

Study material: For B.Sc. part-III

Subject: Organic Chemistry, paper VII

Topic: General Principles

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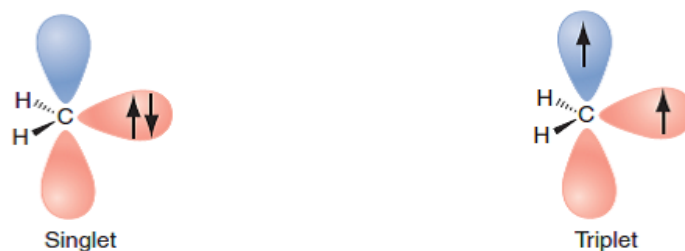
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Other types of reaction intermediates:

Carbene: Carbenes are uncharged divalent carbon derivatives with two unshared electrons. Carbenes are highly reactive species. The parent species (CH_2) is usually known as methylene. There are two types of carbene.

Singlet carbene: If two nonbonded electrons are paired (i.e. both electrons go into one orbital with antiparallel spin), the carbene is a singlet. In singlet carbene the carbon is sp^2 hybridized. Singlet carbene is diamagnetic.

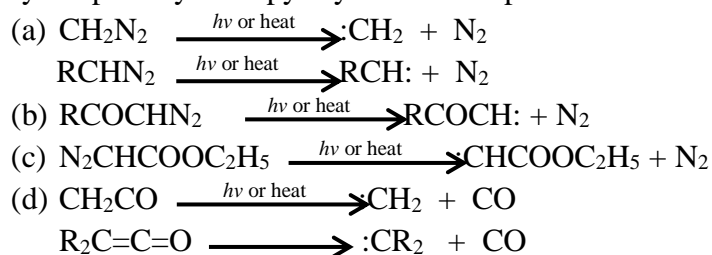
Triplet carbene: If, both nonbonded electrons are unpaired (i.e. two electrons go into different orbital with parallel spin), the carbene is a triplet. The carbene centre is sp hybridized in triplet carbene. Triplet carbene is paramagnetic – a diradical. Singlet methylene should be diamagnetic and triplet methylene be paramagnetic – a diradical.



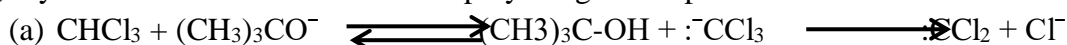
- Triplet carbenes are generally stable in the gaseous state, while singlet carbenes occur more often in aqueous media.
- Alkyl and dialkyl carbenes are generally triplets. Substituents on carbene having electron pair donor ability tend to stabilise the singlet state by electron release into the vacant orbital.
- Carbenes being electron deficient molecules are generally electrophilic.
- Singlet carbenes generally participate in cheletropic reactions. Singlet carbenes with unfilled p-orbital should be electrophilic. Triplet carbenes can be considered to be diradicals, and participate in stepwise radical additions.

Generation of carbene: Carbenes may be generated by following two methods

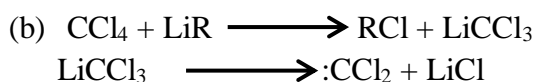
(1) By the photolysis or pyrolysis of the aliphatic diazo compounds or ketenes



(2) By the action of base on a suitable polyhalogen compound.



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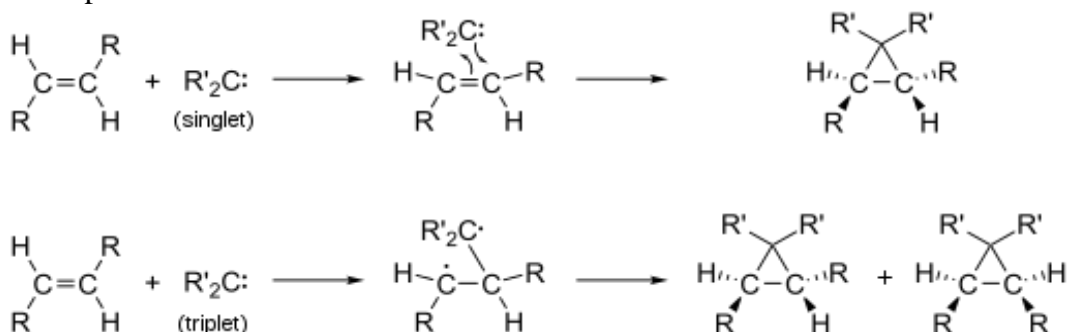


Reactions of carbene: Carbenes undergo several important reactions

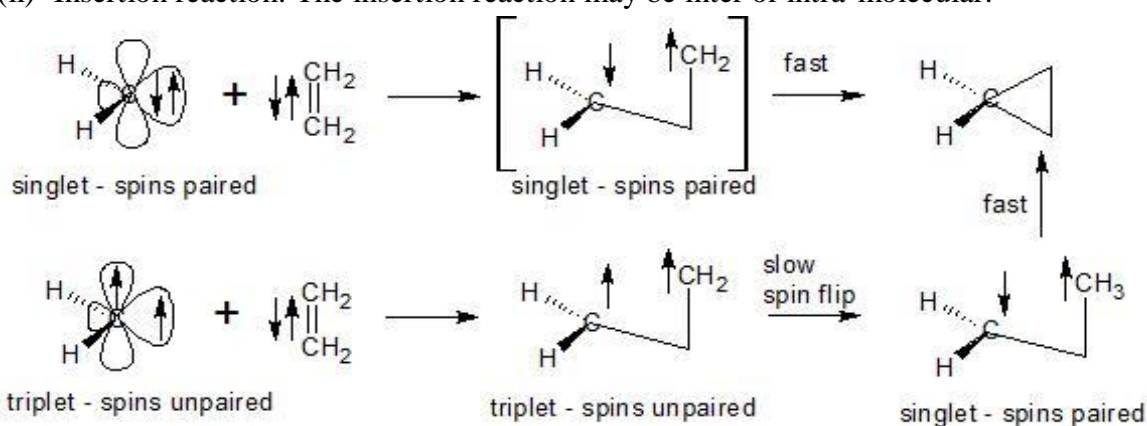
(i) Addition to olefins: Carbenes add on alkenes to form cyclopropane derivatives.

- Singlet carbene add to alkene in a stereospecific manner i.e. stereochemistry of the alkene is retained in the cyclopropane.
- Conversely, the triplet carbene adds on alkene in a non-stereospecifically with the result both the products are formed.

Example:



(ii) Insertion reaction: The insertion reaction may be inter or intra-molecular.



(iii) Ring expansion reactions: Ring expansion reaction involve the addition of a halogenocarbene across a double bond followed by rearrangement.

