

Regioselectivity of the ring opening in the reaction of phenyloxirane, (phenylmethyl)oxirane and (2-phenylethyl)oxirane with K^+ , $K^+(15\text{-crown-5})_2$

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Abstract

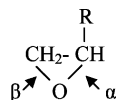
The electron from potassium anion of K^+ , $K^+(15\text{-crown-5})_2$ (**1**) is initially transferred to the aromatic ring of phenyloxirane and (phenylmethyl)oxirane. The oxirane ring is then opened exclusively in the α -position. Two dimeric products, i.e. dipotassium 2,3-diphenylbutane-1,4-dioxide and dipotassium 1,3-diphenylbutane-1,4-dioxide are formed in the case of phenyloxirane. A mixture of several potassium alkoxides involving 3-phenylpropoxide, 3-phenylallyloxide, tetraethylene glycoxide vinyl ether, and appropriate alcohols, i.e. 3-phenyl-1-propanol, 3-phenylallyl alcohol, and tetraethylene glycol vinyl ether, is obtained in the reaction of **1** with (phenylmethyl)oxirane. However, introduction of the second CH_2 group into the substituent results in the β -opening of the oxirane ring in (2-phenylethyl)oxirane. Potassium 4-phenylbutane-2-oxide, and potassium tetraethylene glycoxide vinyl ether are the main reaction products in this case. Organometallic intermediates take part in all these processes.

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1. Introduction

The three-membered oxacyclic ring in monosubstituted oxiranes can be opened in two ways since its two carbon–oxygen bonds are different. The $CH-O$ scission is usually called as the ring opening in the α -position and the CH_2-O one as in the β -position [1]:



In general, a nucleophile attacks the more substituted carbon in acid-catalyzed cleavage (the α -opening), and the less substituted in base-catalyzed cleavage (the β -

opening) [2]. However, some exceptions are known to this rule, e.g. in the case of phenyloxirane reaction with bases.

The regioselectivity of the ring opening in phenyloxirane was discussed firstly in the work [3]. It was found that potassium methoxide opened its ring in the β -position only in 66–75%. The active centres formed in the anionic polymerization of phenyloxirane were more selective giving 83% of the β -cleavage and 17% of the α -cleavage [4]. Similar results were then obtained in the presence of sodium methoxide [5]. The oxirane ring opening occurred in this case in 65% in the β -position and in 35% in the α -position. However, during the polymerization the oxirane ring opening was found to occur almost exclusively in the β -position.

A quite different mechanism of the ring opening was observed in the reaction of phenyloxirane with metallic sodium [6], as well as with lithium naphthalenide or

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potassium biphenylide [7]. Only the α -scission occurred in such cases. This indicated a stabilizing effect of the substituent already during formation of the carbanion [7]. It was suggested that the reaction could be rationalized by a mechanism involving an initial single electron transfer leading to the formation of an intermediate radical anion.

It means that the course of the reaction depended on the kind of the nucleophile. The common bases, as for example alkali metal alkoxides, opened the oxacyclic ring in phenyloxirane in both the possible positions, however, the β -scission was preferred. The electron transfer reagents caused exclusively the α -scission.

In contrast to these findings it was later reported that two electron transfer from the metal anion of K^- , $K^+(18\text{-crown-6})$ to phenyloxirane in tetrahydrofuran solution gave the ring opening to 70% in the β -position and to 30% in the α -position [8]. However, it could not be excluded that such a result was connected with the chemical composition of the alkalide solution used. It contains not only potassium anions and complexed cations but also a mixture of dipotassium oligoethylene glycoxides [9]. The latter are formed already during the preparation of the solution at ambient temperature. The reactions of potassium anions with 18-crown-6 and with products of its destruction proceed in that case. Most likely the potassium glycoxides formed participated in the reaction with phenyloxirane. Each of them possessed two active centres capable to initiate the polymerization with the ring opening mainly in the β -position. That might be one of possible reasons of the results found in the work [8].

The aim of the present work was to explain the influence of an alkyl group in the substituent on the course of the (phenylmethyl)oxirane and (2-phenylethyl)oxirane reaction with potassium anions. A solution of K^- , $K^+(15\text{-crown-5})_2$ (**1**) in tetrahydrofuran was selected for this study. This system had been found as the most stable among known potassium alkalides solutions [10,11]. The concentration of potassium anions in this solution had not been changed during one hour after its preparation at ambient temperature. That warranted that the potassium anion was the only reagent in the potassium solution. Phenyloxirane was used as a model compound.

2. Results and discussion

In the first series of experiments the solution of **1** was added into phenyloxirane tetrahydrofuran solution. The process was conducted in a similar manner as in the work [12], i.e. at the excess of the oxirane compound. The reaction was very fast at ambient temperature. The blue potassium alkalide solution became colorless immediately after mixing with phenyloxirane. Metal an-

ions vanished at this moment [11]. Then, the reaction mixture was treated with methyl iodide to transform non-volatile reaction products to volatile compounds.

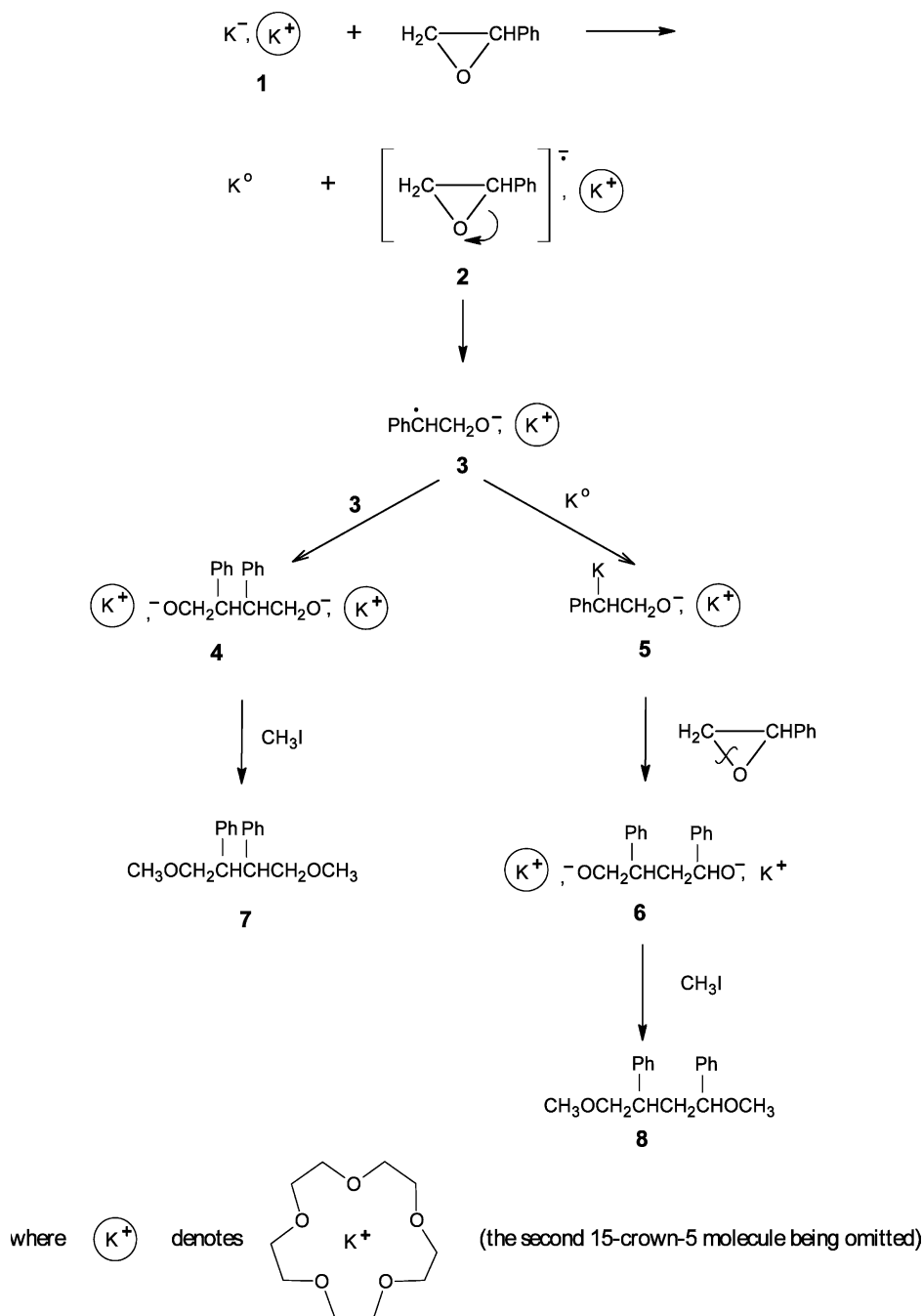
Gas chromatography mass spectrometry (GCMS) analysis of the methylated samples showed the formation of two compounds, i.e. 1,4-dimethoxy-2,3-diphenylbutane (**7**) (in 15% yield) and 1,4-dimethoxy-1,3-diphenylbutane (**8**) (21%). No gaseous products were observed in the liquid and gaseous phase. It means that dipotassium 2,3-diphenylbutane-1,4-dioxide (**4**) and dipotassium 1,3-diphenylbutane-1,4-dioxide (**6**) were formed in the reaction.

Taking into account these results as well as the results of earlier works [6,7] it was assumed that in the initial stage of the process the transfer of one electron from K^- of **1** to the aromatic ring takes place. It leads to the formation of K° and the radical anion **2** (Scheme 1). The existence of the latter was already suggested in Ref. [13]. It decomposes with the oxirane ring opening exclusively in the α -position giving linear radical anion **3**, which then takes part in two reactions. In the first one it undergoes dimerization giving dipotassium 2,3-diphenylbutane-1,4-dioxide (**4**). In the second reaction **3** recombines with K° . The organometallic compound **5** formed reacts with the next phenyloxirane molecule. In this reaction the oxirane ring opening takes place in the β -position leading to the formation of dipotassium 1,3-diphenylbutane-1,4-dioxide without one crown ether molecule **6**. Appropriate ethers **7** and **8** are obtained after methylation.

The β -cleavage during the decomposition of **2** was also taken into account. The resulting radical anion in this case would not only react with **3** to form **6** but it should dimerize, too, giving third isomeric product, i.e. dipotassium 1,4-diphenylbutane-1,4-dioxide. However, appropriate derivatives of this alkoxide were not observed in the reaction mixture after its methylation or benzylation. It confirms our assumption that the β -cleavage does not occur and in fact only the α -opening can be accepted for the reaction of phenyloxirane with **1**.

It is especially remarkable that organometallic compounds were lately found as the crown ring opening reagents [12,14]. In the case of 15-crown-5 such reactions resulted in potassium tetraethylene glycoxide vinyl ether. However, in the present work the methylated derivative of this compound was not found in the first series of experiments. On the other hand, carbanions are known as initiators of the oxirane polymerization [15]. It can be concluded that the reaction of **5** with phenyloxirane is much faster than with crown ether, probably because as a benzylic carbanion it is more nucleophilic and less basic than alkylpotassium compounds.

K° formed from K^- can react with another phenyloxirane molecule similarly as K^- (Scheme 2). A radical anion without crown ether is obtained in this case.



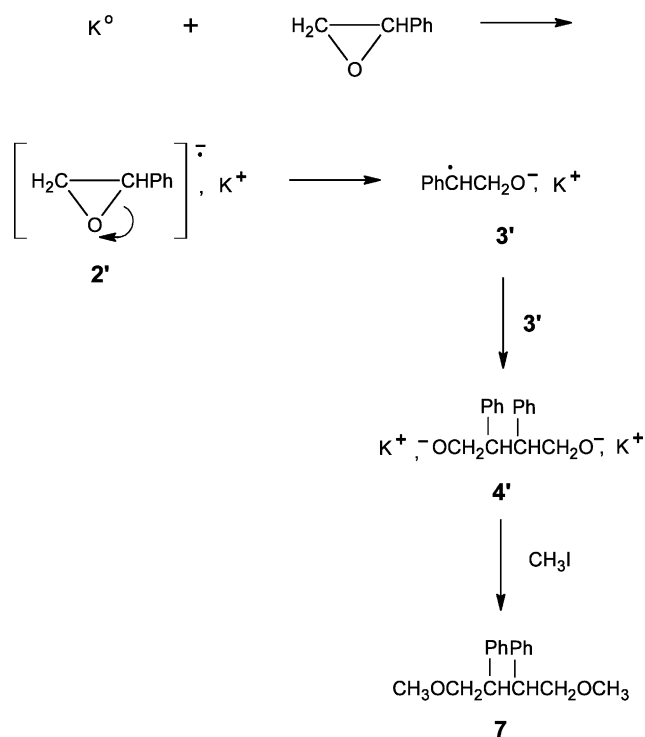
Scheme 1.

However, it can only dimerize giving the final product **7** after methylation.

The reaction of phenyloxirane with potassium biphenylide (**9**) was conducted to confirm the proposed mechanism. The main products of this reaction were the same as in the system containing potassium anions. The difference was connected with the formation of stable biphenyl instead of K^0 . Compound **9** can transfer only one electron to the aromatic ring of phenyloxirane (Scheme 3). Radical anion **3'** formed in this case undergoes dimerization giving **4'** or reacts with the

next molecule of **9** which results in **5'**. The latter can add the phenyloxirane molecule according to the reaction presented in Scheme 1. It is worth noting that Bartmann [7] carried out the reaction of phenyloxirane with **9** at -80°C . The organometallic alkoxide **5'**, stable at this temperature, was the only product of this reaction.

The proposed course of the process is also in a good agreement with the literature data concerning the reaction of metallic sodium with phenyloxirane in tetrahydrofuran [6]. Among three products formed in that system, two were the same as found in the present

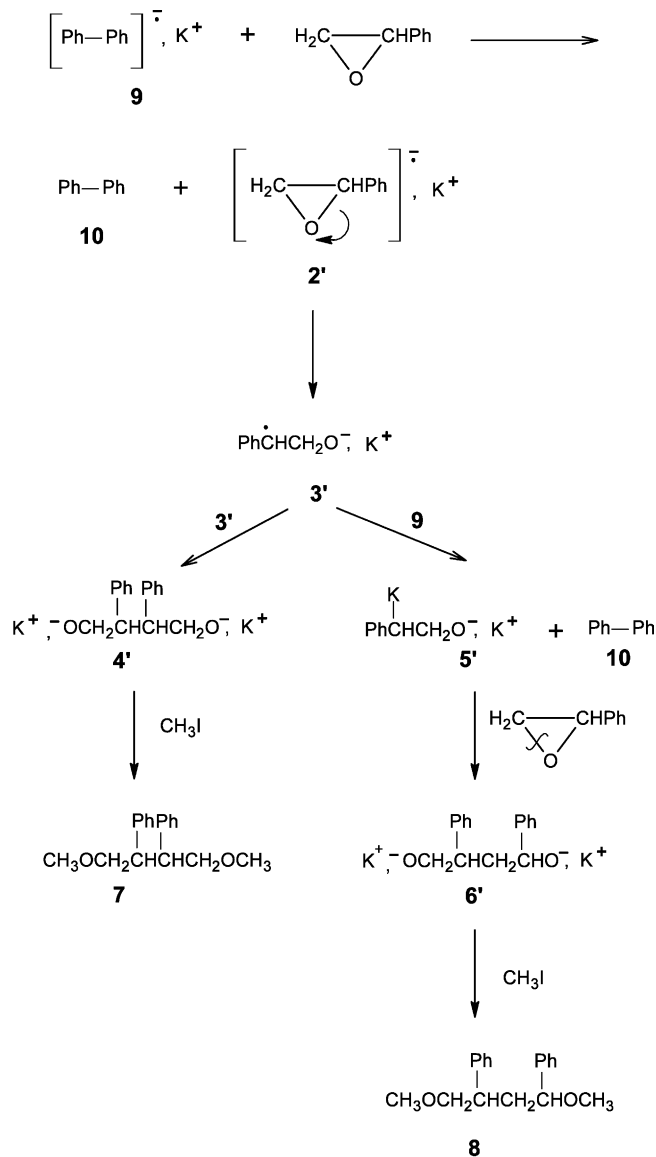


Scheme 2.

work. The third product possessing the cyclic structure was not observed by us.

In the second series of experiments phenyloxirane solution was introduced into **1** solution until its blue color faded. Therefore, potassium anions were still at the excess in the reaction mixture except for the moment of discoloration. After methylation of the reaction mixture the signals of **7**, **8** and several new compounds were found in the chromatogram. Among them was that of tetraethylene glycol methyl vinyl ether, i.e. the methylated product of 15-crown-5 decomposition [12]. It means that the method of substrate delivery influences the course of reaction. A similar effect was observed earlier in the work [16]. Side reactions occurred at the excess of potassium anions. Initial products were destroyed and a mixture of many new compounds was formed. Therefore, such method of substrate delivery can provide to misleading conclusions concerning the reaction mechanism. However, in all these processes $\text{K}^\cdot$ became two-electron-transfer reagent as it has been found in other systems investigated till now [17]. Only one exception is known to this rule [18].

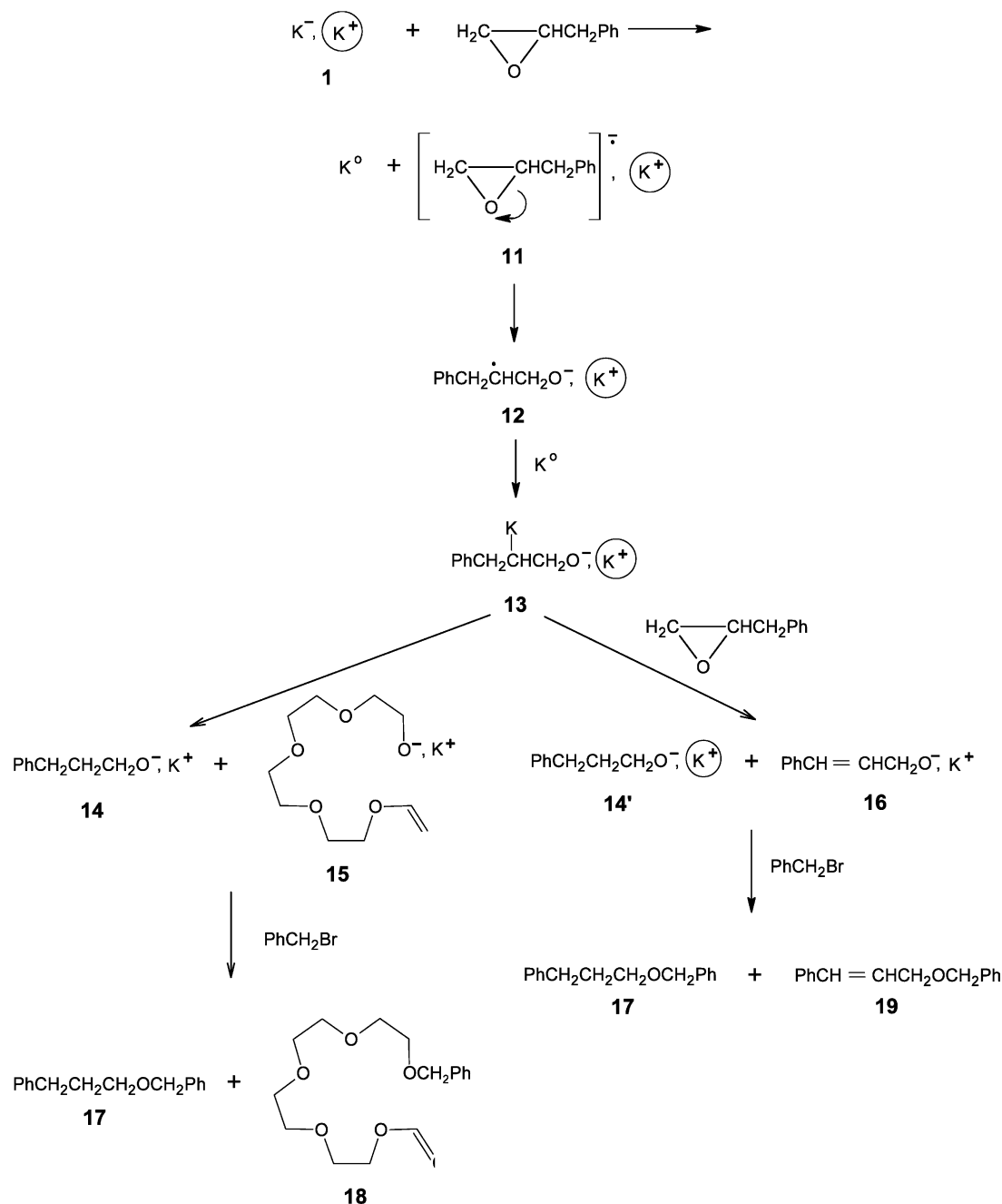
The reaction of **1** with (phenylmethyl)oxirane was studied in the third series of experiments. This reaction was also rapid at ambient temperature. Several products were found in the sample treated with benzyl bromide. They were 3-phenyl-1-propanol (in 5% yield), 3-phenylallyl alcohol (8%), tetraethylene glycol vinyl ether (4%), benzyl 3-phenylpropyl ether (5%), benzyl 3-phenylallyl ether (25%), and tetraethylene glycol benzyl vinyl ether



Scheme 3.

(6%). It showed that the mentioned alcohols and their alkoxides, i.e. potassium 3-phenylpropoxide, potassium 3-phenylallyloxide and potassium tetraethylene glycoxide vinyl ether were formed in this reaction. No gaseous products were found in the liquid and gaseous phase also in this case.

It could be assumed that the initial step of the process is similar to that proposed for phenyloxirane. One electron is transferred from $\text{K}^\cdot$ of **1** to the aromatic ring of (phenylmethyl)oxirane (Scheme 4). The radical anion **12** and K° are the products of this reaction. However, the dimer of **12** was not found in the reaction mixture. Therefore, **12** presumably recombines with K° giving the organometallic compound **13**. It opens the crown ether ring. Potassium tetraethylene glycoxide vinyl ether (**15**) is the product of this reaction as it has been found in our earlier works [12,14]. Potassium 3-

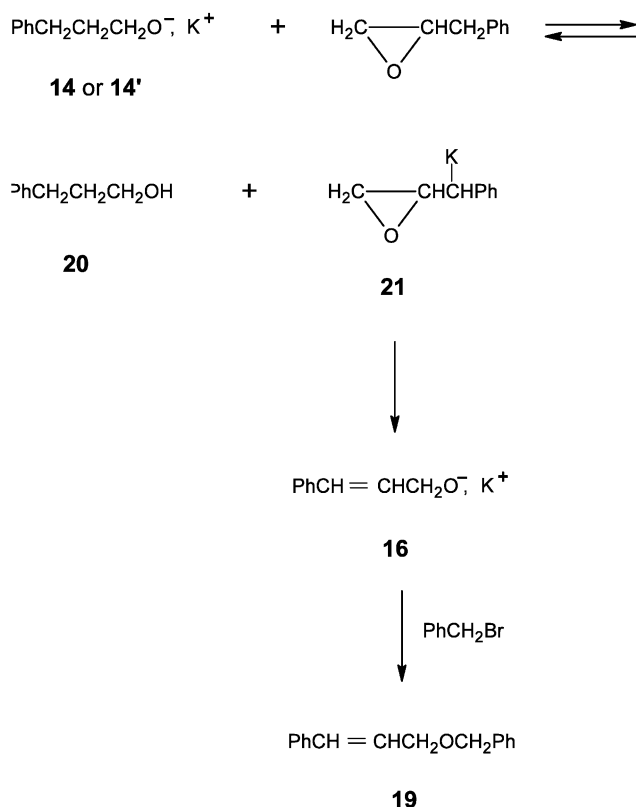


Scheme 4.

phenylpropoxide (**14**) is formed simultaneously. Compound **13** can also react with another (phenylmethyl)oxirane molecule giving **14'** and potassium 3-phenylallyloxide **16**. Then, potassium alkoxides **14**, **14'**, **15** and **16** react with (phenylmethyl)oxirane in a like manner as **13** does. However, it is not a simple addition to the oxirane ring known in the literature [1]; products of such reaction were not found in the reaction mixture. It seems to be a proton transfer process (Schemes 5–7) similar to the chain transfer reaction to the monomer observed for example during the anionic polymerization

of methyloxirane [19–21]. The unsaturated alkoxide **16** and appropriate alcohols, i.e. 3-phenylpropanol (**20**) and tetraethylene glycol vinyl ether (**22**) are formed in this case. Compound **16** can also react in the same manner with another (phenylmethyl)oxirane molecule; **16** is reactivated in this process and 3-phenylallyl alcohol **23** is formed.

It is worth noting that in contrast to **13** the organometallic compound **5** did not deprotonate the crown ether but opened rapidly the oxirane ring of phenyloxirane probably because as a benzylic carbanion



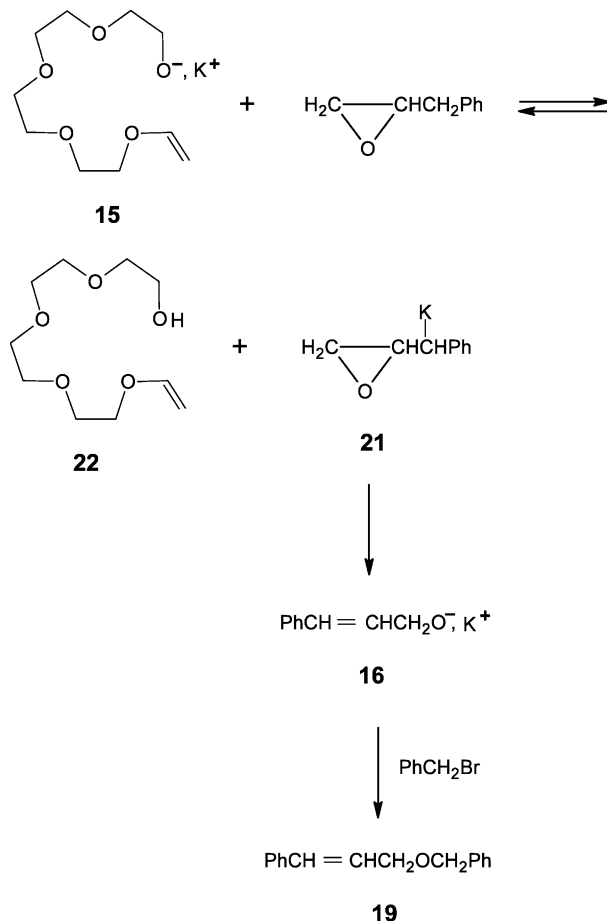
Scheme 5.

it is more nucleophilic and less basic than **13**. On the other hand, protons of the CH_2 group present in the substituent of (phenylmethyl)oxirane are even more acidic than those of the crown ring. Therefore, the reaction involving the proton exchange occurs and the rearrangement of (phenylmethyl)oxirane potassium derivative **21** to **16** takes place.

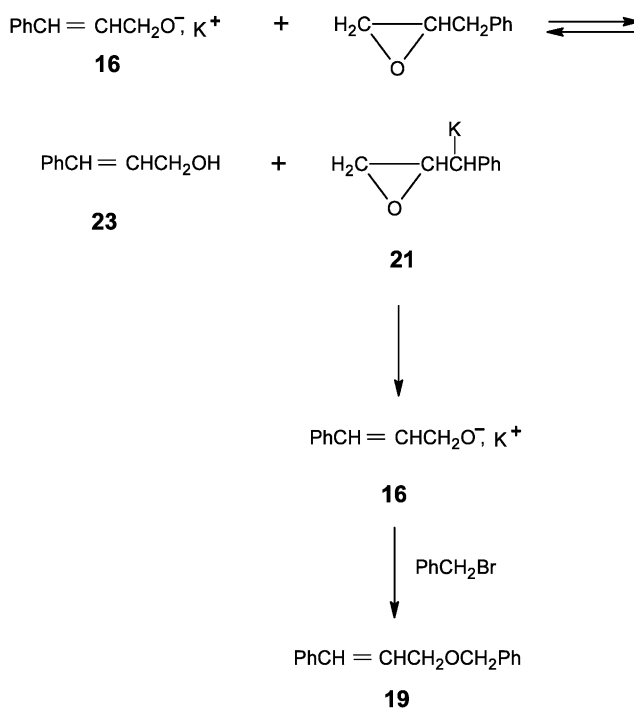
Another direction of the oxirane ring opening, i.e. in the β -position was observed in (2-phenylethyl)oxirane which possesses two CH_2 groups in the substituent. It seems that this reaction followed the electron transfer to the oxirane ring. The organometallic intermediate **26** formed reacted exclusively with the crown ether molecule giving two potassium alkoxides, i.e. potassium 4-phenylbutane-2-oxide (**27**) and potassium tetraethylene glycoxide vinyl ether (**15**) (Scheme 8). Their benzyl derivatives were observed in the reaction mixture after benzylation. They were benzyl-(1-methyl-3-phenylpropyl) ether (**28**) (in 16% yield) and tetraethylene glycol benzyl vinyl ether (**18**) (14%). No dimer or other reaction products were found in this case in the analyzed samples.

3. Conclusions

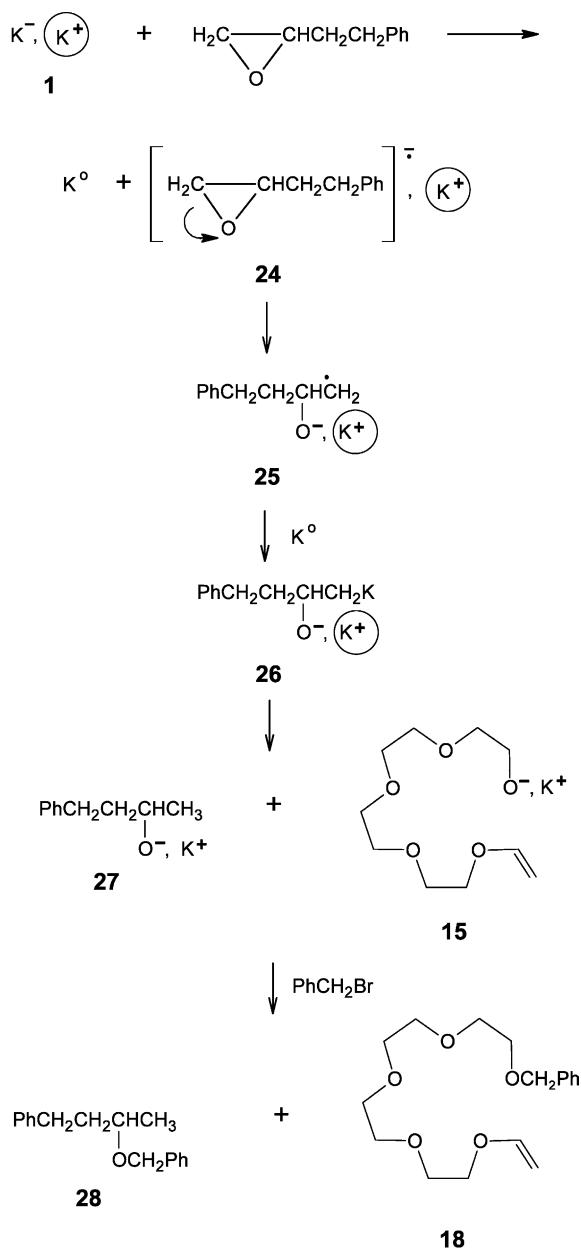
Introduction of one or two CH_2 groups into the substituent at the oxirane ring changes significantly the



Scheme 6.



Scheme 7.



Scheme 8.

electron density in the molecules under study. The polar constants σ^* for Ph, PhCH_2 , and PhCH_2CH_2 groups are equal to 0.60, 0.21 and 0.08, respectively [22]. Therefore, the electron from K^- of **1** is transferred to the aromatic ring of phenyloxirane and (phenylmethyl)oxirane. As a result the oxirane ring is opened exclusively in the α -position. Presumably in the case of (2-phenylethyl)oxirane the electron is transferred to the oxirane ring. The latter is then opened in the β -position. The course of further reactions depends on the kind of substituent and the method of substrates delivery. However, two products in the case of phenyloxirane and (2-phenylethyl)oxirane or a mixture of various ones for (phenylmethyl)oxirane are formed at the excess of these substrates in relation to potassium anions.

Organometallic compounds are intermediate products in all the studied processes. The end products prove their existence in the reaction because they cannot be formed otherwise.

4. Experimental

GCMS analyses were performed on a 30-m fused silica capillary column DB-5 in a Varian 3300 gas chromatograph equipped with a Finnigan MAT SSQ 700 quadrupole detector. Diethylene glycol dimethyl ether was used as an internal standard. Gaseous products were searched for by GC with a 2.4-m long stainless steel column packed with Al_2O_3 , 0.2–0.3 mm, deactivated with 5% K_2CO_3 , in an INCO 505 gas chromatograph equipped with a flame ionization detector. ^1H - and ^{13}C -NMR spectra were recorded with a Varian VXR-300 multinuclear pulsed spectrometer (300 MHz for ^1H and 75 MHz for ^{13}C) at 20 °C. Chemical shifts were referenced to tetramethylsilane serving as an internal standard. Deuterated acetone was used as the solvent. Infrared spectra were measured with a BIO-RAD FTS-40A FTIR spectrophotometer.

Gas chromatography mass spectrometry (GCMS) analyses were run on a 30-m long DB 1701 fused silica capillary column, using a Varian 3300 gas chromatograph equipped with a Finnigan MAT 800 AT ion trap detector. Diethylene glycol dimethyl ether was used as the internal standard for the yield measurement.

Gaseous products were searched for by gas chromatography (GC) with a 2.4-m long stainless steel column packed with Al_2O_3 , 0.2–0.3 mm, deactivated with 5% K_2CO_3 , in an INCO 505 gas chromatograph equipped with a flame ionization detector.

^1H - and ^{13}C -NMR spectra were recorded at 20 °C on a Varian VXR-300 multinuclear pulsed spectrometer operating at the ^1H resonance frequency of 300 MHz, and the ^{13}C resonance frequency of 75 MHz. Chemical shifts were referenced to tetramethylsilane serving as an internal standard. Deuterated acetone was used as the solvent.

Phenyloxirane (Aldrich) and (phenylmethyl)oxirane (Aldrich) were heated over CaH_2 for 6 h and then distilled under dry argon atmosphere; the fraction boiling at 194 °C and 95 °C/16 Torr was collected, respectively. Tetrahydrofuran (POCH) was boiled over CuCl to decompose peroxides and then over CaH_2 for 10 h, and finally it was distilled at 66 °C. This fraction was dried over metallic potassium for 20 h and redistilled prior to use. 15-Crown-5 (Aldrich) was dried under vacuum at 50 °C for 8 h. Potassium (Fluka) was purified in boiling tetrahydrofuran and then distilled under high vacuum into a reactor. 0.1 M blue solution of K^- , K^+ (15-crown-5)₂ was obtained by dissolution of potassium in 0.2 M 15-crown-5 tetrahydrofuran solu-

tion as in Ref. [10]. The metal–solvent contact time was equal to 25 min. Potassium biphenylide was prepared as in Ref. [23].

The reaction of phenyloxirane, (phenylmethyl)oxirane and (2-phenylethyl)oxirane with potassium anions was conducted under dry argon atmosphere at 20 °C in the reactor described in Ref. [11]. 10 cm³ of 0.1 M K⁺, K⁺(15-crown-5)₂ blue tetrahydrofuran solution was dropped into 10 cm³ of 0.5 M appropriate oxirane tetrahydrofuran solution while mixing, i.e. the oxirane compound was still in the excess; one exception to this rule was described in the discussion of results of this work. Then, the reaction mixture was immediately treated with methyl iodide or benzyl bromide as the quenching agent. The obtained volatile compounds were identified matching their mass spectra, retention times, and NMR spectra with those of the authentic compounds.

4.1. (2-Phenylethyl)oxirane

It was prepared according to the method described in Ref. [24]. Its NMR and MS spectra were presented in the same reference.

4.2. 1,4-Dimethoxy-2,3-diphenylbutane (7) and 1,4-dimethoxy-1,3-diphenylbutane (8)

Their mixture was obtained by the reaction of metallic sodium with phenyloxirane as in Ref. [6]. The retention times and MS spectra of these compounds were the same as those obtained in the reaction of phenyloxirane with **1** and **9**. Attempts to separate of **7** and **8** from their mixture were unsuccessful. The analysis of NMR spectra of this mixture was also impossible because many signals of the isomers of **7** and **8** were observed there. Therefore, the problem which compound is which was solved by the comparison of the results of MS analysis to the MS data of **7** presented in Ref. [25]. MS (*m/e*) of **7** found in this work: 270 [4, M⁺]; 238 (17); 206 (32); 193 (28); 179 (10); 165 (10); 135 (100); 121 (22); 102 (23); 91 (24); 75 (9); 45 (57). MS (*m/e*) of **8**: 270 [4, M⁺]; 255 (9); 238 (1); 223 (2); 193 (4); 134 (20); 121 (100); 103 (6); 91 (9); 77 (10); 45 (4).

4.3. Benzyl 3-phenylpropyl ether (17), tetraethylene glycol benzyl vinyl ether (18), and benzyl 3-phenylallyl ether (19)

Their NMR as well as MS spectra were described in Refs. [26,12,27], respectively.

4.4. 3-Phenyl-1-propanol (20)

Its NMR spectra were presented in Ref. [27a]. MS (*m/e*): 136 [56, M⁺]; 117 (100); 91 (81); 77 (25); 65 (32); 51 (16); 39 (12).

4.5. Tetraethylene glycol vinyl ether (22)

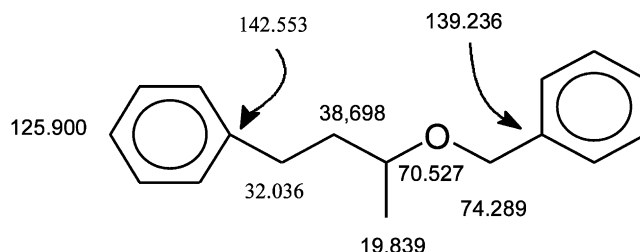
It was prepared according to the method described in Ref. [12], i.e. in the reaction of **1** with methyloxirane. DOWEX 50 WX2 (Fluka) was used in this case as the quenching agent. It allowed to transform **15** into **22**. ¹³C-NMR CDCl₃ δ: 151.6 (OCH=); 86.8 (CH₂=); 72.6 (CH₂=CHOCH₂); 69.8–70.5 (OCH₂, six signals); 61.3 (CH₂OH). ¹H-NMR and IR spectra were presented in Ref. [28]. MS (*m/e*): 177 (1); 133 (6); 89 (20); 73 (11); 45 (100); 43 (21).

4.6. 3-Phenylallyl alcohol (23)

Its NMR spectra were presented in Ref. [27b]. MS (*m/e*): 134 [100, M⁺]; 115 (35); 105 (34); 92 (77); 78 (61); 77 (48); 54 (20); 51 (28); 39 (14).

4.7. Benzyl-(1-methyl-3-phenylpropyl) ether (28)

A mixture of 0.1 mol 4-phenyl-2-butanol, 0.1 mol benzyl chloride, 0.4 mol powdered NaOH, 0.007 mol tetrabutylammonium hydrogensulphate and 50 cm³ benzene was stirred intensively at 70–80 °C in a water bath for 3 h. After cooling 100 cm³ water and 100 cm³ hexane was added. The layers were separated, the organic layer was washed three times with 50 cm³ water and dried with anhydrous MgSO₄. Having removed hexane and benzene on a rotatory evaporator the residue was distilled under reduced pressure. Benzyl-(1-methyl-3-phenylpropyl) ether has been finally obtained in 60% yield (purity >97%; GC). B.p. = 169–170 °C at 2 mmHg. ¹³C-NMR CDCl₃ δ:



128.633–127.622: other aromatic carbons

¹H-NMR CDCl₃ δ: 7.38–7.08 (m, 10H, 2 × Ph-); 4.537 and 4.400 (qAB, 2H, Ph-CH₂-O-, J_{AB} = 11.72 Hz); 3.490 (qdd, 1H, CH₃-CH-, J = 6.35 Hz, J = 6.3 Hz, J = 5.2 Hz); 2.745 (ddd, 1H, Ph-CH₂-CH₂-, J_{gem} = 14.7 Hz, J = 7.8 Hz, J = 3.8 Hz); 2.656 (ddd, 1H, Ph-CH₂-CH₂-, J_{gem} = 14.7 Hz, J = 8.2 Hz, J = 5.3 Hz);

1.890 (dddd, 1H, Ph-CH₂-CH₂-, $J_{\text{gem}} = 11.6$ Hz, $J = 7.8$ Hz, $J = 6.3$ Hz, $J = 5.3$ Hz); 1.730 (dddd, 1H, Ph-CH₂-CH₂-, $J_{\text{gem}} = 11.6$ Hz, $J = 8.2$ Hz, $J = 5.2$ Hz, $J = 3.8$ Hz); 1.190 (d, 3H, Ph-CH₂-CH₂-CH(CH₃)-, $J = 6.35$ Hz). A computer simulation was applied by the analysis of the spectrum using the MestRe-C 2.3a program. MS (m/e): 240 [1, M⁺]; 132 (38); 118 (8); 105 (30); 91 (100); 87 (14); 65 (19).

Acknowledgements

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