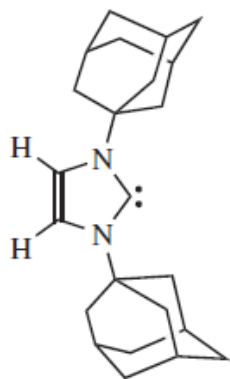
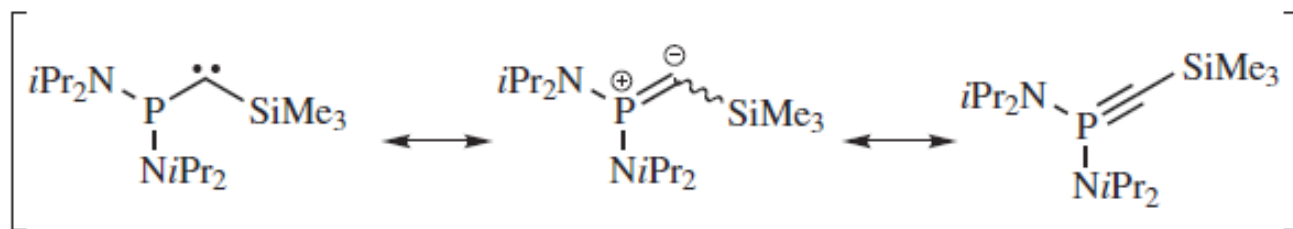


Carbenes

- Highly reactive species with practical lifetimes considerably under 1 s
- Carbenes have been isolated by entrapment in matrices at low temperatures (77 K or less)
- Carbenes that are stable at room temperature have been reported



stable crystals
(m.p. 240–241°C)

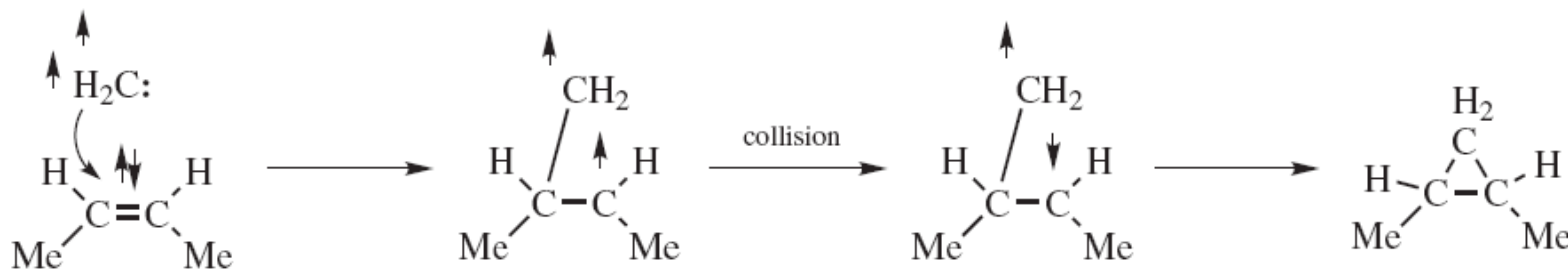
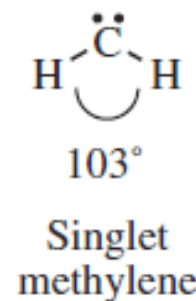
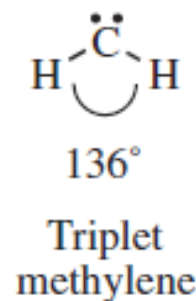
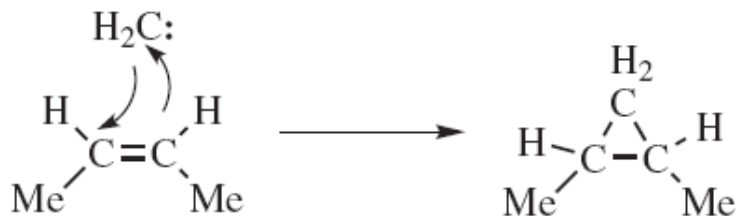


Angew. Chem. Int. Ed. 1991, 30, 674



Carbenes

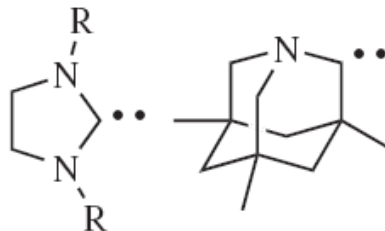
- The two nonbonded electrons of a carbene can be either paired (singlet) or unpaired (triplet)



Examples of carbene

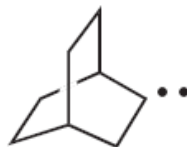
- **Methylene & dichlorocarbene** :CH_2 :CCl_2

- **Heterocyclic carbenes**



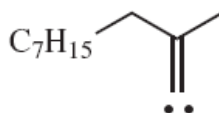
Angew. Chem. Int. Ed. 1997, 36, 2607
Angew. Chem. Int. Ed. 2002, 41, 1290
J. Org. Chem. 2002, 67, 9288

- **bicyclo[2.2.2]octylidene**



Tetrahedron Lett. 2001, 42, 6979

- **alkylidene carbenes**



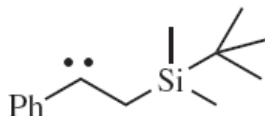
Chem. Rev. 2004, 104, 3795

- **Conformationally restricted cyclopropylcarbenes**



Tetrahedron Lett. 2001, 42, 8761

- **β -Silylcarbenes**

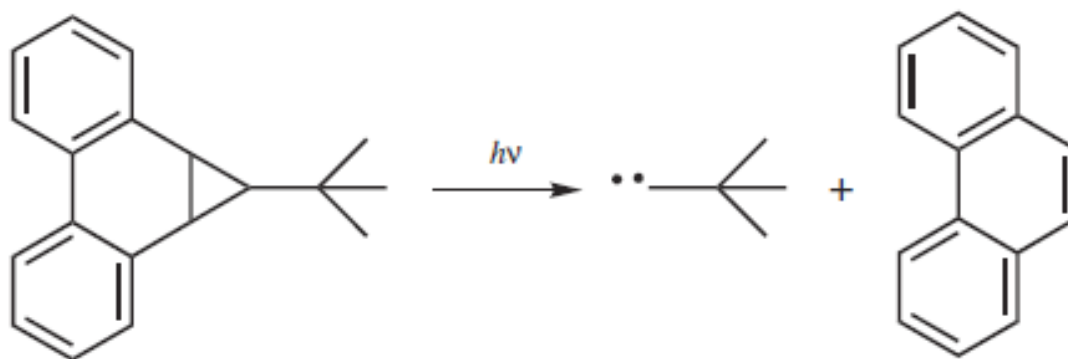
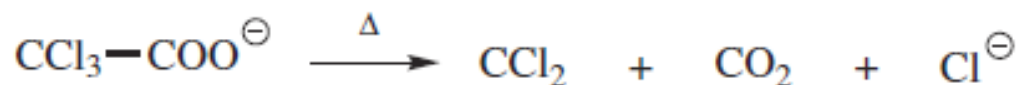
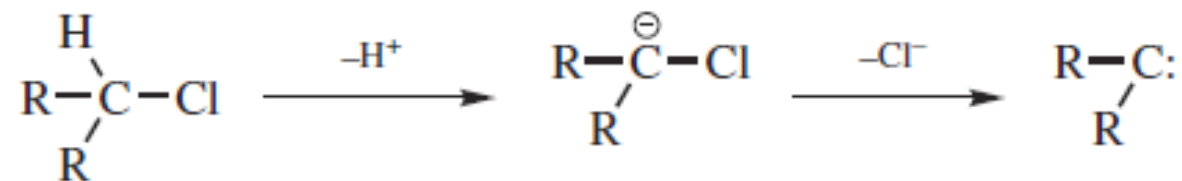


J. Org. Chem. 2002, 67, 112



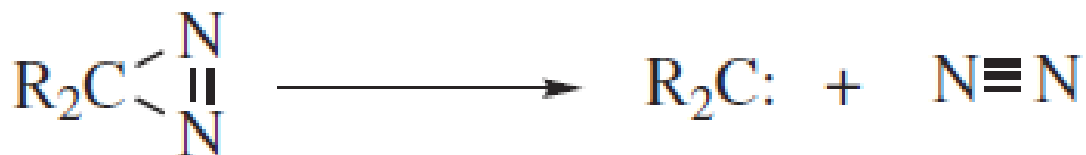
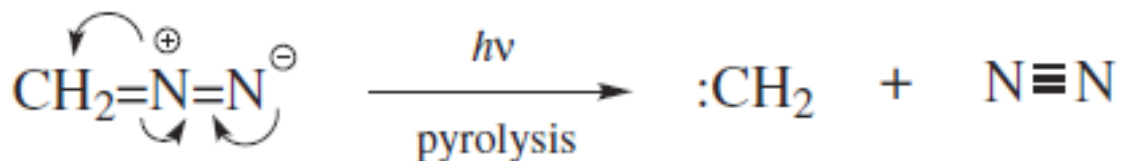
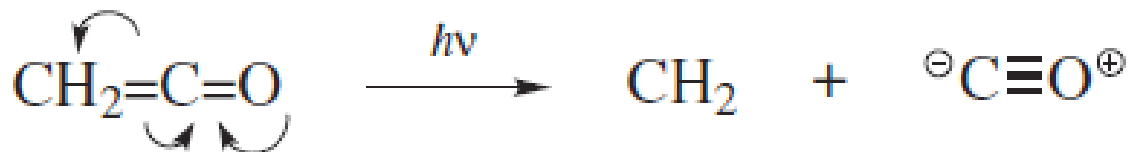
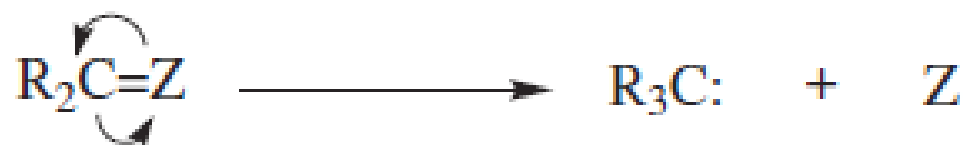
Generation of carbenes

1. α -Elimination



Generation of carbenes

2. Disintegration of compounds containing certain types of double bonds

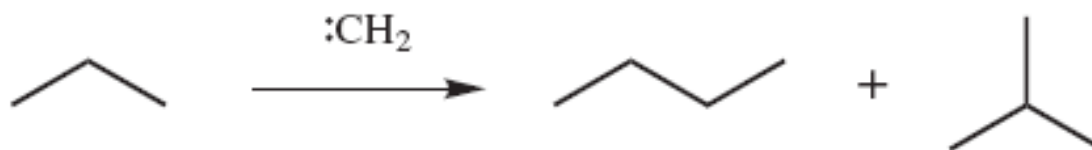


Diazirines are widely used for its photo-affinity in bioactive probes



Reactions of carbenes

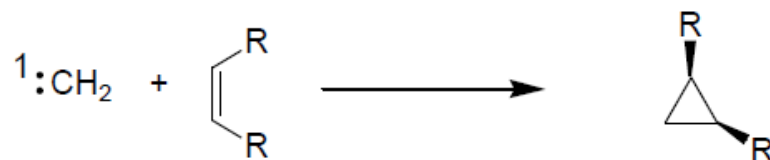
◆ Insertion into C—H bonds



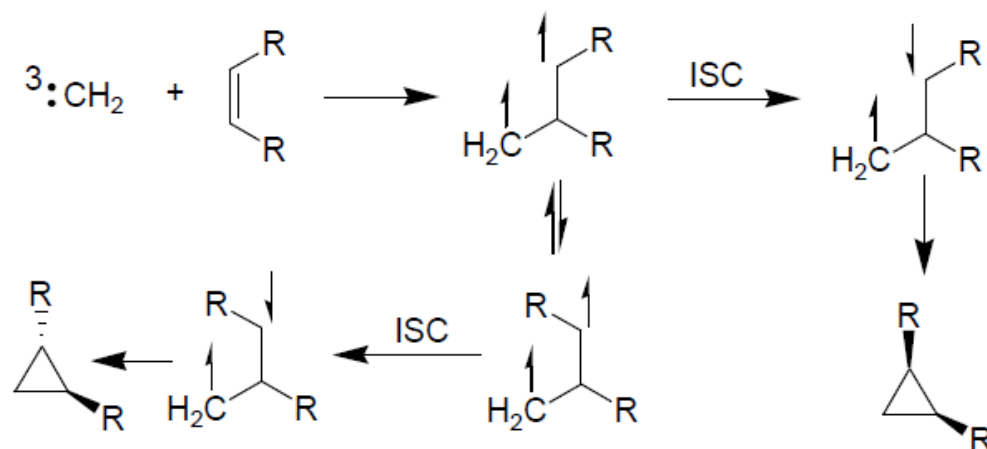
Reactions of carbenes

◆ Additions to C=C

■ **Cyclopropanation** The Skell Rule:



Singlet carbenes add to olefins stereospecifically;



Triplet carbenes add non-stereospecifically

Skell and Woodward *JACS*, 1956, 78, 4496.

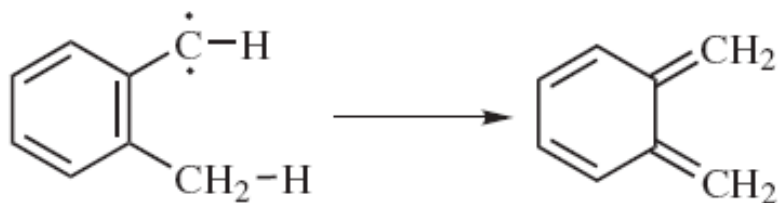
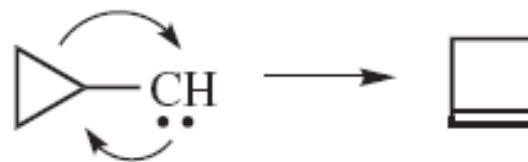
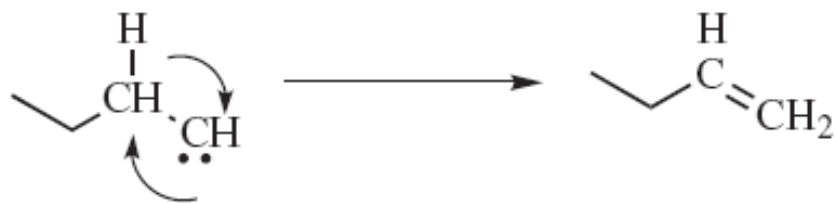


Reactions of carbenes

◆ Dimerization



◆ Rearrangement with migration of alkyl or hydrogen



Reactions of carbenes

- ◆ Triplet carbenes can abstract hydrogen or other atoms to give free radicals



Singlet carbenes can also give this reaction, in this case only halogen atoms are abstracted, not hydrogen.

J. Am. Chem. Soc. 1971, 93, 1527, 4935,
Acc. Chem. Res. 1977, 10, 85

