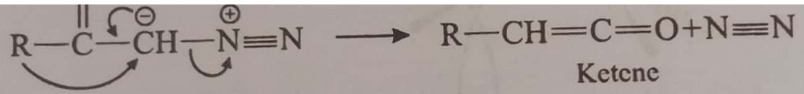
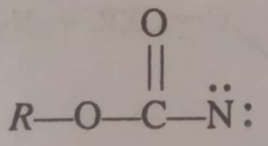


3.12.5 Nitrenes

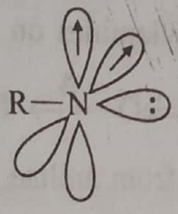
The nitrogen analogues of carbenes are called nitrenes. The nomenclature follows that of carbenes. Substituted nitrenes are simply named as substituted derivative of carbenes. For example :

$C_6H_5-\ddot{N}:$	Phenylnitrene
$CH_3SO_2\ddot{N}:$	Methanesulphonylnitrene
$R-\ddot{N}:$	Alkylnitrene
 $R-O-\overset{\overset{O}{\parallel}}{C}-\ddot{N}:$	Carboalkoxynitrene

Structure and Reactivity : Like carbenes, there is the possibility of two spin states for nitrenes, depending on whether the two non-bonding electrons (the normal nitrogen lone pair remains paired) have their spins paired or parallel

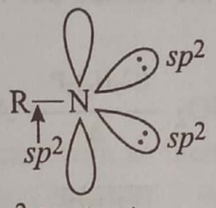
$$R-\overset{\cdot\cdot}{N}: \begin{array}{l}\longleftarrow \text{These two electrons are paired.}\\ \longleftarrow \text{These two electron may be paired or unpaired.}\end{array}$$

In general, nitrenes obey Hund's rule and are ground state triplets with two degenerate *sp*-orbitals containing a single electron each.



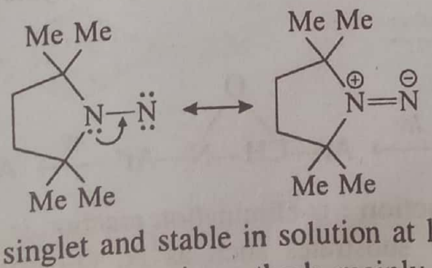
sp-Triplet nitrene

Nitrenes also exist in singlet state. Nitrogen atom in the singlet is usually represented as sp^2-hybridised.



sp^2-Singlet nitrenes

The energy difference between the singlet and triplet states is usually much larger for nitrenes than for carbenes, being estimated at 145 kJ/mole for nitrene ($\ddot{N}H$) itself compared with 32-42 kJ/mole for carbene ($\ddot{C}H_2$). This energy difference is due to the electronegativity difference in carbon and nitrogen. Nitrogen is more electronegative than carbon and therefore holds its electrons closer to the nucleus which decreases energy and hence increases stability. The nature of the substituent on nitrogen affects both the multiplicity and the normal electrophilic reactivity of nitrenes. Strong *pi*-donor substituents such as amino groups greatly stabilise the singlet as well as causing the nitrene to exhibit nucleophilic character in its reaction.



This nitrene is ground state singlet and stable in solution at low temperature.

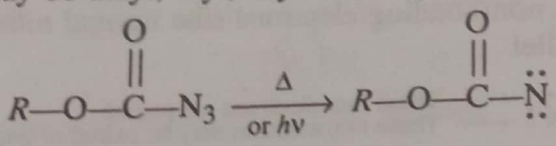
Nitrenes are characterised by spectroscopic methods mainly UV and IR. Nitrene ($\ddot{N}H$) is very transient species and it is extensively characterised by UV spectroscopy. It shows absorption maximum at 336 nm.

(A) Generation of Nitrenes :

(1) From Azides : The most common method for generating nitrene intermediates is by photolysis or thermolysis of azides.

$$R-\overset{\ominus}{N}-\overset{\oplus}{N}\equiv N \xrightarrow[h\nu]{\Delta \text{ or}} R-\ddot{N} + N\equiv N \qquad .(1)$$

In this reaction azides may be alkyl, aryl, acyl and sulphonyl.



$$R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}N_3 \xrightarrow[\text{or } h\nu]{\Delta} R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\ddot{\underset{\cdot\cdot}{N}} \qquad \ldots(2)$$

$$R{-}SO_2{-}N_3 \xrightarrow[\text{or } h\nu]{\Delta} R{-}SO_2{-}\ddot{\underset{\cdot\cdot}{N}} \qquad \ldots(3)$$

(2) From Sulphinylamines : Sulphinylamines on thermolysis give phenyl nitrenes.

$$Ph{-}N{=}S{=}O \xrightarrow{\Delta} Ph{-}\ddot{\underset{\cdot\cdot}{N}} + SO$$

Sulphinylamines are readily prepared from aniline and thionyl chloride.

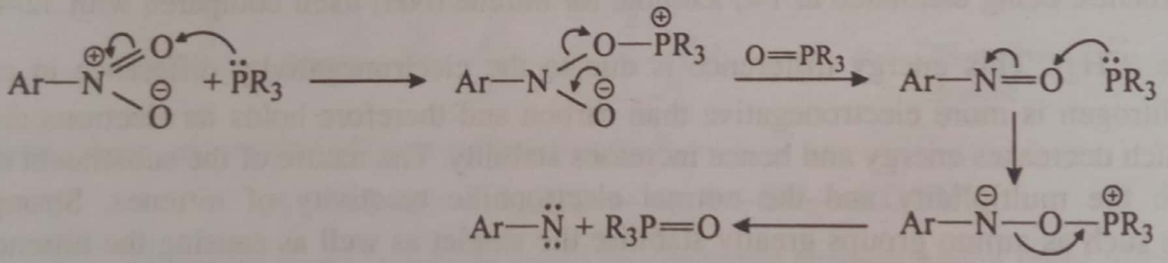
$$Ar{-}NH_2 \xrightarrow{SOCl_2} Ar{-}N{=}S{=}O$$

(3) From Nitro and Nitroso Compounds : Deoxygenation of nitro and nitroso compounds may generate nitrenes. The deoxygenation can the carried out with a variety of reagents but the best result is obtained with triethylphosphite.

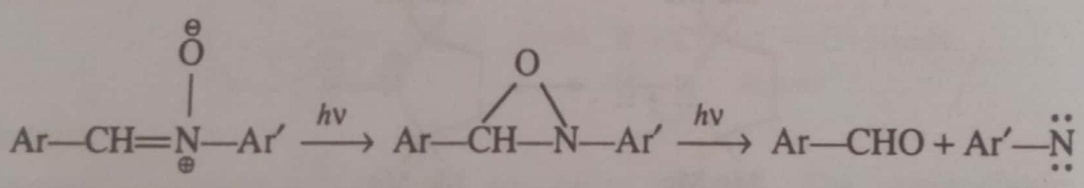
$$Ar{-}NO_2 \xrightarrow[\Delta]{(C_2H_5)_3P} Ar{-}\ddot{\underset{\cdot\cdot}{N}}$$

$$Ar{-}NO \xrightarrow[\Delta]{(C_2H_5)_3P} Ar{-}\ddot{\underset{\cdot\cdot}{N}}$$

Reaction takes place as follows :



(4) From Small Ring Compounds : Nitrones on photolysis give oxaziranes which on further photolysis give nitrene.



(5) From α-Elimination Reaction : α-elimination reaction is not very common reaction for the preparation of nitrenes. Only few substrates such as N, O-bis(trimethylsilyl)hydroxylamines and *O*-arenesulphonylhydroxylamines gives nitrene by α-elimination reaction.