4	20	175	44.85	0.0200	4.67
ED-20 + PEPA (reference)	–	36.0	1.5	100	15–20	0.03	3.8

The constants of the CUEOE obtained (**VI**) are given in Table 1. By vacuum fractionation of VI, we isolated and identified compounds **VII** (34.5 g, yield 53%), **VIII** (17.5 g, yield 27%), and **IX** (11.0 g, yield 17%) (Tables 1, 2). Similar procedure was used for preparing BCUEOE (**X**) and determining its composition by vacuum fractionation (Table 1).

Independent synthesis of VIII. To a mixture of 75.3 g

(0.5 mol) of compound **XV** prepared from allyl alcohol and 1-chloro-2,3-epoxypropane following the procedure described in [20] and of 0.2 mL of boron trifluoride etherate, 9.3 g (0.1 mol) of 1-chloro-2,3-epoxypropane was added dropwise with stirring over a period of 60 min at 20–22°C. After adding the whole amount of 1-chloro-2,3-epoxypropane, the mixture was stirred for an additional 2 h. The catalyst was removed by washing with a 5% aqueous sodium carbonate solution, excess chlorohydrin **XV** was distilled off at 73–75°C (1 mm Hg), and the residue (66 g) was added dropwise into a flask charged with 6.0 g (0.15 mol) of powdered NaOH and 80 mL of diethyl ether. The mixture was stirred for 3.5–4 h at 35–40°C. Then, the ether phase was separated, and the salt precipitate was dissolved in water and extracted with ether. The combined extracts were washed with 5% aqueous acetic acid and water and dried over $MgSO_4$. The ether was distilled off, and the residue was distilled in a vacuum to obtain 14.9 g (72.0%) of **VIII** (Tables 1, 2). Compounds **VII**, **XI**, and **XIV** were synthesized similarly (Tables 1, 2).

CONCLUSIONS

(1) Ionic telomerization of 1-chloro-2,3-epoxypropane with allyl alcohol was studied, and conditions allowing synthesis of halogenated unsaturated epoxy oligoethers or of individual compounds of this type were found.

(2) The synthesized products are well compounded with ED-20 epoxy–4,4'-isopropylidenediphenol resin, and composite materials prepared on their basis exhibit high physicomechanical and dielectric properties and can find use in various branches of electrical engineering.

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