STUDIES ON THE SYNTHESIS AND PYROLYSIS OF GLYCIDIC ESTERS

A THESIS SUBMITTED TO THE
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CERTIFICATE

This is to certify that the thesis entitled, "**Studies on the Synthesis and Pyrolysis of Glycidic Esters**", being submitted by **Mr. Vinod Kumar Sharma** to the Indian Institute of Technology, Delhi for the award of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him.

Mr. Vinod 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 full, to any other university or institute for the award of any degree or diploma.

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(Vinod Kumar Sharma)

Abstract

The thesis entitled, "**Studies on the Synthesis and Pyrolysis of Glycidic Esters**" comprises of six chapters.

The first chapter reviews the mechanistic details of the Darzens condensation. An account of different mechanisms postulated for this reaction has been given. Kinetics of the reaction, effect of solvents, influence of substituents and steric course of the reaction have been discussed.

The second chapter includes the preparation of several new glycidic esters. Several methods are reported in the literature for the synthesis of glycidic esters. These include ring closure of chlorohydrin by a base, epoxidation of α, β unsaturated ester by peracids, reaction of carbonyl compounds with gem-dihalides in the presence of n-butyl lituium, etc. But in the present study glycidic esters have been synthesized through the Darzens condensation. Various α-substituted glycidic esters were synthesized by condensing t-butylchloroacetate, t-butyl α-chloropropionate and t-butyl α-chlorophenylacetate with benzaldehyde and p-substituted benzaldehydes using potassium t-butoxide in dry t-butanol as a base. The structures of the glycidic esters were assigned on the basis of elemental and spectral analysis. The effect of the bulk of β and α-substituents on the progress of the reaction has been studied by condensing different

halogenomethylene compounds with a number of ketones having varied steric demands. The cis- and trans- isomers of some glycidic esters have been reported and their structures confirmed by their stereospecific synthesis.

Phase transfer catalysis is a recent methodology of immense synthetic importance available for achieving many carbanion mediated reactions. Chapter III reports the application of this technique for the Darzens condensation. A number of aldehydes and ketones have been condensed with α-haloester in the presence of tetra-n-butylammonium chloride or benzyl triethylammoniumchloride using dichloromethane or n-hexane as solvents. The use of PTC resulted in better yields of glycidic esters with significant reduction in the reaction time.

The fourth chapter describes the decarboxylation of sodium salts of glycidic acids. This procedure results in the formation of aldehydes or ketones. The sodium glycidates of a number of glycidic esters namely t-butyl β-phenyl -α-phenylglycidate, t-butyl β(p-nitro phenyl) -α- phenyl glycidate and t-butyl β-(p-nitrophenyl)-α-methylglycidate have been decarboxylated under acidic conditions. Three types of products, i.e. rearranged, 'normal' and 'abnormal' have been isolated and identified by a careful HPLC analysis. Mechanistic interpretations for their formation have been discussed.

Pyrolysis of glycidic esters serves as a useful method for obtaining ketones or aldehydes otherwise accessible with difficulty by conventional routes. A number of representative t-butyl glycidates such as t-butyl β-phenyl-α-phenylglycidate, t-butyl β(p-(chlorophenyl) α -phenyl glycidate, t-butyl β-phenyl-α-methylglycidate, ethyl β-phenylglycidate etc. bearing an α-substituent have been pyrolysed to assess the effect of substitution on the nature of product formation. An alternative mechanism has also been postulated for the pyrolysis of t-butyl glycidates.

It is known that the presence of substituents on the oxirane ring plays an important role in directing the fragmentation pathways of glycidic esters. The sixth chapter includes the analysis of the fragmentation patterns of some glycidic esters possessing an α-substituent. These esters have been observed to display some characterstic fragmentation pathways under electron-impact significant among them being (i) transannular cleavage of the oxirane ring (ii) loss of $C(CH_3)_3$ ion (iii) transannular cleavage of the epoxy acid to form an ionised carbene (iv) loss of isobutylene by the Mc Lafferty rearrangement.

CHAPTER III

PHASE TRANSFER CATALYSIS IN THE DARZENS CONDENSATION

CHAPTER IV

DECARBOXYLATION OF GLYCIDIC ESTERS

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