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, $[(Ph_3P)_2N]^+$.

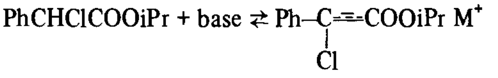
2 A. Martinsen and J. Songstad, *Acta Chem. Scand., A31,* 645 (1977).

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

ISABELLE ARTAUD and PAULETTE VIOUT

Groupe de Recherche No 12, C.N.R.S., B.P. 28, 94320, Thiais, France

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:



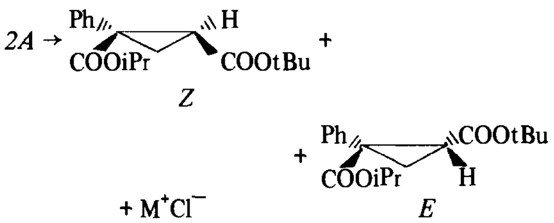
$$PhCHClCOOiPr + base \rightleftarrows Ph\text{–}\underset{Cl}{\underset{|}{C}}\overset{-}{=}COOiPr\ M^+$$

1 *1A*

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

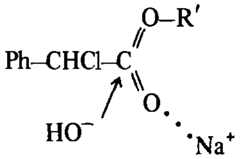
$$Ph\text{–}CCl(COOiPr)CH_2CH\overset{-}{=}COOtBu\ M^+$$

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 $NBu_4^+Br^-$.

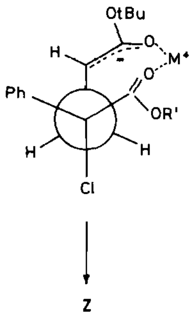
The saponification by NaOH is attributed to the complexation of the carbonyl group by Na^+, which favours the nucleophilic attack of the hydroxide anion:

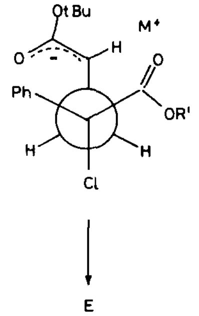


The complexation is weaker with K^+ than with Na^+, and then, the proton abstraction of the α-chloroester is predominant.

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

ESTHER D'INCAN and ANDRE LOUPY

G.R. 12 C.N.R.S. 2 - 8, Rue H. Dunant, 94320 Thiais, France

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