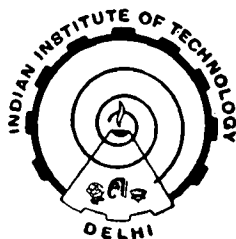


INTRAMOLECULAR *ortho* GROUP PARTICIPATION

BY
SUNIL KUMAR JAIN

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DEDICATED
TO
MY PARENTS

BIO-DATA

Name .. Sunil Kumar Jain
 Father's Name .. Shri M. K. Jain
 Date of birth .. December 5, 1957.

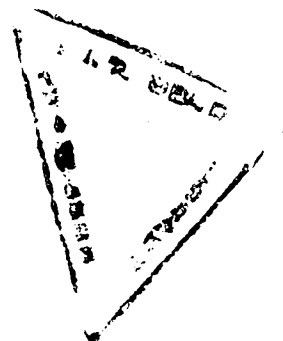
Educational Qualifications -

Exam. Passed	University	Year of passing	Division
Pre-Medical	Kurukshetra Univ., Kurukshetra.	1975	First
B.Sc.	Kurukshetra Univ., Kurukshetra.	1977	First
M.Sc.	University of Roorkee, Roorkee	1979	First

Research Fellowship -

JRF	I.I.T., Delhi	Aug. 1979 to July 1981
SRF	I.I.T., Delhi	Aug. 1981 to present

TM-1081



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(SUHIL KUMAR JAIN)

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-carbonybenzhydryl 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 oxime- 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 p'-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 8.0 in order to examine the participation of the carbonamide group as

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

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