Alkene Reactions – 1- Addition Reactions

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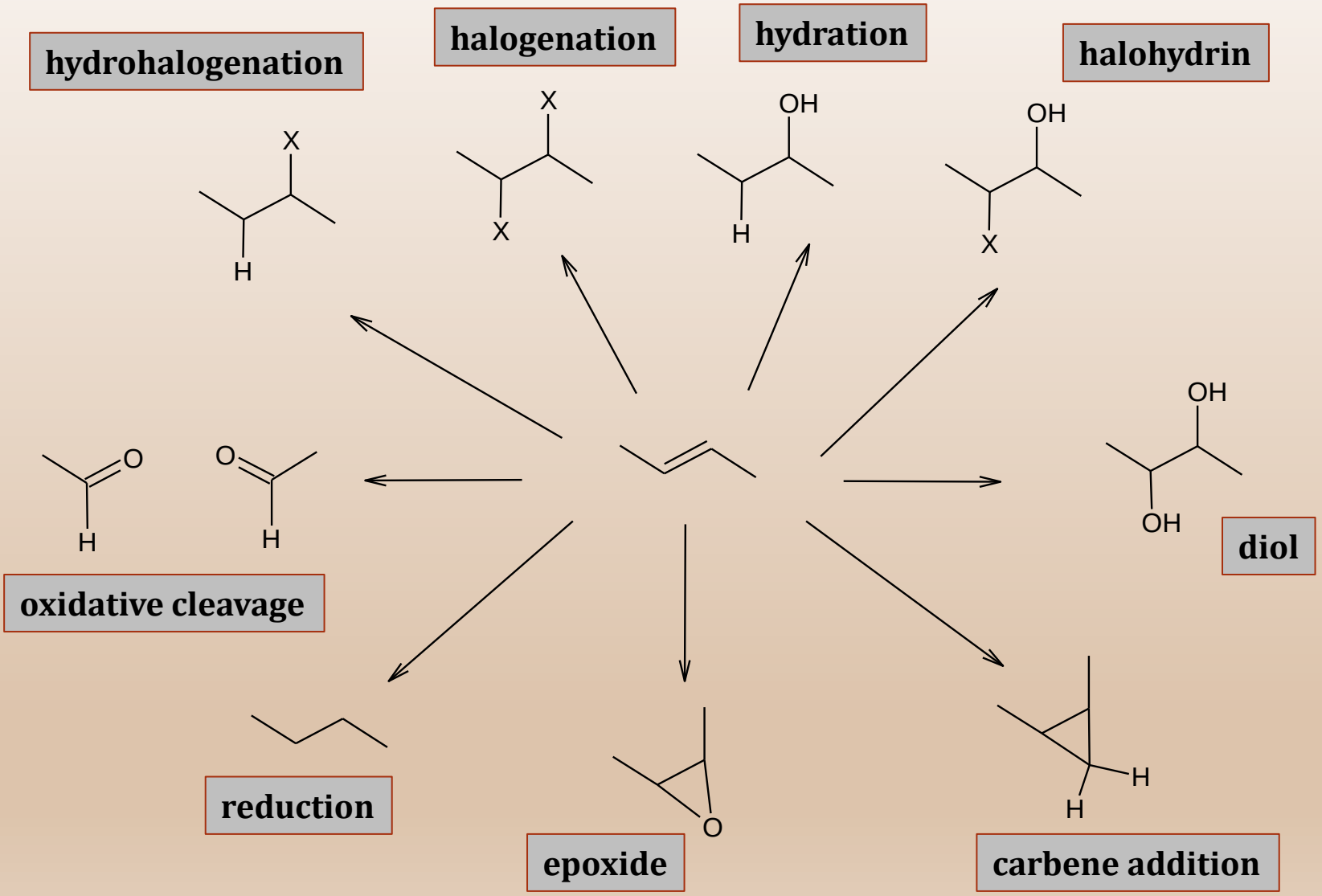
Reactions of Alkenes

1. Most reactions of alkenes are addition because of the unsaturation in the double bond.
2. Other reactions are oxidations
3. Alkenes react with many electrophiles to give useful products by addition (often through special reagents)

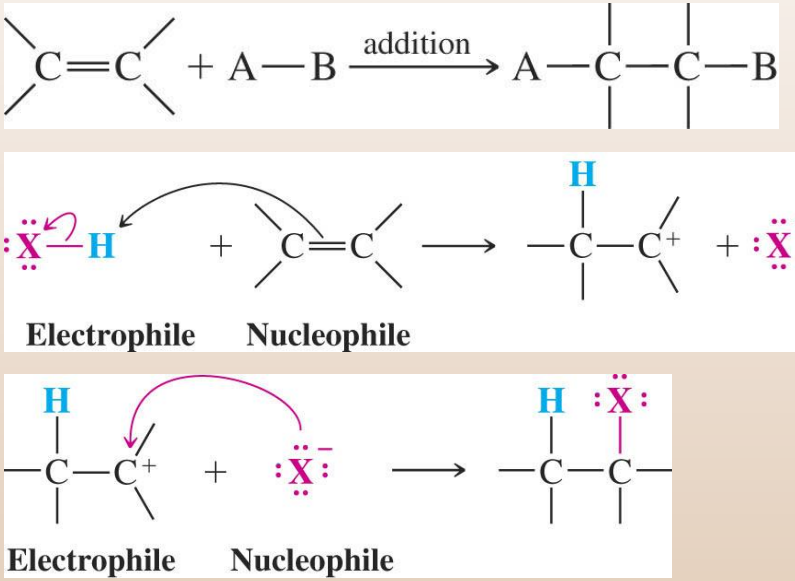
- Addition Reactions
  - Hydrohalogenation (HX)
  - Halogenation (X_2)
  - Hydration (H_2O)
  - Halohydrin ($X_2 + H_2O$)
  - Synthesis of diols
  - Carbene addition ($:CH_2$)
  - Epoxide formation
  - Hydrogenation (H_2) (reduction)
- Oxidative cleavage

All Reactions

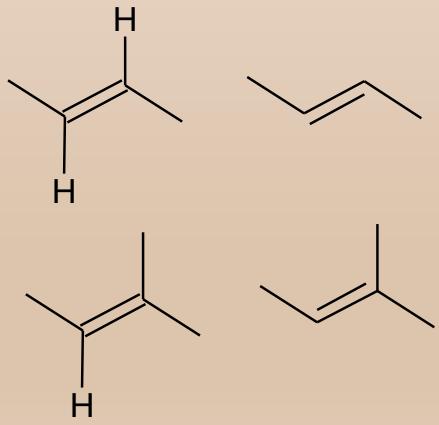


General Mechanism

- The alkene is the nucleophile.
- The reagent is the electrophile

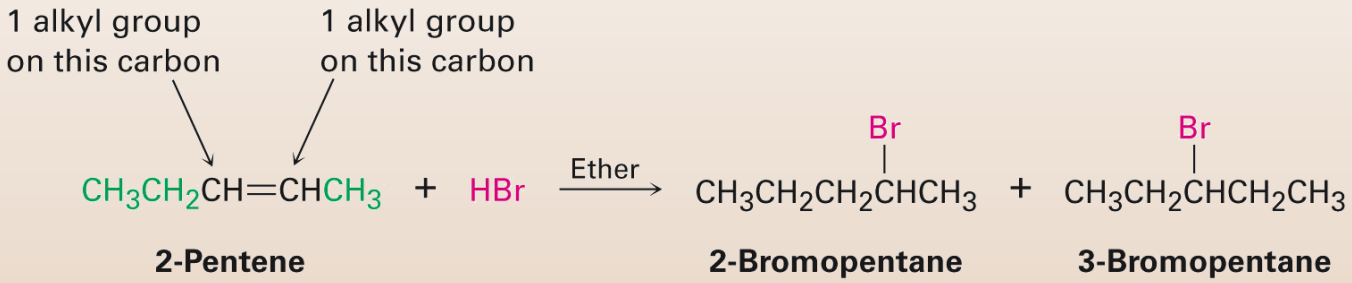


- Alkene types: symmetric – where alkene has equal number of carbons on the double bond and asymmetric where one carbon of the double bond has less carbons.

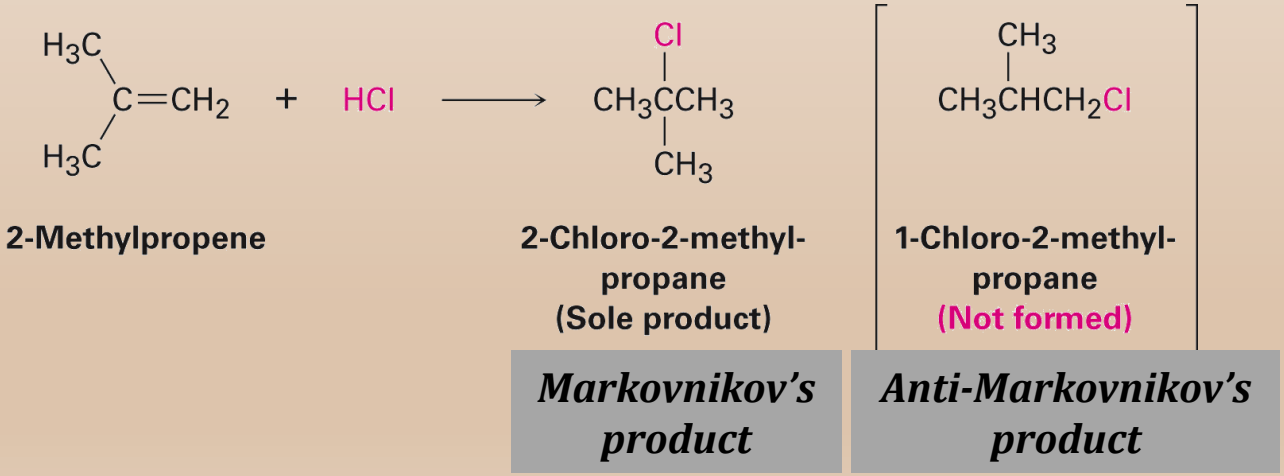


Hydrohalogenation

- Symmetric alkene.

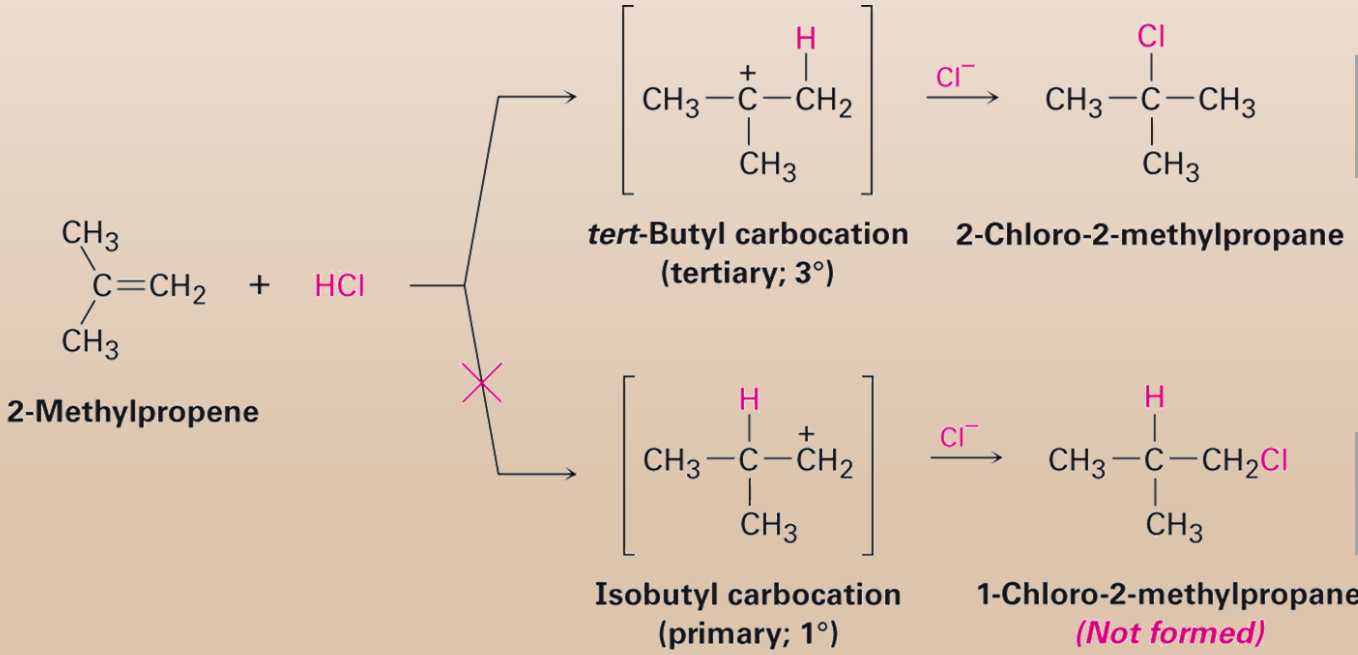


- In an unsymmetric alkene addition of any reagent with H in it, the H will go to the carbon with more H. (***Markovnikov's rule***)

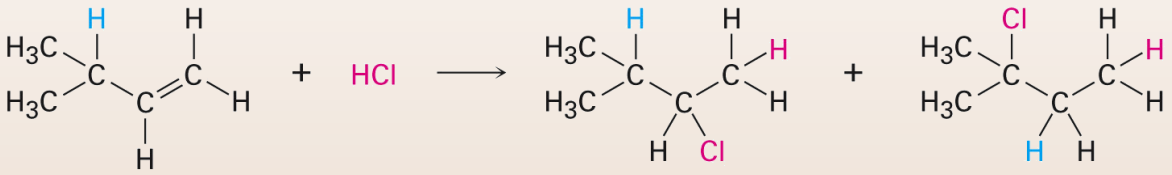


Hydrohalogenation - Mechanism

- This rule was later understood when mechanism of reactions were established.
- During the first step a carbocation is formed – the more stable carbocation will be formed hence give the ***Markovnikov's product***.

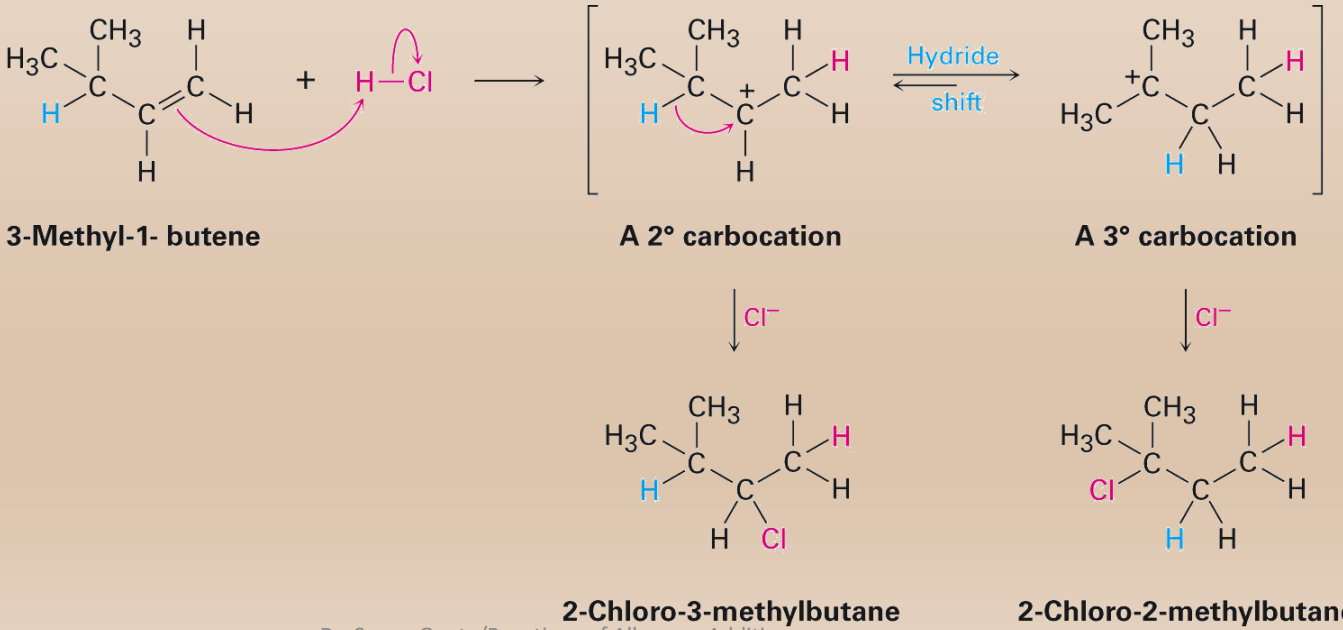


Rearrangement During Addition



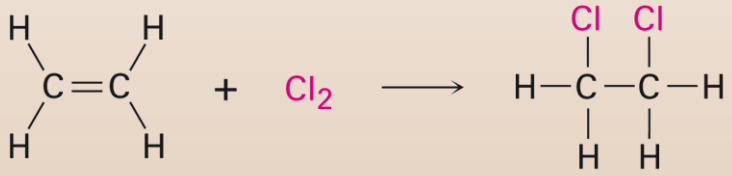
Expected only

- Carbocations undergo structural rearrangements following set patterns
- 1,2-H and 1,2-alkyl shifts occur (H, CH_3, Ph)
- Goes to give most stable carbocation



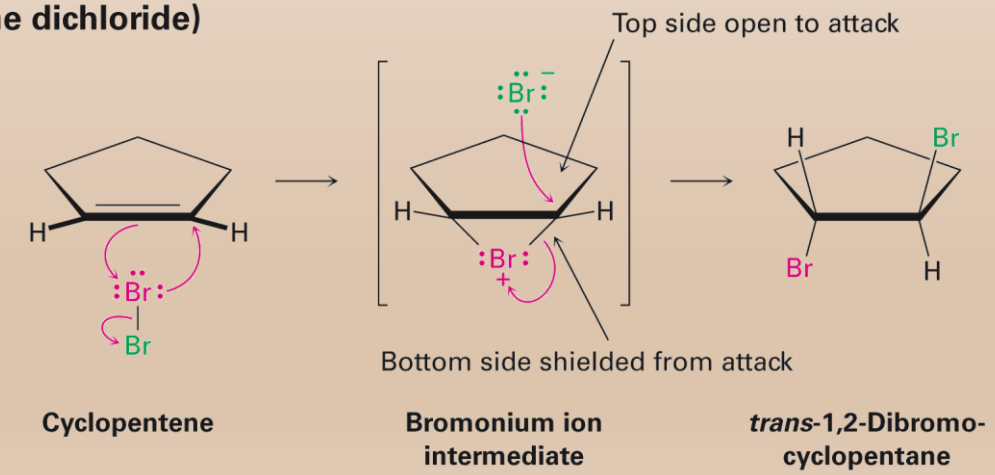
Halogenation

- Bromine and chlorine add to alkenes to give 1,2-dihaldes
- F_2 is too reactive and I_2 does not add
- Cl_2 reacts as Cl^+ Cl^-;
- Br_2 is similar in reactivity ***(QUALITATIVE TEST)***



Ethylene **1,2-Dichloroethane (ethylene dichloride)**

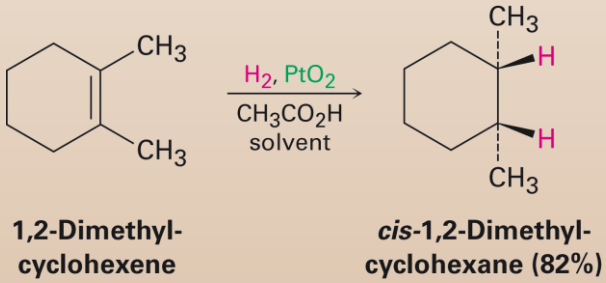
- ***Addition is ANTI (TRANS).***



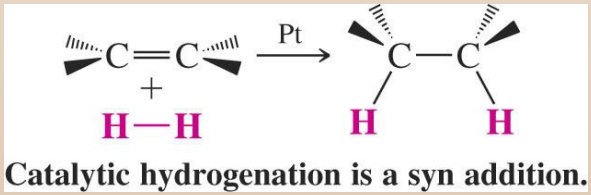
Cyclopentene **Bromonium ion intermediate** ***trans*-1,2-Dibromo-cyclopentane**

Hydrogenation

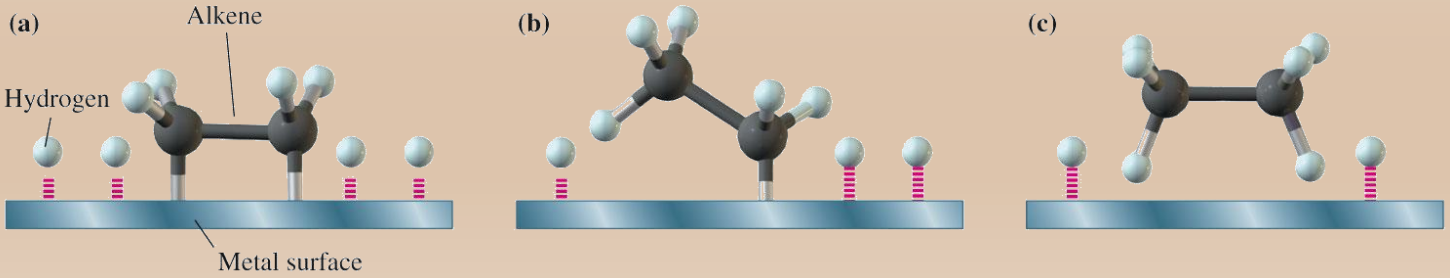
- Addition of H-H across C=C
- Reduction in general is addition of H_2 or its equivalent
- Requires Pt, Pd or Ni as powders on carbon and H_2
- Hydrogen is first adsorbed on catalyst
- ***Addition is SYN***



1,2-Dimethyl-cyclohexene → ***cis*-1,2-Dimethyl-cyclohexane (82%)**

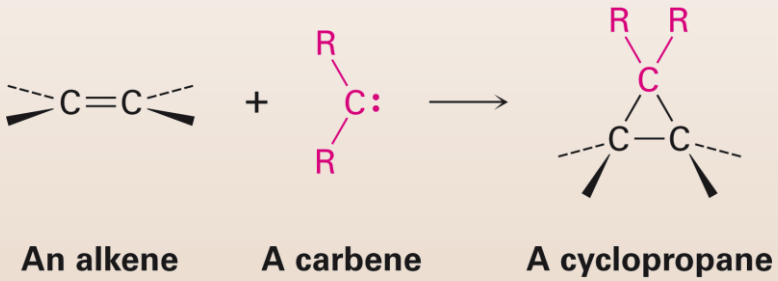


Catalytic hydrogenation is a syn addition.

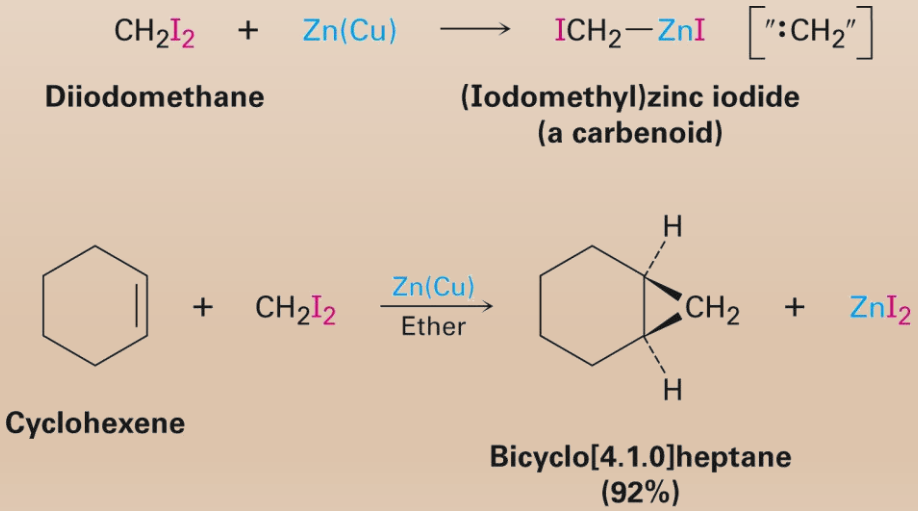


Reaction with Carbene

- The **carbene** is "half of an alkene"
- Carbenes are electronically neutral with six electrons in the outer shell (CH_2:)
- They add symmetrically across double bonds to form cyclopropanes

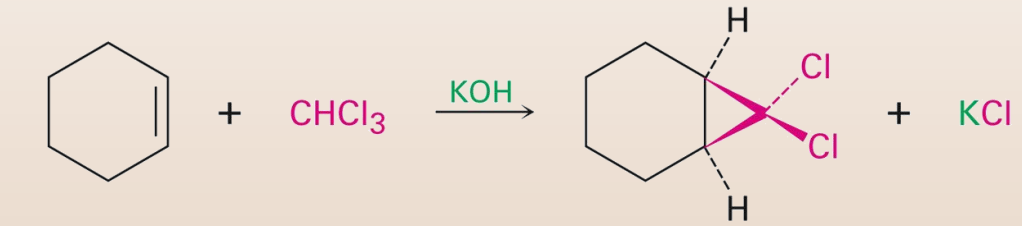


- Another way to generate carbene is the Simmons-Smith reaction



Reaction with Carbene - 2

- Addition of dichlorocarbene is stereospecific ***addition is SYN***



Cyclohexene

Key Words/Concepts

- Electrophilic addition
- Markovnikov's addition
- Syn addition
- Anti addition
- Hydrohalogenation
- Halogenation
- Carbene
- Hydrogenation