

**Organometallic Reagents
in
ORGANIC CHEMISTRY**

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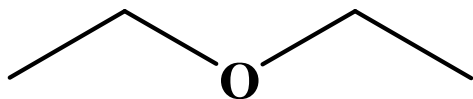
Palayamkottai

Organometallic Compounds

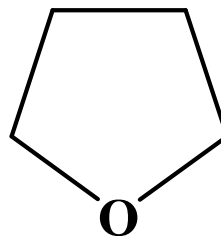
- **Organic Compounds Containing Carbon—Metal Bonds**
- **Bonds Range From Ionic to Primarily Covalent**
- **Ionic C—M Bonds:**
 - **C—Na**
 - **C—K**
- **Primarily Covalent C—M Bonds:**
 - **C—Pb**
 - **C—Sn**
 - **C—Hg**
- **Inetermediate C—M Bonds Include C—Mg and C—Li**
- **Reactivity Increases with Ionic Character of C—M Bond**

Organolithium Reagents

Common Solvents for Organolithium Reagents:

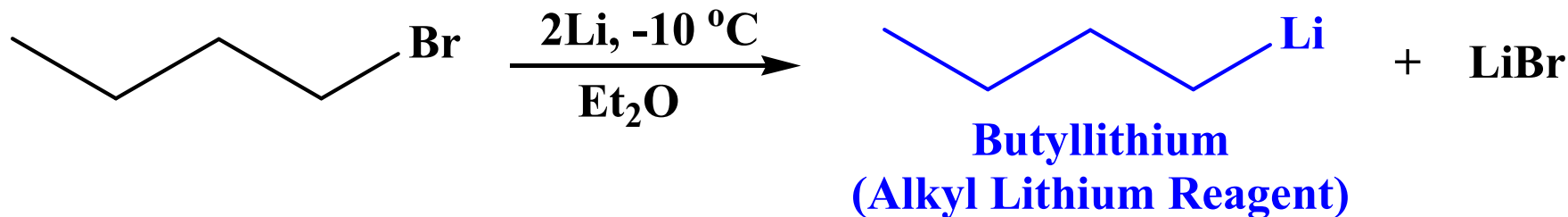


Diethyl Ether



Tetrahydrofuran

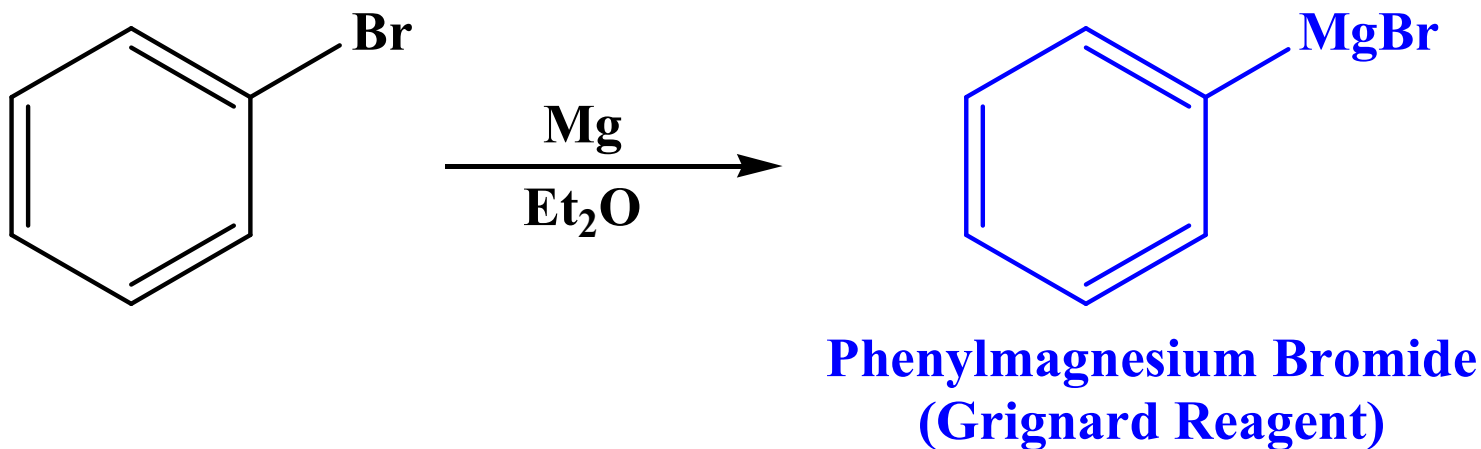
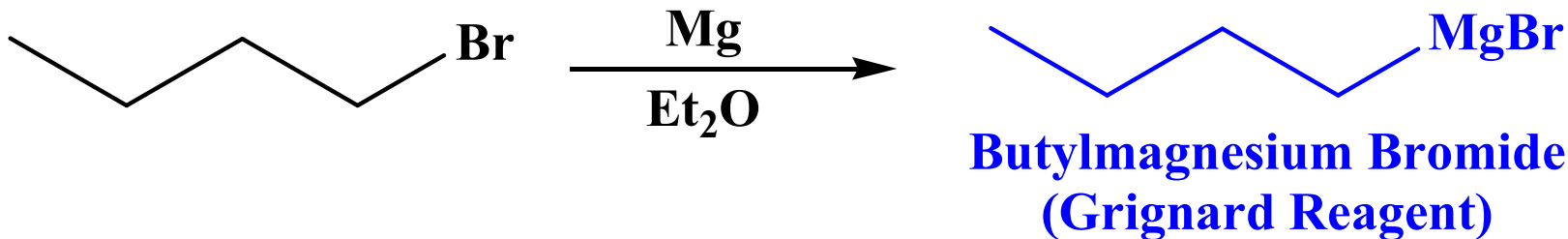
Preparation of Organolithium Reagents:



- **Reactive, Carbanion-Like Species (React Slowly w/ Ethers)**
- **Halide Reactivity: RI > RBr > RCl (F Not Often Used)**

Grignard Reagents

Preparation of Grignard Reagents:

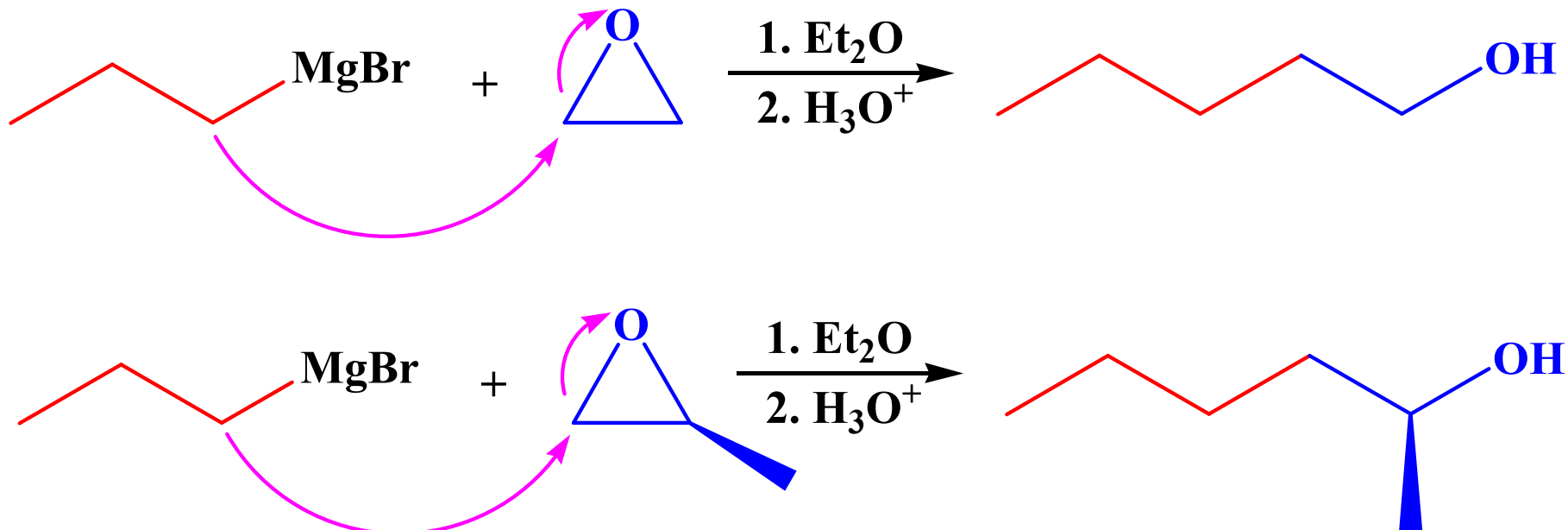


- **Reactivity of Halides Same as for Organolithium Reagents**
- **Generally Exist as Complexes, We'll Use RMgX for Simplicity**

Organometallic Reactions: Notes

- **Can Act as Nucleophiles Towards Polarized Carbonyl Groups**
- **Very Strong Lewis Bases (React with Acidic Protons)**
- **Basicity Necessitates Dry Conditions (Avoid Reaction w/ H₂O)**
- **Reason For Basicity: Carbanion-Like Behavior (pK_a??)**
- **Strong Enough Bases to Deprotonate Terminal Alkynes (pK_a??)**
- **With No Acidic Protons, Can Do Nucleophilic Substitution**

Grignard Reactions: Epoxides

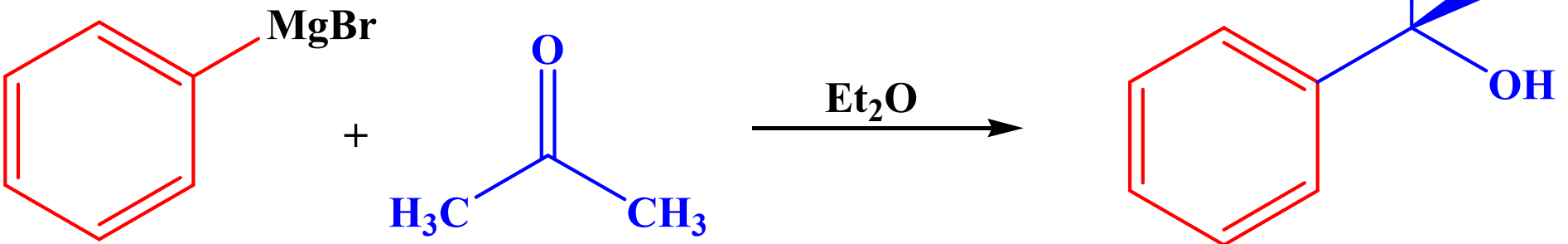
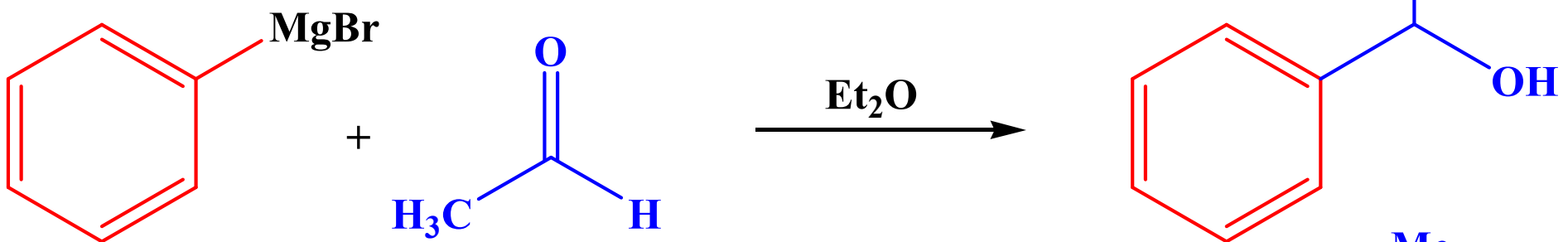
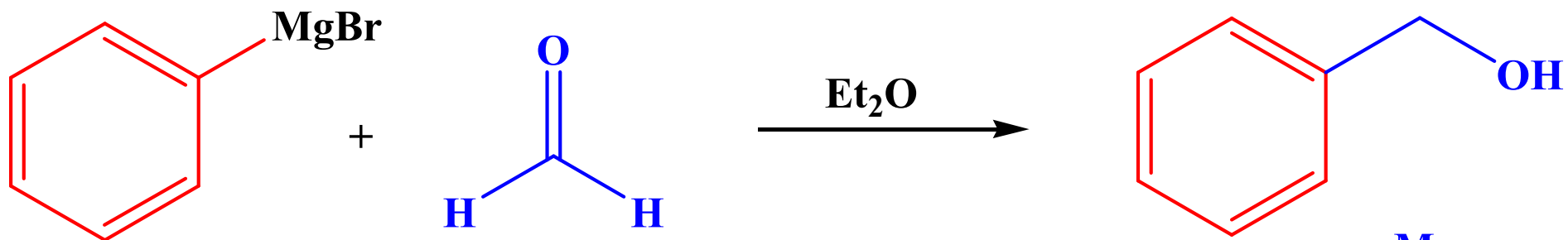


- Grignard Reagents Nucleophilically Open Epoxides
- Generally Attack Less Substituted Carbon (Steric Hindrance)
- View This as Carbanion Attacking in $\text{S}_{\text{N}}2$ Reaction (O L.G.)

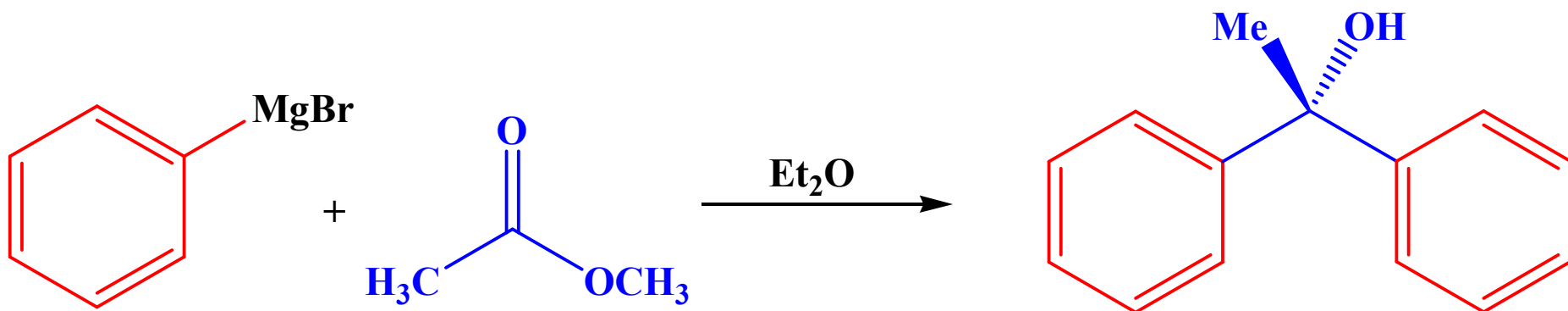
Grignard Reactions w/ Carbonyls

- **Grignard Reagents React With a Variety of Carbonyls**
 - **Formaldehyde → 1° Alcohols**
 - **Higher Aldehydes → 2° Alcohols**
 - **Ketones → 3° Alcohols**
 - **Ester → 3° Alcohols**
- **Attack of Grignard Generates Alkoxide; Protonate to get OH**

Grignard Reactions: Carbonyls



Grignard Reactions: Esters

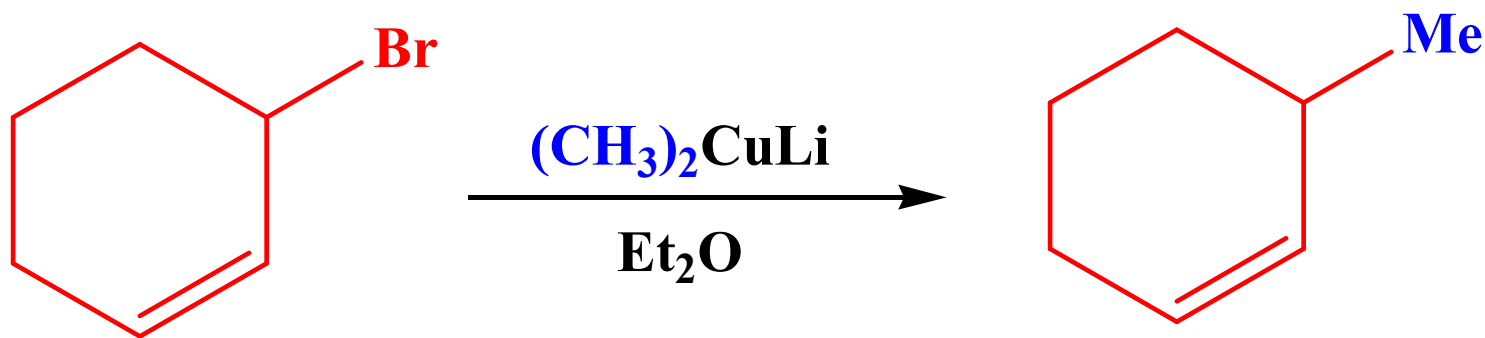
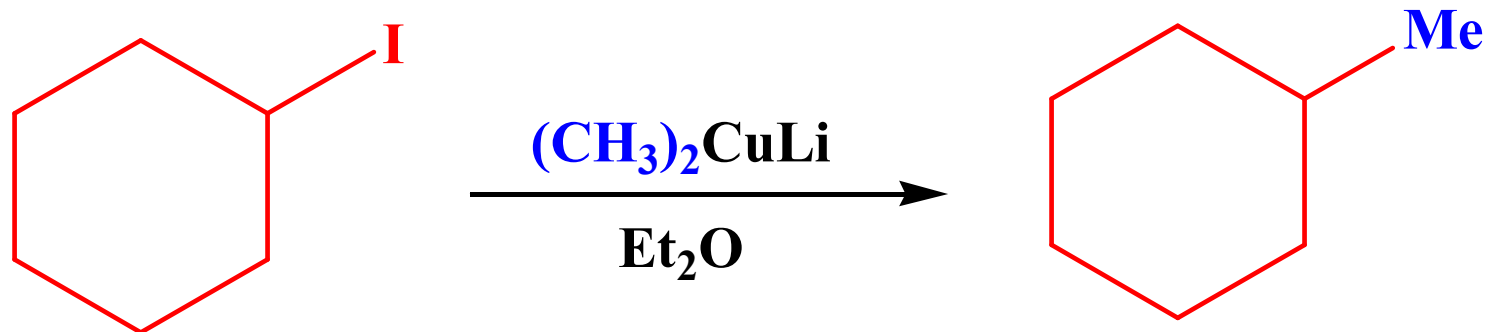


- Grignard Reagents React Twice w/ Esters → 3° Alcohols
- Two Alkyl Groups of Alcohol Correspond to Grignard Reagent
- Grignard Reactions Quite Useful in Wide Range of Alcohol Syntheses (w/ Varying Degrees of Substitution)

Reactions of Organolithium Compounds

- **Organolithium Reagents React Similarly to Grignards**
- **Also Strong Bases, Same Limitations Apply**
- **More Reactive Species Than Grignard Reagents**
- **Routine Syntheses: Prefer to use Grignard Reagents**
- **Sodium Alkynides (Triple Bond Anions) React in Same Manner w/ Aldehydes and Ketones**

Lithium Dialkylcuprates



Quite Versatile C—C Bond Forming Reaction