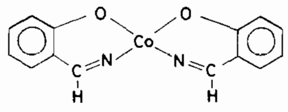
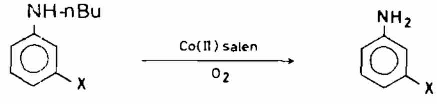
The catalysis of cobalt(II)–Schiff's base complexes has been used mainly in the oxidation of phenols with oxygen. In these cases quinone and quinone dimers were the reaction products.

We investigated the reaction of aromatic amines with oxygen in refluxing methanol in the presence of bis(salicylaldehyde)ethylenediiminecobalt(II) (1).



(1)

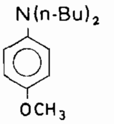
N-n-butylanilines (2–7) gave dealkylation to yield the corresponding primary amine:



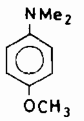
(2) : X = H
(3) : $X = 3\text{-}CH_3$
(4) : $X = 3\text{-}OCH_3$
(5) : X = 3-Cl
(6) : $X = 4\text{-}CH_3$
(7) : $X = 4\text{-}OCH_3$

Neither oxygen alone nor $CoCl_2$ and oxygen were able to perform this transformation under comparable conditions.

Poorer results were obtained in the case of the two tertiary amines (8) and (9):



(8)



(9)

Reactivity measurements based on partial rate factors and kinetic isotope effect obtained by deuterium labelling on the carbon α to nitrogen in aromatic secondary amines gave some mechanistic indications. These are compared with the amino cation radical and nitrenium ion-forming lead tetraacetate oxidation of aromatic secondary amines and the thermolysis of O,N-diacylhydroxylamines occuring *via* a nitrenium ion transition state.

Asymmetric Synthesis at Nitrogen Atom by Oxidation of Imines with *m*-Chloroperoxybenzoic Acid in the Presence of Optically Active Carbinols

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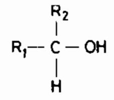
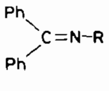
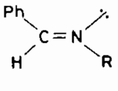
Asymmetric reactions in chiral media may be effected by using optically active additives that do not function as catalysts but only enter into reactions as intermediates complexes or solvates. Optically active oxaziridines, stable at the asymmetric nitrogen atom, can be obtained by oxidation of imines with *m*-chloroperoxybenzoic acid (MCPBA) in the presence of chiral alcohols [1].



I



II

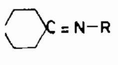


III

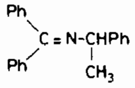
$R_1 = CH_3, CF_3$

$R_2 = C_6H_{11}$, Ph, α-naphthyl

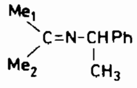
R = Me, Bu^t



IV



V



VI

We have performed a oetailed study on the factors which can influence the stereochemical results of this reaction, by oxidation of imines of type II–VI with MCPBA and in the presence of chiral methyl- or trifluoromethyl-carbinols I. The results obtained show that the optical purity of the reaction products depends on the nature of both the chiral solvent and of the prochiral imine. The highest optical yields (>30%) are obtained when the oxidations are carried out in the presence of chiral trifluoromethylcarbinols and with imines II and V, *i.e.* with substrates which contain the two phenyl substituents at the carbon of the C=N bond. The absolute stereochemistry of all the oxaziridines obtained is correlated to the configuration of the chiral solvent used. From imines II–IV we obtained laevorotatory oxaziridines when (R)-trifluoromethyl- or (S)-methylcarbinols were used as solvents. Oxaziridines with opposite (+)-sign were obtained when the oxidations were induced by (S)-[I; $R_1 = CF_3$] or (R)-[I; $R_1 = CH_3$]. Oxidation of racemic imines V and VI under condition of kinetic control gives different amounts of diastereoisomeric oxaziridines with a predominance of one enantiomer of well established absolute configuration.

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 assymetric 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

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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:

$$RX_{gas} + M^+Y^-_{solid} \xrightarrow[150\ ^\circ C]{cat.} RY_{gas} + M^+X^-_{solid}$$

Material in the Column [3]	Conversion %
a) KI	2
b) KI + $(n\text{-}C_4H_9)_4P^+I^-$	96
c) KI + $n\text{-}C_{12}H_{25}OSO_3^-Na^+$	11
d) KI + silica gel	50
e) KI + silica gel + $(n\text{-}C_4H_9)_4P^+I^-$	93
f) KI + silica gel + $n\text{-}C_{12}H_{25}OSO_3^-Na^+$	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*.

$(CH_3)_4P^+X^-$ *1*

$(n\text{-}C_4H_9)_4P^+X^-$ *2*

$n\text{-}C_{16}H_{33}P^+(CH_3)_3X^-$ *3*

$n\text{-}C_{16}H_{33}P^+(CH_2CH_3)_3X^-$ *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

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