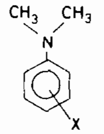		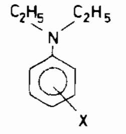	
(*1*)	X = 4-F	(*9*)	X = 4-F
(*2*)	3-Cl	(*10*)	3-Cl
(*3*)	4-Cl	(*11*)	4-Cl
(*4*)	3-Me	(*12*)	3-Me
(*5*)	4-$NHCOCH_3$	(*13*)	4-$NHCOCH_3$
(*6*)	4-*iso*C_3H_7	(*14*)	4-*iso*C_3H_7
(*7*)	4-CN	(*15*)	3-OCH_3
(*8*)	3-NO_2		

obtained for the oxidation of dialkylarylamines with rat liver microsomal P-450 dependent detoxifying system.

Hydrophobic Host–Guest Interactions in Aqueous Media

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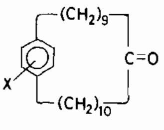
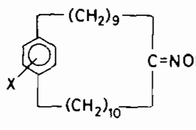
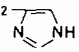
Three fundamental structures can be conceived for designing hydrophobic macrocycles as host molecules which interact with various hydrophobic guest molecules in aqueous media: (a) macrocycles without capping at both top and bottom, (b) macrocycles with a flexible or fixed cap at one end, and (c) macrocycles with a fixed cap at one end and a flexible cap at the other. The author and his coworkers have been mostly concerned with macrocyclic hosts of type (a) structural mode, and prepared various paracyclophanes illustrated by 1, 2, and 3 as typical examples. [*20*] Paracyclophanes provide a hydrophobic binding site much more effective than cyclodextrins for hydrophobic substrates (binding constant $K_b = 10^3$–10^5), and exercise the following catalytic functions in the deacylation of hydrophobic carboxylic esters: nucleophilic-electrostatic [1], nucleophilic-hydrophobic [2], and coordination-nucleophilic [3]. A [*20*] paracyclophane having an ammonium group (1c) provides electrostatic-hydrophobic double-field and a hydrophobic ester undergoes effective aminolysis by glycine [4]. A [*10.10*] paracyclophane bearing two imidazole groups (3e) shows complete turnover behavior in the hydrolysis of hydrophobic esters upon addition of copper(II) ion to the system; the catalysis proceeds through acylation and subsequent deacylation of the cyclophane. [*10.10*] Paracyclophanes exercise two substrate-binding modes depending on the nature of substrates; penetration and face-to-face [5]. Azaparacyclophanes bearing multiple alkyl chains (octopus-cyclophanes) incorporate various substrates by the hydrophobic-electrostatic interaction of induced-fit type (4) [6].

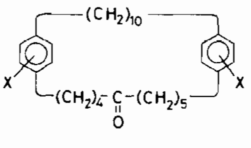


1

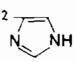


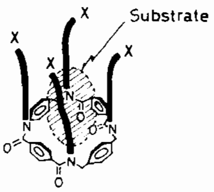
2

X: (a) H ; (b) COOH
(c) $CH_2\overset{+}{N}(CH_3)_3Cl^-$
(d) $CONHCH_2CH_2$ 



3

X: (a) H , (b) COOH
(c) $CH_2N^+(CH_3)_3Cl$
(d) $CO(CH_2)_3COOH$
(e) $CONHCH_2CH_2$ 



4

References

1 Y. Murakami, Y. Aoyama and K. Dobashi, *J. Chem. Soc., Perkin Trans., 2,* 24 (1977).
2 Y. Murakami, Y. Aoyama and K. Dobashi, *ibid.,* 32 (1977).
3 Y. Murakami, Y. Aoyama, M. Kida and J. Kikuchi, *J. Chem. Soc., Chem. Commun.,* 494 (1978).
4 Y. Murakami, Y. Aoyama, K. Dobashi and M. Kida, *Bull. Chem. Soc. Jpn., 49,* 3633 (1976).
5 Y. Murakami, Y. Aoyama, M. Kida, A. Nakano, K. Dobashi, C. D. Tran and Y. Matsuda, *J. Chem. Soc., Perkin Trans, I,* 1560 (1979).
6 Y. Murakami, A. Nakano, R. Miyata and Y. Matsuda, *ibid.,* 1669 (1979).

The Bis (salicylaldehyde) ethylenediiminecobalt (II) Catalysed Oxidation of Aromatic Amines with Oxygen

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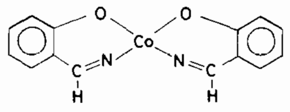
The catalysis of complexed ions in the oxidation of aromatic amines with oxygen could minic biological detoxification reactions.

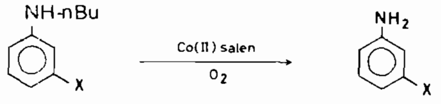
The catalysis of cobalt(II)–Schiff's base complexes has been used mainly in the oxidation of phenols with oxygen. In these cases quinone and quinone dimers were the reaction products.

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



(1)

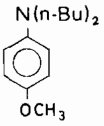
N-n-butylanilines (2–7) gave dealkylation to yield the corresponding primary amine:



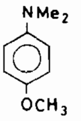
(2) : X = H
(3) : X = 3-CH_3
(4) : X = 3-OCH_3
(5) : X = 3-Cl
(6) : X = 4-CH_3
(7) : X = 4-OCH_3

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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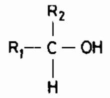
Istituto di Chimica Organica dell'Università, Modena, Italy

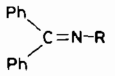
Asymmetric reactions in chiral media may be effected by using optically active additives that do not function as catalysts but only enter into reactions as intermediates complexes or solvates. Optically active oxaziridines, stable at the asymmetric nitrogen atom, can be obtained by oxidation of imines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



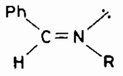
I

R_1 = CH_3, CF_3

R_2 = C_6H_{11}, Ph, α-naphthyl

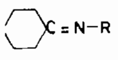


II

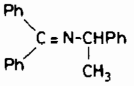


III

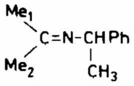
R = Me, Bu^t



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.