

class — U.G. sem — III

paper — MTC-3

Unit — 1

Topic — Reaction Intermediates

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Reaction Intermediates:

Introduction:

In organic reactions, reactants do not change in one step. The change normally takes place via an intermediate product, which is short-lived. From the intermediate product, the reaction passes on to the products. Various reaction intermediates that we come across in the study of organic reactions are:

[i] Carbonium ion [or carbocation]

[ii] Carbanion

[iii] Free radical

[iv] Carbene

[v] Nitrene

[vi] Arynes [Benzynes]

CARBENES:

These are defined as the neutral organic species containing a divalent carbon atom having a sextet of electrons but no charge on it. For example,

[a] $:\text{CH}_2$

Methyl carbene

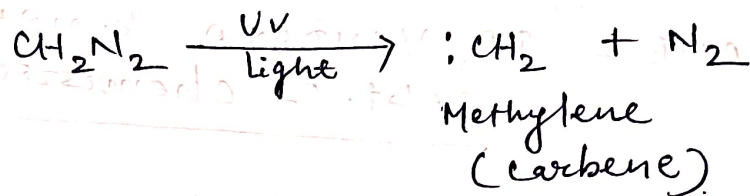
[b] $:\text{CCl}_2$

Dichlorocarbene

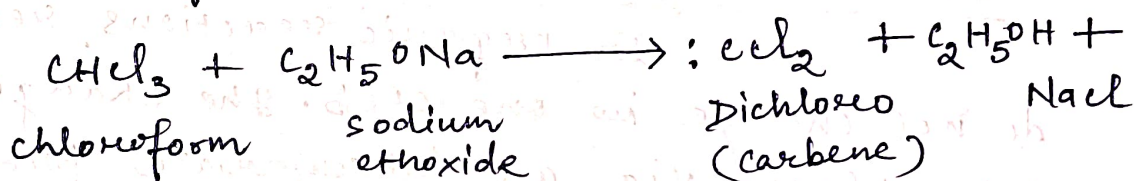
Formation of carbenes :

carbenes can be generated by the following methods :

a.] By the action of UV light on diazomethane

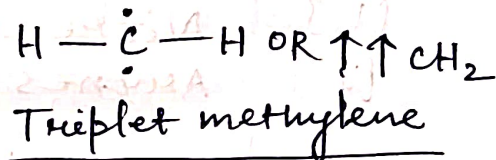
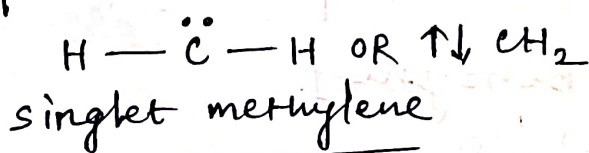


b.] By the action of sodium ethoxide on chloroform.

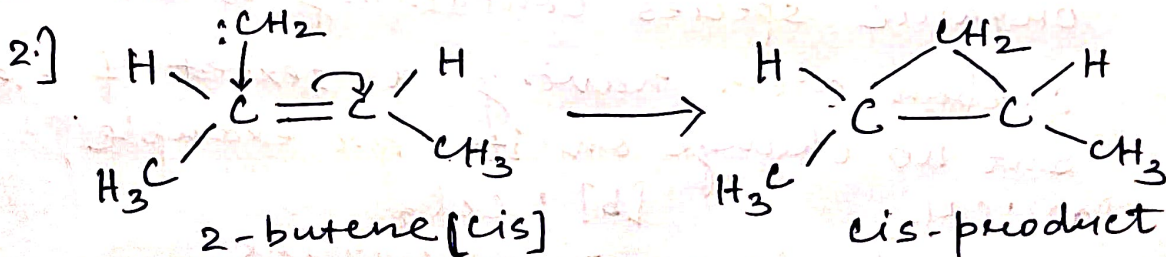


stability of carbenes :

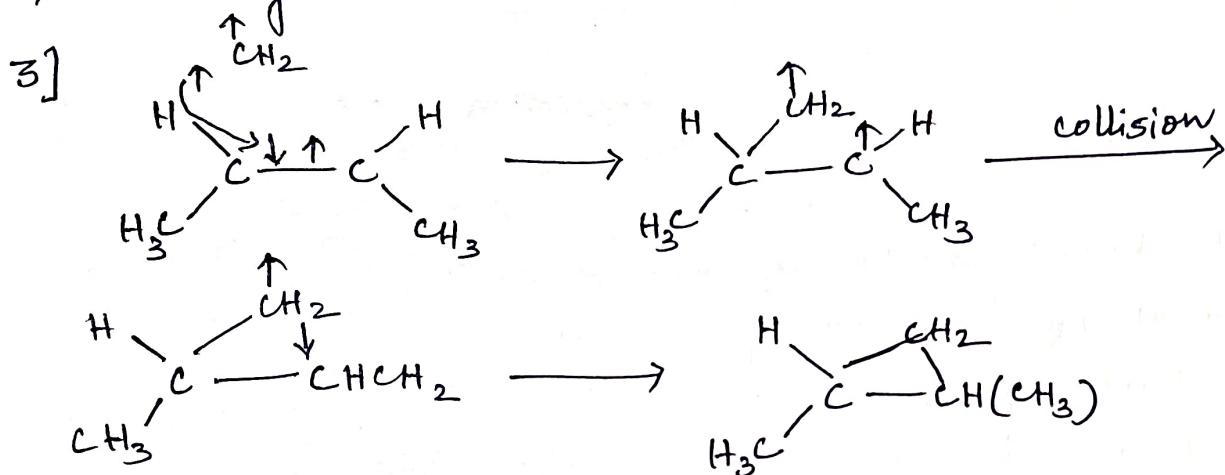
1.] The two unbonded electrons of a carbene may be either paired or unpaired. When the two electrons on the carbon atom are ~~un~~paired, then it is called singlet carbene. In the triplet state, it is called a biradical as the two electrons on carbon atom are unpaired.



In the triplet state, carbene is relatively more stable as it has lower energy content.



The singlet and triplet species can be distinguished by the common addition reaction of carbene to double bond to form cyclopropane derivatives. The addition of singlet species to cis-butene forms a cis-product. The reason is that the movement of two pairs of electrons occurs either simultaneously or with one rapidly succeeding the other.



In the case of triplet carbene, the two unpaired electrons cannot form a new covalent bond simultaneously as they have parallel spins. The bond formation is possible by collision process when one of the electrons can reverse its spin.

During this time of collision, there is a free rotation around C-C single bond and the product formed is a mixture of cis and trans isomers. It has been found that the difference in energy between the singlet and the triplet methylene is about 37-46 kJ/mole.