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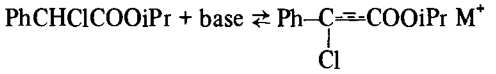
The formation of cyclopropanes by the MacCoy reaction is reinvestigated in the presence of solid sodium or potassium hydroxide, with or without a quaternary ammonium salt, in dioxanne:



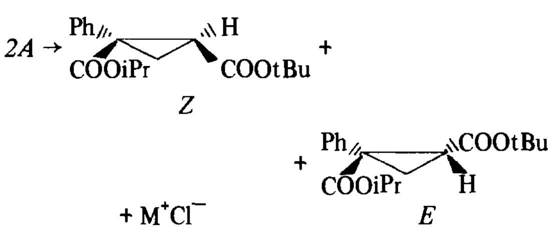
$$PhCHClCOOiPr + base \rightleftarrows Ph{-}\underset{\displaystyle Cl}{C}{=\!=}COOiPr\ M^+$$

1 *1A*

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

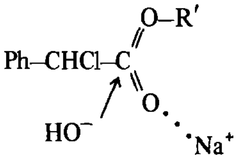
$Ph{-}CCl(COOiPr)CH_2CH{=\!=}COOtBu\ M^+$

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 $NBu_4^+Br^-$.

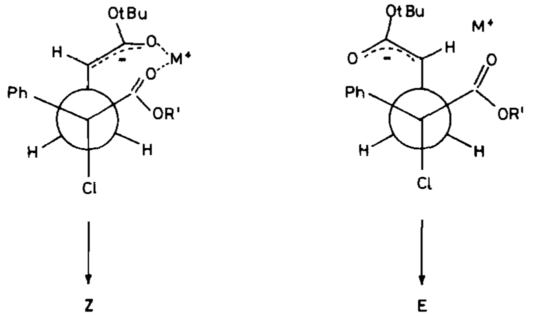
The saponification by NaOH is attributed to the complexation of the carbonyl group by Na^+, which favours the nucleophilic attack of the hydroxide anion:



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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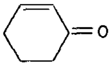
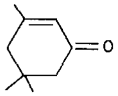
We noticed previously an inversion in the regioselectivity of 2-cyclohexenones reduction with $LiBH_4$ in THF by addition of cryptand [2.1.1]. Therefore, the regioselectivity of attack on the α-enone should be connected to its interaction with the Li^+ cation; that is the reason why we studied the NBu_4BH_4 reduction of 2-cyclohexenones (1 and 2), the interaction $C{=}C{-}C{=}O{-}\cdot{-}N^+Bu_4$ being certainly very loose, inducing thus the 1–4 reduction. Some reactions in phase transfer catalysis conditions have also been investigated.


1


2

The regioselectivity of NBu_4BH_4 reduction of 1 is quasi independent upon the aprotic solvent nature (1–2/1–4 is about 10/90 in 8 aprotic solvents: Et_2O, THF, toluene, DME, HMPA, dioxane, CH_3CN and CH_3NO_2) the yields being nearly quantitative at room temperature. On the other hand, the reaction rates seem to be related to the solvent acceptor power (the rate increases when the solvent A.N. decreases).

The orientation is affected by the intervention of hydrogen bonding with the α-enone carbonyl when the NBu_4BH_4 reduction is performed in CH_2Cl_2, CH_3OH or H_2O (1–2/1–4 ≃ 40/60).

NBu_4BH_4 reduction of 2 in THF or toluene at 60 °C leads to a saturated alcohol, resulting from 1–4 addition followed by reduction, with very good yield and selectivity (about 95%). On the other hand, in the liquid–liquid phase transfer catalysis conditions (toluene–water), a regioselectivity decrease is noticed which can be attributed to an interaction between H_2O and the isophorone carbonyl.

Some experiments performed in solid–liquid phase transfer catalysis conditions give low yields, unless cryptand is used, the ion exchange being difficult.

Phase-Transfer Catalysis in Reaction Promoted by Hydroalogenic Acids

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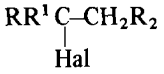
Recently we reported that lipophilic quaternary ammonium and phosphonium salts show a high catalytic activity in reactions promoted by hydroalogenic acids in aqueous-organic two phase systems, such as the conversion of alcohols to the corresponding halides [1] (eqn. 1) and the cleavage of ethers [2] (eqns. 2 and 3).

$$R{-}CH_2{-}OH_{org} + HHal_{aq} \xrightarrow[\Delta]{Q^+X^-} R{-}CH_2{-}Hal_{org} + H_2O \qquad (1)$$

$$R{-}O{-}R'_{org} + 2H\,Hal_{aq} \xrightarrow[\Delta]{Q^+X^-} R{-}Hal_{org} + R'{-}Hal_{org} + H_2O \qquad (2)$$

$$R{-}O{-}Ar_{org} + H\,Hal_{aq} \xrightarrow[\Delta]{Q^+X^-} R\text{-}Hal_{org} + Ar{-}OH_{org} \qquad (3)$$

This catalytic system can also be advantageously utilized in other reactions, such as the facile addition of hydroalogenic acids to carbon–carbon double bonds according to Markownikoff's rule [3](eqn. 4), and the hydrolysis of ethers [4] (eqns. 5 and 6) and of other derivatives of carboxylic acids [4]



$$RR^1C{=}CHR^2_{org} + H\,Hal_{aq} \xrightarrow[\Delta]{Q^+X^-} RR^1\underset{\displaystyle Hal}{\underset{|}{C}}{-}CH_2R_2 \qquad (4)$$

$$R{-}COOR^1_{org} + H\,Hal_{aq} \xrightarrow[\Delta]{Q^+X^-} R{-}COOH_{org} + R^1Hal_{org} \qquad (5)$$

$$R{-}COOAr_{org} + H_2O \xrightarrow[\Delta]{Q^+X^-} R{-}COOH_{org} + ArOH_{org} \qquad (6)$$

The factors which affect the reactions will be discussed.

References

1 D. Landini, F. Montanari and F. Rolla, *Synthesis*, 37 (1974).
2 D. Landini, F. Montanari and F. Rolla, *Synthesis*, 171 (1978).
3 D. Landini and F. Rolla, submitted to *J. Org. Chem.*
4 Unpublished results from our laboratory.