

PART - B

## CHAPTER - V

### A general review on cyclopropane

(a) The chemical bond in the cyclopropane ring<sup>1</sup>:

Three membered ring-cyclopropane gives an interesting case of a bent C-C covalent bond, the  $\pi$ -bond or banana bond. It is planar and the internal bond angles of  $60^\circ$  (strained largely) represent a large deviation from the tetrahedral angle. But carbon can not have hybridized orbitals oriented at less than  $90^\circ$  to each other and since there are four bonds on each carbon, the angles have to be more than even  $90^\circ$ . This would mean that in cyclopropane, the ring  $\sigma$ -bonds can not be formed by the bonding atomic orbitals pointing directly at one another.

According to the MO model of Walsh<sup>2</sup> (Fig. 1) three occupied molecular orbitals determine the nature of the C-C bonds of the three membered ring.

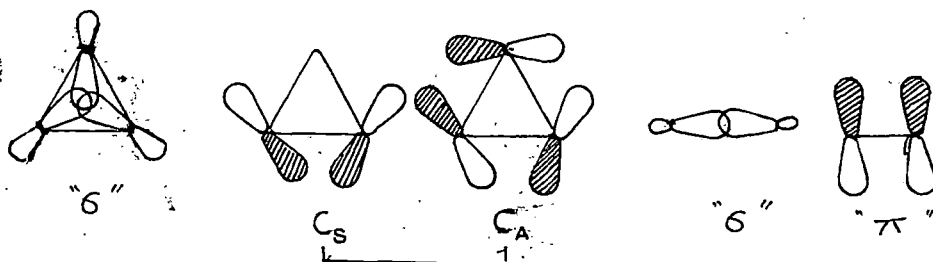
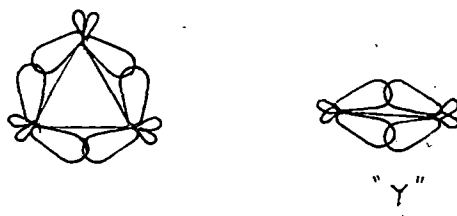


Fig. 1 (MO - representation of cyclopropane and ethylene)

Of these, the orbitals of lowest energy ( $\sigma$ ) is a linear combination of three  $sp^2$ -hybrid atomic orbitals. While the other

two ( $e_g$  and  $e_g'$ ) are equal-energy linear combinations of three p-atomic orbitals differing only in their symmetry properties. This picture is a strong reminding of the commonest description of a Carbon-Carbon double bond by two occupied MOs, one linear combination of two  $sp^2$ -atomic orbitals ( $\sigma$ -MO) and with two p-atomic orbitals ( $\pi$ -MO) [ Fig. 1 ]. By analogy with the letter MO's the Walsh  $e_g$  and  $e_g'$  orbitals are also called  $\pi$  or "quasi  $\pi$ " orbitals of the three membered ring.

Valence bond model of cyclopropane, due originally to Forster<sup>3</sup> and refined by Coulson<sup>4</sup>, however, reflected a significant point arising out of the higher p-character of AO's of the C-C bonds which causes a small but appreciable degree of  $\pi$ -delocalisation around the ring. Actually the C-C bonds are described as resulting from the overlapping of two  $sp^3$ -hybrid orbitals at each carbon atom (Fig. 2) which lie outside the internuclear angles ( $\approx 104^\circ$ ).



(Fig. 2 Valence bond model of Cyclopropane and ethylene).

Since the direction of the orbitals cannot coincide with the directions of bonding but are directed towards relative to the

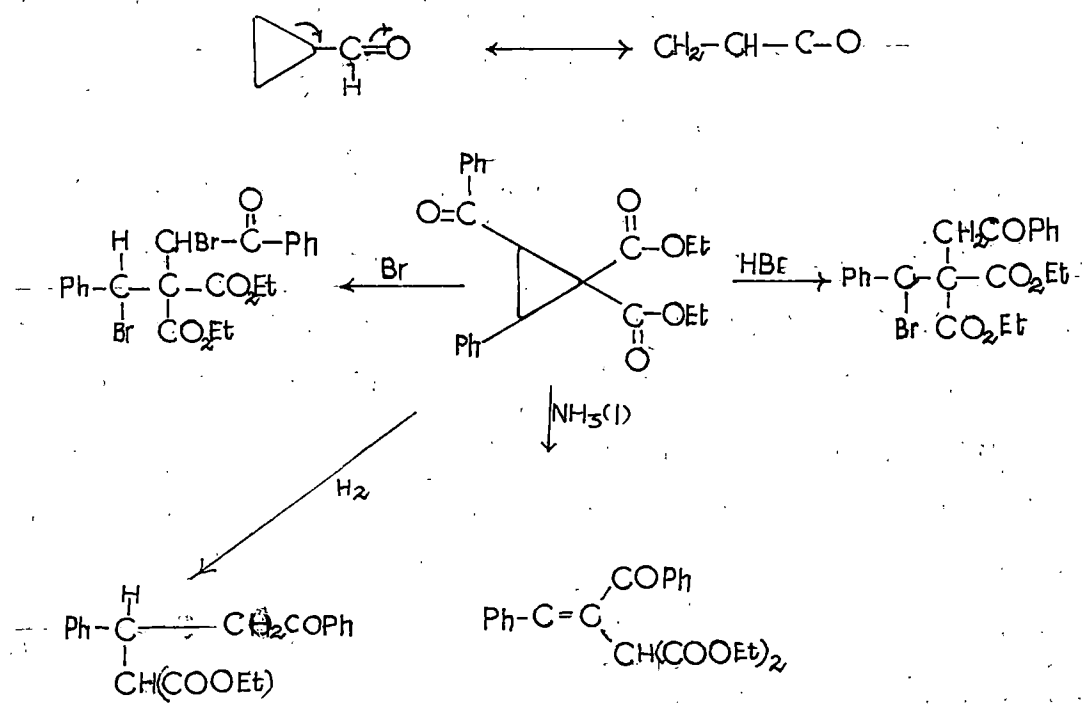
latter, the bond create the impression of being bent. Molecular orbital calculation<sup>5</sup> also show that the carbon-carbon bonds in cyclopropane are not completely  $\sigma$ -in character, the density of the bonding electron is greatest of the C-C connecting line i.e. C-C bonding MO's are not symmetrical about the internuclear axes but are bent giving the appearance of bananas. They also predicted that the C-H bond orbitals in Cyclopropane to have less p-character than normal tetrahedral bonds and hence be more like ethylene than ethane.

Another common feature of the two models is the participation of  $sp^3$ -hybrid orbitals of the C-atoms in C-H bond formations. This is substantiated by experimental facts; for instance, the cyclopropyl C-H bond (like vinylic C-H bonds) are shorter than normal aliphatic C-H bonds<sup>6</sup>, and the  $^{13}\text{C}$ -H coupling constants found for cyclopropane derivatives indicate 32% s-character of the C-H bonding orbitals<sup>7-9</sup>.

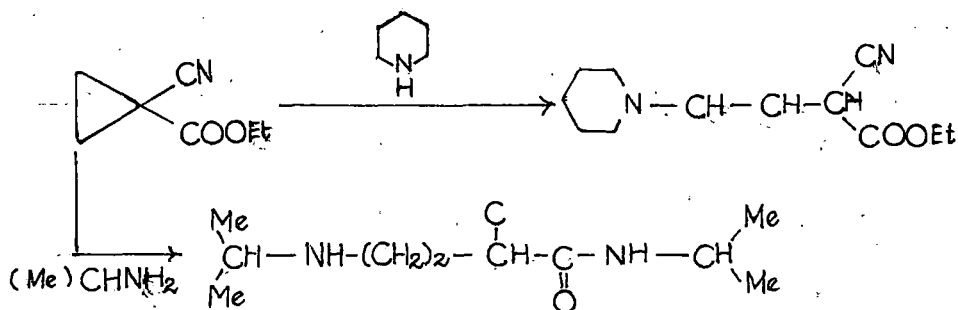
A study of chemical shift<sup>8</sup> in cyclopropane also offers the possibility of giving new insight into the electronic structure of the three membered carbon cycle. A large body of evidence has accumulated which supports the concept that the cyclopropane ring systems possess double bond character. The evidence for double bond character is further supported by measurements of dipole moment, U-V, I.R. spectra, Ionisation potential and chemical results<sup>10</sup>.

**(b) Some reactions of cyclopropane ring compounds:**

Among the cyclic compounds of carbon, cyclopropane and its derivatives in the class of small rings is outstanding by virtue of their unusual structural, spectroscopic and chemical properties. The cyclopropane ring more closely resembles the C=C double bond than the cyclobutane ring. It is a small ring with some "double bond" characteristics. Thus the ring may be hydrogenated to yield propane derivatives. Bromine and iodine react fairly to form 1, 3-dihaloxypropane and halogen acids cause fission<sup>11-13</sup> of the ring giving substituted propyl halides; the manner in which addition takes place is governed by numbers and disposition of the substituted alkyl groups i.e., the Markovnikov's rule is obeyed (enhance electronic transition of  $\pi-\pi^*$  nature of substituents like olefinic, carbonyl groups).

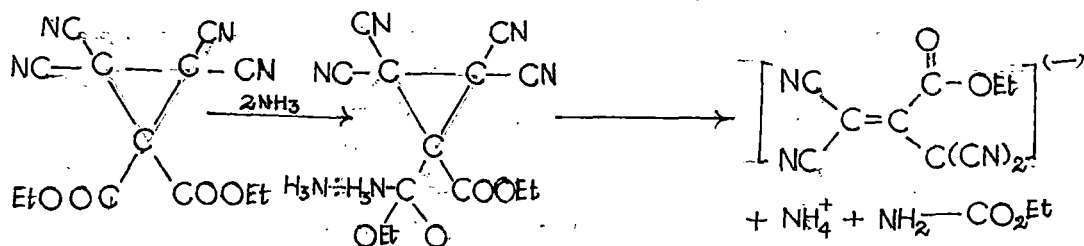


Ring opening addition reactions have been found to take place with various nucleophilic reagents<sup>14</sup> and a series of 1,1-disubstituted (two electrons withdrawing groups) cyclopropane derivatives resulting in 1,1,3-trisubstituted propane derivatives.

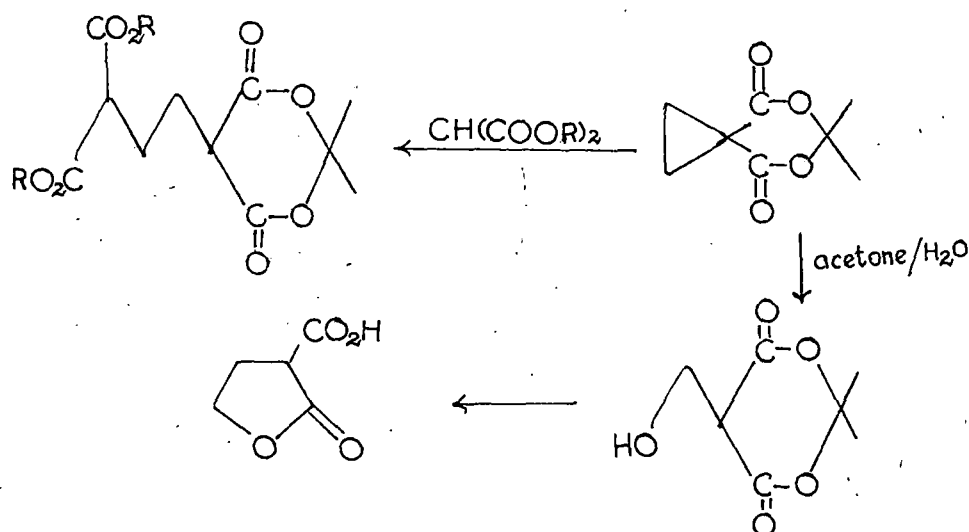


Poly carboxylic esters of cyclopropanes (or similarly functionalized) are generally stable to bases with respect to ring cleavage<sup>14(b)</sup>.

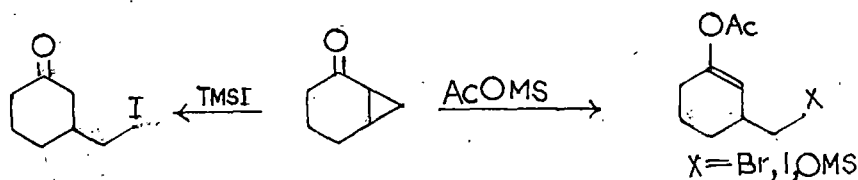
Hydrolysis is often accompanied by decarboxylation but the ring remains intact unless very vigorous reaction conditions are employed. An example of a cyclopropane ring cleavage under very mild conditions<sup>14(c,d)</sup> is cited below.



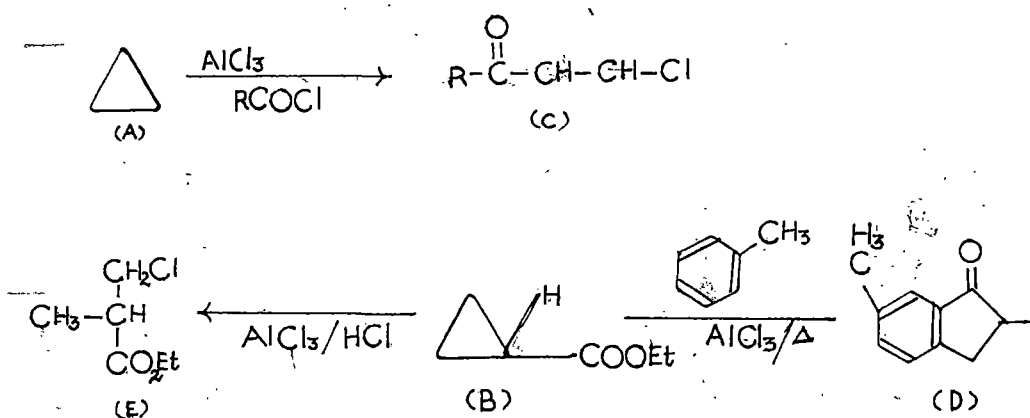
The cleavage of cyclopropyl carbonyl compounds by nucleophilic reagents has also been developed extensively in recent years<sup>15,16</sup>. If sufficiently activated by two electron withdrawing groups such compounds can add various nucleophilic reagents<sup>17</sup>.



Nonactivated cyclopropanes do not react the same way except in special case<sup>15</sup>. Nucleophilic addition to such systems do, however, occur smoothly with the assistance of an electrophile<sup>18-21</sup>. In this way, cyclopropyl ketones are cleaved under mild conditions e.g. by trimethyl silyliodide (TMSI) to  $\gamma$ -iodo-ketones or by acetyl methane sulphonate (AcOMS) together with nucleophiles to give  $\beta$ -substituted enol acetates<sup>21</sup>.



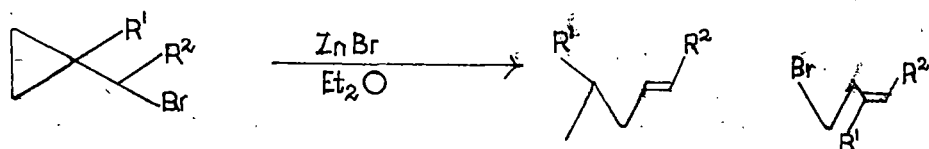
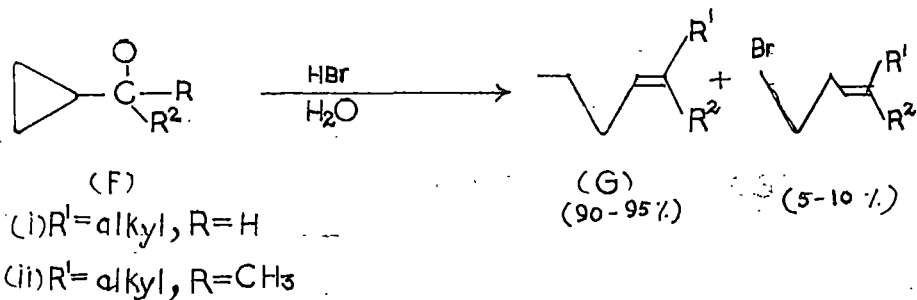
Organic acid in the presence of electrophilic reagent such as  $\text{Et}_2\text{OBF}_3$  converts cyclopropane to propyl ester. When the simple cyclopropane or its derivatives [A] and [B] were treated with anh.  $\text{AlCl}_3$  (Lewis acid) they afford the rearranged products [C], [D] and [E] respectively.



According to Julia et al.<sup>24</sup>, a cyclopropyl  $\alpha$ -hydroxy is treated with 48% hydrobromic acid, secondary alcohol, [F(i)] give the E-olefins [G(i)] with 90-95% stereoselectivity. Treatment of the tertiary alcohols [F(ii)] with magnesium halide in ether also gives E-olefins [G(ii)] in excellent yields<sup>25</sup>.

On the other hand modified procedure of Johnson et al.<sup>26</sup> leads to trisubstituted E-olefins, [I] stereoselectively upon treatment of the secondary cyclopropyl methyl bromides, [H], with zinc bromide in ether.

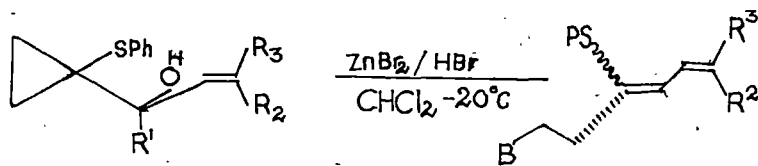




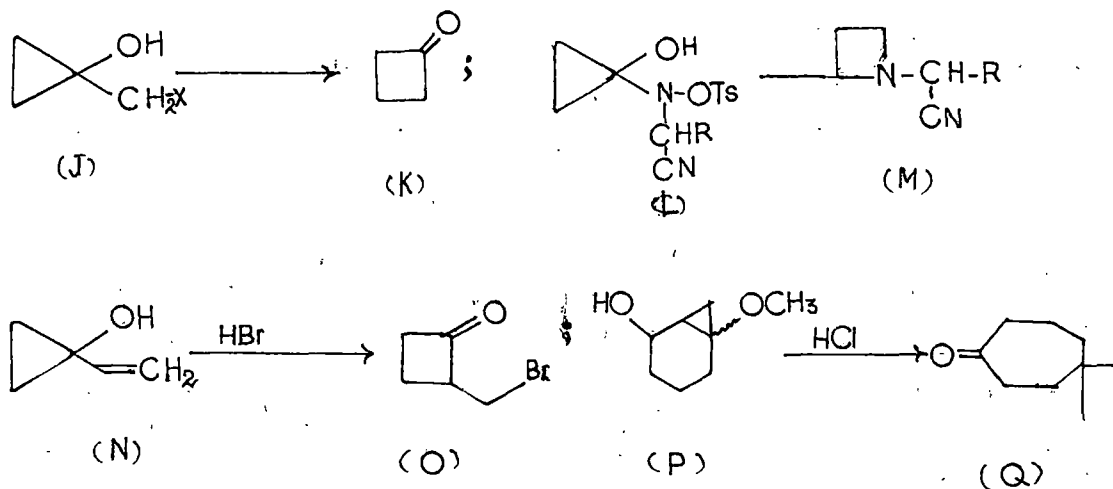
$R^1 = \text{CH}_3, \text{C}_2\text{H}_5$

$R^2 = \text{alkyl, alkenyl}$

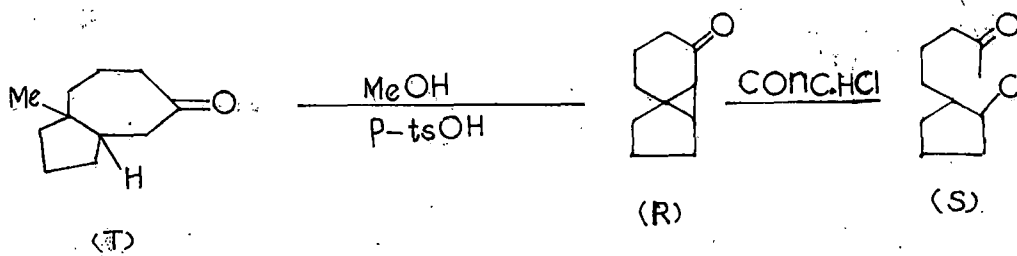
The acid catalyzed rearrangement<sup>27,28</sup> of (phenyl thio-cyclopropyl) vinyl methanol to functionalized conjugated diene is versatile intermediate in synthesis.



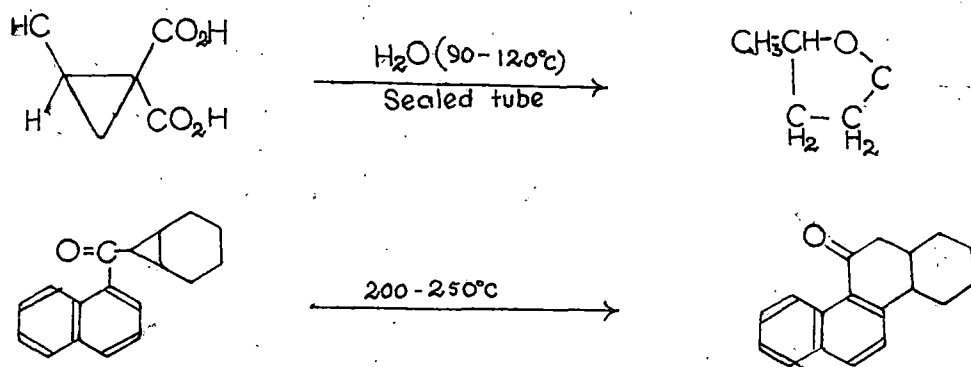
The ring expansion of cyclopropane to higher membered ring derivatives was essential for a number of new synthetic reactions<sup>29-33</sup>, (1-hydroxy cyclopropyl) methyl derivatives, [J], yield cyclobutanone, [K], under appropriate condition<sup>19</sup>. A  $\beta$ -lactam synthesis developed by Hassenman et al<sup>30</sup>, [L  $\rightarrow$  M], is based on the same reaction principle. In a reaction of 1-vinyl cyclopropanol, [N] with electrophilic reagent such as HBr yields derivative of 2-bromo methyl cyclobutanone<sup>31</sup> [O].



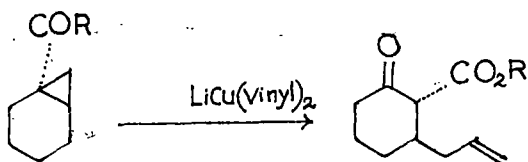
Similarly the following compounds, [R], when treated with electrophilic reagents such as conc. HCl, or methanolic P-tSOH, it gives the rearranged products, [S] and [T] after cleavage of the cyclopropane ring.



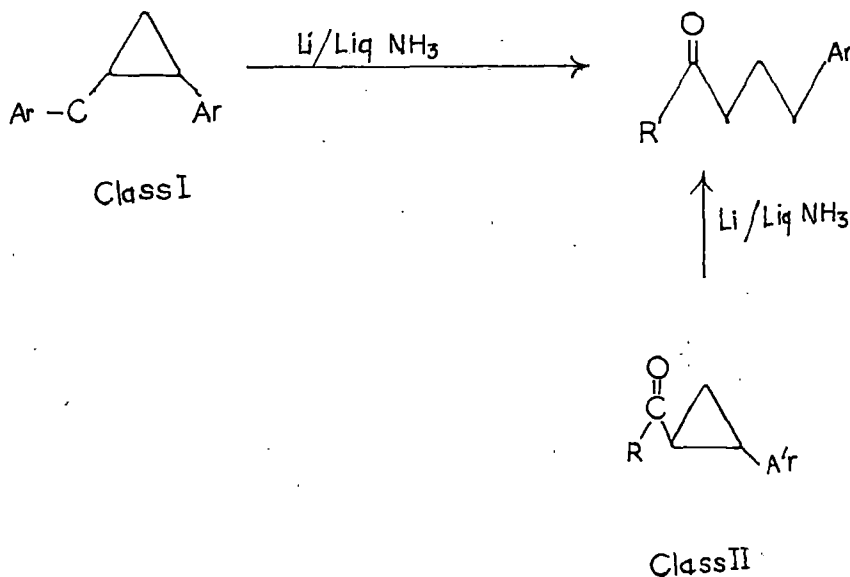
Under the thermal conditions<sup>34,35</sup> (without any acid-base treatments) a few cyclopropane derivatives may be rearranged to the following cleaved products.



A simple reductive cleavage<sup>36,37</sup> of cyclopropyl ketone has been effected by irradiating<sup>38</sup> a methanolic solution of a cyclopropyl ketone and tri-n-butyl hydride with ultraviolet light. Metal reductions have also been done to cleave C-C bonds of cyclopropyl ketones<sup>39</sup>.

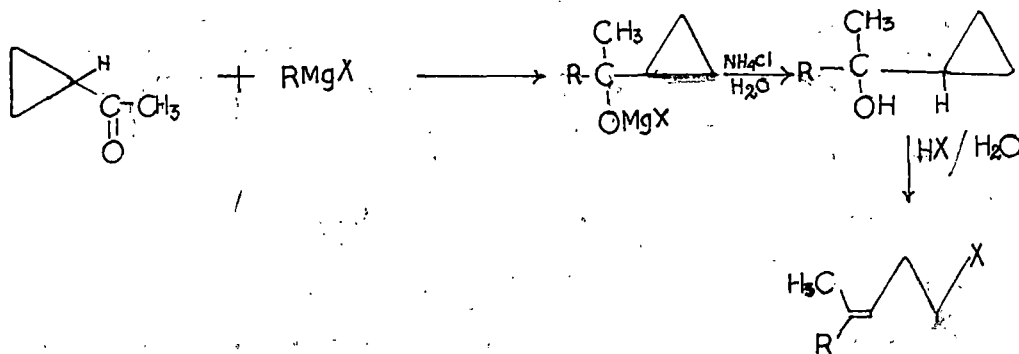


Aryl substituted cyclopropyl ketones are cleaved to acyclic ketones with  $\text{Zn}/\text{ZnCl}_2$  or with  $\text{Zn}$  in refluxing alcohol. For the reductive cleavage<sup>40</sup> of alkyl and aryl cyclopropyl ketones, lithium in liquid ammonia has been employed. There are three classes of cyclopropyl ketones which have been cleaved by this method as shown below:



Jilia et al<sup>24</sup> had isolated cyclopropane carbinol by the grignard reaction of cyclopropyl ketone, acidified with 48% hydrobromic acid. Modification of this method for the preparation of homo-allylic bromides and iodides Biernacksi<sup>41</sup> hydrolysed the carbinol

product with aqueous hydrobromic acid or hydroiodic acid.



In the course of Eli Breuer's report<sup>42</sup> on the homoallylic rearrangement of cyclopropyl-carbinyl borate, it is observed that aryl cyclopropyl ketone (U) is reduced by diborane to the corresponding benzyl cyclopropane (V) without cleavage of cyclopropane ring. It is further reported that the addition of 10% (molar proportion) Boron trifluoride to the reaction mixture indeed catalyzes hydrogenolysis in many other cases of cyclopropyl aryl ketone and cyclopropyl aryl methyl carbinols (W) (with the exception of anisyl cyclopropyl ketone).

