INTRAMOLECULAR *ortho* GROUP PARTICIPATION

BY

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

Department of Chemistry
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
October, 1983

DEDICATED

TO

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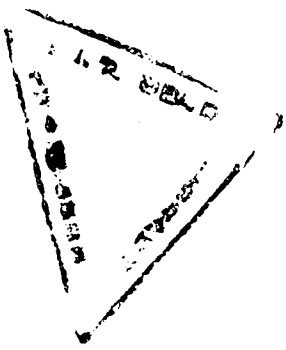

ACKNOWLEDGEMENTS

The author wishes to express his profound gratitute to Dr. Raj Kumar Bansal, Assistant Professor, Department of Chemistry, Indian Institute of Technology, Delhi, for his invaluable guidance, help and encouragement during the course of this work. But for his help, this thesis would not have attained this stage.

It is a great pleasure to thank Professor M. K. Jha, Head, Department of Chemistry, for providing the necessary facilities.

A debt of gratitute is due to Professor F. W. Bachelor, Department of Chemistry, University of Calgary, Calgary, Alberta, Canada, for the mass spectral analysis.

His special thanks are also due to Dr. K. L. Dhar, Assistant Director, Regional Research Laboratory, Jammu Tawi and to Dr. C. R. Jagga, ITMMEC, Indian Institute of Technology New Delhi, for the mass spectral analysis of some samples.

The author also takes this opportunity to express his deep sense of gratitute to his family members and friends for their constant encouragement.

A word of appreciation is due to M/S Durga Singh and J. P. Singh for their assistance in running the UV and IR spectra.

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ABSTRACT

The thesis entitled "Intramolecular ortho-Group Participation," has been divided into five chapters.

The first chapter gives an upto-date survey of the literature on the work regarding a discussion on neighbouring group participation. Various methods, namely, kinetic measurements, isolation of products, trapping of intermediates, stereochemical evidence, spectroscopic methods, etc., which may be employed to assess participation by a nucleophilic substituent, have been described in detail with appropriate examples.

The second chapter deals with the solvolysis of substituted benzhydryl bromides. Isomeric ortho- and para-carbophenoxy and ortho- and para- carboethoxybenzhydryl bromides were prepared and solvolyzed in aqueous acetone and aqueous dioxane. The intramolecular participation capacity of carbophenoxy- and carboethoxy- groups, when placed at the ortho- position to the reaction site in this system, has been compared. An attempt was made to brominate o-benzylbenzoic acid to obtain o-carboxybenzhydryl bromide, but the product obtained was 3-phenylphthalide. The effect of adding silver nitrate to the reaction medium, on the solvolysis rates, was also studied. The thermodynamic constants were also calculated.

The third chapter consists of a study on the solvolysis of isomeric ortho-, meta- and para- nitrobenzal chlorides and unsubstituted benzal chloride. These nitrobenzal chlorides were prepared and solvolyzed in aqueous ethanol in order to see if ortho- nitro group would function as an intramolecular nucleophile. The solvolysis was also carried out in the presence of silver nitrate in order to see its effect on the solvolysis rates.

The fourth chapter gives an account of the hydrazone- and oximino- groups as intramolecular nucleophiles. A series of eleven o-aroylbenzoic acids was prepared and treated separately under Huang-Minlon modification of Wolff-Kishner reduction and with hydroxylamine hydrochloride respectively. The phthalazinones in the first case and the lactones in the second case were isolated and characterized by their elemental and spectral analyses. Appropriate mechanisms for their formation were also postulated. The fragmentation patterns of phthalazinones under electron impact were also examined.

The last chapter deals with the solvolysis of 2'-substituted phthalanilic acids. Phthalanilic acids, with different substituents, such as nitro-, methyl-, chloro-, etc., located in the para-position of aniline ring, were prepared and solvolyzed in aqueous dioxane at an ionic strength of 0.12 M and an apparent pH of 6.0 in order to examine the participation of the carboxamide group as

an intramolecular participant. A Hammett plot was drawn and a probable mechanism for the reaction was suggested. Thermodynamic constants were also calculated

CONTENTS