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The behaviour of organopotassium intermediates derived from oxiranes under the influence of alkalide K^-, $K^+(15\text{-crown-}5)_2$

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Abstract

Organopotassium intermediates derived from monosubstituted oxiranes by alkalide K^-, $K^+(15\text{-crown-}5)_2$ are generally unstable at ambient temperature. They undergo further fast reactions. There are three groups of these organometallic compounds. The first one reacts exclusively with 15-crown-5. The second reacts only with the oxirane substrate. The third reacts both with crown ether and with the appropriate oxirane, and one of these undergoes γ-elimination. The most interesting seems to be the first type of the reaction. It leads to the crown ring cleavage. Potassium tetraethylene glycoxide vinyl ether is the product of the reaction. Crown ether plays a dual role in this case. It takes part in the process both as a complexing agent and as a reagent.
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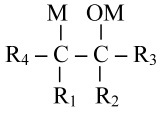
Keywords: Oxiranes; Organopotassium intermediate; Ether bond scission; Alkalide

1. Introduction

It is known that organometallic compounds of a general structure denoted as **1** can be formed in reactions of oxiranes with alkali metals [1–6] or radical anions of aromatic hydrocarbons [7,8]. Most of the synthetically interesting β-metalloalkoxides are stable only at low temperatures [7,9,10].



1

The reaction of oxiranes with alkali metals in protic solvents, e.g. ammonia or amines [1–3,5,6] leads to the formation of simple alkoxides [11]. The compounds of type **1** are obtained as intermediates. If the reaction is performed in aprotic solvents, such as tetrahydrofuran, various products are formed depending on the nature of the metal and the structure of the oxirane [4]. Deoxygenation to olefins is the main reaction in the case of lithium. The rearrangement to carbonyl compounds, reduction to alcohols, and formation of dimeric products occur when oxiranes are treated with sodium. All the reactions could be rationalized by a mechanism involving an initial single electron transfer.

Bartmann [7] successfully synthesized some stable β-metalloalkoxides using salts of aromatic radical anions, i.e. lithium biphenylide or lithium naphthalenide as well as their potassium or magnesium analogues. It was possible to convert them into appropriate derivatives in the reaction with some electrophiles in relatively high yields. For example, cyclohexene oxide smoothly reacted at −80 to −90 °C with lithium biphenylide or lithium naphthalenide in tetrahydrofuran giving lithium β-lithiocyclohexanolate. Formally, two asymmetric centres are formed. However, the subsequent deuteration is not stereoselective. According to ^{13}C-NMR spectrum, *cis*- and *trans*-cyclohexanol are obtained in 1:1 ratio. On the other hand, in the case of a more bulky electrophile, such as diphenyl disulfide, only the *trans*-compound is formed. Monosubstituted oxiranes with the phenyl or ester group give stable **1** at low temperature. However, if the substituent is an alkyl group, side reactions occur which greatly reduce the yield of **1**.

It was recently shown that organometallic intermediates are also formed in the reaction of alkalide K^-,

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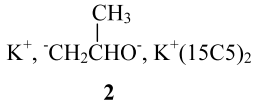
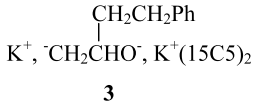
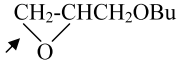
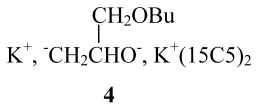
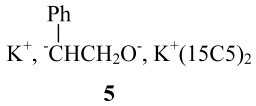
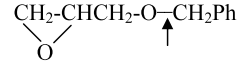
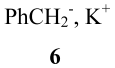
$K^+(15\text{-crown-}5)_2$ with monosubstituted oxiranes and some other compounds [12–20]. Potassium anion behaved in these processes as electron-transfer reagent. All the reactions were carried out in tetrahydrofuran solution at ambient temperature. The aim of this work was to systematize the behaviour of intermediate compounds generated in these reactions.

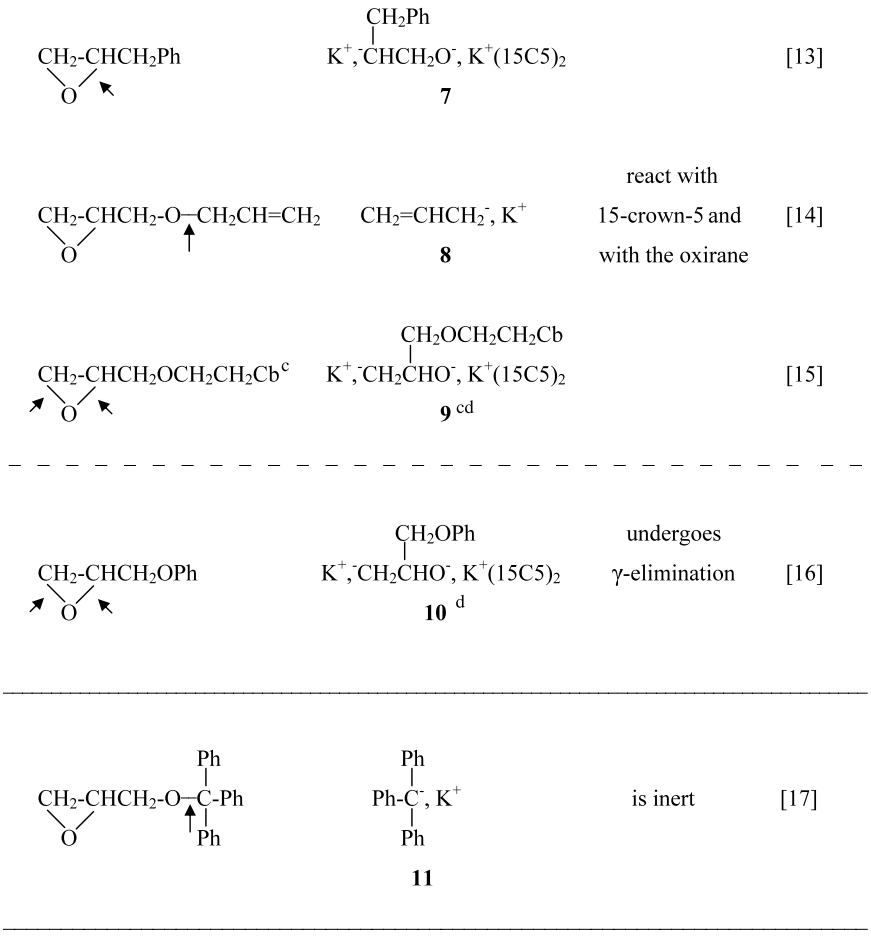
2. Results and discussion

The structure of organopotassium compounds formed during the reaction of selected oxiranes with K^-, $K^+(15\text{-crown-}5)_2$ is presented in Table 1. The greater part of them is a product of the oxirane ring opening. It can occur in the β-position (**2**–**4**) or in the α-position (**5**, **7**) or in both of the positions, however, the β-opening prevails in that case (**9**, **10**). The resulting potassium β-potassioalkoxides possess potassium cation complexed by two 15-crown-5 molecules. On the other hand, **6**, **8**, and **11** obtained by the cleavage of the linear ether bond in the oxirane molecule are not alkoxides and their potassium cations are not complexed. The regioselectivity of the ether bond cleavage depends strongly on the kind of substituent in the oxirane molecule. A detailed discussion concerning this problem is presented in Ref. [21].

The organopotassium intermediate products, except **11**, undergo further rapid reactions in the studied processes. The compounds **2**–**4** react exclusively with

Table 1
Organopotassium intermediates formed in the reaction of selected oxiranes with alkalide K^-, $K^+(15\text{-crown-}5)_2$

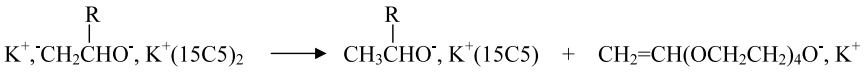
Oxirane[a]	Intermediate organometallic product[b]	Further reactions of organometallic intermediate	Ref.
	 **2**		[12]
	 **3**	react exclusively with 15-crown-5	[13]
	 **4**		[14]
	 **5**		[13]
	 **6**	react exclusively with the oxirane	[17]



$[Oxirane]_o > [alkalide]_o$.
[a]The direction of the ether bond cleavage by K^- is marked by '→'.
[b]15C5 denotes 15-crown-5 molecule.
[c]Cb denotes the carbazolyl group.
[d]The product of the oxirane ring opening in the β-position.

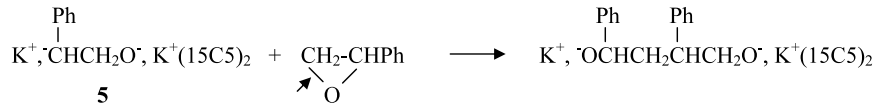
15-crown-5 giving potassium tetraethylene glycoxide vinyl ether and the appropriate alkoxide, i.e. potassium isopropoxide [12], potassium 4-phenylbutane-2-oxide [13], and potassium 3-butoxypropane-2-oxide [14], respectively (Scheme 1).

The opening of the crown ring resulted in potassium tetraethylene glycoxide vinyl ether was reported for the first time in the reaction of K^-, $K^+(15\text{-crown-}5)_2$ with methyloxirane and methyl iodide [12], and then with oxetane [18] and methyl methacrylate [19]. In all the processes, organopotassium intermediates attacked the crown ether molecule. For example, potassium γ-potassiopropoxide was one of them in the case of oxetane [18]. The same result was observed both at +25 and −20 °C. On the other hand, it was earlier reported that this organopotassium alkoxide obtained in the reaction of oxetane with another alkalide, i.e. K^-, K^+(18-crown-6), was stable at −20 °C and it could be protonated or methylated [22,23]. No reaction with crown ether was described in that system. The mechanism different from accepted in Refs. [12,18,19] was also presented for the reaction of K^-, K^+(18-crown-6) with methyloxirane [24], methyl methacrylate [25], styrene [26], and isoprene [27]. The proton exchange was



where: 15C5 denotes 15-crown-5 molecule.

Scheme 1.

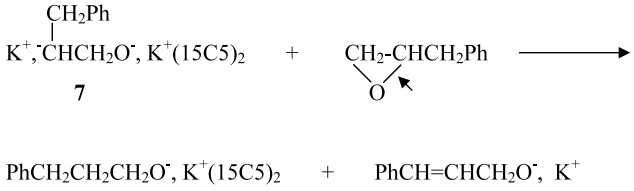


Scheme 2.

assumed to occur between the organometallic intermediate and tetrahydrofuran used as the solvent. However, no evidence was given for such a hypothesis, as well as for the role of the second product expected in the reaction. Thus, it was not clear that what compound really took part in the reaction with the organometallic intermediate in those processes.

A more detailed study of the problem shows, however, that 18-crown-6 is opened during the reaction of K^-, K^+(18-crown-6) with methyloxirane. Potassium isopropoxide and potassium pentaethylene glycoxide vinyl ether are found as the reaction products. Their methylated or benzylated derivatives are obtained when the reaction mixture is treated with methyl iodide or benzyl bromide, respectively. The ring opening of 18-crown-6 is also observed in the reaction of potassium anions with oxetane and methyl iodide. It allows to state that organopotassium intermediates are present in these systems too, and they easily opened up the crown ring. Moreover, it would indicate that potassium oligoethylene glycoxides vinyl ethers can be synthesized in such a way from unsubstituted crown ethers. However, further experiments showed that this is not a rule.

The next two organopotassium compounds, i.e. **5** and **6**, react exclusively with the appropriate oxirane. The mechanism of the process depends on the structure of the oxirane molecule. **5** opens the oxirane ring of phenyloxirane in the β-position which leads to a dimeric product, i.e. dipotassium 1,3-diphenylbutane-1,4-dioxide (Scheme 2) [13]. It is worth noting that K^-, K^+(15-crown-5)$_2$ as well as other electron-transfer reagents, e.g. metallic sodium [4], lithium naphthalenide or potassium biphenylide [7] caused the α-scission in phenyloxirane. Only one exception to this phenomenon was described in literature [24], i.e. both the α- and the β-ring opening were reported in phenyloxirane when using K^-, K^+(18-crown-6). On the other hand, **6** cleaves unexpectedly one of the linear ether bonds of benzyloxymethyloxirane. It results in potassium glycidoxide and bibenzyl (Scheme 3) [17]. The cited work demonstrates for the first time that the possibility of the selective scission of the linear ether bond by K^- or by organopotassium compound without the opening of the oxirane ring present in the same molecule. Moreover, the formation of potassium glycidoxide under such conditions was earlier not

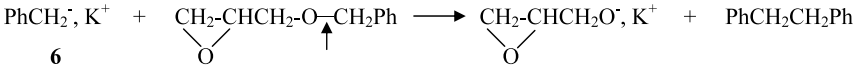


Scheme 4.

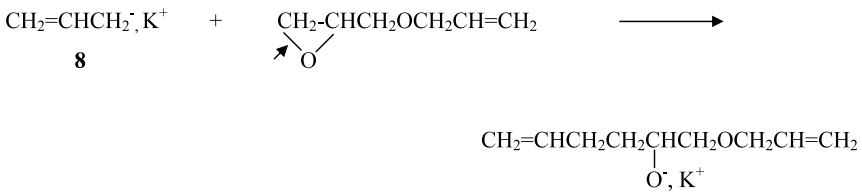
described in the literature. This alkoxide can be used as a substrate in the synthesis of glycidyl ethers or glycidyl esters. Its reaction with aliphatic or aromatic halides in tetrahydrofuran occurs very fast at ambient temperature. Potassium glycidoxide is also a typical inimer [28], i.e. it can both initiate the polymerization as well as take part in this process as a monomer.

Crown ether is found to be stable also during the reaction of K^-, K^+(15-crown-5)$_2$ with carbazole [20]. The process proceeds via organopotassium intermediate. It reacts with the next carbazole molecule giving carbazylpotassium and 1,4-dihydrocarbazylpotassium. A similar behaviour of crown ether was observed in the reaction of K^-, K^+(18-crown-6) with β-lactones [29–33]. It was claimed that an organometallic compound was formed after the C–C bond cleavage in the β-lactone. Then, it reacted exclusively with the next β-lactone molecule. The cleavage of the crown ring was not reported. On the other hand, it is found in this work that the reaction of K^-, K^+(15-crown-5)$_2$ with β-butyrolactone gives not one but several products. However, also in this case the organopotassium intermediate formed reacts only with the next β-butyrolactone molecule. The product of the crown ring opening is not observed.

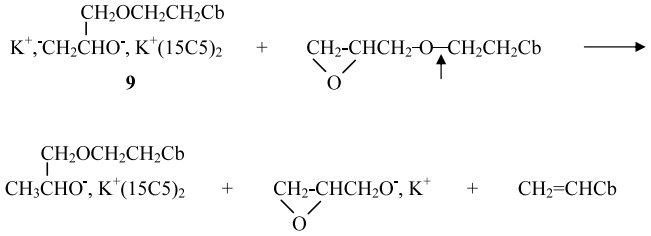
Compounds **7**, **8**, and **9** react both with 15-crown-5 and with the appropriate oxirane. The former results in the crown ring opening, i.e. in potassium tetraethylene glycoxide vinyl ether. The mechanism of the latter depends on the oxirane structure. The reaction of **7** with (phenylmethyl)oxirane [13] is not a simple addition to the oxirane ring known in literature [34]. It seems to be a proton-transfer process similar to the chain-transfer reaction to the monomer observed during the anionic polymerization of methyloxirane [35,36]. Two alkoxides, i.e. potassium 3-phenylpropoxide and potassium 3-phenylallyloxide, are the end products of the reaction



Scheme 3.



Scheme 5.



Scheme 6.

(Scheme 4). The ring opening in the β-position occurs in the reaction of **8** with (allyloxymethyl)oxirane. It results in the potassium alkoxide with two double bonds (Scheme 5) [14]. The behaviour of **9** is more complex. β-Elimination takes place during its reaction with carbazolyl-substituted oxirane giving potassium 3-(9-carbazolyl)ethoxy-2-oxide, potassium glycidoxide, and 9-vinylcarbazole (Scheme 6) [15]. **10** does not react with (phenoxymethyl)oxirane but undergoes γ-elimination to potassium cyclopropoxide and potassium phenoxide (Scheme 7). The elimination reaction is preferred probably due to the formation of phenoxide anion strongly stabilized by resonance [16].

From the midst of organopotassium intermediates, only **11** was found to be stable probably because of a high resonance stability of triphenylmethyl anion [17].

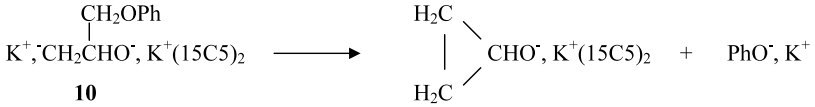
Attention was separately paid to tetrahydrofuran. That cyclic ether had been known to decompose to ethylene and potassium acetaldehyde enolate under the influence of butylpotassium [37]. However, tetrahydrofuran used as the solvent in the studied systems was found to be inert. None of its expected decomposition products were found in the reaction mixture. A higher reactivity of crown ether in comparison with tetrahydrofuran may originate from a specific activating effect of several oxygen atoms in the polydentate ligand as well as from the fact that the crown ether takes part in the reaction in the form of a complex with the potassium cation. The complexation of the cation by crown molecules would tend to make the C–H bond more acidic [12].

To sum up, the proton exchange between β-potassioalkoxide anion and crown ether being in complex with the counterion is much faster in some systems than the addition of the alkoxide to the oxirane molecule. The crown ring opening occurs in this case. However, in other systems, the proton exchange with the oxirane molecule or the resonance stability of the reaction product are the main factors responsible for the behaviour of organopotassium compounds under study.

It is worth noting that the cleavage of the crown ether ring was for the first time observed in K^-, K^+(18-crown-6) tetrahydrofuran solution [38]. A mixture of potassium glycoxides and ethylene were identified as the main reaction products. Next, that phenomenon was observed by Cauliez et al. [39]. The mechanism of the process was recently explained for the K^-, K^+(15-crown-5)$_2$ system [40]. Besides K^-, organopotassium intermediates, i.e. potassium β-potassioethoxide and potassium δ-potassiobutoxide, were found to be additional crown ring opening species. However, organometallic compounds do not take part in the ring opening of cyclohexano- and dicyclohexano-substituted 15-crown-5 or 18-crown-6 ethers under the influence of potassium anion [41]. Arenocrown ethers, i.e. naphtho-15-crown-5, benzo-15-crown-5, and benzo-18-crown-6, undergo Birch reduction by potassium in tetrahydrofuran solution [42]. A mechanism involving single electron transfer from alkali metal to the aromatic ring with the formation of radical anion was accepted in this case. Potassium anions were not detected in such system.

3. Conclusions

The discussion of the literature data shows that the organopotassium intermediates formed in the reaction of oxiranes with K^-, K^+(15-crown-5)$_2$ are generally unstable and they take part in various further processes. There are three groups of these compounds. The first one reacts exclusively with 15-crown-5. The second reacts only with the appropriate oxirane. The third



Scheme 7.

group undergoes miscellaneous processes. The most interesting seems to be the first type of the reaction leading to the crown ring opening. Potassium tetraethylene glycoxide vinyl ether is the product of this reaction. Crown ether plays a dual role in this case. It takes part in the process both as the complexing agent and as the reagent.

4. Experimental

0.1 M K^-, $K^+(15\text{-crown-}5)_2$ blue solution was obtained by dissolution of the potassium mirror in 0.2 M 15-crown-5 tetrahydrofuran solution, as in Ref. [43]. Potassium solution with 18-crown-6 was prepared as in [38]. After the contact time equal to 25 min, the solution was filtered off through a glass frit and used as the reagent. Selected oxiranes, oxetane, and β-butyrolactone were distilled over CaH_2. Tetrahydrofuran was purified as in Ref. [44]. 15-Crown-5 and 18-crown-6 were dried under vacuum at 50 °C for 8 h. Potassium was purified in boiling tetrahydrofuran and then distilled under high vacuum into a reactor.

The reaction was conducted under dry argon atmosphere at 25 °C in the reactor described in Ref. [12]. 10 ml of 0.1 M K^-, $K^+(15\text{-crown-}5)_2$ blue solution was dropped into 10 ml of 0.5 M selected oxirane, oxetane or β-butyrolactone solution while mixing, i.e. the latter was still in the excess. The reaction was instantaneous. Potassium anions vanished immediately in the mixture. That could be easily observed because the blue solution became colourless at the moment. However, a direct identification of organopotassium compounds formed during the process, except **11**, was found to be unsuccessful. Attempts to obtain their volatile derivatives, e.g. by methylation or benzylation of the reaction mixture proved abortive [12–20]. Their intermediate existence in the reaction was proven by the end products because they cannot be formed otherwise. Details are described in Refs. [12–20].

Note: The method of substrate delivery influences the course of studied processes in a decisive way. The use of oxacyclic reagent in the excess allowed to avoid side reactions between alkalide and primary reaction products. In another case, i.e. at the excess of K^-, $K^+(15\text{-crown-}5)_2$ further reactions took place with the participation of potassium anions [13,16–18]. Some initial products were destroyed and various new compounds were observed in the reaction mixture. Even a simple titration of alkalide solution with selected reagent gave the same result. Potassium anions were still in the excess in that case, except the end point and discoloration of the solution. Therefore, such methods might lead to wrong conclusions on the reaction mechanism.

Acknowledgements

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