CH 310 N T TH 2-3:30 LECTURE 6

Textbook Assignment: Chapter 15 Begin

Homework (for credit): POW 3 posted

Today's Topics: Organometallic Reagents

Notice & Announcements:

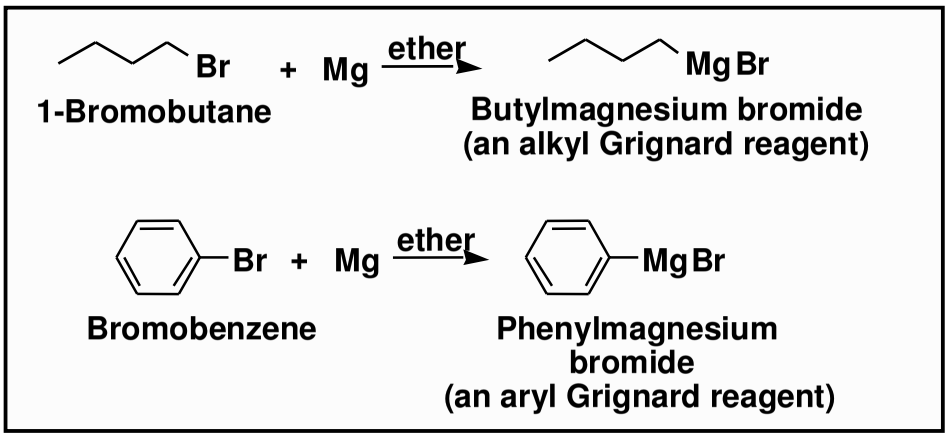
Graded POWs in mailboxes outside WEL 2.246

Organometallic Compound

- Organometallic compound: a compound that contains a carbon-metal bond
- The focus will be on organometallic compounds of **Mg, Li, and Cu**
  - these classes illustrate the usefulness of organometallics in modern **synthetic organic chemistry**
  - the use of organometallics can bring about transformations that cannot be accomplished in any other way

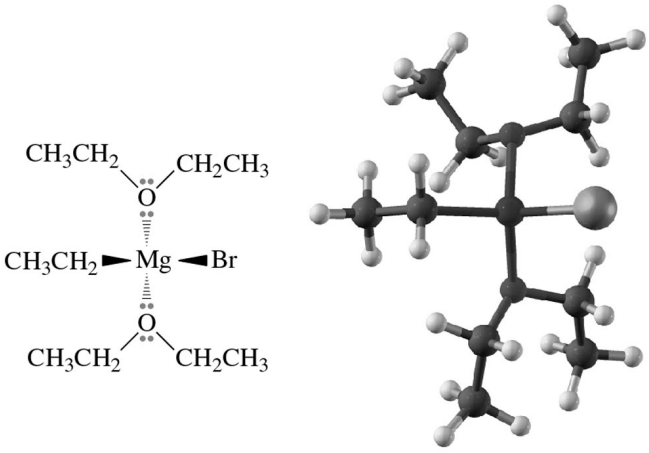
Grignard Reagents

- Grignard reagent: an organomagnesium compound
  - prepared by addition of an alkyl, aryl, or alkenyl (vinylic) halide to Mg metal in diethyl ether or THF



RMgX & RLi

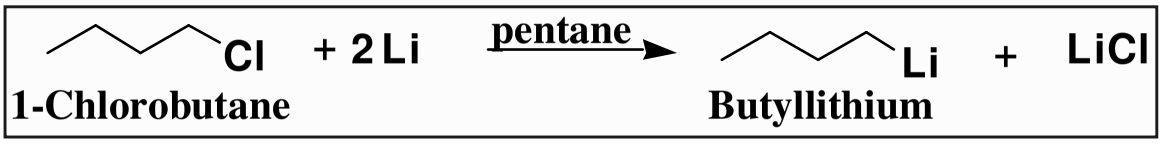
- Grignard reagents dissolve as coordination compounds solvated by ether
  - ethylmagnesium bromide, EtMgBr



Ethylmagnesium bromide dietherate

RMgX & RLi

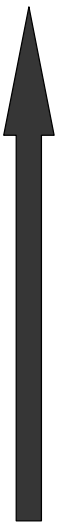
- Organolithium reagents
  - prepared by reaction of an alkyl, aryl, or alkenyl halide with lithium metal



RMgX & RLi

The carbon-metal bonds in RMgX and RLi are polar covalent

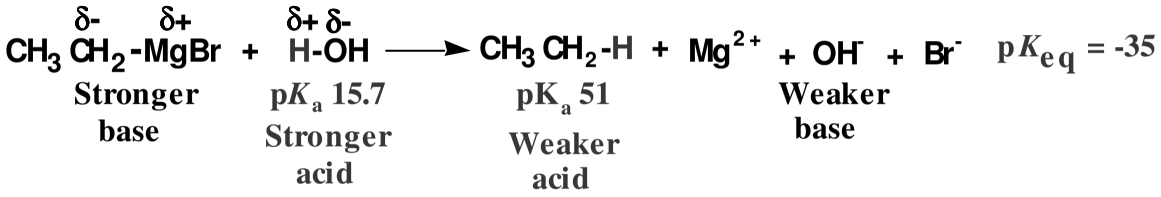
C-M Bond	Difference in Electronegativity	Percent Ionic character*
C-Li	2.5 - 1.0 = 1.5	60
C-Mg	2.5 - 1.2 = 1.3	52
C-Al	2.5 - 1.5 = 1.0	40
C-Zn	2.5 - 1.6 = 0.9	36
C-Sn	2.5 - 1.8 = 0.7	28
C-Cu	2.5 - 1.9 = 0.6	24
C-Hg	2.5 - 1.9 = 0.6	24



Increasing Ionic Character

*Percent ionic character = $\frac{E_C - E_M}{E_C}$ x 100

- Reaction with proton donors:
  - RMgX and RLi are strong bases



  - they react readily with these proton acids

R_2NH	$RC{\equiv}CH$	ROH	HOH	ArOH	RSH	RCOOH
pK_a 38-40	pK_a 25	pK_a 16-18	pK_a 15.7	pK_a 9-10	pK_a 8-9	pK_a 4-5
1° and 2° Amines	Terminal alkynes	Alcohols	Water	Phenols	Thiols	Carboxylic acids

This is often an undesired side reaction-to be avoided!!

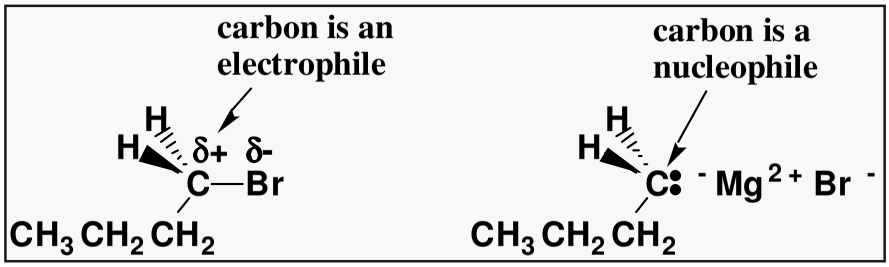
Organometallic reagents have 2 general types of reactions:

1. As Strong bases (Bronsted-Lowry)
2. As nucleophilic reagents:

Regard the alkyl group as "R^-"

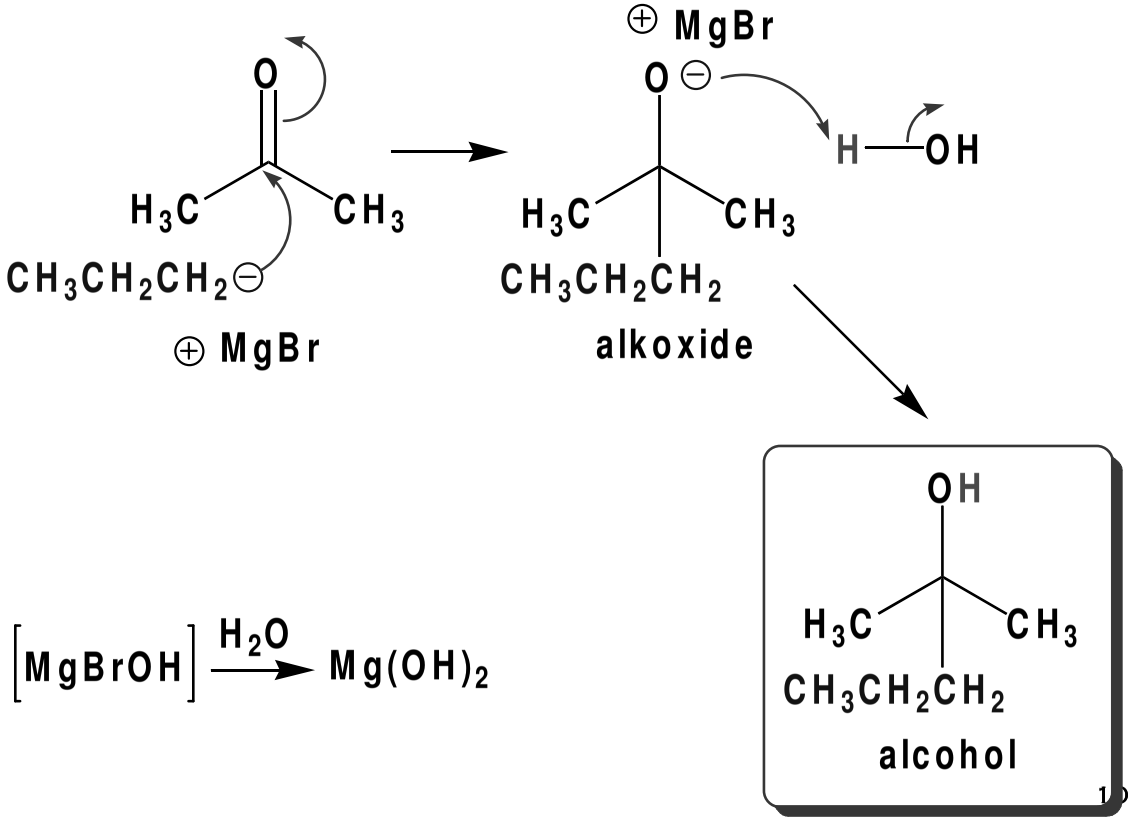
RMgX & RLi

- **RMgX and RLi are valuable in synthesis as nucleophiles**
  - the carbon bearing the halogen is transformed from an electrophile to a nucleophile



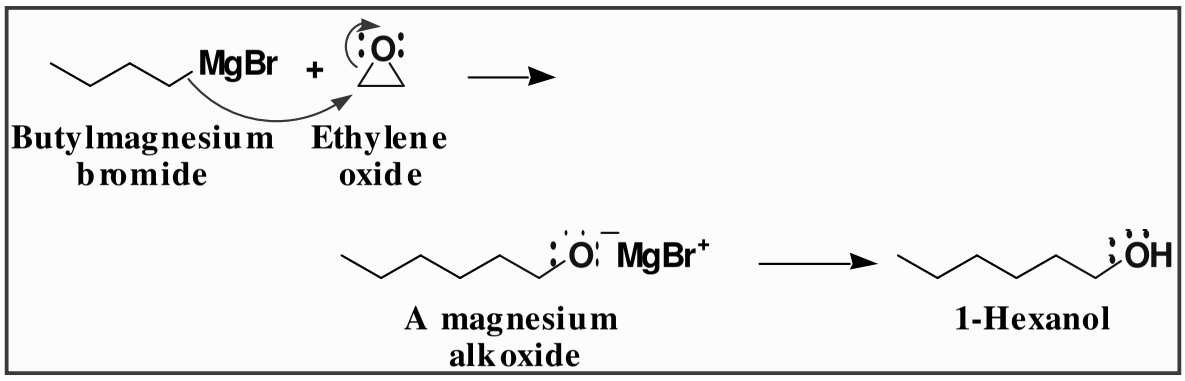
  - their most valuable use is addition to the electrophilic carbon of C=O groups of aldehydes, ketones, carboxylic esters, and acid chlorides to form a new carbon-carbon bonds

A Simple Example:



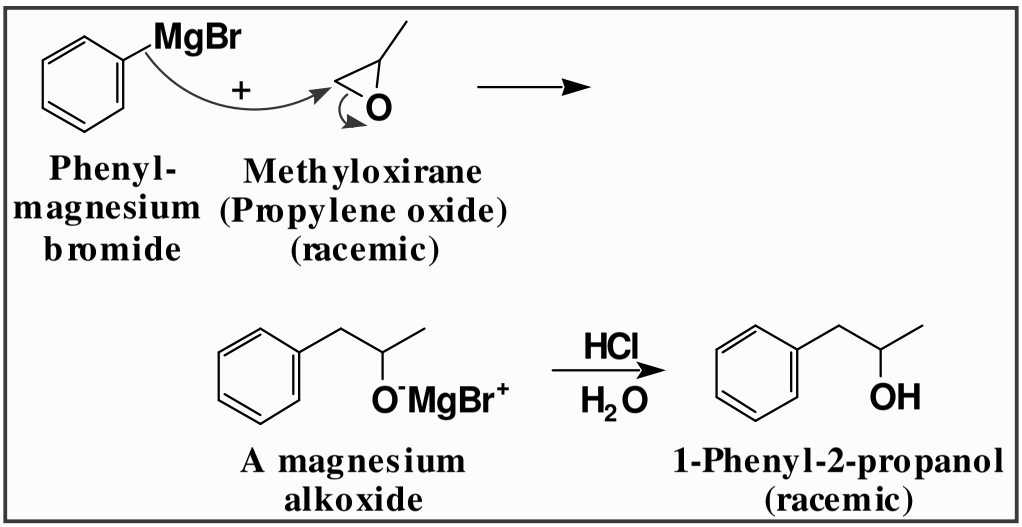
Reactions

- Reaction with oxiranes (epoxides)
  - reaction of RMgX or RLi with an oxirane followed by protonation gives a primary alcohol with a carbon chain two carbons longer than the original chain



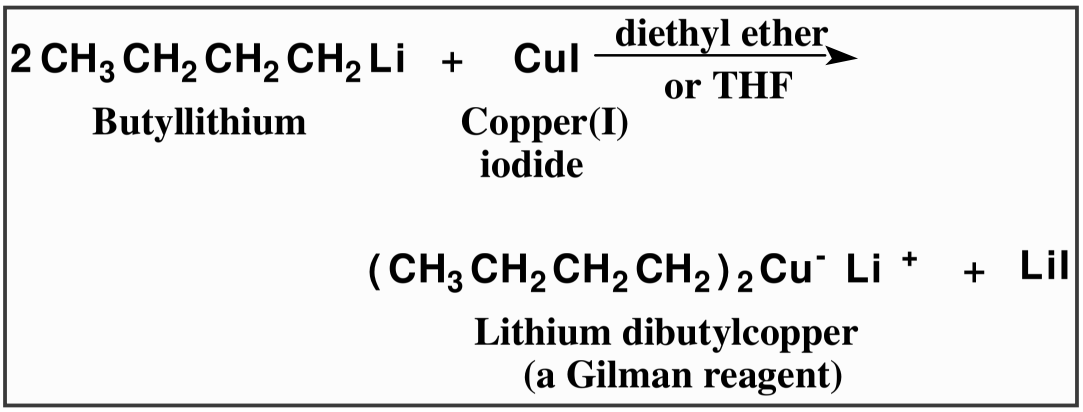
Reactions

- Reaction with oxiranes (epoxides)
  - the major product corresponds to S_N2 attack of RMgX or RLi on less hindered carbon of the epoxide



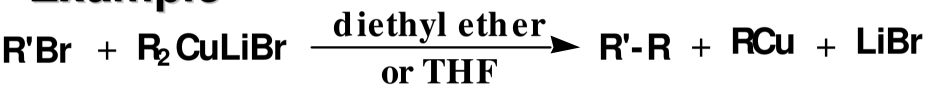
Gilman Reagents

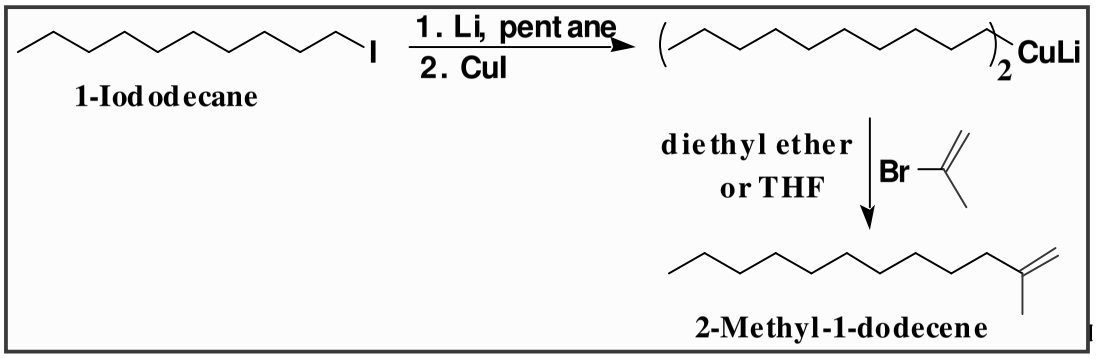
- Lithium diorganocopper reagents, known more commonly as **Gilman reagents**
  - prepared by treating an alkyl, aryl, or alkenyl lithium compound with Cu(I) iodide



Reactions

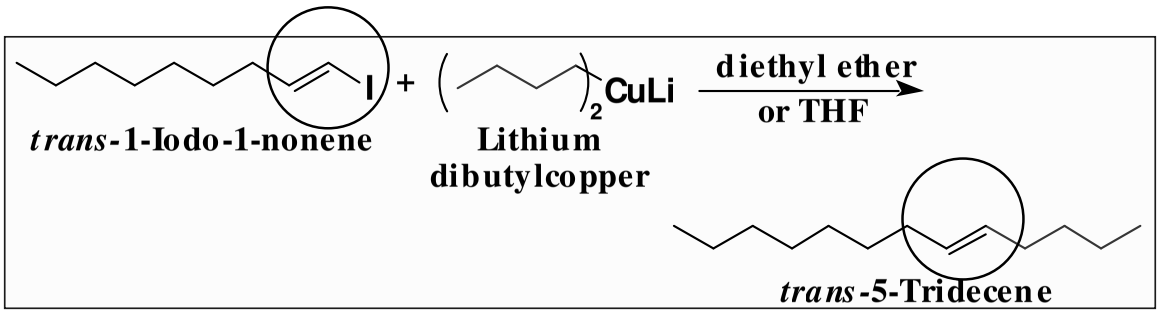
- Coupling within organohalogen compounds
  - form new carbon-carbon bonds by coupling with alkyl and alkenyl chlorides, bromides, and iodides
  - **Example**





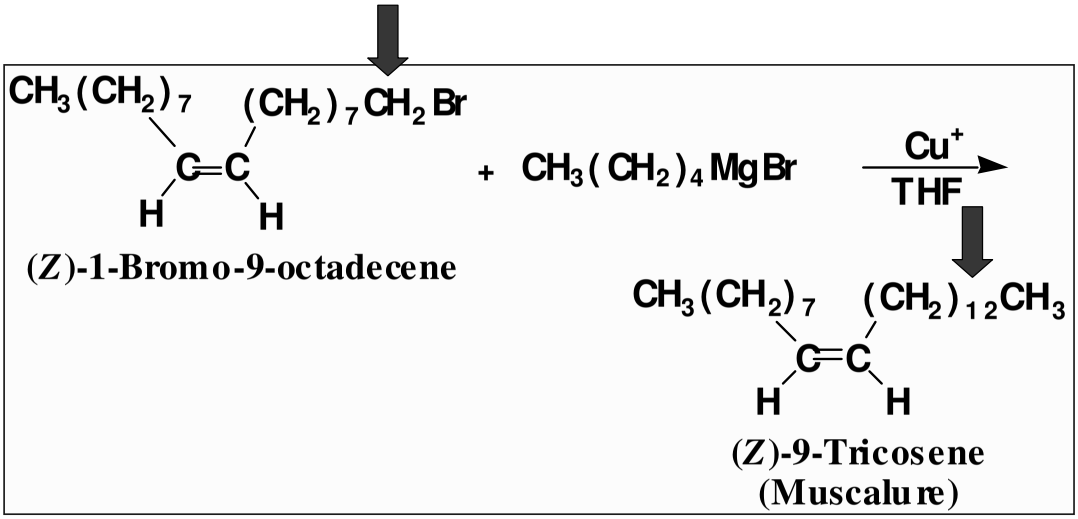
Reactions

coupling with a vinylic halide is stereospecific: the configuration of the carbon-carbon double bond is retained



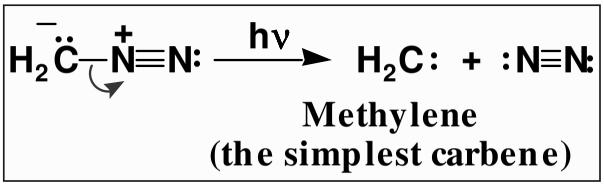
Reactions

- A variation on the preparation of a Gilman reagent is to use a Grignard reagent with a catalytic amount of a copper(I) salt



Carbenes & Carbenoids

- **Carbene**, R_2C: a neutral molecule in which a carbon atom is surrounded by only six valence electrons
- Methylene, the simplest carbene
  - prepared by photolysis or thermolysis of diazomethane

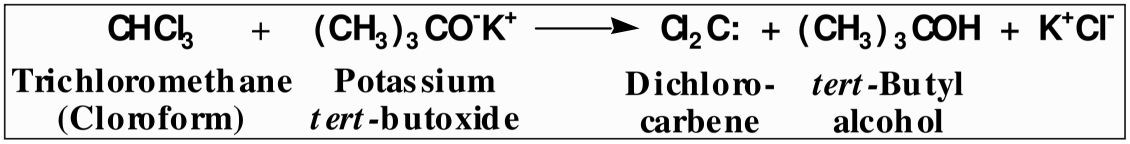


  - methylene prepared in this manner is so nonselective that it is of little synthetic use

Carbenes & Carbenoids

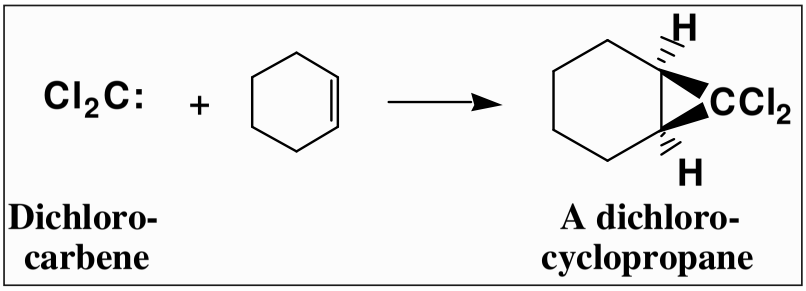
Dichlorocarbene

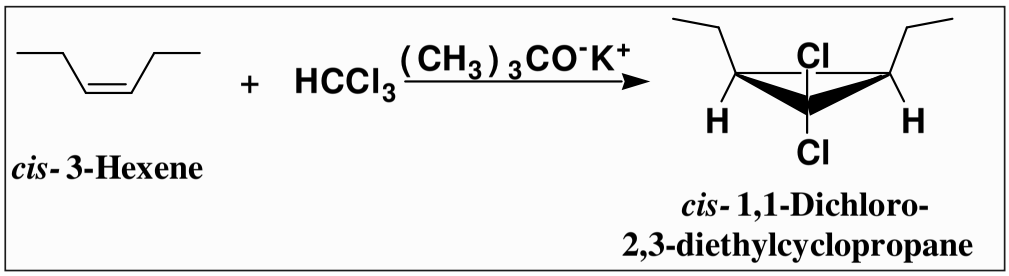
- prepared by treating chloroform with potassium *tert*-butoxide



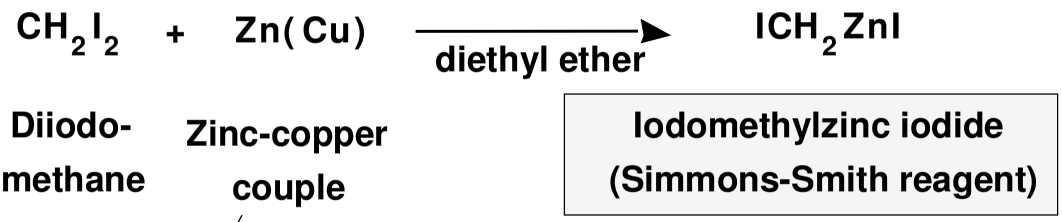
Dichlorocarbene

reacts with alkenes to give dichlorocyclopropanes





- **Simmons-Smith reaction**
  - a way to add methylene to an alkene to form a cyclopropane
  - generation of the Simmons-Smith reagent

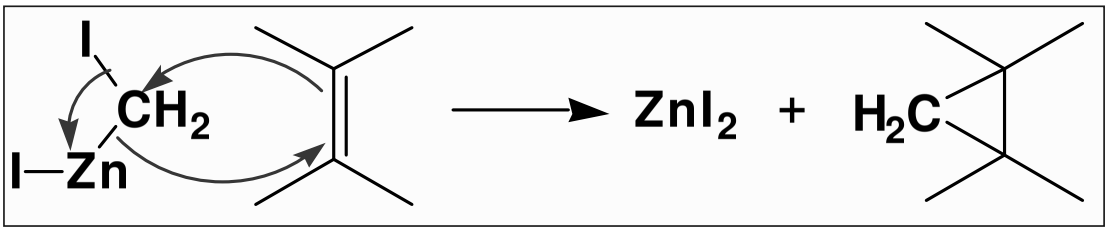


  - this organozinc compound reacts with a wide variety of **alkenes to give cyclopropanes**

(prepared by: Zn dust; CuCl & heat)

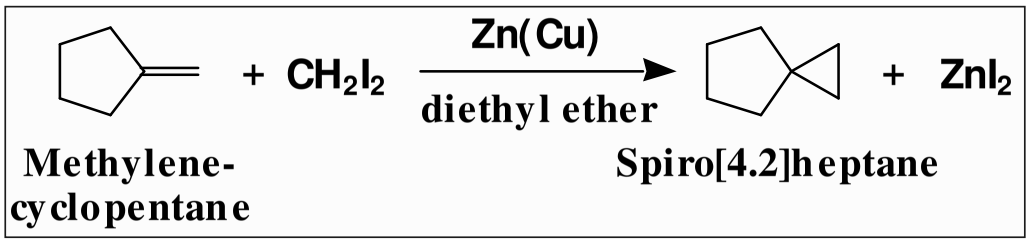
Simmons-Smith reaction:

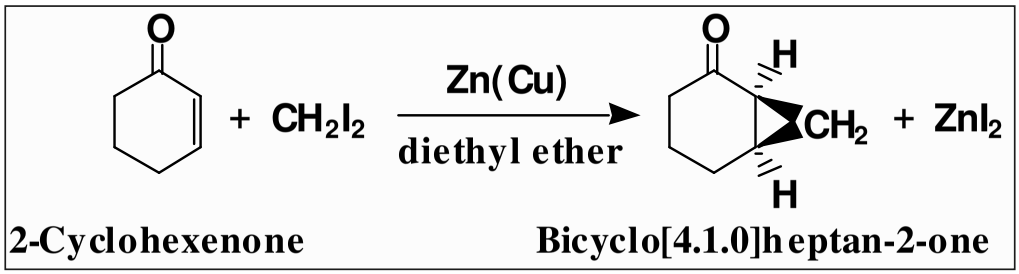
the organozinc compound reacts with an alkene by a concerted mechanism*



***concerted mechanism**-one in which there is simultaneous bond breaking and bond formation.

Uses of the Simmons-Smith reagent:





Aldehydes And Ketones

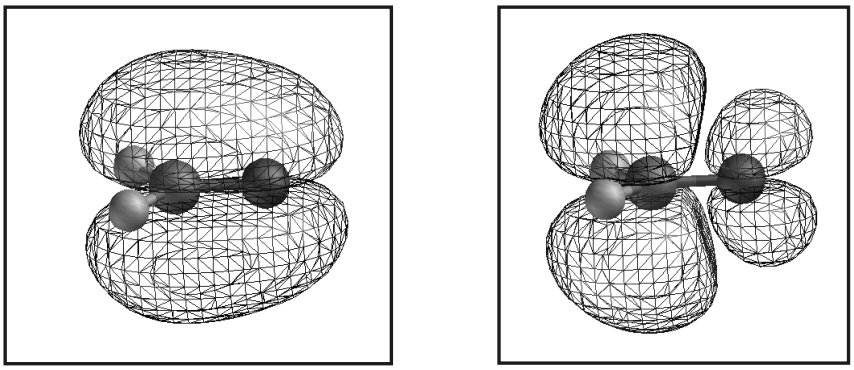
The Carbonyl Group

The next units cover the physical and chemical properties of classes of compounds containing the carbonyl group, **C=O**

- aldehydes and ketones (Chapter 16)
- carboxylic acids (Chapter 17)
- acid halides, acid anhydrides, esters, amides (Chapter 18)
- enolate anions (Chapter 19)

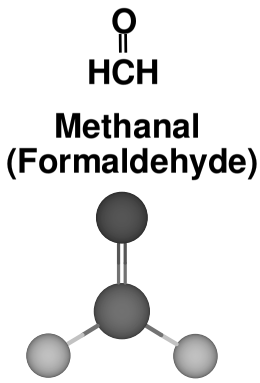
– the carbonyl group consists of **one sigma bond** formed by the overlap of sp^2 hybrid orbitals and **one pi bond** formed by the overlap of parallel 2*p* orbitals

– pi bonding and pi antibonding MOs for formaldehyde

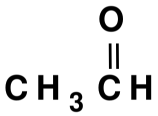


– the functional group of an **aldehyde** is a carbonyl group bonded to a H atom and a carbon atom

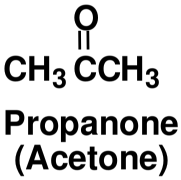
– the functional group of a **ketone** is a carbonyl group bonded to two carbon atoms



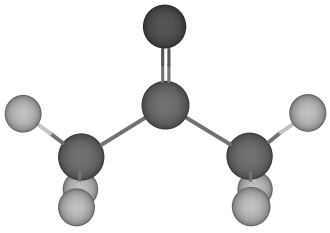
Methanal
(Formaldehyde)



Ethanal
(Acetaldehyde)



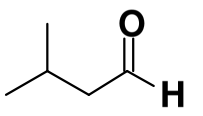
Propanone
(Acetone)



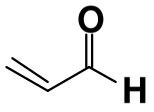
Nomenclature

IUPAC names:

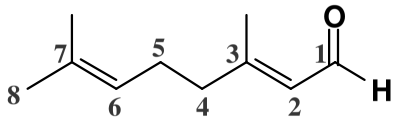
- the parent chain is the longest chain that contains the functional group
- for an aldehyde, change the suffix from -e to -al
- for an unsaturated aldehyde, change the infix from -an- to -en-; the location of the suffix determines the numbering pattern
- for a cyclic molecule in which -CHO is bonded to the ring, add the suffix -carbaldehyde



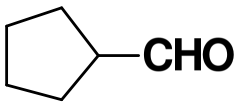
3-Methylbutanal



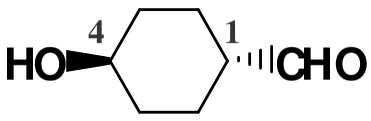
2-Propenal
(Acrolein)



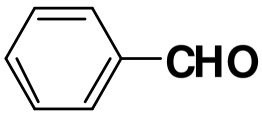
(2*E*)-3,7-Dimethyl-2,6-octadienal
(Geranial)



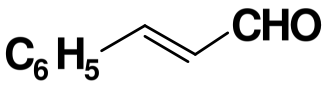
Cyclopentane-
carbaldehyde



trans-4-Hydroxycyclo-
hexanecarbaldehyde



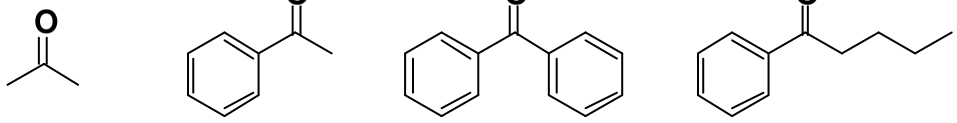
Benzaldehyde



trans-3-Phenyl-2-propenal
(Cinnamaldehyde)

IUPAC names

- the parent alkane is the longest chain that contains the carbonyl group
- for ketones, change the suffix -e to -one
- number the chain to give C=O the smaller number
- the IUPAC retains the common names acetone, acetophenone, and benzophenone

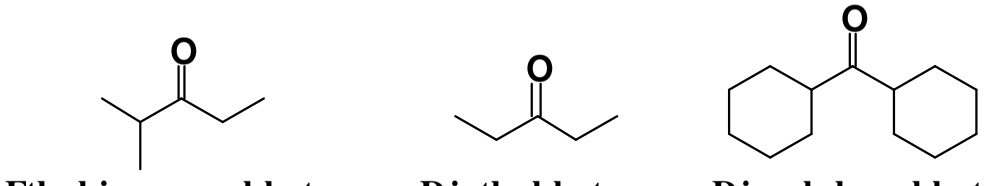


Propanone (Acetone) | Acetophenone | Benzophenone | 1-Phenyl-1-pentanone

Common Names

- **for an aldehyde, the common name is derived from the common name of the corresponding carboxylic acid**
- **for a ketone, name the two alkyl or aryl groups bonded to the carbonyl carbon and add the word ketone**

Formaldehyde | Formic acid | Acetaldehyde | Acetic acid



Ethyl isopropyl ketone | Diethyl ketone | Dicyclohexyl ketone