KINETICS AND MECHANISM FOR THE FORMATION OF THREE-, FOUR-, AND FIVE-MEMBERED OXYGEN-CONTAINING HETEROCYCLES IN THE REACTION OF OLEFIN EPOXIDES WITH β-, γ-, AND δ-HYDROXYALKYL SULFIDES

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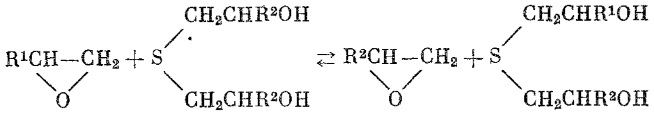
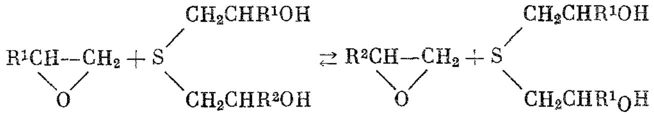
The reaction of olefin epoxides with alcohols leads to the formation of glycol ethers [1]. However, the reaction with olefin epoxides proceeds by a different pathway when the alcohol has a β-sulfur atom. Instead of glycol ethers, the reaction yields an olefin epoxide and sulfur-containing alcohol differing in structure from the original [2, 3], i.e., the reaction becomes an exchange process.

In the present work, we examined the exchange reactions in a system composed of an olefin epoxide and β-hydroxyalkyl sulfide and carefully studied the kinetics of the reaction of the olefin epoxide with mono-β-hydroxyalkyl sulfide. In addition, we studied the possibility of forming four- and five-membered oxygen-containing heterocycles in the reactions of olefin epoxides with γ- and δ-hydroxyalkyl sulfides.

Depending on the nature of the β-hydroxyalkyl sulfides, the reactions of olefin epoxides with these sulfides fall into three categories. For the first group characteristic for bis(β-hydroxyalkyl) sulfides, we encounter the formation of one type of olefin epoxide and two β-hydroxyalkyl sulfides, the second of which is formed due to secondary reaction (2):



(1)

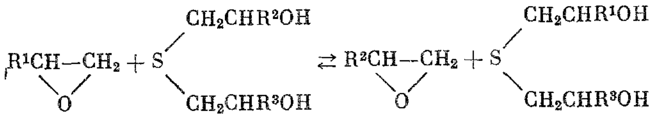


(2)

$R^1 = H, Me, CH_2OPh$ and $R^2 = H, Me.$

Exchange reactions were first discovered specifically for this case [2]; the products of these exchange reactions were identified by various physicochemical methods.

The reactions of the second group featuring β,β'-dihydroxyalkyl sulfides with $R^1 \neq R^2 \neq R^3$ lead to the formation of two olefin epoxides and two β-hydroxyalkyl sulfides. In addition, the formation of further types of β-hydroxyalkyl sulfides is possible due to secondary exchange reactions involving the three types of olefin epoxides and four types of β-hydroxyalkyl sulfides formed in the reactions



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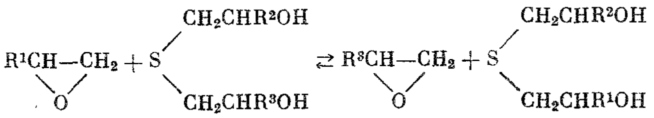

(4)

$R^1 = H, Me, Ph, CH_2OPh; R^2 = H, Me, Ph, CH_2OPh; R^3 = H, Me, Ph, CH_2OPh.$

In the third and most simple group characteristic for mono-β-hydroxyalkyl sulfides, we encounter formation of only two reaction products, namely, an olefin epoxide and monohydroxyalkyl sulfide in equal amounts and the absence of side reactions

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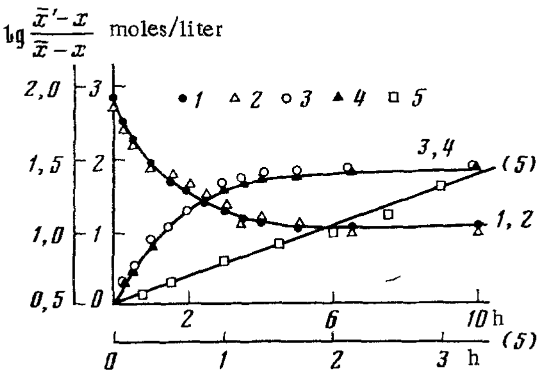
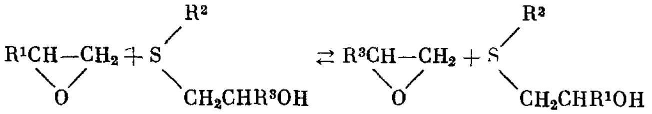


Fig. 1. Kinetic curves for the consumption of octyl β-hydroxypropyl sulfide (1), glycidyl phenyl ether (2), and the accumulation of octyl β-hydroxy-γ-phenoxypropyl sulfide (3) and propylene oxide (4) at 150°C. The dependence of $\log[(\bar{x}' - x)/(\bar{x} - x)]$ on time for the reaction of the system containing glycidyl phenyl ether and octyl β-hydroxypropyl sulfide at 150°C is given by curve 5.



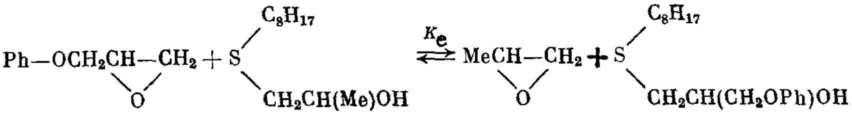
(5)

R^1 = H, Me, Et, $CH=CH_2$, CH_2Cl, CH_2Br, Ph, CH_2OEt, CH_2OBu, CH_2OPh, CH_2OH; R^2 = Ph, CH_2Ph, C_6H_4Me, C_7H_{15}, C_8H_{17}; R^3 = H, Me, CH_2OPh.

The course of the reaction may be controlled at any stage relative to any of the four components of reaction (5).

In all the systems examined, the structure of the olefin epoxide formed is a factor of the structure of the β-hydroxyalkyl group of the initial sulfide. For example, the reaction of β-hydroxyethyl β-hydroxypropyl sulfide $HOCH_2CH_2SCH_2CH(OH)Me$ with glycidyl phenyl ether proceeds with the formation of ethylene epoxides and propylene.

The kinetics of the exchange reactions was studied for the reactions of olefin epoxides with mono-β-hydroxyalkyl sulfides. Thus, the reaction of glycidyl phenyl ether with octyl β-hydroxypropyl sulfide leads to the formation of propylene epoxide and octyl β-hydroxy-γ-phenoxypropyl sulfide



(6)

Reaction (6) is the only process for this system. Side products were not detected as indicated by maintenance of the material balance of the starting compounds and products. The reaction reaches a state of dynamic equilibrium 5.5 h after its onset at 150°C (Fig. 1a). The equilibrium constant K_e = 3.05 (150°C) was found using the equilibrium concentration of the reaction components. This value is virtually independent of the ratio of the starting reagents. (The concentration range for the olefin epoxide was from 0.74 to 4.0 moles/liter and that for the sulfide was from 4.17 to 2.0 moles/liter.) In the reaction of propylene oxide with octyl β-hydroxy-γ-phenoxypropyl sulfide (the reverse direction of reaction (6)), the only products are glycidyl phenyl ether and octyl β-hydroxypropyl sulfide. Equilibrium is reached 9-10 h after the reaction onset. The equilibrium constant K_e' was determined from the equilibrium concentrations of the mixture components (0.33), i.e., $1/K_e'$ = 3.03, which is in accord with the value obtained above. The reaction rate obeys reversible second-order kinetics

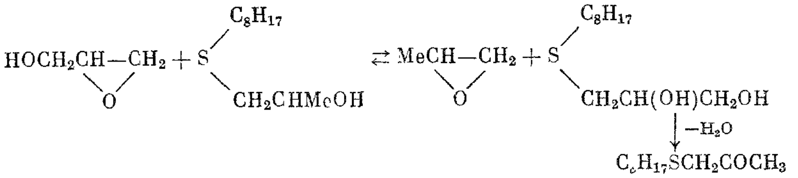
$$W = k_1C_AC_B - k_{-1}C_CC_D \tag{a}$$

TABLE 1. Effective Rate Constants of the Exchange Reactions for Systems Containing an Olefin Epoxide and R-β-Hydroxyalkyl Sulfide

Olefin epoxide		Sulfide			T., °C	k_1, k_{-1}, liters/mole · sec
R^1	C_0, moles/liter	R^2	R^3	C_0, moles/liter		
$PhOCH_2$	4,44	Ph	Me	2,86	118–189	$3{,}3 \cdot 10^2 \exp(-15\,600/RT)$, $15{,}2 \exp(-12\,500/RT)$
Same	4,12	C_6H_4Me	Me	2,64	140,5–180	$1{,}2 \cdot 10^2 \exp(-14\,100/RT)$ $3.85 \exp(-11\,000/RT)$
»	2,78	C_8H_{17}	Me	2,82	140–180	$3{,}54 \exp(-9530/RT)$, $1{,}24 \exp(-9600/RT)$
$EtOCH_2$	2,45–2,83	Same	Me	2,81–3,17	141,5–182	$1{,}8 \cdot 10^2 \exp(-13\,700/RT)$, $2{,}8 \cdot 10^2 \exp(-13\,300/RT)$
$PhOCH_2$	3,75–5,30	»	H	1,25–2,45	140–170	$1{,}1 \cdot 10^2 \exp(-13\,000/RT)$, $6{,}1 \cdot 10^2 \exp(-10\,800/RT)$
Me	0,747	»	H	0,0625	150	$0{,}48 \cdot 10^{-6}$, $1{,}94 \cdot 10^{-3}$

where k_1 and k_{-1} are the effective rate constants of the forward and reverse reactions and C_i are the current concentrations of the starting components and reaction products. The dependence of log $[(\bar{x}' - x)/(\bar{x} - x)]$ on time for this reaction (see Fig. 1b) is characteristic for reversible second-order reactions and permits us to find the rate constants for the forward and reverse reactions [4]. Thus, the rate constants were found for other systems in a broad temperature range (Table 1). Under comparable conditions, an increase is found in the effective reaction rate constants with increasing electron-donor properties of the R^2 substituent in the sulfide and electron-withdrawing properties of the R^1 substituent in the olefin epoxide. For example, for $R^1 = CH_2OPh$ and $R^3 = Me$, the ratio between the k_1 values at 150°C for $R^2 = Ph$, C_6H_4Me and C_8H_{17} is 0.32:0.69:4.6. The enthalpy change of the reverse reaction obtained from Table 1 $\Delta H = 0$–3.0 kcal/mole. On the other hand, the calculation for the same systems carried out using the additivity rule for group properties [5] gives $\Delta H_r^\circ = 0$. This discrepancy may be attributed to use of concentrational values of K_e obtained experimentally in the calculations and, in addition, some contribution to the nonzero value is related to the error in the gas–liquid chromatographic analysis of the reaction mixture components, which was 5-10%.

The reaction of glycidol with octyl β-hydroxypropyl sulfide, in contrast to the reactions examined above, is irreversible. Table 2 shows that glycidol is completely consumed in 11 h at 86°C with conservation of the material balance relative to the consumed reagents, octyl β-hydroxypropyl sulfide and glycidol and the product, propylene oxide (the sulfide product was not analyzed). The irreversible nature of this reaction is apparently attributed to the pinacol rearrangement [6] of the sulfide product. The disappearance of the OH groups in this product hinders the back reaction


(7)

Despite the simplicity of the exchange reactions (5), their mechanism is complex. Thus, overall third-order reaction kinetics is observed for concentrated solutions of the hydroxyalkyl sulfides, first-order relative to the olefin epoxide and second-order relative to the hydroxyalkyl sulfide for all the systems given in Table 1. Figure 2 gives the logarithmic plots for the dependence of the initial reaction rate on the concentrations of glycidyl phenyl ether and octyl β-hydroxypropyl sulfide. In the concentration range studied, first-order kinetics is found relative to the olefin epoxide. First-order kinetics relative to the sulfide was found for concentrations $\leqslant 0.3$ mole/liter, while second-order kinetics relative to this component was found above 0.8–0.9 mole/liter. The lack of accord of the total reaction rate determined experimentally with the value from the stoichiometric equation indicates a multistep mechanism for the exchange reaction. In our previous work [7], we showed that the reaction occurs in several steps. The first step of the forward reaction features the formation of a hydrogen-bonded complex upon the reaction of the sulfide OH group with the oxygen atom of the epoxide ring

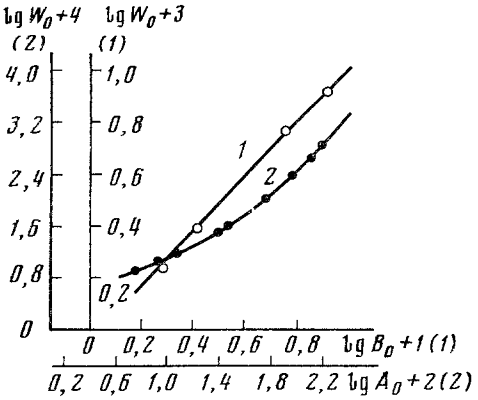
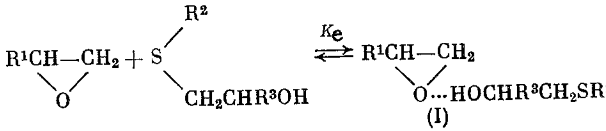


Fig. 2. Logarithmic plot for the dependence of the initial reaction rate on the concentration of glycidyl phenyl ether (1) and octyl β-hydroxypropyl sulfide (2) at 150°C in chlorobenzene.

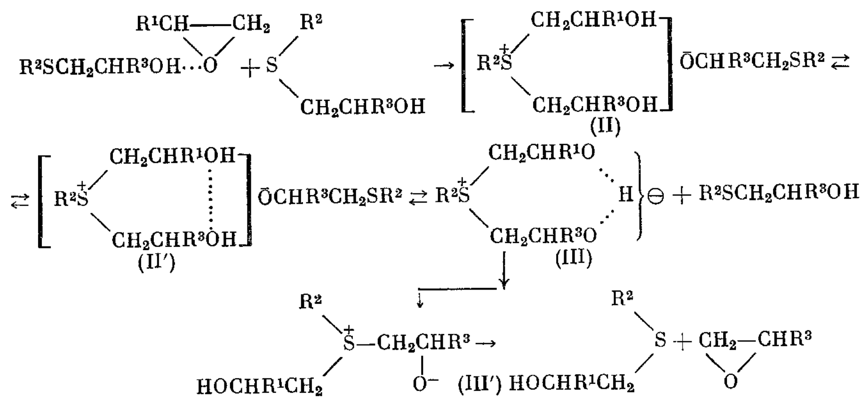
TABLE 2. Gas–Liquid Chromatographic Analysis of the Starting Components and Reaction Products (moles/liter) in the System Consisting Initially of Glycidol and Octyl β-Hydroxypropyl Sulfide at 86°C

Reagent	Time, h									
	0	0,27	0,5	1,0	2,0	3,05	4,5	6,5	9,05	10,6
$HOCH_2\underbrace{CH-CH_2}_{O}$	0,90	0,81	0,72	0,62	0,44	0,36	0,23	0,15	0,04	0,0
$S\begin{matrix}C_8H_{17}\\CH_2CH(CH_3)OH\end{matrix}$	4,26	4,17	4,08	3,97	3,81	3,72	3,61	3,46	3,38	3,37
$Me\underbrace{CH-CH_2}_{O}$	0	0,09	0,17	0,28	0,45	0,54	0,65	0,75	0,86	0,90
Material balance relative to olefin epoxides, %	100	100	104	100,5	102	101	103	99,5	100	100



(8)

Then, complex (I) reacts with a second hydroxyalkyl sulfide molecule to form sulfonium salt (II) in the rate-limiting step to account for the second-order kinetics relative to the hydroxyalkyl sulfide. The decomposition of the sulfonium salt through several intermediate steps leads to the final reaction products.



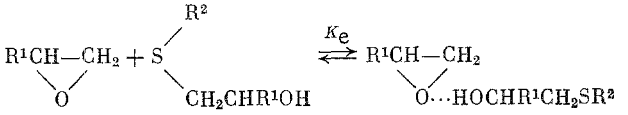
(9)

TABLE 3. Comparison of the THF Yield in the Presence of Catalytic Amounts of Acetic Acid (1) and in the Absence of Acid (2) at 152°C over 1 h for the System Initially Containing Glycidyl Phenyl Ether and Octyl δ-Hydroxybutyl Sulfide

Compound	(1)	(2)
	moles/liter	
Octyl δ-hydroxybutyl sulfide	2,5	2,5
Glycidyl phenyl ether	3,03	3,03
Acetic acid	$9\cdot10^{-2}$	–
Tetrahydrofuran	0,37	0,14

In addition to a sulfonium salt with an intramolecular hydrogen bond (II'), there is also the possibility of formation of dipolar ion (III) with an intramolecular hydrogen bond and delocalized negative charge. Bipolar ion (III') is formed upon localization of hydrogen on one of the oxygen atoms; intramolecular attack of the oxygen atoms of the α-carbon atom occurs in this ion, accounting for the nature of the products formed.

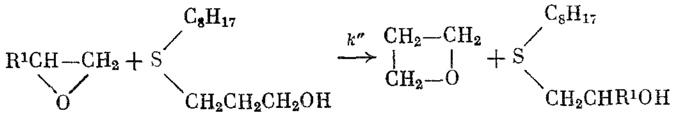
The finding that reaction (5) obeys second-order reversible kinetics (first-order relative to the olefin epoxide and to the hydroxyalkyl sulfide), and not third-order kinetics, is explained by compensation of the loss of the starting hydroxyalkyl sulfide due to the formation of the hydroxyalkyl sulfide product, which, in addition to the initial reagent, participates in the formation of the hydrogen-bonded complex



(10)

The reaction of this complex with a molecule of the starting hydroxyalkyl sulfide, in the final analysis, leads to the same products and the expression for the third-order reaction kinetics is converted to equation (a) for reversible second-order kinetics taking account of the constant sum of the concentrations of the hydroxyalkyl sulfides in the reaction mixture. Thus, a unique example of catalysis by hydroxyalkyl sulfides is revealed.* The results of the present work along with the data of our previous study [8] proving the formation of hydrogen-bonded complex (I) by a spectral method indicate the catalysis of reaction (5) by various classes of proton donors [9].

If the mechanism of the reactions of olefin epoxides and hydroxyalkyl sulfides, which contain an OH group in the γ or δ position relative to the sulfur atom, is analogous to the mechanism of reaction (5), we should expect the formation of four- or five-membered oxygen-containing heterocycles and the corresponding β-hydroxyalkyl sulfides as the final products. For example, the reaction scheme of octyl γ-hydroxypropyl sulfide and octyl δ-hydroxybutyl sulfide with an olefin epoxide should have the form



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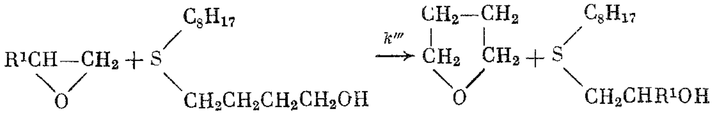

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*The catalytic effect of hydroxyalkyl sulfides was also shown upon their direct introduction into the system.

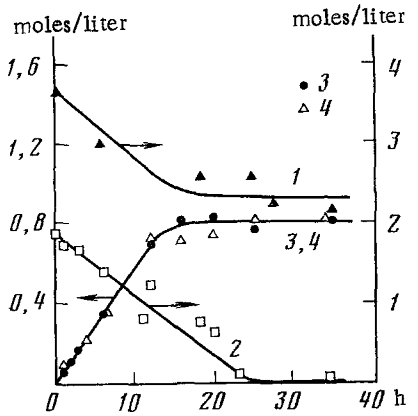


Fig. 3

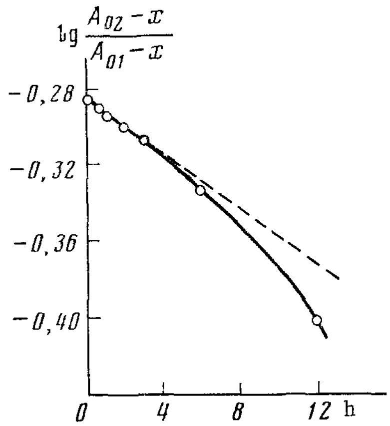
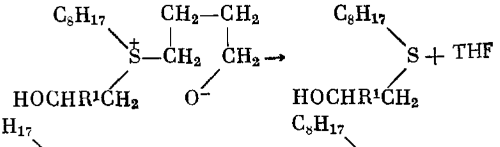


Fig. 4

Fig. 3. Kinetic curves for the consumption of octyl δ-hydroxybutyl sulfide (1) and propylene oxide (2) and of the accumulation of THF (3) and octyl β-hydroxypropyl sulfide (4) at 150°C.

Fig. 4. Dependence of log $[(A_{02} - x)/(A_{01} - x)]$ on time for the reaction of the system containing propylene oxide and octyl δ-hydroxybutyl sulfide at 150°C.

Analysis of the products of reaction (11) (R^1 = Me, CH_2OPh, Ph, and CH_2OBu) showed the formation of the corresponding β-hydroxyalkyl sulfide and absence of trimethylene oxide in all the reaction mixtures in addition to considerable amounts of side products. On the other hand, analysis of the products of reaction (12) (R^1 = Me, Ph, CH_2OBu, and CH_2OPh) in all cases showed tetrahydrofuran (THF) and the corresponding β-hydroxyalkyl sulfide. The THF content in the reaction mixture was determined by chromatomass spectroscopy: The mass spectrum of the volatile fraction unequivocally indicates the formation of THF by reaction (12). Reactions (11) and (12) were shown experimentally to be irreversible. The kinetics of reactions (11) and (12) was studied. Reaction (12) is accelerated in the presence of catalytic amounts of acetic acid, indicating the formation of a more reactive hydrogen-bonded complex of the olefin epoxide and the hydroxybutyl sulfide (Table 3). Figure 3 gives the kinetic curves for the consumption of the starting components and the accumulation of the products of the reaction of propylene oxide with octyl δ-hydroxybutyl sulfide. The kinetic curves for the accumulation of THF and octyl β-hydroxypropyl sulfide virtually coincide (see Fig. 3), but material balance between the reaction products and starting components is not observed for this system. In this regard, the time dependence for log $[(A_{02} - x)/(A_{01} - x)]$ (A_{01} and A_{02} are the initial concentrations of the hydroxysulfide and propylene oxide and x is the current concentration of THF or octyl β-hydroxypropyl sulfide) which is characteristic for irreversible second-order reactions (the hydroxyalkyl sulfide concentration in the system was constant) was found to be nonlinear (Fig. 4). Nevertheless, although without high precision, the effective rate constant of reaction (12) may be evaluated using the slope of the tangent to curve 1: $k''' = 2.6 \cdot 10^{-6}$ liter/mole·sec. The rate constant for reaction (11) was evaluated analogously, $k'' = 2.5 \cdot 10^{-6}$ liter/mole·sec. Since reactions (5), (11), and (12) are apparently related by a common mechanism, the final steps in reactions (11) and (12) may be represented as follows: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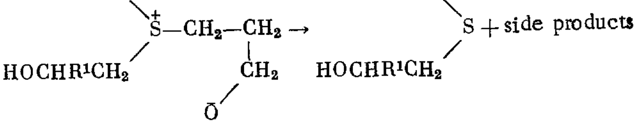
(14)

The reaction is terminated by intramolecular nucleophilic attack of the α-carbon atom by the oxygen atom. Ring closure occurs concurrently with breaking of the $\overset{+}{S}$—C bond and sulfide formation in reaction (13). The decomposition of trimethylene oxide in reaction (14) apparently proceeds at the instant of its formation.

EXPERIMENTAL

The gas—liquid chromatographic analysis and recording of the PMR spectra were carried out as in our previous work [10]. The chromatomass spectroscopic analysis was carried out on a Ribermag K-10-10C Nermag S. A. Chromatomass spectrometer on a 2.1-m column packed with SE-30 on 120 mesh Chromosorb WSE-30. The electron impact energy was 70 eV. The kinetic experiments were carried out as in our previous work [10]. The separation of the hydroxyalkyl sulfides in the reaction of ethylene oxide with bis(β-hydroxypropyl) sulfide was carried out on a 56 cm × 12 mm alumina column with 9:1 benzene—ethanol as the eluent. Samples of octyl β-hydroxypropyl sulfide, octyl γ-hydroxypropyl sulfide (IV), and octyl δ-hydroxybutyl sulfide (V) were prepared according to our previous procedures [11] by the reaction of octyl mercaptan with the corresponding alkylene-halohydrins in 90-95% yield. The purity of the sulfides was monitored by gas—liquid chromatography. For (IV), bp 130°C (2 mm), d_4^{20} 0.9357, n_D^{20} 1.4795. Found: C 63.38; H 11.55%; MR 62.0. Calculated for $C_{11}H_{24}OS$: C 64.65; H 11.84%; MR 62.63.

For (V), bp 185°C (0.5 mm), d_4^{20} 0.9217, n_D^{20} 1.4784. Found: C 66.59; H 11.97%; MR 67.12. Calculated for $C_{12}H_{26}OS$: C 65.99; H 12.00%; MR 67.28. Propylene oxide was obtained as the product of the reaction of ethylene oxide with bis(β-hydroxypropyl) sulfide, mp 34.5°C, d_4^{20} 0.8271, n_D^{20} 1.3667 [1]. The PMR spectrum unequivocally confirmed its structure and corresponds to the spectrum given by Shonin and Ershov [12]. The PMR spectra of β,β'-dihydroxyethylpropyl sulfide and bis(β-hydroxyethyl) sulfide, which are the products of this reaction, coincide with the corresponding PMR spectra of these sulfides obtained by convergent synthesis [11].

The authors express their gratitude to D. Fentsov for taking the chromatomass spectra.

CONCLUSIONS

1. The effective rate constants, activation energies of the forward and reverse reactions, and equilibrium constants were obtained for the exchange reactions of olefin epoxides with β-hydroxyalkyl sulfides. The participation of both the initial and product hydroxyalkyl sulfide in the catalysis of this exchange reaction was demonstrated.

2. The formation of five-membered oxygen-containing heterocycles was shown in the reactions of olefin epoxides with δ-hydroxyalkyl sulfides. The kinetics of this reaction was studied and a possible reaction mechanism was proposed.

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