

Textbook Assignment: Chapter 15
 Homework (for credit): POW 3 posted-
 Today's Topics: Organometallic Reagents

Notice & Announcements:

EXAM 1: MONDAY, 9/22 7-9 PM

Last Name: A-L WEL 1.308

Last Name: M-Z WEL 1.316

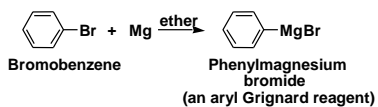
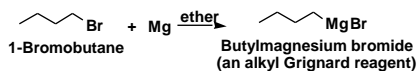
Organometallic Compounds

- 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

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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

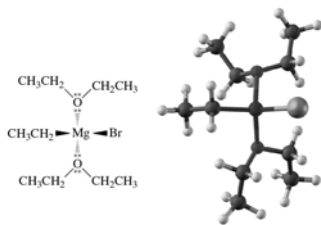


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RMgX and RLi

ORGANIC LECTURE SERIES

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



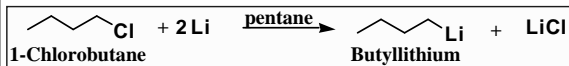
Ethylmagnesium bromide dietherate

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RMgX and RLi

ORGANIC LECTURE SERIES

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



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RMgX and RLi

ORGANIC LECTURE SERIES

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 |

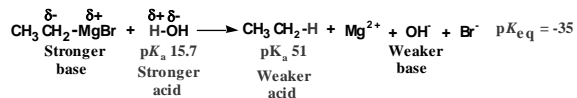


Increasing Ionic Character

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

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



– they react readily with these proton acids

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

This is often an undesired side reaction-to be avoided!! 7

Organometallic reagents have 2 general types of reactions:

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



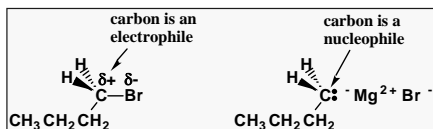
Regard the alkyl group as "R"

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RMgX and RLi

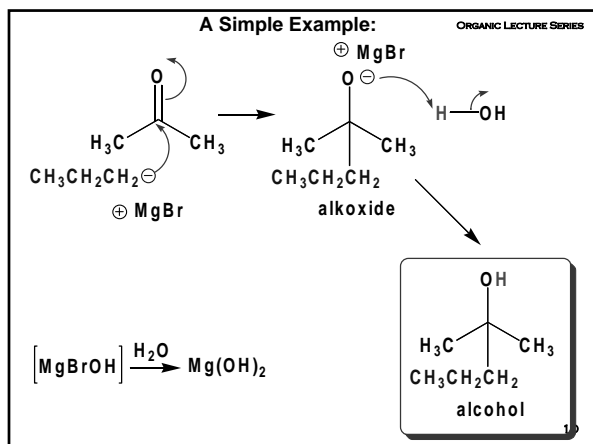
- RMgX and RLi are valuable in synthesis as nucleophiles

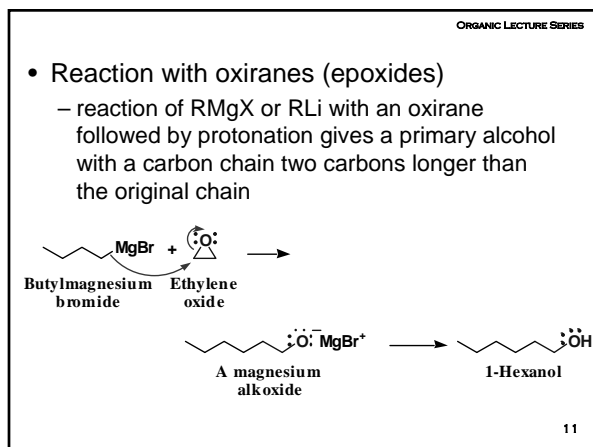
– the carbon bearing the halogen is transformed from an electrophile to a nucleophile

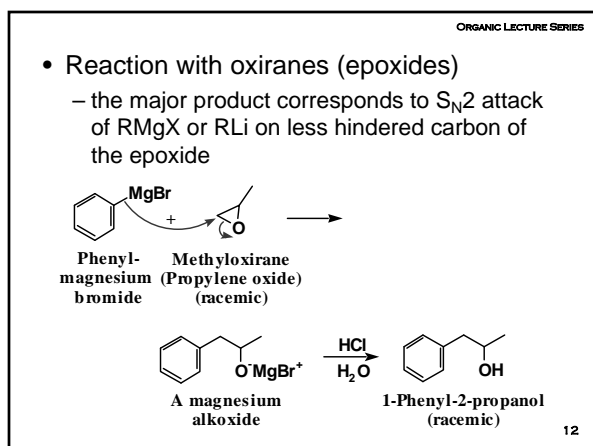


– their most valuable use is addition to the electrophilic carbon of C=O groups of aldehydes, ketones, carboxylic esters, and acid chlorides to form a new carbon-carbon bonds

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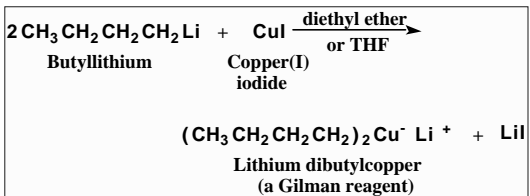






Gilman Reagents

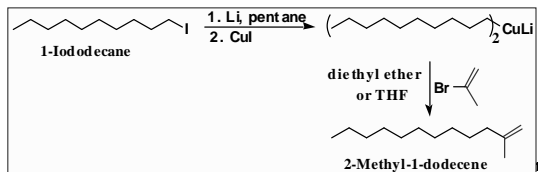
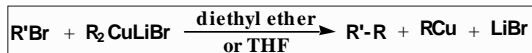
- Lithium diorganocopper reagents, known more commonly as Gilman reagents
 - prepared by treating an alkyl, aryl, or alkenyl lithium compound with Cu(I) iodide



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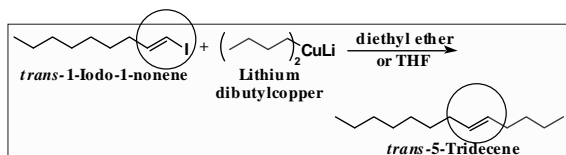
Coupling within organohalogen compounds

- form new carbon-carbon bonds by coupling with alkyl and alkenyl chlorides, bromides, and iodides



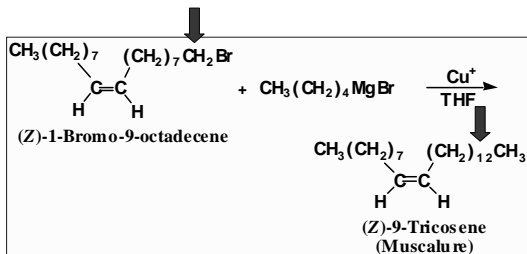
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coupling with a vinylic halide is stereospecific: the configuration of the carbon-carbon double bond is retained



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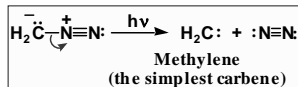
- A variation on the preparation of a Gilman reagent is to use a Grignard reagent with a catalytic amount of a copper(I) salt



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Carbenes and Carbenoids

- Carbene**, $\text{R}_2\text{C:}$: 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



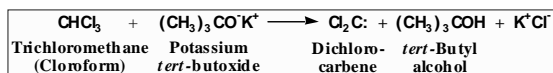
- methylene prepared in this manner is so nonselective that it is of little synthetic use

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Carbenes and Carbenoids

Dichlorocarbene

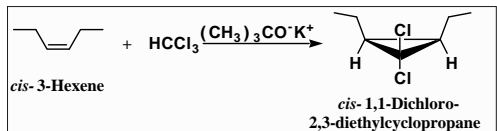
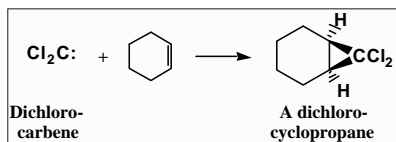
- prepared by treating chloroform with potassium *tert*-butoxide



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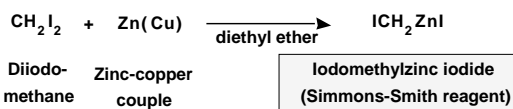
Dichlorocarbene

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



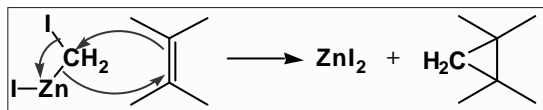
- this organozinc compound reacts with a wide variety of **alkenes to give cyclopropanes**

(prepared by: Zn dust; CuCl & heat)

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Simmons-Smith reaction:

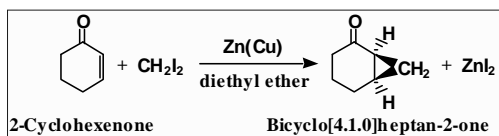
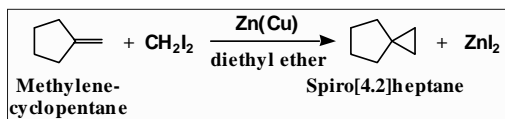
the organozinc compound reacts with an alkene by a concerted mechanism*



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

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Uses of the Simmons-Smith reagent:



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