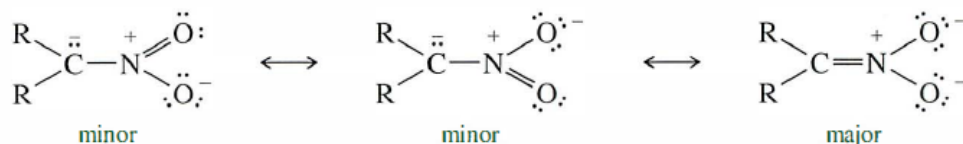
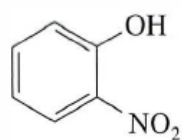


PROBLEM 10-9

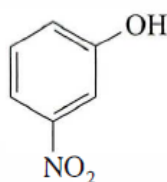
A nitro group ($-\text{NO}_2$) effectively stabilizes a negative charge on an adjacent carbon atom through resonance:



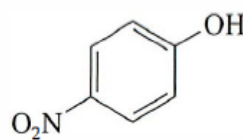
Two of the following nitrophenols are much more acidic than phenol itself. The third compound is only slightly more acidic than phenol. Use resonance structures of the appropriate phenoxide ions to show why two of these anions should be unusually stable.



2-nitrophenol



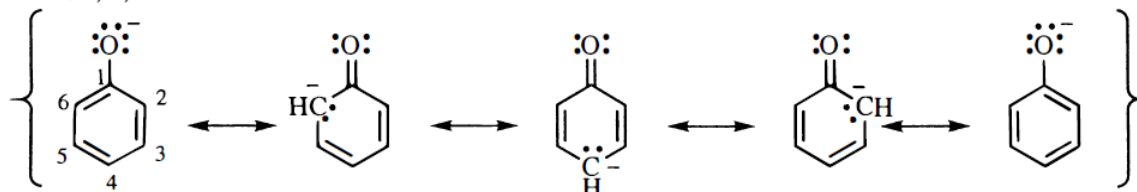
3-nitrophenol



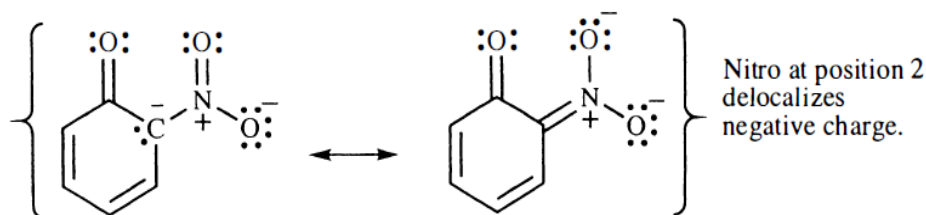
4-nitrophenol

ANSWER

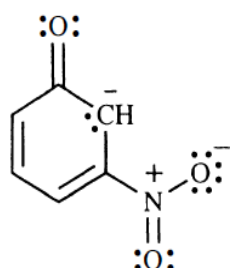
10-9 Resonance forms of phenoxide anion show the negative charge delocalized onto the ring only at carbons 2, 4, and 6:



Nitro group at position 2

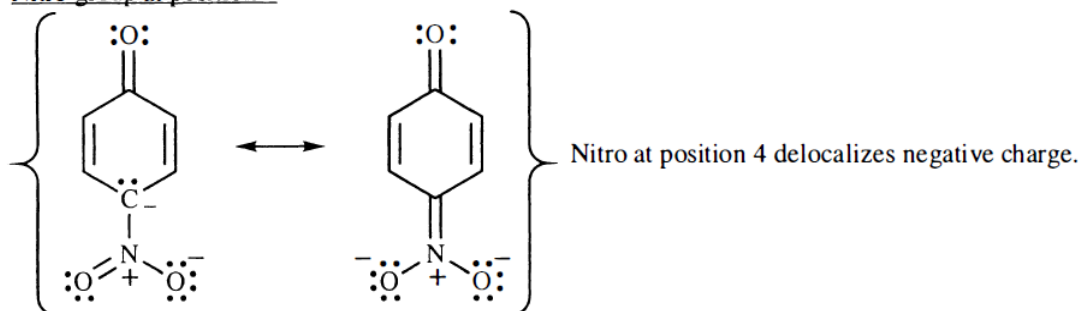


Nitro group at position 3



Nitro at position 3 cannot delocalize negative charge at position 2 or 4—no resonance stabilization.

Nitro group at position 4



Only when the nitro group is at one of the negative carbons will the nitro have a stabilizing effect (via resonance). Thus, 2-nitrophenol and 4-nitrophenol are substantially more acidic than phenol itself, but 3-nitrophenol is only slightly more acidic than phenol (due to the inductive effect).

PROBLEM 10-11

Which of the following compounds are suitable solvents for Grignard reactions?

(a) *n*-hexane

(b) $\text{CH}_3\text{—O—CH}_3$

(c) CHCl_3

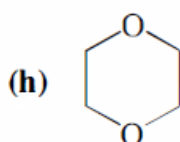
(d) cyclohexane

(e) benzene

(f) $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$



THF
(tetrahydrofuran)



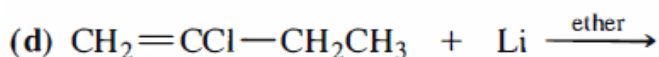
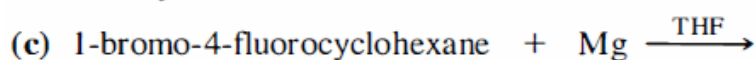
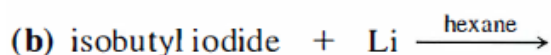
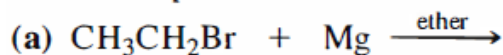
1,4-dioxane

ANSWER

10-11 The Grignard reaction needs a solvent containing an ether functional group: (b), (f), (g), and (h) are possible solvents. Dimethyl ether, (b), is a gas at room temperature, however, so it would have to be liquefied at low temperature for it to be a useful solvent.

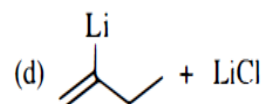
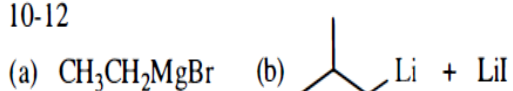
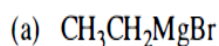
PROBLEM 10-12

Predict the products of the following reactions.



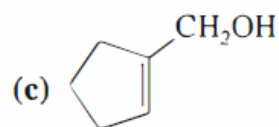
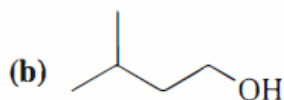
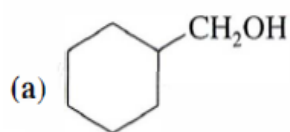
ANSWER

10-12



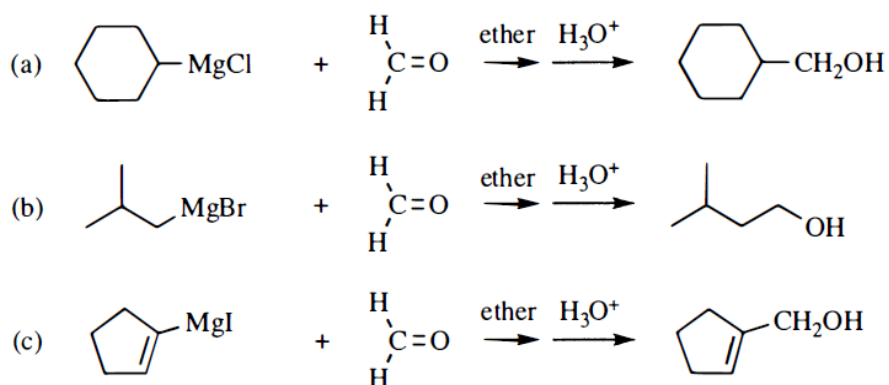
PROBLEM 10-13

Show how you would synthesize the following alcohols by adding an appropriate Grignard reagent to formaldehyde.



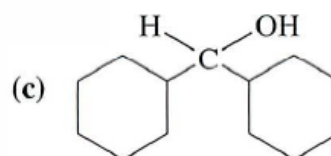
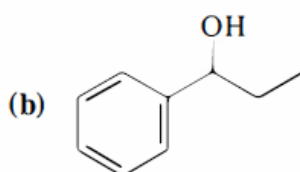
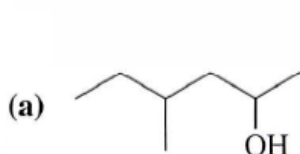
ANSWER

10-13 Any of three halides—chloride, bromide, iodide, but not fluoride—can be used. Ether is the typical solvent for Grignard reactions.



PROBLEM 10-14

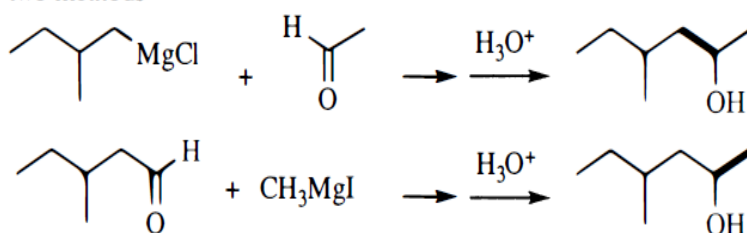
Show two ways you could synthesize each of the following alcohols by adding an appropriate Grignard reagent to an aldehyde.



ANSWER

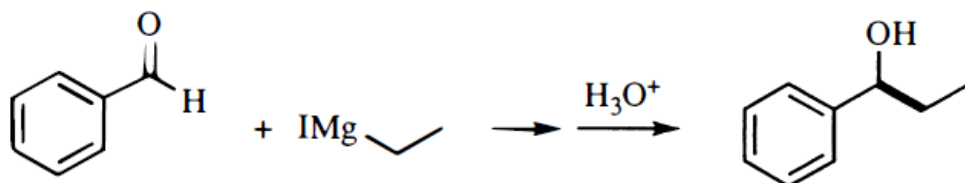
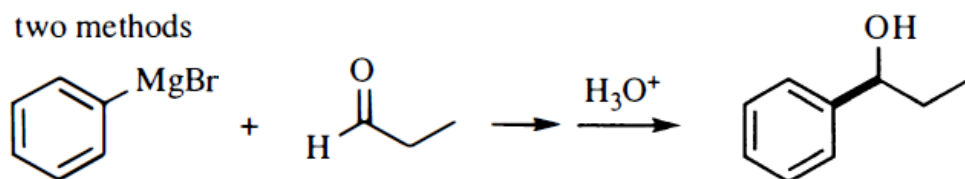
10-14 Any of three halides—chloride, bromide, iodide, but not fluoride—can be used. Grignard reactions are always performed in ether solvent; ether is not shown here.

(a) two methods

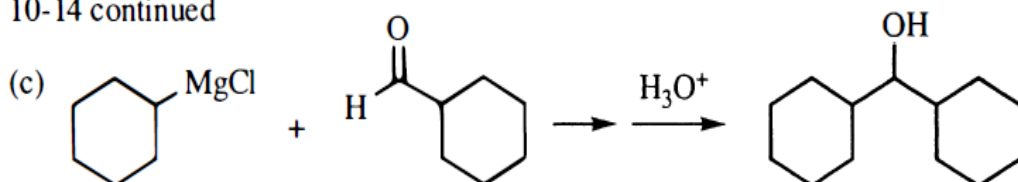


Where two methods can be used to form the target compound, the newly formed bond is shown in bold.

(b) two methods

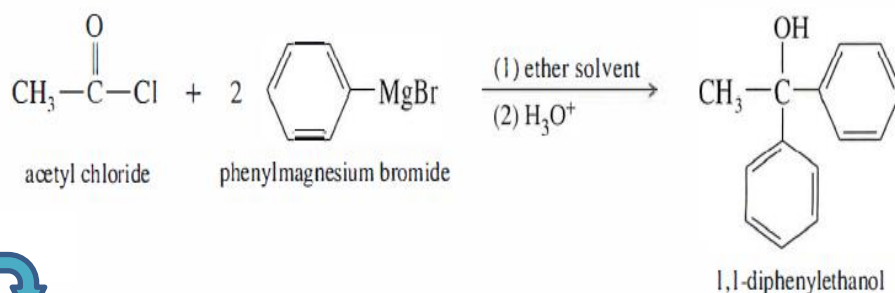


10-14 continued

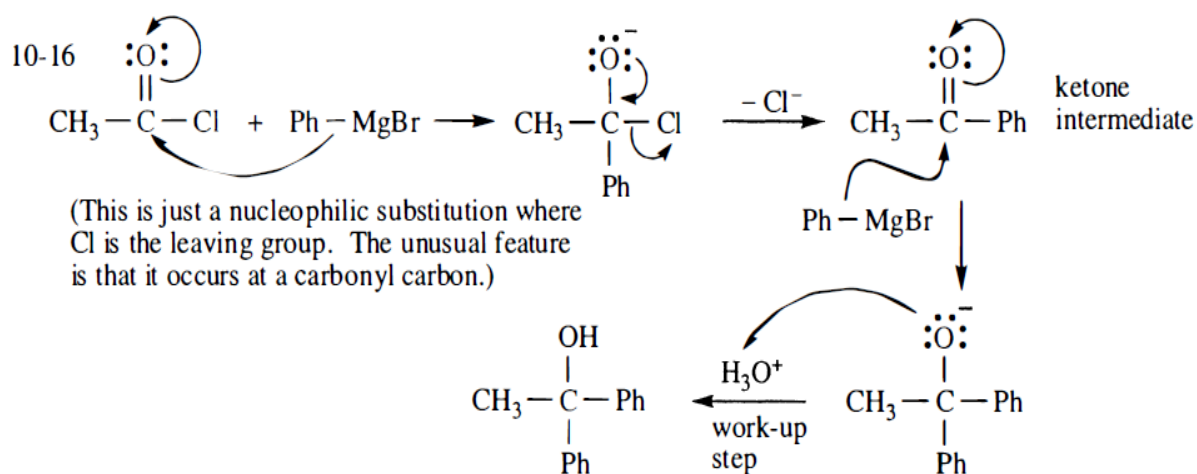


PROBLEM 10-16

Propose a mechanism for the reaction of acetyl chloride with phenylmagnesium bromide to give 1,1-diphenylethanol.



ANSWER

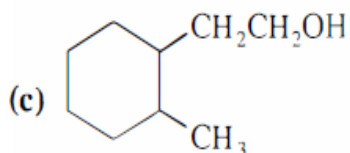


PROBLEM 10-19

Show how you would synthesize the following alcohols by adding Grignard reagents to ethylene oxide.

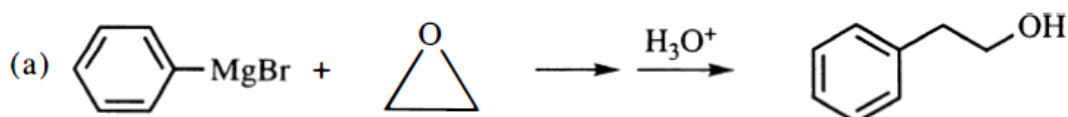
(a) 2-phenylethanol

(b) 4-methyl-1-pentanol



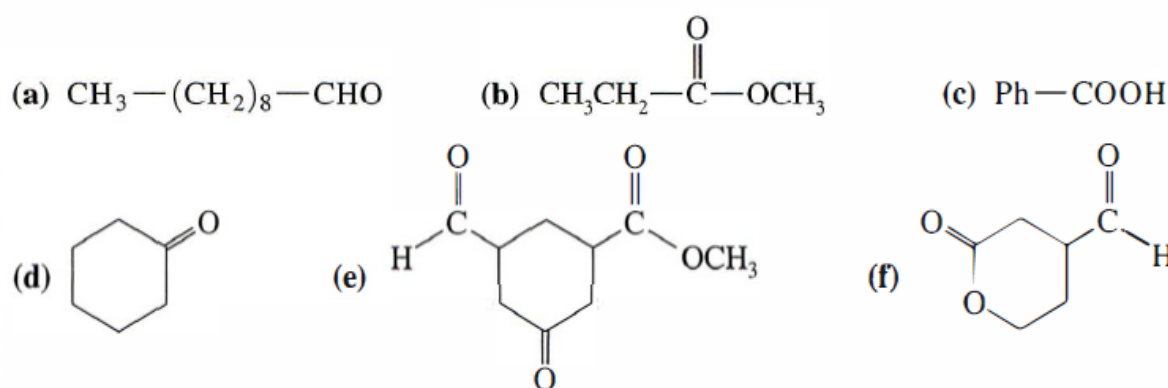
ANSWER

10-19 Ether is the typical solvent in Grignard reactions.



PROBLEM 10-24

Predict the products you would expect from the reaction of NaBH_4 with the following compounds.



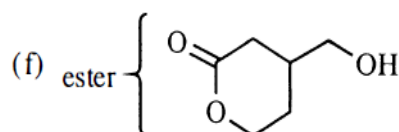
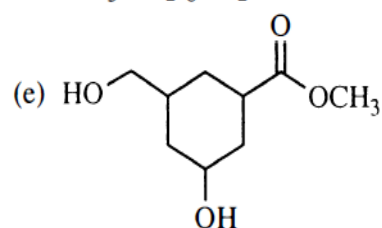
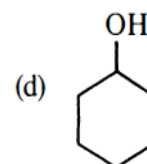
ANSWER

10-24 Sodium borohydride does not reduce esters.

(a) $\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{OH}$

(b) no reaction

(c) no reaction (PhCOO^- before acid work-up)



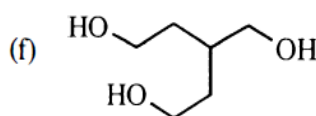
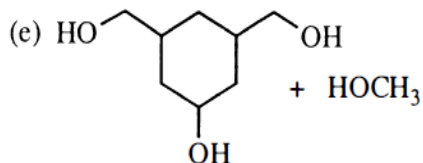
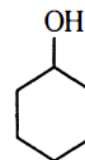
PROBLEM 10-25

Repeat Problem 10-24 using LiAlH_4 (followed by hydrolysis) as the reagent.

ANSWER

10-25 Lithium aluminum hydride reduces esters as well as other carbonyl groups.

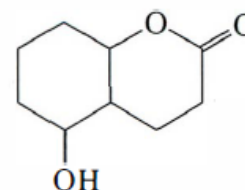
(a) $\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{OH}$ (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{HOCH}_3$ (c) PhCH_2OH (d)



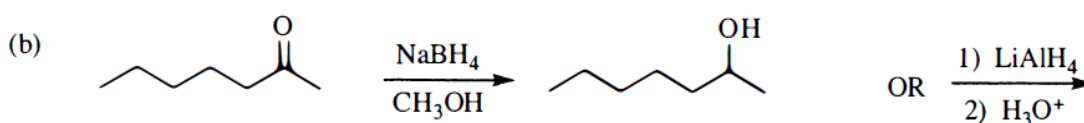
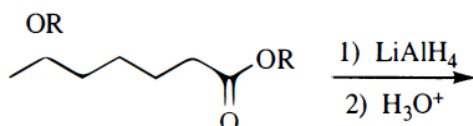
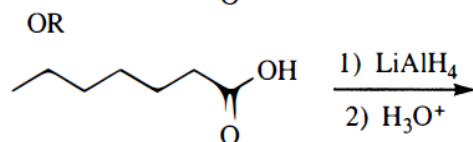
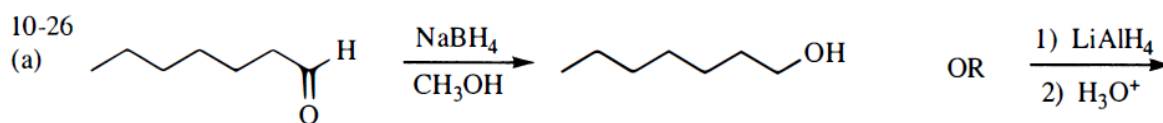
PROBLEM 10-26

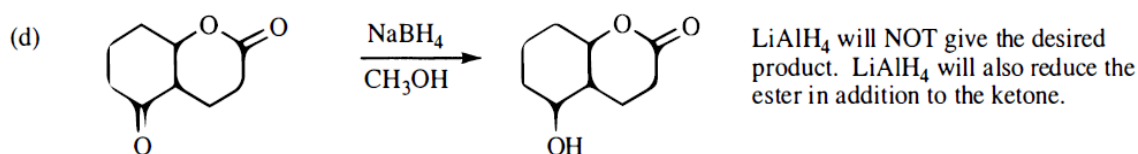
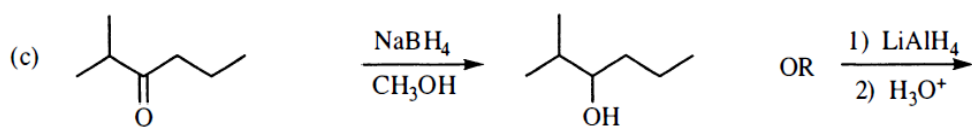
Show how you would synthesize the following alcohols by reducing appropriate carbonyl compounds.

(a) 1-heptanol (b) 2-heptanol (c) 2-methyl-3-hexanol (d)



ANSWER





Reactions of Alcohols

Types of Reactions of Alcohols

PROBLEM 11-2

Predict the products of the reactions of the following compounds with chromic acid and also with PCC.

- | | |
|---|--|
| <p>(a) cyclohexanol</p> <p>(c) 2-methylcyclohexanol</p> <p>(e) cyclohexane</p> <p>(g) ethanol</p> | <p>(b) 1-methylcyclohexanol</p> <p>(d) cyclohexanone</p> <p>(f) acetic acid, CH₃COOH</p> <p>(h) acetaldehyde, CH₃CHO</p> |
|---|--|

ANSWER

