Synthesis of Diols from 1,2-Epoxy-3-butene

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Abstract—The catalytic hydration of 1,2-epoxy-3-butene was studied. The products of the reaction are 3-butenediol-1,2 (BD-1,2) and 2-butenediol-1,4 (BD-1,4). It was shown that the formation of 2-butenediol-1,4 proceeds predominantly in a polar solvent medium in the presence of the catalytic system "nickel iodide (bromide)–tetraethylammonium iodide" at a temperature of 80°C. In the presence of inorganic acids, the main product is 3-butenediol-1,2.

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Glycols have found extensive practical use in many sectors of the national economy and, in terms of growth in their production rate, rank among the leading products of the chemical industry. They are used as solvents, for the manufacture of softeners and antifreezes, and for the syntheses of glycol esters and ethers, polyester resins, and polyurethanes. Hydration of unsaturated epoxides (e.g., 1,2-epoxy-3-butene) leads to the formation of unsaturated diols, which possess wide functional capabilities [1]. They exhibit biological activity and are used for the manufacture of pharmaceuticals and as monomers for a variety of polymeric materials.

The hydration reaction of unsaturated epoxides was studied mainly for alicyclic compounds in the presence of acid catalysts [2, 3, 4]. At the same time, data concerning this reaction for acyclic oxides with multiple bonds are scarce. In [5], it was shown that the hydration of 2,3-epoxypentene-4 yields 4-pentenediol-2,3. In the case of sulfuric acid-catalyzed hydration of butadiene monoxide [1], the main product is 3-butenediol-1,2 (BD-1,2). However, the hydration of this epoxide under certain conditions gives 3-butenediol-1,4 (BD-1,4) along with diol-1,2 [6, 7], i.e., the hydration reaction proceeds via two routes. Thus, investigation of the hydration reaction of 1,2-epoxy-3-butene (**EB**) is of both practical and theoretical interest.

The objective of this work was to study the influence of the type of catalytic system and coordinating solvent on the direction of the EB hydration reaction.

EXPERIMENTAL

1,2-Epoxy-3-butene was obtained via epoxidation of 1,3-butadiene with isopropylbenzene hydroperoxide and isolated by fractional distillation. The mass fraction of the base substance was at least 96%.

Hydration of EB was carried out in a thermostated, hermetically sealed glass reactor with a volume of 30 cm³. The reaction mixture was agitated with the use of a mechanical rocking chair. Water, solvent, and catalyst were heated in the reactor up to the reaction temperature, whereupon EB was introduced into the reactor. The progress of the reaction was monitored by following the conversion of epoxide determined by direct titration with perchloric acid [8].

The products of the reaction were analyzed using a Chrom-5 chromatograph with a flame-ionization detector (a 2.5×0.003 m chromatographic column packed with PEG-20M-coated diatomite CAW, a temperature rise from 80 to 195°C at a rate of 20°C/min, and a carrier gas (nitrogen) pressure of 0.45×10^{-5} Pa).

The diols obtained were isolated by fractional distillation. The boiling point of 3-butenediol-1,2 was 96° C/14 mm Hg, and that of 2-butenediol-1,4 was 131° C/13 mm Hg.

Identification of the obtained products was carried out by means of IR spectroscopy in the region 400-4000 cm⁻¹ with an IR Fourier RXT instrument and Spectrum-2000 software. The terminal vinyl double bond $CH=CH_2$ in the spectrum of 3-butenediol-1,2 is characterized by the stretching vibration band at 1646.86 cm⁻¹, in-plane bending vibrations at 1426 cm⁻¹ δ (CH), and out-of-plane bending vibrations CH at 928 cm⁻¹ and 993 cm⁻¹. The presence of the hydroxyl group is characterized by the band of stretching vibrations at 3367.98 cm⁻¹ and bending vibrations of the C–O group at 1074.11 cm⁻¹. 2-Butenediol-1,4 consists of the mixture of cis- and trans-isomers. The characteristic band of C=C stretching vibrations is observed at 1666.42 cm^{-1} , in-plane bending vibration is at 1406.45 cm^{-1} (C–H-*cis*) and at 1406.45 cm⁻¹ (C–H-*trans*), out-of-plane bending vibrations are at 780 cm⁻¹ (C=C-*cis*) and at 976.74 cm⁻¹ (C=C-trans). Stretching vibrations of the hydroxyl groups are characterized by the band at 3369.17 cm⁻¹ (OH group), and bending vibrations are characterized by the band at 1085.89 cm^{-1} (C–O) [9].

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Catalyst	Solvent	Temperature, °C	1,2-Epoxy-3-butene conversion	Yield of diols on converted-ep- oxide basis, %	BD-1,4/BD-1,2 ratio
Without catalyst	-	80	75, 01	79.62	0
H_2SO_4	-	25	92.92	100.00	0
HClO ₄	-	25	91.41	99.03	0.07
H ₃ PO ₄	-	25	98.21	92.92	0.14
H ₃ PO ₄ *	-	80	98.61	96.05	0.09
H ₃ PO ₄	Acetone**	60	95.17	98.57	0.10
H ₃ PO ₄	N-Methylpyrrolidone**	60	35.00	100.00	0.10

Table 1. Hydration of 1,2-epoxy-3-butene in the presence of inorganic acids at initial 1,2-epoxy-3-butene and catalyst concentrations of 1.30 and 0.004 mol/dm³, respectively; a water : epoxide molar ratio of 40 : 1; and a reaction time of 60 min

Notes: * The reaction time is 20 min.

** The water : epoxide molar ratio is 20 : 1.

RESULTS AND DISCUSSION

On the basis of the data on the reaction kinetics and the product composition for the hydrolysis of monoxides of cycloalkadienes-1,3 [2], the $S_N 1$ (A1) mechanism of the reaction involving the formation of the allyl cation is postulated. Thus, the reaction of acid-catalyzed hydration of EB can be represented by the scheme:



The ratio of diols BD-1,2 (III) and BD-3,4 (IV) will depend on the prevalence of form I or II of the intermediate in the system, the rate of their interaction with water, and the thermodynamic stability of alternative products. Our calculations showed that, in the interval of temperatures studied, the formation of diol IV is thermodynamically favorable. The equilibrium constant of reaction (a) in the liquid phase at 80°C was $K_{(a)} = 1 \times 10^{18}$, and that of route (b) was $K_{(b)} = 24 \times 10^{18}$. However, the data obtained by Ross et al. [2] and our results (Table 1) show that diol III primarily accumulates in the products in the presence of inorganic acids. Hence, the kinetic factor dominates over the thermodynamic one.

Carrying out the reaction in the presence of solvents and elevation of temperature (Table 1) practically did not affect the direction of water addition, although the rate of the reaction considerably decreased in an N-methylpyrrolidone (N-MP) medium. The noncatalytic reaction of epoxides likewise proceeds at lower rates; nonetheless, the activation of the oxirane ring in the intermediate takes place in this case as well [10]. It may be assumed that diol III will also be the main product in a neutral medium. Our experiments showed that only diol III was present in the products of the catalystfree hydration of EB.

The nature of inorganic acid (Table 1) affects, to some extent, not only the rate of the reaction of EB with H_2O , but also the amount of diol IV. However, the hydration route with the participation of intermediate I always prevails considerably.

The products of the hydration of α -oxides in acidic and alkaline media are usually identical [4]; therefore, investigation in this area is not promising.

Earlier [4, 11–13], it was shown that the nature of the solvent and Lewis acid had a considerable effect on the direction of the rearrangement of epoxides including those with multiple bonds. For example, in the presence of LiI, $ZnCl_2$ in an N-MP medium, heterocyclization yielding dihydrofuran occurs instead of the usual isomerization reaction [11]. Hence, it might be expected that the formation of diol IV would occur in an analogous system in the presence of water to a

Catalyst	Reaction time, min	1,2-Epoxy-3-butene conversion	Yield of diols on epoxide converted, %	BD-1,4/BD-1,2 ratio
LiI*	120	63.08	91.88	0.06
LiI	180	55.14	97.10	0.75
MgBr ₂ *	120	85.86	80.78	0.27
MgBr ₂	180	53.21	85.72	0.86
NiF ₂	180	47.02	90.46	0.11
NiCl ₂	180	37.10	86.23	0.27
NiBr ₂	240	62.73	60.86	0.83
NiI ₂	365	68.66	78.62	2.04

Table 2. Hydration of 1,2-epoxy-3-butene in the presence of Lewis acids. Temperature, 80°C; initial molar concentration, mol/dm³: 1,2-epoxy-3-butene, 1.30; catalyst 0.08, water : epoxide molar ratio, 20 : 1; solvent N-methylpyrrolidone

* The solvent-free run at a water : epoxide molar ratio of 40 : 1.

Table 3. Influence of tetrabutylammonium iodide on the direction of water addition to 1,2-epoxy-3-butene at 80°C; an initial molar concentration, mol/dm³: 1,2-epoxy-3-butene, 1.30; Lewis acid, 0.05, $(C_4H_9)_4$ NI 0.65, N-methylpyrrolidone, 3.7, and a water : epoxide molar ratio of 20 : 1

Catalyst	Reaction time, min	1,2-Epoxy-3-butene conversion	Yield of diols on converted-epoxide basis, %	BD-1,4/BD-1,2 ratio
$LiI + (C_4H_9)_4NI$	255	73.87	99.75	1.48
$MgBr_2 + (C_4H_9)_4NI$	360	90.80	95.20	2.67
$NiI_2 + (C_4H_9)_4NI$	270	90.35	66.40	2.93
$NiBr_2 + (C_4H_9)_4NI$	360	90.50	85.18	3.67

greater extent than in the case of the catalysis by protic acids.

For the purpose of corroborating this assumption, we studied the reaction of the hydration of 1,2-epoxy-3-butene in the presence of a number of metal halides in an N-MP medium (Tables 2, 3). As it is seen from Table 2, the yield of 2-butenediol-1,4 is considerably higher when the reaction is carried out in the presence of a Lewis acid and a polar solvent, such as N-methylpyrrolidone. It should be noted that the formation of a catalytic complex similar to the one isolated previously and identified as $MgBr_2 \cdot 2H_2O \cdot 4N-MP$ in the isomerization reaction of 2-methyl-2,3-epoxybutane [14] would occur in the reaction medium in the case of $MgBr_2$.

In the presence of metal bromides and iodides, the 1,4-addition of water becomes progressively more noticeable (Table 2). The highest 2-butenediol-1,4 to 3-butenediol-1,2 ratio was obtained in the presence of nickel iodide, where its value was about 2. But the total yield of the diols does not exceed 80%, because of the formation of glycol esters. Similar ratios between the diols were observed when lithium iodide, magnesium bromide, nickel bromide, and N-methylpyrrolidone were used as catalysts.

Quaternary ammonium bases can considerably alter the properties of a reaction medium. Therefore, we

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examined the hydration of 1,2-epoxy-3-butene in the presence of tetrabutylammonium iodide (TBAI), a Lewis acid, and the solvent N-MP. From the experimental data (Table 3), it follows that the ratio between the diols considerably increases in favor of 2-butene-diol-1,4 for all of the catalysts used, reaching 3.67 : 1 in the case of nickel bromide and TBAI.

The results obtained in this work and published data [4, 15, 16] indicate that the basicity of the oxirane ring, which is determined by its activation with the participation of a catalyst as well, and the double-bond nucleo-philicity, which depends on the electrophilicity of a catalyst, are essential factors that affect the direction of the addition of a nucleophile (H_2O in this case) in the presence of Lewis acid in a coordinating-solvent medium. The rate and direction of the hydration of unsaturated epoxides presumably depend on the structure, configuration, and conformation of oxirane, including those in the transition state involving the catalytic complex. This dependence was noted earlier in the study of the heterocyclization of unsaturated acyclic epoxides under similar conditions [16].

It should be noted that the model proposed earlier [17] for the mechanism of the reaction of epoxides with water as epoxide ring opening via the boundary $S_N 2-S_N 2'$ mechanism also makes it possible to explain these results.

CONCLUSIONS

The noncatalytic reaction of 1,2-epoxy-3-butene with water and its catalysis by protic acids give 3-butenediol-1,2 as the main product. The hydration of 1,2-epoxy-3-butene with the primary formation of 2-butenediol-1,4 proceeds in the polar solvent N-methylpyrrolidone at a temperature of 80°C and in the presence of the catalytic system nickel iodide, nickel bromide-tetraethylammonium iodide. The conversion of 1,2-epoxy-3-butene is 90.5%, the yield of the diols is 85%, and the diol-1,4 to diol-1,2 ratio reached 3.67 : 1.

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