SOME SYNTHETICALLY USEFUL REACTIONS OF HYDRAZONES, SEMICARBAZONES AND CYCLIC IMIDES

by

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DEDICATED TO

MY

NEARS AND DEARS

Certificate

This is to certify that the thesis entitled "SOME SYNTHETICALLY USEFUL REACTIONS OF HYDRAZONES, SEMICARBAZONES AND CYCLIC IMIDES", being submitted by Mrs. Kiran Varsha, 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 carried out by her. Mrs. Kiran Varsha 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 dissertation 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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(Kiran Varsha)

Abstract

The thesis entitled "Some Synthetically Useful Reactions of Hydrazones, Semicarbazones and Cyclic Imides" has been divided into three chapters.

CHAPTER 1:

Allyl, cinnamyl and propargyl ethers of salicylaldehyde and 2-hydroxynaphthaldehyde were prepared by condensation of the phenolic aldehydes with appropriate bromides. Similarly prepared were the allyl and propargyl ethers of 3-methoxy-2-hydroxybenzaldehyde. These aldehydic ethers were converted into their acetyl-, benzoyl- and tosyl- hydrazones, semicarbazones, *thiosemicarbazones* and azines. The acetyl hydrazones and the benzoyl hydrazones underwent intramolecular tandem [3⁺+2] cycloadditions accompanied by the cleavage of the acetyl and benzoyl group on heating in methanol under reflux in the presence of equimolar proportion of hydrochloric acid to give bis-adducts which were found to be either identical (in the cases of propargyl ethers) or diastereoisomeric (in cases of alkenyl ethers) with the products isolated from the acid catalysed intramolecular criss-cross cycloaddition of the corresponding azines under similar conditions. The tosylhydrazones, the semicarbazones and the thiosemicarbazones were recovered unchanged under similar conditions except when they were derived from 2-cinnamyloxynapthaldehyde, in which case the bis-adduct, identical to that given by the corresponding acetyl- or benzoyl-hydrazone, was obtained. 2- Allyloxybenzaldehyde benzoylhydrazone on stirring with $CuCl_2.2H_2O$ in acetonitrile, yielded the same bis-adduct as was obtained from its reaction in methanol in the presence of hydrochloric acid.

CHAPTER II:

Several semicarbazones of aldehydes and ketones were hydrolysed with $CuCl_2.2H_2O$ in refluxing acetonitrile to give the carbonyl compounds in high

yields. The regeneration of the ketones proceeds faster than that of the aldehydes. Ester, amide, alkoxy and phenolic groups and conjugated or isolated double bond survive under the reaction conditions. 2,4-DNP derivatives remain unaffected even under more stringent conditions.

CHAPTER III:

Some hitherto unreported 3-arylamino-4-hydroxybutyranilides were prepared in high yields by highly regioselective reduction of N-aryl-α-arylaminosuccinimmides with sodium borohydride in acetonitrile-methanol (4:1,v/v) medium. The carbonyl group adjacent to the arylamino group was found to be reduced selectively. When the α-substituent was a tertiary amino (N,N-methyl-phenylamino) group, a mixture of both the regioisomeric reduction products were obtained from the reaction showing opposite but poor regioselectivity.

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