CARBENES AND NITRENES REACTION INTERMEDIATES

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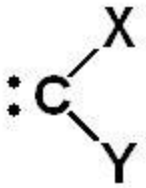
What are Carbenes? Nitrenes?

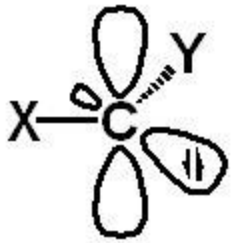


- **Neutral, divalent carbon species containing six valence electrons**

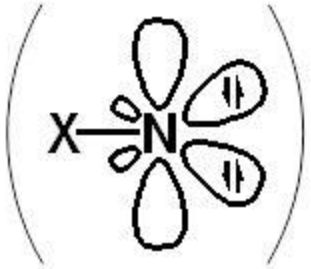
- **Neutral, monovalent nitrogen species containing six valence electrons**

Electron deficient  ***Highly reactive***

Singlet and Triplet States

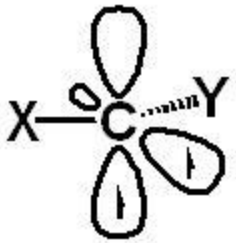


Singlet

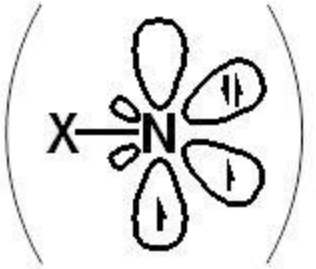


Singlet

- sp^2 hybridized carbon
- non-bonding electrons have opposite spin - occupy an sp^2 orbital
- XCY angle 100-110°



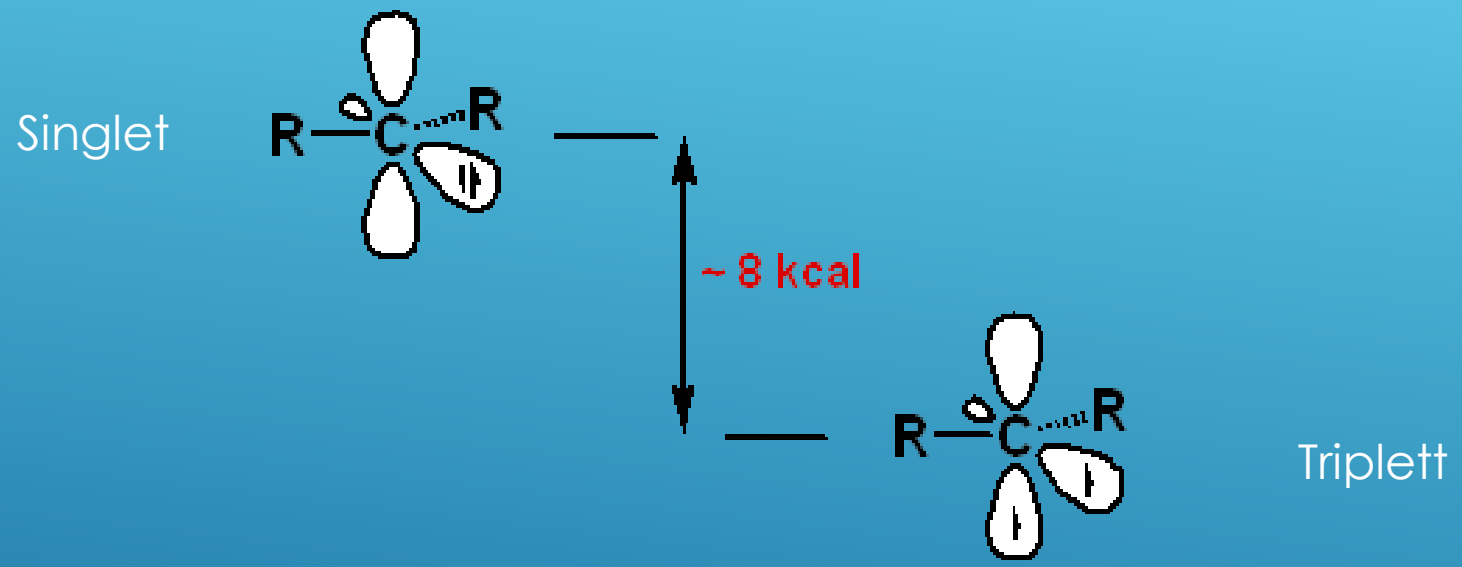
Triplet



Triplet

- sp^2 hybridized carbon (or sp?)
- non-bonding electrons have same spin – occupy an sp^2 and p orbital
- XCY angle 130-150°

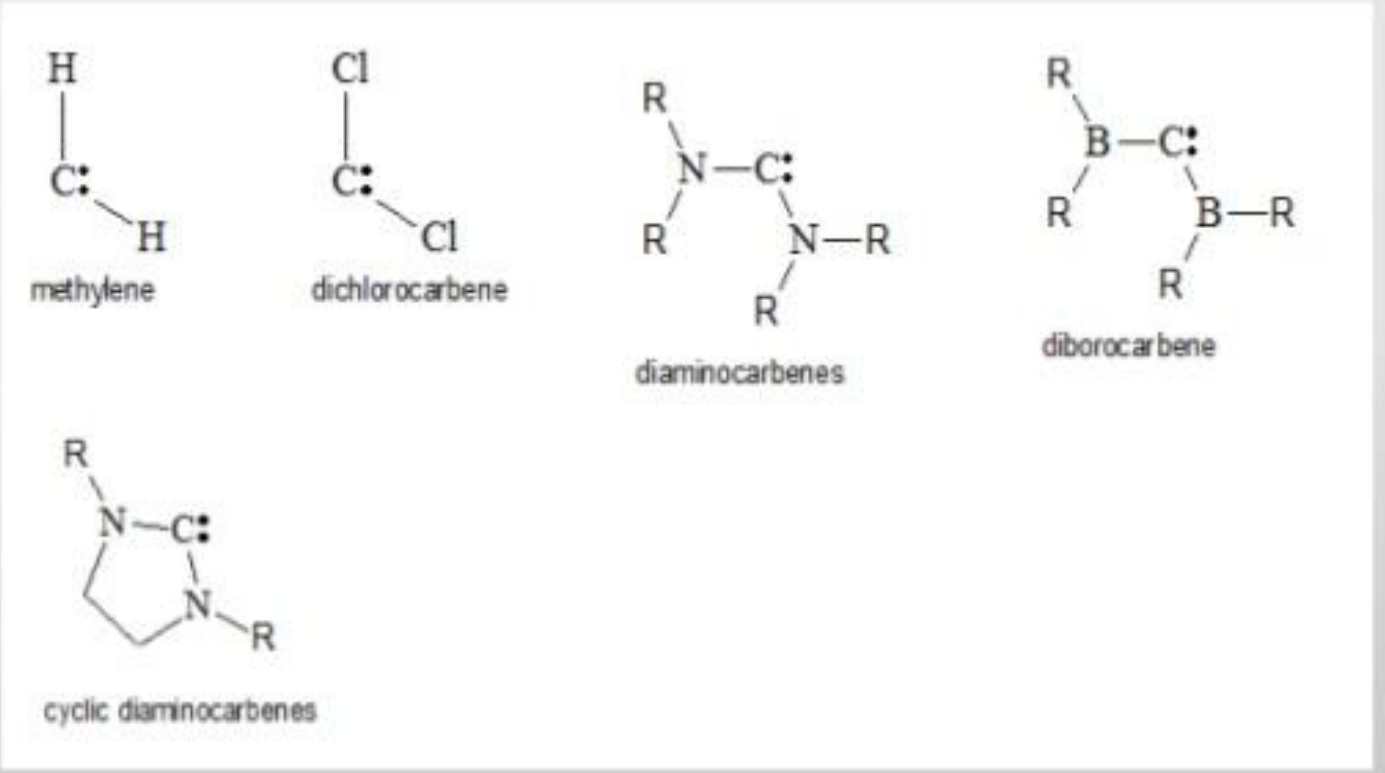
Triplet state is more stable than singlet state



Structure and bonding

- Singlet carbenes are spin-paired. This molecule adopts an sp^2 hybrid structure.
  - Eg- :CH2 :CHPh :CHPh2 :CHR
- Triplet carbenes have two unpaired electrons.
- Most carbenes have a nonlinear triplet ground state, except for those with nitrogen, oxygen, or sulfur atoms, and halides directly bonded to the divalent carbon.
  - Eg:- :CCl2 :CHCl :C(OMe)2

Carbene Examples

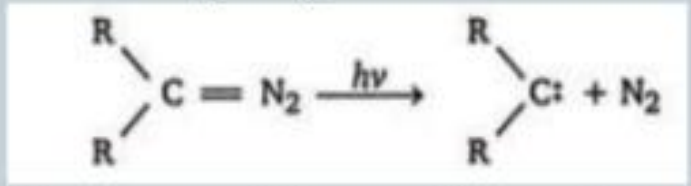


5.Generation Of Carbenes:

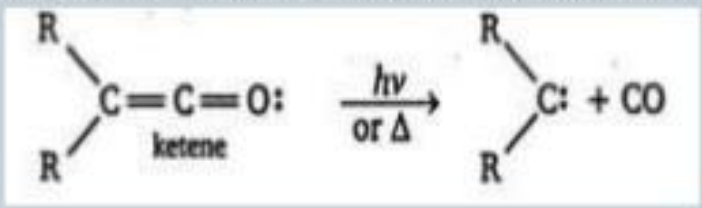
(a) From aliphatic diazo compounds:

Aliphatic diazo compounds can be decomposed either photolytically or thermally to generates carbenes.

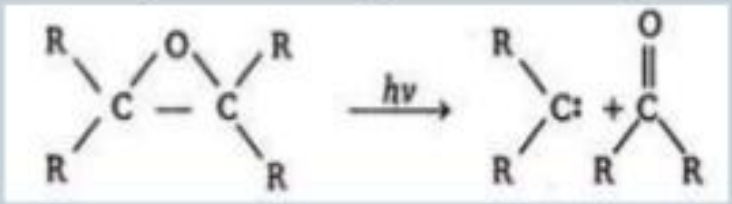
(b) From ketenes:



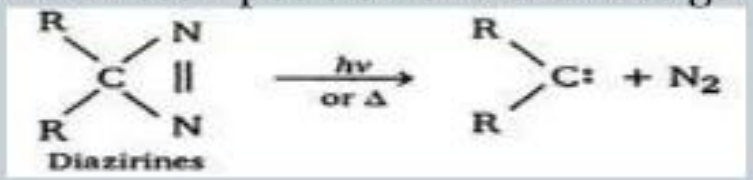
Ketenes can be decomposed thermally or photolytically to generate carbenes.



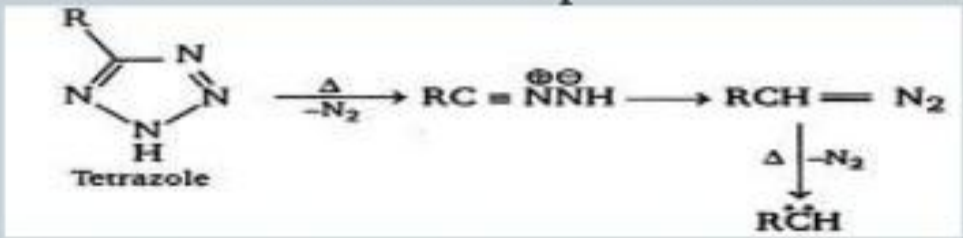
(c) From epoxides: Photolytic decomposition of epoxides to carbene.



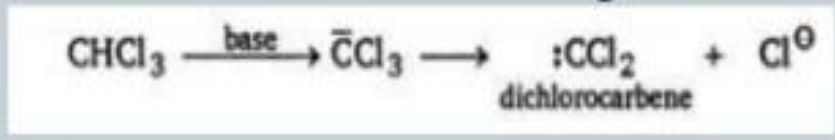
(d) From diazirines:Decomposition of diazarines generates carbenes.



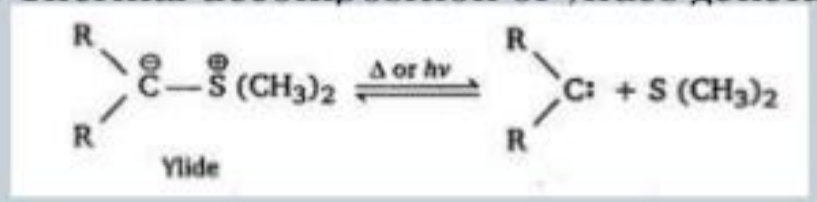
(e) From tetrazoles:Thermal Decomposition of tetrazoles generates carbenes.



(f) From alkyl halide:This method is used for generation of chlorocarbenes.



(g) From ylides: Thermal decomposition of ylides generates carbenes.



Reactions of carbenes

- Carbenes are highly electrophilic species.
- Three major classes of carbene reactions.

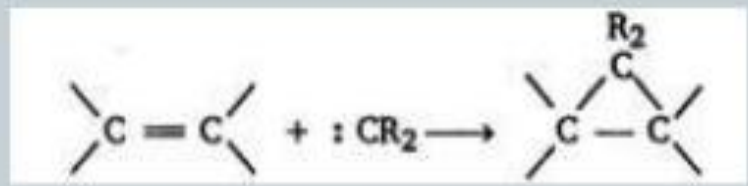
(1) Carbene insertions

(2) Carbene additions

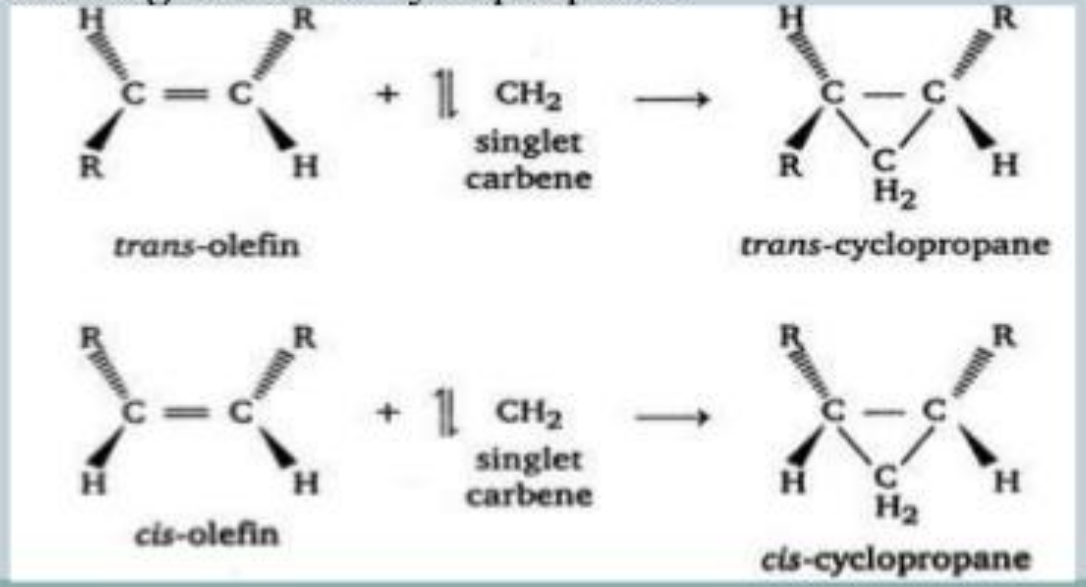
(3) Carbene rearrangements

6.Reactions Of Carbenes:

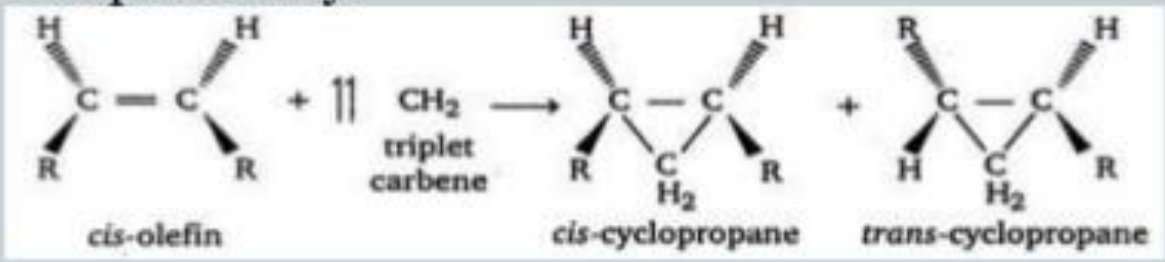
(a) Cycloadditions: Carbenes add on an olfinic double bond giving a cyclopropane derivative



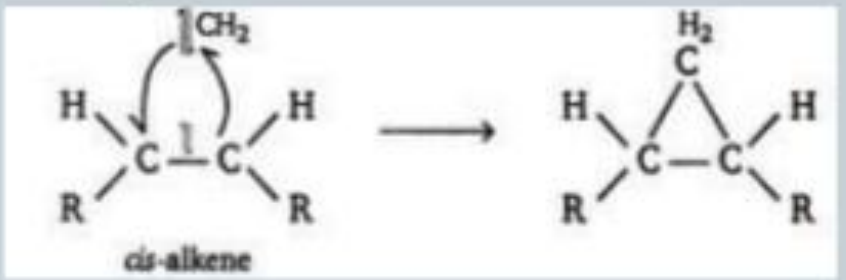
->When the reaction is perfomed in liquid medium singlet carbene is formed, which adds on in stereospecific way. Thus, cis-alkene gives cis-cyclopropane and trans-alkene gives trans-cyclopropane.



->In gaseous medium, the attacking species is triplet carbene, which does not add stereospecifically.



->Addition of singlet carbene to an olfin occurs in a concerted manner and therefore is stereospecific.



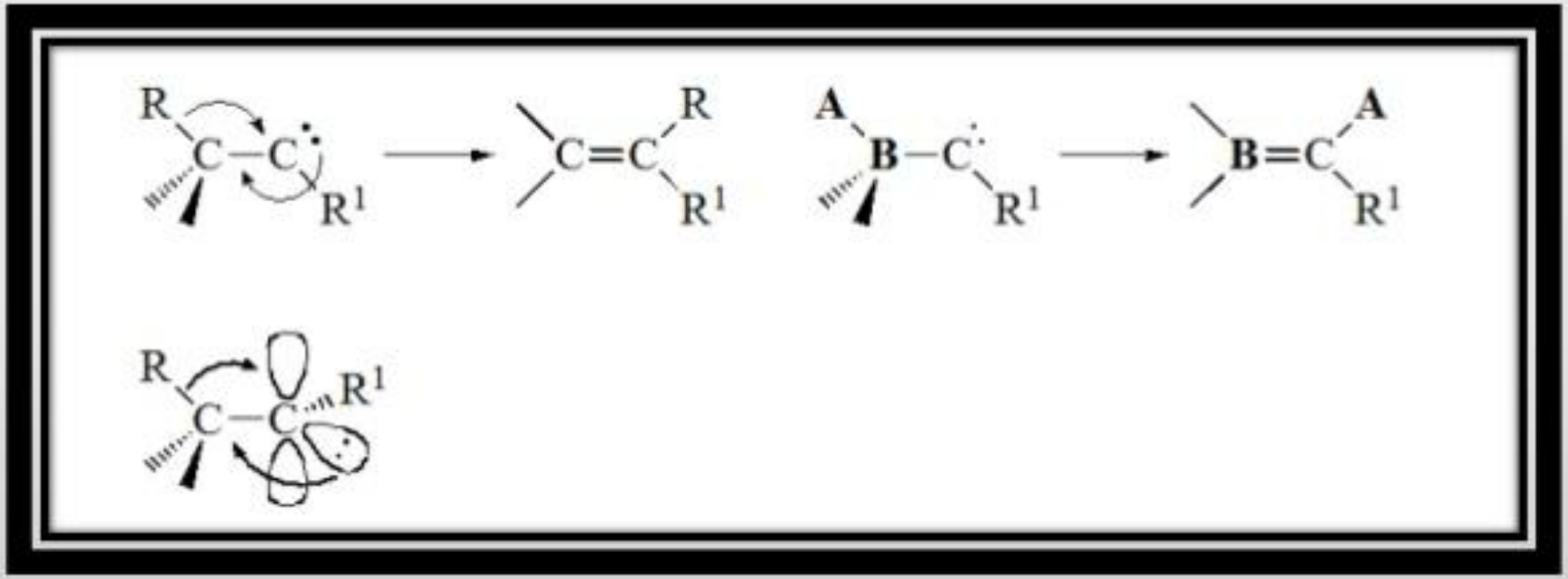
->In triplet carbene the reaction place in two place:

Carbene……..

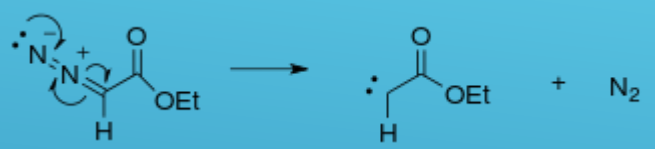
- Insertion

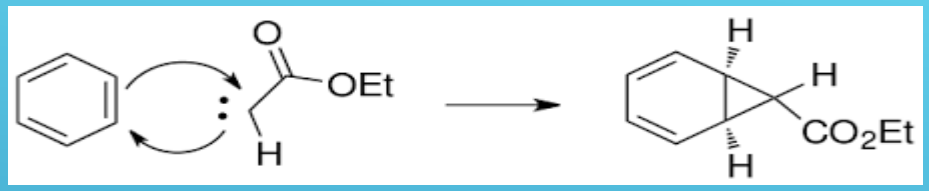
- Addition to multiple bonds

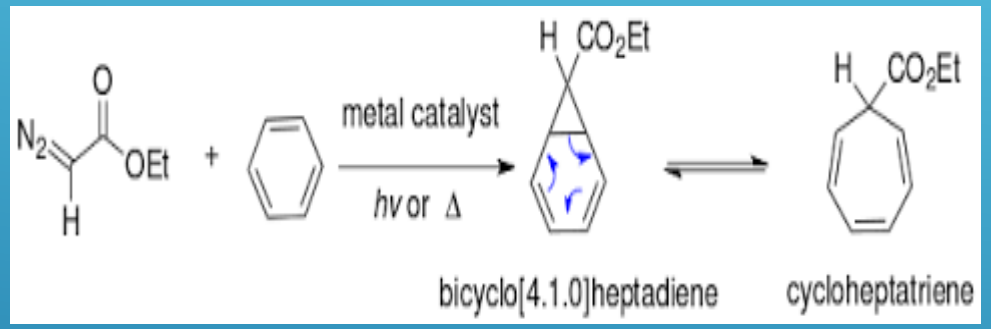
Rearrangement

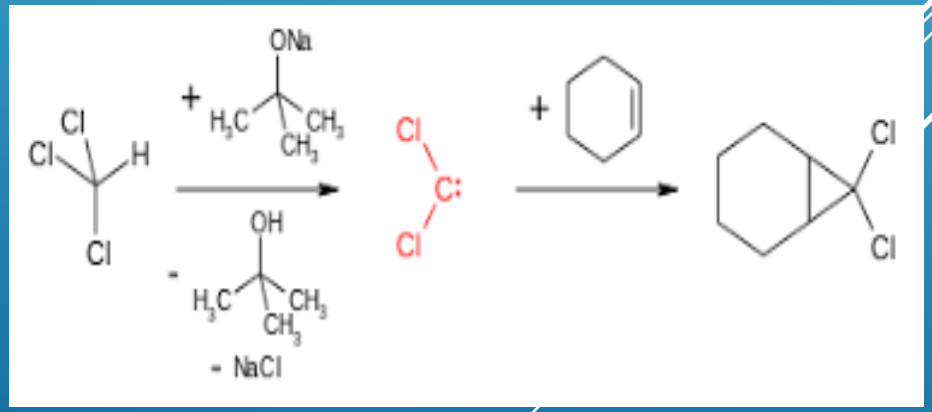


RING EXPANSION REACTION





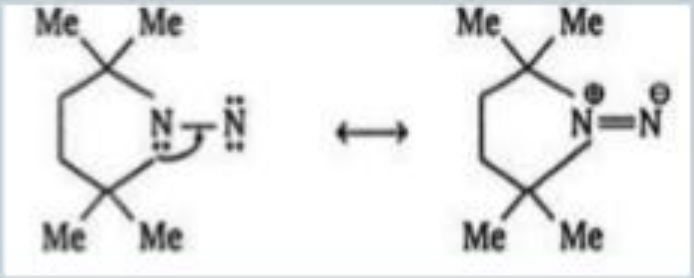




(2) NITRENES

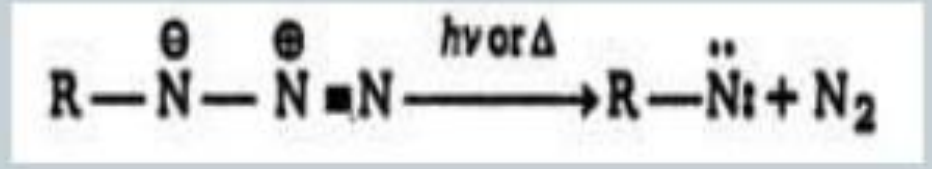
1. Nitrenes are derivatives of the molecule :NH in which nitrogen is monovalent.The nitrogen atom in nitrenes has a sextet of electrons.
2. Similar to carbene, singlet and triplet states are possible for nitrenes.

3. **Stability of Nitrenes**: As nitrogen is more electronegative it holds its electron closer to the nucleus which decreases energy and increases stability.

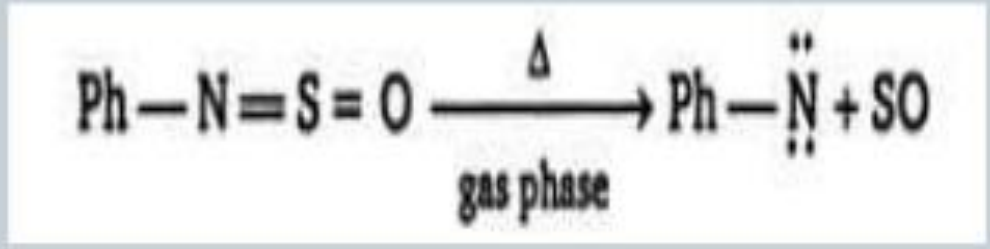


4.Generation Of Nitrenes

(a) From azides: This is most common method for the generation of nitrenes.



(b) From sulfinylamines: Pyrolysis of sulfinylamines generates nitrenes



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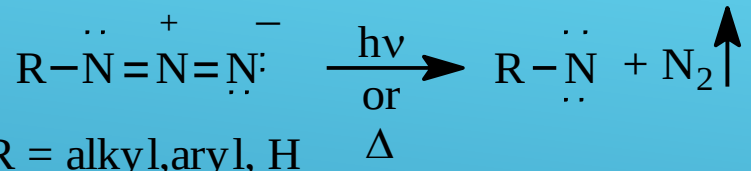
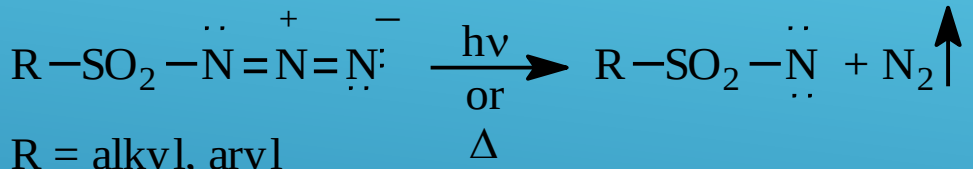
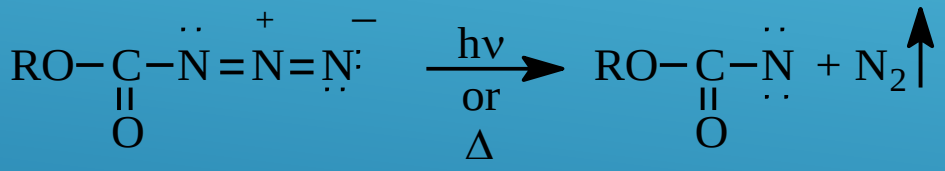
a) 

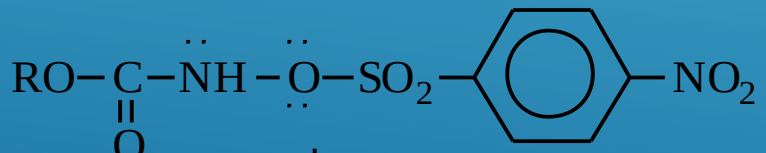
R = alkyl,aryl, H

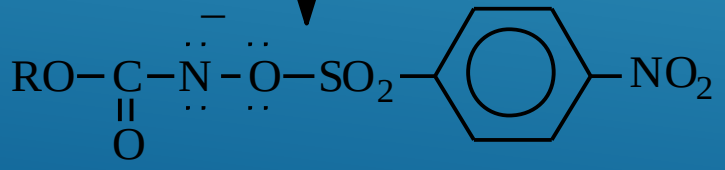
b) 

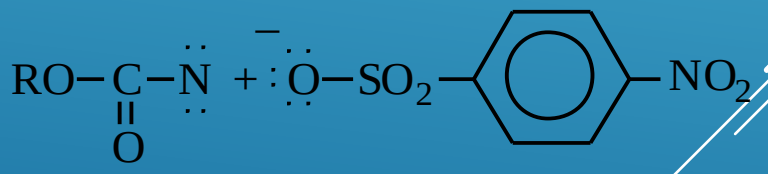
R = alkyl, aryl

c) 

R = alkyl, aryl

d) 

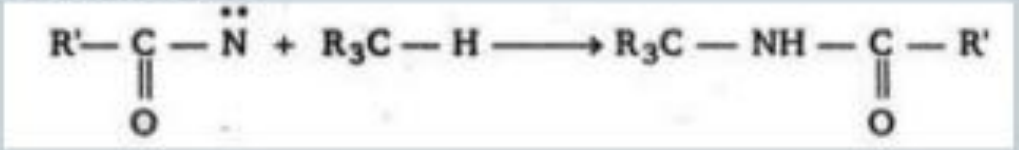




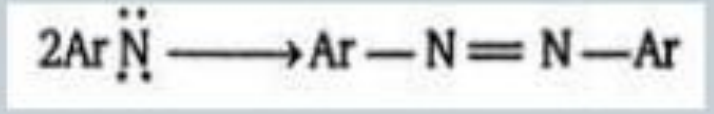
(nosylate)

5. Reactions Of Nitrenes:

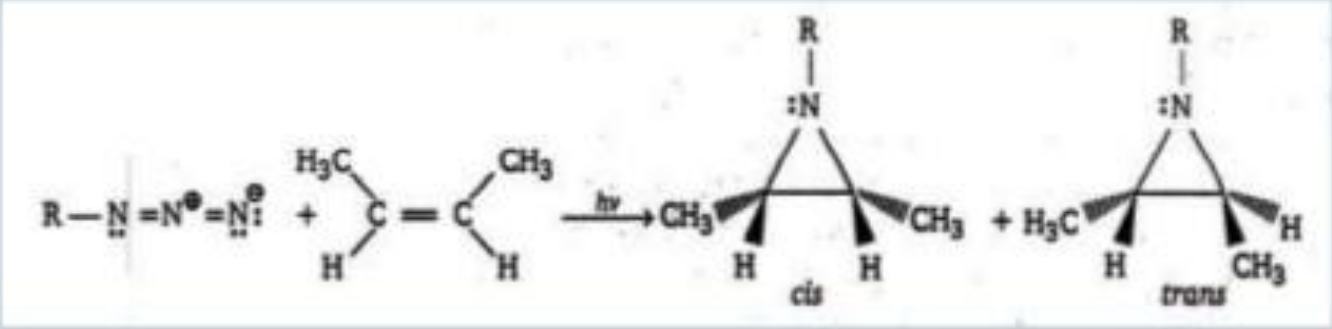
(a) Insertion: Nitrenes, particularly acyl nitrenes and sulfonyl nitrenes can insert into C-H bonds.



(b) Dimerization: The dimerization of nitreres give azobenzene.

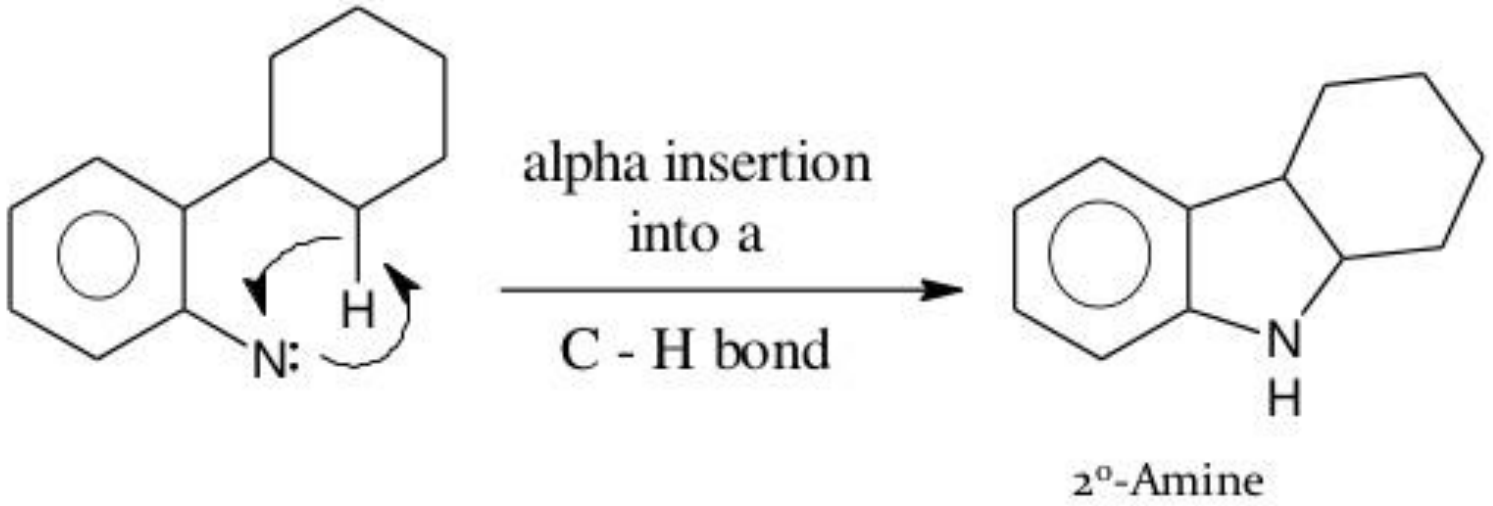


(c) Cycloaddition of alkenes: Addition of inert solvent converts singlet nitrenes to triplet nitrenes and reaction becomes less streospecific.



REACTIONS OF NITRENES

- Singlet nitrene undergoes a σ-insertion to give 2^0 - amines. For eg;



2°-Amine

- π- Insertion of nitrenes into a C=C bond gives aziridines.

Singlet Nitrene

- Acyl nitrenes undergo skeletal rearrangement to give alkyl isocyanates.this rearrangements is involved in Crutius and Hoffmann rearrangements.

Acyl nitrene

Alkyl isocyanate

Thank You