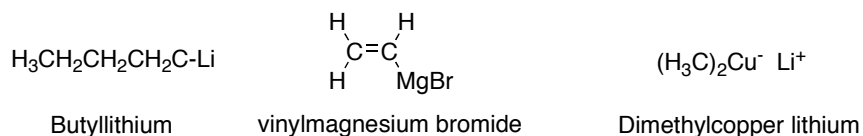
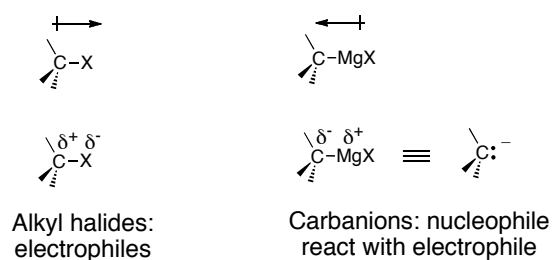


## Chapter 14: Organometallic Compounds - Reagents with carbon-metal bonds

### 14.1: Organometallic Nomenclature (please read)



### 14.2: Carbon-Metal Bonds in Organometallic Compounds

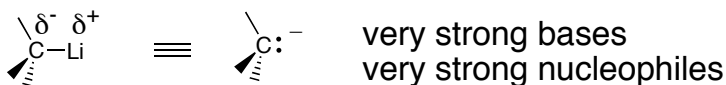
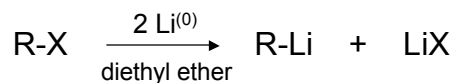


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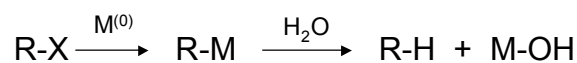
Alkyl halides will react with some metals ( $\text{M}^0$ ) in ether or THF to form organometallic reagents

### 14.3: Preparation of Organolithium Compounds

Organolithium Compounds

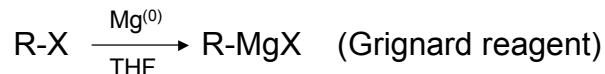


organolithium reagents are most commonly used as very strong bases and in reactions with carbonyl compounds



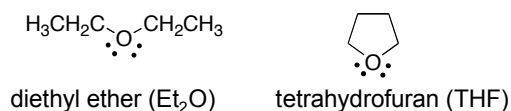
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#### 14.4: Preparation of Organomagnesium Compounds: Grignard Reagents



R-X can be an alkyl, vinyl, or aryl halide (chloride, bromide, or iodide)

Solvent: diethyl ether (Et<sub>2</sub>O) or tetrahydrofuran (THF)



Alcoholic solvents and water are incompatible with Grignard reagents and organolithium reagents.

Reactivity of the alkyl halide: -I > -Br > -Cl >> -F  
alkyl halides > vinyl or aryl halides

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The solvent or alkyl halides can not contain functional groups that are electrophilic or acidic. These are incompatible with the formation of the organomagnesium or organolithium reagent.

Grignard reagents will deprotonate alcohols



Other incompatible groups:

-CO<sub>2</sub>H, -OH, -SH, NH<sub>2</sub>, CONHR (amides)


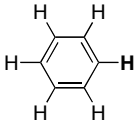
Reactive functional groups:

aldehydes, ketones, esters, amides, halides,  
-NO<sub>2</sub>, -SO<sub>2</sub>R, nitriles

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**14.5: Organolithium and Organomagnesium Compounds as Brønsted Bases** - Grignard reagents (M = MgX) and organolithium reagents (M = Li) are very strong bases.

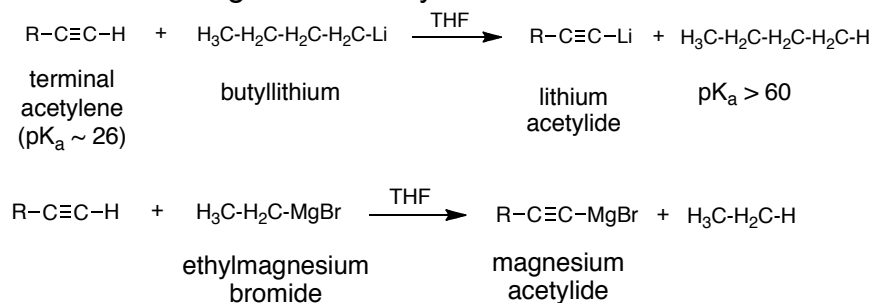


	pKa		pKa
(CH <sub>3</sub> ) <sub>3</sub> C-H	71	H <sub>2</sub> N-H	36
H <sub>3</sub> CH <sub>2</sub> C-H	62	H-C≡C-H	26
H <sub>3</sub> C-H	60	Water	16
	45		
	43		

Hydrocarbons are very weak acids; their conjugate bases are very strong bases.

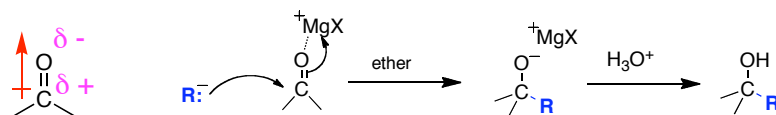
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**Lithium and magnesium acetylides**



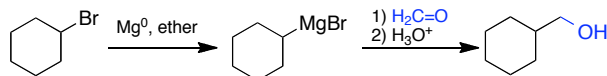
**14.6: Synthesis of Alcohols Using Grignard Reagents**

Grignard reagents react with aldehydes, ketones, and esters to afford alcohols

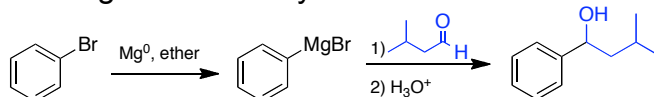


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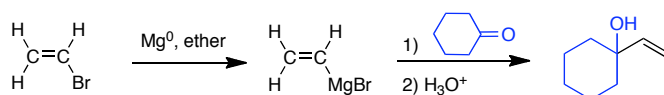
Grignard reagents react with . . .  
formaldehyde ( $\text{H}_2\text{C}=\text{O}$ ) to give primary alcohols



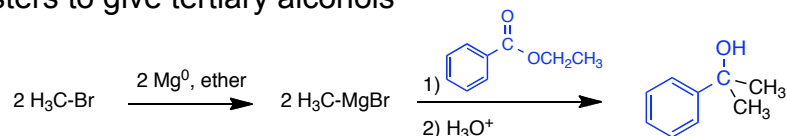
aldehydes to give secondary alcohols



ketones to give tertiary alcohols

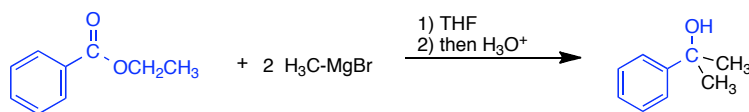


esters to give tertiary alcohols

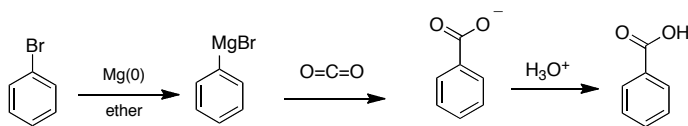


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### 14.10: Preparation of Tertiary Alcohols From Esters and Grignard Reagents - mechanism:



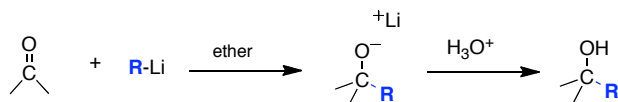
Reaction of Grignard reagents with  $\text{CO}_2$  (Lab, Chapter 19.11)



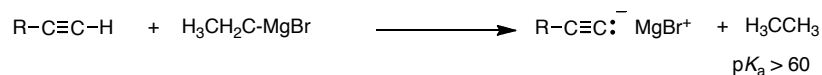
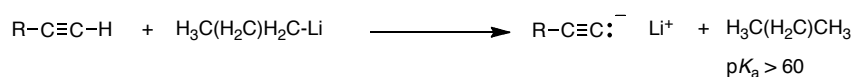
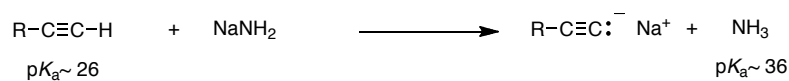
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### 14.7: Synthesis of Alcohols Using Organolithium Reagents

Organolithium reagents react with aldehydes, ketones, and esters in the same way that Grignard reagents do.

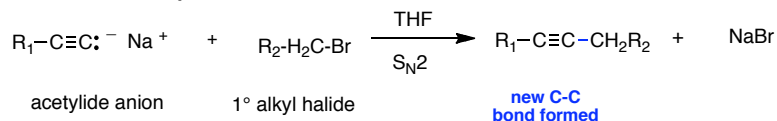


### 14.8: Synthesis of Acetylenic Alcohols

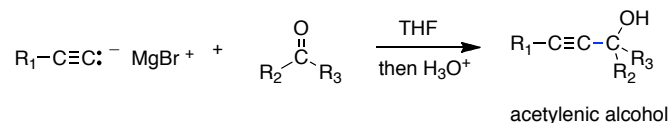


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### Recall from Chapter 9.6



Acetylide anions react with ketones and aldehydes to form a C-C bond; the product is an acetylenic (propargyl) alcohols



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**14.9: Retrosynthetic Analysis** - the process of planning a synthesis by reasoning backward from the the target molecule to a starting compound using known and reliable reactions.

“it is a problem solving technique for transforming the structure of a **synthetic target molecule (TM)** to a sequence of progressively simpler structures along the pathway which ultimately leads to simple or commercially available starting materials for a chemical synthesis.”

The transformation of a molecule to a synthetic precursor is accomplished by:

**Disconnection:** the reverse operation to a synthetic reaction; the hypothetical cleavage of a bond back to precursors of the target molecule.

**Functional Group Interconversion (FGI):** the process of converting one functional group into another by substitution, addition, elimination, reduction, or oxidation

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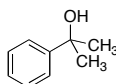
Each precursor is then the target molecule for further retrosynthetic analysis. The process is repeated until suitable starting materials are derived.

Target molecule  $\Rightarrow$  Precursors <sub>1</sub>  $\Rightarrow$  Precursors <sub>2</sub>  $\Rightarrow$   $\Rightarrow$   $\Rightarrow$  Starting materials

Prepare (Z)-2-hexene from acetylene

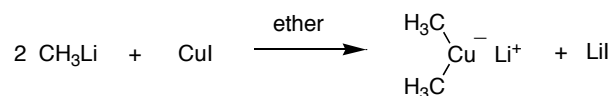


2-Phenyl-2-propanol

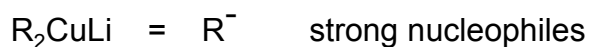


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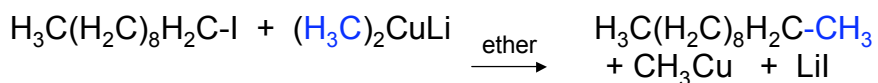
### 14.11: Alkane Synthesis Using Organocopper Reagents



Gilman's reagent  
(dimethylcuprate, dimethylcopper lithium)



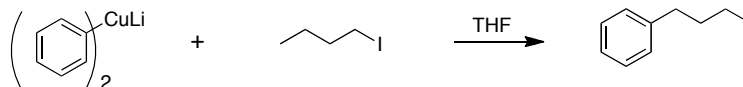
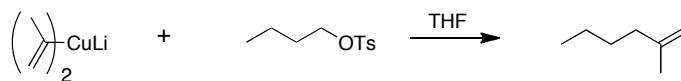
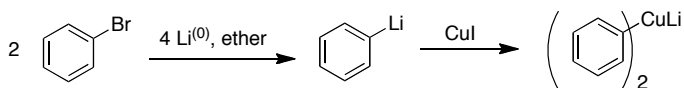
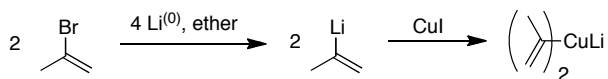
Nucleophilic substitution reactions with alkyl halides and sulfonates (alkylation)



$\text{S}_{\text{N}}2$  reaction of cuprates is best with primary and secondary alkyl halides; tertiary alkyl halides undergo E2 elimination.

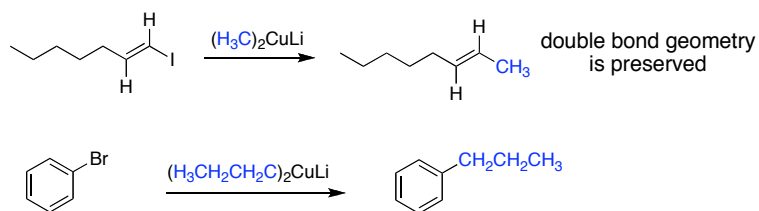
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### Vinyl and aryl (but not acetylenic) cuprates



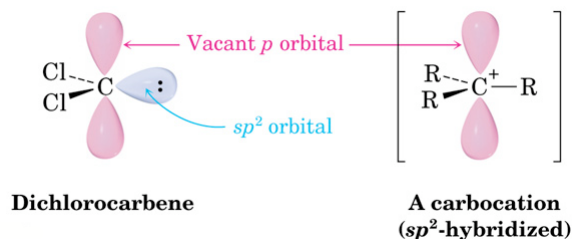
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### Reaction of cuprates with aryl and vinyl halides



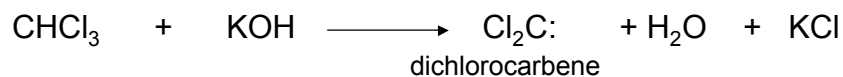
### 14.13: Carbenes and Carbenoids

Carbene: highly reactive intermediate, 6-electron species. The carbon is  $sp^2$  hybridized; it possesses a vacant hybridized p-orbital and an  $sp^2$  orbital with a non-bonding pair of electrons

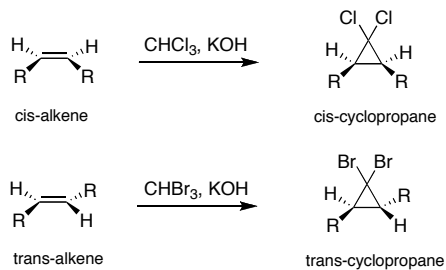


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### Generation and Reaction of Dihalocarbenes:



Carbenes react with alkenes to give cyclopropanes.

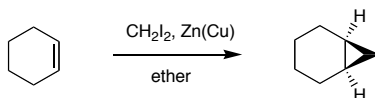
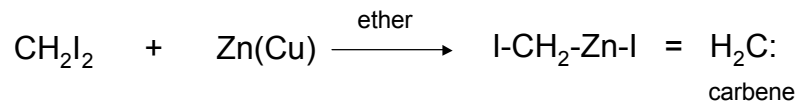


The cyclopropanation reaction takes place in a single step. There is NO intermediate. As such, the geometry of the alkene is preserved in the product. *Groups that are trans on the alkene will end up trans on the cyclopropane product. Groups that are cis on the alkene will end up cis on the cyclopropane product.*

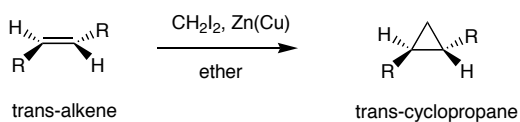
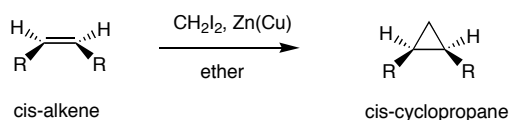
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### 14.12: An Organozinc Reagent for Cyclopropane Synthesis Simmons-Smith Reaction



The geometry of the alkene is preserved in the cyclopropanation reaction.



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### 14.14: Transition-Metal Organometallic Compounds

(please read)

### 14.15: Homogeneous Catalytic Hydrogenation (please read)

$\text{H}_2$ , Pd/C - The catalyst is insoluble in the reaction media:  
heterogeneous catalysis, interfacial reaction

$\text{H}_2$ ,  $(\text{Ph}_3\text{P})_3\text{RhCl}$  - The catalyst is soluble in the reaction media:  
homogeneous catalysis.

### 14.16: Olefin Metathesis (please read)

### 14.17: Ziegler-Natta Catalysis of Alkene Polymerization

(please read)

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