

we have synthesised the cyclopropane by a chemical way, using NaNH_2 in ether from the phenacyl bromide, either in conditions of low concentration or in normal conditions. In the first case just the cyclopropane was obtained. In the second case, where we are reproducing the conditions of the proposed ionic mechanism: high concentration of neutral molecules of phenacyl bromide in the presence of the brominated anion, 2-Br-1,3-diphenyl-3-epoxy-butanone was obtained as exclusive product.

To finish this report, we discuss the experimental results in the formation of the furanones synthesised from several substituted phenacyl bromides, using the following substituents in 4-position: H, Cl, Br, CH_3 , OCH_3 , C_6H_5 , NO_2 .

No trace of the corresponding furanones were obtained when the 4-substituents were OCH_3 , C_6H_5 and NO_2 .

We explain that result considering that the donor substituents OCH_3 and C_6H_5 increase the anion Ph-CO-CH_2^- nucleophilicity. Consequently, the furan formation by nucleophilic addition is favoured instead of the behaviour as a base towards a neutral molecule of phenacyl bromide.

On the other hand, the transpositions to obtain the ketene are unfavored with withdrawing substituents, as NO_2 .

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COMPLEXATION OF ELECTROCHEMICALLY REDUCED CROWN ETHERS INCORPORATING ANTHRAQUINONE NUCLEI WITH ALKALI METAL IONS.

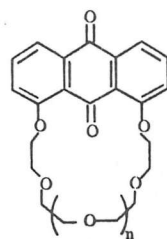
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Selective molecular recognition of organic molecules by metal ions is a very interesting and important subject, because it is the basis of many biochemical processes and has wide application in many areas of chemistry, from the theoretical as well as from the practical point of view. Among the synthetic receptor molecules, ionophores such as macrocyclic crown ethers, have successfully been used for complexation. As well as showing ability to bind metal ions, they can also present characteristics of cationic selectivity owing to their selective complexation properties towards specific cations^(1,2). If the crown ether is appended to electroactive groups which can be reversibly reduced and if they are in a favourable position to interact with the cation, this association behaviour and binding power to the metal ion can suffer a significant change^(3,4). In this way, it is possible to extend this sensitive principle to enhance cation sensitivity and possibly discriminate among metal ions.

The host ligands presented in this study were prepared incorporating an anthraquinone subunit within a macrocyclic crown ether with six or seven oxygen atoms in the macroring (Scheme I). Li^+ , Na^+ and K^+ were the alkali cations studied.

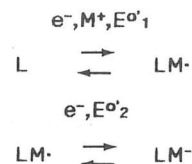


Scheme I

Compound	n
1	1
2	2

Electrochemical characterization and complexation effects were performed in acetonitrile / tetrabutylammonium perchlorate (0.1 mol.dm⁻³) by cyclic voltammetry using a PAR potentiostat model 173 with an interface model 276. A glassy carbon, a platinum wire and a silver wire were used as working, counter and reference electrodes, respectively. In the reduction processes, the current intensity increased linearly with the increase of the scan rate, but the potentials were independent of the potential scan rate.

Compounds 1 and 2 (L) undergo two successive reversible or quasi-reversible one-electron reductions, exhibiting the double redox characteristic in agreement with the two redox carbonyl groups of the anthraquinone subunit and generated the anion radical (L⁻) and the dianion (L²⁻) (Table I). The electrochemical reduction of the macrocyclic ligands in the presence of the alkali metal salts (M⁺) leads to different cyclic voltammograms. New redox couples were observed at more positive potential values which were attributed to the reduced complexing ligands,



since LM⁺ is a very weak complex but LM⁻ is a strong complex. The electrochemical data of the complexation are presented in the Table I where E^{o1} and E^{o2}, E^{o'1} and E^{o'2}, are the formal potentials of the ligand redox couples in the absence and presence of the alkali metal cations, respectively.

The potential shifts ΔE^{o1} and ΔE^{o2} (Table I) translate the electrochemical changes of the ligands in the absence and presence of the cations and can be used to estimate the increase of the degree of association of the ion-pairs formed with each one of the cations (5).

Table I. Electrochemical data of the effects of alkali metal cations on redox potentials of the compounds 1 and 2(a)(b).

Compound	M ⁺ (c)	E ^{o1} (d)	E ^{o2}	E ^{o'1}	E ^{o'2}	ΔE ^{o1} (e)	ΔE ^{o2} (e)
1	-	-1.22	-1.64				
	Li ⁺			-0.82	-1.36	0.40	0.28
	Na ⁺			-0.98	-1.38	0.24	0.26
	K ⁺			-1.06	-1.45	0.16	0.19
2	-	-1.28	-1.72				
	Li ⁺			-0.94	-(f)	0.34	-0.06(g)
	Na ⁺			-1.02	-1.57	0.26	0.15
	K ⁺			-1.06	-1.59	0.22	0.13

(a) all the potentials are reported in volts vs. Ag/Ag⁺ 0.01 M; (b) measures were made in CH₃CN/Bu₄NC₁₀ (0.1 mol.dm⁻³);(c) L/M⁺=2/1;(d) the formal potentials E^{o1} and E^{o2}, and E^{o'1} and E^{o'2}, were taken as the average of anodic and cathodic peak potentials, respectively; (e) ΔE^{o1}=E^{o'1}-E^{o1} and ΔE^{o2}=E^{o'2}-E^{o2}; (f) (-) means that no redox couple was observed;(g) this value was calculated from the reduction potentials.

These increases are a consequence of a cooperative effect of the complexation and redox reactions, being the result of an additional intramolecular charge-charge interaction involving the reduced carbonyl groups of the anthraquinone subunit and the macroring bound-cation. The presence of negative charge on the reduced ligands and specially in the binding sites contributes strongly to the cation binding strength when compared to the unreduced forms.

The positive values of the potential shifts (ΔE°) obtained after the electrochemical reduction of the ligand 1 in the presence of alkali metal ions reflect an effective cation binding enhancement in relation to the corresponding complexation by the neutral ligand. The data also indicate that the reduced ligand 1 is comparatively a strong binder of the lithium ion. Effectively, the electrochemical reduction induced the largest increase of the potential shift observed, $\Delta E^{\circ}_1=0.40$ V, reflecting a very large cation binding enhancement and the greater preference of the reduced ligand 1 by that cation; less strong interactions with the reduced form 1 is manifested in the presence of Na^+ and K^+ , which induced smaller potential shifts, $\Delta E^{\circ}_1=0.24$ V and 0.16 V, respectively. The data obtained for the binding increase of the ligand with the alkali metal ions follows the order: $\text{Li}^+ \gg \text{Na}^+ > \text{K}^+$, which is the decreasing order of the charge/size ratio of the cations. The behaviour of the reduced compound 2 with seven oxygen atoms in the macroring retains in general the characteristic exhibited by the reduced compound 1 and follows a similar pattern to the redox reactions that depend of the cation, while comparatively its association degree suffers a slight decrease with the Li^+ and a slight increase with Na^+ and K^+ .

Factors that contribute to the increase in binding power and the capacity for discrimination between these reduced hosts and the alkali metal cations, include the relative size of the cation and macroring cavity, the geometry of the anion and the flexibility of the crown ether macroring and its reorganization capacity.

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