

Alkali metal supramolecular complexes and their significance in organic chemistry

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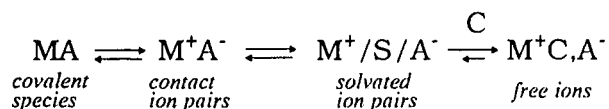
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Abstract - Some reactions of potassium or sodium supramolecular complexes with various heterocycles are presented, the attention being paid to enolization, metallation and carbon - carbon bond scission processes. The mechanisms of new reactions involving electron transfer from alkali metal supramolecular complexes towards some oxa-cyclic compounds are discussed.

1. INTRODUCTION

Discovery of crown ethers and cryptands, being able to complex cations, by Pedersen (ref. 1) , Lehn (ref. 2) and Cram (ref. 3) has opened new doors to interdisciplinary research in chemistry, biology, physics, material science etc.

The equilibrium of ions and ion pairs is shifted to the right after addition of a complexing agent:



where: S - solvent, C - cation complexing agent, e.g. crown ether or cryptand.

The kinetics as well as the mechanism of a given chemical reaction, can be changed by complexation, because reactivities of covalent species, ion pairs and free ions are usually different (ref. 4). This concept has been widely used in the synthetic organic chemistry. The utility of crown ethers and cryptands has been also proven in the alkali metal chemistry (ref. 5). It has been revealed that alkali metals as sodium or potassium can be easily dissolved in an etheral solvent after addition of a crown ether or a cryptand. Solubility of alkali metals in THF is very low, of the order of $5 \cdot 10^{-6}$ - $5 \cdot 10^{-4}$ mol/l. After addition of a suitable organic ligand as 18C6 or C[222] the metal solubility increases dramatically due to metal cation complexation, the total metal concentration in the form of metal ions being in saturated solution twice as high as that of the organic ligand (a crown ether or a cryptand).

Alkali metal "blue" solutions, as described in early papers (ref. 5), contained metal ions and solvated electrons in equivalent amounts. By controlling the kinetics of metal dissolution we are able nowadays to produce alkali metal solutions containing only small, negligible amount of electrons, complexed cations and metal anions being prevailing (ref. 6). So the uniform, well defined reagent can be prepared. However, after some time, especially at higher temperatures, the decomposition of metal blue solution occurs due to side reactions between alkali metal and a solvent (e.g. THF) or a complexing agent (ref. 7). Potassium solutions with 18C6 are usually more stable than those with macrobicyclic ligand C[222].

In early eighties alkali metal solutions have been employed as reducing agents for hydrocarbons (refs. 8-9). Barret, Barton et al. (refs. 10-12) have applied sodium - potassium alloy, dissolved in *tert*-butylamine or another solvent containing crown ether, for reduction of esters or their derivatives. In this paper novel reactions of alkali metal supramolecular complexes are presented. The alkali metal supramolecular complexes have been prepared by dissolution of metal mirror of potassium or sodium - potassium alloy (1:1) in THF or in tetraglyme containing 18C6 or C[222] as described in ref. 6. The composition of a dissolved complex and metal concentration were followed by ^{23}Na or ^{39}K NMR (refs. 13-15).

Alkali metal supramolecular complexes as $\text{K}^+18\text{C}6, \text{K}^-$ or $\text{K}^+18\text{C}6, \text{Na}^-$ can react like strong nucleophiles and reducers, transferring electrons from metal anion towards suitable acceptor or abstracting proton from a substrate. Examples of such reactions are provided.

2. γ - AND β -LACTONES REACTIONS WITH ALKALI METAL SUPRAMOLECULAR COMPLEXES

α -Alkyl- γ -lactones can be synthesized via their enolates in several ways, for example, α -methyl- γ -butyrolactone has been obtained by the reaction with lithium dialkylamide (LDA) and methyl iodide at -78°C in THF.

The procedure now reported is much simpler and can be employed for synthesis of both α -alkyl and α -acyl γ -lactones. Side reactions, such as O-acylation, self-condensation or α, α -disubstitution do not occur. Due to the reaction of $\text{K}^+18\text{C}6, \text{K}^-$ complex with a γ -lactone in THF at room temperature respective lactone enolates are formed (Scheme 1). The enolates (2a and 2b) can react with a variety of alkyl and acyl halides to provide good yields of the corresponding α -substituted γ -lactones (Table 1). We did not observe any significant influence of the methyl substituent in the γ position on the reaction yield (ref. 16).

Scheme 1

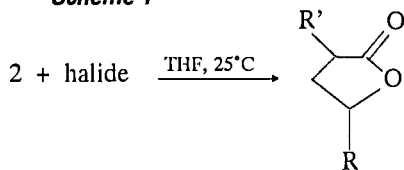


Table 1.
Reaction of alkyl and acyl halides with γ -lactone enolates.

enolate	halide	R	R'	reaction time, h	yield, %
2a	CH_3I	H	CH_3	3	89
2a	$\text{C}_2\text{H}_5\text{I}$	H	C_2H_5	4	82
2a	<i>n</i> - $\text{C}_4\text{H}_9\text{I}$	H	<i>n</i> - C_4H_9	5	80
2a	<i>n</i> - $\text{C}_5\text{H}_{11}\text{I}$	H	<i>n</i> - C_5H_{11}	6	79
2a	PhCH_2Cl	H	PhCH_2	5	86
2a	PhCOCl	H	PhCO	3	93
2a	CH_3COCl	H	CH_3CO	5	85
2b	CH_3I	CH_3	CH_3	4	88
2b	$\text{C}_2\text{H}_5\text{I}$	CH_3	C_2H_5	5	81
2b	PhCH_2Cl	CH_3	PhCH_2	4	85
2b	PhCOCl	CH_3	PhCO	3	95

The reaction of β -lactones with alkali metal complexes proceeds differently, when compared with that of γ -lactones. It is well known that 4-membered ring of β -lactones is very strained and usually alcoholysis or acidolysis induces alkyl-oxygen or acyl-oxygen bond cleavage (ref. 17). However, in the reaction of a β -propiolactone with alkali metal supramolecular complex, e.g. $\text{K}^+18\text{C}6, \text{K}^-$, the ^{35}K NMR measurements have revealed that two electrons are transferred from metal anion to the β -lactone molecule (Fig.1).

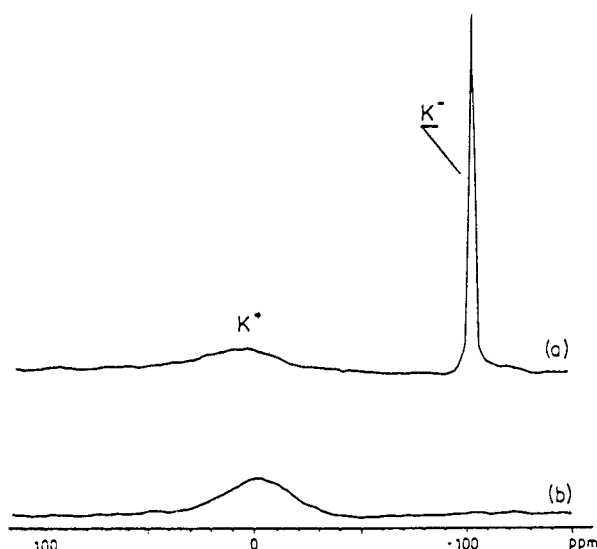
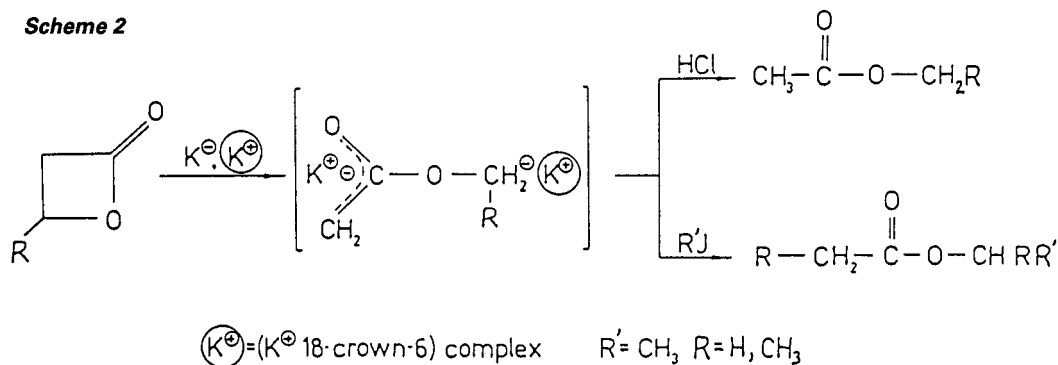
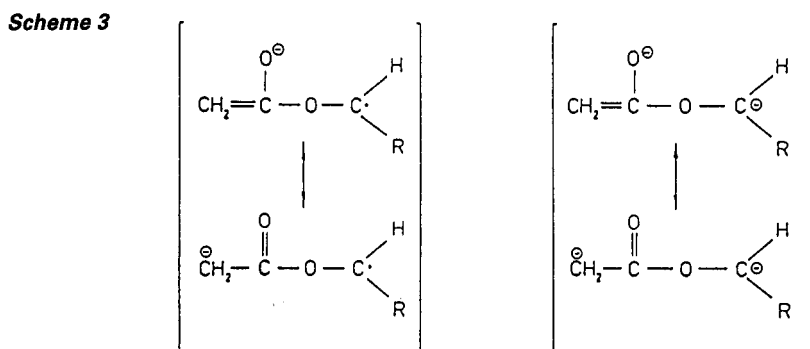


Fig.1 ^{39}K NMR spectra of (a) potassium solution in THF containing 18-crown-6, (b) after addition of water to the solution.

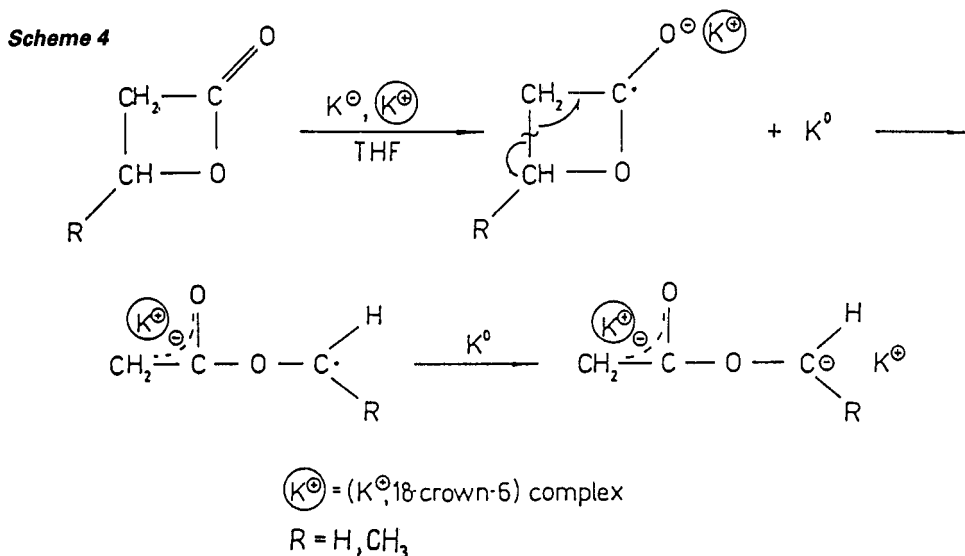
By addition of the β -lactone to the solution of alkali metal supramolecular complex the blue solution decolorized instantly and after protonation or alkylation respective esters have been isolated and identified in good yields (over 70%) (Scheme 2).



These results clearly indicate that at the first step of the reaction between potassium anion and β -propiolactone the corresponding enolate carbanion is formed due to the C-C bond scission of the strained β -lactone ring. The driving force of this reaction is obviously the strong resonance stabilization of the intermediate enolate (Scheme 3).



The ESR measurements have revealed that enolate radical is formed in the reaction of the β -propiolactone with potassium supramolecular complex providing direct evidence for the proposed reaction mechanism (Scheme 4).



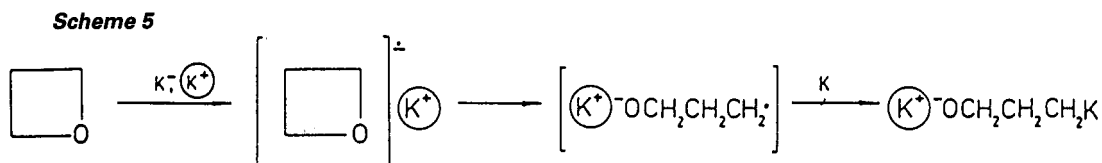
According to our suggestion the single electron is transferred from metal anion to a β -propiolactone to form unstable cyclic radical anion which after ring cleavage, due to β -elimination, yields enolate radical. The latter, due to recombination, produces eventually enolate carbanion.

It is known that C-C bond scission occurs between aliphatic carbon atoms bearing bulky substituents and also in some dibenzyl derivatives resulting from the reaction of alkali metal alloys in suspension (ref. 18), but never such a reaction has been observed in heterocycles. The unique enolate carbanions can serve for many syntheses.

3. OXETANE REACTIONS – NEW METHOD OF CARBANIONS GENERATION

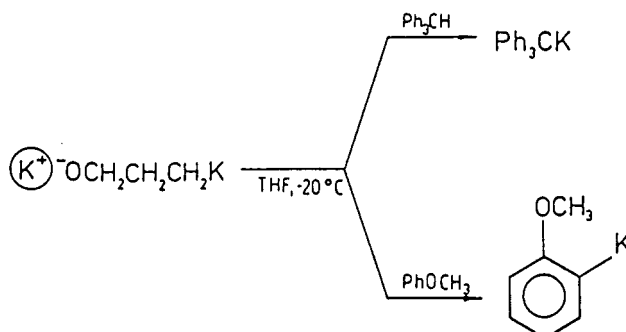
Carbanions are playing significant role as intermediates in organic syntheses, because their reactions with various electrophilic molecules result in the formation of C-C bonds. Carbanions are usually formed by proton abstraction from C-H acidic compounds, alkali metal hydroxides being the most widely used basic reagents in this reaction. Several attempts have been made to improve preparative methods and to avoid side reactions induced by alkali metal hydroxides (refs. 19-21). For this reason also metal-free carbanions are recommended, i.e. ammonium or guanidinium salts of resonance stabilized carbanions (ref. 22).

In this paper we report on the novel method of carbanions generation and its usefulness in organic synthesis. In particular, there is reported the reaction of oxetane with potassium supramolecular complex K^+18C6, K^- , containing potassium anion and complexed by 18-Crown-6 potassium cation dissolved in THF at 20 °C. The reaction with oxetane proceeds via alkyl-to-oxygen bond scission (Scheme 5), yielding the potassium organometallic compound (90%). The course of the reaction has been followed by ^{39}K NMR and ESR measurements.



The experimental results suggest that at first, due to single electron transfer, an oxetane radical anion is produced, which converts next, after ring scission, to potassium propoxide radical. The latter reacts with potassium yielding eventually the organometallic compound, which precipitates. The final product seems to be stable, however it is very efficient in metallation reactions with triphenylmethane and anisol (Scheme 6).

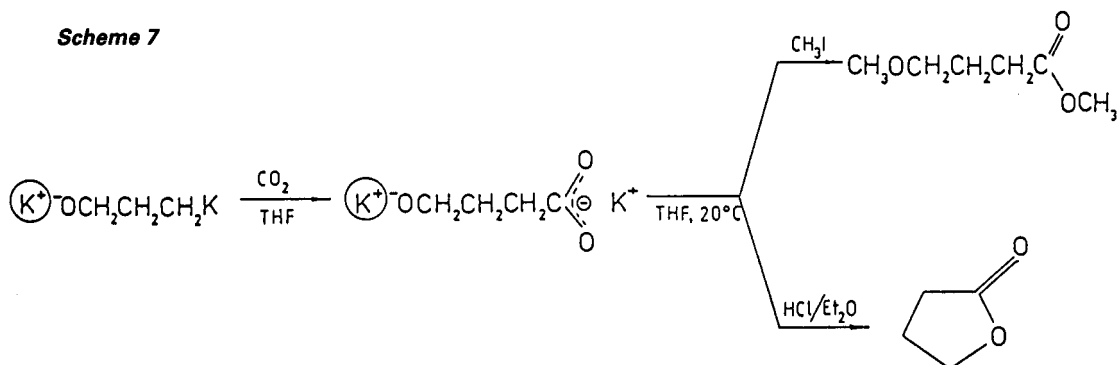
Scheme 6



The yield of metallation is high (above 90%) and reaction conditions milder than those used with traditional metallation reagents, like n-butyllithium with *tert*-butoxide or *tert*-butyllithium.

The described functionalized organometallic compound can be also employed as a useful reagent in carboxylation (Scheme 7) and alkylation reactions (ref. 23).

Scheme 7



Acknowledgements

I am indebted to my coworkers: Dr. H. Janeczek, Dr. A. Misiołek and Mr A. Jankowski for carrying out a part of experiments.

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