

Lecture 7



كلية العلوم التطبيقية
Faculty of Applied Sciences



Special topics in Organic chemistry



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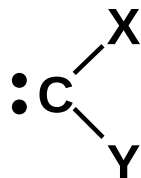
Special Topics in Organic Chemistry

Course code: (4024583-2)



Carbenes and Nitrenes:

What are Carbenes? Nitrenes?



- Neutral, divalent carbon species containing six valence electrons



- Neutral, monovalent nitrogen species containing six valence electrons

*Electron
deficient*



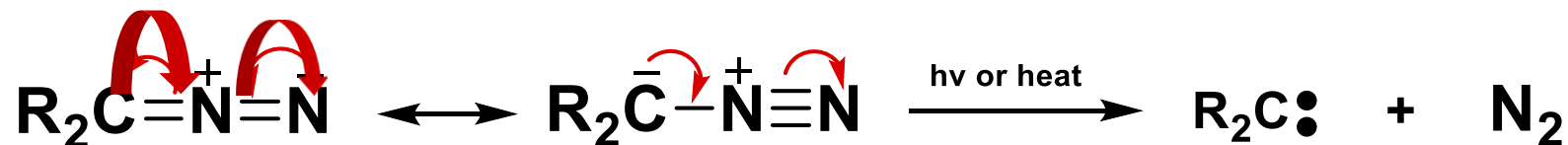
*Highly
reactive*

➤ **Carbenes** are uncharged, electron deficient molecular species that contain a divalent carbon atom surrounded by a sextet of electrons.

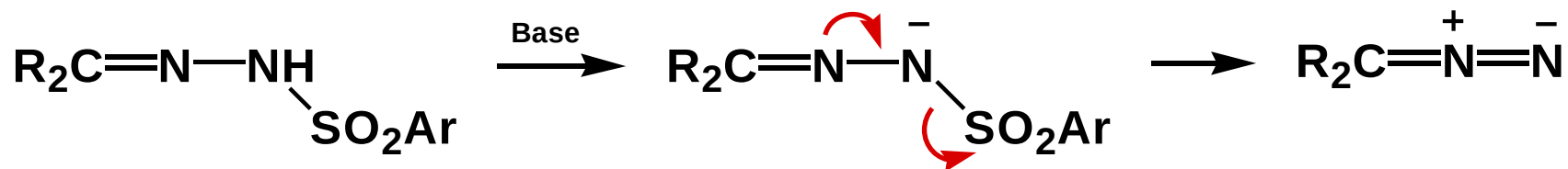
Nitrenes are uncharged, electron deficient molecular species that contain a monovalent nitrogen atom surrounded by a sextet of electrons.

Carbene Formation

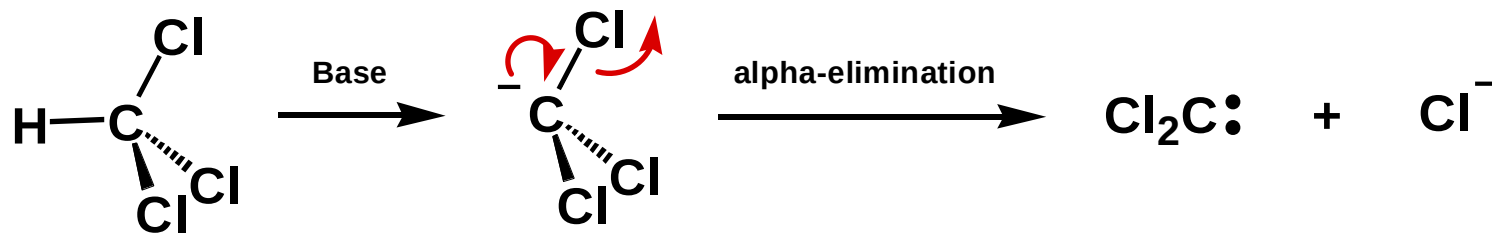
- Diazoalkanes



- Sulfonylhydrazones

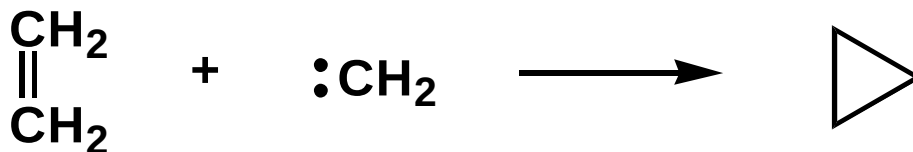


- Halides

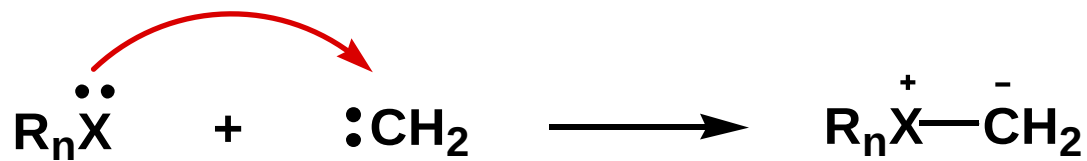


Reactions of Carbenes

- Addition reactions



- Ylide formation



- Insertion reactions

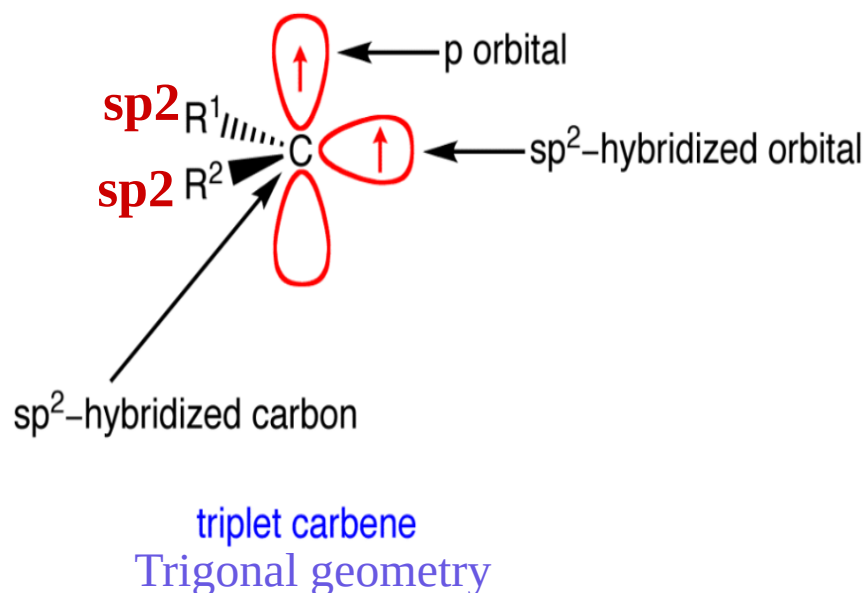
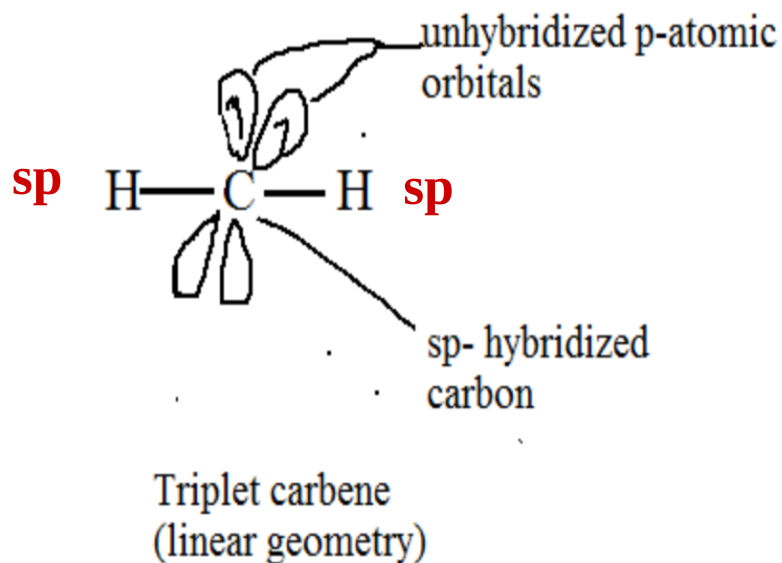


States of Carbenes and Nitrenes

- **Singlet state**
- **Triplet state**

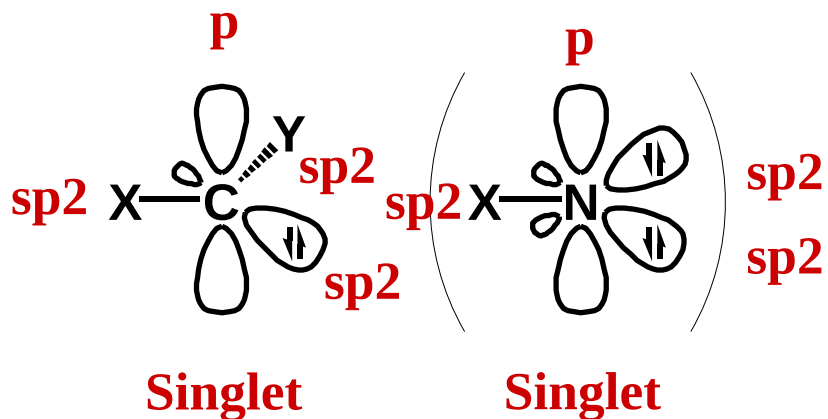
States of Carbenes

- **Singlet state:** carbocation-like in nature, trigonal planar geometry, electrophilic character
- **Triplet state:** diradical-like in nature, linear geometry only in carbenes and trigonal planar in carbenes and nitrenes

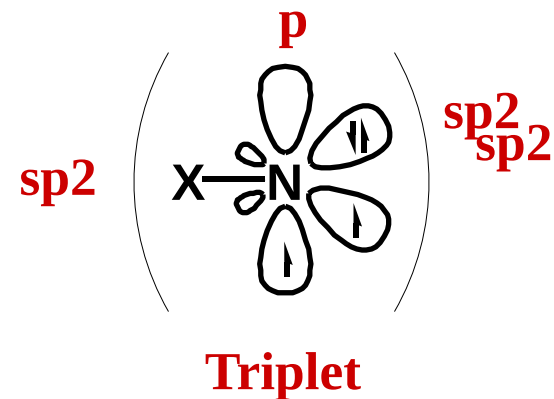


Triplet

Singlet and Triplet States

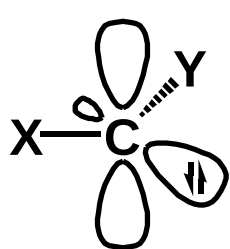


- sp^2 hybridized carbon
- non-bonding electrons have opposite spin - occupy an sp^2 orbital
- XCY angle $100-110^\circ$

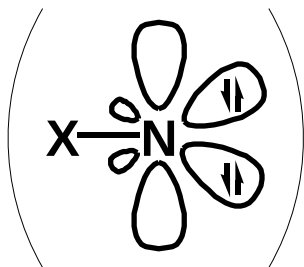


- sp^2 hybridized carbon (or sp ? only in carbenes)
But not **Nitrenes**
- non-bonding electrons have same spin – occupy an sp^2 and p orbital
- XCY angle $130-150^\circ$

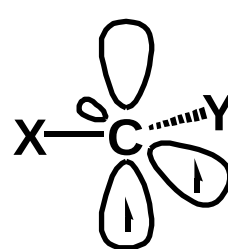
Singlet and Triplet States



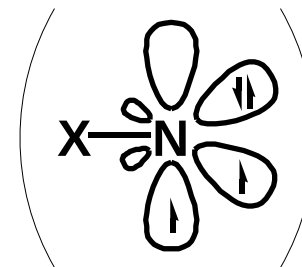
Singlet



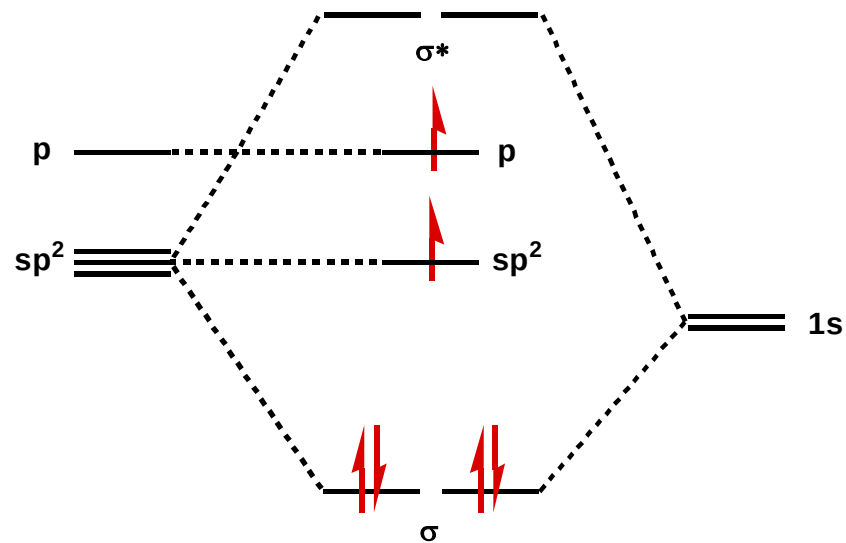
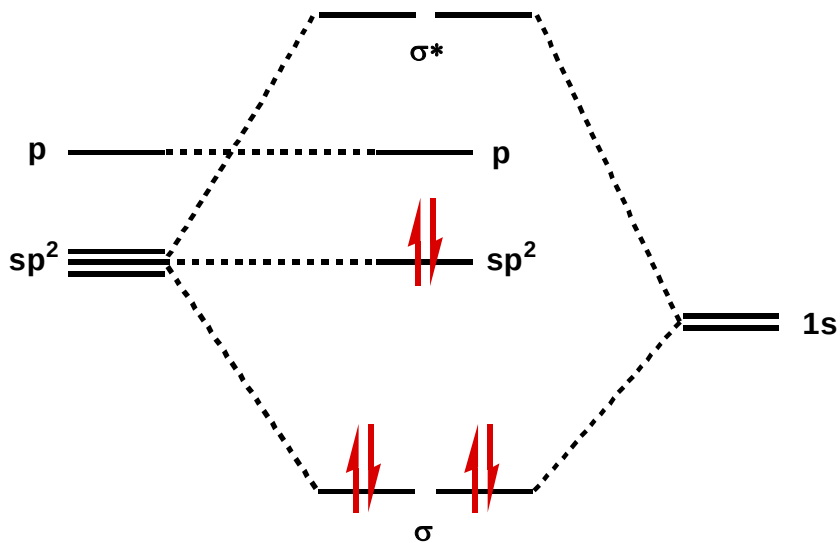
Singlet



Triplet

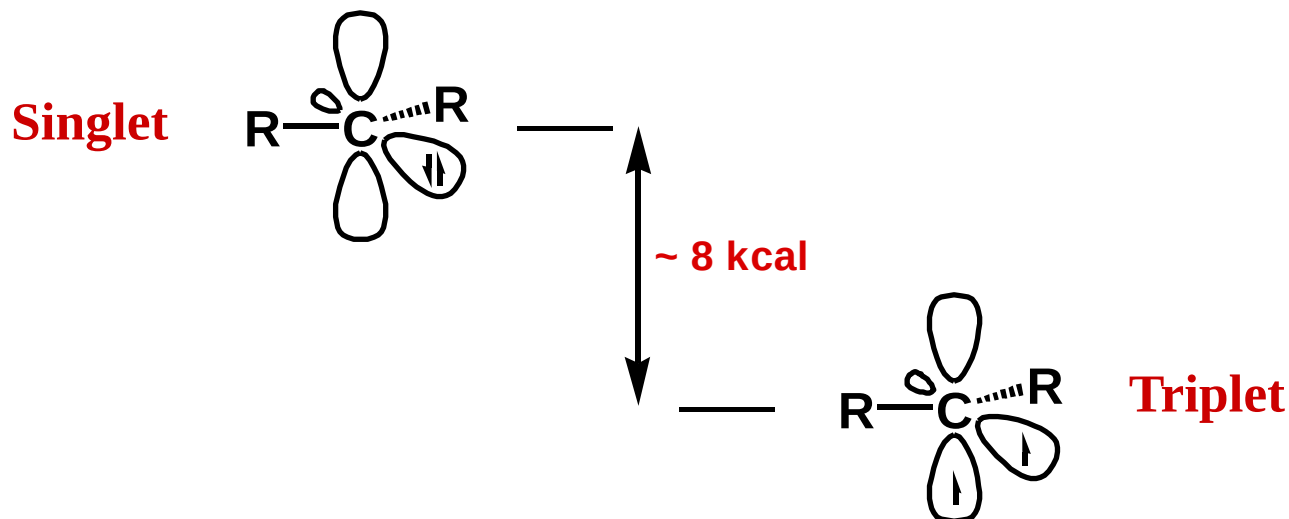


Triplet

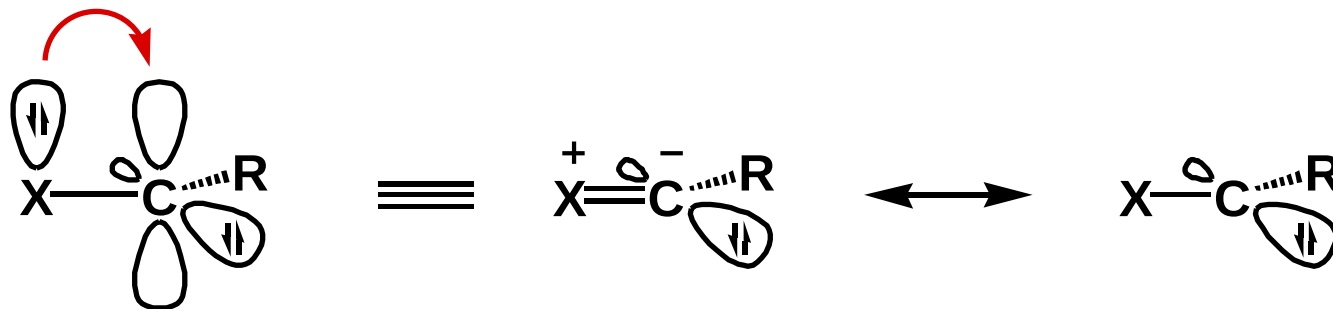


Relative Stability of Singlet and Triplet States

- Triplet more stable than singlet (R=H, alkyl)

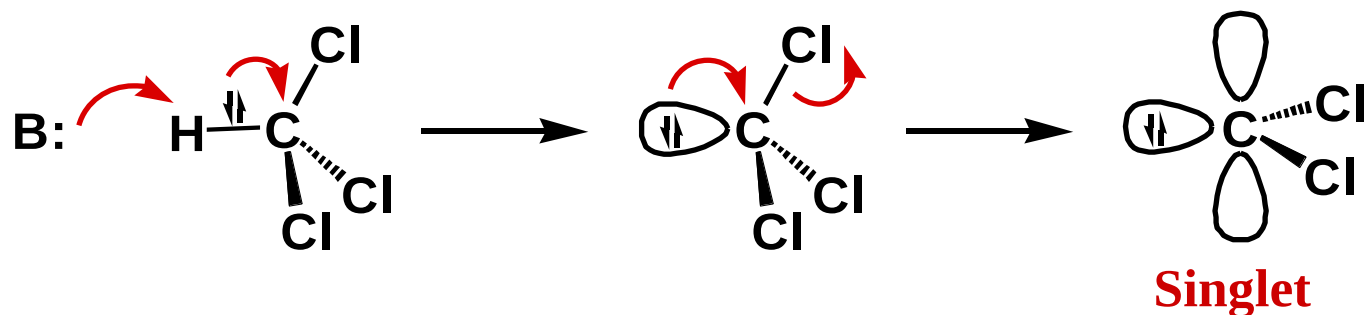


- Unless, added stabilization possible (X=O, N, S, halogen etc.)

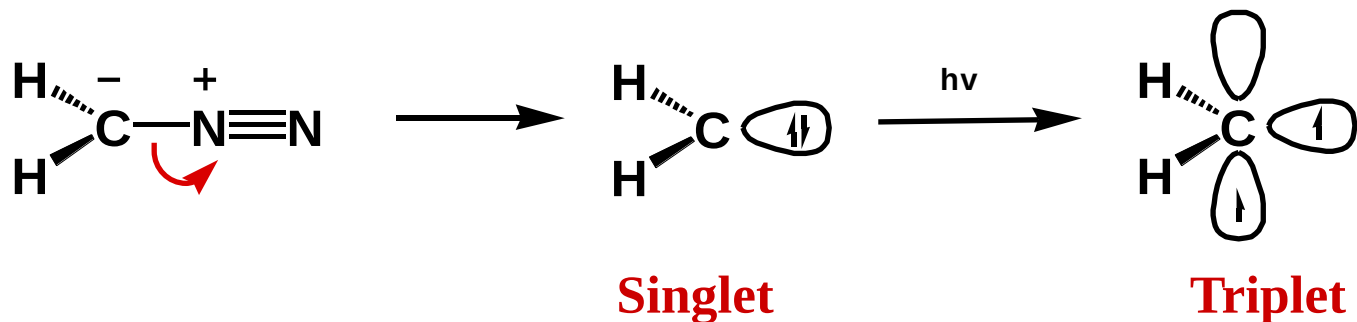


Mode of Preparation – Singlet vs. Triplet

Ionic Mechanism:

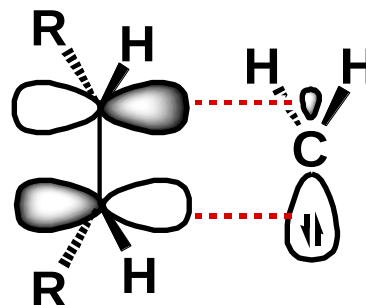
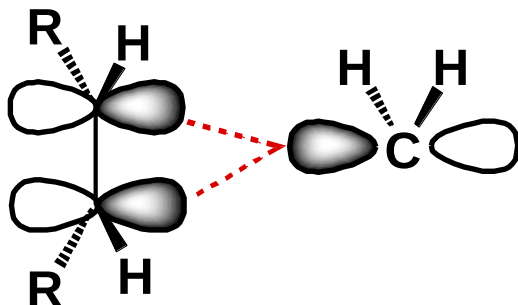


Photolysis:

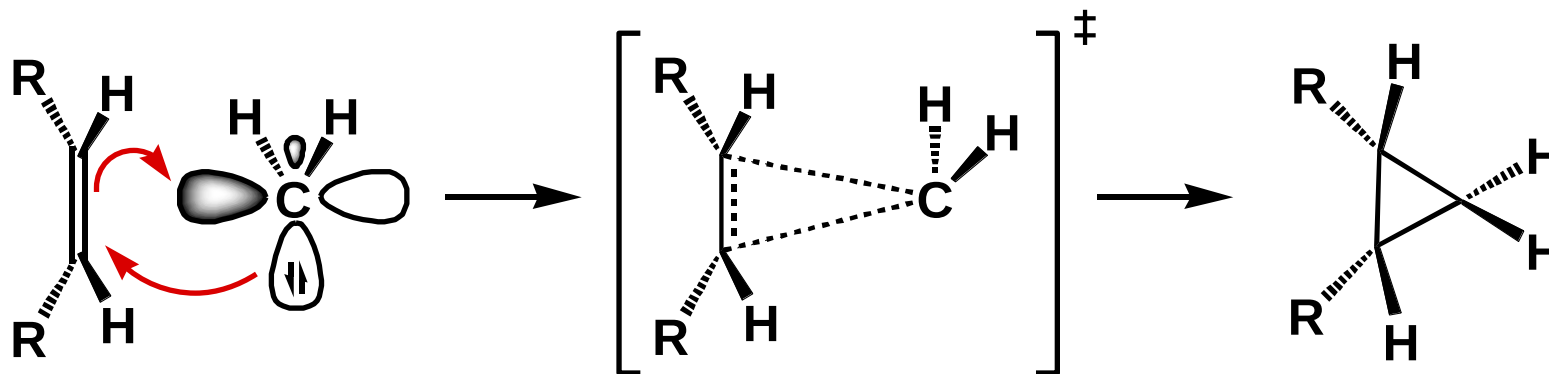


Singlet Carbenes React Stereospecifically

FMO interactions for cyclopropanation with singlet carbene:



Mechanism:



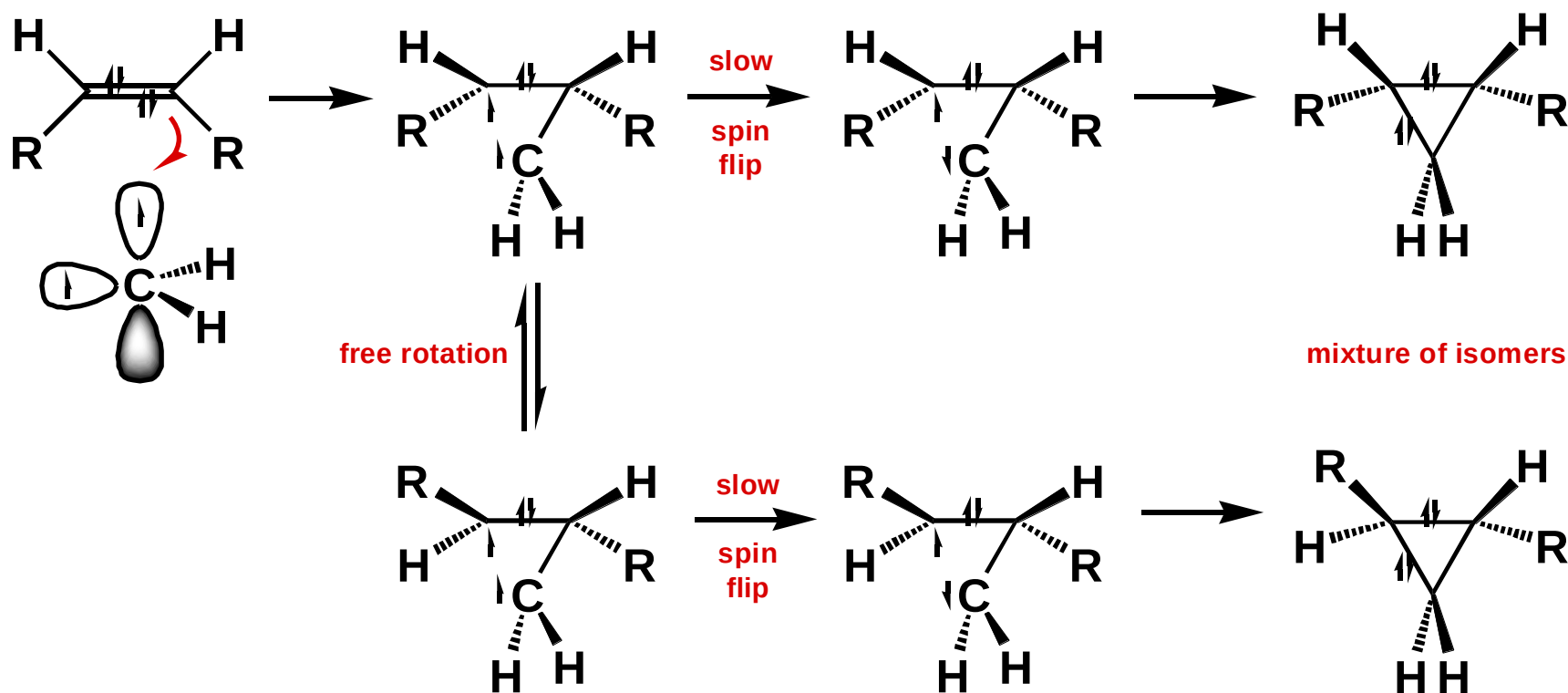
Concerted



Stereospecific

Triplet Carbenes React Stereoselectively

Cyclopropanation with triplet carbenes - radical mechanism:

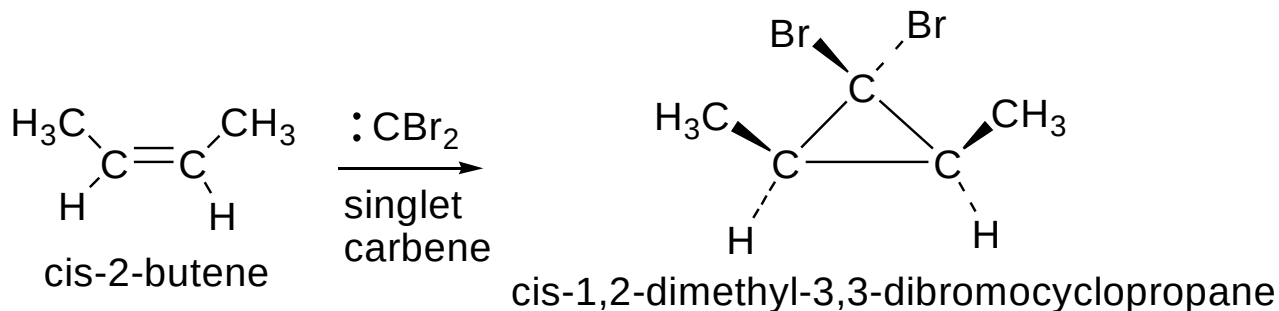
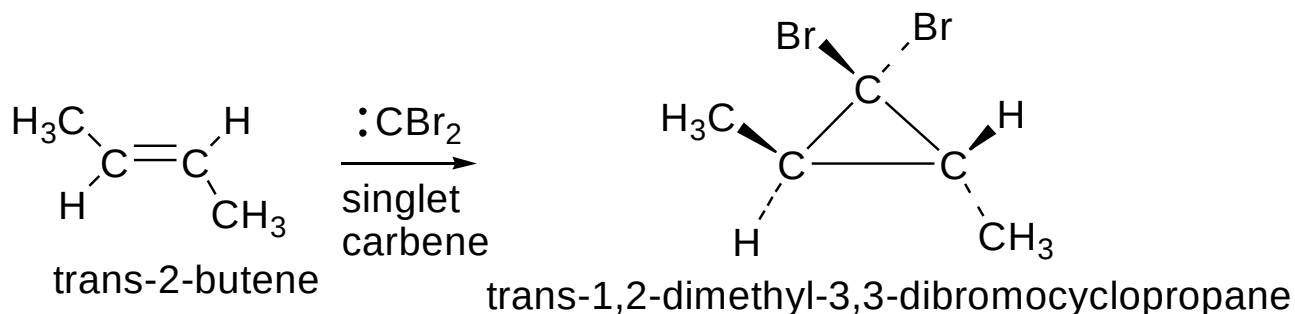


Two pathways  *Stereoselective*

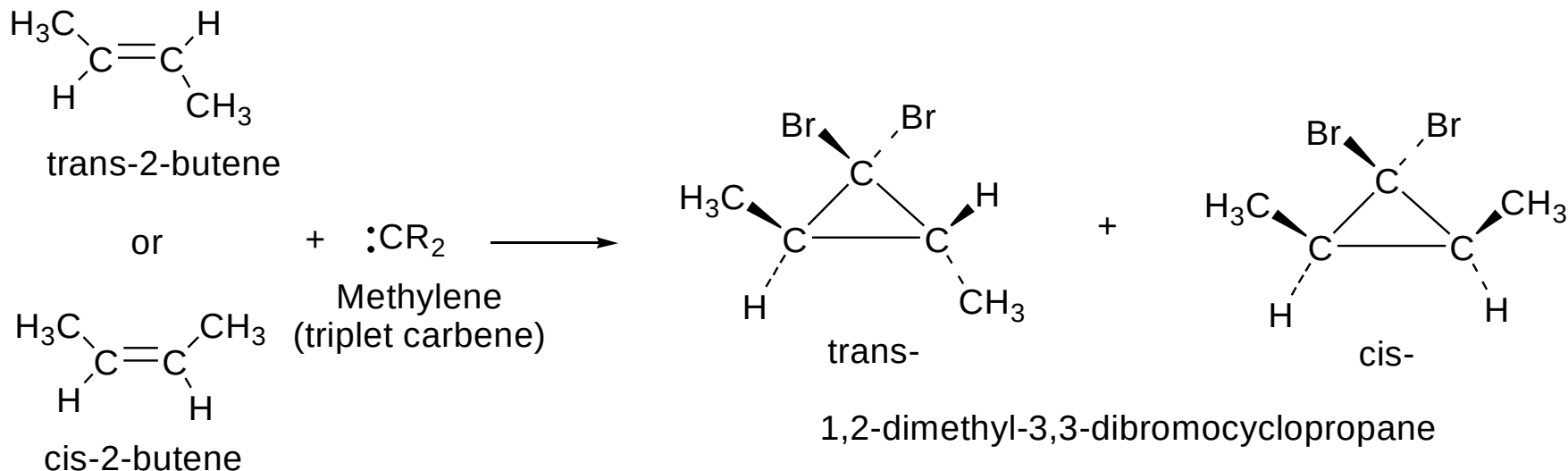
B- Reactions of carbenes:

1) Addition to olefins:

Singlet carbenes add to olefins stereospecifically; i.e. a cis olefin gives a cis 1,2-disubstituted cyclopropane and a trans olefin gives a trans 1,2-disubstituted cyclopropane.

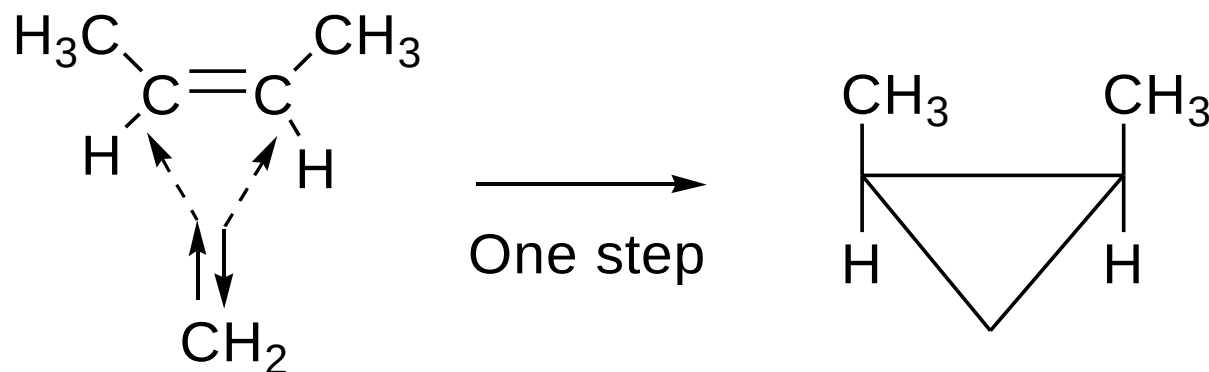


Triplet carbenes (methylene) add to olefins non-stereospecifically; i.e. a mixture of cis and trans-disubstituted cyclopropanes is obtained from either cis- or trans-1,2-disubstituted olefin.

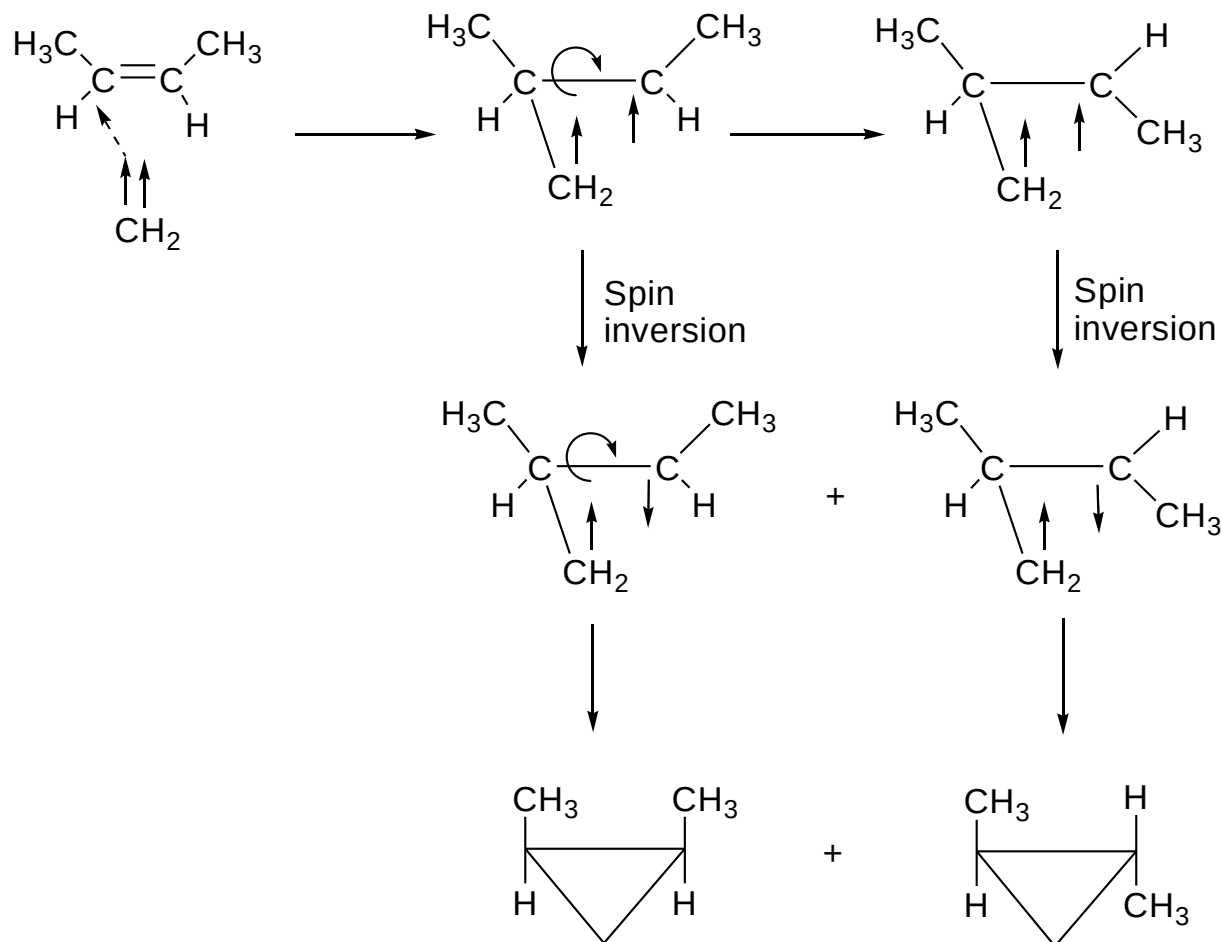


Explanation: Singlet carbenes add in one step (concerted), whereas triplet carbenes (methylene) add in two steps (stepwise).

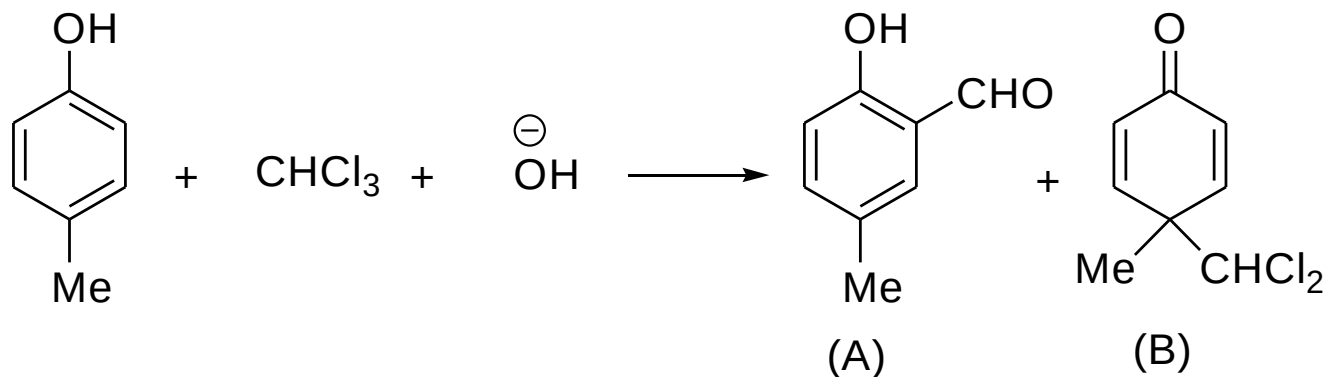
In singlet carbenes, the two electrons have opposite spins. The two electrons can form two C-C bonds simultaneously. Thus, there is no time between the first and the second bond formations, and the reaction therefore is stereospecific.



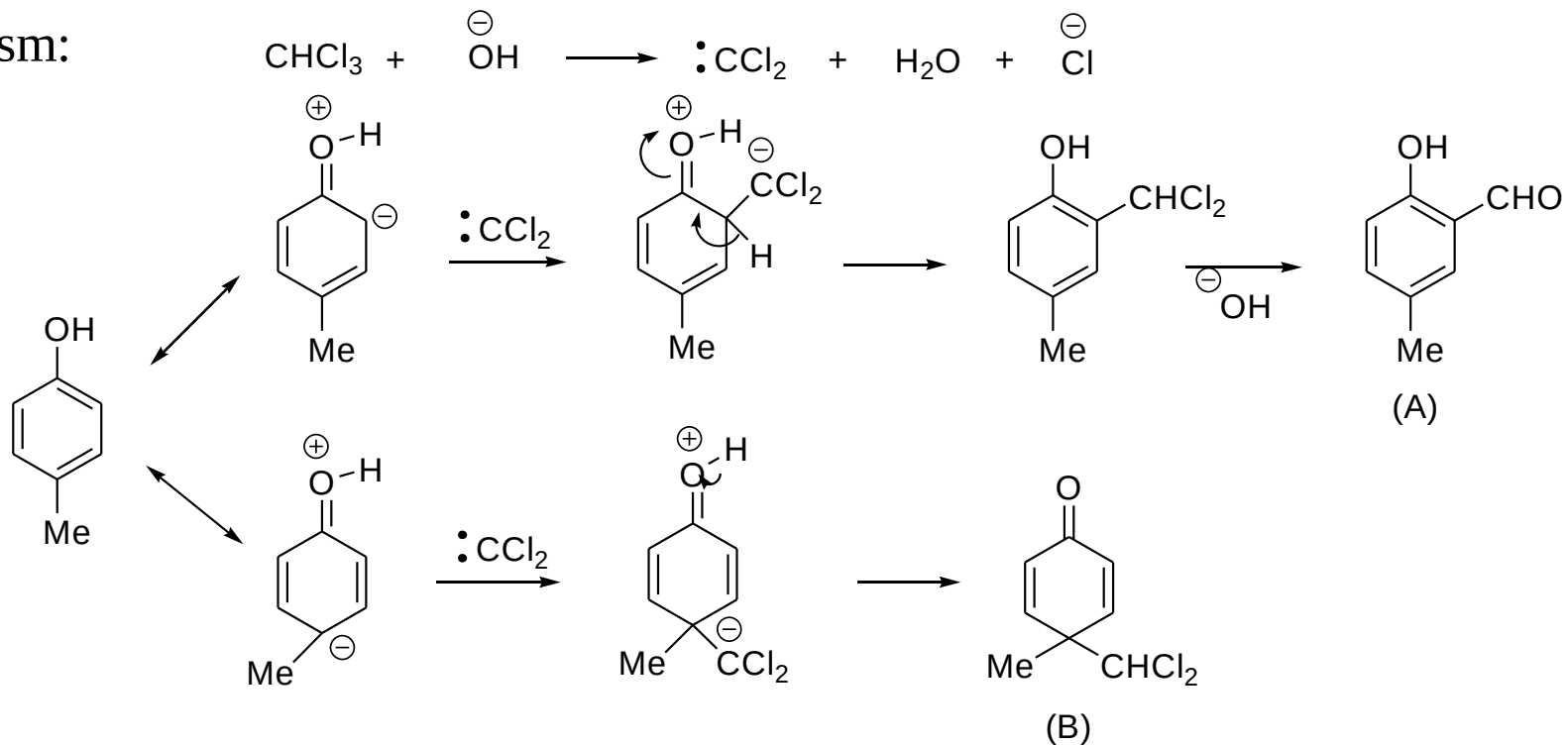
In triplet carbenes (methylenes), the two electrons have parallel spins and they cannot form two bonds simultaneously. The reaction must take place stepwise. After the first bond is formed, the second electron needs time to reverse its spin. During this time, free rotation about the single bond takes place leading to the formation of cis- and trans- isomers.



2) Reimer Tiemann Reaction:

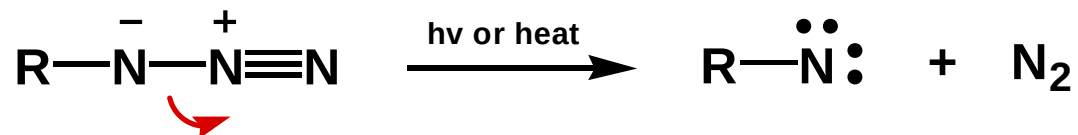


Mechanism:

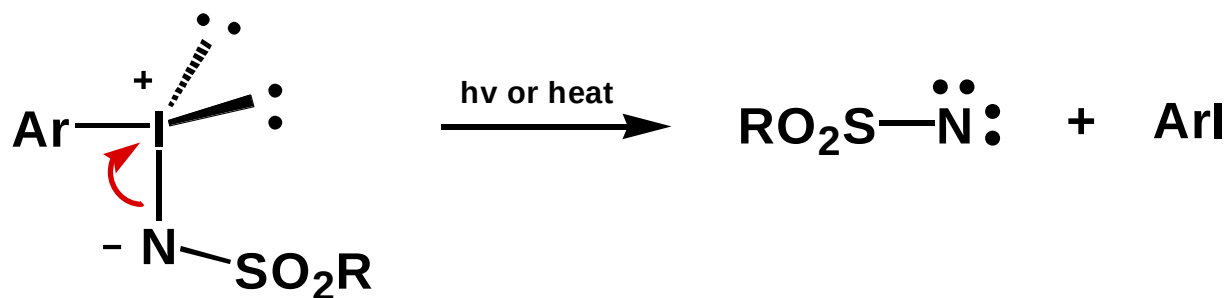


Nitrene Formation

- Azides



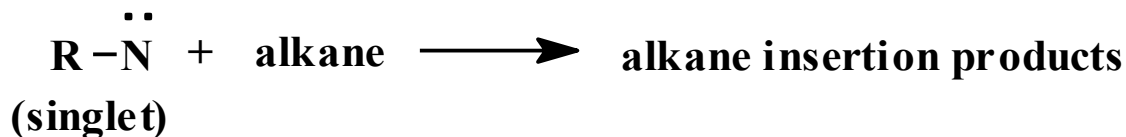
- Iminoiodanes



- Sulfonamides

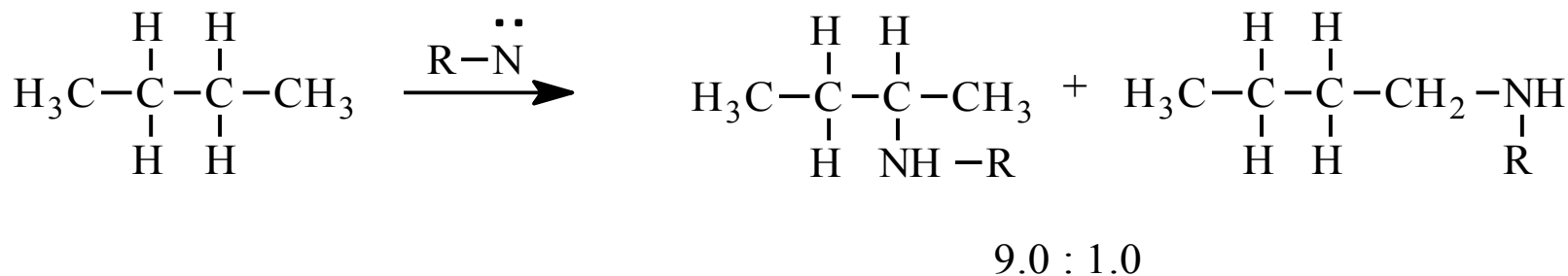
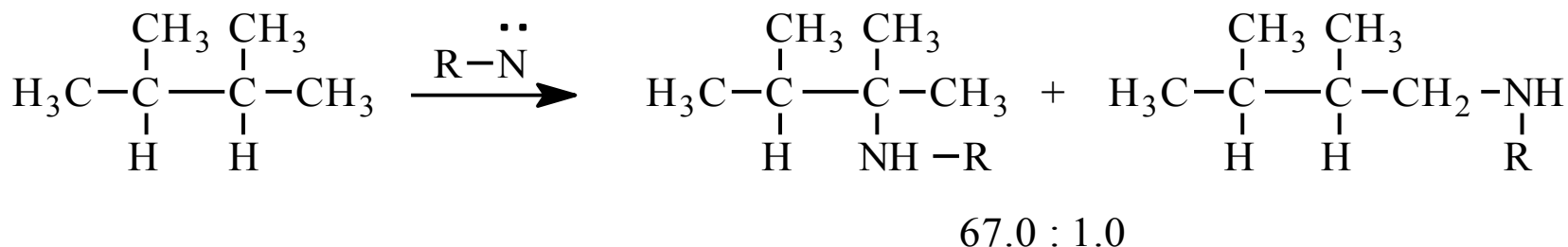


Evidence of Singlet Nitrene C-H Insertion Selectivity



Alkane

Relative reactivities

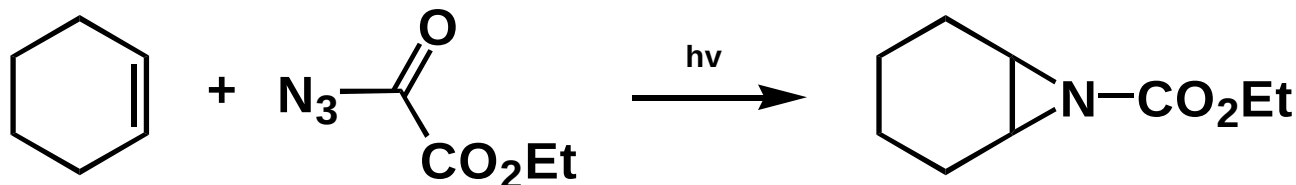


Singlet nitrene C-H insertion selectivity:

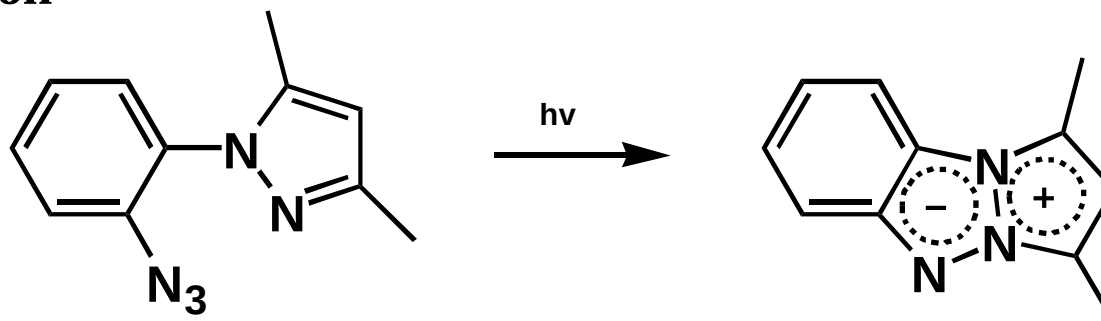
tertiary C-H > secondary C-H > primary C-H

Reactions of Nitrenes

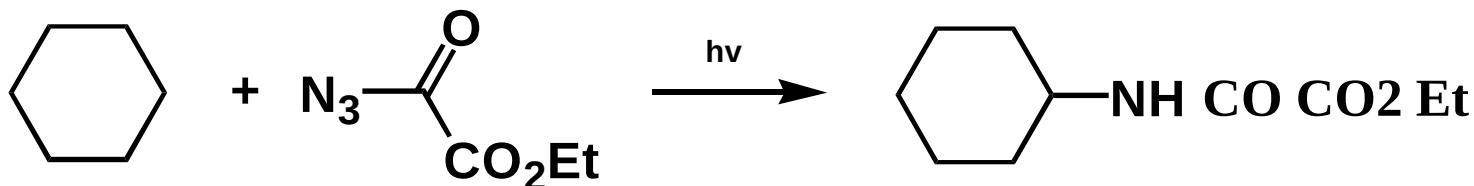
• Addition reactions¹



• Ylide formation²



• Insertion reactions¹



¹Lwowski, W. *Angew. Chem. Int. Ed. Engl.* **1967**, 6, 897. ²Albini, A.; Bettinetti, G.; Minoli, G. *J. Am. Chem. Soc.*, **1997**, 119, 7308.

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.