

Electron-transfer reduction of selected alcohols with alkalide K^- , $K^+(15\text{-crown-5})_2$ via organometallic intermediates

Zbigniew Grobelny^a, Andrzej Stolarzewicz^{a,*}, Adalbert Maercker^b,
Stanisław Krompiec^c, Janusz Kasperczyk^d, Józef Rzepa^e, Holger Frey^f

^a Institute of Materials Science, University of Silesia, Bankowa 12, 40-007 Katowice, Poland

^b Institut für Organische Chemie, Universität Siegen, 57068 Siegen, Germany

^c Department of Analytical and General Chemistry, Silesian University of Technology, 44-101 Gliwice, Poland

^d Chair of Molecular Biology, Biochemistry and Biopharmacy, Medical University of Silesia, 41-200 Sosnowiec, Poland

^e Institute of Chemistry, University of Silesia, 40-007 Katowice, Poland

^f Institut für Organische Chemie, Johannes-Gutenberg-Universität, 55099 Mainz, Germany

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Abstract

The course of the reaction of alkalide K^- , $K^+(15\text{-crown-5})_2$ **1** with selected alcohols depends on the kind of alcohol and the mode of substrate delivery. In the case of methanol, potassium methoxide formed initially undergoes destruction at the excess of **1**. It results in potassium oxide and methylpotassium. The latter opens the crown ether ring giving potassium tetraethylene glycoxide vinyl ether and methane. A similar course of the process is observed for propanol. Potassium glycidoxide is the main product formed in the reaction of **1** with glycidol. Its oxirane ring is opened at the excess of **1**. Organopotassium alkoxides, i.e., potassium potassiummethoxide and dipotassium potassio propane-1,2-dioxide are intermediate products of this reaction. They react then with the crown ether. Potassium methoxide, potassium enolate of acetaldehyde, dipotassium propane-1,2-dioxide and potassium tetraethylene glycoxide vinyl ether are the final products of this process.

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1. Introduction

Alkalides, M^- , M^+C , are salts containing alkali metal anions and cations complexed by a ligand, e.g., crown ether [1–4]. They are known as two-electron-transfer species [5], used in the reactions with alkenes [6–9], alkyne [10], alkyl halides [11,12], silyl halides [13], ketones [14,15], esters [16–20], and ethers [12,20–28]. Organometallic compounds were intermediate products in those systems. They underwent various fast reactions, for example with crown ether applied for the preparation of alkalide [29].

Data concerning the behaviour of alcohols in the presence of alkalides were till now not presented in the

literature. This work describes for the first time the study in such area. Methanol, propanol, glycidol and K^- , $K^+(15\text{-crown-5})_2$ **1** in tetrahydrofuran solution were selected for this study.

Methanol and propanol are simple alcohols. Glycidol possesses two functional groups, i.e., the oxirane ring and the hydroxyl group. Thus, it can take part in two kinds of reaction [30]. For example, the oxirane ring is opened in the presence of alkoxides [31–33]. Cleavage occurs exclusively in the β -position, i.e., between oxygen and the CH_2 group. This mechanism of the ring opening has been also reported for the reaction of chiral glycidol with thiols under basic condition [34]. A similar mechanism is assumed for the reaction of (R)- or (S)-glycidol with phenols in the presence of triethylamine in absolute ethanol or sodium hydroxide in water [35]. On the other hand, the O–H bond is cleaved in reactions of glycidol with vinyl ethers [36]. The appropriate glycidyl ethers

* Corresponding author. Tel.: +48-32-359-14-21; fax: +48-32-259-69-29.

E-mail address: astolarzewicz@silesianet.pl (A. Stolarzewicz).

are formed in this case. The oxirane ring does not take part in this process. A similar phenomenon was recently described in [37]. Glycidol reacted with potassium hydride exclusively as a typical alcohol, giving potassium glycidoxide and hydrogen. This means that the activity of one of the groups present in the glycidol molecule results in the inactivity of another. Further examples supporting this rule are given in [30].

2. Results and discussion

An excess of methanol in relation to **1** was used in the first series of experiments. The blue solution of **1** became colorless when it was dropped into methanol. Potassium anions of **1** vanished at this moment [4]. Hydrogen evolution was observed at the same time. The reaction mixture was quenched by the addition of benzyl bromide. Only one product was detected in the system after its benzylation, i.e., benzyl methyl ether (in 25% yield).

In a separate experiment methanol was dropped into a solution of **1** until the reaction mixture became colorless, i.e., until K^- was decayed. It means that potassium anions were still at the excess in relation to methanol except for the moment of discoloration. The evolution of hydrogen and methane took place in this case. Tetraethylene glycol benzyl vinyl ether was found in the reaction mixture after its quenching with benzyl bromide.

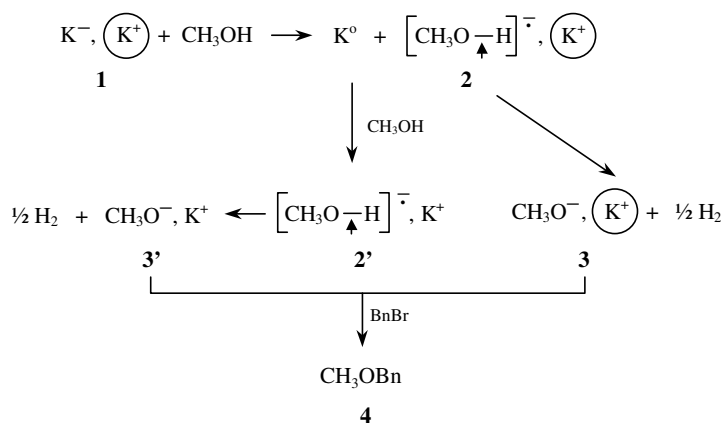
Basing on these results a following mechanism of the process is proposed. The electron-transfer reduction of methanol with **1** leads to the formation of hydrogen and two kinds of potassium methoxide molecules, **3** and **3'** (Scheme 1). However, at the excess of **1** the alkoxide is then destroyed to methylpotassium **6** and potassium oxide. **6** reacts immediately with crown ether giving methane and potassium tetraethylene glycoxide vinyl ether **7** (Scheme 2).

The products obtained in the reaction of **1** with the excess of propanol included hydrogen and potassium propoxide. At the excess of **1** the latter decomposed to potassium oxide and propylpotassium, which opened the crown ether ring giving propane and **7**. It means that methanol and propanol react in the same manner with the alkoxide.

A similar phenomenon was previously described for allylic and benzylic alcohols and their silylated derivatives [38]. It was found that alkoxides obtained in the reaction of these alcohols with butyllithium could be cleaved even with a less reactive lithium powder when using of 4,4'-di-*tert*-butylbiphenyl (DTBB) in a catalytic amount. That resulted in appropriate alkyllithium compounds, which reacted with different electrophiles. Crown ether was not applied in such a system.

The excess of glycidol in relation to **1** was used in the second series of experiments. Hydrogen evolution was observed during the reaction. The process was stopped by the addition of benzyl bromide to identify volatile benzyl derivatives of non-volatile reaction products. Two compounds were detected in the reaction mixture after benzylation, i.e., benzyl glycidyl ether (19%) and 2-benzyloxy-1-propanol (3%). This shows that potassium glycidoxide and potassium 1-hydroxypropane-2-oxide were the original products of the reaction. The experiments were repeated several times with very similar product distribution. Only these two benzylated potassium alkoxides and hydrogen were obtained each time.

Various reaction mechanisms were taken into account to explain these results. The most probable is that the process starts with the electron transfer from K^- of **1** to the glycidol molecule. K° and the radical anion **9** are formed in this reaction (Scheme 3). The unstable **9** can decompose to the radical anion **10** due to the oxirane ring opening in the β -position. Then, K° transfers the second electron to **10** giving the organopotassium compound **11**. It reacts with another glycidol molecule,



where: $\textcircled{K^+}$ denotes $K^+(15\text{-crown-5})$; the second crown ether molecule was omitted.

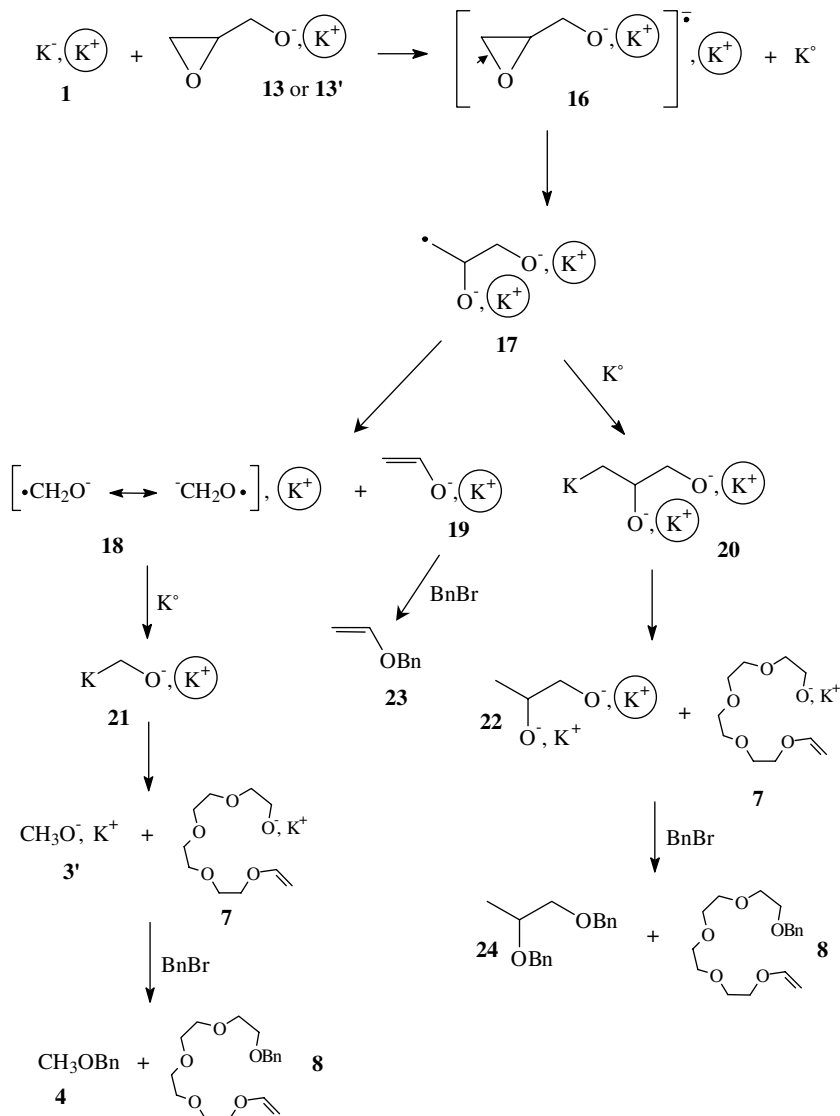
Scheme 1.

12, **13**, and **13'**, although only two benzylated products, i.e., 2-benzyloxy-1-propanol **14** and benzyl glycidyl ether **15** are obtained after benzylation of the reaction mixture.

This means that the system found differs from those known until now [30–37]. Both the oxirane ring and the O-H bond are cleaved in glycidol by K^- . The rule presented in the literature that the activity of one of these groups is connected with the inactivity of another is not valid in the studied system.

In further experiments the reaction of glycidol was conducted in reverse. Glycidol was dropped into a solution of **1** until the reaction mixture became colorless. In this case the benzylated reaction products included benzyl methyl ether (in 12% yield), benzyl vinyl ether (15%), 1,2-dibenzyloxypropane (26%), and tetraethylene

glycol benzyl vinyl ether (15%). Benzyl glycidyl ether, i.e., the benzylated product of potassium glycidoxide was not observed. This means that additional reactions occur in the system containing an excess of **1**. K^- transfers one electron to **13** or **13'**, giving K° and the radical anion **16** (Scheme 4). The oxirane ring of **16** is then opened in the β -position. The radical anion **17** formed may react in two ways. In the first path, it decomposes to the radical anion of formaldehyde **18** [27] and the enolate anion of acetaldehyde **19**, which are stabilized by resonance. Then, K° transfers the next electron to **18** giving potassium potassiomethoxide **21**. It opens the crown ether ring. This in turn results in potassium tetraethylene glycoxide vinyl ether **7** and potassium methoxide **3'**, similar as described in [27]. In the second path the electron is transferred from K° to **17**.



Scheme 4.

Organopotassium glycoxide **20** formed attacks then crown ether. **7** and dipotassium propane-1,2-dioxide **22** are the final products of the process. However, **1** can also react with **12**. It results in the formation of **22** and hydrogen. Thus, at the excess of **1** further reactions took place with the participation of potassium anions. Initial products were destroyed and some new compounds were observed in the reaction mixture. **4**, **8**, **23**, and **24** are their benzylated derivatives found after benzylation.

The processes presented in Schemes 1–4 are very fast, similarly as it has been found in earlier works [22–28]. Organopotassium compounds are formed at the excess of **1**. However, their benzylated derivatives were not detected in the reaction mixture. It means that they underwent further reactions before benzylation, in spite of the fact that the quenching agent was used immediately after mixing of reagents.

This is another example found by us that organopotassium compounds easily open the crown ether ring giving unsaturated alkoxide containing four CH₂CH₂O groups. It seems that this reaction might be applied as a method helpful for checking the presence of short-lived organometallic intermediates in the reaction mixture, i.e., for their qualitative analysis. However, some limitations on this method should be taken into account in this case. The negative result of the experiment, i.e., the absence of the expected alkoxide, cannot be a proof that the studied reaction occurs without the participation of organometallic intermediates [29].

3. Conclusions

The mechanism of the reaction of **1** with selected alcohols depends on the mode of substrate delivery. Deprotonation of alcohol occurs at its excess. It leads to the appropriate alkoxide, which is decomposed at the excess of **1**. Potassium oxide and short-lived organopotassium intermediates are formed in the case of simple alcohols, e.g., methanol or propanol. The organopotassium compounds react then with crown ether giving potassium tetraethylene glycoxide vinyl ether.

The course of the reaction of **1** with potassium glycidoxide differs from that with simple alkoxides. The oxirane ring opening occurs in such a case and potassium oxide is not formed. However, the oxirane ring of glycidol is opened also at its excess resulting in organopotassium alkoxide. The latter reacts with the next glycidol molecule and does not with crown ether.

4. Experimental

GC–MS analyses of liquids were run on a 30-m fused silica capillary column DB-5 in a Varian 3300 gas chromatograph equipped with a Finnigan MAT SSO

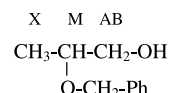
700 quadrupole detector. Diethylene glycol dimethyl ether was used as an internal standard for yield measurements. Gaseous reaction products were searched for by GC with a 2.4-m stainless steel column packed with Al₂O₃, 0.02–0.03 mm, deactivated with 5% K₂CO₃ in an INCO 505 gas chromatograph equipped with a flame ionization detector. ¹H and ¹³C NMR spectra were recorded at 20 °C on a Varian VXR-300 multinuclear spectrometer at the ¹H resonance frequency of 300 MHz, and at the ¹³C resonance frequency of 75 MHz. Deuterated acetone was used as the solvent. Chemical shifts were referenced to tetramethylsilane (TMS) serving as an internal standard.

Glycidol (Merck) was distilled at 61 °C/15 mm Hg. Tetrahydrofuran (POCH) was boiled over CuCl to decompose peroxides and then over CaH₂ for 10 h; finally it was distilled at 66 °C. The fraction obtained was dried over metallic potassium for 20 h and redistilled prior to use. Methanol and propanol were distilled twice. 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.

4.1. 2-Benzyloxy-1-propanol and 1-benzyloxy-2-propanol

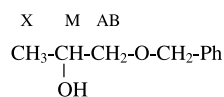
A mixture of 0.3 mol 1,2-propanediol, 0.1 mol benzyl chloride, 50% NaOH (60 mL), 0.005 mol tetrabutylammonium hydrogensulfate, and benzene (60 mL) was stirred intensely at 70–80 °C on a water bath for 3 h. Subsequently cooled water (100 mL) and hexane (100 mL) was added to the mixture. The layers were separated, the organic layer was washed three times with water (50 mL) and dried with anhydrous MgSO₄. After removing hexane and benzene on a rotatory evaporator the residue was distilled under reduced pressure. A mixture of 2-benzyloxy-1-propanol and 1-benzyloxy-2-propanol was finally obtained in 82% yield (40:60). B.p. = 130–131 °C/3 mm Hg. The attempt to separate the mixture was unsuccessful. ¹H NMR spectra were analyzed by a simulation study, using NMR software MestRe-C 2.3a (Unidade de Resonancia Magnetica, Universidade de Santiago de Compostela, La Coruna, Spain).

4.1.1. 2-Benzyloxy-1-propanol (**14**)



¹H NMR (CDCl₃): δ = 7.30 – 7.35 (m, 5 H, Ph); 4.61 (s, 2 H, CH₂); 3.75 (m, 1 H, CH_(M)); J_{AM} = 6.0 Hz, J_{BM} = 4.8 Hz, J_{MX} = 6.3 Hz); 3.55 (q, 1H, CH_(A)); J_{AB} = 10,2 Hz, J_{AM} = 6.0 Hz); 3.45 (q, 1 H, CH_(B)); J_{AB} = 10.2 Hz, J_{BM} = 4.8 Hz); 1.20 (d, 3 H, CH_(X)); J_{MX} = 6.3 Hz). Mass spectrum (*m/e*): 166 [M⁺, 1]; 107 (25); 91 (100); 79 (6); 77 (6); 75 (8); 65 (22); 51 (1).

4.1.2. 1-Benzylxy-2-propanol



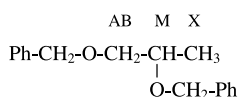
^1H NMR (CDCl_3): $\delta = 7.30 - 7.35$ (m, 5 H, Ph); 4.55 (s, 2 H, CH_2); 3.97 (m, 1 H, $\text{CH}_{(\text{M})}$; $J_{\text{AM}} = 3.0$ Hz, $J_{\text{BM}} = 7.5$ Hz, $J_{\text{MX}} = 6.3$ Hz); 3.42 (q, 1 H, $\text{CH}_{(\text{A})}$; $J_{\text{AB}} = 8.5$ Hz, $J_{\text{AM}} = 3.0$ Hz); 3.26 (q, 1 H, $\text{CH}_{(\text{B})}$; $J_{\text{AB}} = 8.5$ Hz, $J_{\text{BM}} = 7.5$ Hz); 1.12 (d, 3 H, $\text{CH}_{(\text{X})}$; $J_{\text{MX}} = 6.3$ Hz). Mass spectrum (m/e): 165 [M^+ , 30]; 107 (32); 91 (100); 79 (6); 77 (5); 65 (18); 51 (1).

4.2. Benzyl vinyl ether (23)

A mixture of 0.01 mol 2-bromoethylbenzyl ether, 0.01 mol 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and tetrahydrofuran (10 mL) was stirred intensely at 60 °C for 8 h. Subsequently cooled pentane (10 mL) was added and the mixture was left at 0 °C overnight. The salt precipitate was filtered and washed with 10 mL of tetrahydrofuran and pentane mixture (1:1). Volatile fractions were removed by distillation and benzyl vinyl ether was obtained in practically quantitative yield (purity >99%; GC). B.p. = 50–51 °C/16 mm Hg. Mass spectrum (m/e): 134 [M^+ , 4]; 116 (7); 105 (11); 91 (100); 77 (7); 65 (30); 51 (9); 39 (11). ^1H and ^{13}C NMR spectra (in CDCl_3) have been already presented in [39,40].

4.3. 1,2-Dibenzylxypropane (24)

A mixture of 0.1 mol 1,2-propanediol, 0.22 mol benzyl chloride, 50% NaOH (60 mL), 0.007 mol tetrabutylammonium hydrogensulfate, and benzene (60 mL) was stirred intensely at 70–80 °C on a water bath for 3 h. Subsequently cooled water (100 mL) and hexane (100 mL) was added. The layers were separated, the organic layer washed three times with water (50 mL) and dried with anhydrous MgSO_4 . After removal of hexane and benzene the residue was distilled under reduced pressure. 1,2-Dibenzylxypropane was finally obtained in 62% yield (purity >97%; GC). B.p. = 170–171 °C/2 mm Hg.



^1H NMR (CDCl_3): $\delta = 7.25 - 7.37$ (m, 10 H, Ph); 4.61 (s, 2 H, CH_2); 4.55 (s, 2 H, CH_2); 3.76 (m, 1 H, $\text{CH}_{(\text{M})}$, $J_{\text{AM}} = 6.0$ Hz, $J_{\text{BM}} = 4.8$ Hz, $J_{\text{MX}} = 6.3$ Hz); 3.55 (q, 1 H, $\text{CH}_{(\text{A})}$, $J_{\text{AB}} = 10.2$ Hz, $J_{\text{AM}} = 6.0$ Hz); 3.45 (q, 1 H, $\text{CH}_{(\text{B})}$, $J_{\text{AB}} = 10.2$ Hz, $J_{\text{BM}} = 4.8$ Hz); 1.21 (d, 3 H, $\text{CH}_{(\text{X})}$, $J_{\text{MX}} = 6.3$ Hz). ^{13}C NMR (CDCl_3): 138.86 (C_{t} , Ph); 138.37 (C_{t} , Ph); 128.28 (C_{meta} , Ph); 128.24 (C_{meta} , Ph); 127.53 (C_{ortho} , Ph); 127.51 (C_{ortho} , Ph); 127.46 (C_{para} , Ph); 127.35 (C_{para} , Ph); 74.2 ($\text{CH}_2\text{-CH}$); 73.92

(CH); 73.23 ($\text{CH}_2\text{-Ph}$); 71.03 ($\text{CH}_2\text{-Ph}$); 17.25 (CH_3). ^{13}C NMR spectrum was earlier presented in [41]. Mass spectrum (m/e): 256 [M^+ , 1]; 165 (36); 107 (18); 91 (100); 79 (6); 65 (13); 39 (2).

GC–MS and NMR spectra of benzyl glycidyl ether [26], benzyl methyl ether [27], benzyl propyl ether [27], and tetraethylene glycol benzyl vinyl ether [12] have been reported previously.

4.4. General procedure

Preparation of K^- , $\text{K}^+(15\text{-crown-5})_2$ **1** tetrahydrofuran solution was performed at ambient temperature in an apparatus presented in [12]. Potassium (about 1.5 g) was distilled into a reactor under a high vacuum. Then, 0.2 M 15-crown-5 solution in tetrahydrofuran (10 mL) was dropped on the metal mirror. After 25 min of ultrasonic mixing a deep blue 0.1 M solution of **1** was obtained. The solution was finally filtered through a glass frit.

The reaction was conducted in a 50 mL reactor thermostatted at 25 °C. In one series of experiments 0.1 M solution of **1** (10 mL) was gradually introduced into the reactor filled with 0.5 M of selected alcohol in tetrahydrofuran (10 mL) while mixing. In the other experiments the blue potassium solution was titrated with 0.1 M alcohol solution until discoloration of the reaction mixture. Benzyl bromide (10% excess in relation to potassium ions) was used as the quenching agent to transform non-volatile reaction products into the volatile compounds. Then, water (2 mL) was added to the reaction mixture obtained at the excess of **1**. The basicity of the water phase was found in the system with methanol or propanol, which indicated the presence of potassium hydroxide. The products obtained were identified matching their mass spectra, retention times, as well as NMR spectra.

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