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Selective cleavage of the linear ether bond in benzyl glycidyl ether and triphenylmethyl glycidyl ether by potassium alkalide as two-electron-transfer reagent

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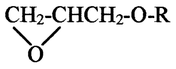
Abstract

The linear ether bond was exclusively cleaved in benzyl glycidyl ether and triphenylmethyl glycidyl ether under the influence of K^-, $K^+(15\text{-crown-}5)_2$ (**1**), whereas the strongly strained three-membered oxacyclic ring remained undisturbed. Potassium glycidoxide and benzylpotassium were found as the primary reaction products of benzyl glycidyl ether with **1**. Subsequently, benzylpotassium reacted with benzyl glycidyl ether giving the next potassium glycidoxide molecule and bibenzyl. Benzyl phenyl ether was used as a model compound to explain the mechanism of bibenzyl formation. The reaction of triphenylmethyl glycidyl ether with **1** resulted in potassium glycidoxide and stable triphenylmethylpotassium. After treating with a quenching agent a new glycidyl ether or glycidyl ester was obtained from potassium glycidoxide. These results were found when the reaction occurred at the excess of glycidyl ether. In another case, i.e. at the excess of **1** further reactions took place with the participation of potassium anions and various new compounds were observed in the reaction mixture after benzylation or methylation. Thus, the method of substrates delivery influences the course of studied processes in a decisive way. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Benzyl glycidyl ether; Potassium alkalide; Linear ether bond cleavage

1. Introduction

Glycidyl ethers possess two kinds of ether bonds, i.e. the cyclic and the linear ones:



$$\underset{\diagdown\,O\,\diagup}{CH_2\text{-}CHCH_2\text{-}O\text{-}R}$$

where R is an alkyl or an aryl group.

The cyclic ether bond can be opened either in the α-position (the CH–O bond scission) or in the β-position (the CH_2–O bond scission). The cleavage of the linear ether bond is also possible in two ways. This occurs either between the oxygen and the carbon atom of the glycidyl group or between the oxygen and the carbon atom of the substituent R. Mechanisms of the ether bond cleavage in the reaction of organo–alkali–metal compounds or alkali metals with linear and cyclic ethers were thoroughly discussed in a review [1].

The oxirane ring opening in glycidyl ethers occurs in the presence of potassium alkoxides [2–4] or potassium hydroxide [5,6] exclusively in the β-position [5]. Recently we have found that the same ring opening took place in the reaction of K^-, $K^+(15\text{-crown-}5)_2$ (**1**) with phenyl glycidyl ether (R: Ph) being at the excess in the system [7]. Cleavage of the cyclic ether bond by **1** was followed in that case by γ-elimination. Potassium phenoxide and potassium cyclopropoxide were the main reaction products. The crown ether ring was opened in a side reaction. Potassium tetraethylene glycoxide vinyl ether was the product of the latter. The rate of the process was very high at ambient temperature. The linear ether bond in phenyl glycidyl ether was stable in the presence of **1** similarly as in all described earlier systems [2–6]. The

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attack of the base occurred only at the oxirane ring of glycidyl ether.

In this work we describe results of our investigations concerning the reaction of benzyl glycidyl ether (R: CH_2Ph) and triphenylmethyl glycidyl ether (R: CPh_3) with **1** in tetrahydrofuran solution. They were model systems for the study of initiation step in the polymerization of these ethers by potassium alkalide (the name introduced by Dye [8] for salts containing alkali metal anions and complexed metal cations). Owing to that the experiments were conducted at the excess of glycidyl ethers in relation to **1**, i.e. under the polymerization conditions [9–11]. However, the influence of increased concentration of **1** on the course of these reactions was also studied.

2. Results and discussion

The reaction of **1** with benzyl glycidyl ether proceeded instantaneously. The blue color of **1** solution vanished immediately after mixing of reagents. It means that all potassium anions took part in the process [12]. After that butyl bromide was added to the mixture as a quenching agent. Two compounds, i.e. butyl glycidyl ether and bibenzyl were then identified in the analysed samples. Their yields were small, about 10% for both products, because the reaction was conducted at the excess of benzyl glycidyl ether. No gaseous products were found before and after butylation. Thus, potassium glycidoxide and bibenzyl were the real reaction products.

Then, the reaction of **1** was carried out with the excess of triphenylmethyl glycidyl ether. Discoloration of the solution of **1** was also instantaneous after its introducing into the ether solution. Butyl glycidyl ether and butyltriphenylmethane were found in the samples treated with butyl bromide. The second product was only identified by the analysis of its mass spectrum. Therefore, in a separate experiment the reaction mixture was quenched by methanol. In this case triphenylmethane was obtained in the system. Gaseous products were not found before quenching as well as in the butylated or protonated samples. It showed that potassium glycidoxide and stable triphenylmethylpotassium were primarily formed in the reaction mixture.

No products of the oxirane ring opening were observed in both series of experiments. It indicated that only the linear ether bond was cleaved by using potassium anions, whereas the strongly strained three-membered ring remained undisturbed. According to our best knowledge such a phenomenon is described in the literature for the first time. A degenerate rearrangement of potassium glycidoxide by an intramolecular nucleophilic attack to the oxirane ring, however, cannot be excluded [13].

The behavior of K^- in chemical processes differs from those of typical anions such as HO^- or RO^- [12,14,15]. The potassium anion possesses two valence electrons in its $4s^2$ orbital. At the beginning of the reaction K^- transfers one electron to an acceptor molecule giving K^o. Subsequently, the potassium atom transfers the second electron, and finally K^+ is formed from K^-, as recently shown by Perrin in his excellent work [14]. It means that the potassium anion behaves as two-electron-transfer reagent. Until now only one exception was found from this rule [16].

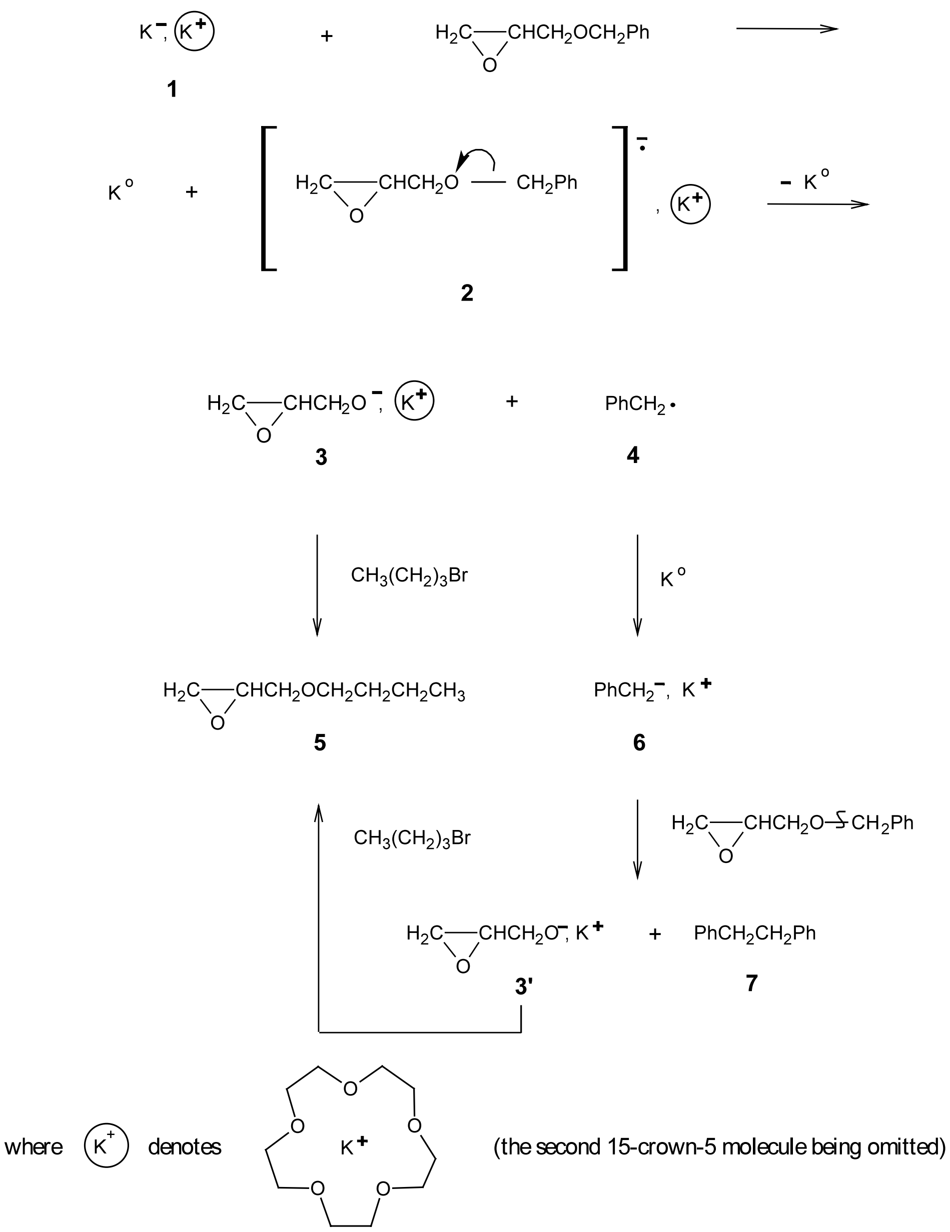
In order to confirm the role of K^o in the present work an additional experiment was carried out using benzyl glycidyl ether. Methanol was introduced into the reaction mixture as the quenching agent. If K^o remained in the system, it should react with methanol giving hydrogen. However, no gaseous products were observed. As mentioned the same result was found for triphenylmethyl glycidyl ether. The lack of hydrogen in the protonated samples indicated that K^o was converted into K^+. Consequently, the two-electron-transfer mechanism was proposed also in these studied systems.

The assumption was made that in the first step of the reaction of **1** with benzyl glycidyl ether one electron is transferred from K^- to the aromatic ring. It results in K^o and the radical anion **2** (Scheme 1). The latter undergoes fragmentation to potassium glycidoxide (**3**) and benzyl radical **4**. The linear ether bond cleavage occurs between the oxygen and the benzyl group. The surprising regioselectivity of the reaction probably is due to the high resonance stabilization of **4**. Butyl glycidyl ether **5** is formed from **3** after its treating with butyl bromide. Benzyl radical recombines with K^o giving benzylpotassium (**6**) which then takes part in the Würtz coupling with benzyl glycidyl ether being in the excess. Bibenzyl **7** and potassium glycidoxide (**3′**) without crown ether are finally formed.

This mechanism, however is questionable. Dimerization of benzyl radical might be expected to occur giving the same final product of the studied process. Proofs that benzyl radicals really do not dimerize to bibenzyl but give benzylpotassium are presented in the further part of this work.

It was then assumed that in the reaction of **1** with triphenylmethyl glycidyl ether the initial products involve potassium glycidoxide (**3**) and triphenylmethyl radical **9** (Scheme 2). The latter recombines with K^o to triphenylmethylpotassium (**10**). However, it does not take part in the Würtz coupling with triphenylmethyl glycidyl ether. Strong mesomeric stabilization of the triphenylmethyl anion, as it was observed earlier [17], and/or steric effects probably play a significant role in this case.

The organometallic compounds **6** and **10** did not cleave the oxirane ring. In contrast to our earlier findings [7,15,18] the reaction of these compounds

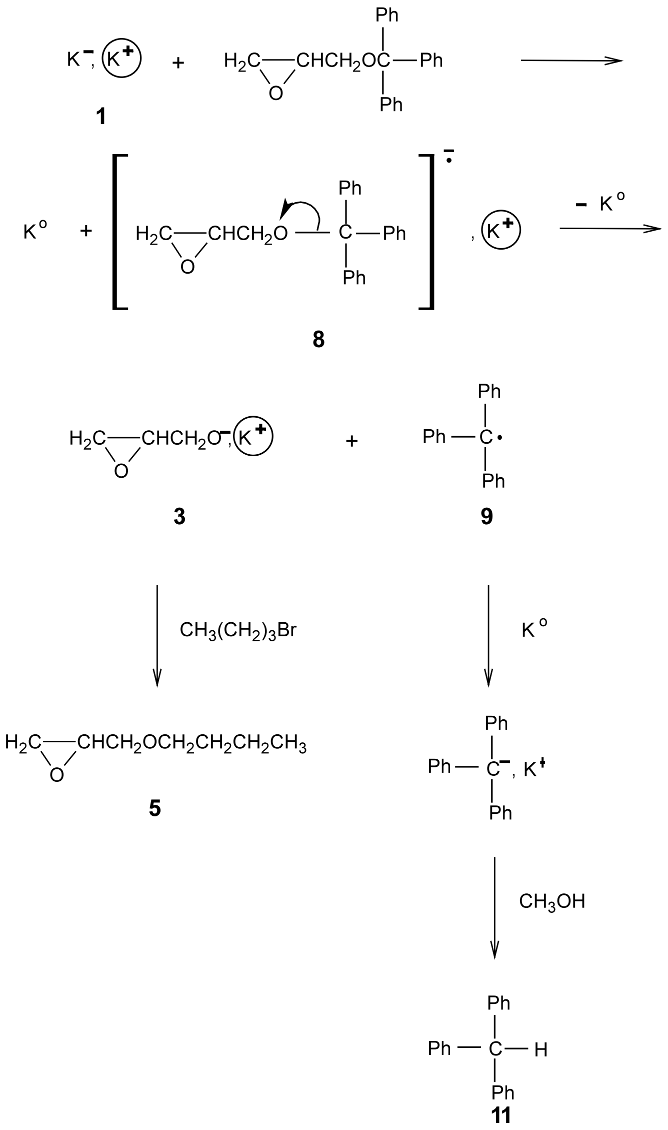


Scheme 1.

with crown ether was also not observed. Therefore, not every organometallic compound opens the crown ring, as it might be considered on the ground of the cited works. The reason of this phenomenon seems to be clear for **10** because of its high stability. It is probable that in the case of **6** the large excess of benzyl glycidyl ether causes the lack of its reaction with crown ether. In conclusion it should be stated that the absence after methylation of the volatile derivative of 15-crown-5 opening product, i.e. tetraethylene glycol methyl vinyl ether, cannot be a proof that the formation of organometallic compounds does not occur.

It is worth noting that **9** obtained in the reaction of metallic zinc with triphenylmethyl chloride was found to exist in an equilibrium with a dimeric form which even prevails in that system [19–21]. Such a phenomenon was not observed in our work.

Results presented in this work differ from those obtained by us in the reaction of **1** with phenyl glycidyl ether [7]. The aromatic ring in that glycidyl ether is connected directly with the oxygen atom possessing an electron donating character. It increases the electron density of the aromatic ring. Therefore, the electron transfer from K^- to the oxirane ring is preferred resulting in such a case in the cleavage of the cyclic ether bond. The introduction of only one carbon atom between the aromatic group and the oxygen changes dramatically the direction of the electron transfer from K^- to the glycidyl ether molecule. A similar effect was observed earlier in the reaction of metallic lithium with



Scheme 2.

1-naphthol in NH_3–C_2H_5OH [22]. In that system a selective reduction of the non-substituted aromatic ring took place due to deactivating influence of the electron donating hydroxyl group connected to the neighboring aromatic ring.

In the present work the cleavage of the ether bond occurred between the oxygen and the benzyl or triphenylmethyl substituent, i.e. the O–R bond is broken. The regioselective carbon–oxygen bond cleavage in aromatic ethers and esters by potassium–18-crown-6–tetrahydrofuran solution at 0 °C were studied earlier by Fish and Dupon [23]. In the case of benzyl phenyl ether two products were found after protonation, i.e. toluene and phenol in almost equimolar amounts. It was claimed that K^+ formed a 1:1 complex with 18-crown-6; K^- gave K° and a solvated electron. Then, the electron provided the cleavage of the benzyl–oxygen bond. Decomposition of the intermediate radical anion to benzyl radical and phenoxide anion was expected before the protonation. The amount of benzyl phenyl ether in the reaction mixture was 10 times lower than that of potassium metal and 18-crown-6 using for the preparation of the metal solution. The relationship between metal and crown ether was initially equal to 1:1 which indicated that half of 18-crown-6 molecules remained free in the solution, i.e. did not complex potassium cations. These free 18-crown-6 molecules can react with potassium anions in the same way as it was proposed by Schué and coworker [24] for cryptands, i.e. giving electrons and potassium cations complexed by the ligand. Thus, electrons prevailed in such system which, therefore, was named by the authors as ‘a blue solution of solvated electrons’.

Angelo [25] investigated the cleavage of several ethers using sodium naphthalenide as the single electron transfer reagent. Benzyl phenyl ether was selected as the model compound. The most likely mechanism of its reaction with naphthalenide was analogous to that elucidated by Kornblum and coworkers [26]. The reduction of the ether lead to the radical anion in which an added electron was situated in the benzyl ring. Ejection of phenoxide anion provided the benzyl radical. That after reduction and protonation was converted into toluene. Traces of bibenzyl were found in the reaction mixture. The authors concluded that it might be formed from the benzyl radical coupling.

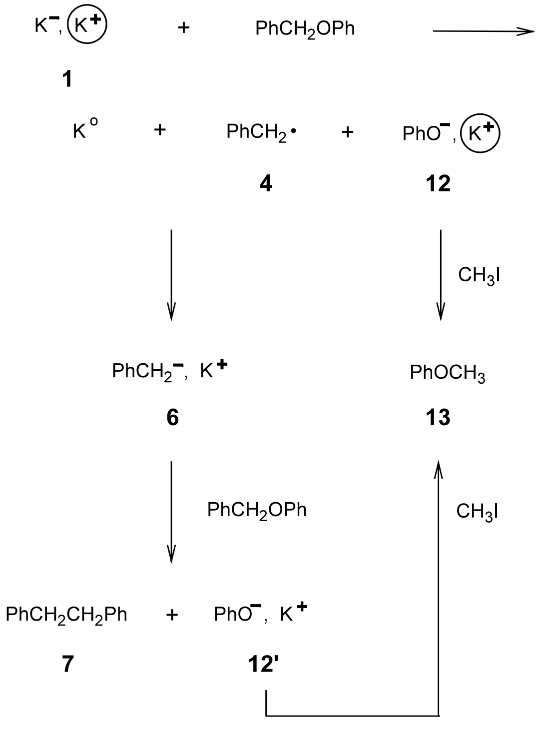
Woolsey and coworkers [27] used a sodium–hexamethylphosphoramide system (prepared at about 2:1 molar ratio of the components) in tetrahydrofuran at ambient temperature and sodium solution in liquid NH_3 with tetrahydrofuran at −78 °C for the reaction with benzyl phenyl ether. The reductive cleavage of the ether was observed also in this case. Bibenzyl as one of the products was formed in 4 and 50% yields, respectively, probably by the coupling of benzyl radicals as the authors mentioned.

Cleavage of nitrosubstituted benzyl phenyl ethers by 2,4,6-tri-*tert*-butylnitrobenzene radical anion was studied by Guthrie and Shi [28]. *p*-Nitrosubstituted ether gave 1,2-bis(4-nitrophenyl)ethane, i.e. di-*p*-nitroderivative of bibenzyl, as the main reaction product. Then, naphthyl benzyl ethers were found to undergo scission of the CH_2–O bond when treated with radical anions of anthracene or fluoranthene [29]. In the case of benzyl 1-naphthyl ether the major product was bibenzyl in 40–75% yields. For benzyl 2-naphthyl ether the main product was toluene, and bibenzyl was produced in only 5–20% yields. That work was continued by using naphthylmethyl phenyl ethers for the reaction involving the electron transfer from fluoranthene radical anion or biphenyl radical anion [30].

The electron transfer from the donor to the ether molecule with the formation of benzyl radical as the intermediate product was postulated in all mechanisms presented in the Refs. [23–31]. However, the kind of the end product depended on the reaction conditions. That could be bibenzyl or a benzylmetallic compound (toluene after protonation).

Therefore, we decided to inspect the course of the reaction of **1** with benzyl phenyl ether, treating it as the model reaction, and to solve the problem of bibenzyl formation in our system. Firstly, benzyl phenyl ether was used in the excess. Bibenzyl and anisole were observed in the reaction mixture after quenching with methyl iodide. Then, **1** was used in the excess and the temperature was diminished to 0 °C. Initially a solution of benzyl phenyl ether in tetrahydrofuran containing *tert*-butanol was slowly dropped into the solution of **1** until its discoloration. This phenomenon was observed at the molar ratio of reagents equal to 4:10, respectively. Toluene, anisole, tetra- and triglyme were obtained in the reaction mixture after quenching with methyl iodide. In other experiments benzyl phenyl ether in tetrahydrofuran solution was slowly introduced into the 10-fold excess of **1**. The mixture was still dark blue. Methyl iodide was then dropped into this mixture until its discoloration in order to destroy unreacted potassium anions. Ethylbenzene, anisole, tetraglyme, triglyme and tetraethylene glycol methyl vinyl ether were found in this case as the reaction products.

It can be concluded that the scission of the ether bond occurred between the oxygen and the CH_2 group in benzyl phenyl ether resulting in potassium phenoxide **12** and benzyl radical **4** (Scheme 3). The latter recombined with K^o and did not dimerize. Benzylpotassium **6** formed could be converted into toluene by *tert*-butanol or it reacted with benzyl phenyl ether being in the excess and bibenzyl **7** was formed after ejection of **12′**. A lack of toluene in the 1:10 experiment shows that in this case benzylpotassium did not react with crown ether. Its ring opening products could be formed in the reaction of **1** with methyl iodide, as described in Ref. [15] or in the reaction conducted in the presence of *tert*-butanol.



Scheme 3.

It is worth noting that by the use of the excess of **1** and at ambient temperature more products were obtained in the sample methylated after discoloration of the reaction mixture, i.e. after the decay of potassium anions. Many of them were identified as toluene, anisole, and 1,2-diphenylpropane. Ethylbenzene, bibenzyl, 1,2,3-triphenylpropane, tetra- and triethylene glycol dimethyl ethers were found only in small amounts. It means that potassium anions reacted also with bibenzyl, which had been formed during the process. The intermediate organometallic compound obtained in this case attacked then the next benzyl phenyl ether molecule. The presence of 1,2,3-triphenylpropane in the methylated sample confirms formation of the metalated bibenzyl as well as the proposed course of its reaction with benzyl phenyl ether. These findings are in a good agreement with the experimental results described by Collins et al. [32]. In that work reactions of sodium–potassium alloy in the solvent system glyme–triglyme (without crown ether) on a series of model compounds were studied to determine whether the Birch–Hückel reduction can be used in this solvent system to cleave carbon–carbon bonds. Sodium anions, potassium cations and small amounts of potassium anions could be expected to exist in such sodium–potassium alloy solution [33]. Ethylbenzene and 1,2-diphenylpropane were obtained in that case as methylated products of the bibenzyl decomposition. Toluene was also formed, however, a mechanism of this reaction was not presented.

It was then found that at the excess of **1** further reactions with the participation of potassium anions occurred also in the case of benzyl glycidyl ether. 1,2,3-Triphenylpropane and toluene were identified among other compounds in the benzylated sample obtained at the 5:1 molar ratio of **1** to benzyl glycidyl ether. The latter was not observed in the reaction mixture. It means that potassium glycidoxide underwent destruction quantitatively. A weak signal of bibenzyl was found in the chromatogram of benzylated samples. On the other hand, toluene, ethylbenzene, 1,2-diphenylpropane, 1,2,3-triphenylpropane, tetraethylene glycol methyl vinyl ether as well as tetra- and triethylene glycol dimethyl ethers were formed in the system when methyl iodide was used as the quenching agent.

The 10:1 molar ratio of **1** to benzyl glycidyl ether and 0 °C was applied in a separate experiment. Ethylbenzene, i.e. the methylated derivative of benzylpotassium, and not bibenzyl was detected in this case in the reaction mixture after methylation. That was in a good agreement with the results obtained with benzyl phenyl ether.

Thus, a method of substrates delivery influences the course of studied reactions in a decisive way. In this work we wanted to explain a possible mechanism of the initiation reaction in the polymerization of selected aromatic glycidyl ethers by **1**. The polymerization occurs always at the excess of monomer in relation to the initiator. Thus, only the results obtained in the first part of this work, i.e. at the excess of glycidyl ethers, can be taken into account in further investigations concerning their polymerization by potassium alkalide. However, a big excess of **1** was needed to use for explanation of the reaction mechanism. These results show additionally that a simple titration of **1** with an ether or other compounds until discoloration of the former, which usually undergoes at the molar ratio of reagents close to 1:1, may provide wrong conclusions.

3. Conclusions

The kind of substituent in the glycidyl ether molecule exerts a great influence on the mechanism of its reaction with potassium alkalide. For the first time to our knowledge it has been demonstrated the possibility of the selective cleavage of the linear ether bond without the opening of the oxirane ring present in the same reagent molecule. Potassium glycidoxide is formed in this reaction. Until now the synthesis of this alkoxide by the use of alkalide solutions has not been described in the literature.

Crown ether does not take part in the studied processes as a reagent. Its role is limited to the complexation of potassium cation in spite of the formation of organometallic intermediates.

4. Experimental

GC-MS 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. The use of quenching agents enabled the analysis of liquid compounds formed from the non-volatile reaction products. Diethylene glycol dimethyl ether was used as the internal standard for the yield measurement. 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-, ^{13}C-, and ^{39}K-NMR spectra were recorded at 20 °C on a Varian VXR-300 multinuclear pulsed spectrometer operating at the ^1H resonance frequency of 300 MHz, the ^{13}C resonance frequency of 75 MHz, and the ^{39}K resonance frequency of 14 MHz. Chemical shifts were referenced to Me_4Si serving as an internal standard for ^1H and ^{13}C measurements. Deuterated C_3H_6O was used as the solvent. IR spectra were taken on a FTS-40A BIO-RAD instrument.

Benzyl glycidyl ether (Aldrich) was heated over CaH_2 for 6 h and then distilled under dry Ar atmosphere; the fraction boiling at 70 °C/11 Torr was collected. Triphenylmethyl glycidyl ether and benzyl phenyl ether (both Aldrich) were dried in vacuum at elevated temperature prior to use. 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. Butyl glycidyl ether, glycidyl butyrate, triphenylmethane and bibenzyl (all Aldrich) were used for GC-MS analyses.

4.1. K^-, K^+(15-crown-5)$_2$ alkalide (0.1 M solution in tetrahydrofuran)

Blue potassium alkalide solution was obtained by dissolution of the potassium mirror in 0.2 M 15-crown-5 tetrahydrofuran solution, as in Ref. [34]. After 25 min contact time the solution was filtered through a glass frit and then used as the reagent.

4.2. Bibenzyl

Its NMR spectra were presented in Ref. 35a Mass spectrum (*m/e*): 182 [M^+, 94]; 178 (7); 165 (7); 91 (100); 65 (12). IR (neat): 3028, 1600, 1492, 752, 700 cm^{-1}.

4.3. Butyl glycidyl ether

Its NMR spectra were presented in Ref. 35b. Mass spectrum (*m/e*): 131 [M^+, 1]; 87 (24); 75 (41); 73 (64); 57 (100); 55 (90); 43 (67); 41 (87). IR (neat): 2960, 2871, 1465, 1253, 913 cm^{-1}.

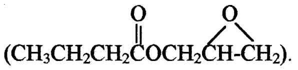
4.4. 1,2-Diphenylpropane

Its NMR and mass spectra were presented in Ref. [36].

4.5. 1,2,3-Triphenylpropane

Its NMR and mass spectra were presented in Refs. [37,38].

4.6. Glycidyl butyrate



$(CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}OCH_2\overset{O}{\overbrace{CH\text{-}CH_2}})$.

Its NMR spectra were presented in Ref. 35c. Mass spectrum (*m*/*e*) 145 [M$^+$, 1]; 116 (21); 89 (2); 71 (100); 56 (14); 43 (92). IR (neat): 1740, 1255, 1180, 911 cm^{-1}.

4.7. Tetraethylene glycol dimethyl ether (tetraglyme)

Its NMR and mass spectra were presented in Ref. [18].

4.8. Tetraethylene glycol methyl vinyl ether

The method of its synthesis as well as its NMR and mass spectra were presented in Ref. [18].

4.9. Triethylene glycol dimethyl ether (triglyme)

Its NMR and mass spectra were presented in Ref. [18].

4.10. Triphenylmethane

Its NMR spectra were presented in Ref. 35d. Mass spectrum (*m*/*e*): 244 [M$^+$, 100]; 165 (78); 152 (16); 139 (4); 77 (29); 51 (6). IR (neat): 3021, 1596, 1492, 757, 699 cm^{-1}.

4.11. General procedure

The reaction was conducted under dry Ar atmosphere at 25 °C in a reactor described in Ref. [12]. K$^-$, K$^+$(15-crown-5)$_2$ (10 cm^3 of 0.1 M) blue solution was dropped into 10 cm^3 of 0.5 M benzyl glycidyl ether or triphenylmethyl glycidyl ether tetrahydrofuran solution while mixing, i.e. the molar ratio of reagents was equal to 1:5, respectively, and glycidyl ethers were still in the excess. In another series of experiments 0.1 M benzyl glycidyl ether tetrahydrofuran solution was dropped into 10 cm^3 of 0.1 M K$^-$, K$^+$(15-crown-5)$_2$ solution until its discoloration, i.e. until all potassium anions were in the system exhausted. Potassium anions were still in the excess in this mixture, except the final moment of the reaction. In both series of experiments the reaction mixture was then treated with one of the appropriate quenching agent, i.e. with butyl bromide, MeOH, MeI, benzyl bromide or butyryl chloride. The products obtained were identified by matching their mass spectra, retention times, as well as NMR and IR spectra with those of authentic compounds. In a separate experiment 1 cm^3 of 0.1 M benzyl glycidyl ether in tetrahydrofuran solution was introduced into 10 cm^3 of 0.1 M K$^-$, K$^+$(15-crown-5)$_2$ solution. That reaction was quenched with MeI.

4.12. Model processes

Benzyl phenyl ether in tetrahydrofuran solution was selected for this purpose. Its reactions with **1** occurred at various molar ratio of reagents, from 5:1 to 1:10, respectively. Initial concentration of benzyl phenyl ether in the solution was equal to 0.5 M in the experiments conducted at its excess. In other experiments it was equal to 0.1 M. The reaction temperature was equal to 25 or to 0 °C. In one experiment *tert*-butanol was present in the benzyl phenyl ether solution; the molar ratio of *tert*-butanol to ether was equal to 2:1. Methyl iodide was used as the quenching agent.

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