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The unusual outcome of the reaction of potassium anions with phenyl glycidyl ether

Andrzej Stolarzewicz *, Zbigniew Grobelny, Marek Kowalczuk

Institute of Polymer Chemistry, Polish Academy of Sciences 41-800 Zabrze, Poland

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Abstract

The formation of potassium phenolate, potassium hydroxide, propylene and ethylene in the reaction of phenyl glycidyl ether ($PhOCH_2\overline{CH{-}CH_2O}$) with the potassium anions has been demonstrated. Evidently, the $PhO{-}CH_2$ bond is remarkably readily cleaved by the K^- ion under these conditions.

Keywords: Potassium anions; Crown ethers; Oxiranes

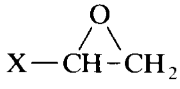
1. Introduction

Organic chemistry textbooks say that linear ethers are inert towards bases and reducing agents but that the strained three-membered oxirane ring is readily opened by such reagents [1,2]. Recently, however, several reports have indicated that not only oxiranes but other cyclic and linear ethers and esters are also cleaved by alkali metal anions [3–6]. Such reactions are very fast and sometimes unexpected products are formed; e.g., enolate carbanions formed by C–C bond cleavage in the case of β-lactones [6].

These reports promted us to examine the products formed in the reaction of potassium anions with phenyl glycidyl ether. The latter possesses both cyclic and linear ether linkages in the molecule allowing us to compare their relative reactivity. A blue solution of the complex K^-, $K^+(15\text{-crown-}5)_2$ in tetrahydrofuran was used as the reagent [7].

2. Results and discussion

The mechanism of the reactions of oxiranes with common bases such as alkali metal hydroxides or alcoholates is well established [8–17]. The reaction takes place via cleavage of the carbon–oxygen bond in the oxacyclic ring. For most monosubstituted oxiranes **1**, e.g. propylene oxide (X = Me) [8–15] and phenyl glycidyl ether ($X = CH_2OPh$) [16,17], the β-carbon–oxygen bond, i.e. the $CH_2{-}O$ linkage, is cleaved.



$$X{-}\overset{\overbrace{\quad O \quad}}{CH{-}CH_2}$$

(1)

The products of such a reaction are the corresponding alkoxides.

Formation of products which do not arise in the manner was observed for the reaction of phenyl glycidyl ether with potassium anions. Dropwise addition of phenyl glycidyl ether in THF into the blue solution containing K^-, $K^+(15\text{-crown-}5)_2$ leads to simultaneous consumption of both reagents and discoloration of the reaction mixture when the molar ratio of oxirane to K^- equals ca. 1 : 2, followed by formation of a precipitate and evolution of gas. The reaction was complete immediately at room temperature and no unchanged phenyl glycidyl ether remained. Upon addition of methanol the precipitate disappeared and the formation of phenol was revealed by GLC–MS analysis. When the mixture was quenched with methyl iodide, anisole was observed in the solution. Thus we concluded that potassium phenolate was the product containing the aromatic moiety. The presence of potassium hydroxide together with potassium phenolate in the precipitate was confirmed by NMR spectroscopy.

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* Corresponding author.

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Quantitative analysis of the non-volatile products (phenolate and KOH) was carried out also by NMR spectroscopy. After evaporation of THF from the reaction mixture, the residue was dissolved in deuterated ethanol. The ^{1}H NMR spectrum revealed that the relative integrals of the signals from KOH, C_6H_5–OD and the CH_2 groups of 15-crown-5 was 0.9 : 5.4 : 80 compared with the theoretical ratio of 1 : 5 : 80 (in the reaction, 1 mmol of K^-, $K^+(15\text{-crown-}5)_2$ was treated with 0.5 mmol of the phenyl glycidyl ether). Thus, ca. 0.5 mmol of KOH and 0.5 mmol of potassium phenolate were formed, indicating a quantitative yield.

Analysis of the gaseous phase by GLC revealed that 0.26 mmol of ethylene and 0.19 mmol of propylene had been formed. Ethylene and traces of propylene were also found in the solution. Thus, the total quantity of gaseous products was ca,. 0.5 mmol (0.3 mmol of ethylene and 0.2 mmol of propylene).

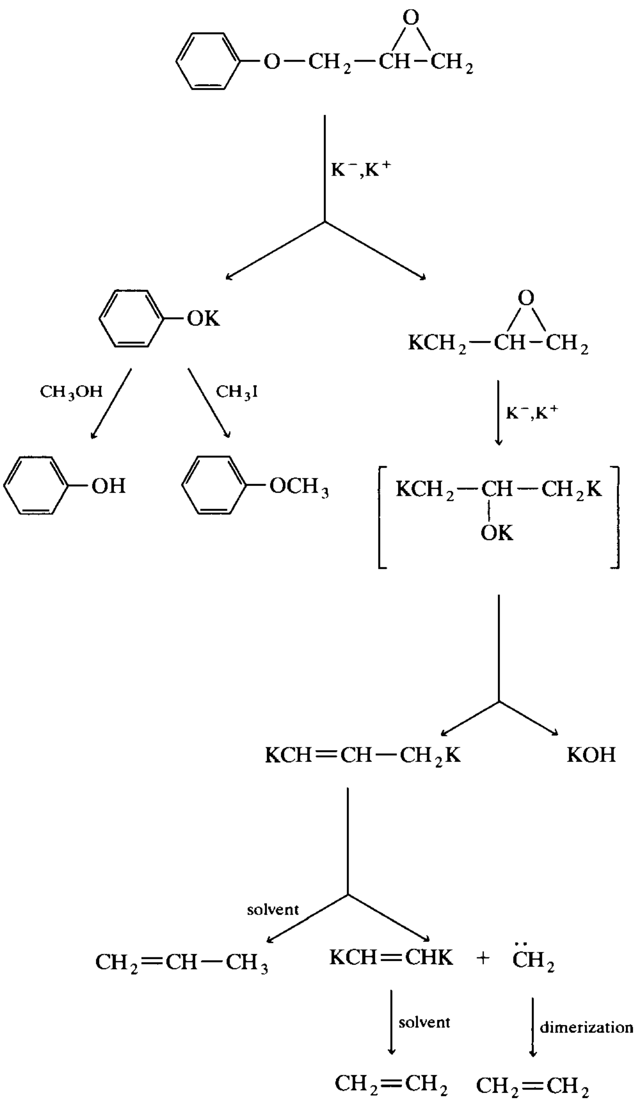
It is noteworthy that these gaseous compounds are present even before the addition of methanol. This indicates that there is a rapid protonation of reactive organopotassium intermediates by the solvent. Such solvent protonation may explain the absence of the corresponding methylation products after treatment of the reaction mixture with methyl iodide.

No other products were revealed in the reaction mixture by GC–MS analysis. In additional experiments carried out in tetraglyme, no products that might have had a retention time overlapping that of THF were detected. This indicates that initially the potassium anion attacks selectively at the linear ether bond of phenyl glycidyl ether. Cleavage of the alkyl–oxygen bond occurs, leading to the formation of potassium phenolate and the anion $KCH_2\overline{CHCH_2O}$. Then oxirane ring-opening occurs and the various decomposition products are formed. The overall process is depicted in Scheme 1.

Further experiments confirmed that alkyl–oxygen bond cleavage also took place in the case of alkyl–aryl ethers such as anisole and phenetole, and led to the formation of potassium phenolate and the corresponding hydrocarbons (methane and ethane). This is in good agreement with earlier reports on regioselective carbon–oxygen bond cleavage in these ethers by metallic potassium in heterogeneous systems [18] and with that of other aromatic ethers by a solution of potassium in THF [19].

Although we could not directly confirm the formation of aliphatic potassium intermediates, we note that the decomposition reactions of alkylpotassium compounds and the elimination of carbene [20,21], the fast protonation of organometallic compounds by solvent molecules [22–24], and the dimerization of methylene [25] have all been reported previously.

It is noteworthy that replacing the phenyl group of the glycidyl ether by an alkyl group leads to an entirely different reaction pattern. Thus addition of butyl glycidyl ether into K^-, $K^+(15\text{-crown-}5)_2$ solution, followed by treatment with methanol gave 1-butoxy-2-propanol, showing that in this case the normal oxirane ring-opening takes place, as depicted in Scheme 2.



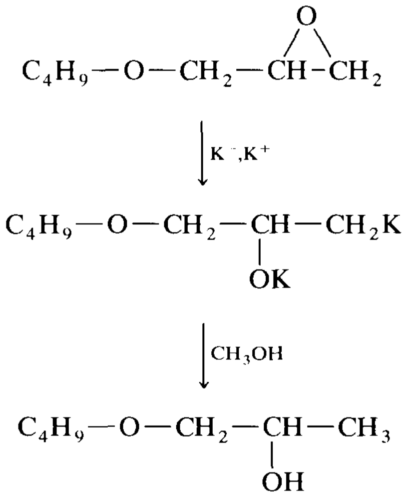
Scheme 1.

It may therefore be concluded that the ease of cleavage of linear ether bond upon treatment with K^- is connected with the presence of the aromatic ring attracted to the oxygen atom.

3. Experimental details

3.1. Materials

The 0.1 M solution of K^-, $K^+(15\text{-crown-}5)_2$ in THF (POCh) or on tetraglyme (Aldrich) were obtained in the presence of 15-crown-5 (Aldrich) as previously de-



Scheme 2.

scribed [7], and 10 ml samples of the solutions containing 1 mmol of potassium anions were used. Phenyl glycidyl ether (Aldrich), butyl glycidyl ether (Koch-Light Laboratories Ltd.), anisole (Aldrich) and phenetole (Aldrich) were distilled and then dried over CaH_2 in a recycling system under a dry argon atmosphere and redistilled before use as 0.1 M solutions in THF.

3.2. General procedure

The reaction was conducted under argon at 293 K (20°C), adding the 0.1 M THF solution of the selected ether drop-wise into the K^-, $K^+(15\text{-crown-}5)_2$ solution until the characteristic blue colour disappeared.

In order to identify the non-volatile potassium phenolate, methanol or methyl iodide was added to the product mixture. The liquid products formed were then analyzed by GLC–MS, and after preparative GC separation also by ^1H NMR spectroscopy.

The GLC–MS analyses were carried out with a 30 m long fused silica capillary column coated with DB-1701 in a Varian 3300 gas chromatograph equipped with a Finnigan MAT 800AT ion trap detector. Preparative GLC separations were conducted on a glass column packed with OV-17, 15% on Chromosorb W, 45–60 mesh using a Varian 2800 gas chromatograph with a semi-preparative scale unit. The MS and NMR spectra of the isolated products were consistent with those of authentic compounds.

Ethylene and propylene were identified by GLC 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 and an electronic integrator.

Identification of KOH was by NMR spectroscopy using a Varian VXR-300 multinuclear spectrometer. After evaporation of the solvent from the reaction mixture, the white residue was dried under vacuum and dissolved in C_2D_5OD. The signal of the potassium cation was observed in the ^{39}K NMR spectrum. In the ^1H NMR spectrum, along with the signals from the aromatic protons at δ 6.8, 6.43 and 6.15 ppm, and those from the CH_2 protons of the crown ether at δ 3.5 ppm, there was also a signal at δ 7.4 ppm. The position of the signal was found to be temperature-dependent, and was attributed to the proton of the OH group. The same signal was observed in the ^1H NMR spectrum of potassium hydroxide solution in this solvent and was absent in the spectrum of the C_2D_5OD used.

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