Reviews

Exchange reaction of oxiranes with β-hydroxyalkyl sulfides, selenides, -amines, and -phosphines

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The results of studies on the exchange reactions of oxiranes with N^{III}, P^{III}, S^{II}, and Se^{II} organic compounds containing β-hydroxyalkyl groups at the heteroatom, which give rise to oxiranes and β-hydroxyalkyl derivatives with different structures, are surveyed. The characteristic features and kinetics of this reaction are analyzed. A quantitative description of the reaction is given.

Key words: oxiranes, β-hydroxyalkyl sulfides, β-hydroxyalkyl selenides, β-hydroxyalkylamines, β-hydroxyalkylphosphines, exchange reaction, kinetics, reaction mechanism, hydrogen bond, onium salt, bipolar adducts, rate constants.

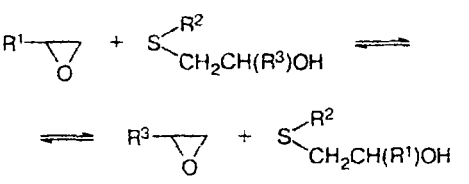
Introduction

Considerable interest in hydroxyalkyl sulfides due to wide application of products synthesized from them requires detailed investigations of their properties and methods for their synthesis. In this connection, attention is attracted to an unusual exchange reaction between oxiranes and β-hydroxyalkyl sulfides leading to oxiranes and β-hydroxyalkyl sulfides with different structures, which has been first observed for the propylene oxide—bis(β-hydroxyethyl) sulfide system.[1] The reaction gave ethylene oxide, (β-hydroxyethyl) (β-hydroxypropyl) sulfide, and bis(β-hydroxypropyl) sulfide. Later, studies of such exchange reactions were extended to organic derivatives of Se, N, and P containing a β-hydroxyalkyl group at the heteroatom. However, the exchange reactions of these derivatives with oxiranes are accompanied by side processes and pathways leading to side products (alkenes, carbonyl compounds, *etc.*) involve the same intermediates.

Some features of the exchange reaction

The reaction of oxiranes with β-hydroxyalkyl sulfides (Scheme 1, $R^1 \neq R^3$) represents the simplest case. This gives only two products: oxiranes and β-hydroxyalkyl sulfides with structures differing from those of the starting compounds.

Scheme 1



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

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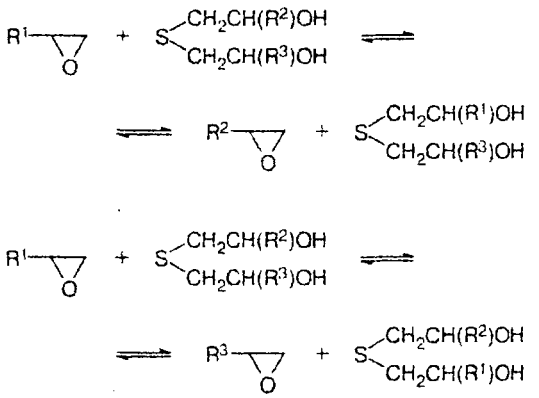
The reactions are usually carried out in glass tubes or in autoclaves (preparative syntheses) in chlorobenzene at 150 °C; the initial oxirane concentrations are 1—4 mol L^{-1} and the sulfide concentrations are 2—4 mol L^{-1}.[2,3]

The number of products increases if the sulfur atom is attached to two different β-hydroxyalkyl groups. Thus when $R^1 \neq R^2 \neq R^3$, pairs of different oxiranes and β-hydroxyalkyl sulfides are initially formed (Scheme 2).

Scheme 2

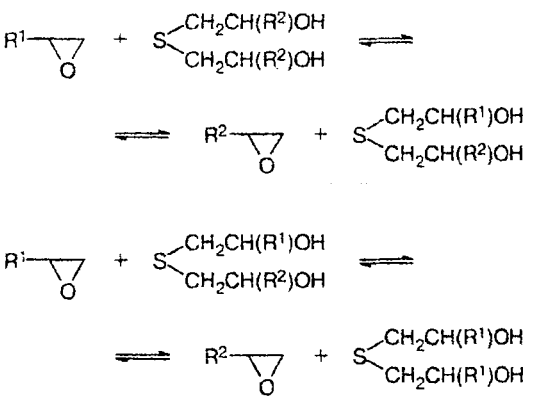


R^1 = H, Me, CH_2OPh; R^2 = H, Me, Ph, CH_2OPh; R^3 = H, Me, CH_2OPh

This is followed by secondary exchange reactions involving three oxiranes and the three β-hydroxyalkyl sulfides present in the mixture and giving rise to all the possible β-hydroxyalkyl sulfides.

In the case where $R^1 \neq R^2 = R^3$ (R^1 = H, Me, CH_2OPh, $R^2 = R^3$ = H, Me), one oxirane and two β-hydroxyalkyl sulfides are produced (Scheme 3).[1,3]

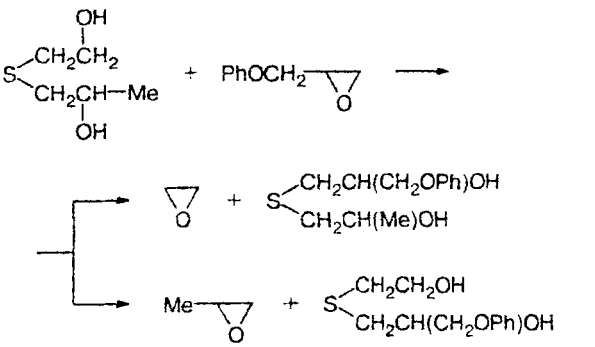
Scheme 3



It should be emphasized that all the above reactions are reversible.

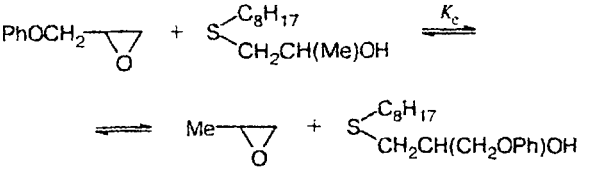
The structures of oxiranes produced in all the systems considered above are determined by the structures of the β-hydroxyalkyl groups present in the starting sulfide.[1—3] Thus the reaction of (β-hydroxyethyl) (β-hydroxypropyl) sulfide with glycidyl phenyl ether yields ethylene oxide and propylene oxide (Scheme 4).

Scheme 4



As a rule, exchange reactions of oxiranes with β-hydroxyalkyl sulfides do not give any side products. For example, the reaction of glycidyl phenyl ether with (β-hydroxypropyl) (*n*-octyl) sulfide yields only propylene oxide and (β-hydroxy-γ-phenoxypropyl) (*n*-octyl) sulfide (Scheme 5).

Scheme 5



This is also confirmed by the fact that the material balance is fulfilled during the whole process. After several hours, the system reaches a dynamic equilibrium (the equilibrium constant K_e = 3.03 at 150°C, Fig. 1). The K_e value for this reaction virtually does not change when the initial concentrations of sulfides vary from 2 to 4.2 mol L^{-1} and those of oxirane vary from 4.1 to 0.7 mol L^{-1} for molar ratios of 1 : 2, 1 : 1, 2 : 1, and 5.5 : 1 (3.0—3.05) and for temperature in the 140—190 °C range (3.0—3.06). The heat of this reaction $Q \approx 0$.

When propylene oxide is made to react with (β-hydroxy-γ-phenoxypropyl) (*n*-octyl) sulfide (the reverse reaction, see Scheme 5), glycidyl phenyl ether and (β-hydroxypropyl) (*n*-octyl) sulfide are formed as the only reaction products. In this system, a dynamic equilibrium is also established, $K_e' = 0.33$, *i.e.*, $1/K_e' = K_e = 3.03$, which is consistent with the value given above.[3] The time it takes to react to equilibrium decreases from

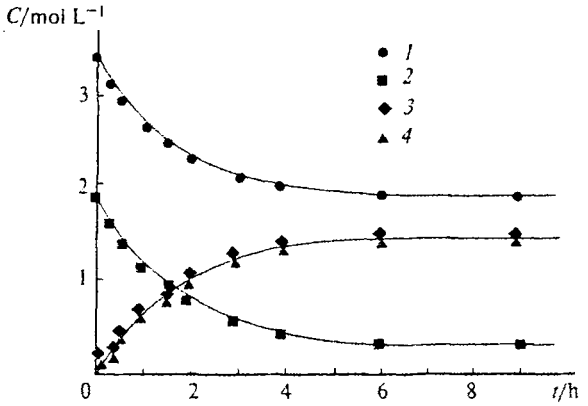


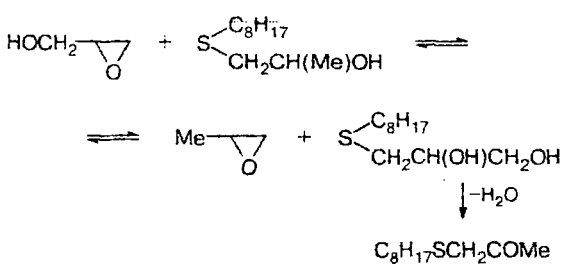
Fig. 1. Kinetic curves for the consumption of glycidyl phenyl ether (*1*) and (β-hydroxypropyl) (*n*-octyl) sulfide (*2*) and accumulation of propylene oxide (*3*) and (β-hydroxy-γ-phenoxypropyl) (*n*-octyl) sulfide (*4*) at 150 °C; chlorobenzene as the solvent.

8—10 h at 140 °C to 2 h at 180°C. For an exchange reaction, this time depends substantially on the structure of the starting compounds. Under comparable conditions (150°C, chlorobenzene as the solvent, oxirane and sulfide concentrations 2.0—3.0 and 2.0—3.0 mol L^{-1}, respectively), equilibrium in the reaction of glycidyl phenyl ether with (β-hydroxyethyl) (*n*-octyl) sulfide is attained in ~50 min. When the concentrations of the initial components are low, the time is much longer. For example, for concentrations of propylene oxide and (β-hydroxyethyl) (*n*-octyl) sulfide of 0.75 and 0.063 mol L^{-1}, respectively, equilibrium in chlorobenzene is attained in ~100 h at 150 °C.

The heats of reactions of glycidyl phenyl ether with (β-hydroxypropyl) [phenyl, (*p*-tolyl), (*n*-octyl)] sulfides are between −3.7 and 0 kcal mol^{-1}.

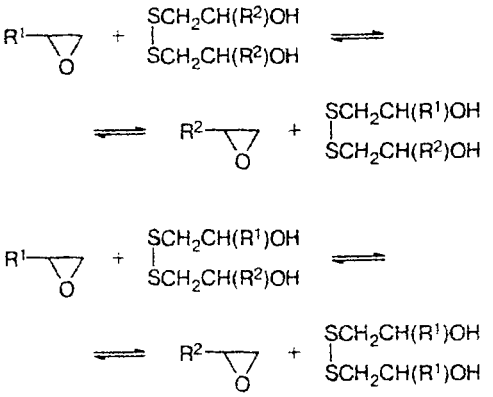
In some cases, the process as a whole becomes irreversible. Thus no dynamic equilibrium is established in the reaction of glycidol with (β-hydroxypropyl) (*n*-octyl) sulfide. This is due to the pinacol rearrangement of the dihydroxyalkyl sulfide formed in the reaction, giving rise to a compound containing no β-hydroxyalkyl group[3,4] (Scheme 6).

Scheme 6



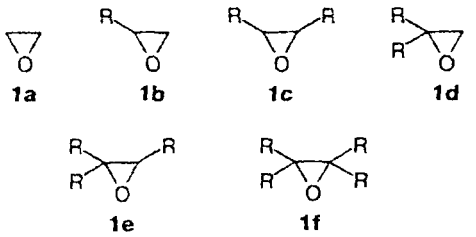
The reactions involving bis(β-hydroxyalkyl) sulfides yield oxathianes as side products resulting from dehydration of sulfides.[5] The exchange reaction in the oxirane—bis(β-hydroxyalkyl) disulfide system follows a similar route; it is accompanied by side processes[2] (Scheme 7).

Scheme 7



R^1 = H, Me, CH_2OPh; R^2 = H, Me

In all the above examples, ethylene oxide (**1a**) and monosubstituted oxiranes **1b** were used; however, one can expect that similar reactions would also proceed for di-, tri-, and tetrasubstituted oxiranes (**1c—f**).



Steric hindrance seems to be the crucial factor influencing the reactivity of compounds of type **1c,e,f**, which should be less reactive than oxiranes **1a,b,d**. This assumption is consistent with the decrease in the relative rate constants *k* for the nucleophilic reaction of $^-SCH_2CH_2OH$ with oxiranes in the sequence **1a** > **1b** > **1c** > **1e** > **1f** ($1.2 \cdot 10^4$, $5 \cdot 10^3$, $5 \cdot 10^1$, $3 \cdot 10^1$, and 1, respectively).[6]

The methods of synthesis and several physicochemical parameters of hydroxyalkyl sulfides and hydroxyalkyl disulfides have been published previously.[7,8]

The mechanism of exchange reaction

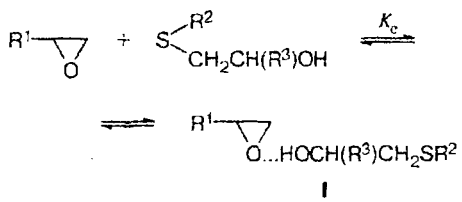
The main kinetic features and quantitative characteristics of exchange reactions were studied in the oxirane—β-hydroxyalkyl sulfide system. In all cases, the order of the reaction with respect to oxiranes is equal to 1, while that with respect to the β-hydroxyalkyl sulfide varies from 1 to 2 as its concentration increases.[3,9] The introduction of proton-donating

compounds into the system accelerates the exchange.[3,10–12]

We considered the possible mechanisms of the exchange reaction for dilute and concentrated solutions of β-hydroxyalkyl sulfides.

The mechanism of exchange reaction for dilute solutions of β-hydroxyalkyl sulfides (the forward reaction). The reaction mechanism in dilute solutions of β-hydroxyalkyl sulfides (concentration ≤0.1–0.15 mol L^{-1}), with allowance for the first order with respect to each component, includes several steps.[1,2,10,13] The first step is the formation of H-complex (**I**) (Scheme 8), which was established by spectral and kinetic methods.[14,15]

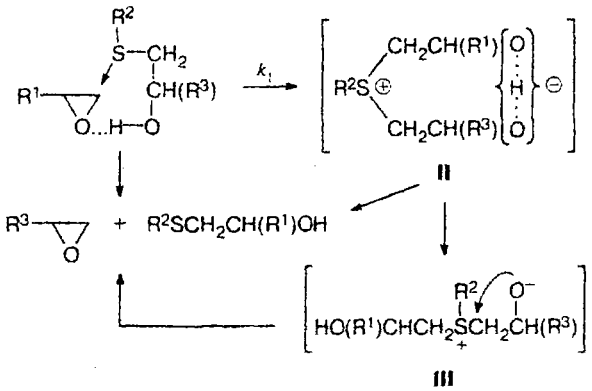
Scheme 8



I

The second step is the nucleophilic attack by the sulfide on the oxide ring within complex **I**: the C—O bond in this complex is highly polarized, which facilitates the attack. As a result, the H-complex undergoes a monomolecular transformation with synchronous cleavage and formation of the corresponding bonds to give the reaction products either directly or through transition into an intermediate unstable cyclic bipolar ion with an intramolecular hydrogen bond (**II**)[3] and then into bipolar ion (**III**).[3,10,16] Closure of the oxirane ring with simultaneous cleavage of the S—CH_2 bond in **III** affords the sulfide (Scheme 9).

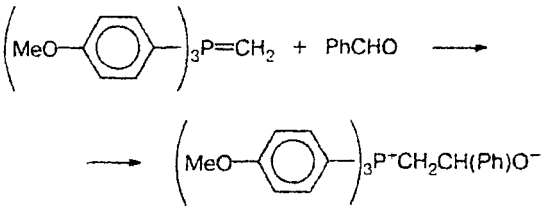
Scheme 9



II

III

It is noteworthy that the existence of complexes with fragments of the $(A...H...B)^+$ and $(A...H...B)^-$ type has been detected in the ionization of organic compounds in solutions of acids and bases.[17–21] The formation of bipolar ions of type **III** as intermediate compounds has been assumed in numerous studies. In the reaction of phosphorane having strong electron-donating substituents with benzaldehyde, a betaine of this type was isolated and proved to be stable.[22]



Thus, the route

I → **II** → **III** → Reaction products

appears to be more probable.

The kinetic parameters and the enthalpies of formation of the H-bonds for the forward exchange reactions of four pairs of oxiranes and β-hydroxyalkyl sulfides are listed in Table 1.[13] The activation energy of the reactions between ethyl oxirane and (β-hydroxypropyl) [phenyl, (*p*-tolyl), and (*n*-octyl)] sulfides decreases in the series Ph > MeC_6H_4 > C_8H_{17}, which is due to the enhancement of the electron-donating ability of the substituents. The heats of formation of the H-complexes correspond to the heats of formation of hydrogen bonds between the oxiranes and alcohols.[23–25]

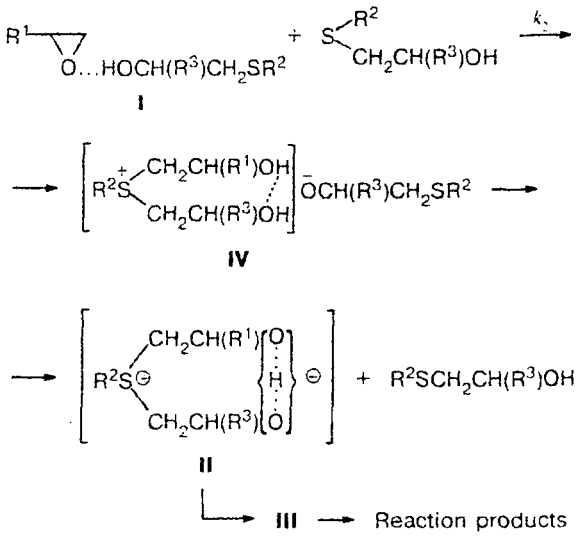
The mechanism of the exchange reaction in concentrated solutions of β-hydroxyalkyl sulfides (the forward reaction). Consideration of reactions for concentrations of β-hydroxyalkyl sulfides of ≥0.3 mol L^{-1}, with allowance for the first order with respect to oxiranes and the second order with respect to sulfides, leads to the conclusion that formation of H-complex **I** is followed by nucleophilic attack on the oxirane ring by a second molecule of β-hydroxyalkyl sulfide to give sulfonium salt (**IV**) as an intermediate species[3,10,16] (Scheme 10).

Sulfonium salts are known to be formed as intermediates or products in the reactions of oxiranes with sulfides.[26–31] These salts can decompose giving rise to oxiranes.[26,32]

Table 1. Kinetic parameters of the exchange reaction and the enthalpy of formation of H-complexes (**I**) for the oxirane–β-hydroxyalkyl sulfide system for dilute solutions (see Scheme 8)

R^1	R^2	R^3	$A \cdot 10^{-9}$ /s^{-1}	E	$-\Delta H$
				kcal mol^{-1}	
Et	Ph	Me	2.2	32.1	2.9
Et	MeC_6H_4	Me	1.6	31.5	2.8
Et	C_8H_{17}	Me	0.17	28.4	3.3
Me	C_8H_{17}	H	1.52	29.4	2.0

Scheme 10



Sulfonium salt **IV** contains two β-hydroxyalkyl groups linked apparently by an intramolecular hydrogen bond, which is favored by its pyramidal structure.[33]

The formation of the sulfonium salt is the rate-determining step of the whole process. It was found[16] for the forward exchange reaction in the propylene oxide—(β-hydroxyethyl) (*n*-octyl) sulfide system that $k_2 = 2.37 \cdot 10^5\{\exp[-19350/(RT)]\}$ L mol^{-1} s^{-1}; the values of k_2 for other systems at 150 °C are listed in Table 2.

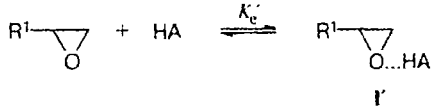
Decomposition of salt **IV** starts with deprotonation of the OH group, which is facilitated by the presence of the sulfonium group in the β-position. This gives rise to bipolar ion **II** with an intramolecular hydrogen bond and delocalized negative charge; simultaneously, the initial β-hydroxyalkyl sulfide molecule is regenerated. Decomposition of bipolar ion **II** results in ion **III**, which is converted into the same final products as in dilute solutions.

Catalytic effect of proton-donating compounds. Replacement of chlorobenzene used as the solvent by benzene, a mixture of decane with chlorobenzene, or acetonitrile did not result in any changes in the exchange reaction rates.[16] However, the reaction rate sharply increased in the presence of proton-donating additives (HA).[11,12] The influence of these additives on the reaction rates in concentrated solutions follows directly from the scheme of the exchange process; in terms of the proposed mechanism, it is due to the formation of H-complex (**I'**) in the first step of the reaction (Scheme 11).

Table 2. Rate constants for the exchange reaction (k_2) for concentrated solutions of β-hydroxypropyl sulfides at 150 °C (see Scheme 10, R^3 = Me)

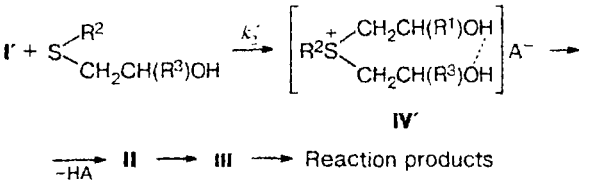
R^1	R^2	$k_2 \cdot 10^4$ /kcal mol^{-1} s^{-1}
CH_2OPh	C_8H_{17}	8.4
CH_2OPh	C_6H_4Me	1.9
CH_2OPh	Ph	0.7
CH_2OEt	C_8H_{17}	3.7

Scheme 11



In the presence of proton-donating compounds, the processes presented in Schemes 8—10 can be accompanied by other reactions[11,12] (Scheme 12).

Scheme 12



Sulfonium salt (**IV'**) and bipolar ions (**II** and **III**) are formed as intermediates. Decomposition of **III** leads to the same compounds as in the absence of HA.

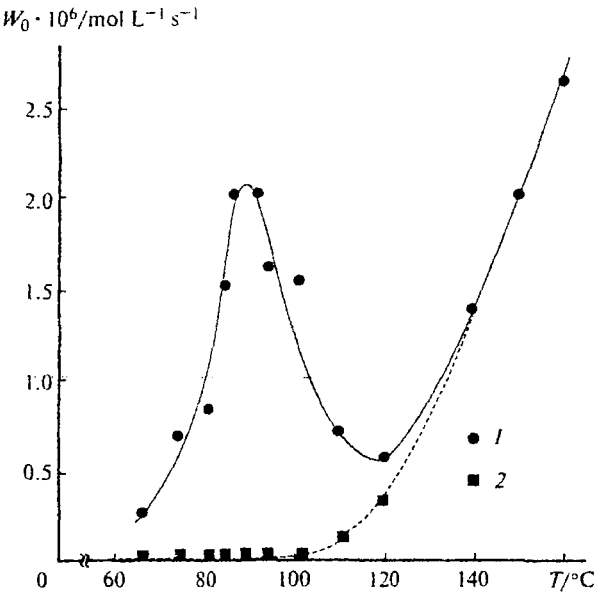


Fig. 2. Temperature dependence of the initial rate of the reaction of propylene oxide (C_0 = 0.55 mol L^{-1}) with (β-hydroxyethyl) (octyl) sulfide (C_0 = 2.5 mol L^{-1}) (*1*) and that taking into account only pathways with k_1 and k_2 (*2*); chlorobenzene as the solvent.

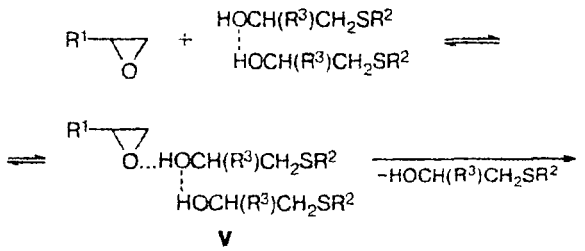
In terms of the catalytic activity in this reaction, the proton-donating additives can be arranged in the following order[12] ($k_2' \cdot 10^4$/L mol^{-1} s^{-1} in chlorobenzene at 150°C): $C_8H_{17}SCH_2CH_2OH$ (0.23) < PhOH (2.5) ≈ CD_3COOD (2.7) < MeCOOH (7.46) < $CH_2ClCOOH$ (160).

The phenomenon of negative temperature coefficient in exchange-type reactions.[16] The dependence of the initial rate (W_0) of the forward reaction of propylene oxide with (β-hydroxyethyl) (*n*-octyl) sulfide on temperature in the 60—100°C range passes through a maximum at 90°C (Fig. 2). This finding cannot be explained in terms of Schemes 8—10. The initial rates calculated taking into account Schemes 8, 9, and 10 (W_0') for the temperature range of 60—120°C amount to 50, 10, and ≤1—2.5% of the overall reaction rate W_0 at 120, 110, and 60—95°C, respectively.

As a rule, abnormal temperature dependences are due to a change in the ratios of concentrations of various forms of self-associates of alcohols and the difference between their reactivities.[34]

The effect observed in this particular case can be rationalized by assuming the formation of H-complex (**V**) from the oxirane molecule and β-hydroxyalkyl sulfide dimer, which is more reactive than H-complex **I** and participates in the exchange reaction (Scheme 13).

Scheme 13



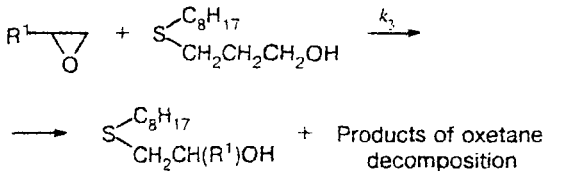
The proton-donating ability and nucleophilicity of β-hydroxyalkyl sulfide increase upon dimerization; this increases the probability of migration of the proton of the OH group to oxygen of the oxide ring and charge redistribution in associate **V**[35]; in other words, the role of the second β-hydroxyalkyl sulfide molecule, like any other proton-donating compound in the associate, is eventually reduced to the activation of the epoxide ring.

The products of the exchange reaction involving associate **V** are formed *via* the corresponding intermediates **II** and **III**, *i.e.*, in the same way as in dilute solutions of β-hydroxyalkyl sulfides.

The regularities of proton transfer in systems with hydrogen bonds have been considered previously.[36,37]

Exchange reaction of oxiranes with γ- and δ-hydroxyalkyl sulfides. Reactions of oxiranes with (γ-hydroxypropyl) (*n*-octyl) sulfide afford the corresponding (β-hydroxyalkyl) (*n*-octyl) sulfides. This was accompanied by the formation of side products, apparently, due to decomposition of oxetane[3] (Scheme 14).

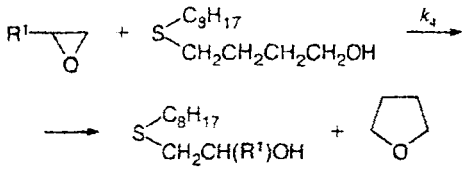
Scheme 14



R^1 = Me, Ph, CH_2OBu, CH_2OPh;
for R^1 = Me $k_2^{eff} = 2.5 \cdot 10^{-6}$ L mol^{-1} s^{-1} (150 °C, chlorobenzene)[3]

The reactions of oxiranes with (δ-hydroxybutyl) (*n*-octyl) sulfide yield the corresponding (β-hydroxyalkyl) (*n*-octyl) sulfide and tetrahydrofuran[3] (Scheme 15).

Scheme 15



R^1 = Me, Ph, CH_2OBu, CH_2OPh;
for R^1 = Me $k_4^{eff} = 2.6 \cdot 10^{-6}$ L mol^{-1} s^{-1} (150 °C, chlorobenzene)

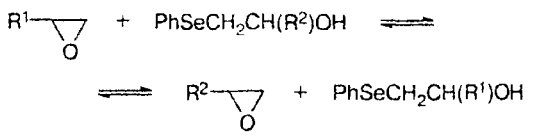
In both reactions, the formation of sulfonium salts without an intramolecular H-bond is possible; decomposition of this salt is accompanied by elimination of one proton of the OH-group under the action of the counter-ion; this gives rise to bipolar ion **III**, which is converted into the reaction products.

Exchange reactions of oxiranes with β-hydroxyalkyl selenides, β-hydroxyalkylamines, and -phosphines

The assumption that exchange reactions pass through the formation and decomposition of intermediate onium derivatives suggests that processes of this type can also occur for compounds of other elements of the Periodic Table that are able to form onium salts. These salts are known for Se, N, and P compounds; some of them were prepared using oxiranes.[38—42] It should be noted that exchange reactions involving Se, N, and P derivatives, accompanied by the formation of side products, can be interpreted as being due to decomposition of onium derivatives (*via* the corresponding bipolar ions $Z^+CH_2CH(R)O^-$ (see below)).

It was found[43] that the exchange reaction of oxiranes with β-hydroxyalkyl phenyl selenides performed at 150 °C without a solvent follows Scheme 16.

Scheme 16



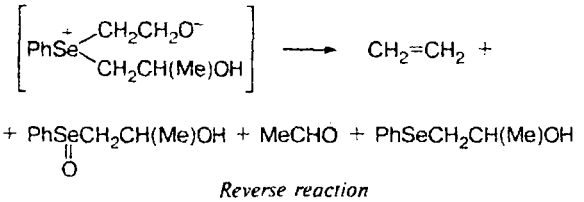
R^1 = Me, CH_2Cl, $CH{=}CH_2$, Ph, CH_2OEt, CH_2OBu, CH_2OPh; R^2 = H, Me

The reversibility of the reaction was demonstrated with a pair of β-hydroxyalkyl selenides, *viz.*, $PhSeCH_2CH_2OH$ and $PhSeCH_2CH(Me)OH$. The formation of alkenes, carbonyl compounds, and other compounds was observed. For example, in the propylene oxide (8.67 mol L^{-1})—(β-hydroxyethyl) (phenyl) selenide (2.71 mol L^{-1}) system, small amounts of ethylene, propylene, acetaldehyde, acetone, and other products were detected in addition to the exchange reaction products at 60% conversion of the selenide (159 °C, 3.5 h).

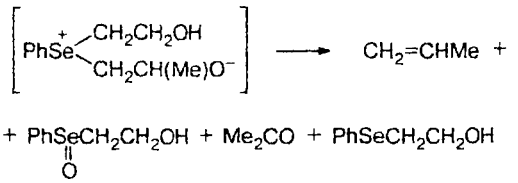
The formation of side products can be presented by Scheme 17.

Scheme 17

Forward reaction

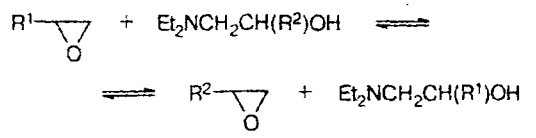


Reverse reaction



Oxiranes and dialkyl(β-hydroxyalkyl)amines also undergo exchange reactions[44] (Scheme 18).

Scheme 18



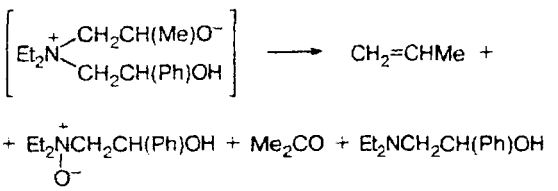
R^1 = Me, $CH{=}CH_2$, Et, CH_2OPh; R^2 = Me, Ph

The reversibility of these processes was shown for the reactions of styrene oxide with $Et_2NCH_2CH(Me)OH$ and of propylene oxide with $Et_2NCH_2CH(Ph)OH$. The side products obtained included carbonyl compounds, alkenes, and other compounds. For example, the reaction of styrene oxide (4.39 mol L^{-1}) with 1-diethylaminopropan-2-ol (3.27 mol L^{-1}) at 150 °C for 12 h was found to give propylene ($1.4 \cdot 10^{-2}$ mol L^{-1}), styrene ($4.1 \cdot 10^{-2}$ mol L^{-1}), acetone ($0.6 \cdot 10^{-2}$ mol L^{-1}), and acetophenone (0.83 mol L^{-1}), together with the expected propylene oxide (0.39 mol L^{-1}) and the corresponding amine (1.3 mol L^{-1}). The oxiranes (both the starting compound and the product), apparently, partly polymerize.

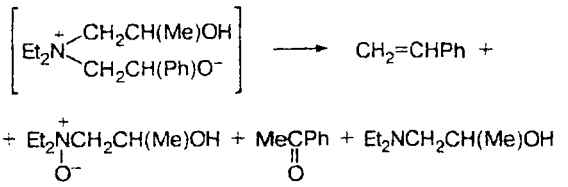
The formation of side products can be illustrated by Scheme 19. The *N*-oxide seems to be unstable under experimental conditions.

Scheme 19

Forward reaction



Reverse reaction



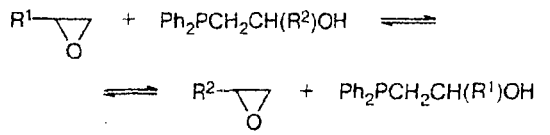
Some of the compounds formed according to Schemes 18 and 19 were also detected upon decomposition of choline and its derivatives.[38]

The major products obtained from oxiranes and dialkyl(β-hydroxyalkyl)phosphines are alkenes, carbonyl compounds, and other compounds. For instance, the reaction of (β-hydroxyethyl)diphenylphosphine (0.65 mol L^{-1}) with propylene oxide (3.0 mol L^{-1}) carried out in chlorobenzene at 150°C for 1 h gave ethylene (0.47 mol L^{-1}), acetaldehyde (0.014 mol L^{-1}), propylene (0.022 mol L^{-1}), acetone ($4.6 \cdot 10^{-4}$ mol L^{-1}), and a small amount of ethylene oxide (0.031 mol L^{-1}). The degree of conversion of the starting phosphine was ~83%; ethylene oxide accounts for 5%.[45]

The formation of ethylene oxide is presented in Scheme 20.

The reaction was carried out at 90—150°C in chlorobenzene. It was found[45] to be reversible for pairs of reactants in which R^1 = H, R^2 = Me and R^1 = Me, R^2 = H; R^1 = Ph, R^2 = Me and R^1 = Me, R^2 = Ph.

Scheme 20



R^1 = Me, $CH{=}CH_2$, Ph, CH_2OEt, CH_2OBu; R^2 = H, Me, Ph

The reversibility of reactions involving S, Se, N, and P compounds might be due to the prototropic tautomeric equilibrium established between bipolar ions and a bipolar ion with an intramolecular hydrogen bond formed as an intermediate adduct.

A general scheme of the formation of all the products indicated above using the reaction of oxiranes with (β-hydroxyalkyl)diphenylphosphine as an example should take into account the possibility of formation of bipolar ions of the $R_3P^+CCO^-$ type and a bipolar ion with an intramolecular bond. Adducts of the $R_3P^+CCO^-$ type are known to arise when phosphonium ylides react with carbonyl compounds[22] or oxiranes react with tertiary phosphines.[46] They decompose according to four pathways to give the following products: alkenes and phosphine oxides,[46] ketones and phosphines,[47] ylides and carbonyl compounds,[46] or oxiranes and phosphines[45,48] (Scheme 21). This type of decomposition is also known for analogous compounds of nitrogen[38] and arsenic.[49]

For the reaction of (β-hydroxyethyl)diphenylphosphine with oxiranes, the ratio of the rates of accumulation of ethylene oxide and ethylene in the reaction mixture (W_1/W_2) was found; this value was defined as the ratio of the yields of these products during the first hour of the reaction. This ratio was found to increase in the following series of the oxirane substituents R^1: Me (0.07), $PhOCH_2$ (0.50), Ph (1.50), $CH_2{=}CH$ (20). In other words, when $R^1 = CH_2{=}CH$, the decomposition of the bipolar ion follows predominantly the pathway leading to ethylene oxide, whereas for R^1 = Me, ethylene is the major product.

Now we compare the influence of Se and P atoms in the corresponding bipolar ions on the yields (mol L^{-1}) of the products of forward reactions

$PhSeCH_2CH_2OH$ + propylene oxide →

→ ethylene oxide, (1.52); ethylene, ($3.4 \cdot 10^{-3}$); acetaldehyde ($0.6 \cdot 10^{-3}$)

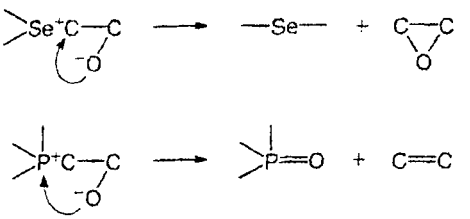
and

$Ph_2PCH_2CH_2OH$ + propylene oxide →

→ ethylene oxide, (0.03); ethylene, (0.47); acetaldehyde, (0.014)

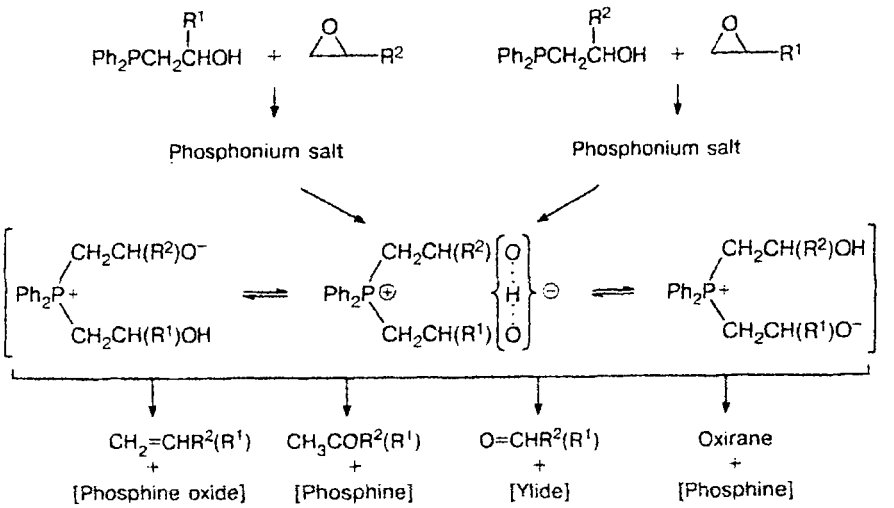
In the former case, ethylene oxide is formed predominantly (99.7%) (the attack in the bipolar ion is directed at C_α), while in the latter case, the major product is ethylene (91.4%) (the attack in the bipolar ion is directed at phosphorus) (Scheme 22).

Scheme 22



In conclusion we would like to note that the results of studies surveyed in this paper reflect only a minor fraction of the potentialities inherent in the exchange reaction and in the accompanying reactions. In our opinion, studies of the exchange reactions involving organic compounds containing other Group VA and Group VIA elements would be equally interesting.

Scheme 21



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