

CHAPTER - VI

Scope, Objectives and Summary of the work

The Chemistry of cyclopropane compound is highly interesting and multidirectional. One colourful facet of the study covers the cleavage of cyclopropane ring systems. To be more relevant to our systems, the cleavage of cyclopropyl keto systems may be summarized as cleavage with (i) hydrolysis⁴³ (ii) protonolysis⁴⁴ (iii) lithium/ammonia reduction⁴⁵ (iv) Lewis acid treatment⁴⁶ (v) reductive cleavage^{40(b)} etc.

The cleavage of α -hydroxy cyclopropanes^{41(a,b)} through 48% HBr^{41(c)} or magnesium halides²⁵ has been effected. The cleavage of cyclopropanes through mercuric acetates⁴⁷ and other electron transfer process⁴⁸ is also possible.

The skatibol rearrangement is the rearrangement of the formally vinyl cyclopropane and is a pericyclic reaction⁴⁹.

The Trost sec-alkylation reaction based on organo-sulphur chemistry may also be mentioned in connection with the cleavage of cyclopropane compounds⁵⁰.

The collapse to allene is also known⁵¹. The presence of trimethylsilyl ether on the ring also aids easy cleavage of the ring⁵².

Another broad aspect of the study is concerning with the functionality transformations in which the cyclopropane ring would retain its identity. Combined the above two aspects (viz. cleavage and functionality transformation) one can have the knowledge to

use masterly new routes to synthesize new compounds or natural products via a cyclopropane route.

Apart from the above scopes of the study of cyclopropane systems it has a huge potentiality of theoretical interests.

Ring opening reactions have been found to occur with various acid and basic reagents and a series of cyclopropane compounds substituted at one carbon of the ring by two electron withdrawing groups. These reactions result in the formation of 1,1,3-tri substituted propenes.

The cyclopropane compounds used in this study were diethyl cyclopropane 1,1-dicarboxylates, ethyl 1-cyano cyclopropane, 1-carboxylate, 1-cyano cyclopropane-1-carboxamide, 1,1-diacetyl cyclopropane and 1-acetyl, 1-benzoyl cyclopropane. Here we observed that the first two cyclopropane ester derivatives remain unattacked by cold strong acids such as conc. H_2SO_4 and HBr (48%) in the cleavage of the three membered ring.

Again it was reported that cyclopropane ester derivatives underwent ring opening addition reaction when heated with secondary amines¹⁴ e.g. piperidine and isobutyl amine either with solvent or without solvent. In this correlation we have performed reactions of 1,1-disubstituted cyclopropane compounds with primary amine such as isopropyl amine. In addition, the reaction of aq. ammonia (28%) on the some cyclopropane derivatives were studied. The details of experimental facts and results of all the reactions

are recorded in the following chapters. In another broad spectrum of study, cyclopropane keto derivatives underwent simultaneous cleavage and rearrangement when acted on with different reagents. Ring cleavage by the action of grignard reagents viz. methyl magnesium iodide, phenyl magnesium bromide and vinyl magnesium bromide and subsequent reaction with acid had been recorded by the previous workers⁵⁴ in this laboratory.

Julia et al⁵⁵ found homo allylic compounds by rearrangement of cyclopropyl carbinols derivatives with the action of 48% hydrobromic acid. An advantageous modification has been reported by using dil. acid in stead of conc. acid. Here the cyclopropane adduct has been reacted with grignard reagent especially with allyl magnesium halide resulting the grignard adduct and this adduct on treatment with dilute mineral acids gave the homoallylic halide derivatives.