Electron-Transfer Processes Mediated by Alkalides: A Critical Approach

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Abstract: The objectives of this review are mainly reactions of alkalides with various classes of organic compounds. Mechanisms of these processes are discussed taking into account our present stage of knowledge. A new method for the preparation of crystalline nanomaterials *via* homogeneous reduction of transition and post-transition metal salts is also presented.

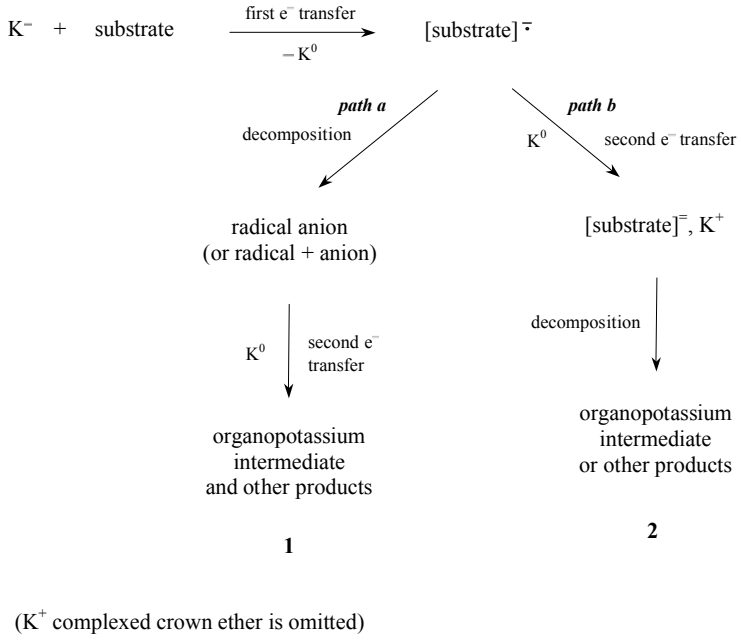
Keywords: Alkalides, potassium anions, two-electron-transfer, reduction, vinyl compounds, ethers, esters.

1. INTRODUCTION

Alkali metal solutions had been for the first time obtained in 1863 by Weyl [1] with the use of liquid ammonia. In further works various amines and ethers were applied to dissolve alkali metals [2-6] Their solutions had conductive and paramagnetic properties [3,7-9] due to the presence of solvated electrons (e^-) [10-14]. Some authors assumed the possibility of electron pairing resulting in the formation of diamagnetic dielectrons ($e_2^{=}$) [2,15]. The discovery of crown ethers and cryptands, i.e. macrocyclic ligands (L) afforded to prepare high concentrated alkali metal solutions in aprotic solvents [16-20].

Using alkali metal NMR technique Dye [20] stated clearly that diamagnetic species present in sodium solutions containing a ligand were sodium anions (Na^-) possessing two electrons in the outer *s* orbital. That was also proved for K^- , Rb^- and Cs^- [21,22]. Lithium anions are not detected in any solvent. No alkali metal anions are found in metal solutions prepared in liquid ammonia. Clusters such astriple ions e^-, M^+, e^- or eventually other aggregates as $(e^-, M^+)_2$ and $e_2^{=}$, M^+ are rather existing in this solvent than the genuine M^- [15]. However, it cannot be excluded that the concentration of metal anions in these cases is below the detection limit.

Alkali metal anions and complexed cations are able to produce crystalline compounds called by Dye [23,24]. alkalides (M^-, M^+L_n where n = 1 or 2). Their ions can derive from the same metal, e.g. Na^-, $Na^+(C222)$ or two different metals, e.g. Na^-, $Rb^+(15C5)_2$. The crystal structure of alkalides can be classified according to the relation of M^- to neighboring species [24]. They can form separated ions (for example in Cs^-, $Cs^+(18C6)_2$), contact ion-pairs (in Na^-, $K^+(HMHCY)$), dimers of anions ($K_2^{=}$ in K^-, $K^+(C222)$) or chains of anions (Cs_n^{n-} in Cs^-, $Cs^+(C222)$) [24,25]. Finally, Rb^-, $Rb^+(18C6)$ combines two structural features, i.e. the chain formation and ion-pairing that yield chains of Rb^-, each Rb^- being in contact with one Rb^+.



Scheme 1. Mechanism of stepwise two-electron-transfer (TET) reactions mediated by the potassium anion of alkalide.

Alkalides were obtained most frequently by cooling the metal solution and evaporation of the solvent [23]. Recently, a new method is proposed to prepare crystalline potassium sodides, i.e. by a direct reaction of NaK alloy with crown ether in a non-polar medium, as for example hexane [26].

Alkalides can be attractive for various investigators because of the variety of solid-state properties that might be achieved. They also open new ways for application of their solutions to chemical synthesis.

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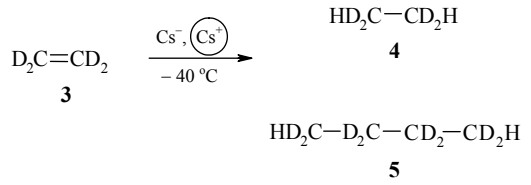


Scheme 2. Reduction of deuterated ethylene with Cs^-, Cs^+(18C6); circled Cs^+ denotes the complex of this cation with crown ether.

2. REACTIONS OF ALKALIDES WITH ORGANIC COMPOUNDS

2.1. General Data

Electron-transfer reactions are important in organic synthesis, biochemistry and medicine [27-30]. They are induced chemically [31-37], photochemically [38-42], and electrochemically [42-47]. Chemical methods usually involve the application of alkali metals (M) [48-54], alkali metal salts of aromatic radical anions ($Ar^{\bullet-}$, M^+) [35,55-57], alkalides (M^-, $M^+(L_n)$) [37], and low-valent transition metal compounds, as for example SmI_2, $CrCl_2$, $TiCpCl_2$ or $[V_2Cl_3(THF)_6][Zn_2Cl_6]$ [58-63].

First reports about the use of alkalides in organic synthesis had concerned Na^-, K^+(18C6) and K^-, K^+(18C6) in tetrahydrofuran solution. Both the alkalides effectively reduced some alkynes [64], alkenes [65,66] linear ethers [67], and esters [67-69]. K^-, K^+(18C6) was applied to the reduction and polymerization of several lactones [70-72], cyclic ethers [73-75], and vinyl compounds [76-79]. However, this alkalide is unstable at ambient temperature. Nearly half of the metal anions vanishes irreversibly during the preparation of K^-, K^+(18C6) tetrahydrofuran solution [80]. Its autocatalytical reaction with crown ether effects in a mixture of dipotassium glycoxides and ethylene. Therefore, the results obtained with this alkalide should be treated rather with criticism.

The use of 15C5 instead of 18C6 allows to prepare the markedly more stable alkalide K^-, $K^+(15C5)_2$ [81]. This alkalide does not decompose during one hour after its preparation in tetrahydrofuran at ambient temperature. It was successfully applied to the reduction of alcohols [82], linear and cyclic ethers [37,83] and esters [84-86]. It was also proved as a very convenient reagent to determine or to correct the mechanisms of several reactions in which organopotassium intermediates were formed [37,73].

The alkali metal anion is nearly as thermodynamically powerful reducing agent as a solvated electron, the most powerful reductant [87]. It does not react as a typical base or nucleophile. In the reaction with organic compounds it behaves as two-electron-transfer (TET) reagent which transfers stepwise two valence electrons to an acceptor molecule (Scheme **1**) and not simultaneously as electron pair $e_2^=$ [88]. *Path a* concerns various classes of compounds, among them linear and cyclic ethers, and *path b* is till now limited only to cyclic esters.

Alkali metals are widely applied to the reduction in organic synthesis (Birch reduction) [89]. These reactions occur in heterogeneous systems whereas the use of alkalides allows to carry out such processes under mild homogeneous conditions. This work reviews the most representative among them.

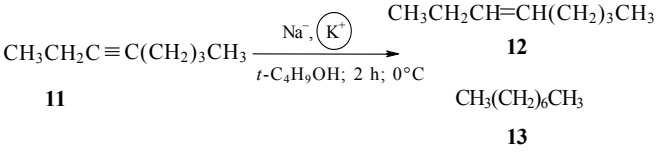
2.2. Hydrocarbons with Double or Triple Bonds

Unusual reduction of ethylene was observed during the decomposition of crystalline Cs^-, Cs^+(18C6) [90]. Fully deuterated ethylene **3** was used to demonstrate that gaseous ethylene could be reduced by this alkalide and gave ethane **4** (25 %) and butane **5** (70 %) at low temperature (Scheme **2**).

The strongly negative electron affinity of ethylene in the gas phase makes this observation particularly intriguing. Presumably ethylene in a polar environment of the solid alkalide traps an electron [91]. The resulting radical anion produces ethane and butane by various sequences of protonation or hydrogen abstraction, further electron-transfer, and dimerization. However, the authors of [90] did not propose the real source of protons and that problem remained unresolved.

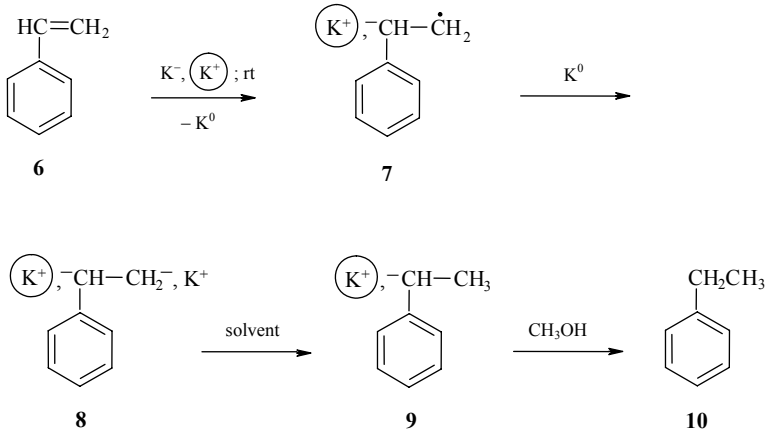
The reduction of styrene **6** with K^-, K^+(18C6) in tetrahydrofuran solution proceeds in three steps (Scheme **3**) [73,76]. The first electron transfer from K^- results in styrene radical anion **7**. Then, the styrene dianion being organopotassium intermediate **8** is formed after the second electron transfer. Evidence for that is given by the detection of ethylbenzene **10**, which is the main product of protonation caused by the subsequent addition of methanol to the reduced solution. It was assumed that **8** containing non-complexed K^+ was protonated by the solvent. However, the product of solvent deprotonation was not determined.

The course of K^-, K^+(18C6) reaction with isoprene in tetrahydrofuran is similar to that presented in Scheme **3** for **6** [78].



Scheme 4. Reduction of 3-octyne to 3-octene and octane by the use of Na^-, K^+(18C6).

Alkynes, such as 3-octyne **11** and 4-octyne are reduced by Na^-, K^+(18C6) tetrahydrofuran solution to the corresponding octenes as

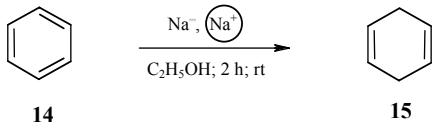


Scheme 3. Reduction of styrene with K^-, K^+(18C6); circled K^+ denotes the complex of this cation with crown ether.

for example **12** (72 %, 1 : 3 mixture of *cis* and *trans* isomers) in Scheme (**4**) [64]. Octane **13** (18 %) is produced after 2 h of the reaction resulting from further reduction of **12**.

2.3. Aromatic Compounds

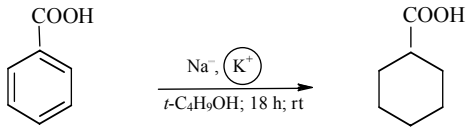
Alkalide Na^-, $Na^+(12C4)_2$ in 12C4 solution was found to reduce benzene **14** to cyclohexa-1,4-diene **15** (60 %) (Scheme **5**) [92].



14 **15**

Scheme 5. Partial reduction of benzene with Na^-, $Na^+(12C4)_2$.

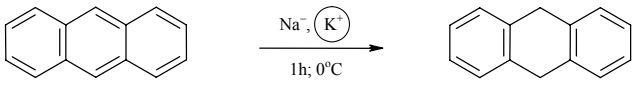
A complete reduction of the aromatic ring was observed in the reaction of benzoic acid **16** with Na^-, $K^+(18C6)$ in tetrahydrofuran to **17** (86 %) (Scheme **6**) [64].



16 **17**

Scheme 6. Complete reduction of the aromatic ring in benzoic acid with Na^-, $K^+(18C6)$.

Anthracene **18** was reduced by Na^-, $K^+(18C6)$ in tetrahydrofuran to 1,8-dihydroanthracene **19** (67 %) regardless to whether *tert*-butanol was present or not (Scheme **7**) [64]. The source of protons in the system without alcohol was not established.



18 **19**

Scheme 7. Reduction of anthracene to 1,8-dihydroanthracene with Na^-, $K^+(18C6)$.

A partial reduction of the aromatic system was stated in the reaction of K^-, $K^+(15C5)_2$ with carbazole **20** in tetrahydrofuran (Scheme **8**) [93].

The single-electron-transfer from K^- to the aromatic ring resulted in K^0 and carbazolyl radical anion. The latter rapidly decomposed with the liberation of hydrogen and the formation of carbazylpotassium **21** and **21'**. 1,4-Dihydrocarbazylpotassium **22** was formed in further reactions. The yield of methylated derivative of **21** and **21',** obtained in the reaction of the latter with methyl iodide, was equal to 70 % and that of **22** to 28 %.

2.4. Halides

The course of methyl iodide **23** reaction with K^-, $K^+(15C5)_2$ was proposed in ref. [94] (Scheme **9**). It was for the first time demonstrated there that organopotassium compound **24** deprotonates crown ether molecules. 15C5 was decomposed in that reaction with ring opening to potassium tetraethylene glycoxide vinyl ether **27**. In the same way 18C6 was deprotonated to potassium pentaethylene glycoxide vinyl ether [37]. A helpful method for checking of the formation of short-lived organopotassium intermediates was proposed on this ground [95]. This method works till now in 17 from 27 processes described in the literature for 15C5. It makes 63 % probability that the test is successfully conducted. Crown ethers considered, with some exceptions, to be stable in organic synthesis are found to act both as activators and as reagents. Thus, the possibility of crown ether decomposition should be taken into account if organoalkali metal compounds are formed in the studied system. Tetrahydrofuran used as the solvent is inert in this process. The products of its deprotonation [96] were not found in the reaction mixture. The deprotonation of the crown ether and not the solvent is preferred because the crown ether forms a complex with the potassium cation. It increases the acidity of the hydrogen atoms in the CH_2 groups of the crown ether [94].

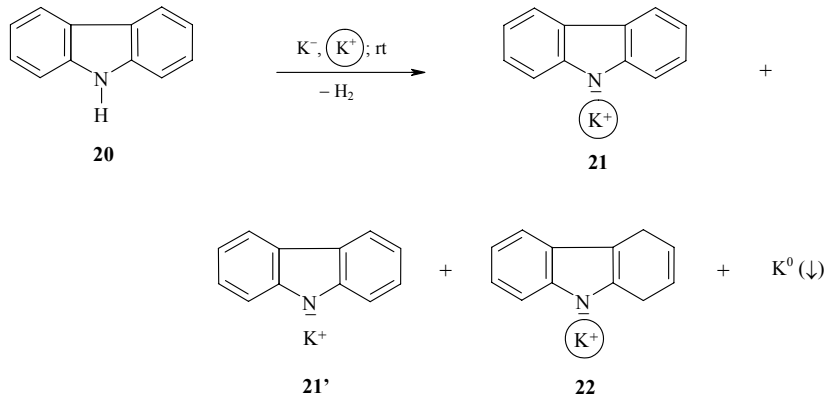
According to that finding it is very probable that organometallic intermediates produced during the reduction of **6** (Scheme **3**) or **18** (Scheme **7**, the appropriate formula is not given) do not deprotonate the solvent but rather the crown ether, i.e. 18C6. Deprotonation of this ligand existing in the stable $K^+(18C6)$ complex should be even easier than $K^+(15C5)_2$ because of a higher acidity of its hydrogen atoms.

The coupling of benzyl bromide **28** proceeded smoothly with K^-, $K^+(18C6)$ (Scheme **10**) [97]. Bibenzyl **29** was the main reaction product. The mechanism of this reaction was not proposed. Presumably, benzyl radical formed initially receives one electron from K^0 (Scheme **1**) giving benzylpotassium, which reacts then with benzyl bromide producing finally **29**.

Poly-coupling occurred if difunctional α,α'-dibromo-*p*-xylene was used in the reaction with K^-, $K^+(18C6)$ yielding poly(*p*-xylene) [97]. It was also reported that polysilanes and cyclic silane oligomers were produced in the polymerization of methylphenyldichlorosilane with K^-, $K^+(18C6)$ [98].

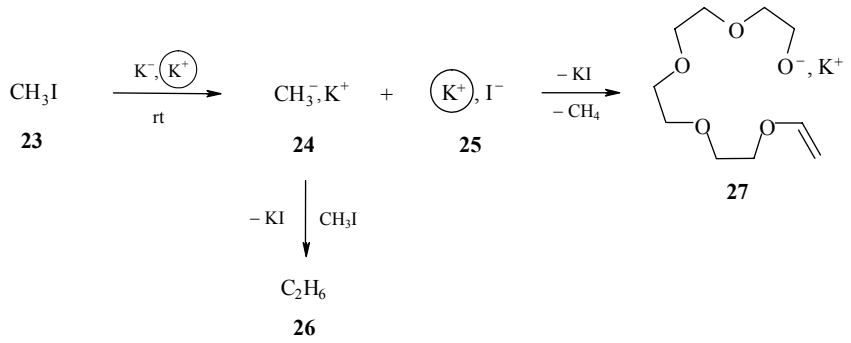
2.5. Alcohols and Alkoxides

Alcohols and alkoxides can be efficiently reduced with K^-, $K^+(15C5)_2$ [82]. A simple alcohol **30** (Scheme **11**), e.g. methanol or

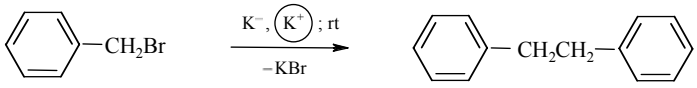


20 **21** **21'** **22**

Scheme 8. Transformation of carbazole to carbazylpotassium and 1,4-dihydrocarbazylpotassium in the presence of K^-, $K^+(15C5)_2$.

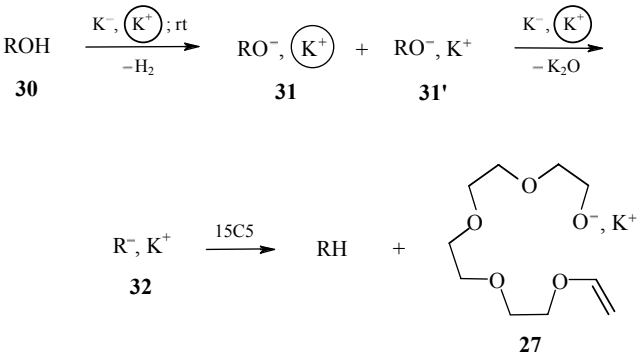


Scheme 9. Decomposition of crown ether in the reaction of methyl iodide with K^-, $K^+(15C5)_2$.



Scheme 10. Coupling of benzyl bromide with the use of K^-, $K^+(18C6)$.

propanol, gives the appropriate potassium alkoxides **31** and **31'** which can be further reduced at the excess of alkalide by carbon-oxygen bond cleavage to organopotassium intermediate **32**. The latter reacts immediately with crown ether giving potassium tetraethylene glycoxide vinyl ether **27**.



where R: CH_3, C_3H_7.

Scheme 11. Reduction of alcohols and resulting alkoxides by the use of K^-, $K^+(15C5)_2$.

Glycidol **33** behaves in the presence of K^-, $K^+(15C5)_2$ both as alcohol and as oxirane (Scheme **12**) [82]. The reduction of primary reaction products by alkalide being in the excess results in several alkoxides, which are formed *via* organopotassium intermediates (Scheme **13**).

The yields of benzylated derivatives of the final reaction products, obtained in the reaction of the latter with benzyl bromide, are given in brackets: **27** (15 %), **34** and **34'** (19 %), **36** (3 %), **38** (15 %), **40** (12 %) and **41** (26 %).

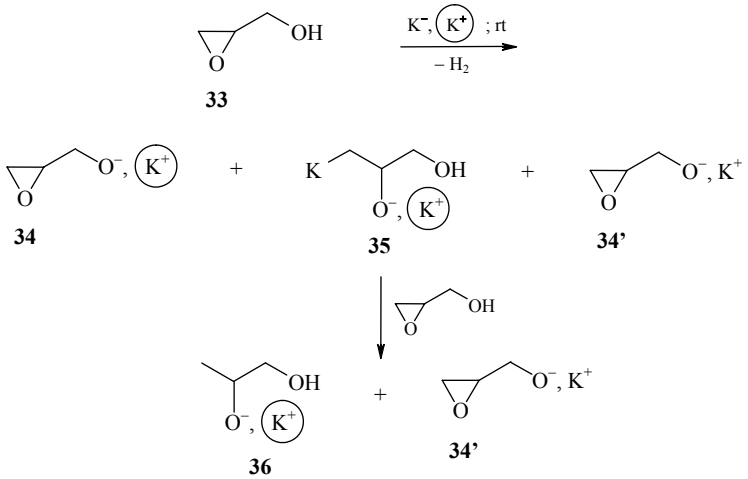
2.6. Ethers

Reactions of alkalides with ethers have been investigated in details by several authors [37,67,94,99-105]. The regioselectivity of ether bond cleavage was the most important aspects of those studies. It was stated [37,67] that the process occurred by decomposition of the ether radical anion formed initially according to *path a* in Scheme 1. The direction of ether bond cleavage as well as the further reaction course depended on the kind of substituent.

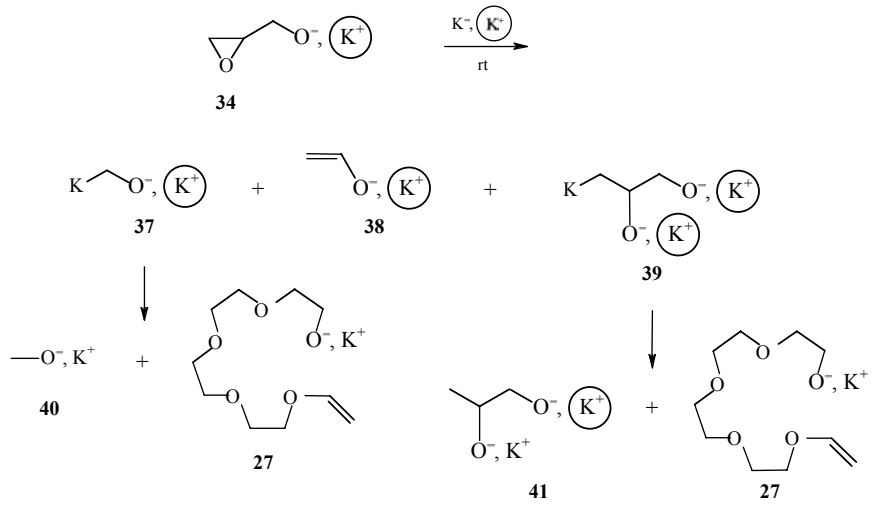
2.6.1. Linear Ethers

Reductive carbon-oxygen bond cleavage in aromatic ethers under the influence of K^-, $K^+(18C6)$ is presented in Scheme (**14**) [67].

The intermediacy of a radical anion was assumed rather than a dianion. Probably the phenyl radical formed by decomposition of the radical anion did not receive the second electron from K^0 but it



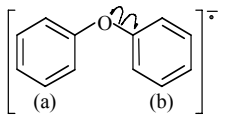
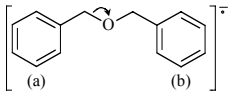
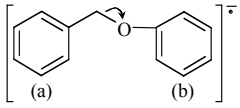
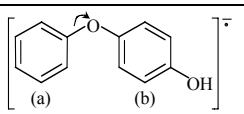
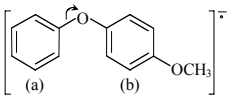
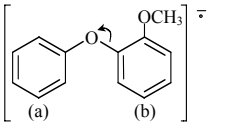
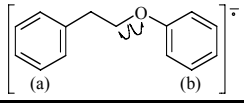
Scheme 12. Mechanism of the reaction of glycidol with K^-, $K^+(15C5)_2$.



Scheme 13. Oxirane ring opening in potassium glycidoxide under the influence of K^-, $K^+(15C5)_2$.

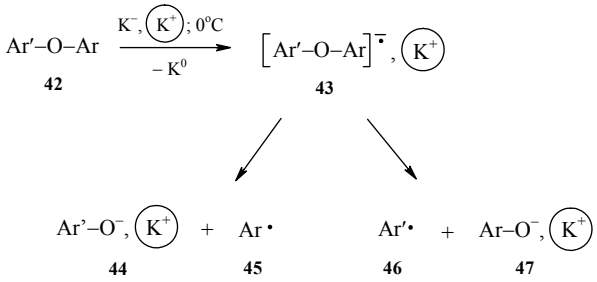
abstracted a hydrogen atom from the solvent, e.g. tetrahydrofuran, giving benzene. However, the product of tetrahydrofuran decomposition was not shown.

Table 1. The Mechanism of C-O Bond Cleavage in Aromatic Ethers by Alkalide K^-, $K^+(18C6)$ [67]. The Aromatic Rings are Denoted (a) and (b)

Electron-transfer occurs to the LUMO orbital localized mainly on:	C-O bond cleavage in ether radical anion [a] formed after the electron-transfer from K^-
(a)	homolytic 
(a)	heterolytic 
(a)	heterolytic 
(a)	heterolytic 
(a)	heterolytic 
(b)	heterolytic 
(b)	homolytic 

[a] $K^+(18C6)$ counter ion is omitted

Regiochemistry of the reaction of K^- with aromatic ethers is shown in Table **1**. A preference for benzyl-oxygen bond cleavage is found in the case of benzyl phenyl ether. Substitution of the hydroxy or methoxy group in the position 4 in diphenyl ether results in selective cleavage between the unsubstituted aryl group and oxygen. The presence of the 2-methoxy group in diphenyl ether changes the regiochemistry. The cleavage undergoes between the substituted aryl group and oxygen. The methoxy group does not show the effect on relative rates of ether bond cleavage whereas the hydroxy group dramatically decreases the reaction rate.



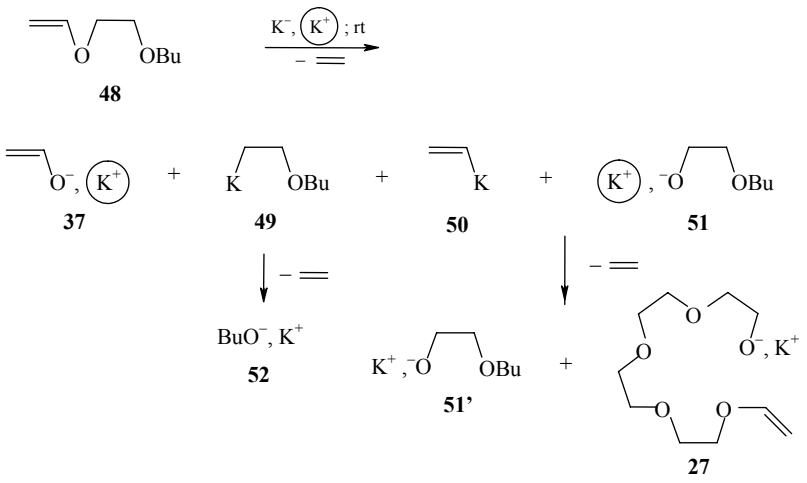
Scheme 14. Reductive C-O bond cleavage in aromatic ethers with K^-, $K^+(18C6)$.

The course of K^-, $K^+(15C5)_2$ reactions with aliphatic and aliphatic-aromatic ethers has been presented in several articles [37,83,95,104]. These reactions were also regioselective. The regioselectivity was correlated with the direction of electron-transfer from K^- to the LUMO orbital of the ether molecule. Organometallic intermediates were formed in all studied systems. They reacted immediately with crown ether or with a substrate molecule or underwent elimination. The reaction of alkalide with ethylene glycol butyl vinyl ether **48** is presented as an example in Scheme (**15**) [104].

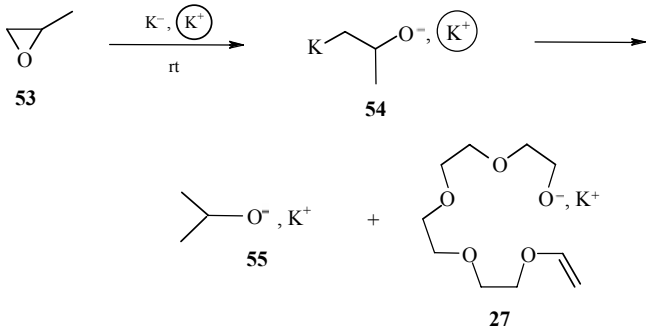
2.6.2. Cyclic Ethers

Oxiranes are the smallest cyclic ethers. The simplest of them, i.e. oxirane (ethylene oxide) had been selected in the first work concerning reactions of K^-, $K^+(18C6)$ with that group of compounds [74].

Then, it was suggested for the reaction of K^-, $K^+(18C6)$ with methyloxirane (propylene oxide) **53** that the organopotassium compound, i.e. potassium 2-potassio-1-methylethoxide **54**, was formed initially as the intermediate which reacted with tetrahydrofuran being the solvent [106]. Potassium isopropoxide **55** and an unidentified derivative of tetrahydrofuran were proposed as the final products of that process. However, it is already known that the solvent is stable in reactions mediated with alkalides. The organometallic product formed from methyloxirane reacts exclusively with crown ether, i.e. 18C6 [37] or 15C5 [94] causing its ring



Scheme 15. Reaction of ethylene glycol butyl vinyl ether with K^-, $K^+(15C5)_2$.



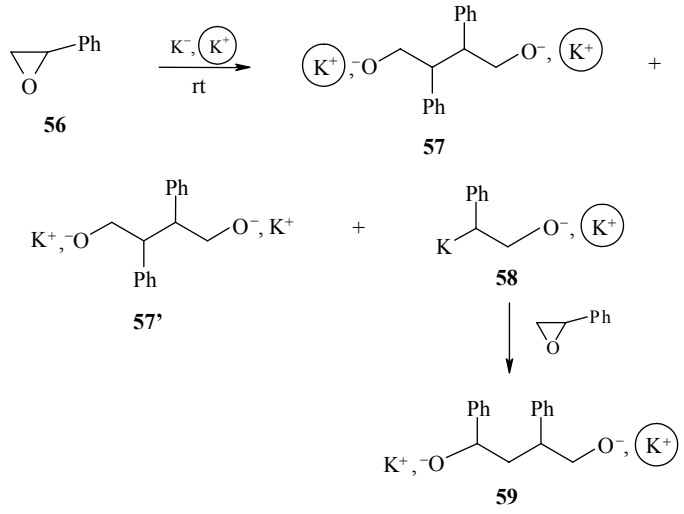
Scheme 16. Ring opening in methyloxirane and crown ether in the presence of K^-, $K^+(15C5)_2$.

opening. Therefore, the course of this process has to be formulated as in Scheme (**16**).

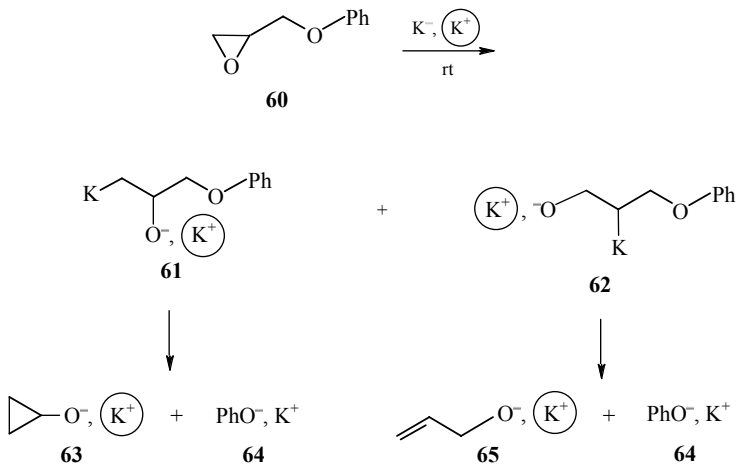
The oxacyclic ring in methyloxirane is opened in the β-position as it usually does in the presence of anionic species. The same mechanism was stated for 3-butenyloxirane whereas in vinyloxirane the α-opening was observed [107].

Phenyloxirane **56** is opened by K^-, $K^+(15C5)_2$ or K^-, $K^+(18C6)$ exclusively in the α-position [83,108] and not both in the α- and β-positions as that was earlier reported [106]. Organometallic compound **58** formed from this oxirane unexpectedly does not react with crown ether but reacts with the substrate (Scheme **17**).

The earlier proposed mechanism of K^-, $K^+(15C5)_2$ reaction with phenoxymethyloxirane **60** [102] had to be also corrected (Scheme **18**) [103]. The oxygen atom of the substituent has an electron-donating character and, therefore, it increases the electron density of the aromatic ring [101]. This may be one of the reasons why the electron is transferred from K^- to the oxirane ring and mainly to the CH_2-O bond and not to the substituent. It results in oxirane ring opening both in the α- and in the β-position but the latter prevails. The yields of benzylated derivatives of the final reaction products are given in brackets: **63** (28 %), **64** (62 %) and **65** (< 10 %).



Scheme 17. Reduction of phenyloxirane with K^-, $K^+(15C5)_2$.



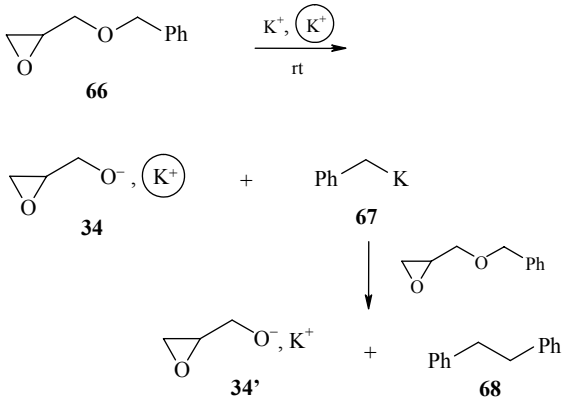
Scheme 18. Reaction of phenoxymethyloxirane with K^-, $K^+(15C5)_2$.

A similar reaction course was observed for carbazolylethoxymethyloxirane [109]. In this compound the oxygen atom of the substituent is separated from the aromatic group by the ethylene bridge and the electron transfer to the carbazolyl group would be rather expected than to the oxirane ring. However, the latter is really cleaved and in both possible positions. A role in this case as well as for **60** might play an intramolecular bond existing between the hydrogen atom of the oxirane ring and the aromatic substituent, as that had been found for phenoxymethyloxirane [110] and trimethylsilyloxymethyloxirane [111].

Data concerning directions and mechanism of ether bond cleavage in the reaction of K^-, $K^+(15C5)_2$ with various monosubstituted oxiranes are collected in Tables **2** and **3**.

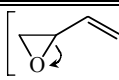
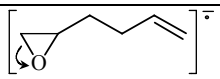
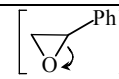
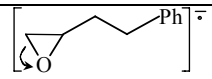
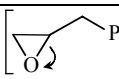
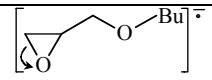
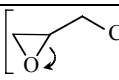
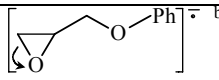
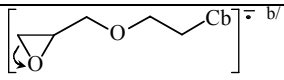
The linear radical or radical anion is formed after decomposition of the substrate radical anion. It receives the electron from K^0 giving an organopotassium compound. The latter is extremely reactive. It deprotonates crown ether or reacts with the oxirane substrate or undergoes elimination [95].

Particularly interesting results were obtained for allyloxymethyloxirane [112], benzyloxymethyloxirane **66** (Scheme **19**) and triphenylmethoxymethyloxirane [101], i.e. for glycidyl ethers, and butyryloxymethyloxirane being a glycidyl ester [86]. The oxirane ring in those compounds was stable under electron-transfer conditions. Linear ether bond cleavage in glycidyl ethers resulted in potassium glycidoxide **34** and allylpotassium, benzylpotassium **67** and triphenylmethylpotassium, respectively.



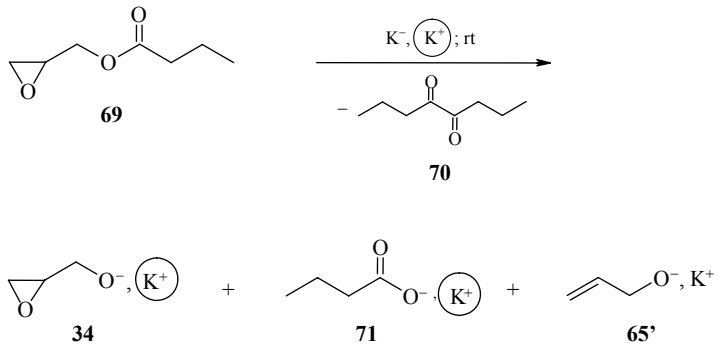
Scheme 19. Unexpected behavior of benzyloxymethyloxirane in the reaction with K^-, $K^+(15C5)_2$.

Table 2. The Mechanism of Ring Opening in Monosubstituted Oxiranes by Alkalide K^-, $K^+(15C5)_2$[a/]

Oxirane Ring Opening in the β-Position	Literature	Oxirane Ring Opening in the α-Position	Literature
	[94]		[107]
	[107]		[108]
	[108]		[108]
	[112]		[113]
 b/	[103]		
 b/	[109]		

[a/] $K^+(15C5)_2$ counter-ion is omitted

[b/] oxirane ring opening in the α-position occurs in a side reaction



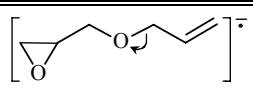
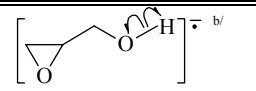
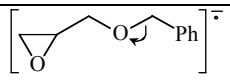
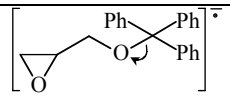
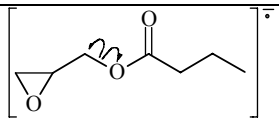
Scheme 20. Decomposition of butyryloxymethyloxirane by K^-, $K^+(15C5)_2$. The yields of benzylated derivatives of the final reaction products are given in brackets: **34** (38 %), **65'** (16 %) and **71** (25 %).

Alkyl-oxygen bond cleavage occurred in the substituent in the case of glycidyl ester **69** (Scheme **20**) [86]. No organopotassium intermediate product was formed in that process, similarly to the systems containing cyclic ketones [114]. Potassium glycidoxide was generated in the further step of the reaction.

Oxetane **72** had been selected to the study from the family of four-membered ethers. The organopotassium compound formed in its reaction with K^-, K^+(18C6), i.e. potassium 3-potassiopropoxide **73**, had been proposed to be stable enough at –20 °C to take part in metallation, carboxylation and alkylation [99]. The yield of metallation had been reported to be high and reaction conditions milder than with traditional reagents, as for example with n-butyllithium. However, further experiments indicated that the same organometallic product obtained in the system containing K^-, $K^+(15C5)_2$ was extremely reactive even at –20 °C and it deprotonated immediately crown ether (Scheme **21**) [36]. No of its derivatives, e.g. methylated or benzylated ones was identified. The reaction of oxetane with K^-, K^+(18C6) gave the same result [113]. Evidently, the behavior of this organopotassium compound did not depend on the kind of crown ether used.

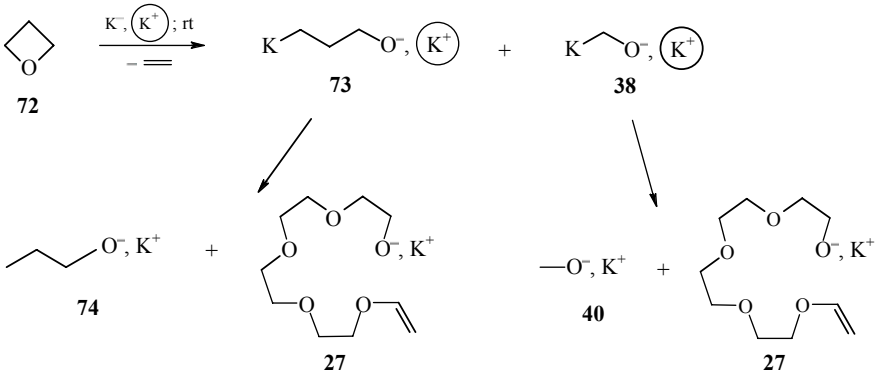
Cyclic ethers having five-membered rings, i.e. tetrahydrofuran and 2-methyltetrahydrofuran **75** used for dissolution of metallic

Table 3. The Mechanism of C-O or O-H Bond Cleavage in the Substituent of Some Oxiranes by Alkalide K^-, $K^+(15C5)_2$.[a/]

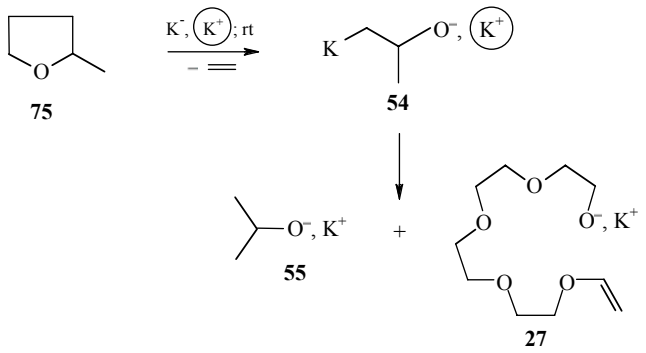
Cleavage of the C-O Bond	Literature	Cleavage of the O-H Bond	Literature
	[112]	 [b/]	[82]
	[101]		
	[101]		
	[86]		

[a/] $K^+(15C5)_2$ counter-ion is omitted

[b/] oxirane ring opening in the β-position occurs in a side reaction



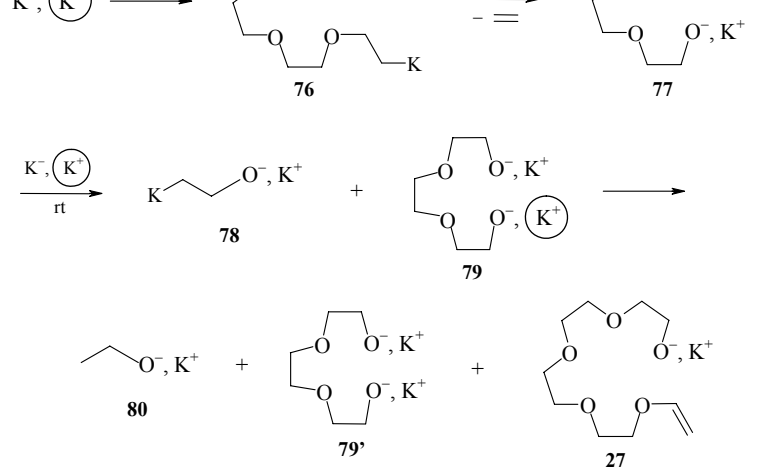
Scheme 21. Decomposition of oxetane *via* two organometallic compounds in the presence of K^-, $K^+(15C5)_2$. The yields of benzylated derivatives of the final reaction products are given in brackets: **27** (38 %), **40** (22 %) and **74** (25 %).



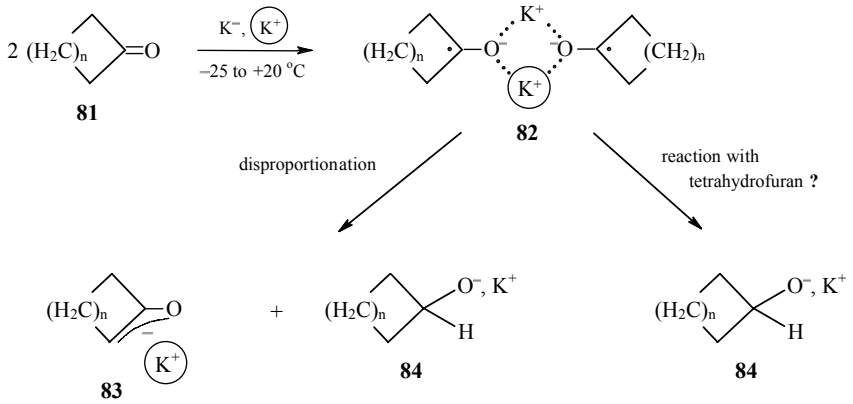
Scheme 22. Destruction of 2-methyltetrahydrofuran used as the solvent in autocatalytic decomposition of K^-, $K^+(15C5)_2$.

potassium are reduced during autocatalytic decomposition of alkalide solutions in the absence of other species. Their rings are opened by K^-, $K^+(15C5)_2$ giving potassium 4-potassiobutoxide and potassium 2-potassio-1-methylethoxide **54** (Scheme **22**), respectively [100]. The latter is formed after the elimination of ethylene from 2-methyltetrahydrofuran radical anion being the intermediate product (Scheme **1**).

Unsubstituted crown ethers being in the complex with K^+, i.e. ethers of larger rings, are decomposed by K^- in alkalide solution to a mixture of dipotassium glycoxides and ethylene [80,100]. An example of such reaction is presented for 15C5 in Scheme (**23**) [100]. Under the same conditions cyclohexano- and dicyclohexano-substituted crown ethers undergo decomposition giving the appropriate dipotassium glycoxides as well as ethylene and cyclohexene [105]. The ether bonds in cyclohexano-15C5 or cyclohexano-18C6 are cleaved in five or six positions, respectively, whereas in dicyclohexano-15C5 in two positions and in dicyclohexano-18C6 only in one position. Extremely unstable organopotassium compounds are formed in all these systems and they decompose rapidly by elimination of unsaturated hydrocarbons.

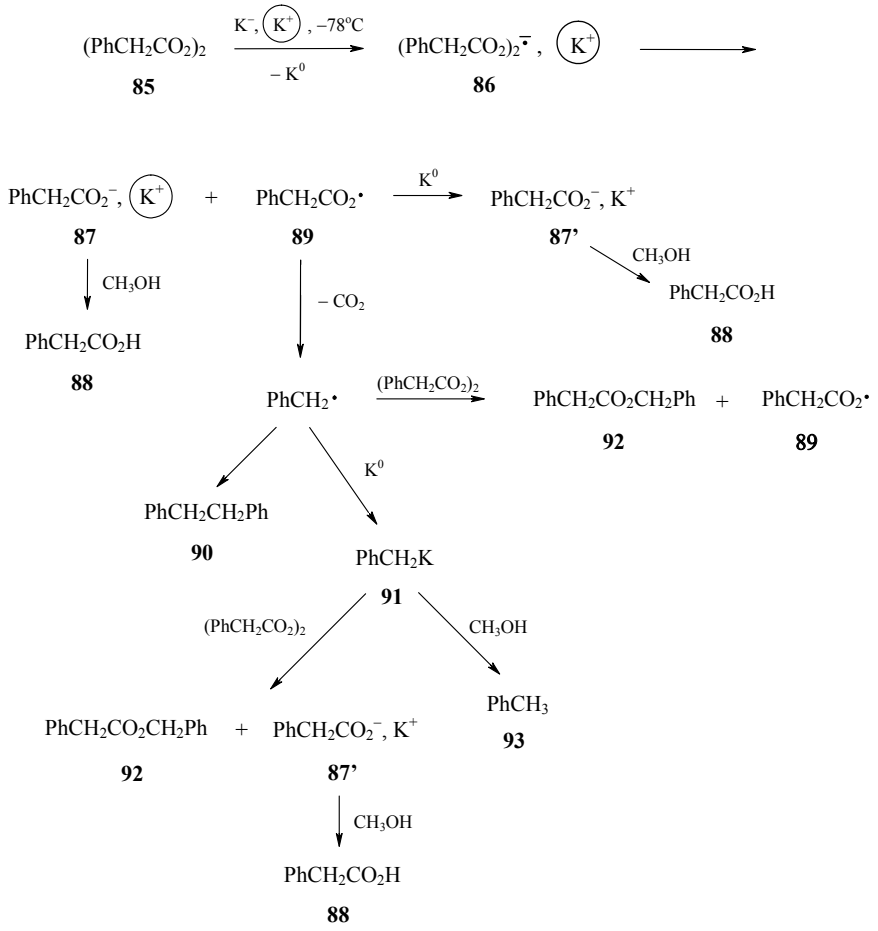


Scheme 23. Decomposition processes taking place in K^-, $K^+(15C5)_2$ solution. The yields of methylated derivatives of the final reaction products are given in brackets: **27** (2 %), **77** (64 %), and **79** and **79'** (15 %). The yield of benzylated derivative of **80** was equal to 4 %.



where n = 1 to 3.

Scheme 24. Reduction of cyclic ketones with K^-, $K^+(18C6)$.



Scheme 25. Reaction of phenacetyl peroxide with K^-, K^+(18C6).

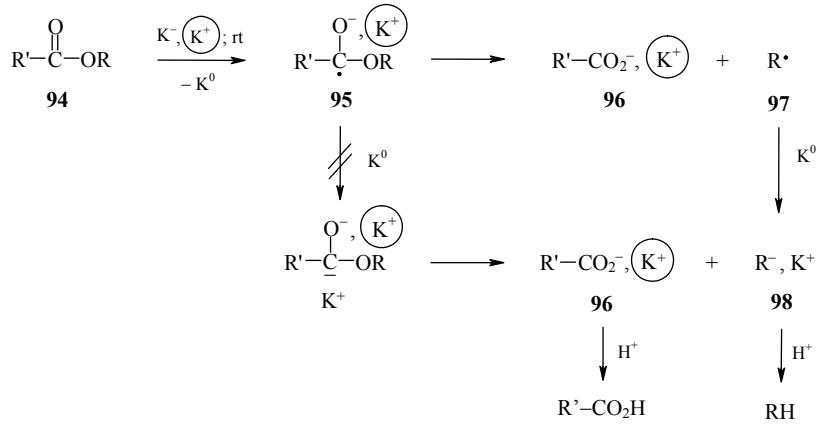
2.7. Ketones

K^-, K^+(18C6) had been described as the reductant of cyclic ketones: cyclobutanone, cyclopentanone and cyclohexanone [114]. According to the mechanism proposed (Scheme **24**) ketyl radical anion **82** was formed in the first step of that process. After disproportionation it yielded the appropriate potassium enolate and potassium alkoxide. Such reaction was possible because the selected ketones had hydrogen atoms in the α-position in respect to the carbonyl group. Compound **82** might also abstract hydrogen from tetrahydrofuran used as the solvent. However, the product of its decomposition was not determined.

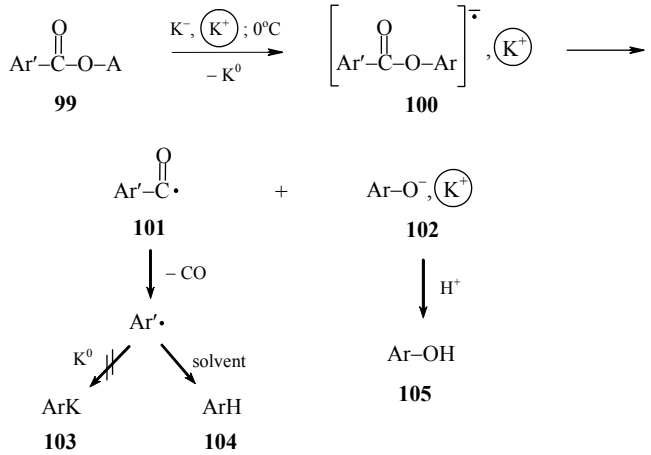
Stable radical anions are formed in the case of benzophenone due to the lack of the hydrogen atom in the α-position making disproportionation impossible [115].

2.8. Peroxides

Phenacetyl peroxide **85** had been selected as an excellent model compound which for the first time allowed to explain the mechanism of electron-transfer reaction mediated by alkalides [88]. The reaction of K^-, K^+(18C6) with this peroxide in tetrahydrofuran solution produced bibenzyl **90**, benzyl phenylacetate **92**, phenylacetic acid **88** and toluene **93** (Scheme **25**). Two last compounds are formed after the addition of methanol at the end of the process.



Scheme 26. Deoxygenation mechanism of the linear ester by the use of alkalide.



Scheme 27. Reductive C-O bond cleavage in aromatic esters with K^-, K^+(18C6).

The formation of toluene, bibenzyl and benzyl phenylacetate was conclusive evidence for the intermediacy of phenylacetoxy radical and, consequently, the stepwise two-electron-transfer from K^-. If concerted two-electron-transfer had occurred, bypassing this radical, then the only product would have been phenylacetate anion **87**. A control experiment with benzoyl peroxide showed that the dominant product was benzoic acid. Decarboxylation of the benzoyloxy radical followed by induced decomposition of peroxide, which was not competitive with the transfer of the second electron from K^0.

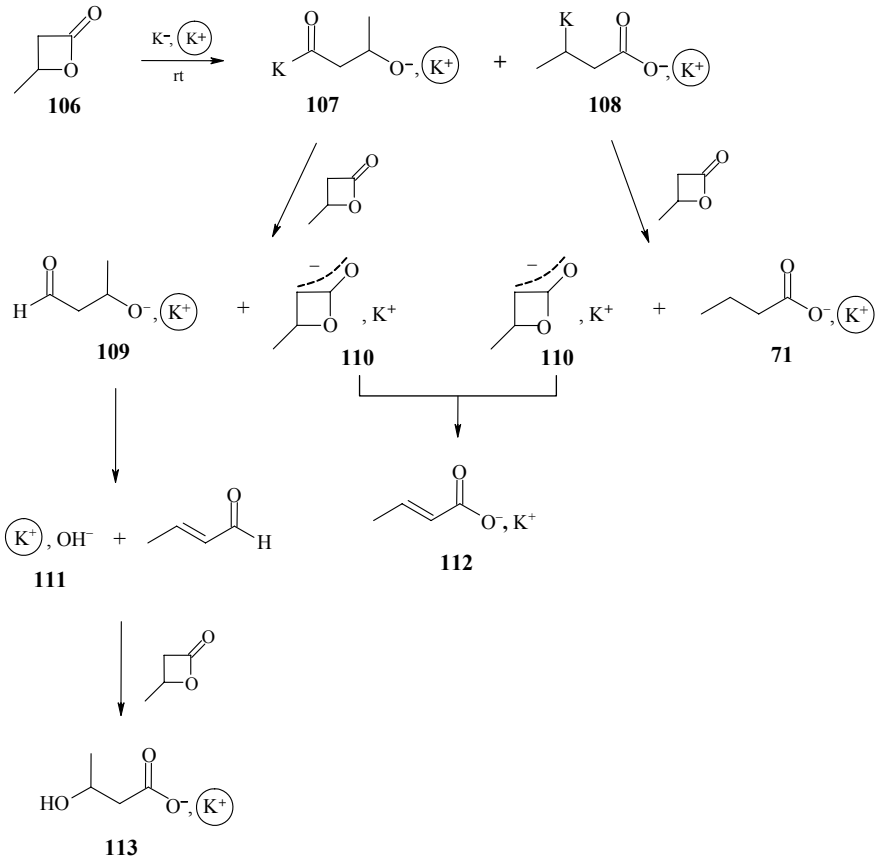
2.9. Esters

The reduction of esters by alkalides had been studied in details in several papers [67-69,73,84-86]. It was established that the reaction mechanism depended on the structure of the substrate. Linear ester reduction occurred according to *path a* in Scheme **1**, i.e. with the formation and decomposition of the ester radical anion. Cyclic esters formed mainly dianions (*path b* in Scheme **1**).

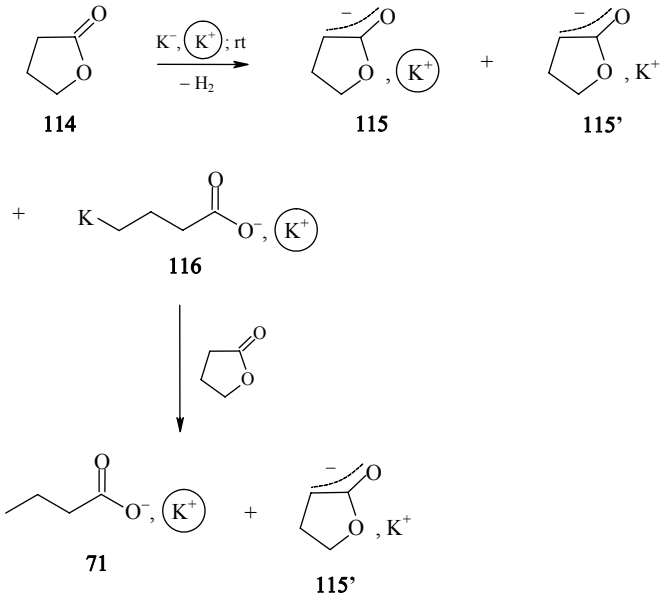
2.9.1. Linear Esters

Na^-, K^+(18C6) or K^-, K^+(18C6) reactions with aliphatic linear ester **94** in *tert*-butylamine or tetrahydrofuran solutions were reported in refs. [68,69]. As shown in Scheme (**26**), ester radical anion **95** is formed in the first step of this process. It decomposes immediately by alkyl-oxygen bond cleavage. Products of this reaction involve carboxylate anion **96** and an alkyl radical. The latter becomes carbanion **98** after receiving the second electron from K^0. This process was called deoxygenation.

The reduction of 3β,5α-cyclocholestan-6β-yl acetate afforded a hydrocarbon fraction which gave cholest-5-ene and 3β,5α-



Scheme 28. Reduction of β-butyrolactone with alkalides *via* acyl-oxygen and alkyl-oxygen bond cleavage and not *via* C-C one.



Scheme 29. Mechanism of γ-butyrolactone reaction with potassium anions of K^-, $K^+(15C5)_2$. The yields of benzylated derivatives of the final reaction products are given in brackets: **115** and **115'** (85 %), and **71** (12 %).

cyclocholestane [68]. That result was consistent with the pathway proceeding with decomposition of the ester radical anion since the rapid rearrangement of 3β,5α-cyclocholestan-6β-yl radical into the more stable cholest-5-en-3-yl radical is a well established process. Conversely, the reduction of ergosteryl pivaloate gave 3α,5α-cycloergosta-7,22-diene and ergosta-7,22-dien-3β-ol. Both reactions supported the belief that the deoxygenation occurred predominantly, if not exclusively, *via* fragmentation of the radical anion. The reduction of carboxylic esters to alkanes by photolysis was shown to occur with a similar mechanism [116].

The reaction of carboxylic esters with alkali metals (classical organic transformation) at the excess of sodium in ethanol provides two alcohols (Bouveault-Blanc) [117] whereas the molten sodium in refluxing toluene gives acyloin [118]. Both the reactions occur *via* acyl-oxygen fragmentation subsequent to the electron-transfer.

Acyl-oxygen bond cleavage occurred exclusively in the reaction of K^-, $K^+(18C6)$ with aromatic esters **99** in tetrahydrofuran solution (Scheme **27**) [67]. However, the acyl radical formed by ester radical anion decomposition did not receive the second electron from K^0 as well as did not dimerize but eliminates carbon monoxide giving the aromatic radical. It is proved by the use of acetic acid-d_4 that at least the phenyl radical abstracted a hydrogen atom from the solvent giving benzene [67]. Such results suggested that radical anions, and not dianions, were predominantly formed in the reaction of alkalide with aromatic esters.

2.9.2. Cyclic Esters

It had been reported that β-lactones could be reduced with unique C-C bond cleavage under the influence of K^-, $K^+(18C6)$ [119]. A strong resonance stabilization of an intermediate enolate had been proposed as a driving force of that reaction. The enolate had been assumed to be stable at ambient temperature enough for protonation or methylation by HCl or CH_3I, respectively.

In fact, organopotassium compounds are generally unstable at ambient temperature [37,95]. Their methyl and benzyl derivatives are not obtained after the use of alkalides. Triphenylmethylpotassium is until now the only one exception to this rule [101]. Thus, there was no reason to expect the enhanced stability of organopotassium enolates formed from β-lactones. Moreover, Szwarc [120] analyzing the mechanism of K^- reaction with β-lactones stated that the rupture of the C-C bond instead of the expected opening of the CO-O or O-CH_2 bonds calls for verification.

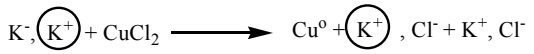
Indeed, using K^-, $K^+(15C5)_2$ for the reaction with β-butyrolactone **106** it was found that the mechanism involving C-C bond cleavage did not operate at all [85]. A real mechanism is proposed according to the Szwarc's suggestion. The main course of this process is shown in Scheme (**28**). It is worth noting that intermediate **107** is formed by the decomposition of lactone dianion and **108** by the decomposition of lactone radical anion.

Application of K^-, $K^+(15C5)_2$ allowed also to correct the earlier suggestion concerning the reduction of γ-butyrolactone **114** [121]. It was demonstrated that the potassium anion really took part in that process as electron-transfer reagent and not as deprotonating species. A new mechanism is presented in Scheme (**29**) [84].

3. PREPARATION OF INORGANIC NANOMATERIALS

The use of alkali metals for reduction of metal salts, often in combination with aromatic radical anions or dianions, had been pioneered by Rieke [122,123]. This method had been applied to produce highly reactive metal powders for organometallic syntheses. Solutions of alkali metal organoborohydride, e.g. $NaB(C_2H_5)_3H$ were used in more recent developments. They yielded both single metals or alloys of the iron group elements as well as noble metals [124].

A new method for the preparation of nanoscale metal particles is based on a homogeneous reduction of metal salts with alkalides. Compounds of transition and post-transition metals such as $AuCl_3$, $CuCl_2$, $TeBr_4$ or $PtCl_4$ dissolved in dimethyl ether or in tetrahydrofuran are rapidly reduced by K^-, $K^+(15C5)_2$ at –30 °C to produce crystalline metal particles of sizes from 2 to 15 nm [125-127]. An example of the reaction between the metal salt and alkalide is shown in Scheme (**30**).



Scheme 30. The use of alkalide K^-, $K^+(15C5)_2$ for the preparation of crystalline transition metal nanoparticles.

It is proposed that in these systems simultaneous two-electron-transfer occurs [128] and not stepwise as it is observed in reactions with organic substrates [88].

The formation of metal alloys or intermetallic species took place when a mixture of precursor compounds was used [125-127]. It was demonstrated for Au-Zn, Au-Cu, Cu-Te and Zn-Te by their XP spectra. Au-Zn and Au-Cu were identified by their selective area electron diffraction patterns. A major advantage of this method is the simple ability to control overall stoichiometry by adjusting initial compositions. It has potential applicability to metal and alloy production in the form of powders on inert supports and in the pores of zeolites as well as to the synthesis of organometallic compounds.

The use of alkalide was shown to be a good route to nanocrystalline metal compounds. Y_2O_3 nanoparticles were obtained by subambient homogeneous reduction with alkalide solution and subsequent oxidation [129a]. α-Mo_2C and α-WC nanoparticles were formed that way [129b]. Their heating resulted in crystalline materials. α-Mo_2C nanoparticles were found to have the average diameter of 3 nm. Much broader size distribution ranging from 3 to 50 nm had α-WC nanoparticles. Both carbides possessed high surface areas. Transition metal nitrides like for example Mo_2N, Ta_3N_5, Fe_3Mo_3N and a mixture of niobium nitride phases were synthesized by heating nanoscale metal particles under flowing gaseous N_2 or NH_3 [130].

Using Na^-, $K^+(15C5)_2$ as the reducing agent it was possible to produce sodium tantalate nanorods in a multistage process [128]. The end product was a black, free-flowing powder of orthorombic $NaTaO_3$, which was demonstreated by its X-ray diffraction.

As mentioned above, the decomposition of alkalides involves the reductive cleavage of the complexant to unsaturated hydrocarbon and alkali metal glycoxides. It is possible that the latter can stimulate the nanorod growth and serve as a source of oxygen for the reaction with Ta nanocrystals [125]. Additional data on the synthesis of inorganic nanomaterials with the use of alkalides were recently described in ref. [131].

4. CONCLUSIONS

Alkali metal anions of alkalides effectively reduce many organic compounds by stepwise two-electron-transfer (TET). These processes occur under mild homogeneous conditions. Organoalkali metal intermediates are the primary reaction products. Generally, they are extremely reactive at ambient temperature and immediately deprotonate crown ether used as the complexing agent or undergo elimination or react with the substrate.

Inorganic salts are reduced with alkalides to crystalline nanomaterials, namely transition and post-transition metals, their alloys and derivatives. This method opens a new way for the synthesis of species useful in nanotechnology. It is suggested that the metal anion transfers simultaneously its two valence electrons to the inorganic acceptor. However, a proof of such assumption is till now not shown and this problem needs verification.

ABBREVIATIONS

Bu	=	Butyl
12C4	=	1,4,7,10-Tetraoxacyclodecane (12-crown-4)
15C5	=	1,4,7,10,13-Pentaoxacyclopentadecane (15-crown-5)
18C6	=	1,4,7,10,13,16-Hexaoxacyclooctadecane (18-crown-6)
C222	=	4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo-[8.8.8]-hexacosan (cryptand [2.2.2])
Cb	=	Carbazolyl
HMHCY	=	Hexamethylhexacyclen
Ph	=	Phenyl

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