STUDIES ON ORGANISED MOLECULAR ASSEMBLIES AND THEIR UTILIZATION IN MODIFICATION OF CHEMICAL REACTIVITY

THESIS SUBMITTED
IN FULFILMENT FOR THE REQUIREMENTS
OF THE DEGREE OF
DOCTOR OF PHILOSOPHY

by

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November, 1989

DEDICATED TO

MY

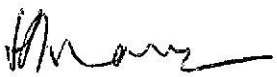
PARENTS

CERTIFICATE

This is to certify that the thesis entitled 'Studies on Organised Molecular Assemblies and their Utilization in Modification of Chemical Reactivity' being submitted by Miss Manisha Pathak to Indian Institute of Technology, New Delhi, for the award of the degree of Doctor of Philosophy, is a record of bonafide research work carried out by her.

Miss Manisha Pathak has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis which to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.



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ACKNOWLEDGEMENT

It gives me an immense pleasure to express my profound sense of gratitute to Dr. H.M. Chawla, for his guidance, invaluable suggestions and constant encouragement throughout the research work embodied in this thesis.

I wish to express my sincere thanks to the Head of the Department, Department of Chemistry, Indian Institute of Technology, New Delhi for providing facilities available in the Department.

I am also thankful to my colleagues who have helped me all through my research project.

My regards are also due to my parents who have always encouraged and assisted me to persue higher studies.

I would also like to thank Mr. Akhilesh Chippli and Mr. Sanjay Arora for typing and wordprocessing the manuscript.

Manisha Pathak

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NOTES

1. All the melting points reported in this thesis are uncorrected and were taken on an electric melting point apparatus (Adair Dutt and Co. Calcutta, India).
2. UV spectra were taken on Perkin Elmer's [Lambda-3B] spectrophotometer.
3. IR spectra were recorded in KBr disc or chloroform on a [5-DX] Nicolet FT-IR spectrophotometer. The abbreviations such as s,w,m, sh,bs,w-sh and m-sh refers to strong, weak, medium, sharp, broad and strong, weak and sharp, medium and sharp respectively.
4. PMR and ^{13}CNMR spectra were recorded in $CDCl_3$ on Jeol [JNM-FX100] FT-NMR spectrometer using TMS as an internal standard and valves reported are in scale. The abbreviation such as s,bs,d,t,q and m indicate singlet, broad singlet, doublet, triplet, quartet and multiplet respectively.
5. Mass spectra were recorded on [JMS-D300] Jeol mass spectrometer at 70 eV and 15 eV.
6. The molecular mass of several calix(n)arenes synthesized was determined by Vapour Pressure Osmometry using Vapour Pressure Osmometer (Knauer, W. Germany).
7. The completion of the reaction, and the purity of the synthesized compounds were checked by TLC performed on silica gel (BDH, Bombay) plates using iodine for visualising the spots.
8. The solvents used were purified and dried before use.
9. Pet. ether refers to the fraction with boiling point range of 60-80°C.

10. The abbreviations used for various surfactants CTAB, CTAC, SDS, KDC, DODCl, DCC, HDTCl, DTAC, HDTBr refer to cetyltrimethylammonium bromide, cetyltrimethylammonium chloride, sodium dodecylsulphate, potassium dodecanoate, dioctadecylcarbodiimide, dicyclohexyl carbodiimide, hexadecyltrimethylammonium chloride, dodecyltrimethylammonium chloride, hexadecyltrimethylammonium bromide respectively.

ABSTRACT

The thesis entitled **"Studies on Organised Molecular Assemblies and their Utilization in Modification of Chemical Reactivity"** has been divided into six chapters. The first chapter describes the available literature on the use of organised media and molecular assemblies employed for achieving selectivity in organic reactions and includes the principles required to be understood for using micelles microemulsions, functionalised polymers and constrained organic and inorganic molecular systems for regioselectivity.

The second chapter includes the synthesis, structure and properties of macrocycles represented by calix(n)arenes. 53 compounds belonging to this class have been synthesized and characterized by spectroscopic methods (UV, IR, NMR and Mass). Some of the calix(n)arenes synthesized are already known compounds while others have been prepeared for the first time. The exact experimental procedures have been developed for the synthesis of these calix(n)arenes and ambiguities reported in the literature have been settled. The conformational analysis of the synthesized calix(n)arene derivatives have been studied by ^{1}HNMR and ^{13}CNMR spectroscopy. Experimental conditions for obtaining calix(4)arenes, calix(6)arenes and calix(8)arenes have been standardized.

Singlet oxygen which is believed to be involved in many chemical, biological and environmental phenomena has been used as a reagent to study the model reactions for a long term goal of exploring photooxidative deactivation of certain enzymes. A series of N-substituted-4,5-imidazolin-2-ones have been synthesized and subjected to dye sensitized photooxygenation. The products have been identified as

dibenzoylureas by UV, NMR and Mass spectroscopic analysis. In order to study the mechanism of photooxygenation of imidazolin-2-ones the reactions have also been carried out in the presence of cationic, anionic and neutral surfactants. A plausible mechanism involving zwitterionic perepoxides has been proposed in Chapter III.

In order to further explore the reaction of singlet oxygen with N-substituted imidazolin-2-ones, photooxygenation reactions have also been carried out in the presence of calix(6)arene, calix(4)arenes, calix(8)arenes and their derivatives. It has been observed that the reaction is catalyzed by the presence of calix(n)arenes which themselves remain unaffected by singlet oxygen. Calix(6)arenes appear to be more effective catalysts as compared to calix(8)arenes and calix(4)arenes. The effect of substituents on calix(n)arenes have also been studied and it has been observed that calix(n)arenes containing long hydrocarbon chains are more effective than calix(n)arenes having short hydrocarbon chains. A plausible mechanism in which the calix(n)arenes effect the reaction rates is discussed in Chapter IV.

Since calix(n)arenes have a basket or wheel type structure they are expected to behave analogous to cyclodextrins. In chapter V, the results of alkaline hydrolysis of p- and m-substituted phenyl benzoates in the presence of calix(n)arenes have been described. It has been observed that the calix(n)arenes instead of facilitating hydrolysis of phenyl benzoates, suppress the release of phenols from them on treatment with alkali. It has also been observed that the structure and conformation of calix(n)arenes affect the release of phenol differently. The results presented in this chapter suggest the

utility of further kinetic and isotopic studies on alkaline hydrolysis of esters in the presence of calixarenes.

Chapter VI describes the results obtained from the reaction of CAN with some aromatic ethers in the presence and absence of various surfactants. The study clarify the earlier investigations from our laboratories which afforded the synthesis of bisethoxynaphthalenes. A plausible rationale for the formation of the products has been described.

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