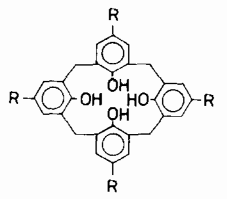
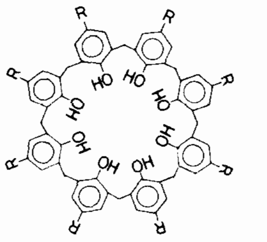


II

R= C(CH$_3$)$_3$



III

Both compounds have been used as *ordered building blocks* for open chain cation ligands [4] obtained by alkylation of the phenolic OH with different binding groups [I, R' = CH_3, CH_3CO–, –$(CH_2CH_2O)_n$-CH_3].

The alkylation of II and III destroys the cup-like structure of the starting compounds, which is mainly determined by intramolecular hydrogen bonds, giving products with different geometries and complexing abilities toward cations. Derivatives of the tetrameric oligomer (II) are a mixture of stereoisomers which do not interconvert at ambient temperature and have non convergent binding groups. Their complexation toward Li^+, Na^+, K^+, NH_4^+, $[C(NH_2)_3]^+$ picrates is very poor, these salts being not extracted by the ligands from water to $CDCl_3$ and CH_2Cl_2.

Derivatives of the octamer (III) have chains which easily pass through the central hole and are able to wrap the cations as the *octopus* molecules [4]. Methyl and acetyl derivatives of III do not complex any tested cation, while compounds with even short poliethers chains [I, R' = –$CH_2CH_2OCH_3$, –$(CH_2$-$CH_2O)_2CH_3$] are able to extract picrates from water to CH_2Cl_2 and $CDCl_3$.

A remarkable strong complexation of the latter compounds is observed toward guanidinium cation whose tetraphenylborate is dissolved in CDCl3 up to a ratio [salt]/[ligand] = 1.3–1.5 and picrate extracted from H_2O to CH_2Cl_2 with an extraction constant $K_e \simeq 2 \times 10^4$ M^{-2}.

Results obtained with other ligands built on cyclic oligomers derived from *p*-cresol and *p*-octylphenol will be also reported.

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Solvent Effects upon Dielectric, Spectroscopic and Thermodynamical Manifestations of EDA Interaction between Iodine and Pyridines

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Dipole moments and the contributions of the dative structure (F_N) in the ground state of pyridine and γ-picoline complexes with I_2 in non-polar and weakly polar solvents were determined. The results thus obtained were compared with those arising from the solvent effect on the spectroscopic behaviour of the amine–I_2 adducts. Correlations were found between the solvent induced enhancement of the dative structure contribution determined from dipole moment measurements and calculated from the force constants of ν(I–I) and ν(N–I) vibrations. A similar correlation of F_N was found with respect to the solvent shift of the transition energy $^3\pi_{ou^+} \leftarrow {}^1\Sigma_{g^+}$ in the I_2 molecule bounded to amines. Solvent effects were also discussed using formation enthalpies ΔH_{AD} for pyridine–I_2 complex on the basis of the thermodynamic cycle. The dependence of F_N and complex stability upon the solvation type were analysed in terms of the Onsager reaction field theory and also through correlations with empirical parameters of solvent activities, such as k_M and E_T.

Solution Chemistry of $[PNP]^+$-Salts in Water and Methanol

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The $[PNP]^+$-cation [1] has been shown to be a valuable alternative to the usually employed onium cations for studies of anions in alcohols and various aprotic solvents [2].

$[PNP]^+Cl^-$, which serves as the starting material, is simple to synthesize in high yield and is fairly cheap. Due to the considerable solubility of this salt in warm water, other salts can be easily prepared by precipitation. These salts are generally easy to purify, are very soluble in most alcohols and dipolar aprotic solvents and are non-hygroscopic.

Various studies, including conductivity, surface tension, compressibility, emf-measurement, vapour phase osmometry, solubility and density, have been performed on $[PNP]^+$–halides in water and methanol. It is concluded that these salts are very well dissociated in methanol while in water, $[PNP]^+Cl^-$, the most soluble salt, appears to have a critical micelle concentration, 'cmc-value', at ~0.005 mol l^{-1}.

References

1 $[PNP]^+$ designs the bis(triphenylphosphine)iminium cation, $[(Ph_3P)_2N]^+$.

2 A. Martinsen and J. Songstad, *Acta Chem. Scand., A31,* 645 (1977).

Cation Effect on the Course of Anionic Reactions in the Presence of a Solid Base

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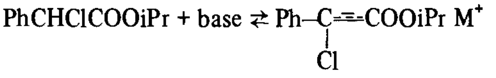
The formation of cyclopropanes by the MacCoy reaction is reinvestigated in the presence of solid sodium or potassium hydroxide, with or without a quaternary ammonium salt, in dioxanne:



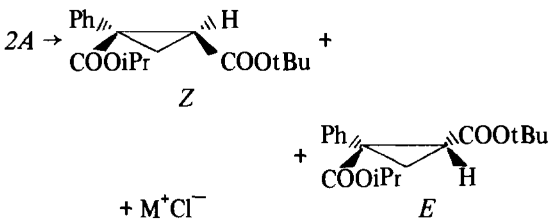
$$PhCHClCOOiPr + base \rightleftarrows Ph{-}\underset{Cl}{\underset{|}{C}}{=\!\!-}COOiPr\ M^+$$

1 *1A*

$1A + CH_2{=}CHCOOtBu \rightarrow$

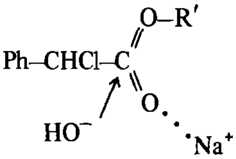
$$Ph{-}CCl(COOiPr)CH_2CH{=\!\!-}COOtBu\ M^+$$

2A



With NaOH alone, the major reaction is the saponification of the α-chloro-ester *1*; the cyclopropanes formation is the only reaction observed using either KOH,or the two bases with $NBu_4^+Br^-$.

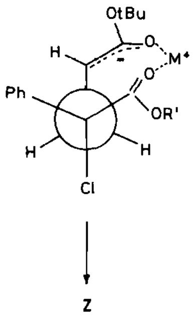
The saponification by NaOH is attributed to the complexation of the carbonyl group by Na^+, which favours the nucleophilic attack of the hydroxide anion:

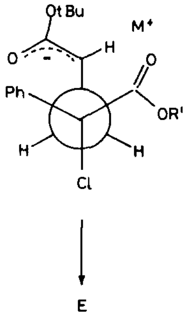


The complexation is weaker with K^+ than with Na^+, and then, the proton abstraction of the α-chloro-ester is predominant.

These results show that metallic cations have a similar behaviour in a crystalline network and in solution.

The stereoselectivity is known to be determined during the cyclisation step. The predominant formation of the Z isomer is explained by chelate formation of metal cation with the two carbonyl groups, while the E isomer is favoured when the size of the cation is too large to allow such a chelate formation.





The different stereochemical results obtained by addition of the ammonium salt involve the association of the intermediate anion *2A* with $NBu_4^+Br^-$. Furthermore, the condensation should occur in the organic phase with the phase transfer reagent, and on the solid surface when the bases are used alone.

NBu_4BH_4 Reduction of 2-Cyclohexenones

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We noticed previously an inversion in the regioselectivity of 2-cyclohexenones reduction with $LiBH_4$ in THF by addition of cryptand [2.1.1]. Therefore, the regioselectivity of attack on the α-enone should