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Selective Reductive Cleavage of Arenocrown Ethers by Alkali Metals in THF

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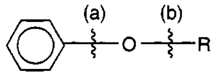
Alkali metal solutions in tetrahydrofuran containing the arenocrown ethers naphtho-15-crown-5, benzo-15-crown-5, and benzo-18-crown-6 were investigated using ^{39}K NMR, ESR, and GC−MS techniques. The cleavage of carbon−oxygen bonds in the crown ethers studied is discussed.

Introduction

Solubilization of alkali metals such as sodium and potassium in ethereal solvents was demonstrated in the late 1960's.[1] It is now well-known that alkali metals can in fact be solubilized in aprotic solvents like dimethyl ether[2] or THF[3−6] after addition of suitable crown ethers, e.g., 18-crown-6 (18C6), 15-crown-5 (15C5), or [2.2.2]-cryptand. Due to modifications of the metal solubilization process, solutions containing metal ion pairs (M$^+$/crown ether, M$^-$) and a negligible number of solvated electrons (e^-_s) can now be prepared.[7] Solutions containing oxacyclic ligands are relatively stable and can be utilized as novel chemical reagents[8−10] and efficient polymerization initiators.[11−14]

On the other hand, the reductive cleavage of simple aryl alkyl ethers by alkali metals has been reported.[15] The influence of ether structure and solvent effect on the regioselectivity of aryl−oxygen (a) and alkyl−oxygen (b) bond cleavage has been studied for simple aryl ethers:



The aim of this work was to study the process of alkali metal solubilization in THF containing the selected arenocrown ethers (Figure 1) as complexing agents for metal cations. The influence of the aromatic substituents on the stability of crown ethers to Birch reduction by alkali metals is discussed.

Experimental Section

Materials. 18-Crown-6 (18C6) and 15-crown-5 (15C5), both from Fluka, were purified as described previously.[7] Benzo-15-crown-5 (B15C5) and benzo-18-crown-6 (B18C6) were purchased from Aldrich. Naphtho-15-crown-5 (N15C5) was synthesized according to Pedersen.[16] The crude product was purified on a silica gel column using CH$_2$Cl$_2$ and CHCl$_3$ as eluents, and after that it was crystallized from *n*-heptane.[17] THF was purified according to ref 7.

General Procedure for Sample Preparation. The apparatus used for preparation of alkali metal solutions, made from borosilicate glass, is shown in Figure 2.

Small pieces of the metallic potassium (ca. 2−3 g) were placed in part A, melted, and degassed at elevated temperature under a continuous flow of argon. Due to the distillation of alkali metal in high vacuum (10^{-4}−10^{-5} Torr), the walls of the receiving container (B) are covered with the metal mirror. Then 15 mL of a 0.1 or 0.2 M solution of macrocyclic ligand were introduced into the receiver under ultrasonic mixing. After the specified time of alkali metal contact with the ligand dissolved in THF (Table 1), the resulting solution was filtered off through the glass frit (C) to the NMR and ESR tubes (Figure 2) and after that to the receivers for samples used in GC−MS and chemical analyses.

Measurements. A multinuclear pulsed NMR spectrometer operating at the ^{39}K resonance frequency of 14 MHz was used. Chemical shifts in the ^{39}K NMR spectra were measured relative to the K$^+$ signal from potassium fluoride solution in D$_2$O. The measurements were carried out at 293 K.

ESR measurements were carried out in the temperature range of 223−293 K, employing 100 kHz field modulation and a microwave frequency of ca. 9.4 GHz. In order to determine the concentration of paramagnetic species, a double rectangular cavity was used and a solution of 2,2-bis(4-*tert*-octylphenyl)-1-picrylhydrazyl served as a reference.

GC−MS analyses of arenocrown ether decomposition products were run on a 30 m DB 1701 fused silica capillary column, using a gas chromatograph equipped with an ion trap detector. Nonvolatile organic potassium compounds were protonated or methylated with methyl iodide for chromatographic identification. The retention times and MS spectra of the detected products were consistent with those of original samples of the authentic compounds, and the MS spectra recorded were in

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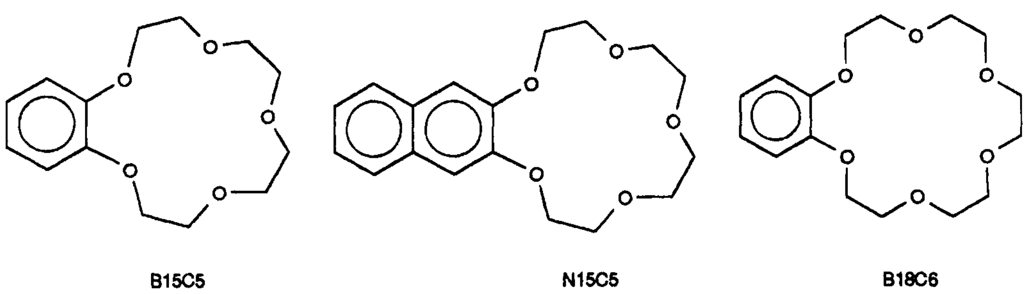

B15C5 N15C5 B18C6

Figure 1. Arenocrown ethers studied.

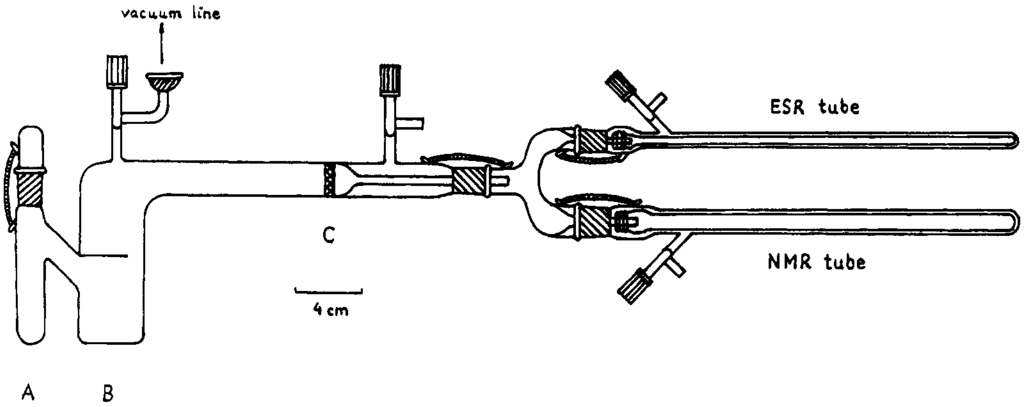

Figure 2. Apparatus used for preparation of alkali metal solutions.

Table 1. Influence of the Type of Crown Ether on the Composition of the Potassium Solutions in THF

no.	type of crown ether	concentration of crown ether	t_c (min)	concentration of paramagnetic species	total concentration of potassium in solution (M)[c]	concentration of potassium anions (M)
1	18C6	0.1	1	10^{-1} [a]	0.1	0.01
2	18C6	0.1	15	10^{-2} [a]	0.2	0.08
3	15C5	0.2	1	10^{-3} [a]	0.09	0.045
4	15C5	0.2	15	10^{-3} [a]	0.19	0.095
5	N15C5	0.2	1	10^{-8} [b]	0.07	
6	N15C5	0.2	15	10^{-10} [b]	0.3	
7	N15C5	0.2	30	10^{-11} [b]	0.7	
8	B18C6	0.1	1		0.2	
9	B18C6	0.1	15		0.42	
10	B15C5	0.2	1	10^{-9} [b]	0.08	
11	B15C5	0.2	15	10^{-13} [b]	0.4	

[a] Solvated electrons. [b] Radical anions. [c] The total potassium concentration was determined by titration with 0.02 mol/L hydrochloric acid, using bromothymol blue as indicator.

good agreement with those included in the NIST mass spectral library, as revealed by computer comparison.

Results and Discussion

The characterization of the potassium solutions containing cyclic ligands (18-crown-6 (18C6) and 15-crown-5 (15C5)) as well as that of arenocrown ethers (benzo-15-crown-5 (B15C5), benzo-18-crown-6 (B18C6), and naphtho-15-crown-5 (N15C5)) included determination of the total concentration of the metal by means of titration, ESR analysis of the paramagnetic species, ^{39}K NMR analysis of the solutions, and chromatographic analysis of the decomposition products.

According to the results presented in Table 1, the homogeneous potassium solutions obtained in the presence of nonaromatic ligands, like 15C5 or 18C6, contain complexed metal cations, anions, and small amounts of solvated electrons. The total concentration of the metal ions depends on the ligand employed, its concentration, and time of contact (t_c) between the metal and the solvent.[4,7] This concentration was measured by titration of the samples after addition of water.

The potassium solutions containing arenocrown ethers were heterogeneous, and white sediment was observed. The ^{39}K NMR spectra of the potassium solutions with arenocrowns revealed extremely weak resonance lines due to K^+ regardless of the time of contact between the metal mirror and THF solution of these crown ethers. Moreover, the signals of the metal anions were not detected. The difference between a high metal content in the reaction mixture determined by titration (Table 1) and the lack of the signals typical for the metal anions and complexed cations[3-5,18,19] in the NMR spectra can be explained by the decomposition reactions of the arenocrown ethers, presumably taking place during the solution preparation.

The ESR studies of the solutions containing N15C5, B15C5, or B18C6 and obtained at t_c of 1 or 15 min reveal that the concentration of radical anions for the systems with N15C5 and B15C5 is extremely low (of the order of 10^{-8}–10^{-11} M) and not detectable for B18C6 (Table 1).

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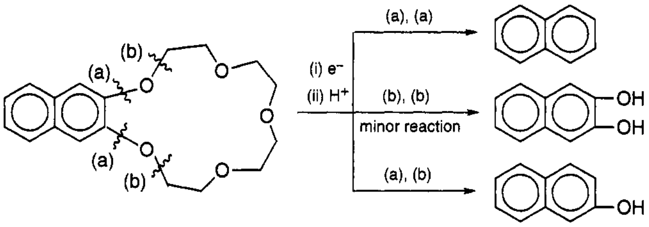
Table 2. Yields of the Aromatic Products of Arenocrown Ether Cleavage

entry no.[a]	arenocrown ether	reaction pathway (Scheme 1)	products	yields[b] (%)
6	N15C5	(*a*), (*a*)	naphthalene	26.3
		(*a*), (*b*)	β-naphthol	73.5
		(*b*), (*b*)	2,3-dihydroxy-naphthalene	0.2
9	B18C6	(*a*), (*a*)	benzene	29.0
		(*a*), (*b*)	phenol	70.9
		(*b*), (*b*)	*o*-cresol	0.1
11	B15C5	(*a*), (*a*)	benzene	27.3
		(*a*), (*b*)	phenol	72.5
		(*b*), (*b*)	*o*-cresol	0.2

[a] Entry no. corresponding to that in Table 1. [b] Yield in mol % recalculated from uncorrected GC areas.

Scheme 1



It is worth noting that, in contrast to the K solutions with 15C5 or 18C6, the ESR spectra reveal no signal due to solvated electrons.

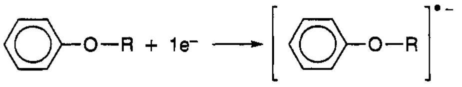
GC–MS analysis revealed that the arenocrown ethers decompose during contact with alkali metals. Some results are summarized in Table 2.

Both aryl–oxygen (a) and alkyl–oxygen (b) bonds are cleaved, yielding β-naphtholate and naphthalene in the case of N15C5 and phenolate and benzene in the B15C5 and B18C6 systems, indicating high regioselectivity.

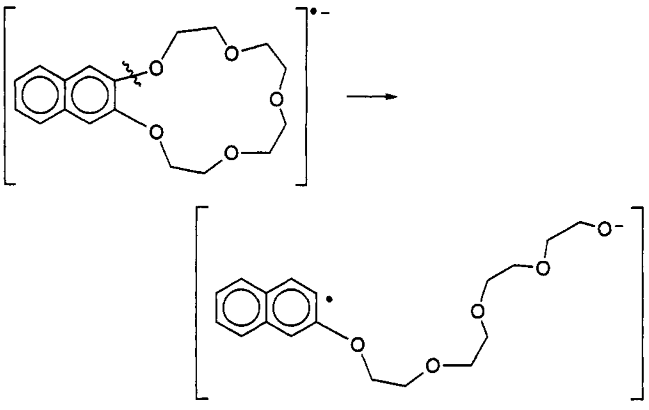
Initial cleavage of bond (a) occurs almost exclusively (Scheme 1), followed by preferential cleavage at bond (b) to give roughly a 3:1 ratio of naphtholate to naphthalene. Then, the random scission of oxygen–carbon bonds of oligoether takes place.[20]

Similar results were obtained when the solutions were quenched with methyl iodide. β-Methoxynaphthalene and naphthalene were detected in case of N15C5; anisole and benzene were found for B15C5 and B18C6.

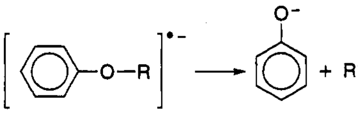
According to previous results, reductive cleavage of ethers containing an oxygen atom adjacent to an aromatic ring occurs due to the reaction with alkali metals. The accepted mechanism of this cleavage involves single electron transfer from alkali metal to the aromatic ring with the formation of a radical anion:[15b]



Scheme 2



The radical anion then decomposes to yield the corresponding anion and radical:



The radical anions obtained from alkali metal reduction of simple aryl alkyl ethers undergo unimodal fragmentation, which can take place either by Ar–O or R–O bond scission. It has been found, similarly as reported previously,[15c] that the rate of Ar–O bond scission increases with decreasing π-bond order of the Ar–O bond in the radical anion. The experimental results presented in Table 2 indicate that in the case of cyclic aromatic–aliphatic ethers, aryl–oxygen bond cleavage is favored initially, yielding the radical anion.

Thus, aryl–oxygen reductive cleavage of N15C5 (Scheme 2) followed by both aryl– and alkyl–oxygen bond ruptures leads to formation of naphthalene and naphtholate. In the case of B15C5 or B18C6, similar reaction pathways can be proposed since benzene and phenolate are the predominant products formed. Only traces of *o*-cresolate (*o*-cresol after protonation) were detected in the reaction mixtures.

Conclusions

Significant differences in the course of alkali metal solubilization carried out in the presence of various crown ethers were observed. It has been found that in the case of the arenocrown ethers studied, alkali metal cation complexation is suppressed by Birch reduction.

The regioselectivity of the reductive cleavage of these cyclic aromatic–aliphatic ethers was demonstrated.

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