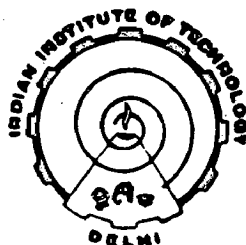


**STUDIES ON
SOME REGIOSELECTIVE CHEMICAL TRANSFORMATIONS
AND
PHYTOCHEMICAL INVESTIGATION OF *Erythrina variegata* FLOWERS**

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

by
SHIV KUMAR SHARMA



**Department of Chemistry
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
JANUARY, 1988**

DEDICATED

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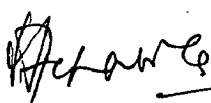
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CERTIFICATE

This is to certify that the thesis entitled, "STUDIES ON SOME REGIOSELECTIVE CHEMICAL TRANSFORMATIONS AND PHYTOCHEMICAL INVESTIGATION OF Erythrina variegata FLOWERS" being submitted by Mr. Shiv Kumar Sharma to the Indian Institute of Technology, Delhi, for the award of the degree of 'Doctor of Philosophy in Chemistry', is a record of bonafide research work carried out by him.

Mr. Shiv Kumar Sharma 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 in full, to any other University or Institute for the award of any degree or diploma.


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(SHIV KUMAR SHARMA)

ABSTRACT OF THE THESIS

The thesis entitled, 'STUDIES ON SOME REGIOSELECTIVE CHEMICAL TRANSFORMATIONS AND PHYTOCHEMICAL INVESTIGATION OF Erythrina variegata FLOWERS' has been divided into six chapters.

Chapter-I describes a review of organic reactions mediated by cerium(IV) salts especially the ones that have been employed for synthetic purposes. It also contains the present work on reactions of different substituted alkylarylketones and dimethylphenols with cerium(IV) ammonium nitrate in conjunction with hydrogen peroxide. It has been observed that the reaction leads to the formation of (i) acids (ii) nitro substituted acids and acetophenones and (iii) oxidatively coupled products such as dimers, trimers, dibenzodioxanes and dibenzofurans. Plausible mechanism for the formation of these products has been suggested.

Recently, cerium salts have been determined to be potent single electron transfer agents and therefore, can be used to produce hydroxyl radicals from hydrogen peroxide. These hydroxyl radicals can be stabilized by predetermined molecular organization constructed out of amphiphatic molecules and made to effect aromatic hydroxylations. The reaction of some simple aromatic hydrocarbons and phenols with cerium(IV) ammonium nitrate/hydrogen peroxide/acetic acid in the molecular assemblage of amphiphatic molecules as a procedure for aromatic hydroxylation is presented in Chapter-II of the thesis.

A novel one-pot good yield synthesis of 2-aryl-3-arylidene-2,3-dihydro-4H-1-benzopyran-4-ones from hydroxyacetophenones and aromatic aldehydes has been described in Chapter-III. The conditions for obtaining regio-selectivity and better yields of 3-arylidenebenzo-

pyrones have been optimized by taking advantage of the hydrophobic environment created by amphiphatic molecules. The reactant concentration and substituent effects on the yield of new products have also been studied which reflect upon the nature of major byproducts of Claisen-Schmidt chalcone synthesis. To further establish the structure of new compounds and to study their transformations, the base catalyzed reactions of 2-aryl-3-arylidene-2,3-dihydro-4H-1-benzopyran-4-ones with hydrazine and phenylhydrazine have been carried out to give new benzopyrano-(4,3-C)-pyrazolines in good yield. Plausible mechanisms for the formation of above mentioned products has also been presented in this chapter.

Chapter-IV starts with a brief discussion on singlet molecular oxygen and then describes the present work on its reactions with 2'-aryl-3-arylidene-2,3-dihydro-4H-1-benzopyran-4-ones and 2'-hydroxyphenylstyrylketones. It has been observed that 2-hydroxyphenylstyrylketones lead to the formation of 2-arylidene coumaran-3-ones and 3-hydroxy-2-phenyl-4H-1-benzopyran-4-ones depending upon the substituents present on the styryl moiety, whereas 2-aryl-3-arylidene-2,3-dihydro-4H-1-benzopyran-4-ones give the corresponding 2-aryl-3-aroxy-4H-1-benzopyrones in good yield. Some compounds like 2-(4'-chlorophenyl)-3-(4"-chlorobenzylidene)-2,3-dihydro-4H-1-benzopyran-4-one have been observed to give degradation side products but regioselective formation of 3-aroxyated benzopyrones can be achieved by using critical micelle concentration of sodium dodecyl sulphate in the reaction media. A study of the reaction of 2'-hydroxyphenylstyrylketones with cerium(IV) ammonium nitrate in conjunction with hydrogen peroxide to yield 2-arylidene coumaran-3-ones and 2-phenyl-4H-1-benzopyran-4-ones is also described in this chapter.

Chapter-V describes the ^{13}C -NMR spectra of the 2-hydroxyphenylstyrylketones and 2-aryl-3-arylidene-2,3-dihydro-4H-1-benzopyran-4-ones that have not been reported so far with a view to rationalize the application of this technique to structural elucidation of some groups of polyphenols. The various signals recorded in the spectra of these compounds have been assigned to different carbon atoms and the assignments have been confirmed by the analysis of their off-resonance spectra.

Erythrina variegata (Family-Leguminosae) is a tall ornamental tree with many useful medicinal properties. Chapter-VI gives a brief account of the chemical work carried out by various workers on different Erythrina species and also the extractive methodology adopted in the present work for determining the chemical constituents of Erythrina variegata flowers (not examined so far), which led to the isolation of eighteen different chemical compounds. The identification of the chemical components isolated and structural elucidation of three new alkaloidal natural products by spectroscopic methods are also described in this chapter.

RESEARCH PAPERS PUBLISHED/COMMUNICATED

1. A Novel Conjunction Catalyst for Aromatic Hydroxylations.
"Recent Advances in Catalysis and Catalytic Reaction Engineering". RRL, Hyderabad (India), 1986, p. 294-305.
2. Novel One Pot Convenient Synthesis of 3-Benzylidene-2-phenyl-2,3-dihydro-4H-1-benzopyran-4-ones
Heterocycles, 1987, 26(6), 1527-34.
3. Hydroxylation of Alkylphenols by Cerium(IV) in Conjunction with Hydrogen peroxide and Sodium dodecyl sulphate.
J. Chem. Soc., Chem. Commun., 1988 (in press).
4. A Novel and Convenient One-Pot Synthesis of 2-Phenyl-3-benzylidene-2,3-dihydro-4H-1-benzopyran-4-ones.
J. Chem. Res. (M), 1988, 1901-13.
5. Cerium(IV) Induced Aromatic Hydroxylation of C-Alkylated Hydrocarbons and Phenols.
Tetrahedron, 1988 (in press).
6. A Novel and Convenient One-Pot Synthesis of 2-Phenyl-3-benzylidene-2,3-dihydro-4H-1-benzopyran-4-ones.
J. Chem. Res. (Synopsis), 1988 (in press).
7. A Novel Cerium(IV) Based Conjunction Catalyst for Aromatic Hydroxylations.
J. Mol. Catalyst, 1988 (in press).
8. Novel One-Pot Synthesis of 3-Benzal-2,3-dihydro-4H-1-benzopyran-4-ones.
Indian J. Chem., 1987, 26B, 1075-77.
9. Dye-Sensitized Photooxygenation of 2-Phenyl-3-benzylidene-2,3-dihydro-4H-1-benzopyran-4-ones.
XIIIth International Conference on Photochemistry, Budapest, Hungary, Aug. 9-14, 1987.
10. Dye-Sensitized Photooxygenation of 3-Benzylidene-2-phenyl-2,3-dihydro-4H-1-benzopyran-4-ones in the Micellar Media
3rd National Conference on Surfactants, Emulsions and Biocolloids, Aligarh Muslim University, Aligarh, Dec. 28-30, 1987, PSS 22.
11. Novel Dye-sensitized Photooxygenation of 2-Aryl-3-arylidene-2,3-dihydro-4H-1-benzopyran-4-ones.
Tetrahedron, 1988 (Communicated).
12. Micelle mediated Regioselective Photooxygenation of 2-hydroxy-phenylstrylketones
J. Org. Chem., 1988 (Communicated).

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 330-Hitachi spectrometer in methanol.
3. IR spectra were recorded in KBr disc or chloroform on a SP-1200 Grating IR spectrophotometer and 5-DX-Nicolet FT-IR spectrophotometer. The abbreviations such as s, w, m, sh, bw, bs and m-s refer to strong, weak, multiplet, sharp, broad and weak, broad and strong and medium to strong respectively.
4. PMR and ^{13}C -NMR spectra were recorded in CDCl_3 , $(\text{CD}_3)_2\text{CO}$ or DMSO on Nicolet-99.55 Mz Jeol-FT-NMR spectrometer using TMS as the internal standard and values reported are in scale. The abbreviation such as s, bs, d, dd, t, q and m indicate singlet, broad singlet, doublet, double doublet, triplet, quartet and multiplet respectively.
5. Mass spectra were recorded on JMS-D 300 Jeol mass spectrometer at 70 eV.
6. The $[\alpha]_D$ values were recorded at laboratory temperature (ca. 25°C).
7. The time allowed for the completion of the reaction and the purity of the prepared compounds were monitored by means of TLC performed on silica gel (BDH, Bombay) plates using iodine for visualizing the spots.
8. Organic solvent extracts were usually dried over anhydrous Na_2SO_4 and solvents used were freshly distilled and purified before use.
9. Petroleum ether solvent refers to the fraction with boiling point range of 60-80°C.
10. The derivatives like hydrazones, acetates, benzoates, of the compounds were prepared according to the procedure given in the 'Text Book of Practical Organic Chemistry', A.I. Vogel, Longman Press, London, 1973.

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CERTIFICATE

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