

# NITRENES

The generic structure of nitrene group  $R-\ddot{N}$ .  
A nitrene is the nitrogen analogue of a carbene. The nitrogen atom has only 6 valence electrons and is therefore considered an electrophile. A nitrene is a reactive intermediate and is involved in many chemical reactions.

In the most simple nitrene linear imidogen ( $:\text{N}-\text{H}$ ) two of the six available electrons form a covalent bond with hydrogen, two other create a free electron pair and the two remaining electrons occupy two degenerate orbitals consistent with Hund's rule the low energy form of imidogen is a triplet with one electron in each of the p orbitals and the high energy form is the singlet state with an electron pair filling one p orbital and other one vacant.

As with carbenes, a strong correlation exist between the spin density on the nitrogen atom which can be calculated in silico and the zero field splitting parameter D which can be derived experimentally from electron spin resonance. Small nitrenes such as  $\text{NH}$  or  $\text{CF}_3\text{N}$  have D values around  $1.8 \text{ cm}^{-1}$  with low D ( $< 0.4$ ) values and spin density of 1.2 to 1.4 such as 9-anthrylnitrene and 9-phenanthryl.

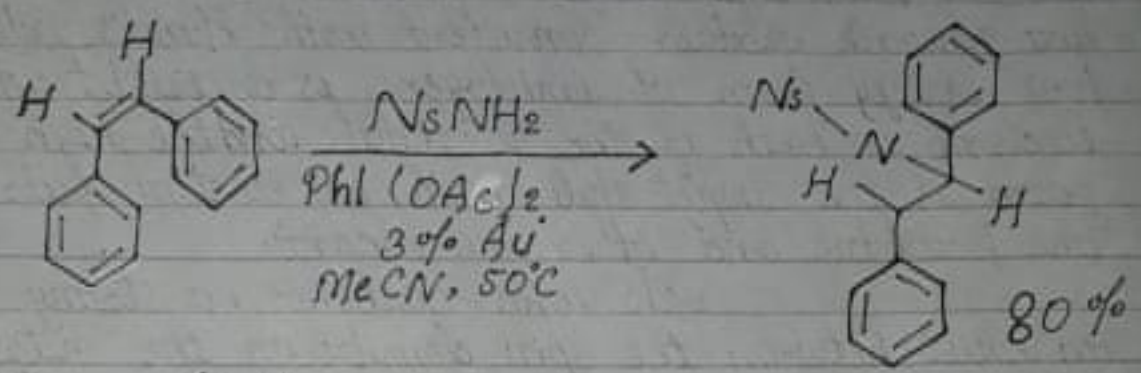
## Formation:

Nitrenes are so reactive, they are not isolated. Instead they are formed as reactive intermediate during a reaction.

From azides by thermolysis or photolysis of nitrogen gas. This method is analogue to the formation of carbene from diazocompounds.

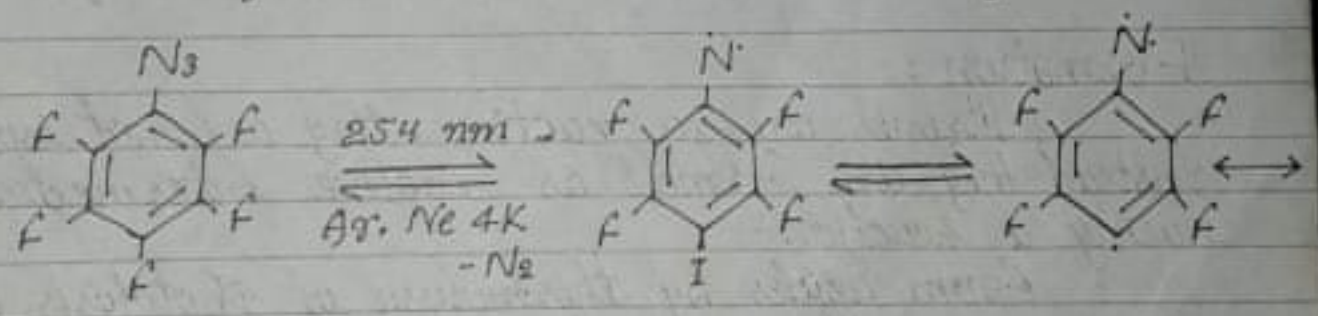
### Chemical reaction:

Nitrene cycloaddition: - With alkenes nitrenes react to aziridines, very often with nitrenoid precursors such as nosyl- or tosyl-substituted [N-(Phenylsulfonyl)imino] phenyl-iodine (PhI = NNs) or PhI = NTs respectively) but the reaction is known to work directly with the sulfonamide in presence of a transition metal based catalyst such as copper, palladium, or gold



### Nitrino radicals:

For several compounds containing both a nitrene group and a free radical group a ESR high-spin quartet has been recorded. One of these has a amine oxide radical group incorporated. another system has a carbon radical group.



A carbene nitrogen radical (Imidyl radical) resonance structure makes a contribution to the total electronic picture.