

Organometallic compounds
Introduction
Part 1

For Semester 3 (CC7)

By

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Associate Professor

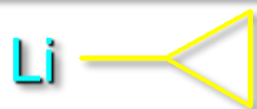
Department of Chemistry

Organometallic compounds

- In this chapter, we focus on synthesis of organometallic compounds of Mg, Li, Cu, Cd and Zn
- Illustration of the usefulness of organometallics in modern synthetic organic chemistry
- Comparative reactivity

A compound that contains a carbon-metal bond

Examples:



Cyclopropyllithium



Vinylsodium

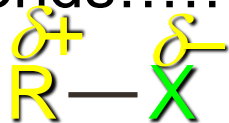


Diethylmagnesium



Methylmagnesium
iodide

Polarity of the bonds.....



Alkyl halide

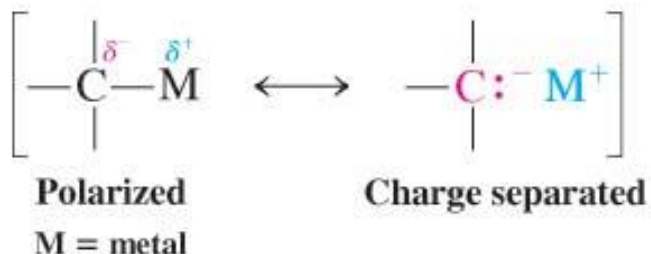


Organometallic compounds

The alkyl metal bond is strongly polar.

- The carbon-lithium bond in CH_3Li has about 40% ionic character, and the carbon-magnesium bond in CH_3MgCl has about 35% ionic character.
- The metal atom is strongly electropositive and is at the positive end of the dipole.

Carbon-Metal Bond in Alkyl lithium and Alkylmagnesium Compounds



Methyl lithium



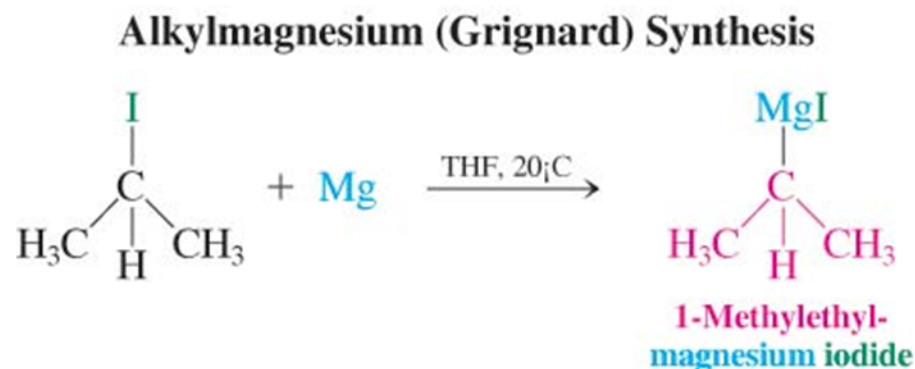
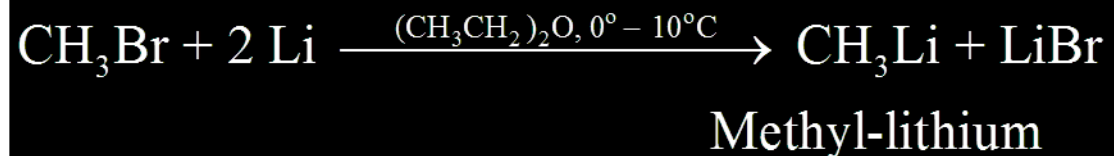
Methylmagnesium chloride

The formation of a Grignard reagent is an example of **reverse polarization**. In the haloalkane, the carbon atom attached to the halogen was electrophilic. In the Grignard reagent, the carbon atom has become nucleophilic.

Alkyl lithium and alkylmagnesium reagents are prepared from haloalkanes.

Alkyl lithium and **alkylmagnesium** compounds can be prepared by reaction of alkyl halides with **lithium** or **magnesium** in ethoxyethane (diethylether) or oxacyclopentane (THF).

The order of reactivity of the haloalkane is:



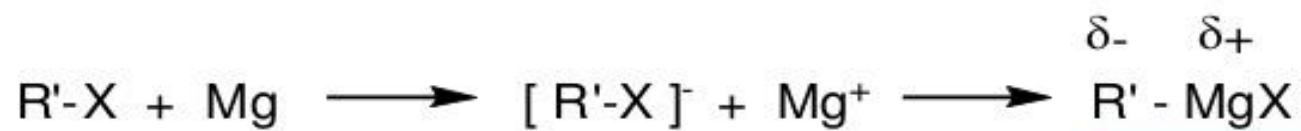
Forbidden Group: Certain groups cannot be present in the solvent, or the halide from which the Grignard reagent is prepared, or the substance with which the Grignard reagent reacts.

- Anything with an OH, SH, or NH group Therefore, cannot use H₂O, CH₃OH, CH₃CH₂OH, etc. as solvents.
- Cannot prepare Grignard reagent from substances such as HOCH₂CH₂Br, etc

Grignard reagents, RMgX, can be formed from primary, secondary and tertiary haloalkane, as well as from haloalkenes and halobenzenes.

➤ **Grignard reagents** are highly reactive organometallic reagents generated by treating alkyl or aryl halides with magnesium metal in the presence of an anhydrous ether.

➤ The reaction proceeds like a strong base reaction.

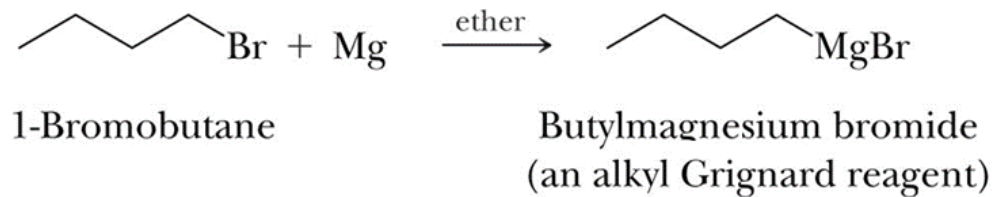
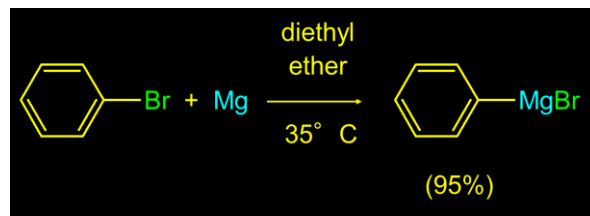
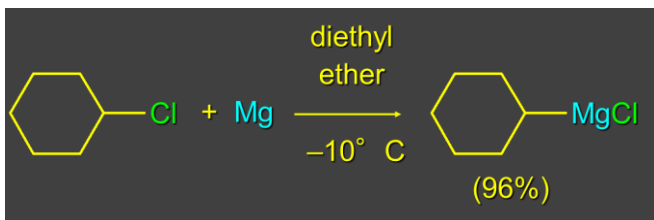


➤ This reagent was discovered by **Victor Grignard** around 1900.



Grignard reagents are very sensitive to moisture and air and are formed in solution and used immediately. The metal atoms in a Grignard reagent are electron-deficient and become coordinated to two solvent molecules:

Examples:



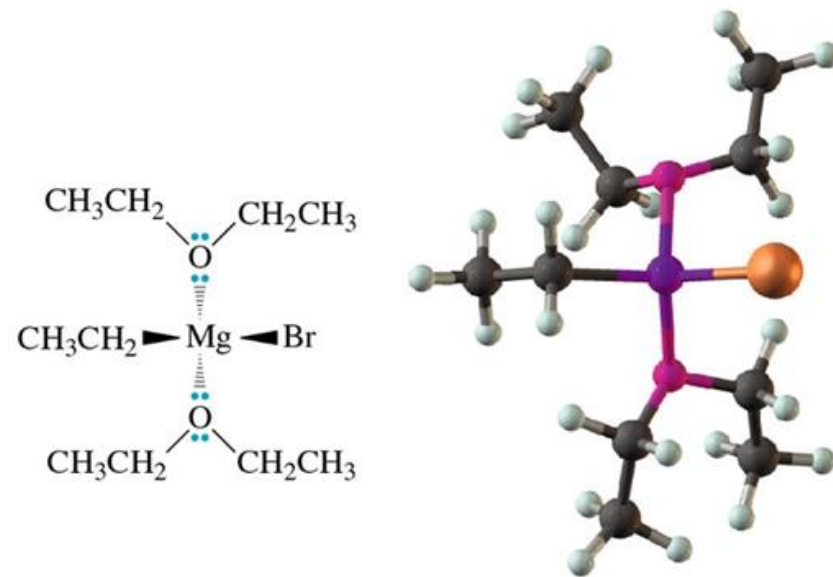
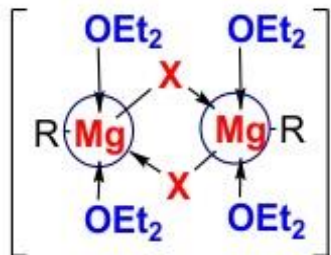
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Grignard Reagents - Structure

The Grignard reagent was existing in **dimeric form** (stabilization of Grignard reagent) which is in equilibrium with dialkyl magnesium compound and magnesium dihalide.



The X-ray diffraction studies -



Ethylmagnesium bromide dietherate

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Reactivity.....

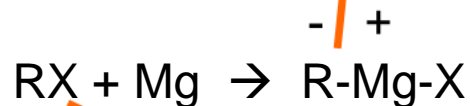
Recall the SN2 reaction where the alkyl group, R, is converted from electrophile to nucleophile.

Forming the Grignard converts the R from electrophile to a potential nucleophile. A wide range of new reactions opens up with R as nucleophile.

The alkyl group in alkylmetals is strongly basic.

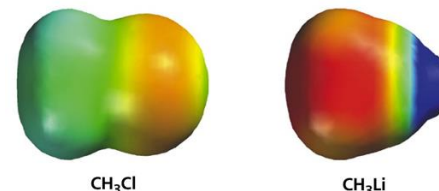
Carbanions are the conjugate bases of alkanes (estimated pKa's of about 50), and as a result are extremely basic, much more so than amines or alkoxides. Because of their basicity, carbanions are extremely sensitive to moisture or other acidic functional groups.

Grignards are destroyed by (weak) protic acids: amines, alcohols, water, terminal alkynes, phenols, carboxylic acids. The Grignard, RMgX, is converted to a Mg salt eventually and RH. The liberation of RH can serve as a test for protic hydrogens.



Nucleophile

Electrophile



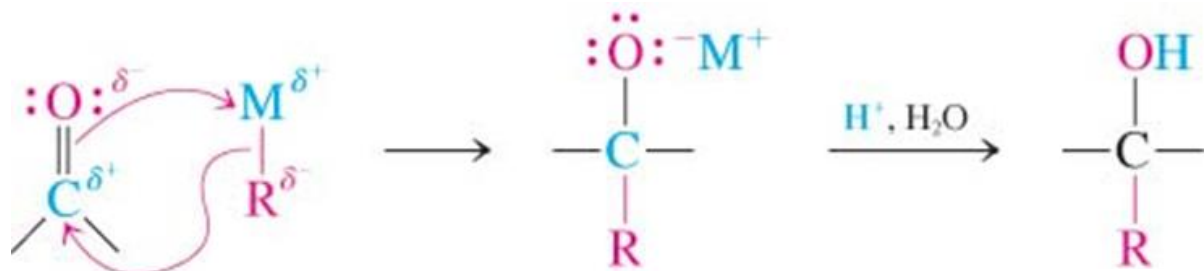
Electrostatic potential map



This reaction is one method which can be used to convert alkylhalides into alkanes.

Synthesis of Alcohols

organometallic reagents react with carbonyl compounds giving an alcohol containing a new C-C bond

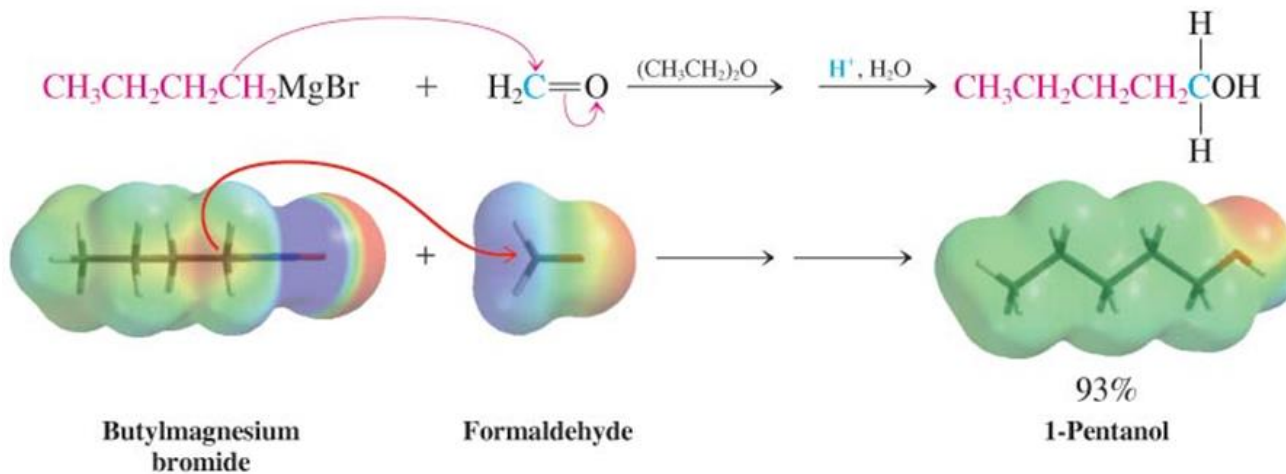


M = Li or MgX

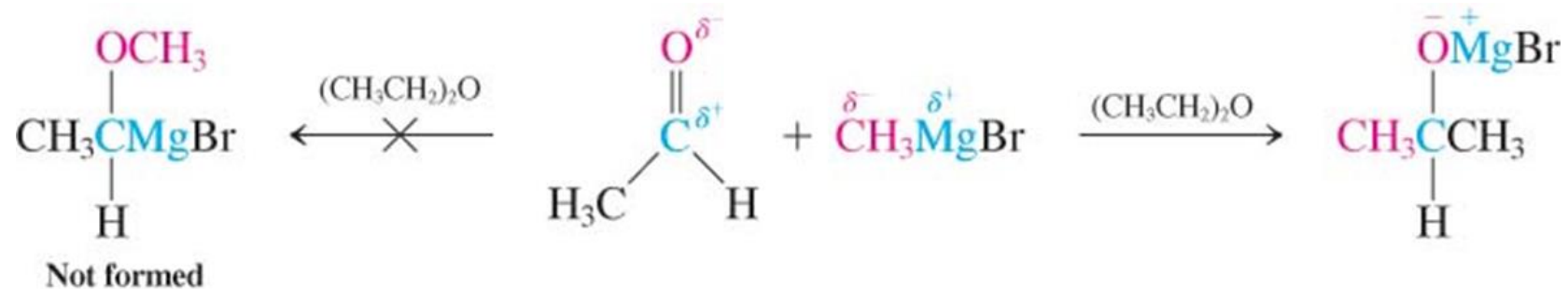
Formation of a Primary Alcohol from a Grignard Reagent and Formaldehyde



Reaction with formaldehyde:

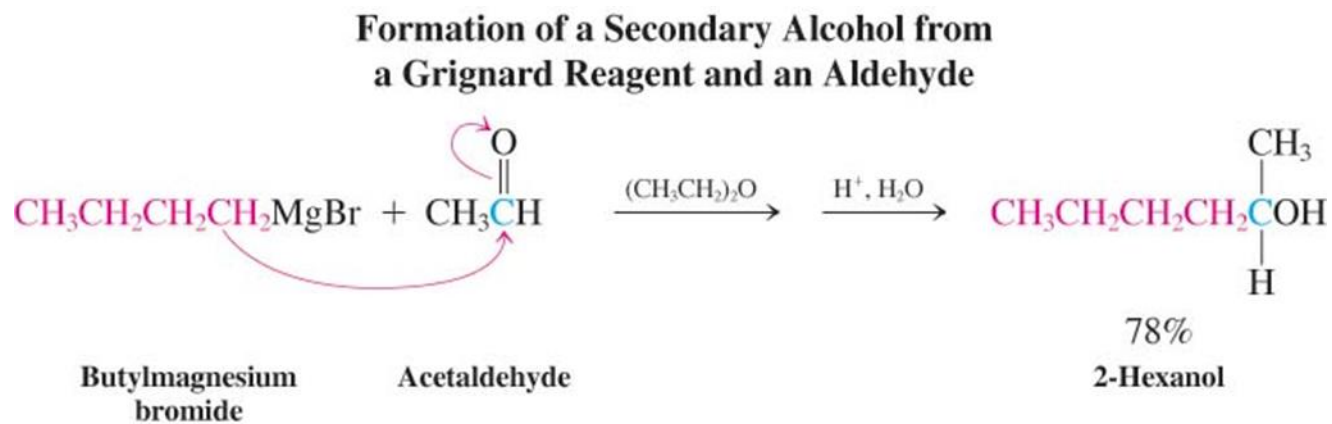


How does a Grignard reagent add to a carbonyl group?

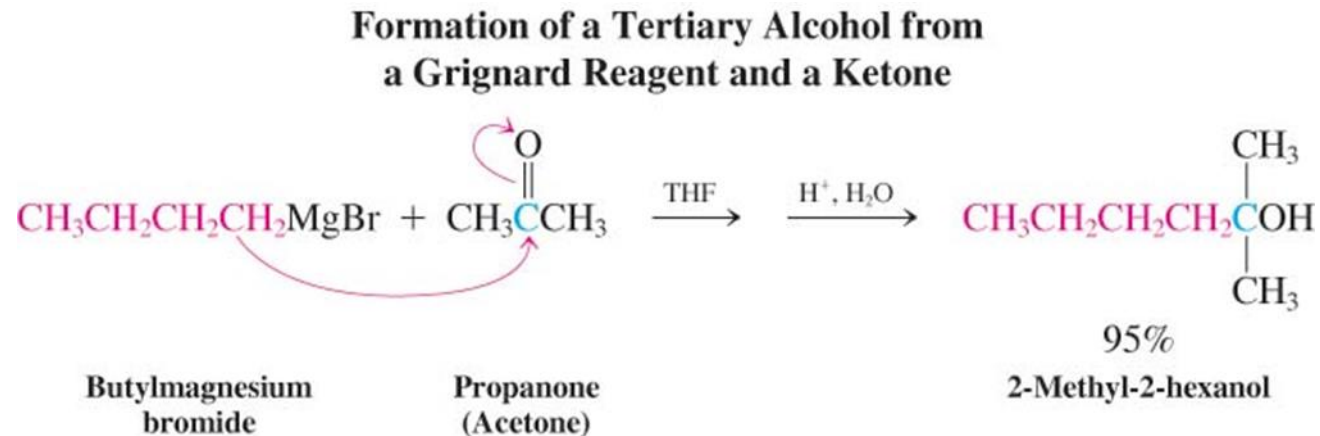


The negatively polarized alkyl group in the organometallic reagent attacks the positively polarized carbonyl carbon in the carbonyl group.

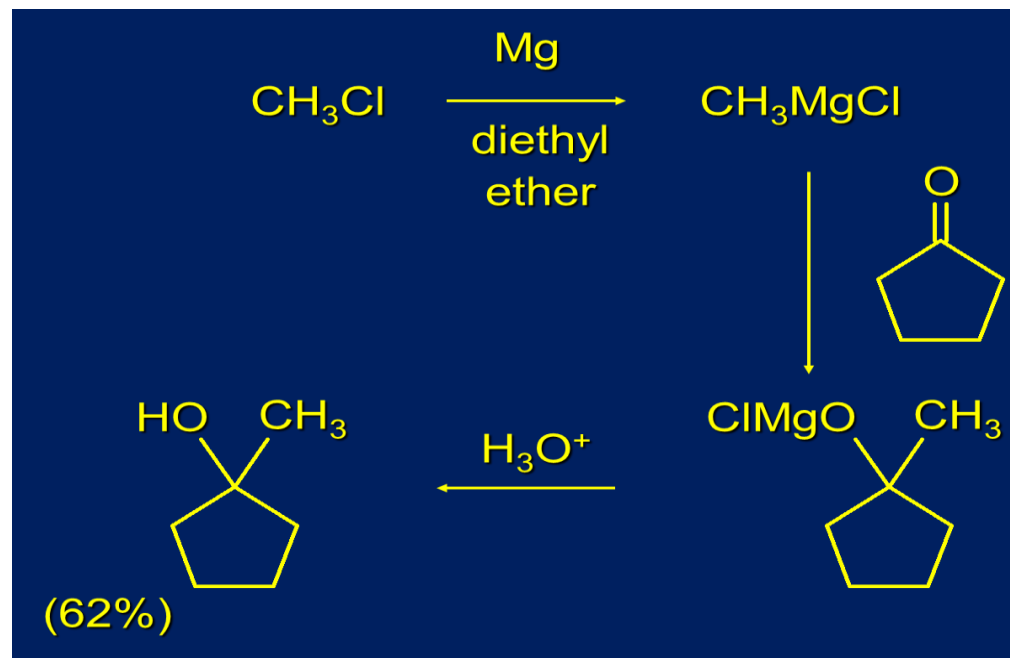
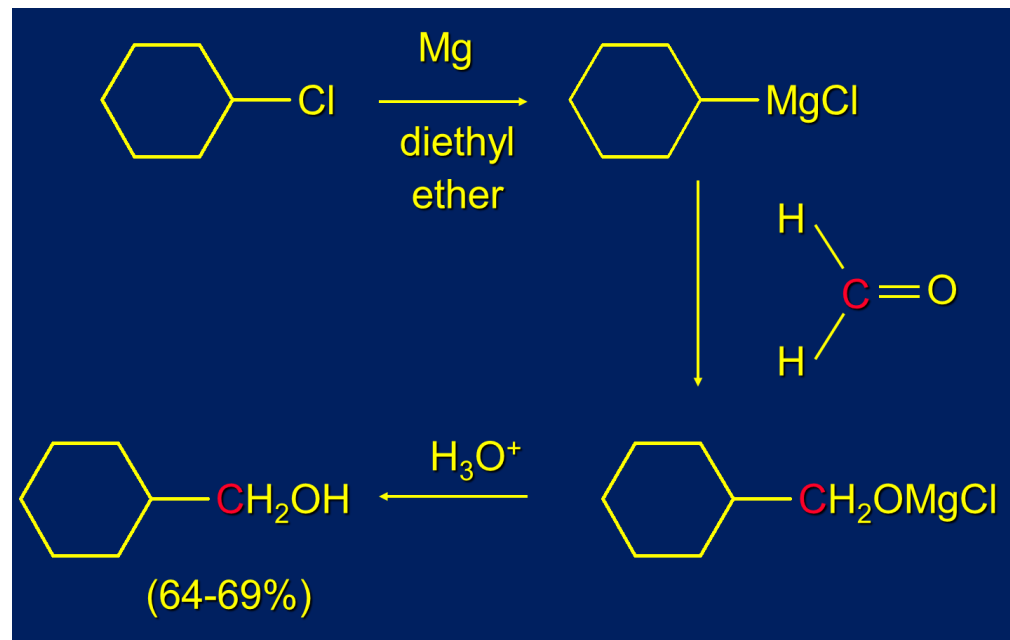
Reaction with aldehydes
other than formaldehyde

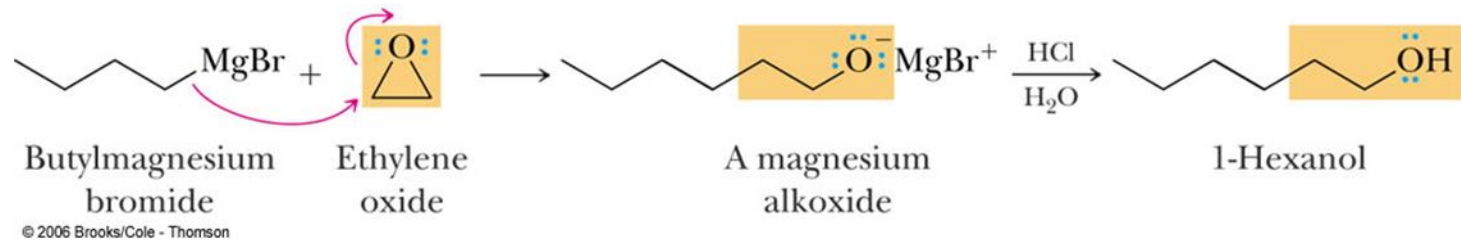


Reaction with ketone



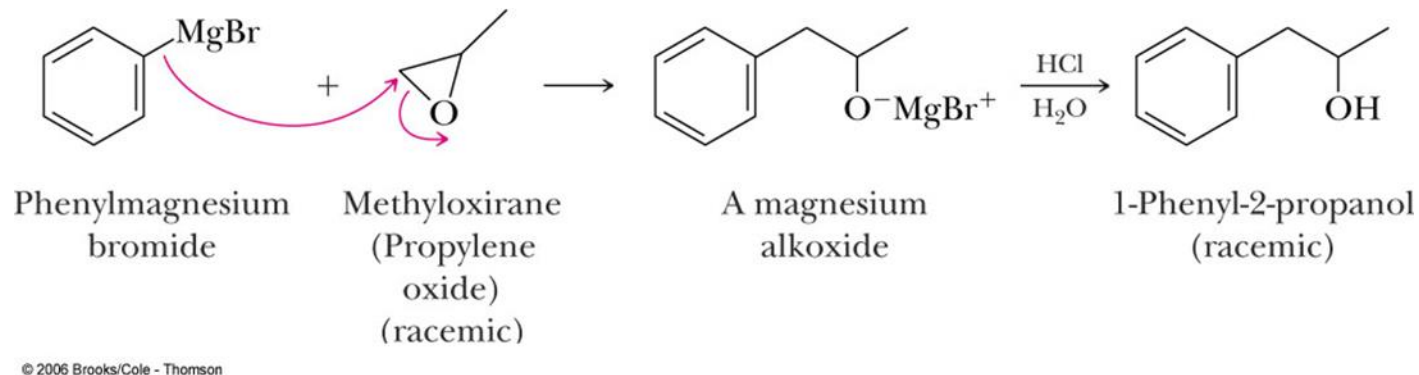
Few more examples.....





Reaction with oxirane

The size of the alkyl group has increased by 2. The functionality (OH) has remained at the end of the chain. We could make it even longer by repeating the above sequence.



Attack at less hindered carbon.

Synthesis of acetylenic Alcohols using acetylenic Grignard reagent



diethyl ether

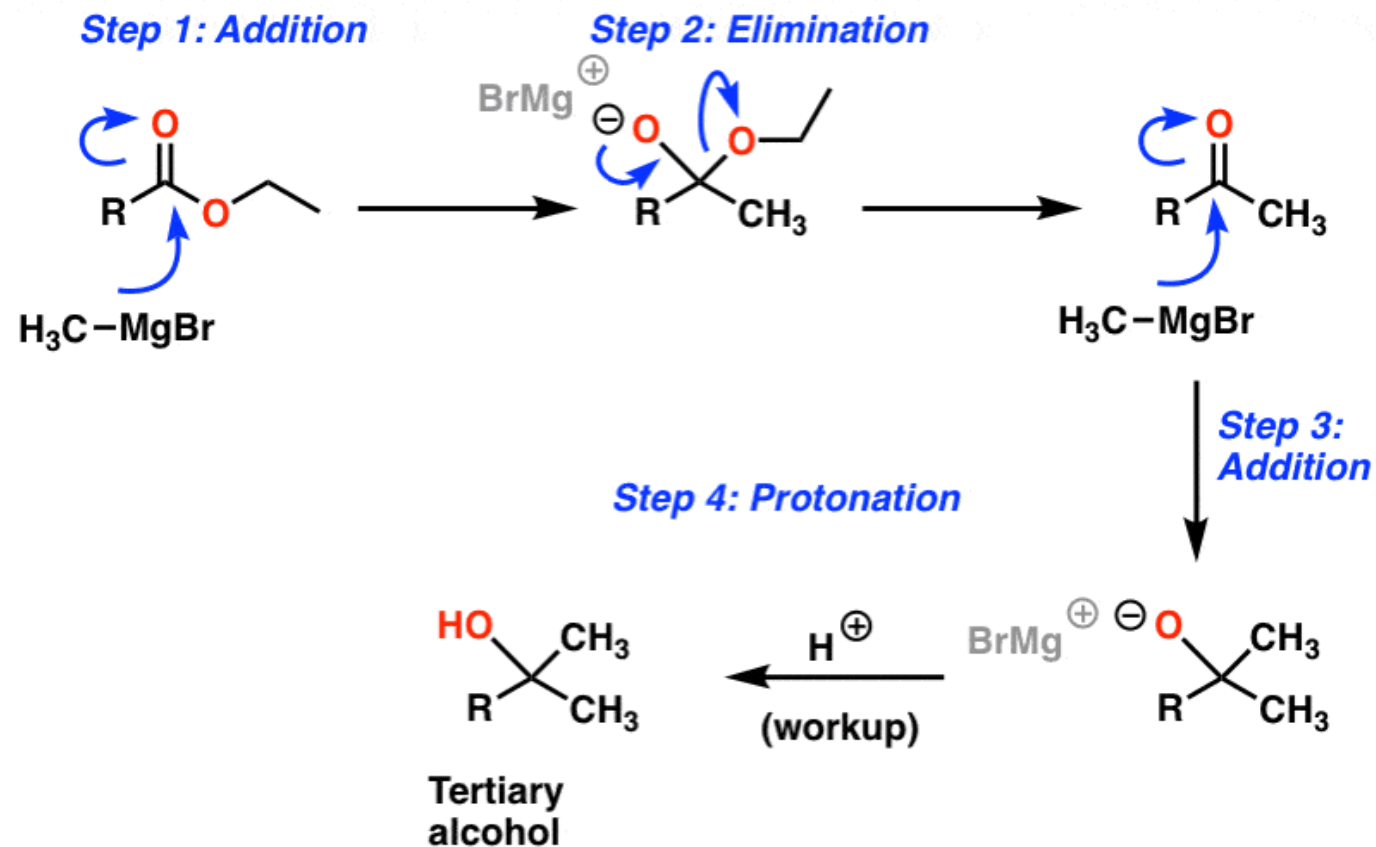


(82%)

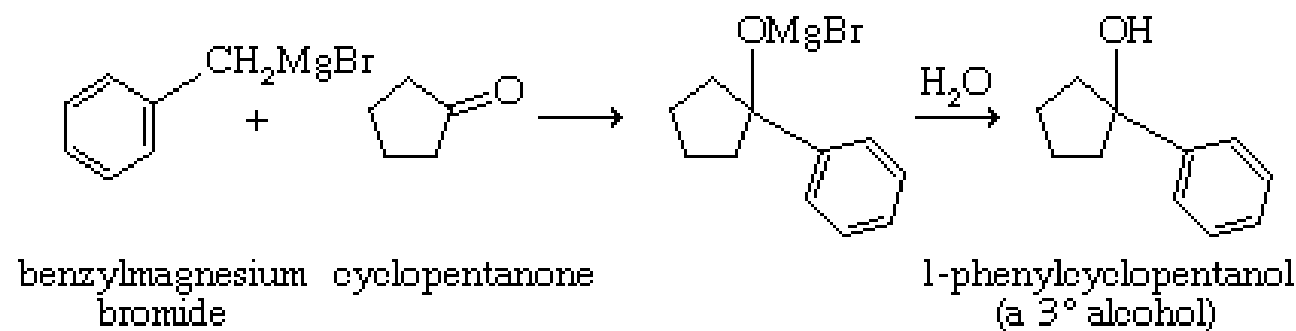
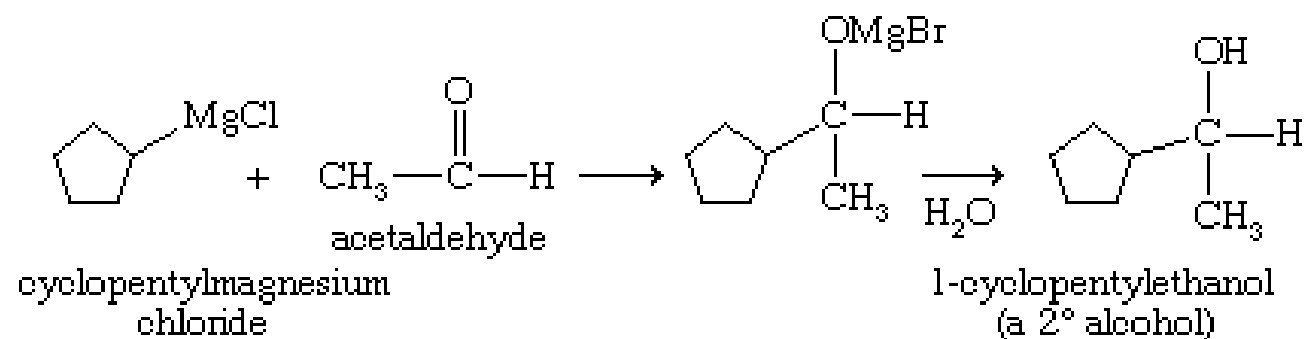
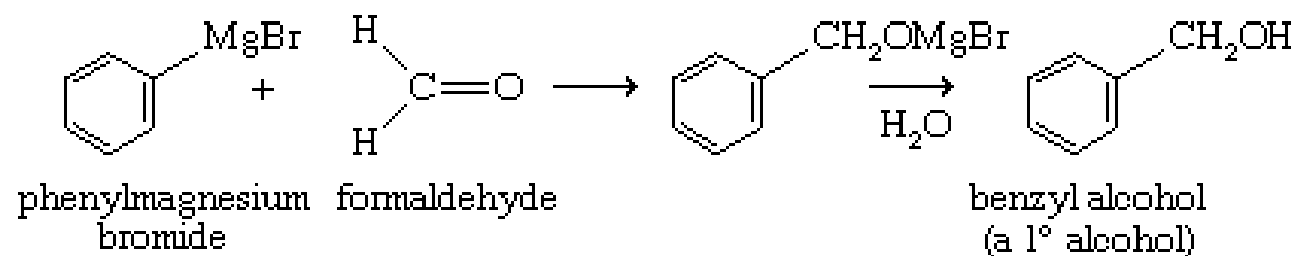
Synthesis of alcohols from esters

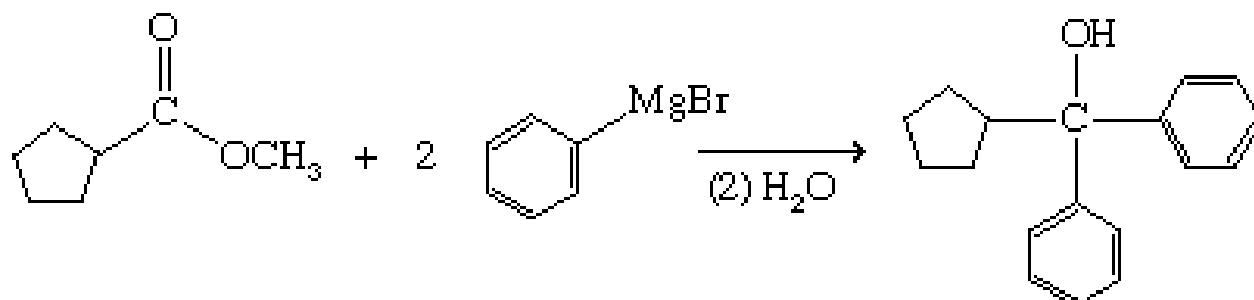
Addition of Grignard Reagents To Esters: How It Works

- In the first step, the nucleophile (Grignard) attacks the carbonyl carbon in an addition reaction (essentially the same step as for ketones/aldehydes).
- THEN, the C–O π bond re-forms, displacing a leaving group (alkoxide, RO⁻). This is a ketone!
- The ketone is then attacked by a second equivalent of nucleophile, leading to formation of a new alkoxide. Workup (addition of water or acid) completes the reaction.



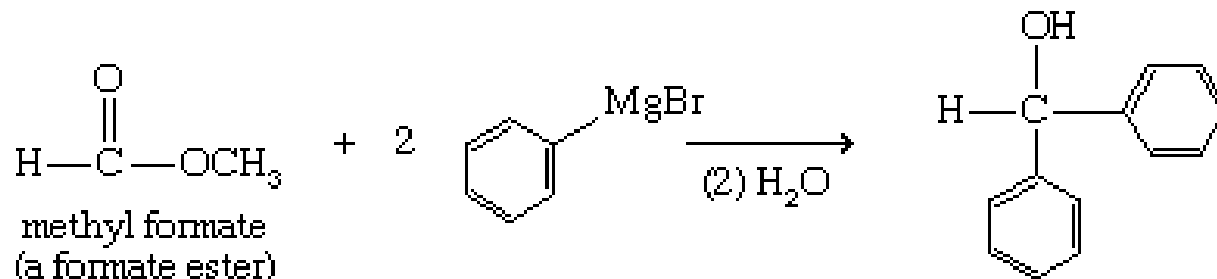
Few more examples.....





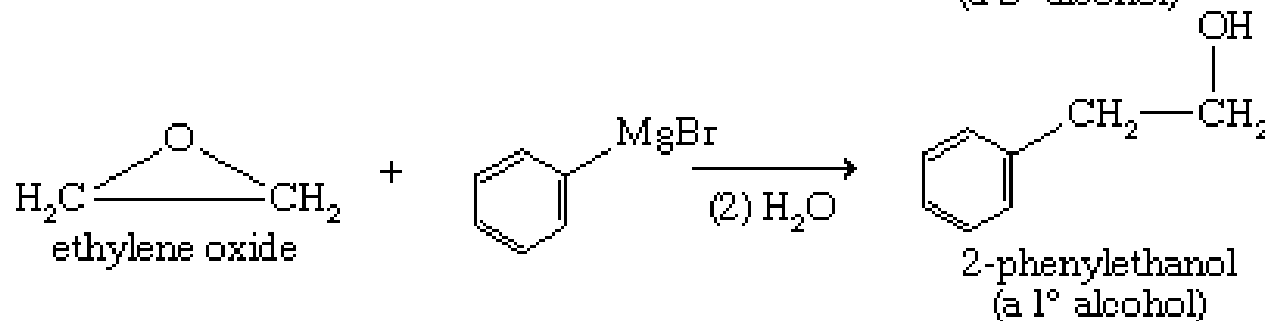
methyl cyclopentanecarboxylate
(an ester)

cyclopentylidiphenylmethanol
(a 3° alcohol)



methyl formate
(a formate ester)

diphenylmethanol
(a 2° alcohol)



ethylene oxide

2-phenylethanol
(a 1° alcohol)