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Novel Electron-Transfer Reactions Mediated by Alkali Metals Complexed by Macrocyclic Ligand

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Introduction

Electron-transfer processes are today a strongly developing area of modern chemistry. Numerous biochemical reactions in living organisms proceed via electron-transfer mechanisms, being controlled by various enzymatic systems.¹ In synthetic chemistry, electron-transfer reactions are usually mediated by organometallic complexes of transition metals,² charge-transfer interactions,³ photoinduction or radiation induction,⁴ or alkali metal complexes of arenes, e.g. those of naphthalene.⁵ Moreover, the electron-transfer mechanism has been found to operate in polymerization processes of vinyl compounds,⁶ dienes,⁷ or acrylic⁸ monomers if the sodium naphthalene complex is used as an initiator. It has recently been postulated that aromatic nucleophilic substitution of

hydrogen in nitroarenes and in some heterocyclic compounds,^{9,10} as well as aromatic electrophilic halogenation,¹¹ can proceed via electron transfer. Thus, electron-transfer reactions in synthetic chemistry have attracted growing attention. Theoretical considerations by Marcus¹² and Hush,¹³ as well as experimental studies in liquid or gaseous phases and on the solid-liquid interface, have shown new perspectives and have stimulated further research in this promising field.

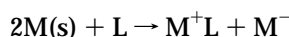
Numerous papers have recently appeared on electron-transfer reactions mediated by alkali metal complexes with macrocyclic ligands; however, a general review has not been published. Thus, it is appropriate to report on reactions that have already been performed, as well as to discuss new perspectives of alkali metals in organic synthesis.

It has been demonstrated that alkali metals such as potassium and sodium can be readily dissolved to form blue metal solutions in an aprotic etheral solvent, e.g. tetrahydrofuran or an aliphatic amine.¹⁴

In contrast to alkali metals in ammonia, blue solutions of alkali metals in ethers or amines contain not only solvated electrons and crowned metal cations but also metal anions. The presence of the M^- species (metal anions) was first proposed on the basis of optical spectra¹⁴ and was later verified for nonammonia metal solutions by alkali metal NMR spectra.¹⁵ The preparation of concentrated alkali metal solutions could be accomplished by addition of a crown ether or a cryptand to an aprotic solvent. The composition of such metal solutions depends on the chemical nature and concentration of the complexant, as well as on the procedure and the temperature of the dissolution process. Preparation of solutions that contain alkali metal complexes with macrocyclic ligands is very simple and has previously been described in detail.¹⁵⁻¹⁷ Usually, to a potassium mirror or potassium-sodium alloy dispersion in tetrahydrofuran (or other ether) is added a complexant that is soluble in THF, e.g. 18-crown-6. Due to the contact of the metal surface with the complexant, the metal dissolves and crowned potassium cations, potassium anions (or sodium anions), and solvated electrons are present in the blue solution.

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Such solutions have been used in organic synthesis, as strong reducing agents^{18–21} or as initiators of polymerization.^{22–25} To achieve reproducibility of these reactions, well-defined metal solutions should be used. Recently, the kinetics of metal dissolution has been examined and the process rationalized.^{16,17} If the contact time between potassium metal and complexant is about 15 min and the solution is separated from the solid metal, the concentration of solvated electrons is very small, on the order of 10^{-4} M, while the concentration of metal anions is equal to that of metal cations and to the concentration of added complexant (which usually is on the order of 0.1–0.5 M). This means that the concentration of solvated electrons is negligible in this case, the main active species in such solutions being alkali metal ion pairs, e.g. K^+L, K^- , accordingly to the equation

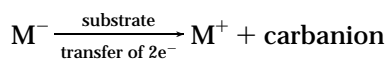


where M is the alkali metal, e.g. potassium or sodium, and L is the complexant, e.g. 18-crown-6.

The process of metal dissolution and the composition of the resulting solution can be monitored by ESR and alkali metal NMR.^{15,26,27} For practical purposes, it is sometimes more convenient to dissolve K/Na alloy instead of a pure metal such as potassium or sodium because the preparation of a metal mirror is not necessary and the metal alloy forms a dispersion in the solvent. In this case, however, mixed metal ion pairs are formed, e.g. K^+18C6, Na^- . So far, the following alkali metal complexes, soluble in ethereal solvents and forming metal ion pairs in solution, have been characterized:²⁸ $K^+/15C5, K^-$; $K^+/Glyme, K^-$; $K^+/18C6, Na^-$; and $K^+/18C6, K^-$ (where 18C6 = 18-crown-6 and 15C5 = 15-crown-5).

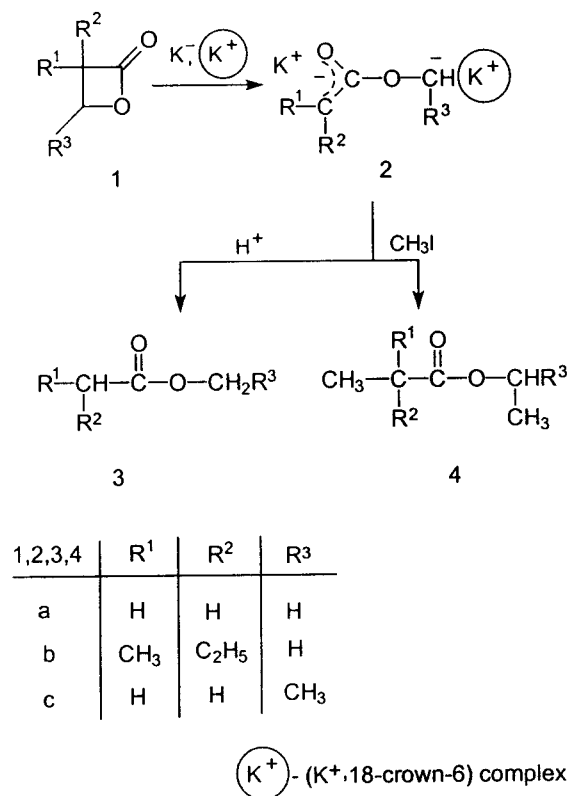
The stability of the metal solution depends on the temperature and on the kind of a ligand used. Potassium or sodium–potassium ion pairs in THF blue solutions that contain 18C6 or 15C5 are stable under an inert gas (e.g., argon) atmosphere at low temperatures. At an ambient temperature of 20 °C the stability of such solutions is limited, up to several hours.

Alkali metal complexes are important because of their unique metal ion pair structure in solutions and their ability to transfer electrons to suitable substrates, a fact that has been utilized in many organic syntheses and catalytic processes. In most cases, K^- and Na^- transfer two electrons from the outer orbital to a substrate to form a carbanion or enolate anion:



where $M = K$ or Na . The reactions are different than those of the solvated electron⁵ (e.g., sodium naphthalenide or Birch-type reactions). This observation was made in our work and confirmed by Ohsawa experiments²⁹ and discussed also by Dye.³⁰

Scheme 1



Reactions of Oxacyclic Compounds with Alkali Metals Complexed by 18-Crown-6

Since 1983, when for the first time well-defined alkali metal complexes (metal ion pairs) were used in homogeneous electron-transfer catalysis,³¹ it has been known that the alkali metal anion, M^- , can act as an electron donor. Electron-transfer reactions and their versatility and utility in synthetic chemistry will be discussed in the following sections.

Reactions of Lactones. It is well-known that hydrolysis, alcoholysis, and acidolysis of four-membered β -lactone rings proceed via alkyl–oxygen or acyl–oxygen bond cleavage.³² However, an unusual C–C bond scission in the strained β -lactone ring by the potassium metal supramolecular complex K^+18C6, K^- in THF solution leading to enolate carbanion 2 formation has been observed³³ due to electron transfer from the metal anion outer orbital (Scheme 1). The evidence for the two-electron transfer from the metal anion to a lactone was provided by ³⁹K NMR of the metal solution before and after the reaction (Figure 1). The driving force of this unique C–C bond cleavage in β -lactones is obviously the strong resonance stabilization of the intermediate enolate carbanion. This functional intermediate carbanion can serve as a useful synthon in various reactions, such as protonation, alkylation, and acylation. Such a course of this reaction is valid for all unsubstituted and substituted β -lactones.³⁴

The mechanism of this unusual ring cleavage in the reaction of β -propiolactones with the potassium supramolecular complex has been elucidated²⁸ (Scheme 2), and direct evidence for the electron transfer was provided

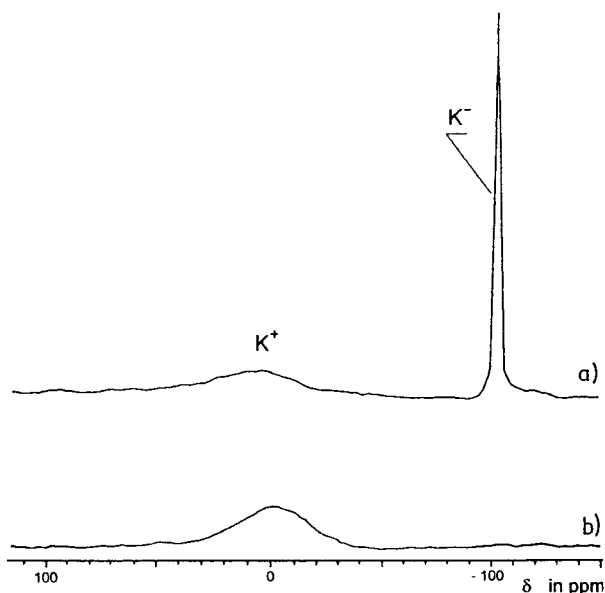
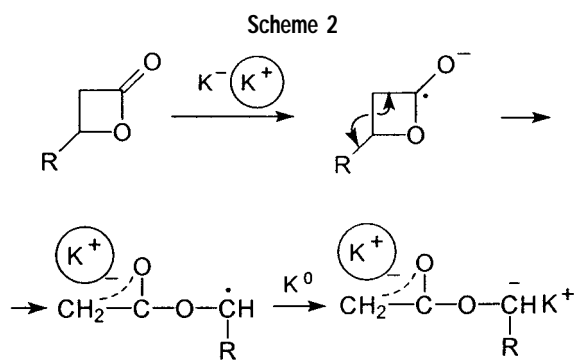
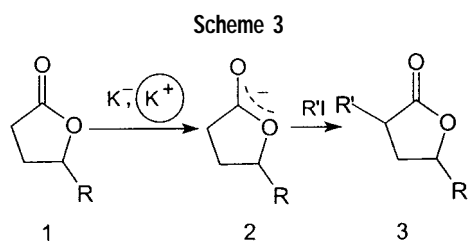
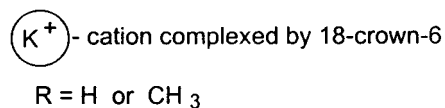


FIGURE 1. (a) ^{39}K NMR of the potassium ion pair with 18-crown-6 in THF solution before a reaction. (b) ^{39}K NMR of this solution (a) after reaction.

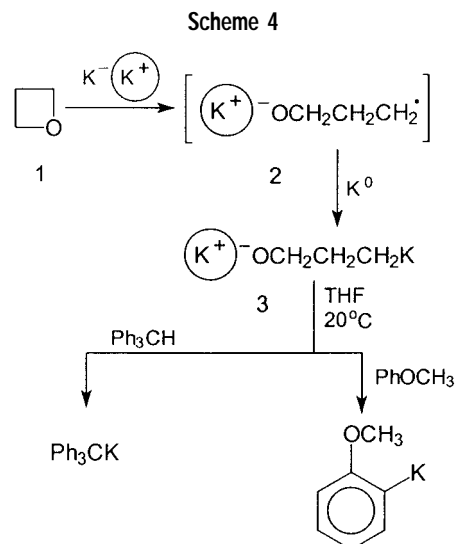


where:

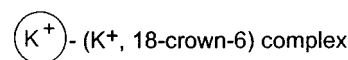


1,2,3: $\text{R} = \text{H}$ or CH_3

by ESR measurements. It is known that C–C bond scission can occur between aliphatic carbon atoms that bear bulky substituents, e.g. arenes, in the reactions with alkali metal alloys in a suspension,³⁵ but prior to the work described here, C–C bond cleavage in heterocycles has not been reported. This novel reaction of β -lactones has been applied to the synthesis of many types of polyesters. Polymerization of (*S*)- β -butyrolactone proceeds with in-



where:

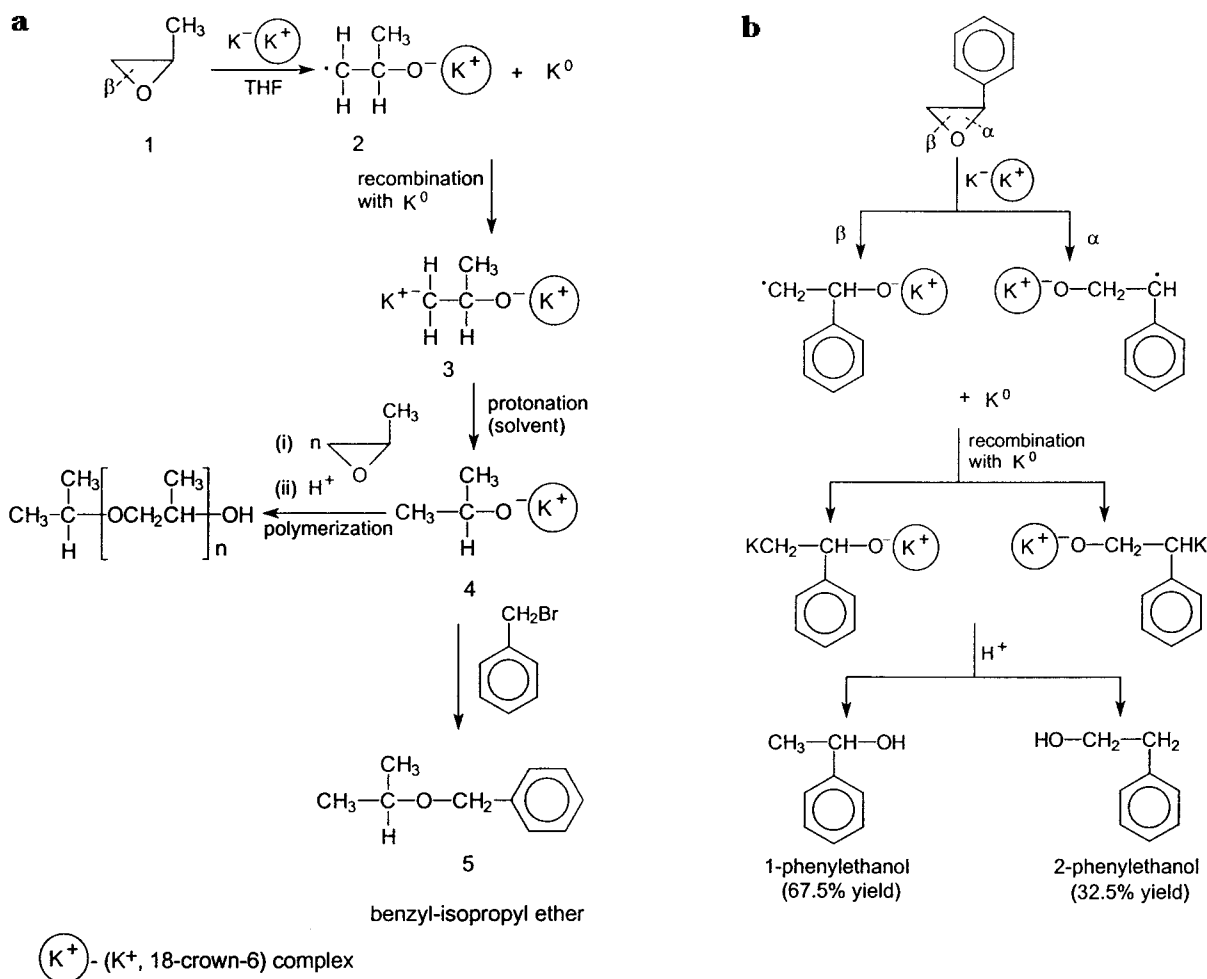


version of configuration and yields a polymer which is similar to the natural poly[(*R*)-3-hydroxybutyric acid]. This physiologically important organic biopolymer is produced by enzymes in prokaryotic and eukaryotic living cells.

The reaction of the thermodynamically stable γ -lactones with the potassium complex $\text{K}^+18\text{C}6, \text{K}^-$ in THF at room temperature yields the respective enolates of γ -lactones 2 (Scheme 3). The enolates produce α -substituted γ -lactones in good yields³⁶ on reaction with a variety of alkyl or acyl halides. 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 of γ -lactone with lithium dialkylamide (LDA) and methyl iodide at -78°C in THF. The procedure reported here is much simpler and can be employed for synthesis of both α -alkyl and α -acyl γ -lactones at 20°C . Side reactions, such as O-acylation, self-condensation, and α, α -disubstitution, do not occur. Thus, due to the stability of five-membered γ -lactones, the chemistry of their reactions with alkali metal complexes is different from that of the unstable, strained four-membered β -lactones.

Reactions of Cyclic Ethers. Oxetane is known to be stable toward nucleophilic reagents. However it has been demonstrated that it reacts easily with the potassium supramolecular complex $\text{K}^+18\text{C}6, \text{K}^-$ in THF at 20°C (Scheme 4). The reaction proceeds via alkyl–oxygen bond scission, yielding a functional carbanion.³⁷ Experimental results suggest that, at first, the oxetane radical anion is produced by single electron transfer and, after ring cleavage, reacts with potassium via recombination, eventually yielding the organometallic compound potassium propoxide carbanion 3. The latter is very efficient in metalation reactions, e.g. with phenylmethane or anisole (Scheme 4). The yield of metalation is high (around 85%) and reaction conditions are milder than those used with traditional metalation reagents, such as *n*-butyllithium or *tert*-butyllithium ethers. The functionalized carbanion 3

Scheme 5



obtained from oxetane can also be employed as a useful reagent in carboxylation and alkylation reactions.³⁸

Small cyclic ethers such as epoxides are very versatile in their reactions with both electrophilic and nucleophilic reagents. The reductive cleavage of epoxides to alcohols is a well-known reaction in organic chemistry.³⁹

The mechanism of reduction of epoxides via one-electron transfer mediated by lithium naphthalenide and metals dissolved in liquid ammonia or amines have recently been discussed and regioselectivity of epoxy ring cleavage has been elucidated on the basis of theoretical calculations.⁴⁰ It is interesting to compare the results of experiments that involve single electron transfer with electron transfer induced by alkali metal supramolecular complexes. In the latter reaction, the direction of the ring scission depends on the nature of a substituent at the ring. Thus the reaction of simple propylene oxide proceeds regiospecifically (Scheme 5a). However, a phenyl substituent in the styrene oxide induces both α and β scission (Scheme 5b) as revealed by NMR and ESI-MS analyses. Carbanions that are formed bearing alcoholate groups are effective synthons able to enter into various substitution reactions.⁴¹

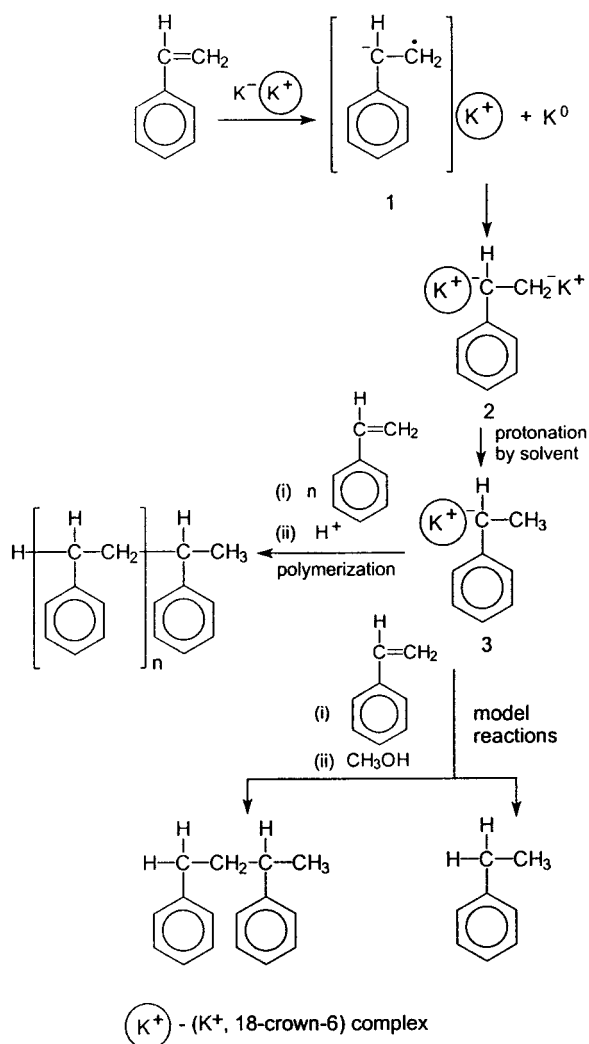
Electron Transfer to Double Bonds in Vinyl Compounds

The electron transfer to styrene from sodium naphthalenide has been known for many years.^{6,7} In this reaction the transfer of one electron yields a radical anion. The recombination of two radical anions gives a dimeric dianion. If a supramolecular complex of potassium is used as the electron donor the reaction proceeds differently and the direct formation of a unique dianion of styrene is observed.⁴² Similar unusual two-electron transfer to α -methylstyrene has also been demonstrated. The transfer of two electrons to styrene or α -methylstyrene, respectively, occurs and the styrene dianions formed are capable of transferring their charge to neutral molecules, thus inducing various reactions as well as polymerization processes.⁴² Using this method, facile synthesis of styrene-ester block copolymers can be accomplished.

Electron Transfer toward Cyclic Ketones: Ketone Enolate Formation

Enolates of cycloalkanones **2** (cyclobutanone, cyclopentanone, and cyclohexanone) along with corresponding alcoholates **3** can be smoothly prepared by the reaction of a ketone **1** with a solution of the potassium supramo-

Scheme 6



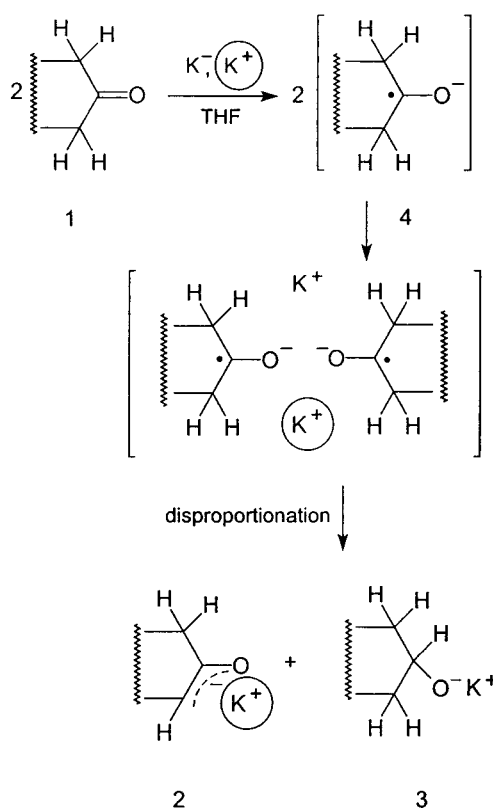
lecular complex $\text{K}^+18\text{C}6, \text{K}^-$ at low or at room (20 °C) temperatures^{43,44} due to α -hydrogen transfer and disproportionation reactions of radical anion intermediates (Scheme 7). The ketone enolates thus obtained can easily undergo alkylation or acylation to produce corresponding α -alkylated or α -acylated products.

Ketones that have no hydrogen atoms in the α -position, e.g. benzophenone, form only stable radical anions.⁴⁵

Reactions of Organic Halides Mediated by Alkali Metal Complexes with Crown Ethers

The typical Wurtz reaction, reductive coupling of alkyl halides or silyl halides, is known to proceed with mediation by dispersed metallic sodium in hydrocarbon solvents. The mechanism of this reaction, as well as of the recently reported reactions with sodium arene complexes, e.g. sodium naphthalenide, is believed to include one-electron transfer with formation of radical anions as intermediates. However, side reactions are very common in the Wurtz process, and in polymerization, polymodal polymers are usually produced.⁴⁶ The mechanism of the coupling reaction of alkyl and silyl halides mediated by soluble alkali metal complexes, e.g. $\text{K}^+18\text{C}6, \text{K}^-$, is different

Scheme 7



from that operating in the common radical Wurtz coupling. The intermediates (carbon or silicon anions) formed on the electron transfer from the alkali metal crown ether complex are obviously responsible for the effective homogeneous reductive coupling.

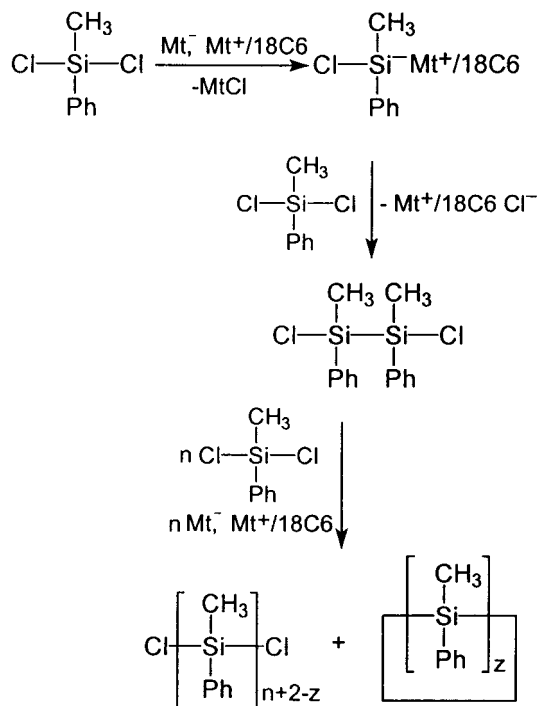
Spectacular examples of such reactions are provided by the recently published coupling of methylphenyldichlorosilane⁴⁷ and that of dibenzyl dibromide.⁴⁸ In the latter, dibenzyl oligomers and poly(xylylene) are formed, whereas in the former, linear polysilanes and cyclic silane oligomers are produced (Scheme 8). The facile novel method of synthesis of macrocyclic polysilanes, as well as of linear polymers, is of interest for practical applications, e.g. for producing novel materials for electronics.

It is known that nucleophilic substitution of halogen in alkyl halides proceeds smoothly and halogen is displaced as a halide ion. However, aryl halides, contrary to alkyl halides, undergo nucleophilic substitution with difficulty. The nucleophilic substitution of aryl halides can be facilitated by introduction of an electron-withdrawing group like NO_2 , CN , SO_3H , etc., to an aromatic ring in the ortho or para position to the halogen.⁴⁹

It has been demonstrated that under specific conditions, e.g., if the attacking carbanion contains a suitable leaving group, hydrogen can be displaced instead of halogen in arene⁵⁰ and azine rings.¹⁰ It has been found recently that alkali metal supramolecular complexes are unexpectedly capable of the selective hydrogen or halogen displacement in nitro arenes; however, reduction of the nitro group also occurs.⁵¹

Concluding Remarks. Due to kinetic and mechanistic studies on alkali metal dissolution in aprotic organic

Scheme 8



where: $Mt = K$ or Na ; $Ph = \text{phenyl}$

$z = 5, 6$

solvents containing crown ethers or other complexants, performed by Dye and other researchers, alkali metal solutions containing complexed metal cations, metal anions, and solvated electrons were discovered. These solutions attracted the attention of inorganic and physical chemists, who were able to prepare from them solid-state materials exhibiting interesting properties, as well as organic chemists, who used these solutions as strong reducers in organic syntheses.

Rationalization of the process of potassium or sodium dissolution in THF containing 18-crown-6 as a complexant enabled preparation of metal ion pairs in the solution (crowned M^+, M^-) and only a very small, negligible concentration of electrons. The existence of unique alkali metal ion pairs soluble in aprotic organic solvents was evidenced experimentally as described in this paper. This observation is important because it extends our knowledge of alkali metal ions and ion pairs in aprotic solvents.

Moreover, these precisely defined metal ion pairs behave as strong bases and electron donors and are useful as reagents and catalysts in many organic reactions and polymerization processes. The enormous versatility of alkali metal supramolecular complexes results in the formation of different types of short-lived intermediates in reactions of aliphatic as well as aromatic compounds.

Taking into account the versatility of reactions and flexibility of the methodology, the electron-transfer reactions mediated by alkali metal supramolecular complexes offer novel opportunities in chemical synthesis. On the other hand, some theoretical aspects such as, e.g. simultaneity of the transfer of both electrons from a metal anion

in the course of a single encounter with styrene, are still under consideration.⁵²

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