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Communication

Decomposition of the crown ether ring in the reaction of K^-, $K^+(15\text{-crown-}5)_2$ with oxetane

Zbigniew Grobelny [a], Andrzej Stolarzewicz [a,*], Adalbert Maercker [b]

[a] *Centre of Polymer Chemistry, Polish Academy of Sciences, 41-819 Zabrze, Poland*

[b] *Institut für Organische Chemie, Universität Siegen, D-57068 Siegen, Germany*

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Abstract

A cleavage of both oxacyclic rings occurs in the reaction of K^-, $K^+(15\text{-crown-}5)_2$ with oxetane in tetrahydrofuran solution. Oxetane ring opening leads to the formation of organometallic compounds, which react with the crown molecule. Potassium methoxide, potassium *n*-propoxide as well as potassium tetra(ethylene glycoxide) vinyl ether are the main reaction products. It means that crown ether can act both as an activator and as a reagent under studied conditions. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Potassium anion; Oxetane; 15-Crown-5

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1. Introduction

The mechanism of reaction of K^-, $K^+(15\text{-crown-}5)_2$ with methyloxirane was studied in our previous work [1]. It was a model reaction of the initiation step of methyloxirane polymerization by the potassium supramolecular complex. Unexpectedly, it turned out that in this process, both the oxirane and crown ether rings were opened. The reaction of a metal anion with methyloxirane resulted at first in the formation of an organometallic compound. The latter reacted with the crown ether causing its decomposition. The main reaction products included potassium isopropoxide and potassium tetra(ethylene glycoxide) vinyl ether. Therefore, it was shown for the first time that the crown ether ring can be opened during a reaction with an organometallic compound.

Further investigations on the 15-crown-5 ring opening are presented in this work. Oxetane, i.e. a cyclic oxide with a larger ring than that of oxirane, was used in the study. This compound was useful for the experiments because it does not polymerize anionically.

2. Results and discussion

The literature concerning the ring opening reaction of oxetane in an anionic process is rather scanty. According to our knowledge only three papers were presented in this field until now. In the first [2], oxetane was cleaved at 0°C in tetrahydrofuran (THF) by lithium 4,4′-di-*tert*-butylbiphenylide, giving lithium γ-lithiopropoxide. A similar product, i.e. potassium γ-potassiopropoxide, was found as the product of reaction of oxetane with K^-, $K^+(18\text{-crown-}6)$ complex at −20°C [3,4]. However, other results were observed in the present work.

Benzyl methyl ether, benzyl *n*-propyl ether and tetra(ethylene glycol) benzyl vinyl ether in 22, 25 and 38% yield, respectively, were found as the main benzylated products of the reaction of K^-, $K^+(15\text{-crown-}5)_2$ with oxetane at 25°C. Ethylene (9 cm^3) evolved during the

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* Corresponding author. Tel.: +48-32-2716077; fax: +48-32-2712969.

E-mail address: polymer@uranos.cto.us.edu.pl (A. Stolarzewicz).

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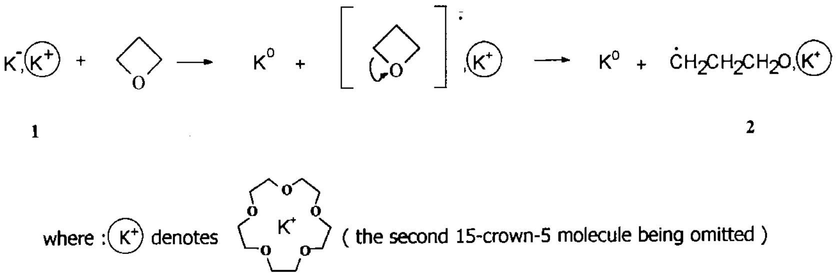


1 2

Scheme 1.

process. The liquid phase was then analyzed by ^{13}C-NMR. In the spectrum the carbon signals assigned to CH_3O, $CH_3CH_2CH_2O$ and $CH_2{=}CHO$ groups were observed. The carbon signals from the $PhCH_2O$ group were also present.

In order to analyze the side-products formed in the studied system the reaction mixture was treated with methyl iodide. Tri- and tetra(ethylene glycol) dimethyl ethers in 15% total yield were found similarly, as in the case of methyloxirane [1].

It was assumed that in the beginning of the examined process a transfer of one electron from K^- to the oxetane molecule occurs resulting in the carbon–oxygen bond cleavage, similarly as described earlier [3,4]. In the case of the system with 15-crown-5, the following scheme for the reaction is proposed.

The unstable radical anion **2** undergoes two reactions. In the first one, **2** recombines with K^0 as usual giving potassium γ-potassiopropoxide **3**.

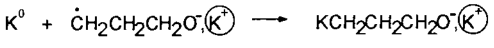
In the second reaction observed for the first time in the system with 15-crown-5 **2** decomposes to ethylene **4** and the radical anion of formaldehyde **5** which is stabilized by mesomerism.

Recombination of **5** with K^0 gives potassium potassiomethoxide **6**.

Then, both organometallic compounds, i.e. **3** and **6**, react with the crown ether molecule.

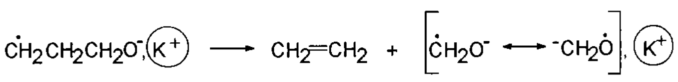
The reactions presented in Schemes 1–6 are very fast. No benzylated or methylated derivatives of **3** and **6** were found in the reaction mixture. Likewise, no products of the reaction of organometallic compounds **3** and **6** with oxetane or the solvent were present in the system.

It is worth noting that **3** formed in the reaction of oxetane with K^-, K^+(18-crown-6) at -20°C was found to be relatively stable [3,4], e.g. it could be protonated or methylated. No reaction with crown ether was observed in that system. Therefore, we have repeated the reaction of oxetane with K^-, K^+(15-crown-5)$_2$ at -20°C. Again benzyl methyl ether, benzyl *n*-propyl ether and tetra(ethylene glycol) benzyl vinyl ether were found in the reaction mixture after benzylation. It means that the same main products were formed at -20°C as at $+25$°C. However, tetra(ethylene glycol) dimethyl ether and tri(ethylene glycol) dimethyl ether were not observed after methylation at the lower temperature, i.e. the destruction of potassium tetra(ethylene glycol) vinyl ether under the influence of K^- to the former side-products did not occur in this case.



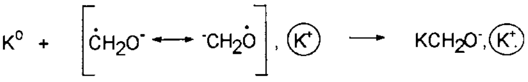
2 3

Scheme 2.



2 4 5

Scheme 3.



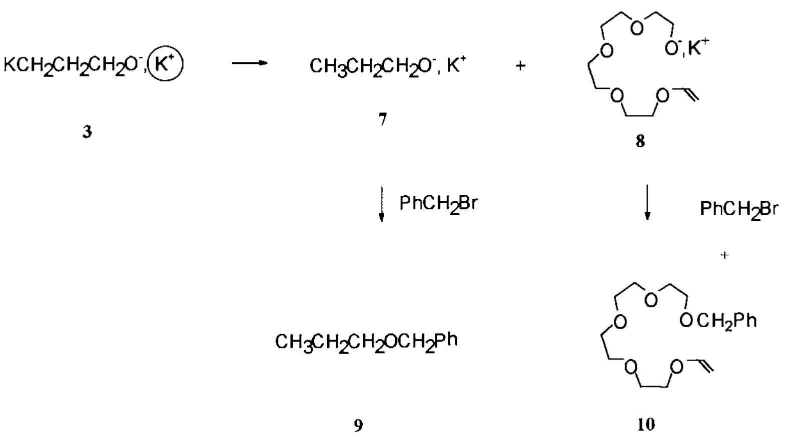
5 6

Scheme 4.

The differences in the reaction mode when using the K^-, K^+(15-crown-5)$_2$ system [1] or the K^-, K^+(18-crown-6) system [5], respectively, were already observed in the reaction with methyloxirane.

3. Conclusions

Until now crown ethers were known, with some exceptions concerning the reaction with metal anions [6–9], as the stable compounds able to enhance the reaction rate in chemical processes. The results of the present work confirm our earlier finding [1] that cleavage of the 15-crown-5 ring occurs also in the presence of organometallic compounds resulting in potassium tetra(ethylene glycoxide) vinyl ether. It provides evidence for a more general character of the phenomenon that the crown ether unexpectedly acts both as an activator and as a reagent.



Scheme 5.

It seems that the kind of crown ether decides on the process. Potassium anion and the 18-crown-6 flat 1:1 complex with potassium cation gives the relatively stable organometallic product [3,4], whereas the use of 15-crown-5 forming a sandwich 2:1 complex with K^+ results in unstable compounds. The latter react instantaneously with the crown ether and its oxacyclic ring is opened.

4. Experimental

Gas chromatography (GC) analysis of ethylene as well as gas chromatography–mass spectrometry (GC–MS), ^{1}H- and ^{13}C-NMR analyses of benzylated or methylated products were carried out as described in Ref. [1].

Oxetane (Aldrich) was heated over CaH_2 for 3 h followed by distillation under dry argon atmosphere, the fraction boiling at 50°C being collected. Potassium and tetrahydrofuran were purified as in Ref. [1].

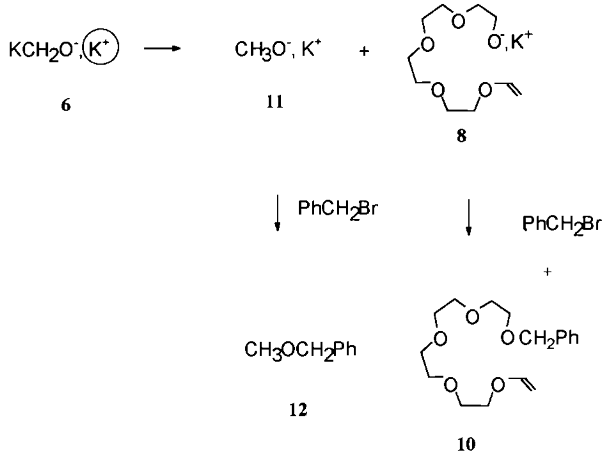
The K^-, K^+(15-crown-5)$_2$ solution in THF was prepared as in Ref. [8]. Its reaction with oxetane was conducted at 25°C under dry argon atmosphere. A 10 cm^3 sample of 0.1 M K^-, K^+(15-crown-5)$_2$ was added dropwise to 10 cm^3 of 1.0 M THF solution of oxetane. The mixture was then treated with benzyl bromide or methyl iodide. The same procedure was used for the process conducted at −20°C. However, the benzylation or methylation of reaction products occurred this time after several hours. The products were identified by matching their mass spectra, retention times, and ^{1}H- and ^{13}C-NMR spectra with those of model compounds.

4.1. Benzyl methyl ether (**12**)

Potassium hydride (0.10 g, 2.5 mmol) and THF (10 cm^3) were introduced into the reactor under dry argon atmosphere. Then, methanol (0.08 g, 2.5 mmol) was added dropwise while stirring at 25°C. The course of the reaction was followed by measuring of the amount of hydrogen evolved. After 8 h, benzyl bromide (0.43 g, 2.5 mmol) was added to the mixture. The precipitated potassium bromide was filtered off, and benzyl methyl ether was distilled from the solution; the fraction boiling at 170°C was collected in 85% yield. ^{1}H-NMR acetone-d_6 δ: 7.30–7.24 (m, 5H, Ph); 4.34 (s, 2H, OCH_2); 3.24 (s, 3H, OCH_3). ^{13}C-NMR acetone-d_6 δ: 139.3 (C_{Ph} *ipso*); 128.7 (C_{Ph} *meta*); 128.0 (C_{Ph} *ortho*); 127.8 (C_{Ph} *para*); 74.7 (OCH_2); 57.9 (OCH_3). MS (*m*/*e*): 122 (92, M^+), 105 (4), 91 (100), 77 (45), 65 (33), 51 (23), 39 (20).

4.2. Benzyl *n*-propyl ether (**9**)

Potassium hydride (0.10 g, 2.5 mmol) and THF (10 cm^3) were introduced into the reactor under dry argon atmosphere. Then, *n*-propanol (0.15 g, 2.5 mmol) was added dropwise while stirring at 25°C. The further



Scheme 6.

procedure was the same as in the case of the synthesis of benzyl methyl ether. Finally, the product was distilled from the solution; the fraction boiling at 200°C was collected in 88% yield. ^{1}H-NMR acetone-d_6 δ: 7.36–7.15 (m, 5H, Ph); 4.42 (s, 2H, OCH_2); 3.35 (t, $J = 6.5$ Hz, 2H, OCH_2); 1.56 (m, $J = 7.4$, 6.5 Hz, 2H, CH_2); 0.9 (t, $J = 7.4$ Hz, 3H, CH_3). ^{13}C-NMR acetone-d_6 δ: 139.8 (C_{Ph} *ipso*); 128.7 (C_{Ph} *meta*); 127.8 (C_{Ph} *ortho*); 127.7 (C_{Ph} *para*); 73.0 (OCH_2Ph); 72.3 (OCH_2); 23.5 (CH_2); 10.9 (CH_3). MS (*m*/*e*): 150 (10, M^+), 107 (15), 91 (100), 79 (25), 65 (30), 51 (11), 39 (15).

The preparation of tetra(ethylene glycol) benzyl vinyl ether (**10**) and its ^{1}H-, ^{13}C-NMR and mass spectra as well as of tetra(ethylene glycol) dimethyl ether and tri(ethylene glycol) dimethyl ether are described in Ref. [1].

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