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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 glycidyl-potassium **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.

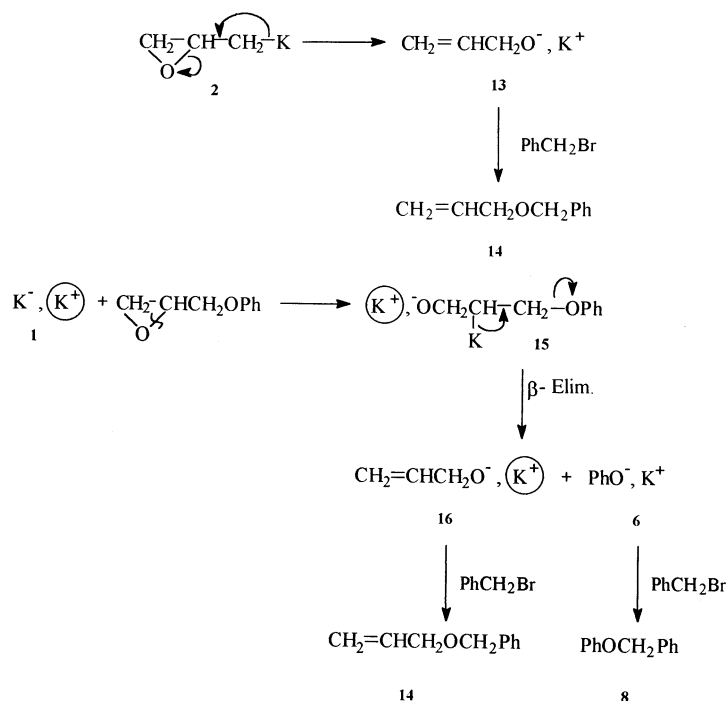
The signals of two main reaction products were found in the chromatogram of the GC–MS analysis. One of them was identified as benzyl cyclopropyl ether, i.e. benzyl derivative of potassium cyclopropoxide, in 28% yield. The other product was found to be benzyl phenyl ether, e.g. the benzyl derivative of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

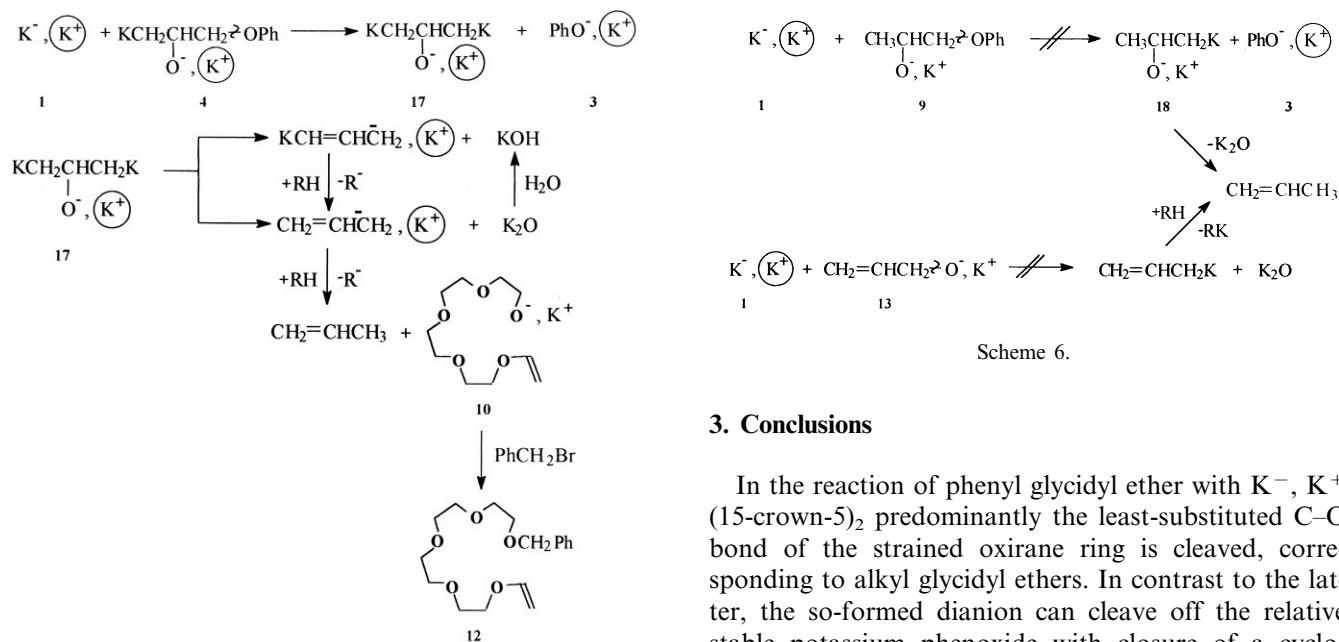
The presence of benzyl cyclopropyl ether in the reaction mixture was also proven by NMR spectroscopic analysis (^1H and ^{13}C). All signals of the authentic sample were found in the NMR spectra of the reaction

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Scheme 4.



Scheme 6.

3. Conclusions

In the reaction of phenyl glycidyl ether with K^- , K^+ (15-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

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.

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. ^1H - 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 ^1H 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). ^1H -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*). ^1H -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 ($\text{M} - 1$, 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 ($\text{HO}[\text{CH}_2\text{-CH}_2\text{O}]_4\text{CH}_2\text{Ph}$): 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 transesterification 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. ^1H -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. ^1H -NMR acetone- d_6 δ : 7.5–6.9 (m, 10H, $\text{Ph} + \text{OPh}$); 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 (OCH₂Ph); 71.5 (CH₂OPh); 17.5 (CH₃). 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**)

¹H-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, CH₂=); 5.14 (ddt, *J* = 10.5, 2, 1.5 Hz, 1H, CH₂=); 4.5 (s, 2H, OCH₂Ph); 4.0 (dt, *J* = 5.3, 1.5 Hz, 2H, OCH₂). ¹³C-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 (=CH₂); 72.5 (OCH₂Ph); 71.6 (OCH₂). 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**)

¹H-NMR acetone-*d*₆ δ : 7.5–6.9 (m, 10H + OPh); 5.1

(s, 2H, OCH₂). ¹³C-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 (OCH₂). Mass spectrum (*m/e*): 184 (M⁺, 92); 91 (100); 77 (10); 65 (78); 51 (19); 39 (36).

References

- [1] A. Stolarzewicz, Z. Grobelny, M. Kowalczyk, J. Organomet. Chem. 492 (1995) 111.
- [2] Z. Grobelny, A. Stolarzewicz, in: Proceedings of the Scientific Conference PTChem, Wrocław, 1998, p. 118.
- [3] W. Moene, M. Schakel, G.J.M. Hoogland, F.J.J. de Kanter, G.W. Klumpp, A.L. Spek, Tetrahedron Lett. 31 (1990) 2641.
- [4] J. Furukawa, N. Kawabata, J. Nishimura, Tetrahedron 24 (1968) 53.
- [5] E.J. Corey, J.D. Bass, R. LeMahieu, R.B. Mitra, J. Am. Chem. Soc. 86 (1964) 5579.
- [6] W.H. Watanabe, L.E. Comlon, J. Am. Chem. Soc. 79 (1957) 2828.