

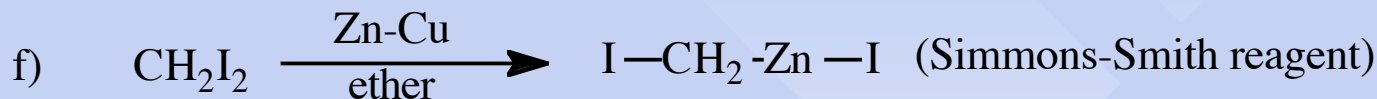
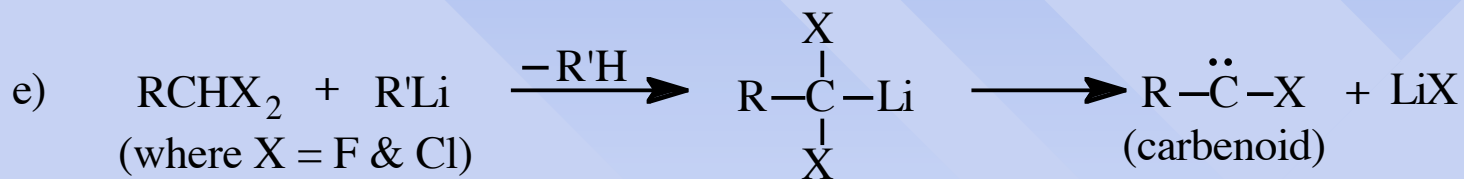
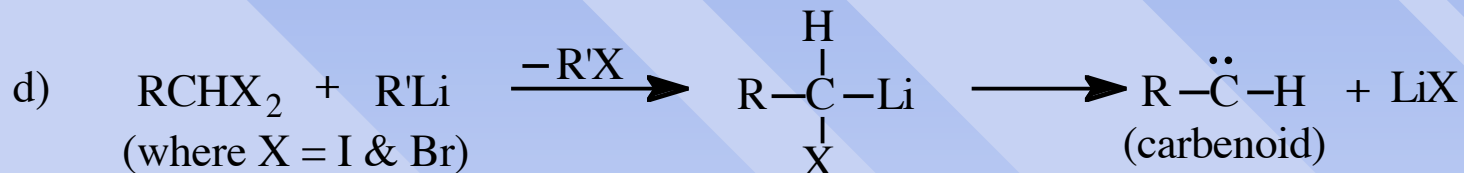
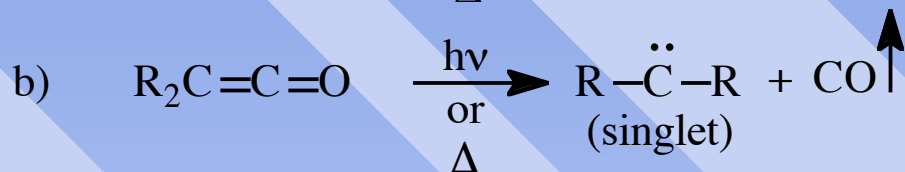
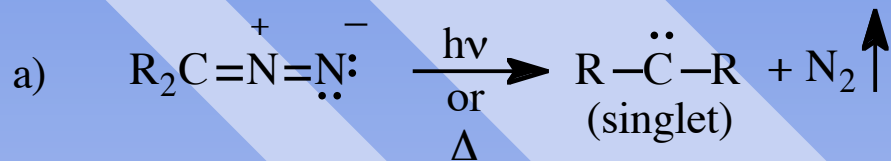
# Carbenes and Nitrenes

- ✱ **Carbenes are uncharged, electron deficient molecular species that contain a divalent carbon atom surrounded by a sextet of electrons.**
- ✱ **Nitrenes are uncharged, electron deficient molecular species that contain a monovalent nitrogen atom surrounded by a sextet of electrons.**

# *States of Carbenes and Nitrenes*

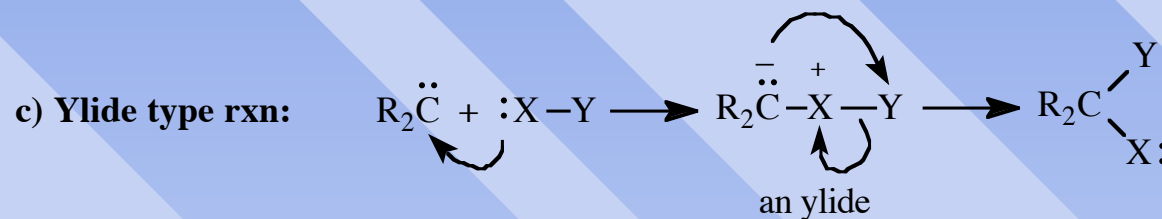
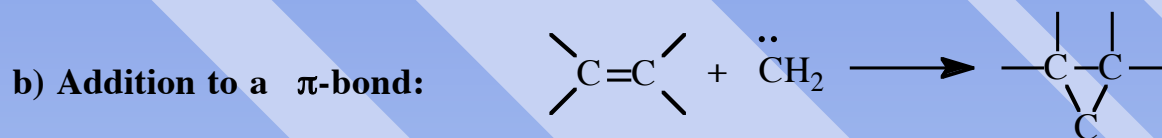
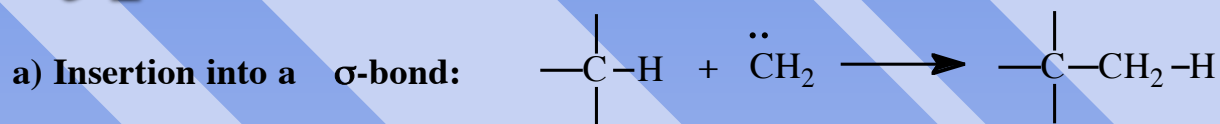
- \* **Singlet state: carbocation-like in nature, trigonal planar geometry, electrophilic character**
- \* **Triplet state: diradical-like in nature, linear geometry**

# Formation reactions of carbenes

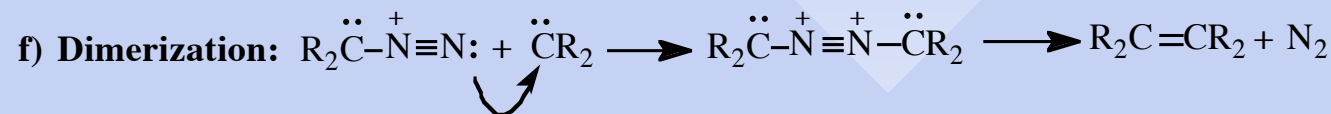
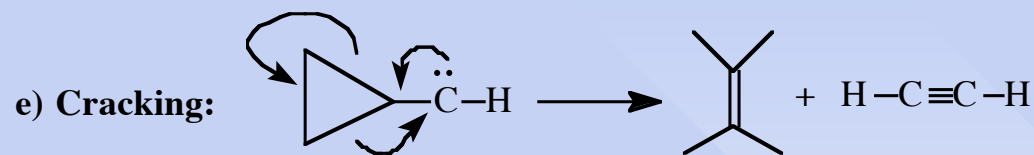
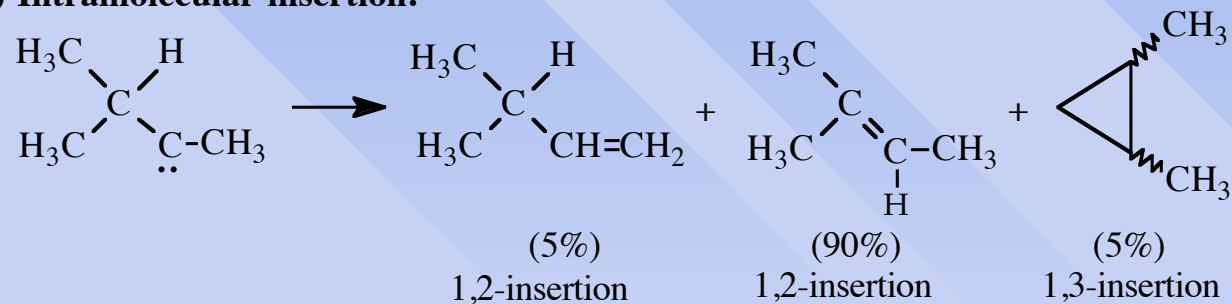


a carbenoid species that reacts stereospecifically with alkenes to give cyclopropanes but does not insert into alkane C-H bonds

# Typical Carbene Reactions



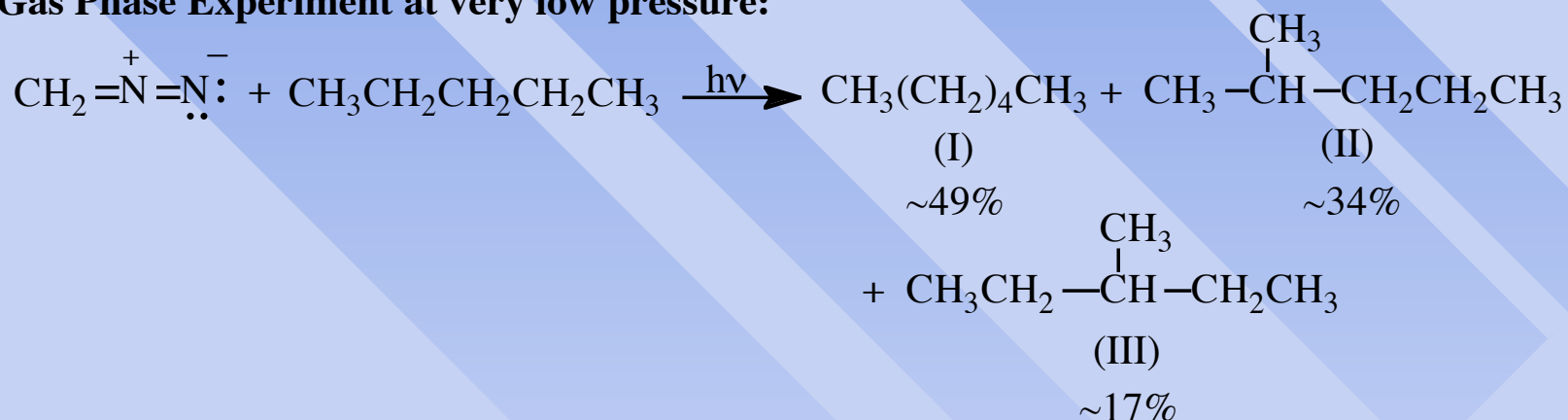
d) **Intramolecular insertion:**



# Mechanistic Aspects of Carbene Chemistry

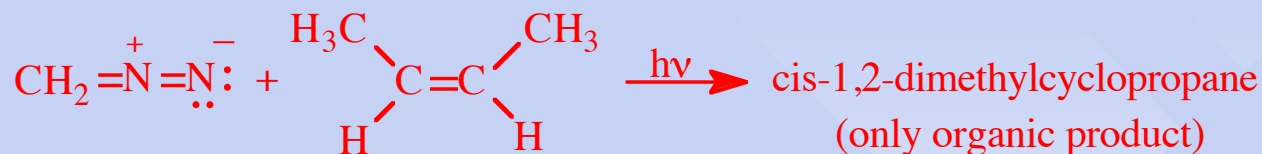
## Observations

### A. Gas Phase Experiment at very low pressure:



Point of Information: As the pressure of the system is increased (nitrogen or argon added), the yields of (II) and (III) increase at the expense of (I).

### B. Liquid phase experiment :



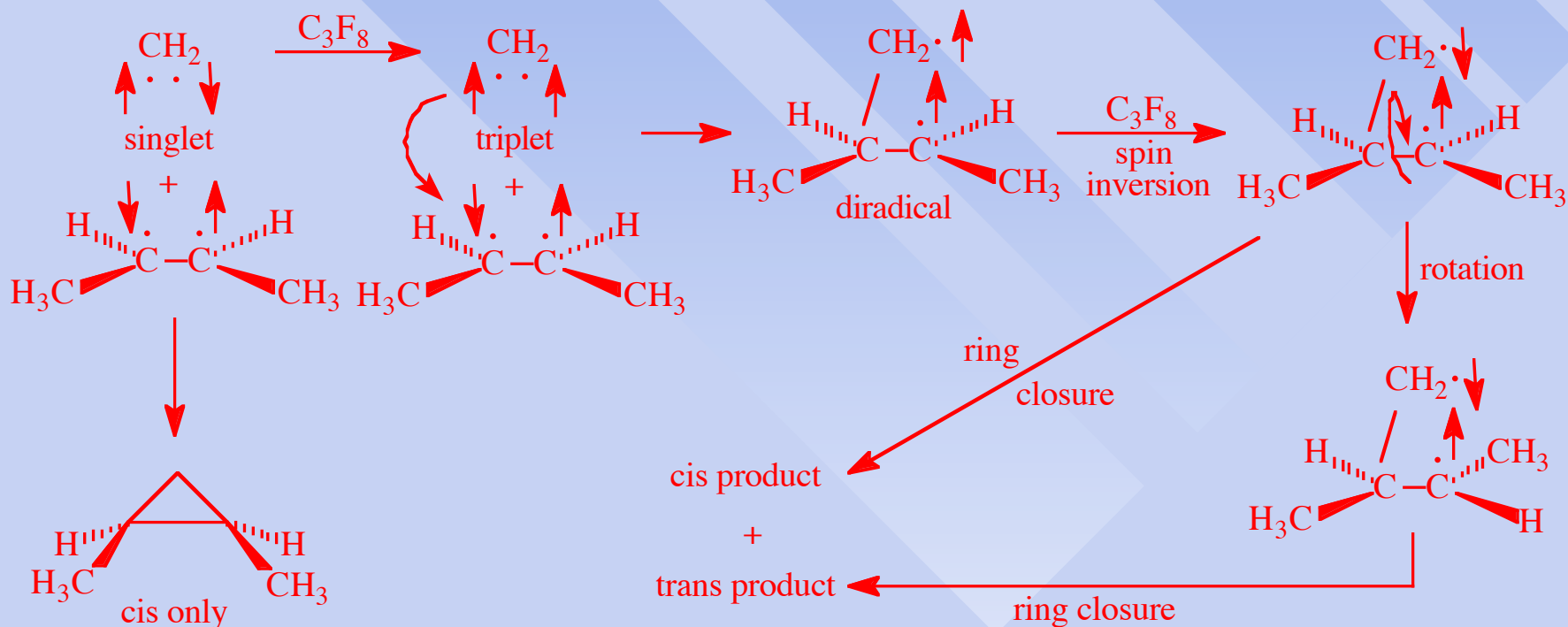
Point of Information: When an inert diluent such as perfluoropropane is added to the starting materials, a mixture of cis- and trans-1,2-dimethylcyclopropanes is obtained.

# Mechanistic Aspects of Carbene Chemistry

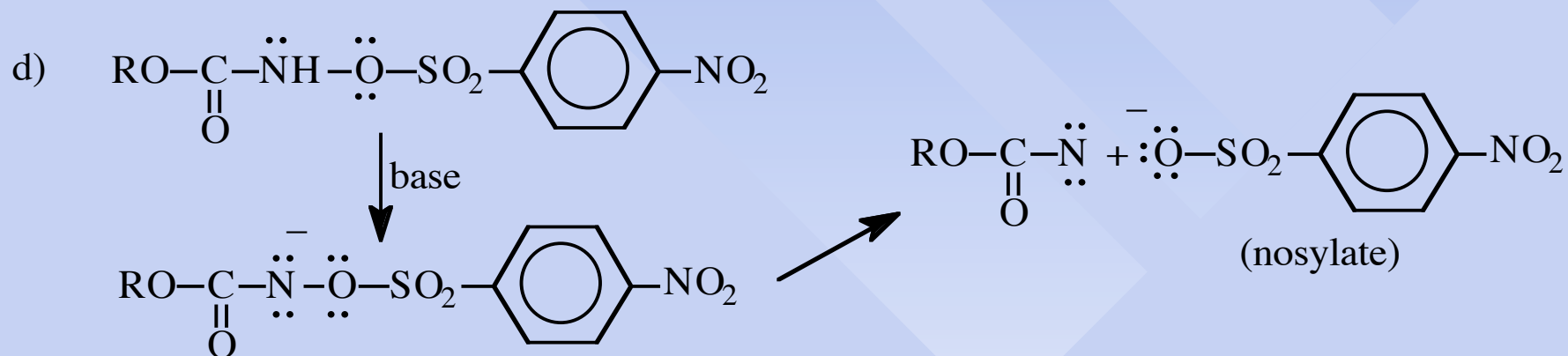
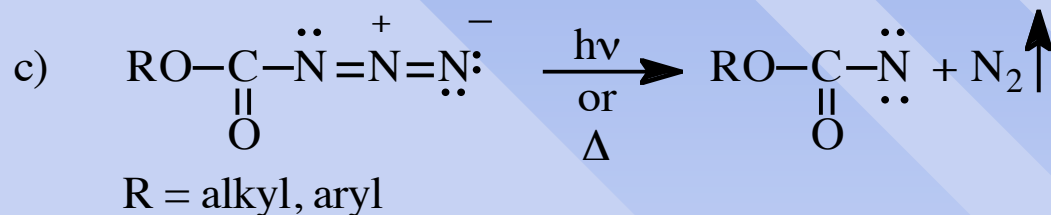
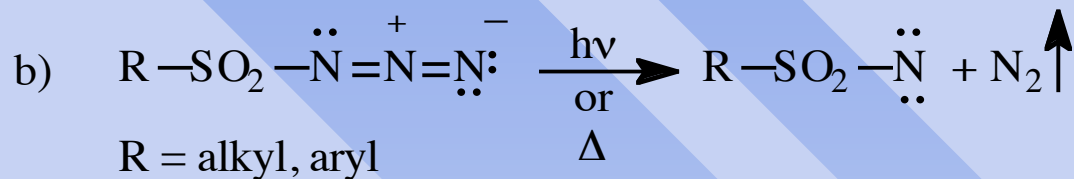
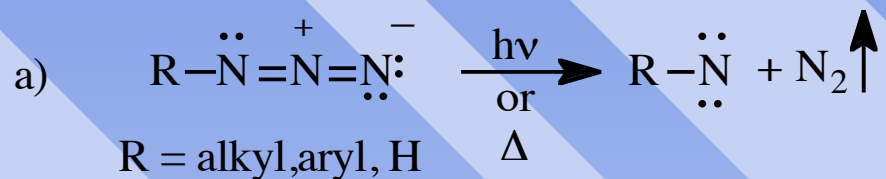
## Explanation for Gas Phase Experiment:

At very low pressure, reactive, singlet carbene inserts in the alkane C-H bonds in a completely random, statistical manner. However, upon addition of nitrogen or argon gas to the reaction, singlet carbene reverts to less reactive (more selective) triplet carbene via non-productive collisions with the inert diluent. Triplet carbene shows a preference for attacking tertiary and secondary hydrogen atoms rather than primary hydrogen atoms. Hence, formation of more tertiary and secondary abstraction products at the expense of primary abstraction product.

## Explanation for Liquid Phase Experiment:



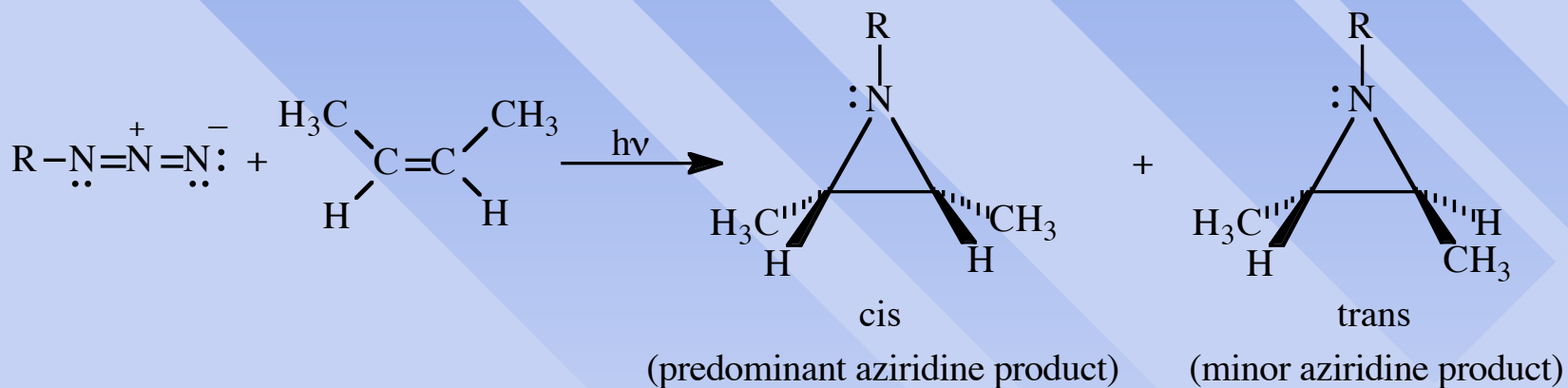
# NITRENE FORMATION REACTIONS



# Mechanistic Aspects of Nitrene Chemistry

## Cycloaddition - Observations

### Liquid phase experiment



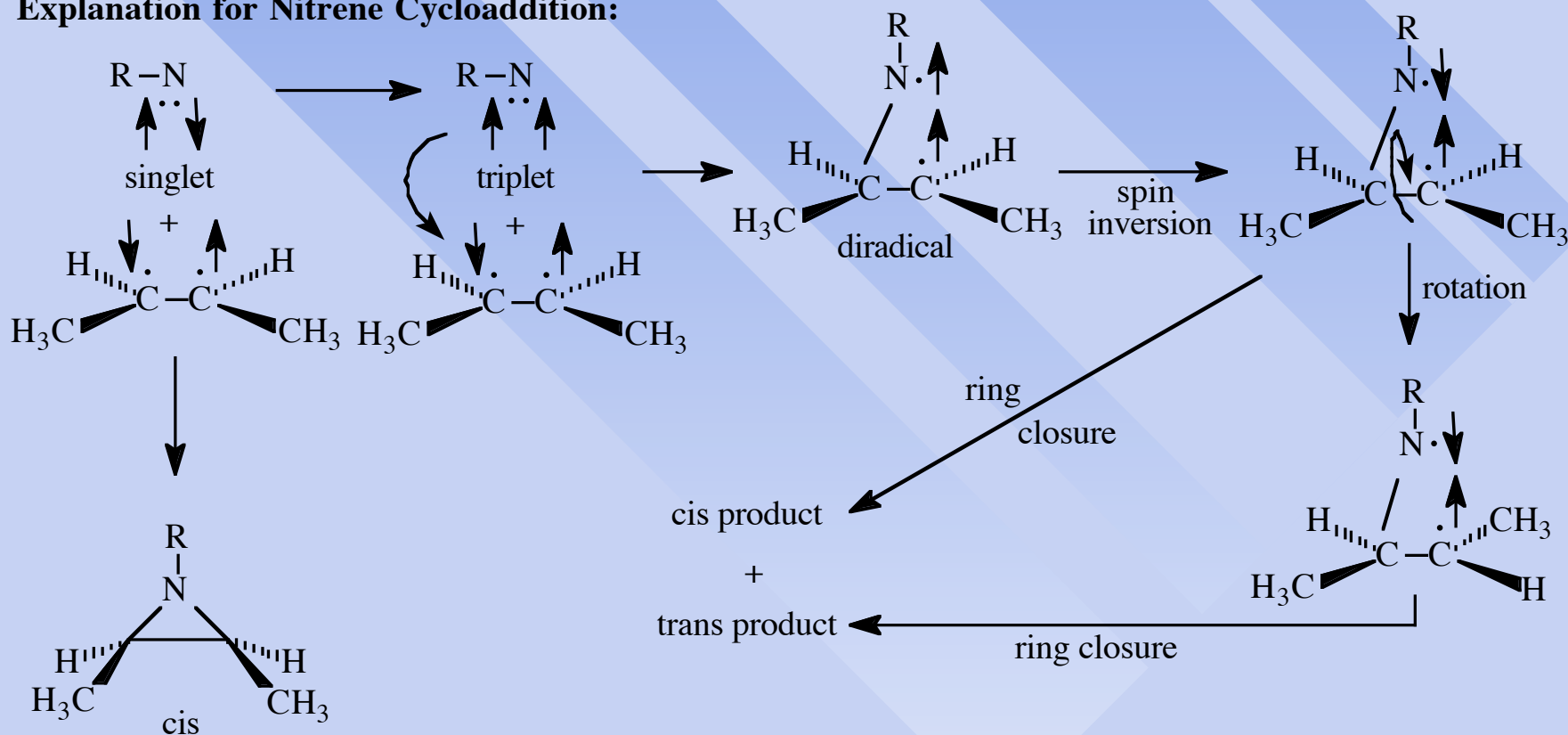
Point of Information: When an inert solvent is added to the reaction mixture, more trans-product is obtained at the expense of the cis-product.



# Mechanistic Aspects of Nitrene Chemistry

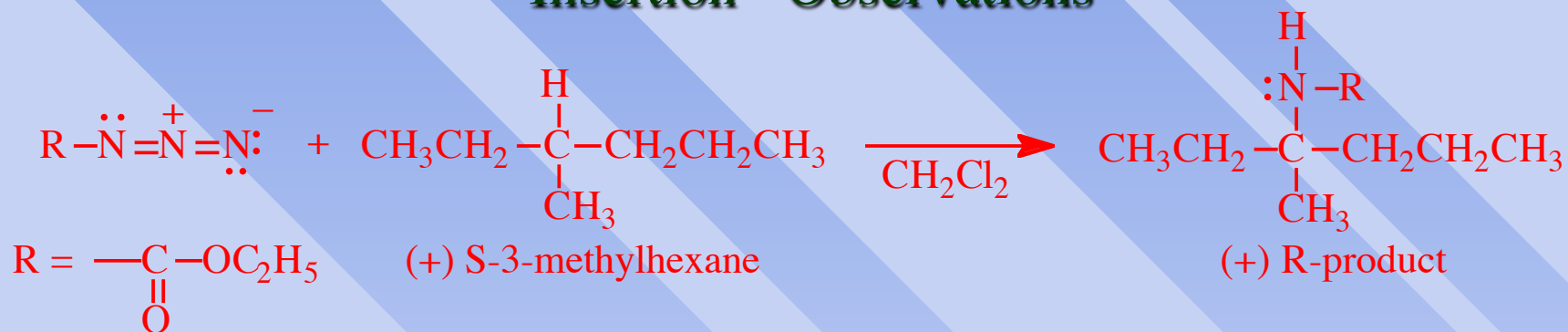
## Cycloaddition

Explanation for Nitrene Cycloaddition:



# Mechanistic Aspects of Nitrene Chemistry

## Insertion - Observations

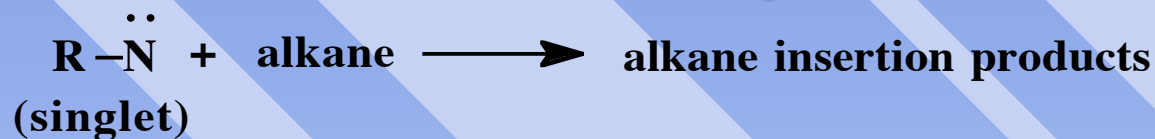


<u>Method of Generation</u>	<u>Conc. of Alkane</u>	<u>Obs. rot. of prod.</u>	<u>Retention of Config</u>
$\text{R}-\text{N}_3 \xrightarrow{\Delta}$	100%	$+1.69^\circ$	99%
$\text{R}-\text{N}_3 \xrightarrow{h\nu}$	1.2%	$+1.71^\circ$	100%
$\text{R}-\text{N}_3 \xrightarrow{h\nu}$	26.8%	$+1.69^\circ$	99%
$\text{R}-\text{N}_3 \xrightarrow{h\nu}$	100%	$+1.68^\circ$	98%

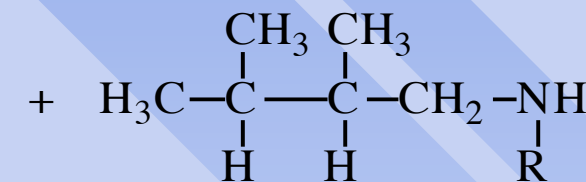
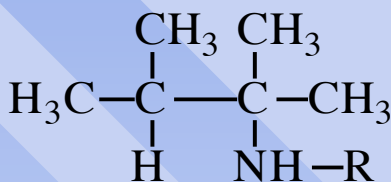
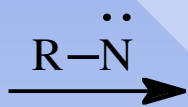
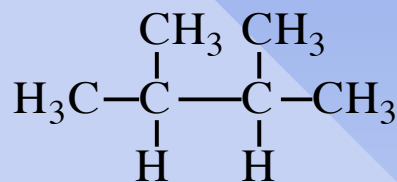
# *Explanation of Nitrene Insertion*

- \* Observed rotation is independent of chiral alkane concentration.*
- \* At less than 100% chiral alkane concentration (more inert solvent present), more triplet nitrene is formed at the expense of initially produced singlet nitrene.*
- \* The fact that higher concentration of triplet nitrene does not affect the observed rotation of chiral product is indicative of the inability of the triplet species to insert into alkyl C-H bonds.*

# Evidence of Singlet Nitrene C-H Insertion Selectivity

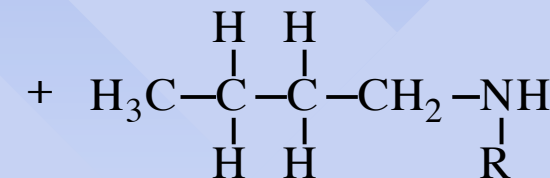
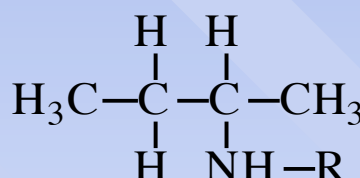
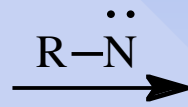
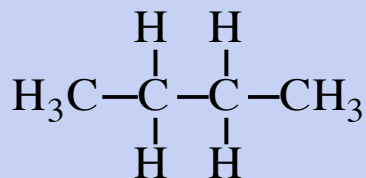


Alkane



67.0 : 1.0

Relative reactivities



9.0 : 1.0

**Singlet nitrene C-H insertion selectivity:**

tertiary C-H > secondary C-H > primary C-H

# Summary of Carbene/Nitrene Chemistry

- + Singlet carbenes and singlet nitrenes add to C=C bonds in a one-step, stereospecific manner.**
- + Triplet carbenes and triplet nitrenes add to C=C bonds in a two-step, non-stereospecific manner.**
- + Singlet carbenes insert into alkyl C-H bonds randomly, whereas singlet nitrenes do so selectively. Both singlet species insert into alkyl C-H bonds with retention of configuration.**
- + Triplet carbenes insert into alkyl C-H bonds selectively, but not stereospecifically.**
- + Triplet nitrenes do not insert into alkyl C-H bonds.**