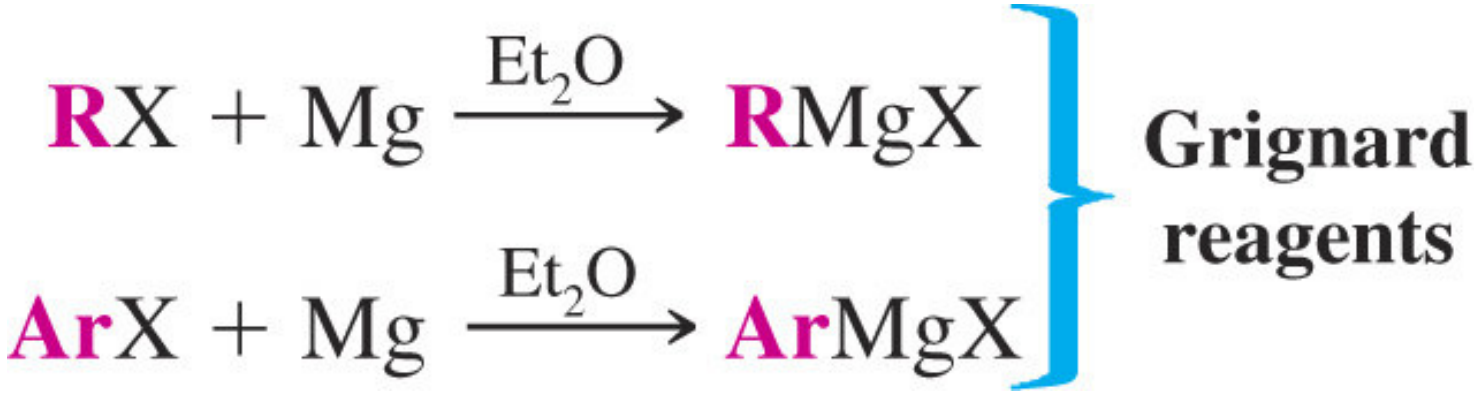
9.9 Grignard Reagents

- Grignard reagents are prepared by the reaction of organic halides with magnesium turnings
  - An ether solvent is used because it forms a complex with the Grignard reagent which stabilizes it

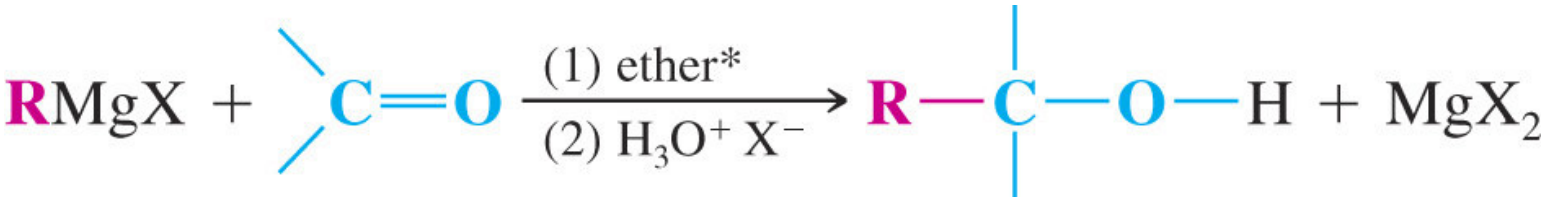


Methylmagnesium iodide (95%)

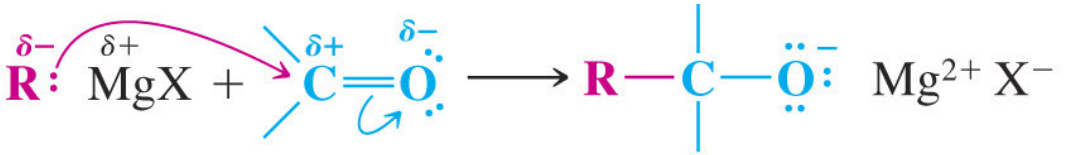
Phenylmagnesium bromide (95%)

– Reaction of Grignard Reagents with Carbonyl Compounds

- Nucleophilic attack of Grignard reagents at carbonyl carbons is the most important reaction of Grignard reagents
  - Reaction of Grignard reagents with aldehydes and ketones yields a new carbon-carbon bond and an alcohol



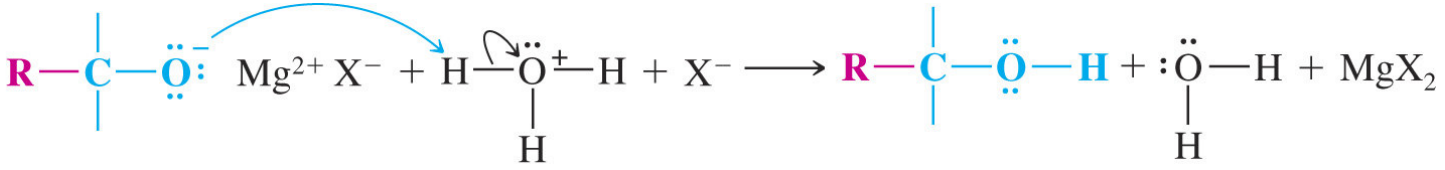
Step 1



Grignard reagent **Carbonyl compound** **Halomagnesium alkoxide**

The strongly nucleophilic Grignard reagent uses its electron pair to form a bond to the carbon atom. One electron pair of the carbonyl group shifts out to the oxygen. This reaction is a nucleophilic addition to the carbonyl group, and it results in the formation of an alkoxide ion associated with Mg^{2+} and X^-.

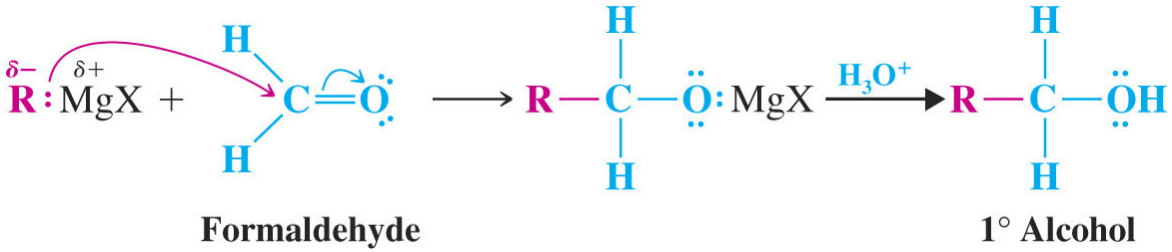
Step 2



Halomagnesium alkoxide **Alcohol**

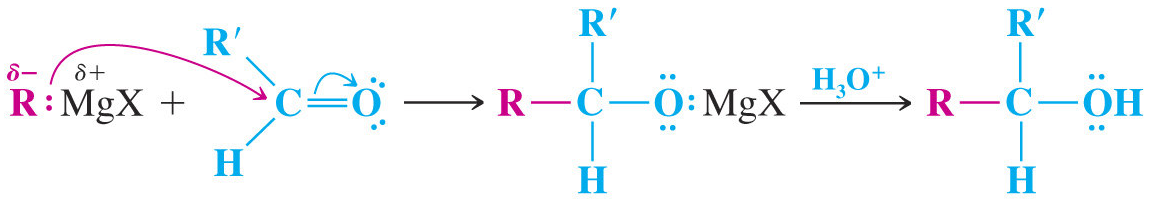
In the second step, the addition of aqueous HX causes protonation of the alkoxide ion; this leads to the formation of the alcohol and MgX_2.

- Alcohols from Grignard Reagents
  - Aldehydes and ketones react with Grignard reagents to yield different classes of alcohols depending on the starting carbonyl compound



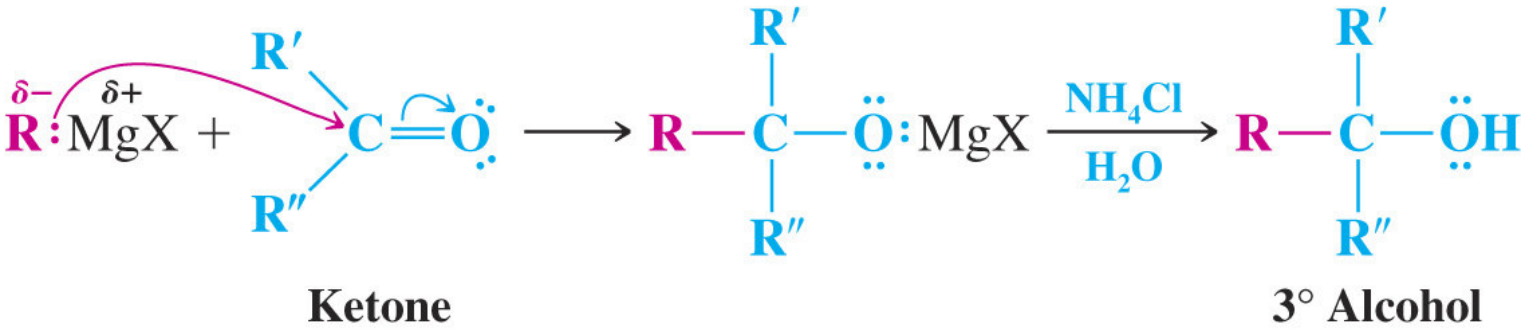
Formaldehyde

1° Alcohol



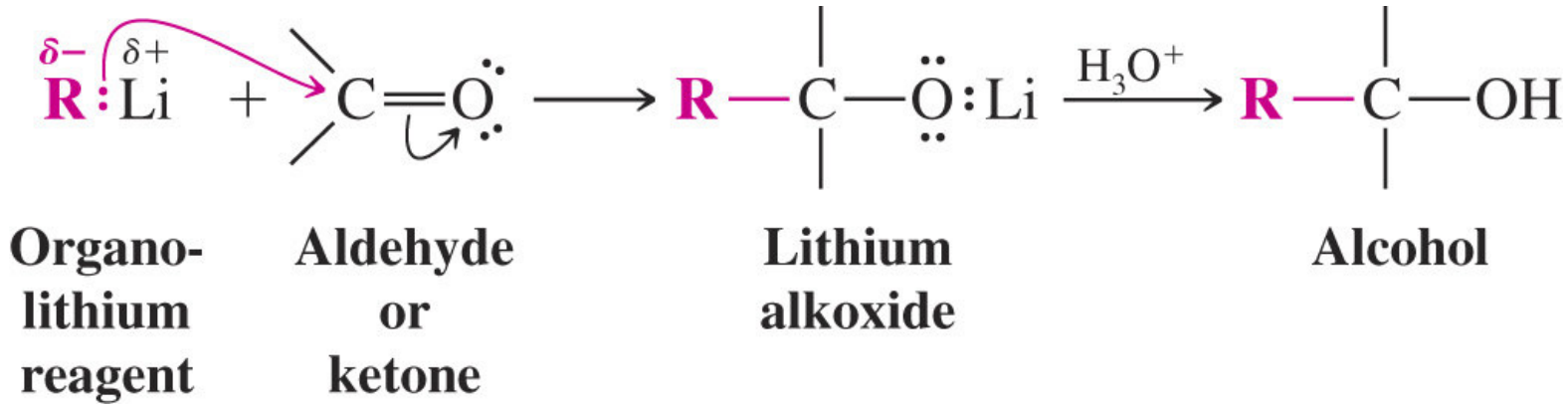
Higher aldehyde

2° Alcohol


δ−
δ+
R:MgX +
R′
R″
C=O
R—C—O:MgX
NH4Cl
H2O
R—C—OH
Ketone
3° Alcohol

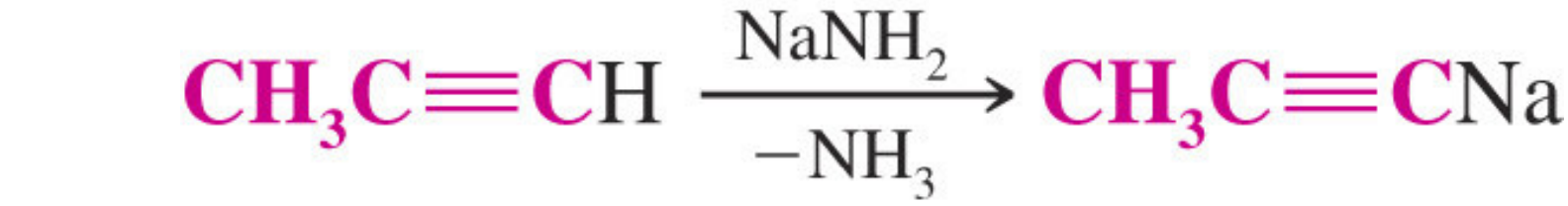
– The Use of Lithium Reagents

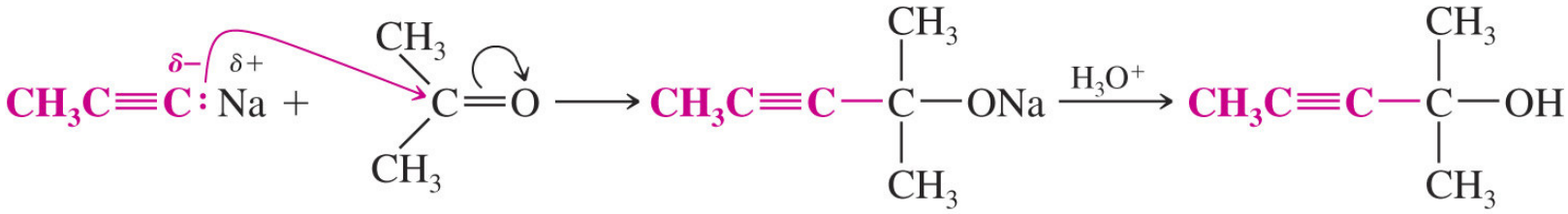
- Organolithium reagents react similarly to Grignard reagents
  - Organolithium reagents tend to be more reactive



– The Use of Sodium Alkynides

- Sodium alkynides react with carbonyl compounds such as aldehydes and ketones to form new carbon-carbon bonds



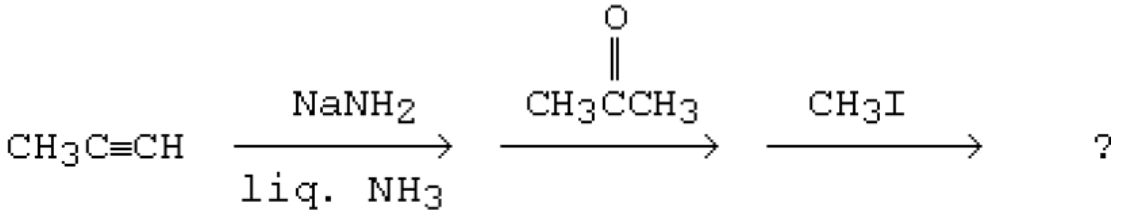


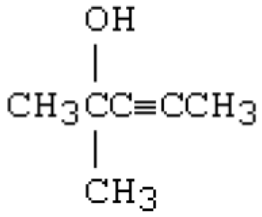
Solved Problems

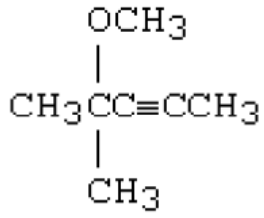
3. Which reagent(s) will distinguish between cyclopentanol and cyclopentane?

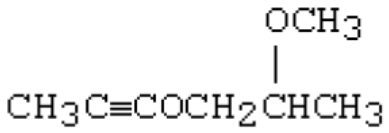
A) Br_2/CCl_4
B) $KMnO_4$ (cold)
C) CrO_3/aqueous H_2SO_4
D) NaOH (aq)
E) A) and B)

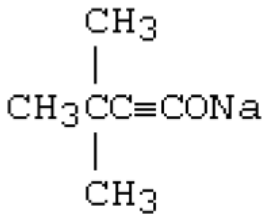
21. What is the final product?



A) 

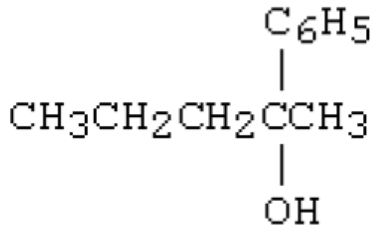
B) 

C) 

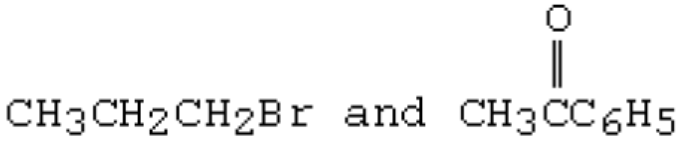
D) 

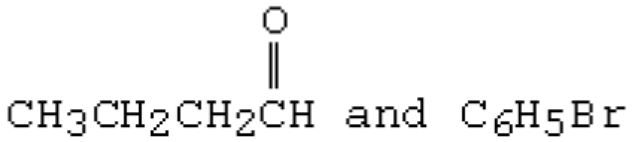
E) None of these

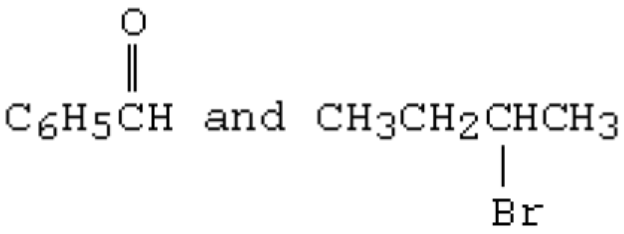
27.



Your task is to synthesize through a Grignard synthesis. Which pairs of compounds listed below would you choose as starting materials?

A) 

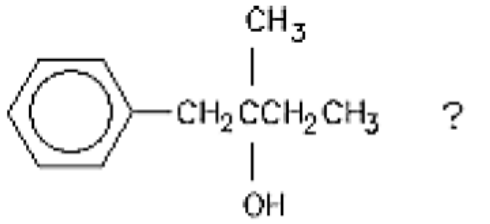
B) 

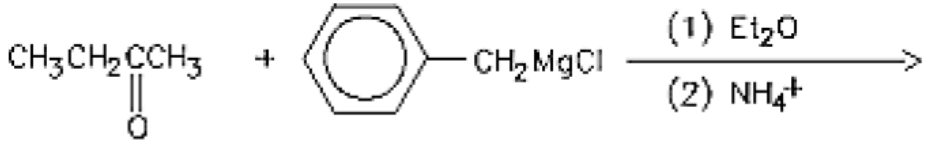
C) 

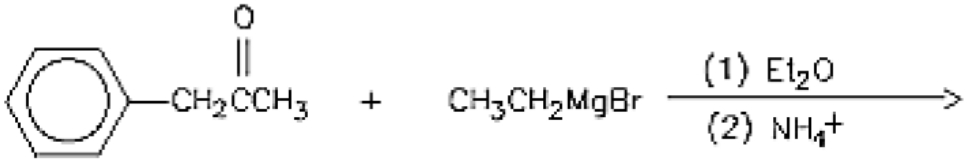
D) More than one of these

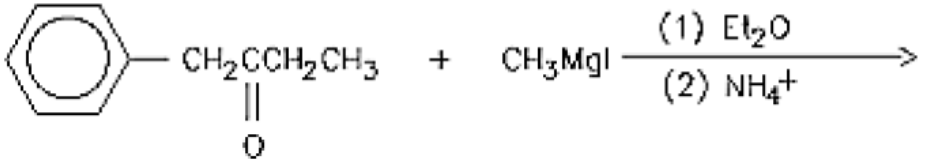
E) None of these

38. Which of the following would serve as a synthesis of racemic:



I 

II 

III 

A) I
B) II
C) III
D) All of the above
E) None of the above