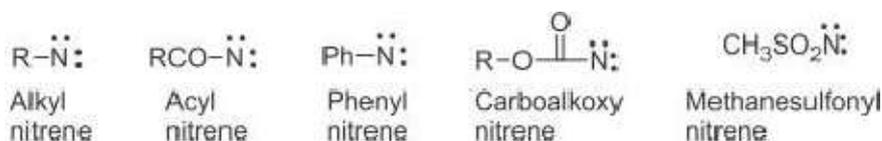


**Nitrene:**

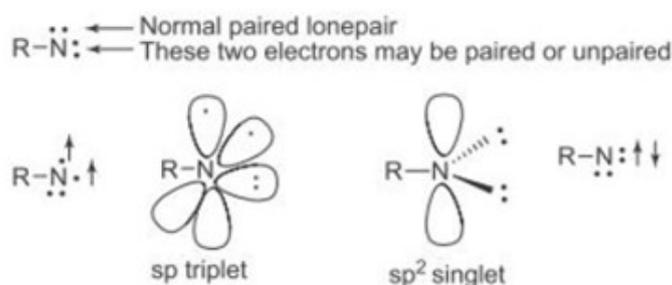
A **nitrene** or **imene** ( $R-\dot{N}$ ) is the nitrogen analogue of a carbene. The **nitrogen** atom is **uncharged**; it has **only six valence electrons**. It is therefore considered an **electrophile**.

**Examples:****Structure of Nitrene:**

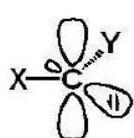
**Simple nitrene has:**

- Singlet state,  $sp^2$**  with **non-bonding electrons have an opposite spin** in  **$sp^2$  orbital**.
- Triplet state,  $sp$**  with **non-bonding electrons has the same spin** in  **$sp^2$  orbital and p orbital**.

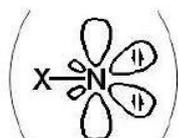
The triplet state is lower in energy than the singlet state.



### *Singlet and Triplet States*

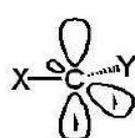


**Singlet**

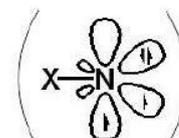


**Singlet**

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



**Triplet**

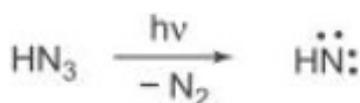
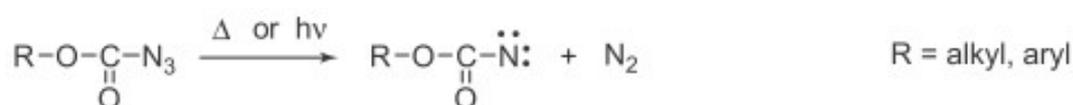
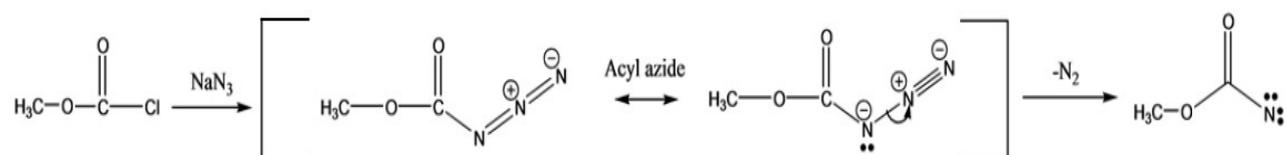
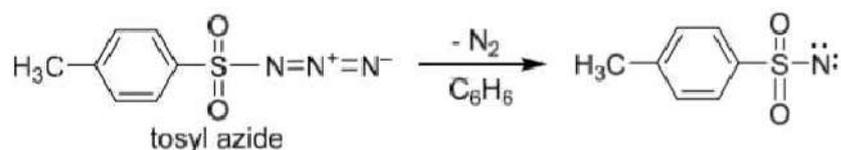
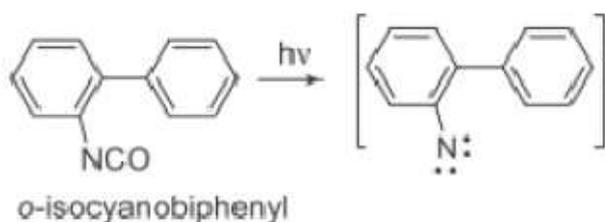
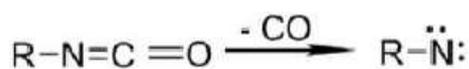


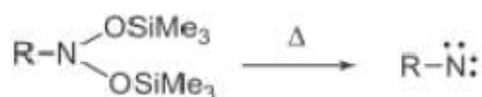
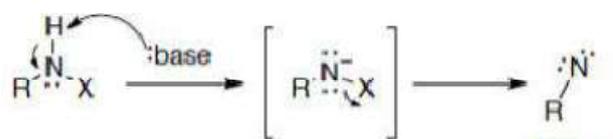
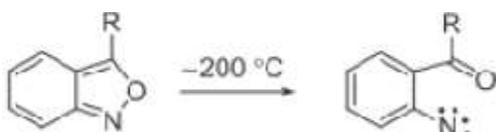
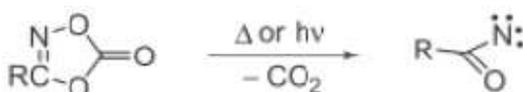
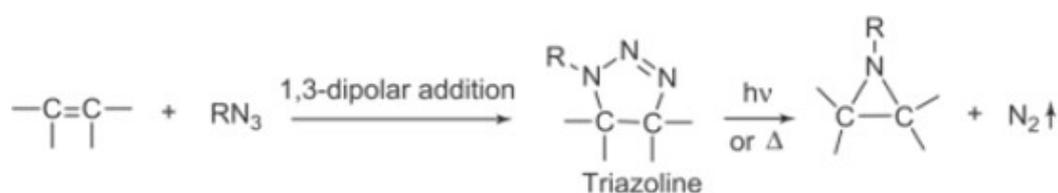
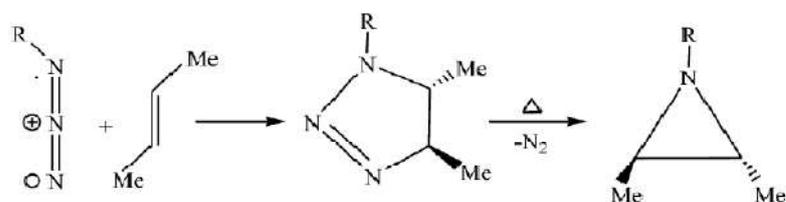
**Triplet**

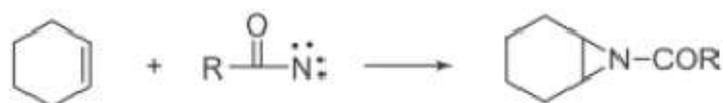
- $sp^2$  hybridized carbon (or sp)
- non-bonding electrons have same spin - occupy an  $sp^2$  and p orbital
- XCY angle 130-150°

**Formation of Nitrene:**

**Four** general methods are used for the generation of nitrene:

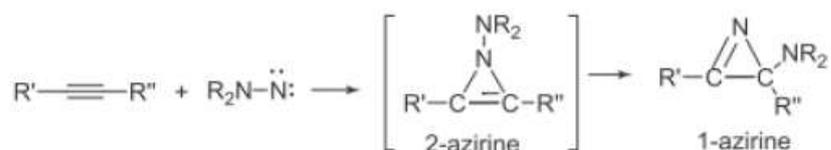
**1- Thermolysis or Photolysis of azides.****Examples:****Mechanism:****2- From isocyanates with expulsion of CO.****Examples:**

3- From  $\alpha$ -elimination.Examples:4- From heterocyclic compounds.Examples:Reactions of nitrenes:1- Cycloaddition with alkenes.Examples:

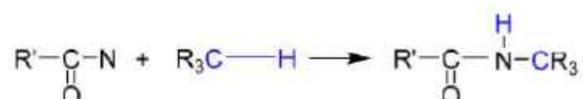


## 2- Cycloaddition with alkynes.

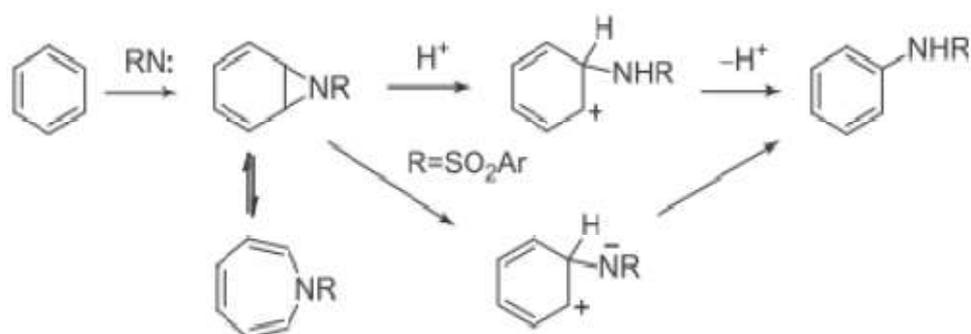
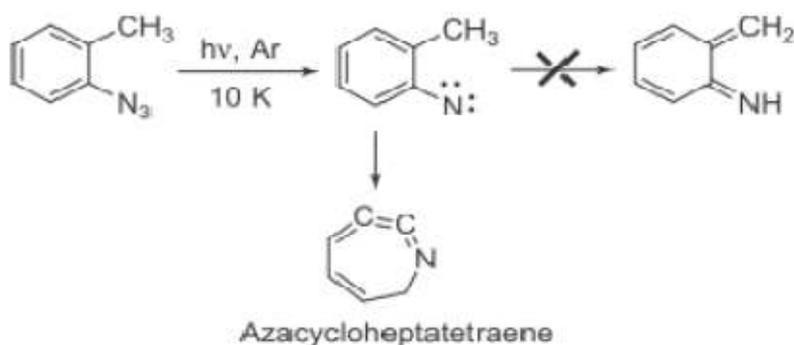
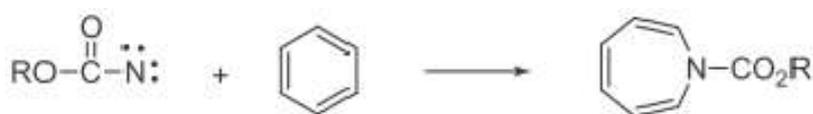
### Example:

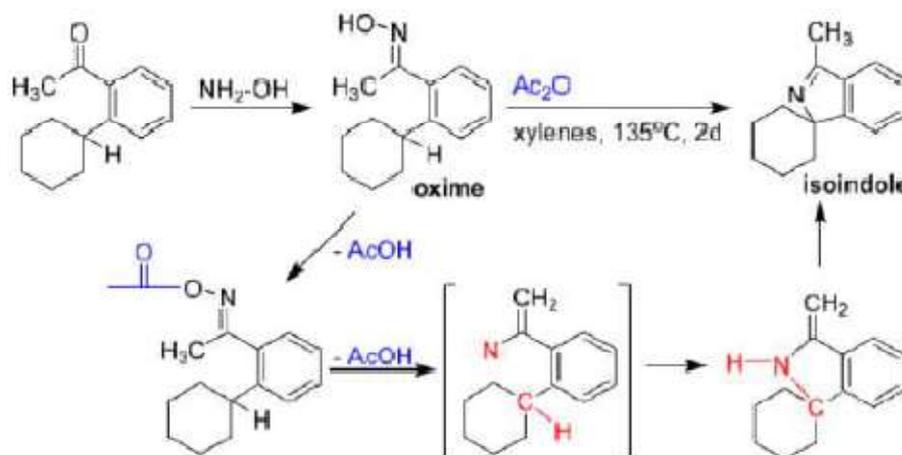


## 3- Insertion reaction of nitrenes (ring expansion): (nitrene C-H insertion) a nitrene can **easily insert** into a **C-H bond** yielding an **amine** or **amide**.



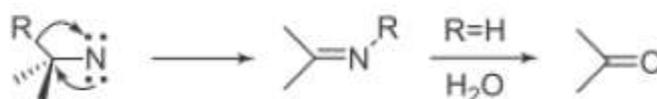
### Examples:





#### 4- Rearrangement of nitrenes:

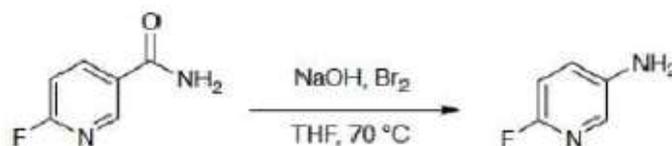
##### a- 1,2- hydrogen shift:



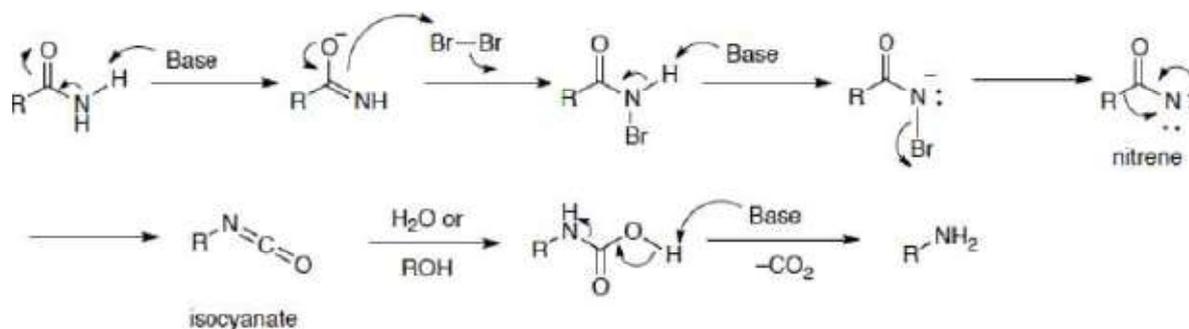
##### Example:



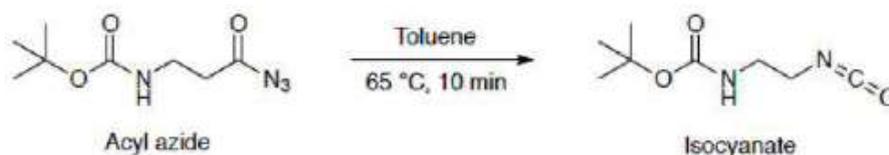
##### b- Hoffman rearrangement:

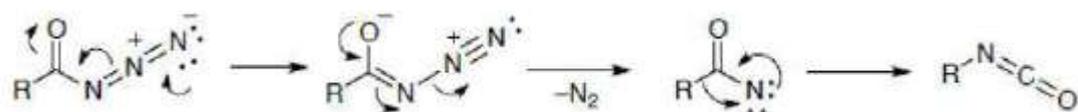
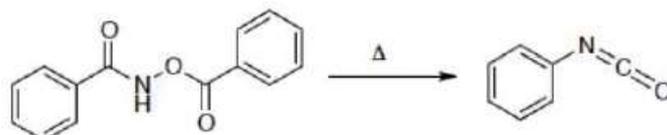
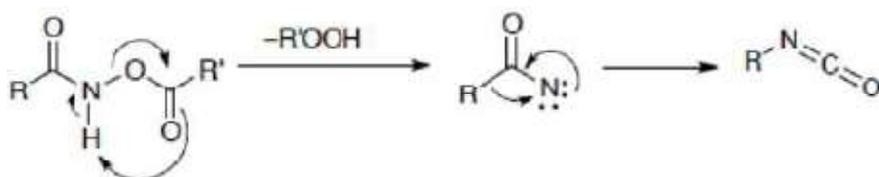
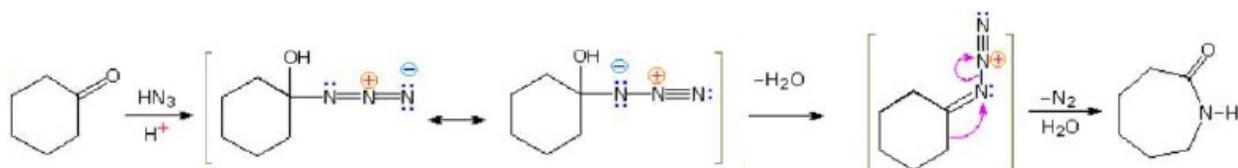


##### Mechanism:



##### c- Curtius rearrangement:



**Mechanism:****d- Lossen rearrangement:****Mechanism:****e- Schmidt rearrangement of ketones:****Mechanism:**