MECHANISM OF THE DARZENS CONDENSATION AND PYROLYSIS OF GLYCIDIC ESTERS

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CERTIFICATE

This is to certify that the thesis entitled, "Mechanism of the Darzens Condensation and Pyrolysis of Glycidic Esters" being submitted by Kanta Sethi to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy, is a record of bonafide research work carried out by her. Kanta Sethi has worked under my guidance and supervision and has fullfilled the requirements for the submission of this thesis, which to my knowledge, has reached the requiste 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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ABSTRACT

The thesis comprises of four chapters and each chapter is subdivided into four sections namely introduction, results and discussion, experimental and references.

The first chapter deals with the kinetic investigation of the Darzens condensation. The rates of condensation of benzaldehyde and its p-methoxy, p-methyl, p-chloro, p-bromo and p-nitro derivatives with phenacyl chloride in the presence of NaOH has been measured in dioxane-water solvent mixture at two temperatures i.e. 15° and 25°. The third order rate constants have been evaluated from the plots and the activation parameters have been calculated. The Hammett equation has been found to apply well to this reaction.

The second chapter includes the preparation, purification and isolation of cis-trans glycidic esters. Several t-butyl glycidic esters were prepared by condensing t-butyl chloroacetate with benzaldehyde and p-substituted benzaldehydes, acetophenone and p-substituted acetophenones, propiophenone and p-substituted propiophenones, isobutyrophenone and benzophenone using potassium t-butoxide in dry t-butanol as a base. In addition some ethyl glycidic esters were also synthesized by condensing ethyl chloroacetate with benzaldehyde and substituted benzaldehydes, acetophenone and p-substituted acetophenones using powdered sodium in dry

xylene as a base. The structures of the glycidic esters were assigned on the basis of elemental and spectral analyses. The effect of bulk of β -substituents on the overall yield has been studied. The cis-trans-isomers were separated in various cases by fractional recrystallization or fractional distillation as the case may be. A Scheme has been devised to prepare the trans-isomer of t-butyl β -methyl- β -(p-bromophenyl)-glycidate exclusively.

The third chapter reports the study on the pyrolysis and decarboxylation of the glycidic esters and briefly the reaction of piperidine with a few glycidic esters. A number of representative t-butyl glycidic esters were pyrolysed directly at 360-80°. The potassium salts were prepared from the corresponding esters and were decarboxylated by treating with glacial acetic acid.

The fourth chapter consists of the mass spectral fragmentation of several ethyl- and t-butyl glycidic esters. Structures of the significant ions and mechanism of their formation have been proposed. A comparison of the fragmentation of the two types of esters has been made under electron impact.

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