

Details of the absolute conformational behaviour of chiral alcohol-imine solvates, which are considered responsible of the reported results, have been studied by ^1H NMR enantiomeric non-equivalence technique, by registering the spectra of partially optically active (R)-[V] and (R)-[VI] in the presence of chiral trifluoromethylcarbinols I. In every case, the field position of the signals corresponding to enantiotopic groups of (R) and (S)-imine, is correlated to the absolute configuration of the alcohol used. The quantitative and qualitative aspects of the NMR spectra and of the asymmetric oxidations of imines V and VI, carried out in the presence of chiral carbinols I, can be explained by means of specific carbinol-imine solvation models, which take into account the ability of the hydroxy-hydrogen of the chiral alcohol to primary bonding interactions with basic sites of the solute molecule, and the ability of the other substituents of the interacting molecules to secondary attractive forces.

Extension of these models to the results observed in the oxidation of imines II-IV allows (+)-(R) and (-)-(S) configurational assignment to the asymmetric nitrogen atom of all the corresponding optically active oxaziridines obtained.

Reference

- 1 A. Forni, I. Moretti and G. Torre, *J. Chem. Soc. Chem. Comm.*, 731 (1977).

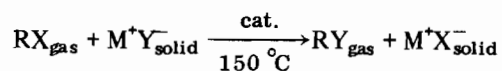
Molten Phosphonium Salts: Exchange Catalysts between a Gaseous and a Solid Phase

PIETRO TUNDO* and PAOLO VENTURELLO

Istituto di Chimica Organica dell'Università, via Bidone 36, 10125 Turin, Italy

Phosphonium salts are stable at high temperature, and when they are molten can give eutectic mixtures with inorganic salts; when a gaseous alkyl halide is allowed to diffuse into this liquid phase, the nucleophilic reaction occurs. If at the same time it occurs that the new eutectic produced with the inorganic salt of the reaction has a higher melting point, the phosphonium salt can act as a catalyst [1]

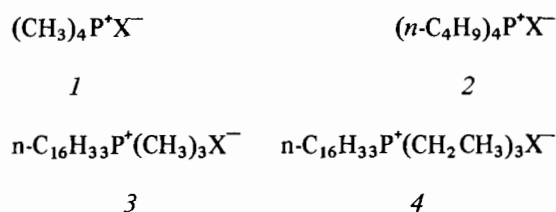
In this way, without the use of solvents some reactions can be made ready, by allowing to pass through a column a gaseous flow of the alkyl halide:



Material in the Column [3]	Conversion %
a) KI	2
b) KI + $(n\text{-C}_4\text{H}_9)_4\text{P}^+\text{I}^-$	96
c) KI + $n\text{-C}_{12}\text{H}_{25}\text{OSO}_3^-\text{Na}^+$	11
d) KI + silica gel	50
e) KI + silica gel + $(n\text{-C}_4\text{H}_9)_4\text{P}^+\text{I}^-$	93
f) KI + silica gel + $n\text{-C}_{12}\text{H}_{25}\text{OSO}_3^-\text{Na}^+$	46

In the synthesis of alkyl iodides starting from bromides and chlorides [2], the presence of a cationic salt and the importance of silica gel as a solid support have been emphasised.

According to this new methodology, the synthesis of esters will be shown with regards to the factors controlling the catalytic activity of the phosphonium salts 1, 2, 3 and 4.



The difference with the classic liquid-liquid phase-transfer catalysis will be also discussed.

References

- 1 P. Tundo, *J. Org. Chem.*, 44, 2048 (1979).
 2 P. Tundo and P. Venturello, *Synthesis*, printer's proofs.
 3 a). Column completely filled with finely ground potassium iodide, b) and c) onium salt and anionic surfactant evenly distributed on finely ground potassium iodide; d) silica gel added to a solution of potassium iodide in water and then dried; e) and f) onium salt and anionic surfactant with silica gel added to a solution of potassium iodide in water/methanol (7/3) and then dried.

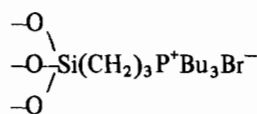
Phosphonium Salts Immobilized on Silica Gel: Phase-Transfer Catalysts in Two Phase Systems and Micellar Catalysts in Water

PIETRO TUNDO* and PAOLO VENTURELLO

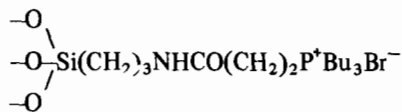
Istituto di Chimica Organica dell'Università, via Bidone 36, 10125 Turin, Italy

Phase-transfer catalysis have been immobilized on polystyrene matrices [1] and on silica gel [2]; the

phosphonium salts supported on silica gel (1, 2, 3 and 4)



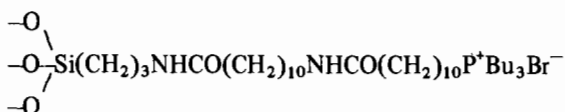
1



2



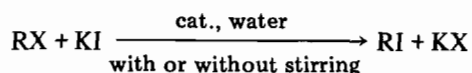
3



4

are different from those immobilized on polystyrene matrices because the catalyzed reaction occurs on the adsorbed substrate and in a microenvironment constituted by the water present on the inorganic matrix.

Kinetic measurements on the reaction:



are carried out. The accessibility of both organic and inorganic phase on such a system is facilitated by the peculiar structure of the silica gel functionalized phosphonium salts: the silica skeleton and the covering organic functions are permeable to both organic and aqueous phase.

Nevertheless the anions exchange in the inner catalytic centers, without stirring, is the more difficult process. Our results (by Arrhenius plots, kinetics without or with different stirring speed, *etc.*) well agree with a mechanism in which only a molar ratio (function of stirring speed and of the alkyl chain in the catalyst) of the catalytic centers catalyze full time the reaction; all the remainder is equal to the mechanism of the soluble onium salts.

Because such systems are constituted by a polar domain (silica gel and onium salt) and by a hydrophobic one (organic chain), and, moreover, work *via* substrate adsorption, they are able to catalyse the

reaction carried out in water, as the micelles do. In the decarboxylation of 6-nitrobenzoxazole-3-carboxylate (test reaction for micellar catalysis) catalytic amounts of 3 (0.05 molar equiv. with respect to the carboxylate) give 2-cyano-5-nitrophenolate with a $k_{\text{dec}} = 1.1 \times 10^{-4} \text{ s}^{-1}$ in water at 30 °C; this value is higher or comparable with the other micellar agents as the cationic polysoaps [4] and the polycrown ethers [5].

References

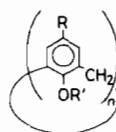
- a) S. L. Regen, *Angew. Chem. Internat. Ed.*, **18**, 421 (1979), and references cited therein; b) H. Molinari, F. Montanari, S. Quici and P. Tundo, *J. Am. Chem. Soc.*, **101**, 3920 (1979), c) S. L. Regen and J. J. Besse, *J. Am. Chem. Soc.*, **101**, 4059 (1979).
- a) P. Tundo, *J. Chem. Soc. Chem. Comm.*, 641 (1977); b) P. Tundo and P. Venturello, *J. Am. Chem. Soc.*, **101**, 6606 (1979).
- P. Tundo and P. Venturello, submitted for publication in the *J. Am. Chem. Soc.*
- T. Kwnitake, S. Shinkai and S. Hirotsu, *J. Org. Chem.*, **42**, 306 (1977).
- S. C. Shah and J. Smid, *J. Am. Chem. Soc.*, **100**, 1426 (1978).

Complexing Properties of Phenol–Formaldehyde Cyclic Oligomers and Their Derivatives

ROCCO UNGARO*, ANDREA POCHINI and PAOLA MELEGARI

Istituto di Chimica Organica dell'Università, Via D'Azeglio 85, 43100 Parma, Italy

Cyclic oligomers (I, $R' = H$) obtained from the base-catalyzed reaction of *p*-substituted phenols and formaldehyde are an old class of compounds [1] which are experiencing new interest because of their



1

cone-shape that brought them the name of *calixarenes* [2]. The tetramer (II) we isolated from the reaction of *p*-*t*-butylphenol and formaldehyde forms a stable 1:1 chlatrate of cage-type with toluene which is held into the cavity as guest [3]. Chlatrates, whose structures are under investigation, are also formed by the octamer (III) which has been isolated from the same reaction mixture.