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New facts concerning the reaction of K^-, $K^+(15\text{-crown-}5)_2$ with phenyl glycidyl ether: unexpected formation of potassium cyclopropoxide

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Abstract

A new mechanism of the reaction of K^-, $K^+(15\text{-crown-}5)_2$ with phenyl glycidyl ether is presented. The linear ether bond is attacked only to a small extent, if at all. As the main reaction path the oxirane bond in the β-position is cleaved, followed by the γ-elimination of potassium phenoxide and the formation of potassium cyclopropoxide. Crown ether ring opening also occurs in reactions with organometallic intermediates. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In our previous paper [1] preliminary results on the investigation of the phenyl glycidyl ether reaction with K^-, $K^+(15\text{-crown-}5)_2$ **1** were presented. Anisole and potassium hydroxide as well as propylene and ethylene were found in the reaction mixture after treating it with methyl iodide. It was postulated that in the first step the metal ion attacks the linear ether bond of phenyl glycidyl ether, leading to the formation of glycidylpotassium **2** and potassium phenoxide **3** (Scheme 1).

In the present work we report new experimental results concerning the study on this process. A new reaction mechanism is proposed.

2. Results and discussion

The addition of phenyl glycidyl ether into the blue K^-, $K^+(15\text{-crown-}5)_2$ solution caused its discoloration at a molar ratio of reagents equal to 1:2. The disappearance of potassium anions occurred at the same moment, as it was found in Ref. [1]. The reaction mixture was then treated with benzyl bromide. That enabled the chromatographic analysis of liquid benzylated products formed from non-volatile organometallic compounds.

The signals of two main reaction products were found in the chromatogram of the GC–MS analysis. One of them was identified as benzyl cyclopropyl ether, i.e. benzyl derivative of potassium cyclopropoxide, in 28% yield. The other product was found to be benzyl phenyl ether, e.g. the benzyl derivative of potassium phenoxide, in 62% yield.

The chromatogram also exhibited small signals due to allyl benzyl ether, 2-benzyloxypropyl phenyl ether and tetraethylene glycol benzyl vinyl ether in total yield of about 10%. The latter was observed earlier by us as the benzylated product of a crown ring-opening reaction [2].

The presence of benzyl cyclopropyl ether in the reaction mixture was also proven by NMR spectroscopic analysis (^1H and ^{13}C). All signals of the authentic sample were found in the NMR spectra of the reaction

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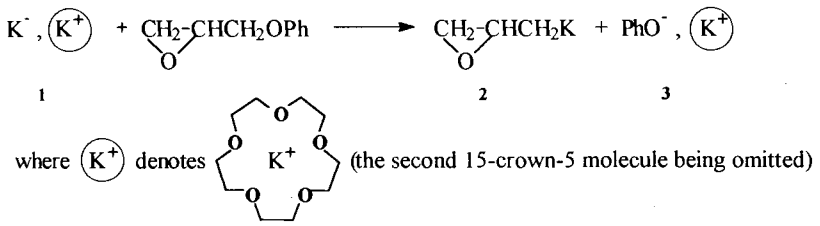


Scheme 1.

mixture. The presence of potassium hydroxide, propylene and ethylene in the reaction mixture was confirmed in separate experiments.

The formation of potassium cyclopropoxide **5** as the main reaction product shows that cleavage of the linear ether bond (Scheme 1) is not the main reaction path, because glycidylpotassium **2** cannot rearrange to **5** for stereoelectronic reasons. Therefore, the oxirane ring bond is assumed to cleave in the β-position by electron transfer from K^-, followed by formation of **4** and γ-elimination (Scheme 2).

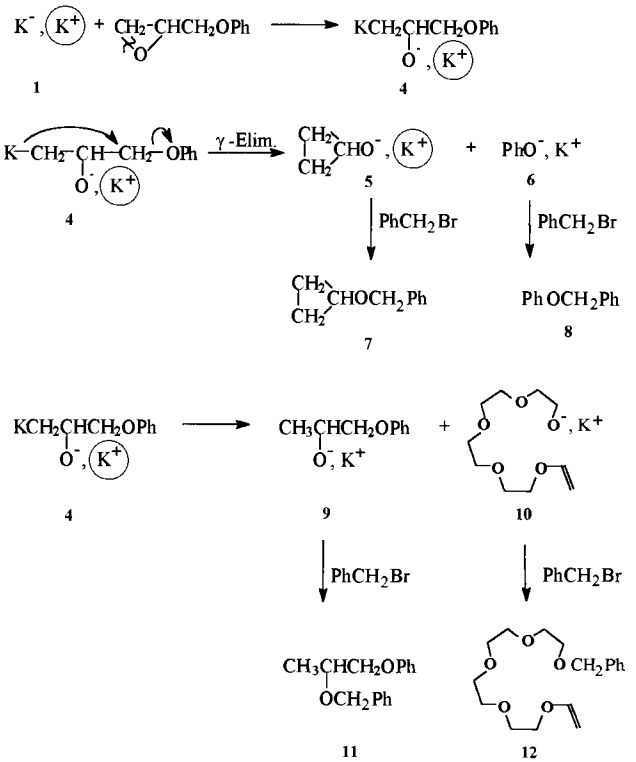
The intermediate **4** is partly trapped by protonation to **9**, finally yielding the 2-benzyloxypropyl phenyl ether **11** upon benzylation and tetraethylene glycol benzyl vinyl ether **12** as the benzylated crown ether ring-opening product **10**. An example for a similar ring closure to a cyclopropane derivative is known in the literature [3] (Scheme 3).

That glycidylpotassium **2** does rearrange into potassium allyloxide **13** was indirectly confirmed by an independent synthesis of glycidylsodium yielding exclusively sodium allyloxide. However, the allyloxide **16** obtained in our reaction starting with phenyl glycidyl ether need not be formed via glycidylpotassium **2** because cleavage of the other oxirane ring bond followed by β-elimination would yield the same product (Scheme 4).

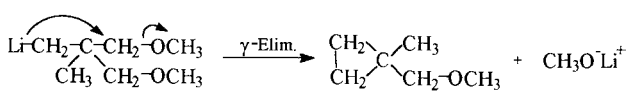
Finally the formation of propylene and potassium hydroxide has to be mentioned. Propylene is found only with excess of K^-, $K^+(15\text{-crown-}5)_2$, i.e. when the phenyl glycidyl ether solution is dropped into the K^-, $K^+(15\text{-crown-}5)_2$ solution. Scheme 5 shows the most probable path to propylene.

Additional K^-, $K^+(15\text{-crown-}5)_2$ is used to cleave the ether bond of **4** to form **17**, which could eliminate KOH or K_2O to give unstable organopotassium intermediates. Protonation of these intermediates by crown ether finally yields propylene and **10**, which is known to decompose under the influence of metal anions into ethylene and potassium glycoxides [2].

Two further paths that could lead to propylene were excluded by us as shown in Scheme 6. Compound **18**, which we prepared by treatment of propylene oxide with K^-, $K^+(15\text{-crown-}5)_2$, does not give propylene. Compound **18** might also be formed by cleavage of **9** with K^-, $K^+(15\text{-crown-}5)_2$, but we did not find the benzyl derivative of **18**. In another experiment we treated **13** with K^-, $K^+(15\text{-crown-}5)_2$ and did not get any propylene.



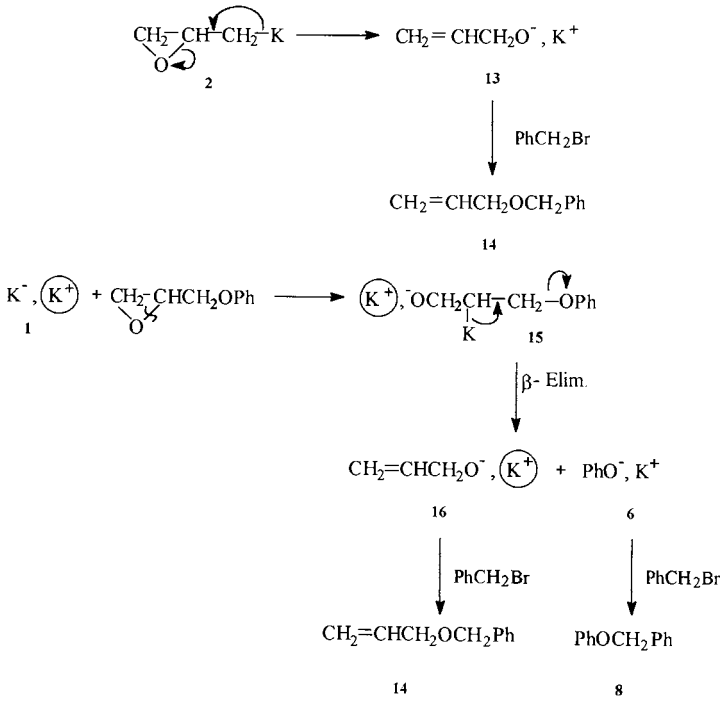
Scheme 2.



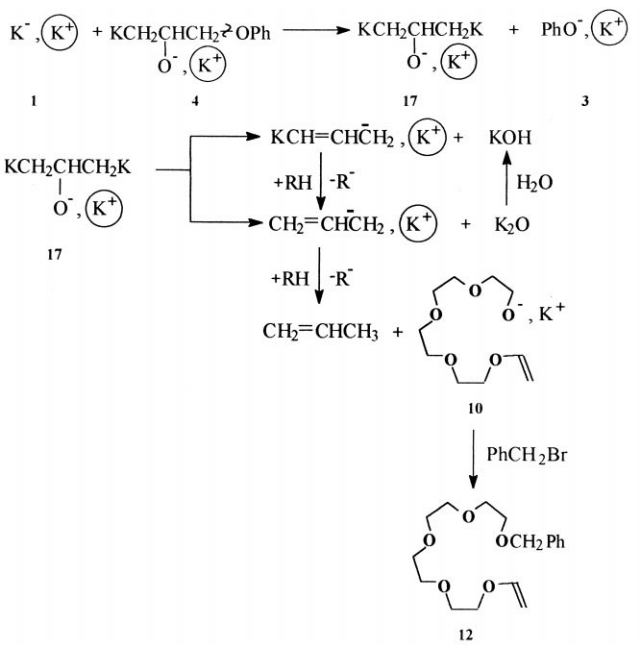
Scheme 3.

It was assumed that another gaseous product, namely ethylene, is formed in a side reaction of potassium anion with **10**.

In one experiment we dropped the K^-, $K^+(15\text{-crown-}5)_2$ solution into an excess of phenyl glycidyl ether solution (molar ratio 1:10). In this case no propylene and ethylene, as well as potassium hydroxide, were formed and only a small amount of tetraethylene glycol benzyl vinyl ether **12** was observed. The other products of ether cleavage remained unchanged.

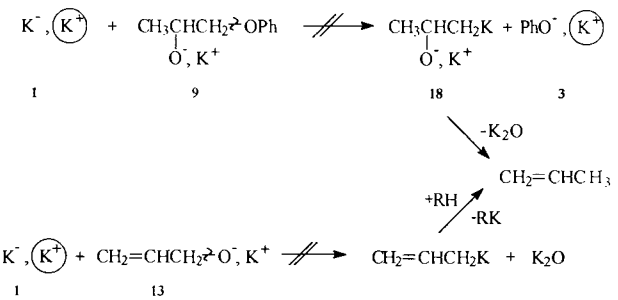


Scheme 4.



Scheme 5. RH is crown ether or other compounds losing hydrogen.

All the reactions are very fast. It was very important to use benzyl bromide as derivatising agent to detect the products **5** and **16**. The analysis of the samples treated with methyl iodide as reported in Ref. [1] did not give the information we needed for the explanation of the reaction mechanism.



Scheme 6.

3. Conclusions

In the reaction of phenyl glycidyl ether with K^-, K^+ $(15\text{-crown-}5)_2$ predominantly the least-substituted C–O bond of the strained oxirane ring is cleaved, corresponding to alkyl glycidyl ethers. In contrast to the latter, the so-formed dianion can cleave off the relative stable potassium phenoxide with closure of a cyclopropane ring (γ-elimination). This reaction is an interesting new route to the anion of cyclopropanol.

4. Experimental

Gas chromatography–mass spectrometry (GC–MS) analyses were conducted on a 30 m-long fused silica column coated with DB 1701 using a Varian 3300 gas chromatograph equipped with a Finnigan MAT 800

AT ion trap detector; the mass spectrum of benzyl cyclopropyl ether was obtained with a Hewlett–Packard HP 5988 A quadrupole mass spectrometer. Diethylene glycol dimethyl ether was used as the internal standard for the yield measurement. ^{1}H- and ^{13}C-NMR spectra of benzyl cyclopropyl ether were taken at 200 MHz on a Bruker AC 200 spectrometer; those of the reaction mixture were recorded at 20°C on a Varian VXR-300 spectrometer operating at the ^{1}H resonance frequency of 300 MHz and the ^{13}C resonance frequency of 75 MHz.

Starting materials and the reaction procedure were described in Ref. [1]. In order to identify non-volatile organometallic compounds, benzyl bromide was added to the reaction mixture to form liquid products. Allyl benzyl ether and benzyl phenyl ether (both Aldrich) were used as model compounds.

4.1. Benzyl cyclopropyl ether (7)

Benzyl cyclopropyl ether (**7**) was prepared according to a general method of Furukawa et al. [4]. To a stirred mixture of benzyl vinyl ether [5] (6.7 g, 50 mmol) and $ZnEt_2$ (4.0 ml, 40 mmol) in 25 ml of dry diethyl ether was added CH_2I_2 (17.5 g, 65 mmol) dropwise during 30 min at room temperature under N_2 atmosphere. The reaction mixture was poured slowly into ice–diluted HCl under stirring. The organic layer was washed with water and diluted $NaHCO_3$ solution, and dried over $MgSO_4$. After evaporation of Et_2O, the residue was distilled through a short column. Several fractions were collected, b.p. 88–92°C (30 mbar), which consisted mainly of benzyl cyclopropyl ether contaminated with benzyl alcohol and some benzyl vinyl ether (total 4.2 g). The last of these fractions, b.p. 92°C (30 mbar) was stirred over night with lithium metal and redistilled to give pure (> 98%) benzyl cyclopropyl ether, b.p. 46°C (2 mbar). ^{1}H-NMR $CDCl_3$ δ: 7.30 (m, 5H, C_6H_5); 4.52 (s, 2H, Ph–CH_2); 3.32 (m, 1H, OCH); 0.63 (m, 2H, CH_2 *cis*); 0.46 (m, 2H, CH_2 *trans*). ^{1}H-NMR C_6D_6 δ: 7.28 (m, 2H, C_6H_5); 7.15 (m, 3H, C_6H_5); 4.38 (s, 2H, Ph–CH_2); 3.10 (m, 1H, OCH); 0.58 (m, 2H, CH_2 *cis*); 0.23 (m, 2H, CH_2 *trans*). ^{13}C-NMR $CDCl_3$ δ: 138.17, 128.35, 127.88, 127.60 (C_6H_5); 72.79 (Ph–CH_2); 53.01 (OCH); 5.69 (CH_2). ^{13}C-NMR C_6D_6 δ: 139.04, 128.30, 127.84, 127.58 (C_6H_5); 72.65 (Ph–CH_2); 53.08 (OCH); 5.84 (CH_2). Mass spectrum (*m*/*e*): 147 (M − 1, 0.3); 130 (0.7); 104 (25); 91 (100); 77 (4); 65 (20); 63 (6); 51 (6); 39 (11).

4.2. Glycidylsodium

Glycidylsodium was prepared as an unstable intermediate from bromomethyloxirane and sodium in tetrahydrofuran solution at room temperature. It could not be detected itself, but decomposed spontaneously to sodium allyloxide.

4.3. Tetraethylene glycol monobenzyl ether

Tetraethylene glycol monobenzyl ether ($HO[CH_2CH_2O]_4CH_2Ph$): a 80% dispersion of NaH (7.8 g containing 0.26 mol NaH) in paraffin was washed twice with *tert*-butyl methyl ether and decanted; the NaH was suspended in 100 ml tetrahydrofuran and then a mixture of tetraethylene glycol (48.5 g, 0.25 mol) and 50 ml tetrahydrofuran was added dropwise. After the evolution of hydrogen had stopped, benzylbromide (25.6 g, 0.15 mol) was added and the reaction mixture stirred for 2 h. Water was added, the organic layer separated and the aqueous phase extracted with *tert*-butyl methyl ether. The combined organic phases were dried and the solvents removed under reduced pressure. The crude product (37 g) was used in the next step without further purification.

4.4. Tetraethylene glycol benzyl vinyl ether (11)

Tetraethylene glycol benzyl vinyl ether (**11**) was prepared by the transetherification method [6]. A stirred solution of crude tetraethylene glycol monobenzyl ether (37 g, 0.13 mol), butyl vinyl ether (60 g, 0.60 mol) and mercury trifluoroacetate (1.2 g, 2.8 mmol) was heated for 1 h under reflux, then anhydrous potassium carbonate (2 g, 20 mmol) was added and the excess of butyl vinyl ether was removed under reduced pressure. A sample of the residue was distilled in a Kugelrohr apparatus; the fraction boiling at 145°C (0.05 mbar) consisted of tetraethylene glycol benzyl vinyl ether. ^{1}H-NMR $CDCl_3$ δ: 7.34 (m, 5H, C_6H_5); 6.50 (dd, $J = 14.4$, 6.8 Hz, 1H, OCH=); 4.56 (s, 2H Ph–CH_2); 4.23 (dd, $J = 14.4$, 2.2 Hz, 1H, CH_2=); 3.97 (dd, $J = 6.8$, 2.2 Hz, 1H, CH_2=); 3.63–3.86 (m, 16H, OCH_2). ^{13}C-NMR $CDCl_3$ δ: 151.7 (OCH=); 138.2, 128.3, 127.7, 127.5 (C_6H_5); 86.5 (CH_2=); 73.2 (Ph–CH_2); 67.1–70.7 (OCH_2, six signals). Mass spectrum (*m*/*e*): 310 (M^+, 2); 223 (1); 177 (5); 133 (15); 105 (17); 91 (100); 73 (19); 45 (62); 43 (30).

4.5. 2-Benzyloxypropyl phenyl ether (10)

Potassium hydride (0.10 g, 2.5 mmol) and tetrahydrofuran (10 cm^3) were introduced into the reactor. Then, 1-phenoxy-2-propanol (0.61 g, 2.5 mmol) was added dropwise while stirring at 25°C. The course of the reaction was followed by measuring the amount of hydrogen evolved. After 6 h benzyl bromide (0.43 g, 2.5 mmol) was added to the mixture. The precipitated potassium bromide was filtered off, and 2-benzyloxypropyl phenyl ether (**10**) was distilled from the solution; the fraction boiling at 140°C at 0.1 mbar was collected in 80% yield. ^{1}H-NMR acetone-d_6 δ:7.5–6.9 (m, 10H, Ph + OPh); 4.64 (s, 2H, OCH_2Ph); 4.10–3.98 (m, 1H, OCH); 3.96–3.83 (m, 2H, CH_2OPh); 1.27 (d, $J = 6.1$ Hz, 3H, CH_3). ^{13}C-NMR acetone-d_6 δ: 159.9

(C_{OPh} *ipso*); 140.1 (C_{Ph} *ipso*); 130.2 (C_{OPh} *meta*); 128.9 (C_{Ph} *meta*); 128.2 (C_{Ph} *ortho*); 128.0 (C_{Ph} *para*); 121.3 (C_{OPh} *para*); 115.3 (C_{OPh} *ortho*); 74.0 (OCH); 72.2 (OCH_2Ph); 71.5 (CH_2OPh); 17.5 (CH_3). Mass spectrum (*m*/*e*): 242 (M^+, 30); 135 (9); 91 (100); 77 (25); 65 (16); 51 (7); 39 (7).

4.6. Allyl benzyl ether (**13**)

^{1}H-NMR acetone-d_6 δ: 7.36–7.24 (m, 5H, Ph); 5.95 (m, $J = 17.4$, 10.5, 5.3 Hz, 1H, CH=); 5.29 (d of apparent q, $J = 17.4$, 2 Hz, 1H, CH_2=); 5.14 (ddt, $J = 10.5$, 2, 1.5 Hz, 1H, CH_2=); 4.5 (s, 2H, OCH_2Ph); 4.0 (dt, $J =$ 5.3, 1.5 Hz, 2H, OCH_2). ^{13}C-NMR acetone-d_6 δ: 139.8 (C_{Ph} *ipso*); 136.3 (CH=); 129.0 (C_{Ph} *meta*); 128.3 (C_{Ph} *ortho*); 128.2 (C_{Ph} *para*); 116.5 (=CH_2); 72.5 (OCH_2Ph); 71.6 (OCH_2). Mass spectrum (*m*/*e*): 148 (M^+, 2); 118 (2); 107 (16); 91 (100); 79 (21); 51 (11); 39 (16).

4.7. Benzyl phenyl ether (**8**)

^{1}H-NMR acetone-d_6 δ: 7.5–6.9 (m, 10H + OPh); 5.1 (s, 2H, OCH_2). ^{13}C-NMR acetone-d_6 δ: 158.8 (C_{OPh} *ipso*); 137.1 (C_{Ph} *ipso*); 129.5 (C_{OPh} *meta*); 128.6 (C_{Ph} *meta*); 127.9 (C_{Ph} *para*); 127.5 (C_{Ph} *ortho*); 120.9 (C_{OPh} *para*); 114.9 (C_{OPh} *ortho*); 69.9 (OCH_2). Mass spectrum (*m*/*e*): 184 (M^+, 92); 91 (100); 77 (10); 65 (78); 51 (19); 39 (36).

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