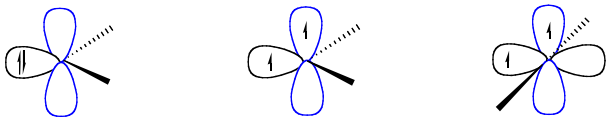
Carbenes In Organic Synthesis

Features of Carbene Reactions

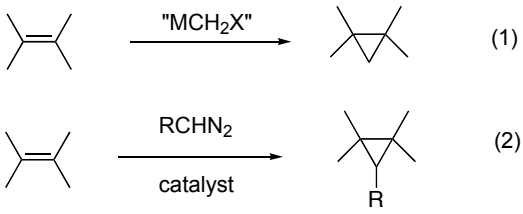
• A carbene is a highly reactive organic molecule with a divalent carbon atom with only six valence electrons. The carbene comes in two varieties - a singlet and triplet. The singlet type has its carbon atom sp2 hybridized with an empty p-orbital extending above and below a plane containing R1 and R2 and the free electron pair. Typically these molecules are very short lived, although persistent carbenes are now known.

• Singlet carbenes have a pair of electrons and sp2 hybrid structure. Triplet carbenes have two unpaired electrons. They may be either sp2 hybrid or linear sp hybrid. Most carbenes have nonlinear triplet ground state with the exception of carbenes with nitrogen, oxygen, sulfur atoms, and dihalocarbenes.



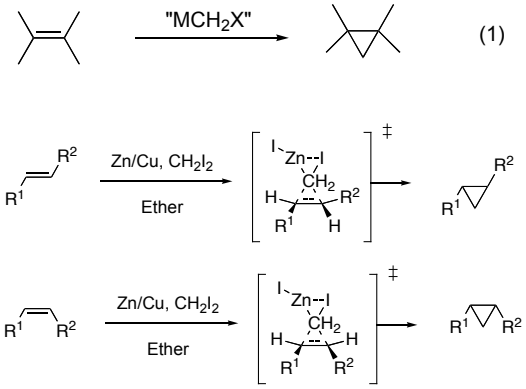
singlet triplet triplet

Carbene Additions to Alkenes

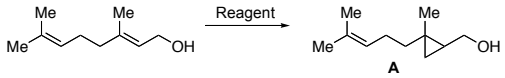


Lebel, H.; Marcoux, J. F.; Molinaro, C.; Charette, A. B., "Stereoselective cyclopropanation reactions." *Chem. Rev.* **2003**, *103*, 977-1050.

Halomethylzinc Additions to Alkenes



Lebel, H.; Marcoux, J. F.; Molinaro, C.; Charette, A. B., "Stereoselective cyclopropanation reactions." *Chem. Rev.* **2003**, *103*, 977-1050.

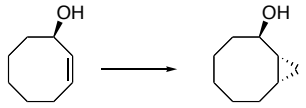


A

Reagent	A : B : C
Et_2Zn, CH_2I_2	74 : 2 : 3
iBu_3Al, CH_2I_2	1 : 76 : 4
Sm(Hg), ICH_2Cl	98 : 0 : 0
Et_2Zn, $IZnCH_2I$	91 : 2 : 3

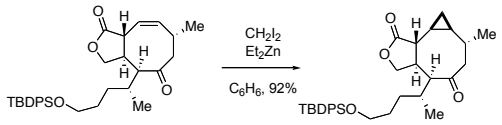
B

C

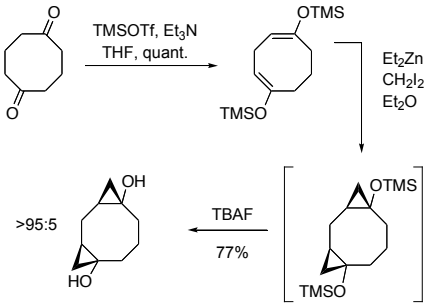


anti:syn

Zn/Cu, CH_2I_2	9:1
$Sm/HgCl_2$, CH	>40:1



Schreiber's bis-cyclopropanation:



Carbene Insertions - Intramolecular C-H Bond Insertion

Taber, D. F.; Yu, H.; Incarvito, C. D.; Rheingold, A. L., "Synthesis of (-)-isonitrin B." *J. Am. Chem. Soc.* **1998**, *120*, 13285. The intramolecular insertion proceeds with retention of absolute configuration.