EXCHANGE REACTIONS IN OLEFIN OXIDE – PHENYL β-HYDROXYALKYL SELENIDE SYSTEM

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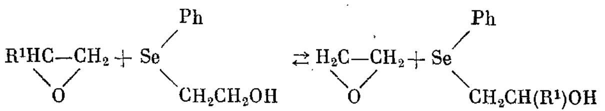
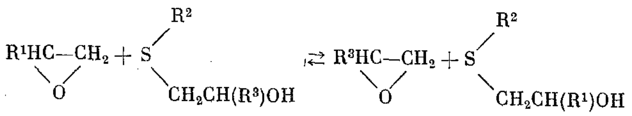
We checked the possible progress of the exchange reaction for the olefin oxide–phenyl β-hydroxyethyl selenide system. The reaction equation for this system can be written as follows:


(1)

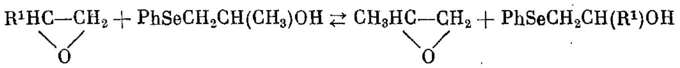
where $R^1 = CH_3$, CH_2Cl, $CH{=}CH_2$, C_6H_5, $CH_2OC_2H_5$, $CH_2OC_4H_9$, $CH_2OC_6H_5$

Together with ethylene oxide, which is formed in all cases, a second reaction product was detected, which was assigned to the corresponding phenyl β-hydroxyalkyl selenide. The structure of the formed selenide should be determined by the structure of the starting olefin oxide, the same as for the analogous olefin oxide–R β-hydroxyalkyl sulfide system in the exchange reaction given in [1]:


(2)

Some of the properties of the selenides obtained by the reaction are given in Table 1. The degree of conversion for the first three olefin oxides varies from 10 to 50% at an ~1:2 ratio of the starting components, and for the others it varies from 7 to 20% at a 1:1 ratio, a temperature of 159°C, and a reaction time of 5.5 h.

When $R^1 = CH_3$, we obtained $PhSeCh_2CH(CH_3)OH$ by reaction (1), which when reacted with ethylene oxide and phenyl glycidate gave propylene oxide and the corresponding selenide:


(3)

$R^1 = H$, CH_2, OC_6H_5

The formation of propylene oxide in reaction (3) indicates that the starting selenide contains the β-hydroxypropyl group.

An examination of reactions (1) with $R^1 = CH_3$ and (3) with $R^1 = H$ points to the reversible character of the process.

By analogy with the olefin oxide–R β-hydroxyalkyl sulfide system [2], exchange reaction (1) can be depicted as going via the formation of the intermediate selenonium salt (I), whose decomposition leads to the formation of zwitterion (II). Further transformations of (II) gives the end reaction products:

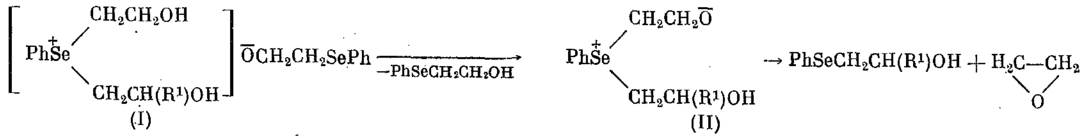

(4)

TABLE. 1. τ_{sp} and R_f Values of Selenides $PhSeCH_2CH(R')OH$ Obtained by Reaction (1)

R^1	τ_{sp}, min	R_f	R^1	τ_{sp}, min	R_f
CH_3	2,1	0,59	$CH_2{=}CH$	7,5	0,73
H	2,9	0,61	$C_6H_5OCH_2$	11,8	0,89
$C_2H_5OCH_2$	4,2	0,62	C_6H_5	13,5	0,89
$C_4H_9OCH_2$	6,65	0,72			

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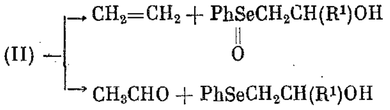
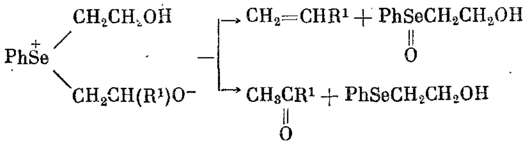
The reversible character of the reaction is also explained by such a scheme, and also the formation of a small amount of by-products when the direction of the decomposition of zwitter ion (II) is different (direct direction of the reaction):



$$(II) \rightarrow \begin{cases} CH_2{=}CH_2 + PhSe(O)CH_2CH(R^1)OH \\ CH_3CHO + PhSeCH_2CH(R^1)OH \end{cases} \quad (5)$$

Zwitterion (II') is characteristic for the reverse direction, during whose decomposition by-products can be formed.



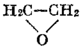
(II')

(6)

EXPERIMENTAL

The GLC analysis was run on an LKhM-8MD chromatograph equipped with a flame-ionization detector and using N_2 as the carrier gas; for the gaseous and low-boiling compounds we used a 2 m × 3 mm column packed with 10% PEG-400 deposited on C-545 and a temperature of 60-150°; for the selenides we used a 1 m × 3 mm column packed with 15% PEGA deposited on C-22 and a temperature of 190-250°. Except for phenyl β-hydroxyethyl selenide, the selenides were not analyzed quantitatively. The TLC analysis was run on Silufol (ethanol:benzene, 2:8) at ~20°, and detection was with iodine vapors. The PMR spectra were recorded on a Varian HA-100 spectrometer at 29° using 30-50% CCl_4 solutions and HMDS as the internal standard; the chemical shifts are given on the δ scale and the accuracy of the measurements is ±0.02 ppm; the accuracy of measuring the spin–spin coupling constants is ±0.2 Hz. The exchange reactions were run without a solvent in 0.04-ml glass ampuls, which were thermostatted at 159°.

Reaction of Propylene Oxide with Phenyl β-Hydroxyethyl Selenide. A mixture of propylene oxide (III) (8.67 moles/liter) and phenyl β-hydroxyethyl selenide (IV) (2.71 moles/liter) was kept in glass ampuls for 3.5 h at 159°. The starting components and reaction products were identified and quantitatively determined by GLC. Analysis results, moles/liter (the selenoxides were not identified):

(III)	(IV)		$PhSeCH_2CH(CH_3)OH$	$CH_2{=}CH_2$	CH_3CHO	$CH_2{=}CHCH_3$	CH_3COCH_3.
6,97	1,10	1,52	1,61 (consumption of starting selenide)	$3.4 \cdot 10^{-3}$	$0.61 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	$0.55 \cdot 10^{-3}$

The degree of conversion based on selenide is 60%. The formation of the exchange reaction products, namely ethylene oxide and phenyl β-hydroxypropyl selenide, is the main direction. The secondary directions constitute 0.25% of the main direction.

Synthesis of Phenyl β-Hydroxyethyl Selenide. With stirring, to 2.37 ml (3.52 g, 0.022 mole) of benzeneselenol was added in an argon atmosphere 9.1 ml of 10% aqueous NaOH solution (0.023 mole). Then 1.61 ml (1.93 g, 0.024 mole) of ethylene chlorohydrin was added in 15 min and the mixture was stirred for another hour. The lower layer was separated, dried over Na_2SO_4, and then vacuum-distilled to give the chromatographically pure phenyl β-hydroxyethyl selenide in 90% yield, bp 148-149° (1-2 mm), $d_4^{23.5}$ 1.43 02 g/cm³, n_D^{25} 1.6072. Found: C 47.62; H 4.90; Se 39.09%. $C_8H_{10}OSe$. Calculated: C 47.77; H 5.01; Se 39.26%. PMR spectrum: 2.83 t (2H, $SeCH_2$; J = 7.0 Hz), 3.57 t (2H, OCH_2; J = 7.0 Hz), 3.79 s (1H, OH), 6.95-7.45 m (5H, C_6H_5).

CONCLUSIONS

Exchange reactions proceed in the olefin oxide–phenyl β-hydroxyalkyl selenide system with the probable intermediate involvement of the selenonium salt.

LITERATURE CITED

1. A. D. Malievskii, V. V. Vints, and V. N. Parfenov, Izv. Akad. Nauk SSSR, Ser. Khim., 1559 (1973).
2. A. D. Malievskii and V. V. Vints, Izv. Akad. Nauk SSSR, Ser. Khim., 2702 (1977).