

CH 318 N

LECTURE 8

Textbook Assignment: Chapter 15-Organometallic Compounds

Homework (for credit): POW 3 posted

Today's Topics: Organic Reactions-Organometallic Reagents

Notice & Announcements:

Exam I:

JGB 2.216 7-9 PM

ORGANIC LECTURE SERIES

Organometallic Reagents

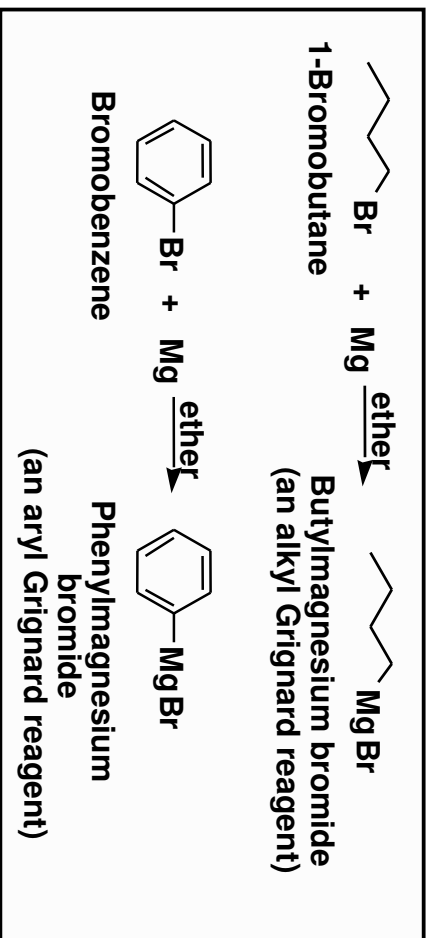
Organometallic Compound

- 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

3

Grignard Reagents

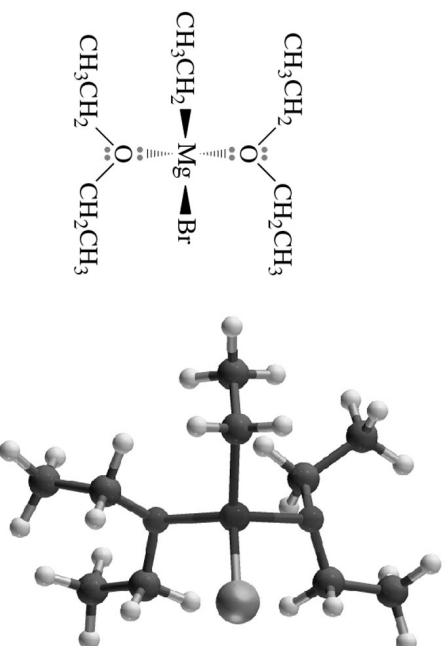
- Grignard reagent: an organomagnesium compound
 - prepared by addition of an alkyl, aryl, or alkenyl (vinyllic) halide to Mg metal in diethyl ether or THF



4

RMgX & RLi

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



Ethylmagnesium bromide dietherate

5

RMgX & RLi

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



6

RMgX & RLi

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

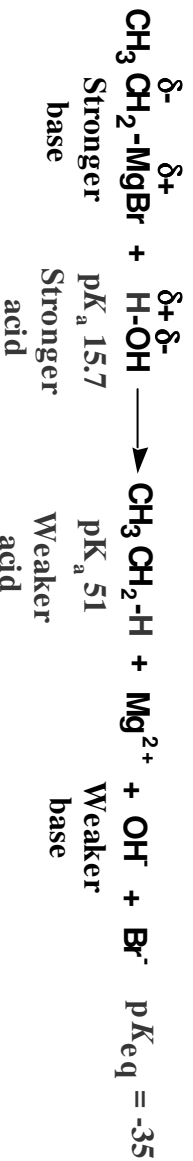
C-M Bond	Difference in Electronegativity character*	Percent Ionic character*
C-Li	2.5 - 1.0 = 1.5	60
C-Mg	2.5 - 1.2 = 1.3	52
C-Al	2.5 - 1.5 = 1.0	40
C-Zn	2.5 - 1.6 = 0.9	36
C-Sn	2.5 - 1.8 = 0.7	28
C-Cu	2.5 - 1.9 = 0.6	24
C-Hg	2.5 - 1.9 = 0.6	24

Increasing Ionic Character

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

7

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



– they react readily with these proton acids

R ₂ NH	RC≡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!!

8

Organometallic reagents have 2 general types of reactions:

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



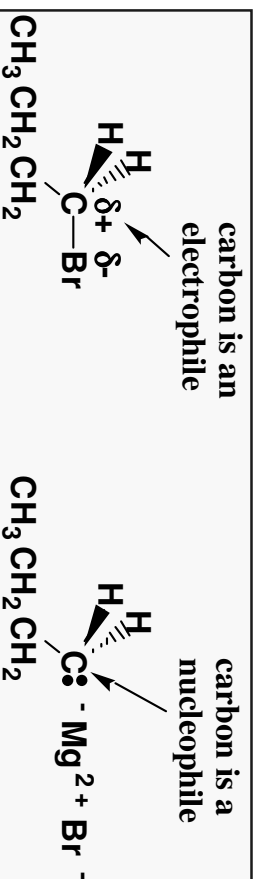
Regard the alkyl group as "R⁻"

9

RMgX & RLi

- **RMgX and RLi are valuable in synthesis as nucleophiles**

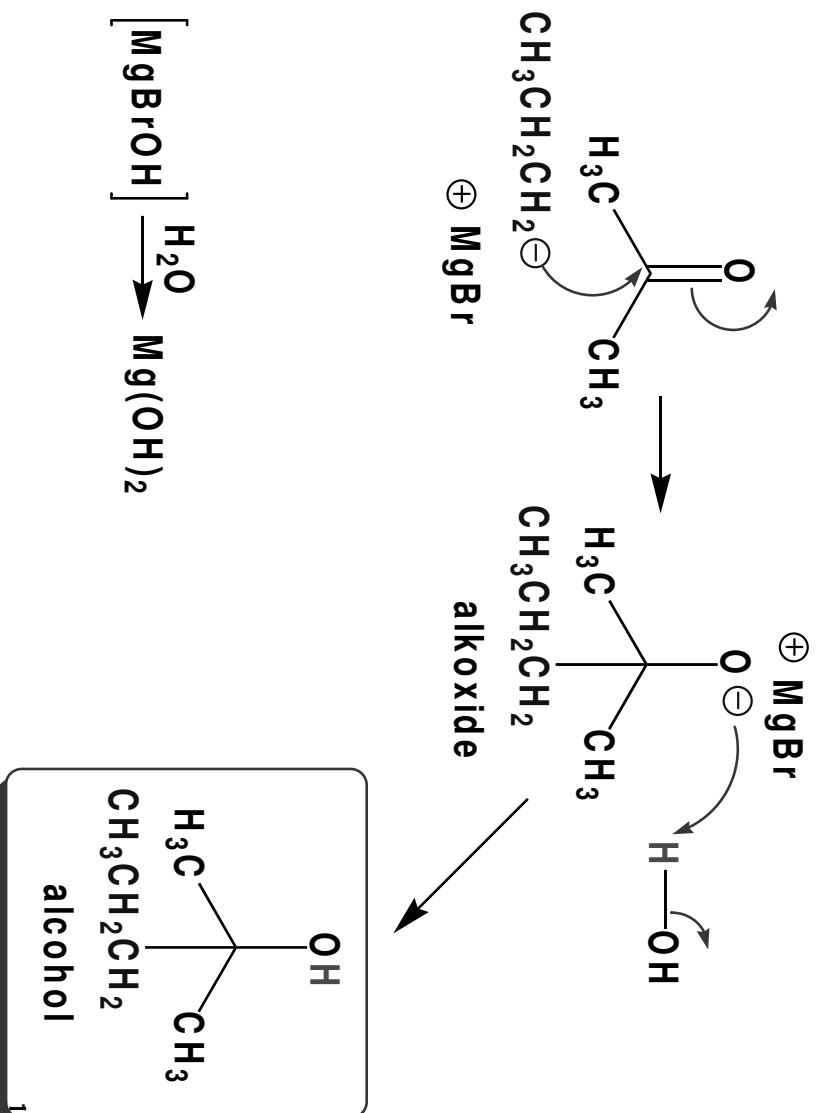
– the carbon bearing the halogen is transformed from an electrophile to a nucleophile



– 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

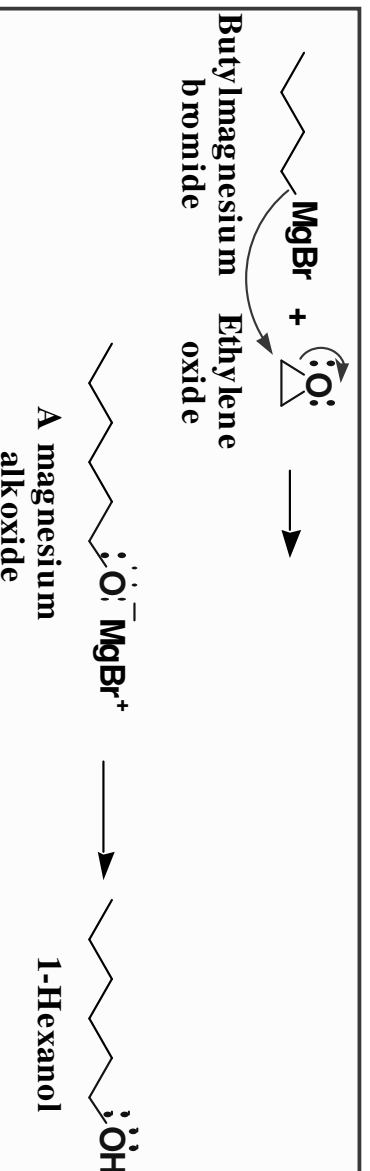
10

A Simple Example:



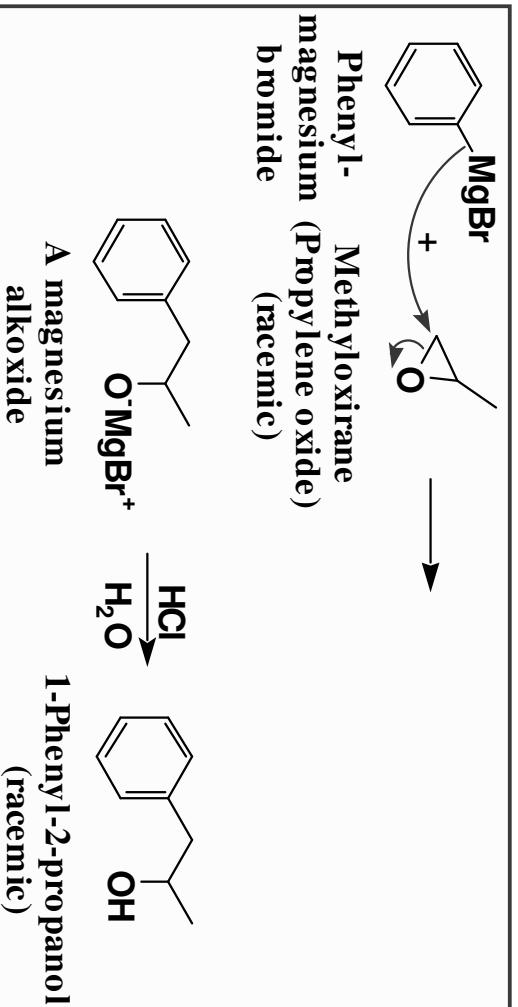
Reactions

- 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

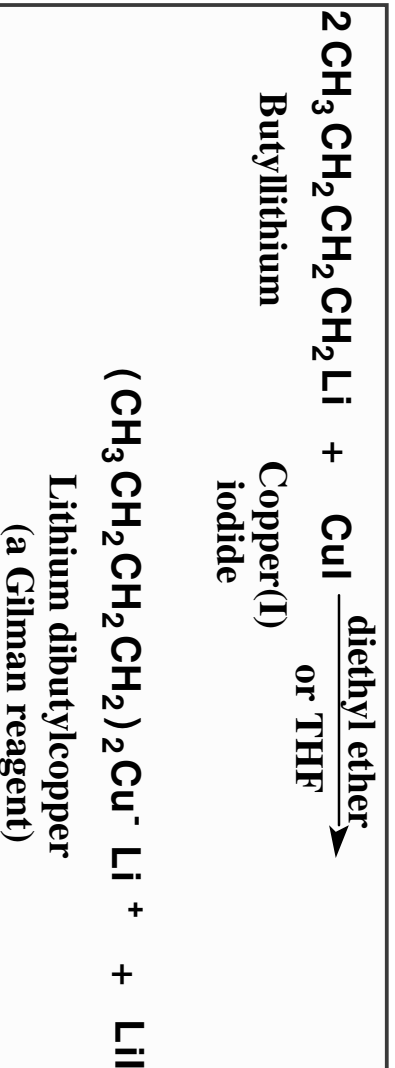
- Reaction with oxiranes (epoxides)
 - the major product corresponds to S_N2 attack of $RMgX$ or RLi on less hindered carbon of the epoxide



13

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

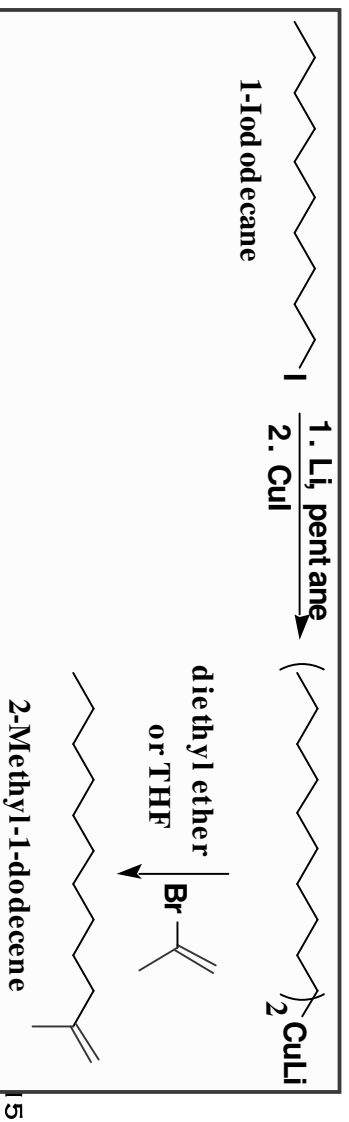


14

Reactions

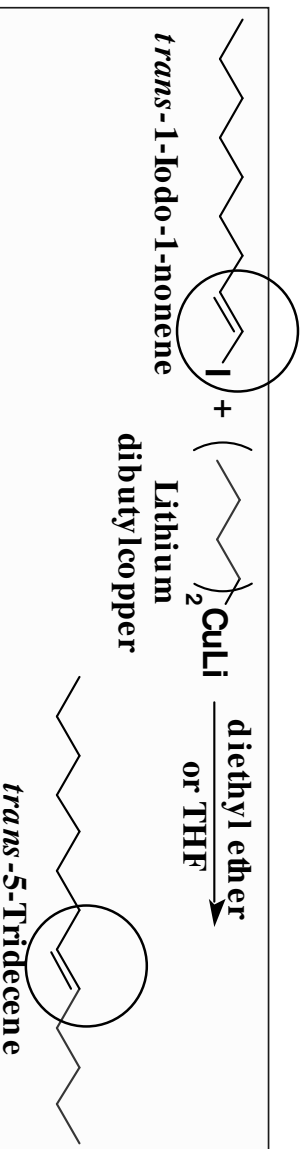
- Coupling within organohalogen compounds
 - form new carbon-carbon bonds by coupling with alkyl and alkenyl chlorides, bromides, and iodides

– **Example**



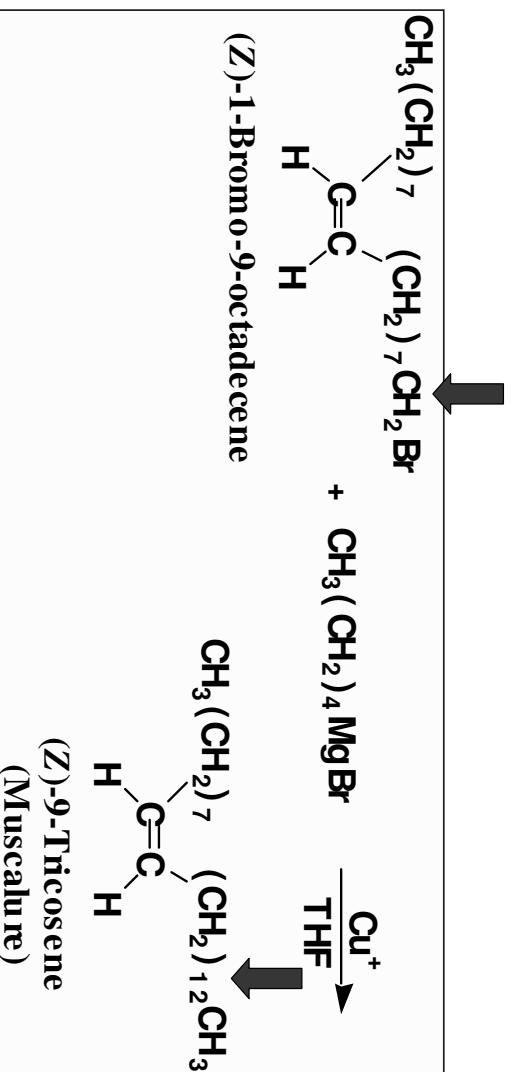
Reactions

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



Reactions

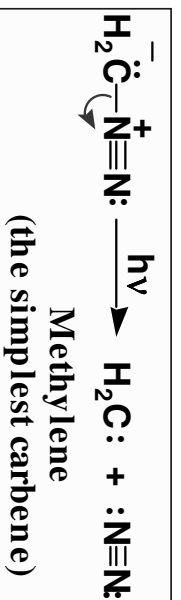
- A variation on the preparation of a Gilman reagent is to use a Grignard reagent with a catalytic amount of a copper(I) salt



17

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



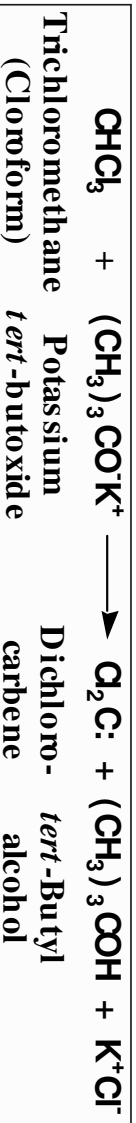
- methylene prepared in this manner is so nonselective that it is of little synthetic use

18

Carbenes & Carbenoids

Dichlorocarbene

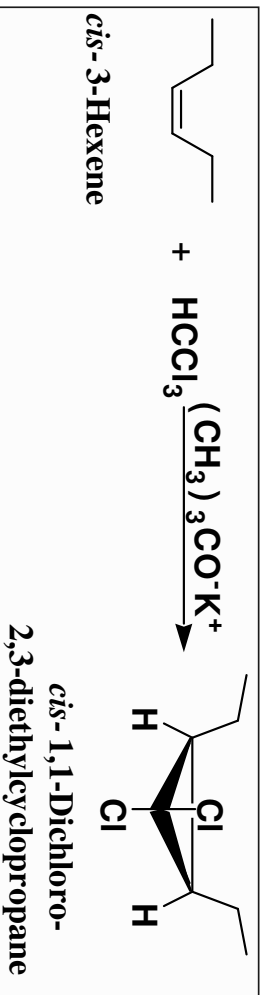
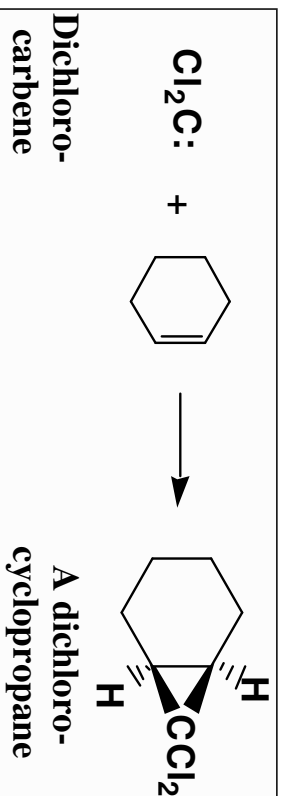
- prepared by treating chloroform with potassium *tert*-butoxide



19

Dichlorocarbene

reacts with alkenes to give dichlorocyclopropanes



20

- **Simmons-Smith reaction**

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



Diiodo- Zinc-copper
methane couple

Iodomethylzinc iodide
(Simmons-Smith reagent)

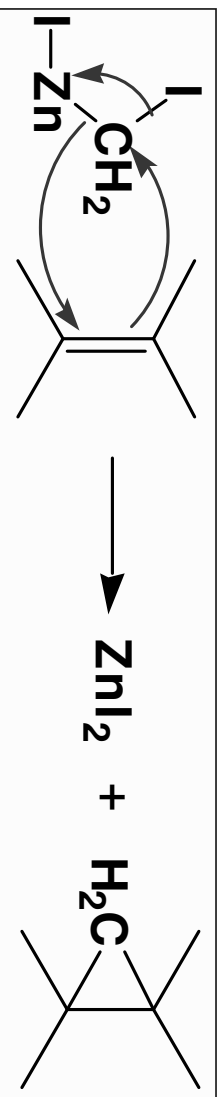
- this organozinc compound reacts with a wide variety of **alkenes to give cyclopropanes**

(prepared by: Zn dust; CuCl & heat)

21

Simmons-Smith reaction:

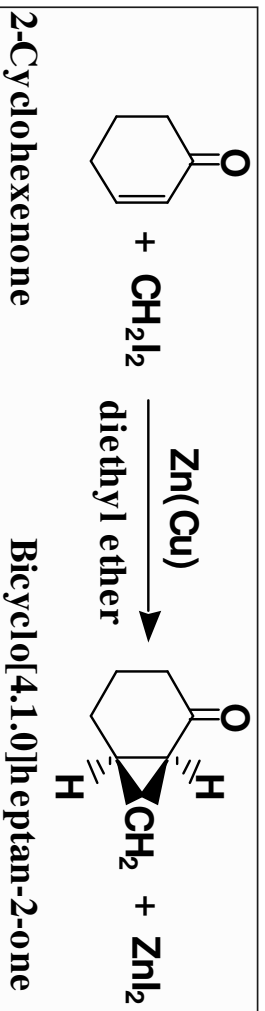
the organozinc compound reacts with an alkene by a concerted mechanism*



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

22

Uses of the Simmons-Smith reagent:



23

Alddehydes And Ketones

24

The Carbonyl Group

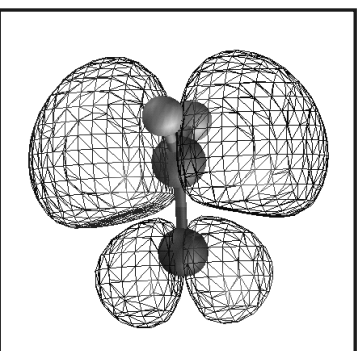
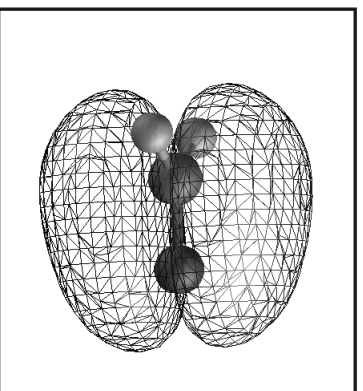
The next units cover the physical and chemical properties of classes of compounds containing the carbonyl group,



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

25

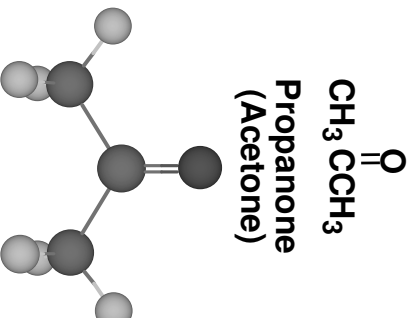
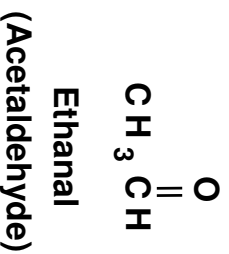
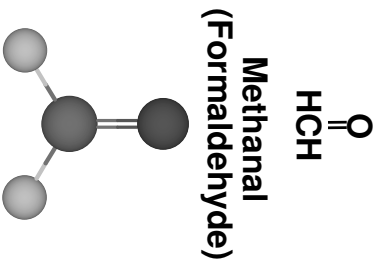
- the carbonyl group consists of **one sigma bond** formed by the overlap of sp^2 hybrid orbitals and **one pi bond** formed by the overlap of parallel $2p$ orbitals
- pi bonding and pi antibonding MOs for formaldehyde



26

– 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



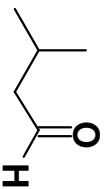
27

Nomenclature

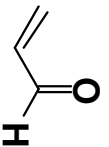
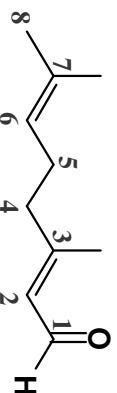
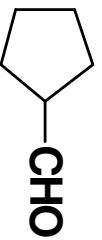
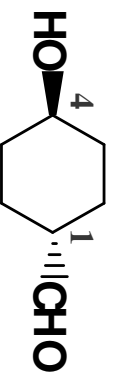
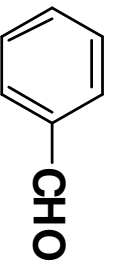
IUPAC names:

- 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**

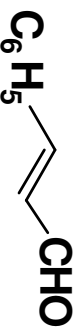
28



3-Methylbutanal

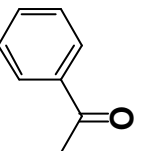
2-Propenal
(A crolein)(2E)-3,7-Dimethyl-2,6-octadienal
(Geranial)Cyclopentane-
carb aldehyde*trans*-4-Hydroxycyclo-
hexane carbaldehyde

Benzaldehyde

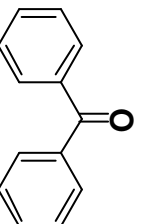
*trans*-3-Phenyl-2-propenal
(Cinnamaldehyde)

IUPAC names

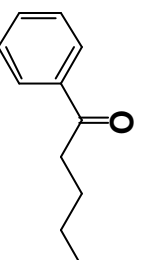
- the parent alkane is the longest chain that contains the carbonyl group
- for ketones, change the suffix -e to -one
- number the chain to give C=O the smaller number
- the IUPAC retains the common names acetone, acetophenone, and benzophenone

Propanone
(Acetone)

Acetophenone



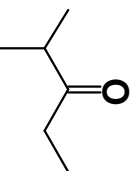
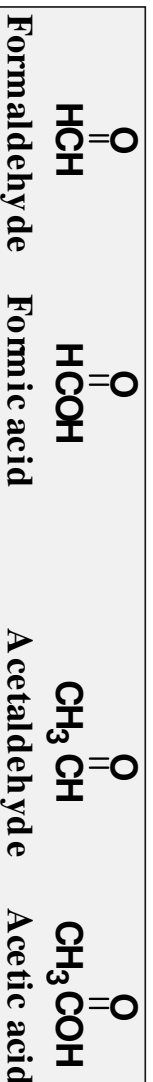
Benzophenone



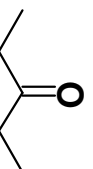
1-Phenyl-1-pentanone

Common Names

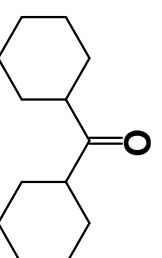
- for an aldehyde, the common name is derived from the common name of the corresponding carboxylic acid
- for a ketone, name the two alkyl or aryl groups bonded to the carbonyl carbon and add the word ketone



Ethyl isopropyl ketone



Diethyl ketone



Dicyclohexyl ketone