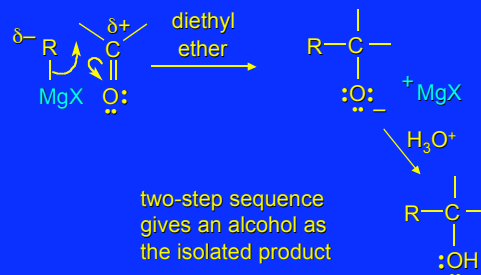


Synthesis of Alcohols  
Grignard or Organolithium Reagents

Organolithium reagents react with carbonyls in the same general way that Grignard reagents do.

Grignard reagents act as nucleophiles toward the carbonyl group



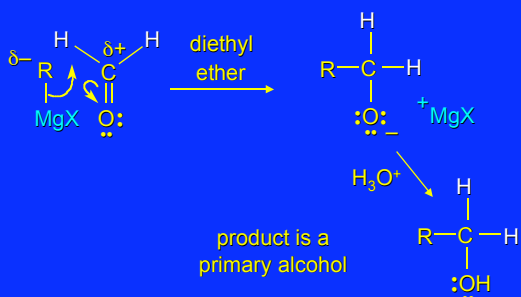
Grignard reagents react with:

- formaldehyde to give primary alcohols
- other aldehydes to give secondary alcohols
- ketones to give tertiary alcohols
- esters to give tertiary alcohols

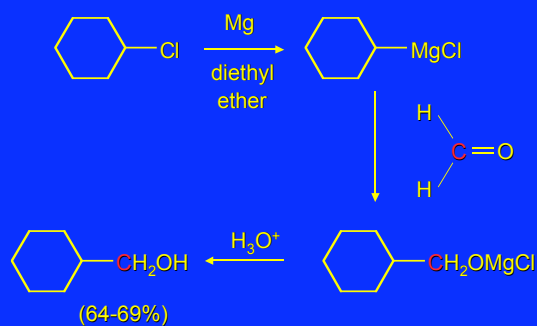
Grignard reagents react with:

- formaldehyde to give primary alcohols

Grignard reagents react with formaldehyde



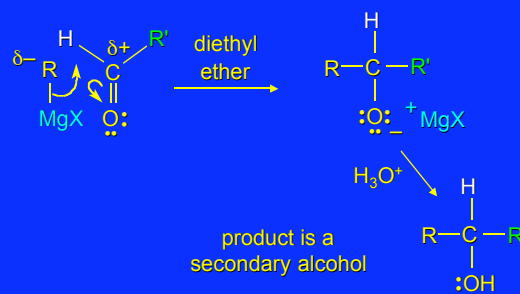
Example



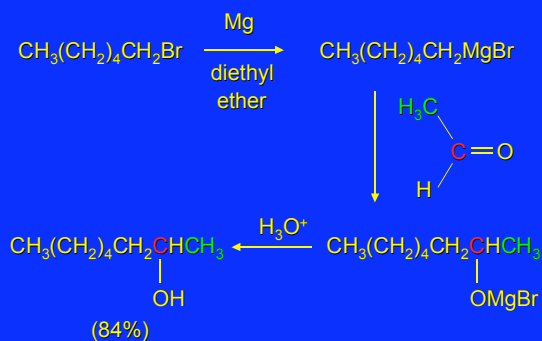
*Grignard reagents react with:*

formaldehyde to give primary alcohols  
aldehydes to give secondary alcohols

*Grignard reagents react with aldehydes*



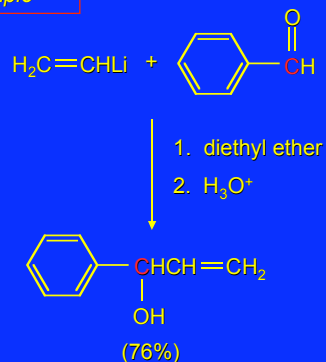
*Example*



Question

- What is the product of the reaction of ethylmagnesium bromide ( $\text{CH}_3\text{CH}_2\text{MgBr}$ ) with butanal ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{O}$ ) followed by dilute acid?
- A) 2-hexanol
- B) 1-butanol
- C) 3-hexanol
- D) 3-pentanol

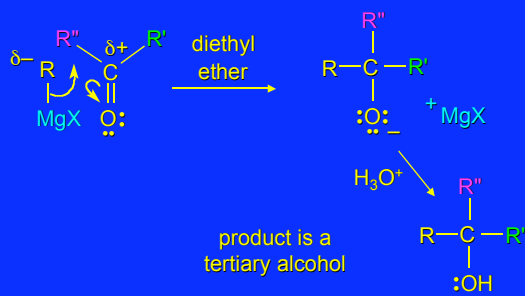
*Example*



*Grignard reagents react with:*

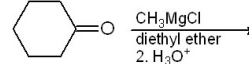
formaldehyde to give primary alcohols  
aldehydes to give secondary alcohols  
ketones to give tertiary alcohols

Grignard reagents react with ketones



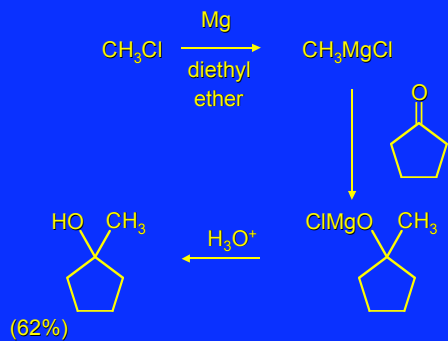
Question

- What is the product of the reaction shown at the right?



- A)
- B)
- C)
- D)

Example

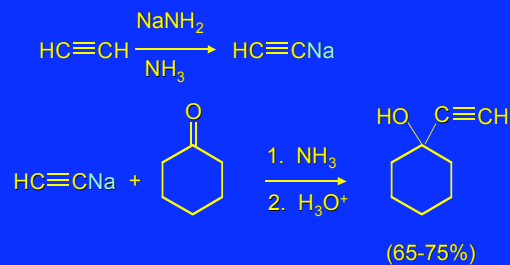


Question

- Two alcohols, each having the molecular formula  $C_{11}H_{22}O$ , are formed in the reaction of methyl lithium with 3-(R)-*tert*-butylcyclohexanone. These two alcohols are
- A) constitutional isomers.
- B) enantiomers in equal amounts.
- C) enantiomers in unequal amounts.
- D) diastereomers.

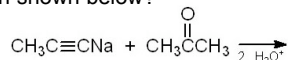
Synthesis of Acetylenic Alcohols

Remember: Sodium Salts of Acetylenes



## Question

- What compound will be obtained from the reaction shown below?



- A)  $\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_2\text{C}\equiv\text{CCH}_3$
- B)  $(\text{CH}_3)_2\overset{\text{OH}}{\text{C}}\text{C}\equiv\text{CCH}_3$
- C)  $(\text{CH}_3)_2\overset{\text{OH}}{\text{C}}\text{CH}_2\text{C}\equiv\text{CH}$
- D)  $\text{CH}_3\overset{\text{OH}}{\text{C}}\text{C}\equiv\text{CCH}_3$

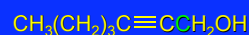
## Using Acetylenic Grignard Reagents



diethyl ether



- $\text{H}_2\text{C}=\text{O}$
- $\text{H}_3\text{O}^+$



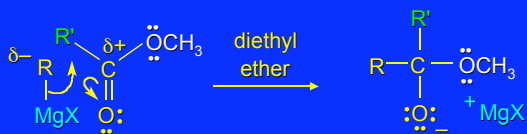
(82%)

## Preparation of Tertiary Alcohols From Esters and Grignard Reagents

## Question

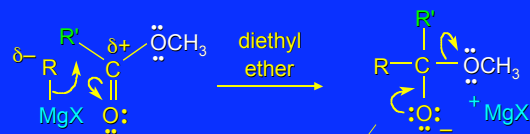
- Which one of the compounds below will be produced when methylmagnesium bromide is added to propanoic acid ( $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ )?
- A)  $\text{CH}_3\text{CH}_2\text{COCH}_3$
- B)  $\text{CH}_3\text{CH}_2\text{CO}_2\text{-MgBr}$
- C)  $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$
- D)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

## Grignard reagents react with esters



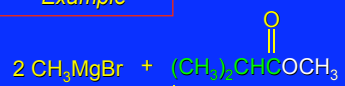
but species formed is unstable and dissociates under the reaction conditions to form a ketone

## Grignard reagents react with esters

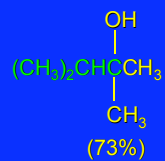


this ketone then goes on to react with a second mole of the Grignard reagent to give a tertiary alcohol

*Example*



1. diethyl ether
2.  $\text{H}_3\text{O}^+$



Two of the groups attached to the tertiary carbon come from the Grignard reagent

## Question

- Which one of the compounds below will be produced when methylmagnesium bromide is added to methyl propanoate ( $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3$ ) followed by acid?
- A)  $\text{CH}_3\text{CH}_2\text{COCH}_3$
- B)  $\text{CH}_3\text{CH}_2\text{CO}_2\text{-MgBr}$
- C)  $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$
- D)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- E) 2-methyl-2-butanol