Alkane/Alkene Synthesis

Organocopper Reagents

Lithium Dialkylcuprates

Lithium dialkylcuprates are useful synthetic reagents.

They are prepared from alkyllithiums and a copper(I) halide.

$$2RLi + CuX \longrightarrow R_2CuLi + LiX$$

[customary solvents are diethyl ether and tetrahydrofuran (THF)]

Lithium Diorganocuprates are Used to Form C—C Bonds

$$R_2CuLi + R'X \longrightarrow R{-}R' + RCu + LiX$$

$$Ar_2CuLi + R'X \longrightarrow Ar{-}R' + ArCu + LiX$$

Example: Lithium Dimethylcuprate

$$(CH_3)_2CuLi + CH_3(CH_2)_8CH_2I \xrightarrow{\text{diethyl ether}} CH_3(CH_2)_8CH_2CH_3$$

(90%)

Primary alkyl halides work best (secondary and tertiary alkyl halides undergo elimination).

Vinylic Halides Can be Used

$$(CH_3CH_2CH_2CH_2)_2CuLi + \text{C}_6\text{H}_5\text{Br} \xrightarrow{\text{diethyl ether}} \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$$

(80%)

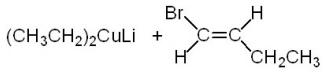
Aryl Halides Can be Used

$$(CH_3CH_2CH_2CH_2)_2CuLi + \text{C}_6\text{H}_5\text{I} \xrightarrow{\text{diethyl ether}} \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$$

(75%)

Question

- What is the principal organic product of the reaction of *trans*-1-bromo-1-butene with lithium diethylcuprate?



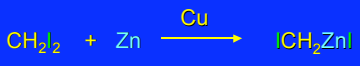
- A) *cis*-3-hexene
- B) *trans*-3-hexene
- C) 3-ethyl-3-hexene
- D) *trans*-2-hexene

Organozinc Reagent

Cyclopropane Synthesis

Iodomethylzinc Iodide

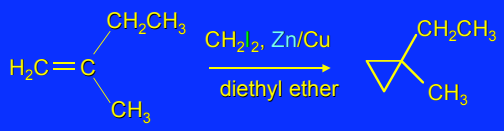
Formed by reaction of diiodomethane with zinc that has been coated with copper (called zinc-copper couple).



Reacts with alkenes to form cyclopropanes.

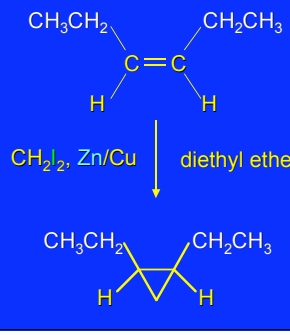
Reaction with alkenes is called the Simmons-Smith reaction.

Example

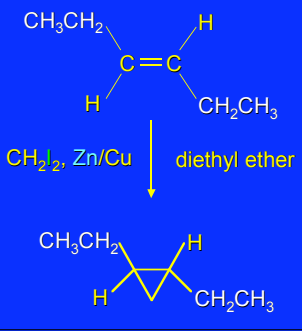


(79%)

Stereospecific syn-Addition



Stereospecific syn-Addition



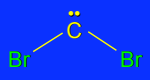
Question

- Give the major product of the reaction of (*E*)-2-pentene with CH_2I_2 and Zn(Cu).
- A) *cis*-1-ethyl-2-methylcyclopropane
- B) *trans*-1-ethyl-2-methylcyclopropane
- C) 1-ethyl-1-methylcyclopropane
- D) an equimolar mixture of products A and B

Carbenes and Carbenoids

Carbene

Name to give to species that contains a divalent carbon (carbon with two bonds and six electrons).

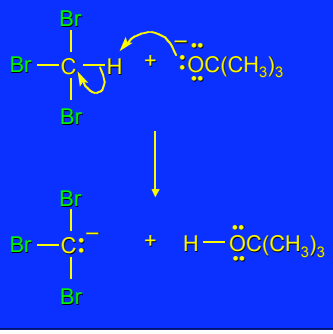


dibromocarbene

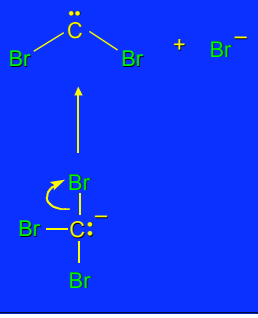
Carbenes are very reactive; normally cannot be isolated and stored.

Are intermediates in certain reactions.

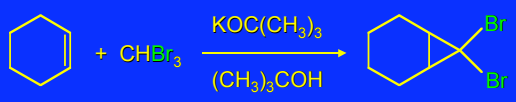
Generation of Dibromocarbene



Generation of Dibromocarbene



Carbenes React with Alkenes to Give Cyclopropanes



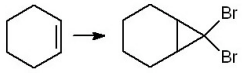
(75%)

CBr_2 is an intermediate

stereospecific syn addition

Question

- Which combination of reagents would accomplish the transformation shown at the right?



- A) $CHBr_3$, $KOC(CH_3)_3$, $(CH_3)_3COH$
- B) CH_2Br_2, Zn(Cu), ether
- C) CH_2Br_2, $KOC(CH_3)_3$, $(CH_3)_3COH$
- D) $CHBr_3$, NaOH, CH_3CH_2OH

Homogeneous Catalytic Hydrogenation

Wilkinson's Catalyst

Wilkinson's Catalyst

Ni, Pt, Pd, and Rh can act as a heterogeneous catalyst in the hydrogenation of alkenes. However, tris(triphenylphosphine)rhodium chloride was found to be soluble in organic solvents. This catalyst was developed by Sir Geoffrey Wilkinson, who received a Nobel Prize in 1973.

Olefin Metathesis

The catalytic breaking and remaking of carbon - carbon bonds in alkenes

Olefin Metathesis

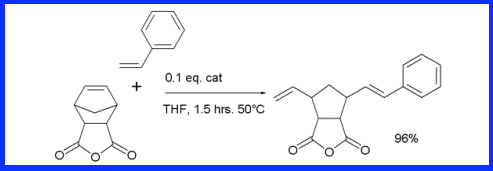
The reaction is generally catalyzed a transition metal complex. Typically Ni, Ru, W, or Mo are used.

Olefin metathesis was first commercialized in petroleum reformation for the synthesis of higher alkenes. There are many types:

Cross-metathesis (CM)
Ring-closing metathesis (RCM)
Enyne metathesis (EM)
Ring opening metathesis (ROM)
Ring opening metathesis polymerisation (ROMP)
Acyclic diene metathesis (ADMET)
Alkyne metathesis (AM)
Alkane metathesis

Olefin Metathesis

Example Cross Olefin Metathesis :



Ziegler-Natta Catalysis of Alkene Polymerization

The catalysts used in coordination polymerization for many polymers are transition-metal organic compounds.

Ziegler-Natta Catalysts

Early Ziegler-Natta catalyst were a combination of $TiCl_4$ and $(CH_3CH_2)_2AlCl$, or $TiCl_3$ and $(CH_3CH_2)_3Al$.

Currently used Ziegler-Natta catalyst combinations include a metallocene such as bis(cyclopentadienyl)zirconium dichloride.