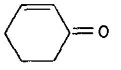
be connected to its interaction with the Li^+ cation; that is the reason why we studied the NBu_4BH_4 reduction of 2-cyclohexenones (1 and 2), the interaction $C{=}C{-}C{=}O{-}\cdot{-}N^+Bu_4$ being certainly very loose, inducing thus the 1–4 reduction. Some reactions in phase transfer catalysis conditions have also been investigated.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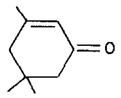
2

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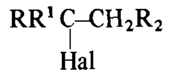
Recently we reported that lipophilic quaternary ammonium and phosphonium salts show a high catalytic activity in reactions promoted by hydroalogenic acids in aqueous-organic two phase systems, such as the conversion of alcohols to the corresponding halides [1] (eqn. 1) and the cleavage of ethers [2]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