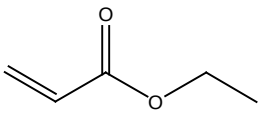
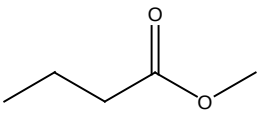
Ch. 13 Carbonyl (1) Answers

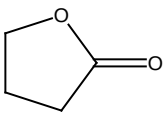
1. Name the carboxylic acid and alcohol from which each ester is derived.

(a) 

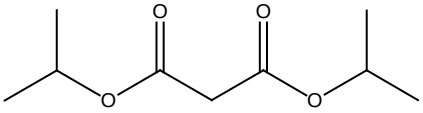
acrylic acid, ethanol
or ethyl propenoate

(b) 

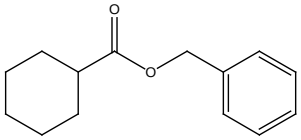
butyric acid, methanol

(c) 

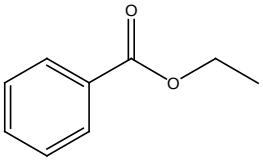
4-hydroxybutanoic acid

(d) 

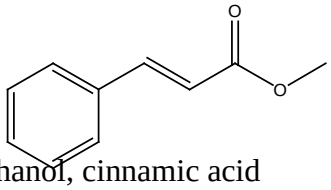
malonic acid, isopropyl alcohol or
2-propanol

(e) 

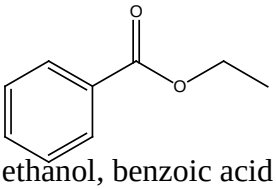
benzyl alcohol,
cyclohexanecarboxylic acid

(f) 

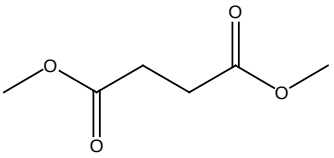
ethanol benzoic acid

(g) 

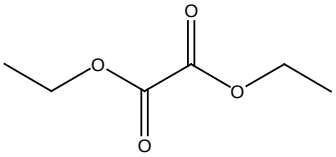
methanol, cinnamic acid

(h) 

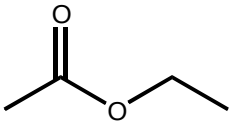
ethanol, benzoic acid

(i) 

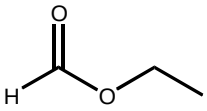
methanol, succinic acid

(j) 

ethanol, oxalic acid

(k) 

ethanol, acetic aicd (or ethanoic aicd)

(l) 

ethanol, formic acid

2. Using an alcohol or alkyl halide to make each of the following esters:

(a) methyl butyrate

$$CH_3OH + CH_3CH_2CH_2COOH \xrightarrow{H^+}$$

$$CH_3Cl + CH_3CH_2CH_2COONa \xrightarrow{\Delta}$$

(b) propyl acetate

$$CH_3CH_2CH_2OH + CH_3COOH \xrightarrow{H^+}$$

$$CH_3CH_2CH_2Cl + CH_2COONa \xrightarrow{\Delta}$$

(c) Ethyl butyrate

$$CH_3CH_2OH + CH_3CH_2CH_2COOH \xrightarrow{H^+}$$

$$CH_3CH_2Cl + CH_2CH_2CH_2COONa \xrightarrow{\Delta}$$

(d) Methyl phenylethanoate

$$CH_3OH + C_6H_5CH_2COOH \xrightarrow{H^+}$$

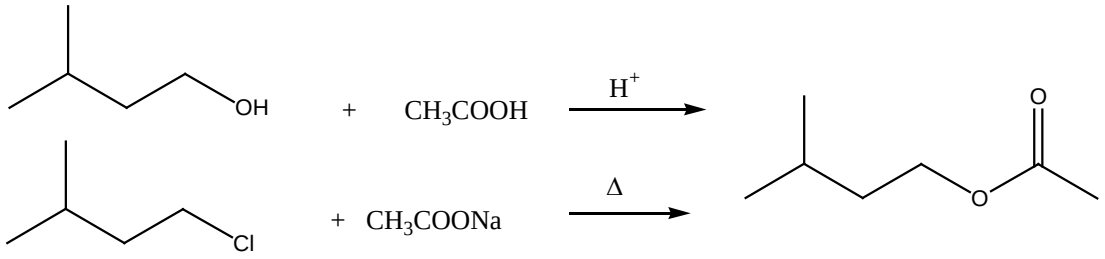
$$CH_3Cl + C_6H_5CH_2COONa \xrightarrow{\Delta}$$

(e) octyl acetate

$CH_3(CH_2)_7OH + CH_3COOH \xrightarrow{H^+}$

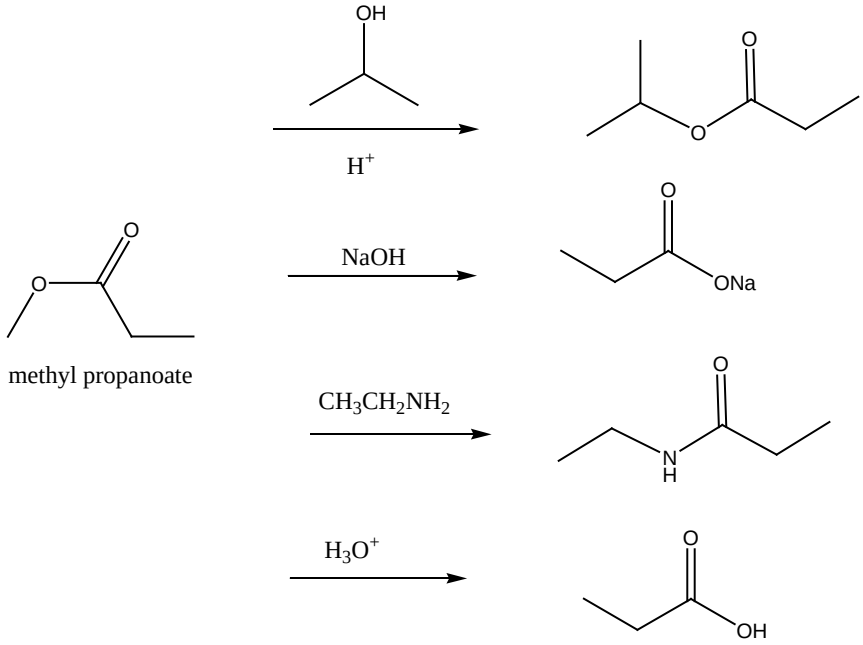
$CH_3(CH_2)_7Cl + CH_3COONa \xrightarrow{\Delta}$

(f) isopentyl acetate

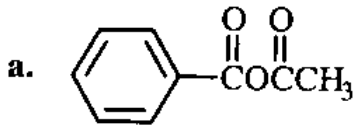


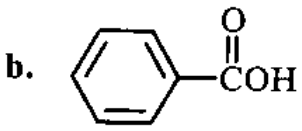
3. What reagents would you use to convert methyl propanoate into the following compounds?

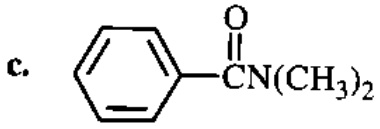
(a) isopropyl propanoate (b) sodium propanoate (c) N-ethylpropanamide (d) propanoic acid

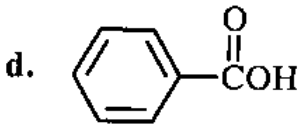


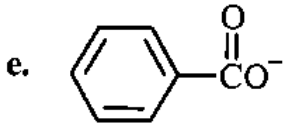
4. What products would be formed from the reaction of benzoyl chloride with the following reagents?
a. sodium acetate b. water c. dimethylamine d. aqueous HCl e. aqueous NaOH f. cyclohexanol g. benzylamine h. 4-chlorophenol i. Isopropyl alcohol j. aniline

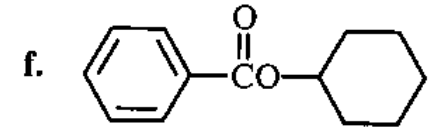


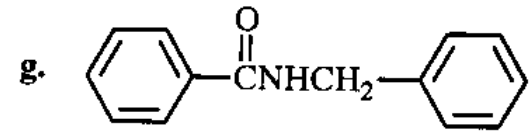


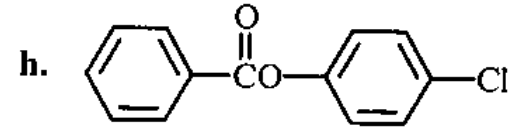


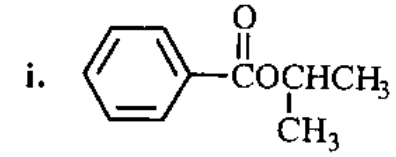


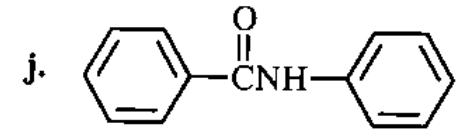




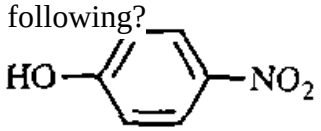






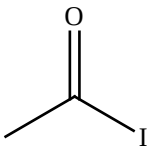


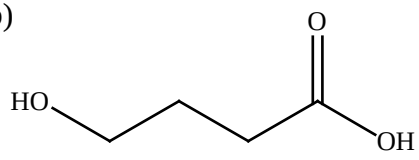
5. Starting with acetyl chloride, what would you use to make each of the following?

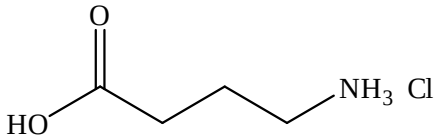
a. $CH_3CH_2CH_2OH$ c. $(CH_3)_2NH$ e. 

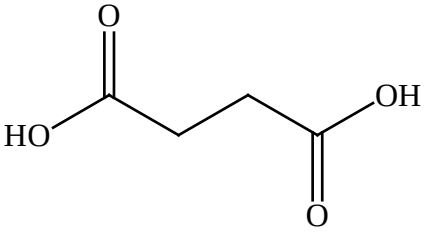
b. $CH_3CH_2NH_2$ d. $CH_3\overset{O}{\overset{\|}{C}}O^-$ f. H_2O

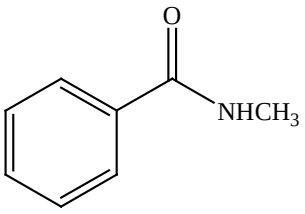
5. The product of the following reactions:

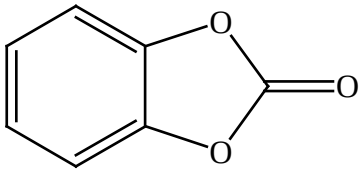
(a) 

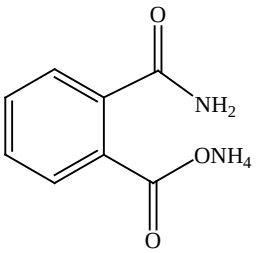
(b) 

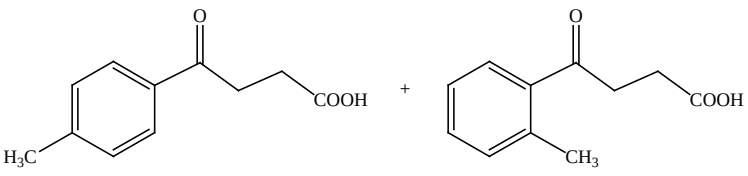
(c) 

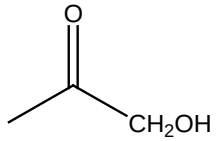
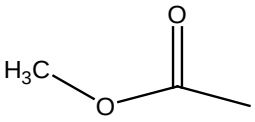
(d) 

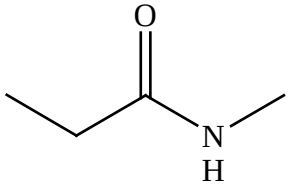
(e) 

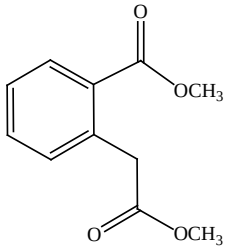
(f) 

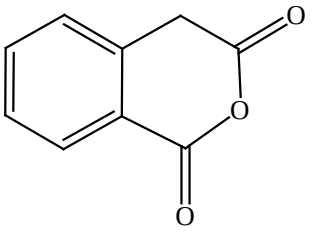
(g) 

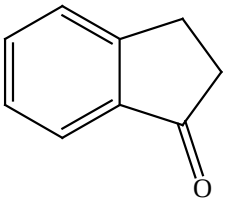
(H) 

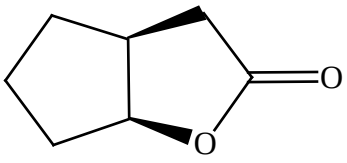
(I)  + 

(j) 

(K) 

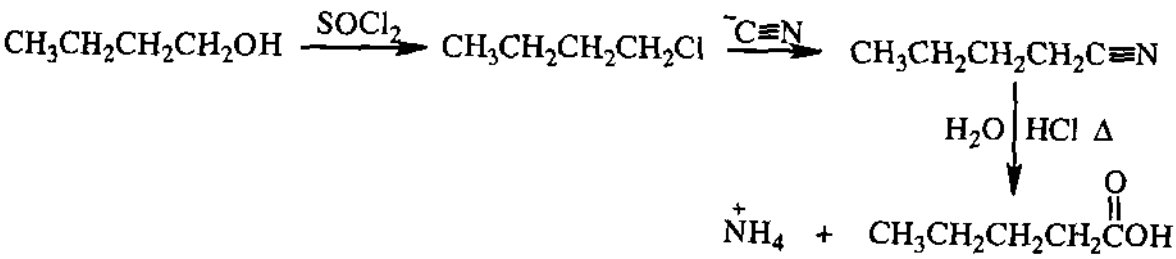
(L) 

(M) 

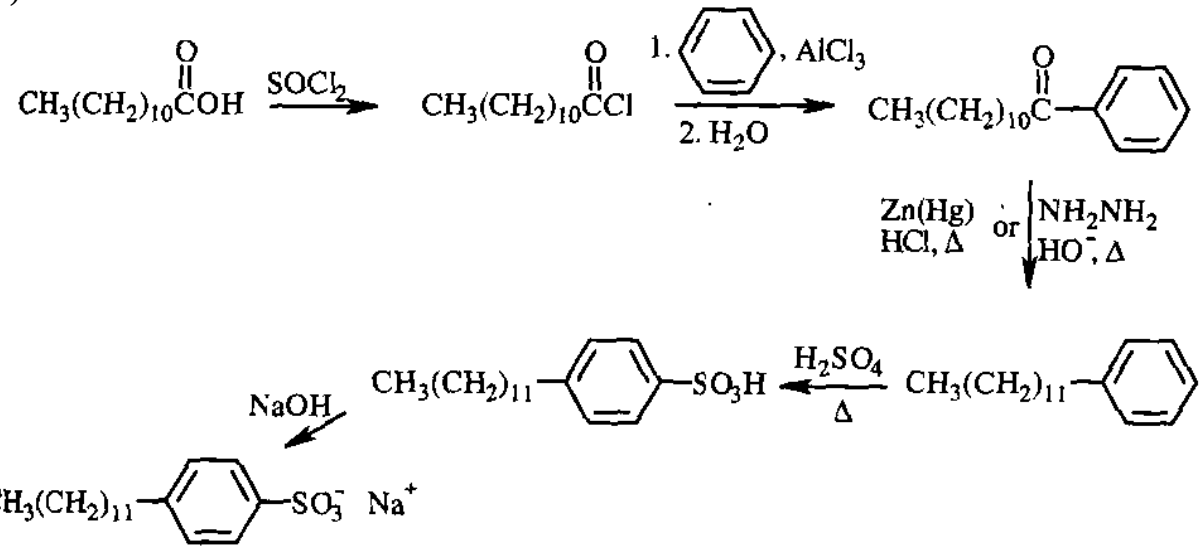
(N) 

6. Show how the following compounds could be prepared from the given starting materials. You can use any necessary organic or inorganic reagents:

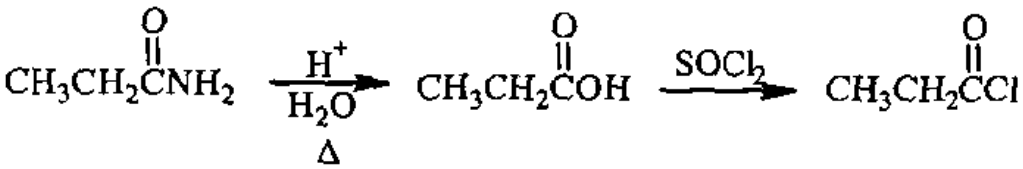
(a)



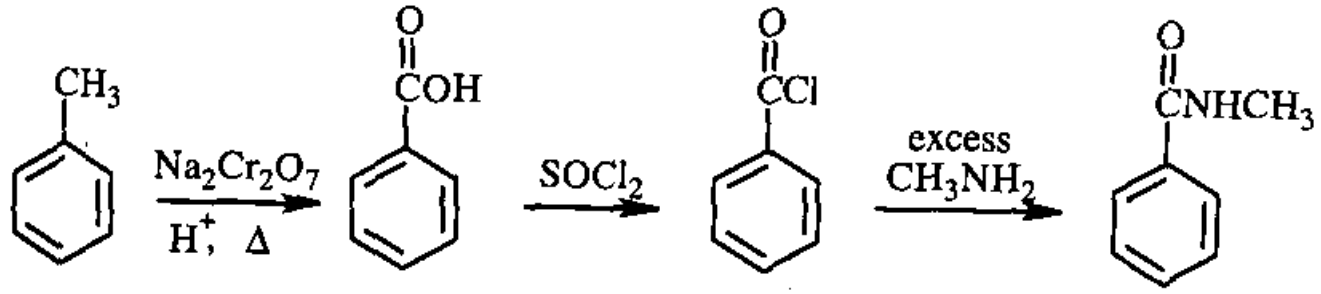
(B)



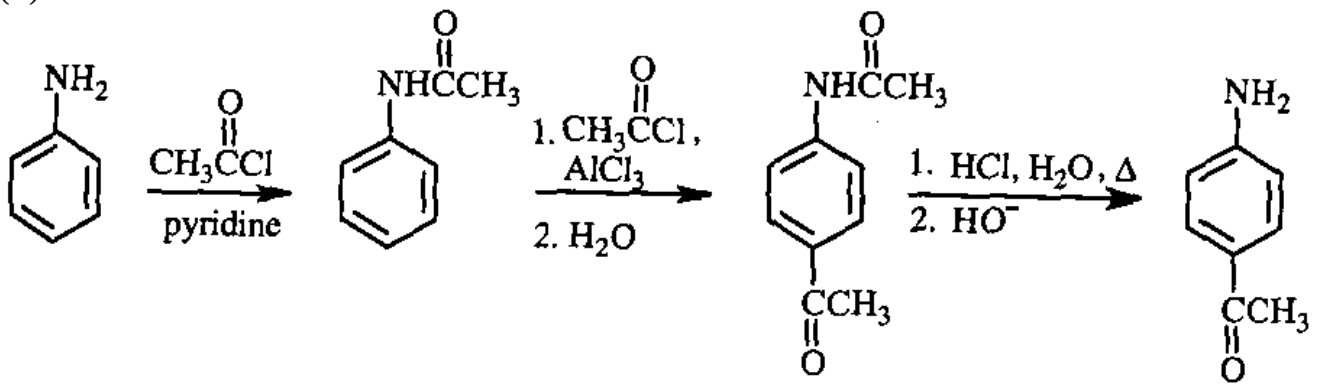
(C)



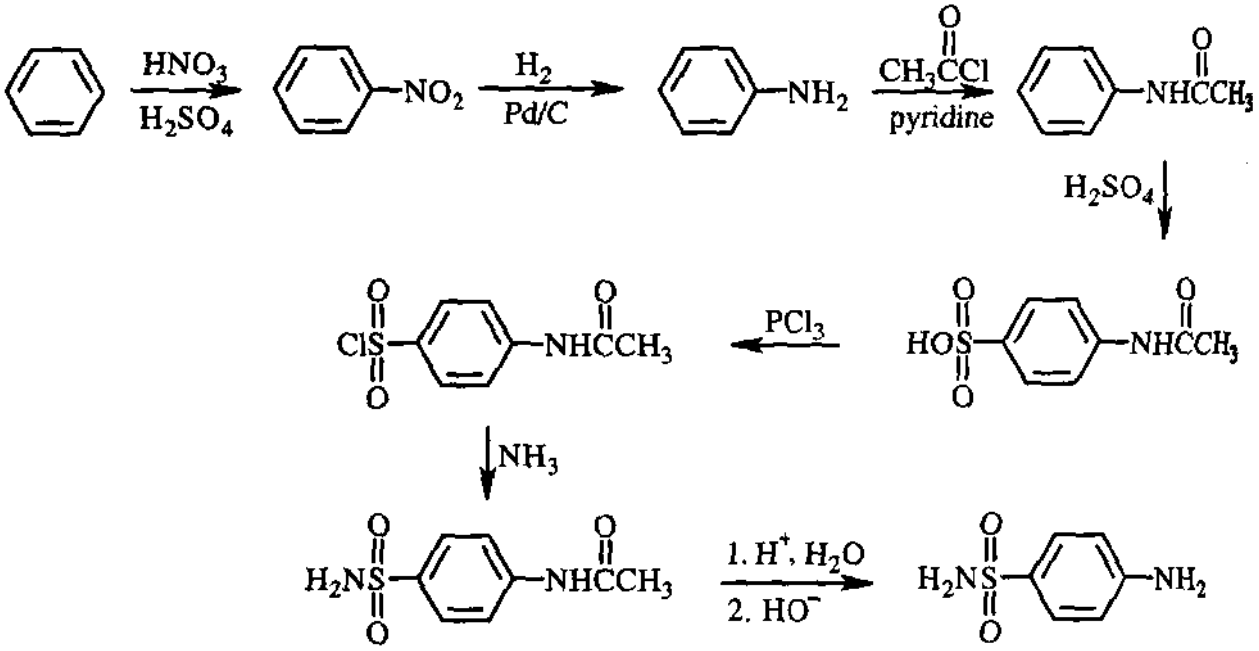
(D)


CH3
Na2Cr2O7
H+, Δ
COH
SOCl2
CCl
excess
CH3NH2
CNHCH3

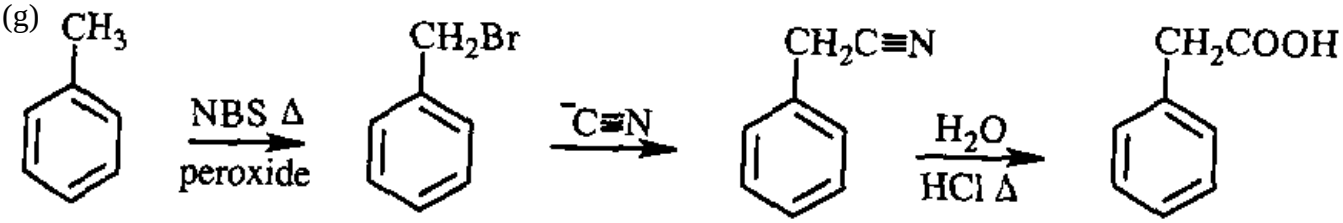
(E)


NH2
CH3CCl
pyridine
NHCCH3
1. CH3CCl,
AlCl3
2. H2O
CCH3
1. HCl, H2O, Δ
2. HO−

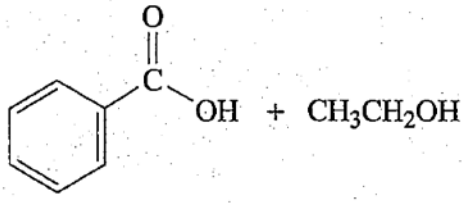
(F)

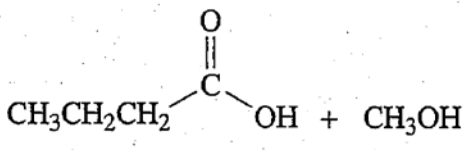

HNO3
H2SO4
NO2
H2
Pd/C
NH2
CH3CCl
pyridine
NHCCH3
H2SO4
PCl3
ClS
HOS
NH3
H2NS
1. H+, H2O
2. HO−

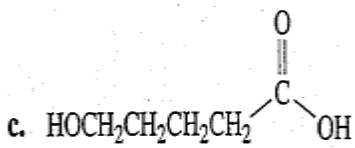
(g)


CH3
NBS Δ
peroxide
CH2Br
−C≡N
CH2C≡N
H2O
HCl Δ
CH2COOH

7.

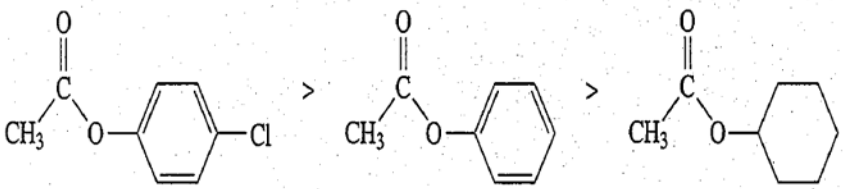
a. 

b. 

c. 

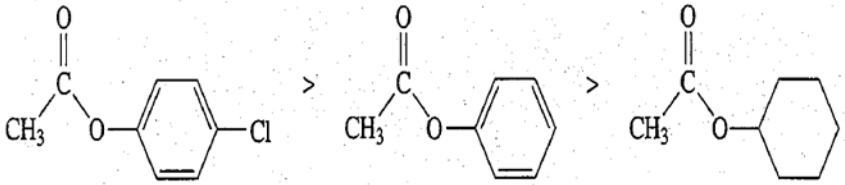
8

a. The weaker the base attached to the acyl group, the stronger its electron-withdrawing ability; therefore, the easier it is to form the tetrahedral intermediate. *para*-Chlorophenol is a stronger acid than phenol so the conjugate base of *para*-chlorophenol is a weaker base than the conjugate base of phenol.



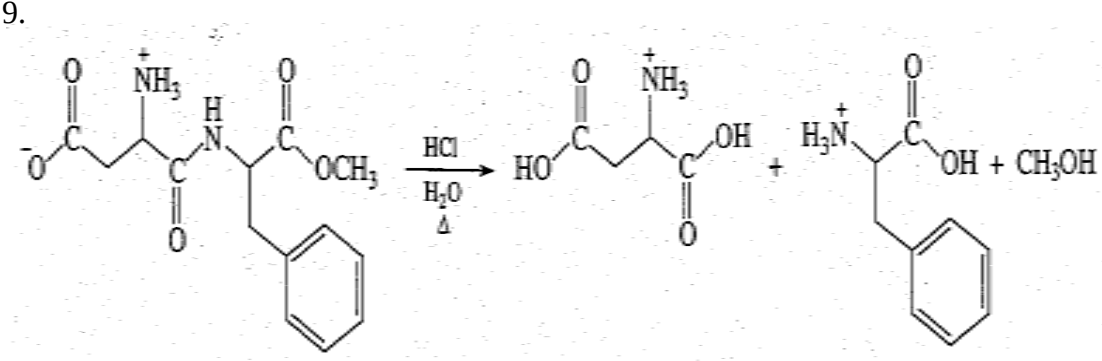
C A B

b. The tetrahedral intermediate collapses by eliminating the OR group. The weaker the OR group is as a base, the easier it is to eliminate it.

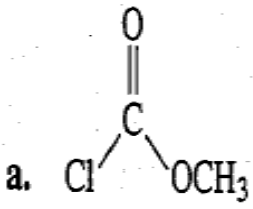


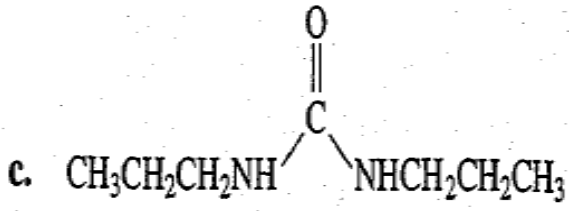
Thus, the rate of both formation of the tetrahedral intermediate and collapse of the tetrahedral intermediate is decreased by increasing the basicity of the OR group.

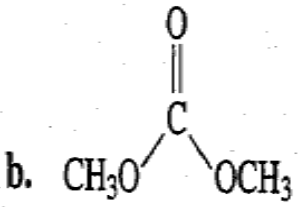
9.

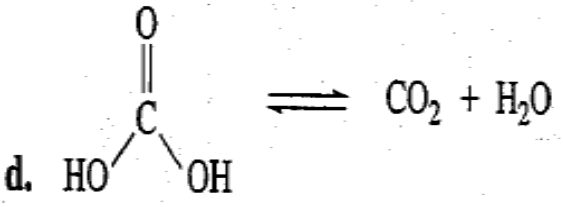


10









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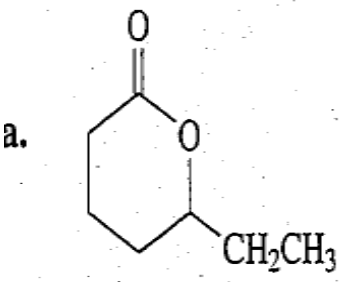
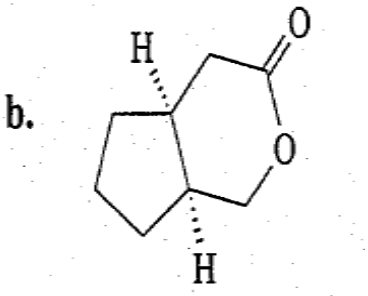
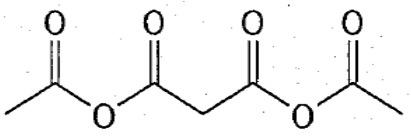
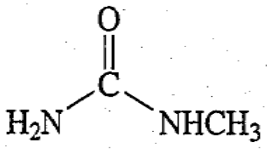


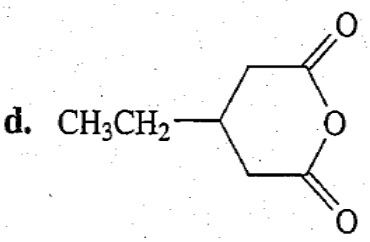


+ CH_3CH_2OH

12.





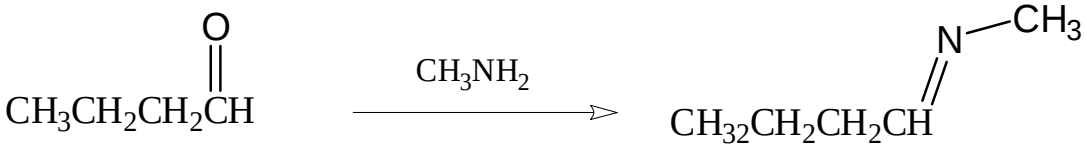


c. no reaction; an amide will not react with water without a catalyst

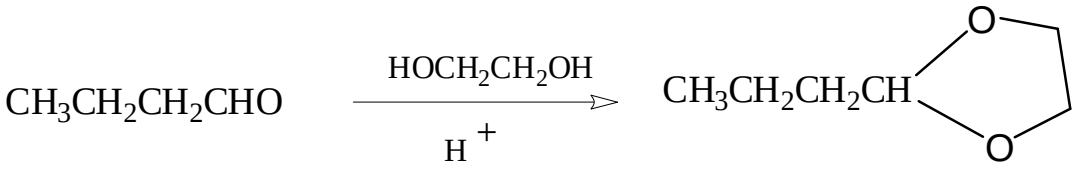
Ch 14 Carbonyl (II) Answers

1. Show the product expected from reaction of butanal with each of the following reagents:

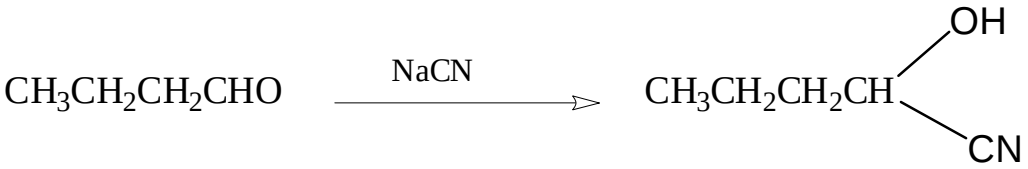
(a) methylamine



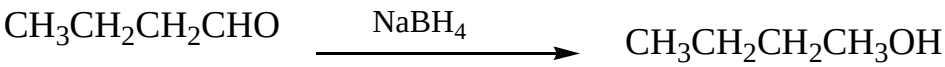
(b) ethylene glycol and a trace of acid



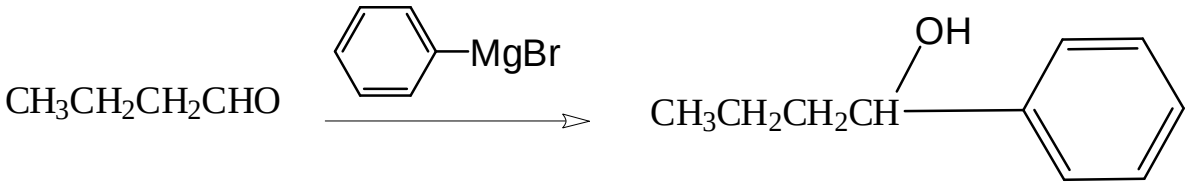
(c) sodium cyanide (NaCN) at pH 10



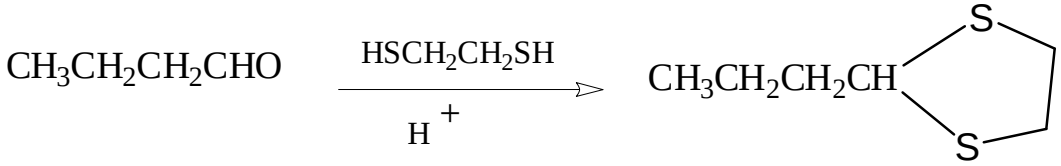
(d) sodium borohydride (NaBH4)



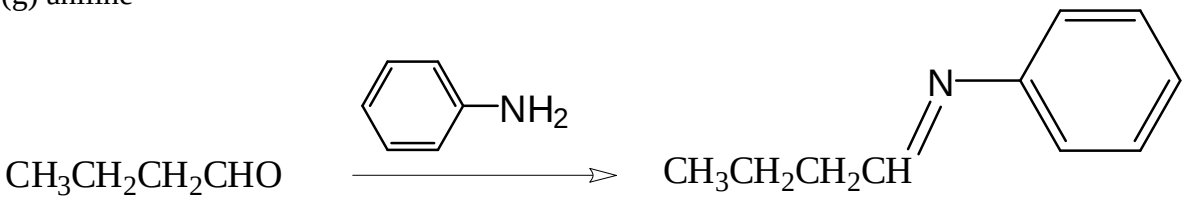
(e) phenylmagnesium bromide



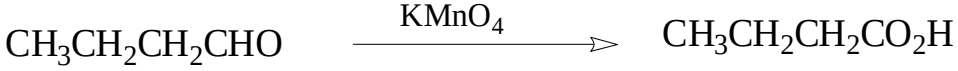
(f) ethanedithiol and acid



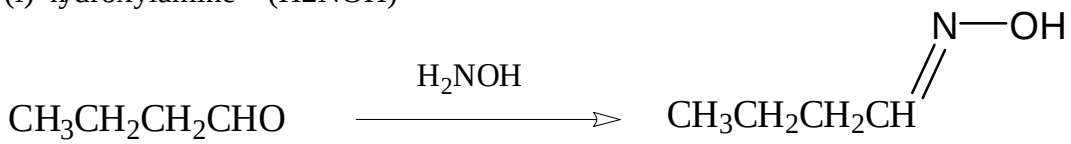
(g) aniline



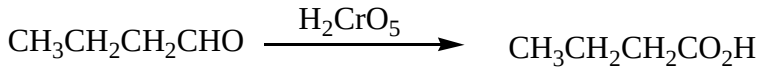
(h) potassium permanganate



(i) hydroxylamine (H2NOH)

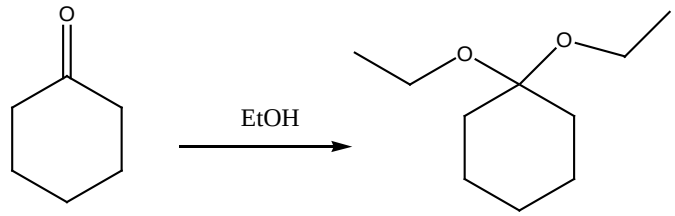


(j) Jones' reagent (chromic acid)

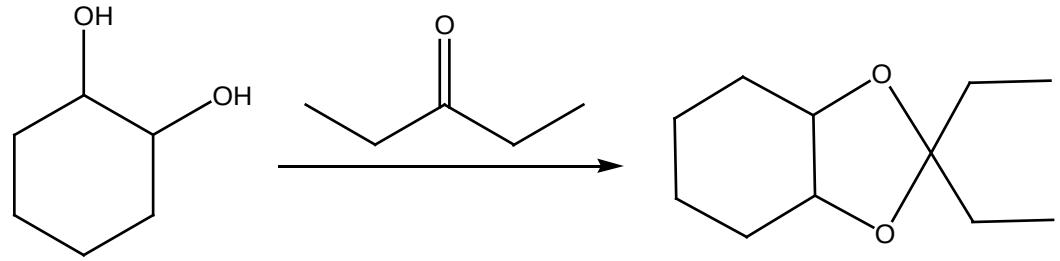


2. Show the structure of the acetal formed from each of the following reactions, using H2S04 as a catalyst:

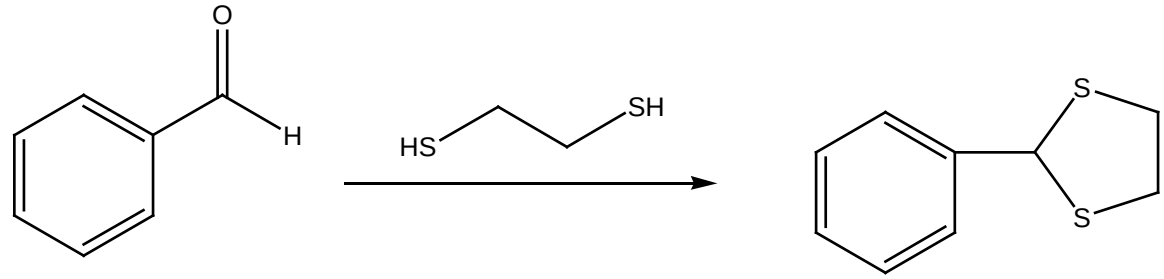
(a) cyclohexanone and ethanol



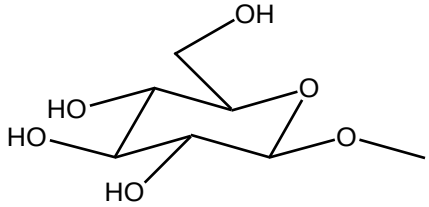
(b) cis-1,2-cyclohexanediol and diethyl ketone

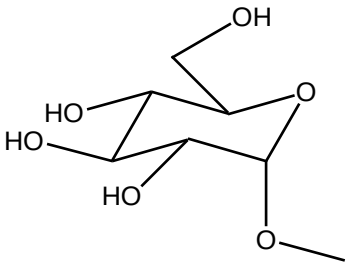


(c) benzaldehyde and ethanedithiol



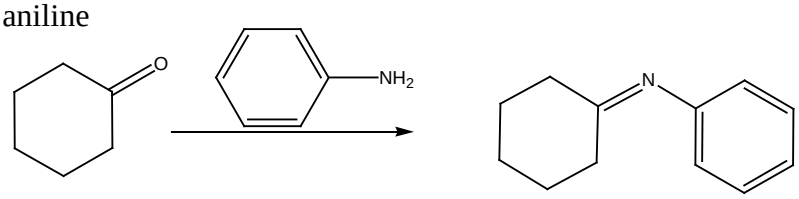
(d) glucose and methanol



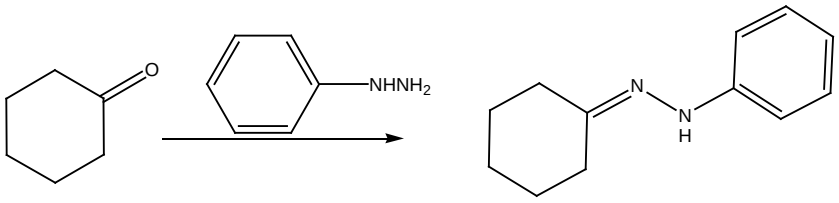


3. Show the product of the reaction of cyclohexanone with each of the following compounds:

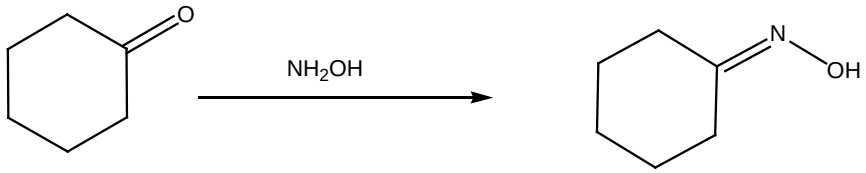
(a) aniline



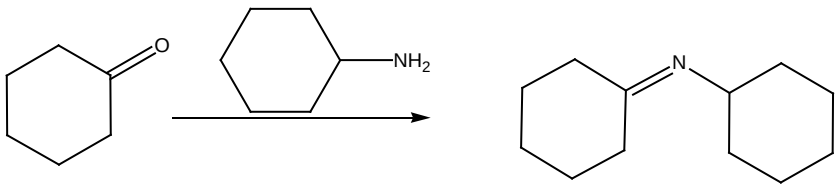
(b) phenylhydrazine (C6H5NHNH2)



(c) hydroxylamine (H2NOH)

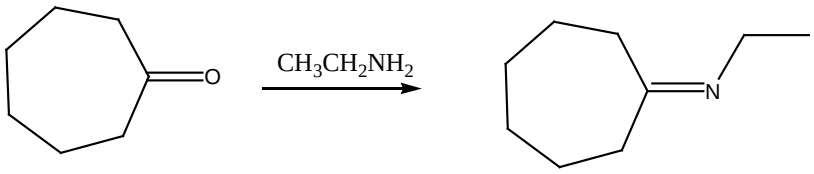


(d) cyclohexylamine

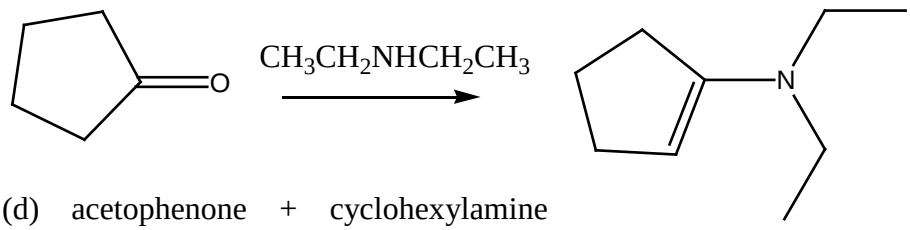


4. Give the product of the following reaction:

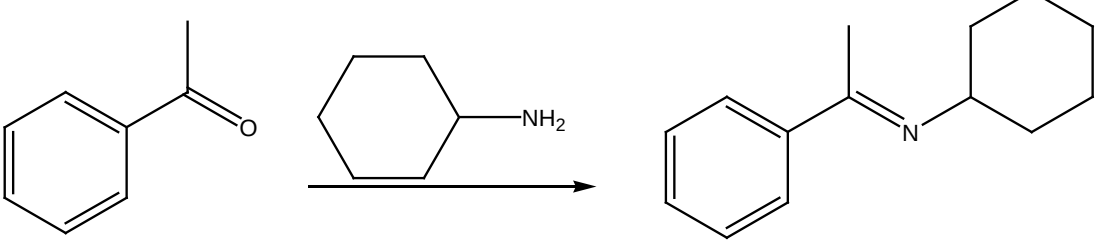
(a) cycloheptanone + ethylamine



(b) cyclopentanone + diethylamine

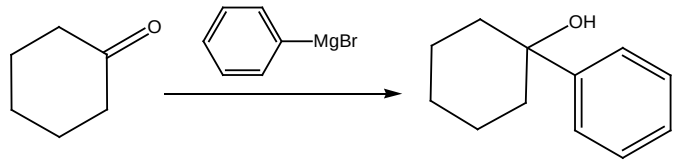


(d) acetophenone + cyclohexylamine

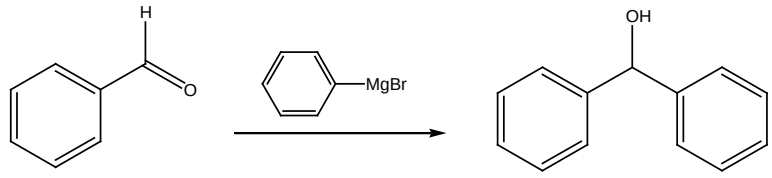


5. Show the product of the reaction of phenylmagnesium bromide with each of the following compound:

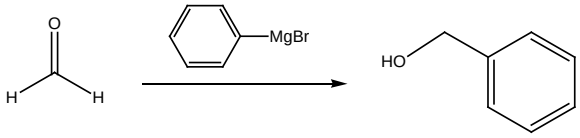
(a) cyclohexanone



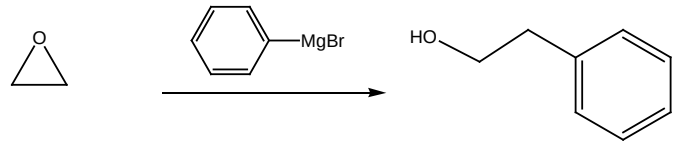
(b) benzaldehyde



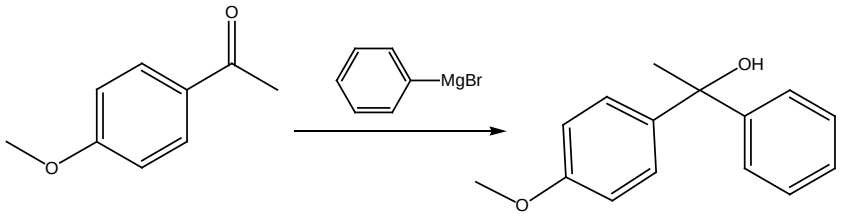
(c) formaldehyde (HCHO)



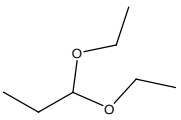
(d) ethylene oxide

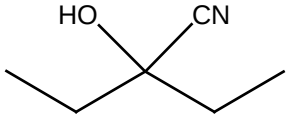


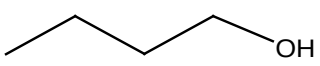
(e) p-methoxyacetophenone



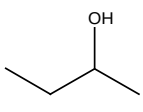
5. Give the products of the following reactions:

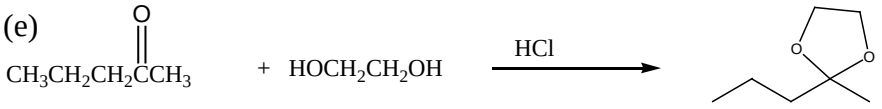
(A) $CH_3CH_2\overset{O}{\overset{\|}{C}}H + CH_3CH_2OH \xrightarrow{HCl}$ 

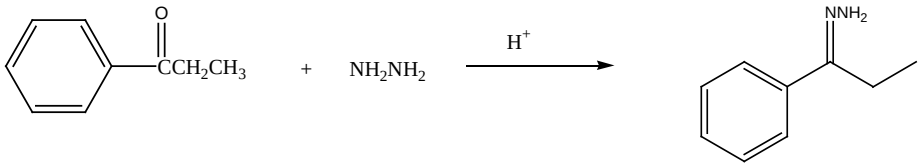
(b) $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3 + NaCN \xrightarrow{HCl}$ 

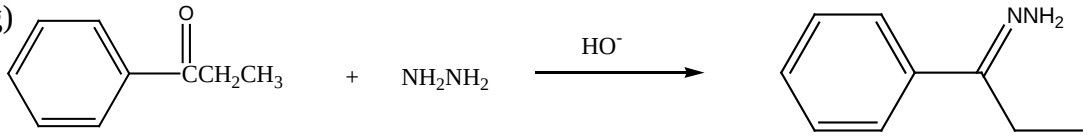
(c) $CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3 \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4}$ 

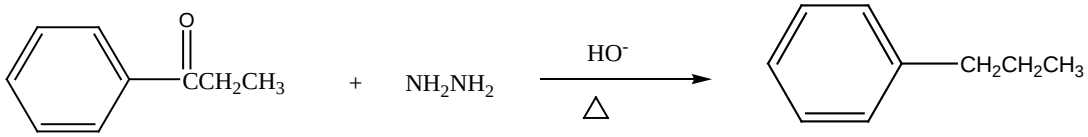
$+ \ CH_3CH_2OH$

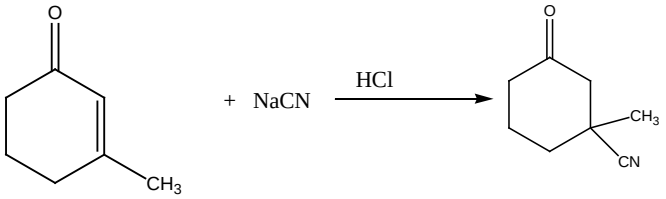
(d) $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[2.\ H_3O^+]{1.\ NaBH_4}$ 

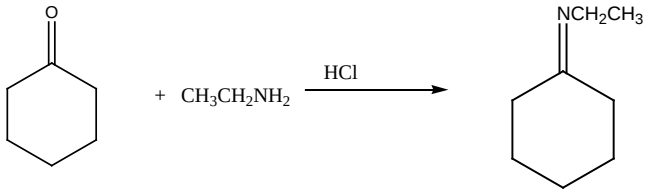
(e) 

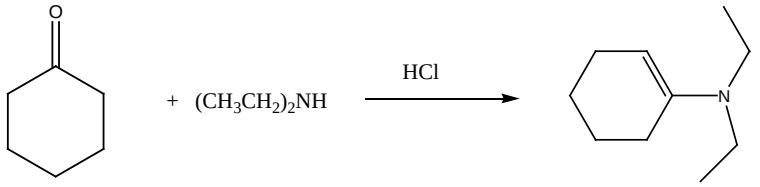
(f) 

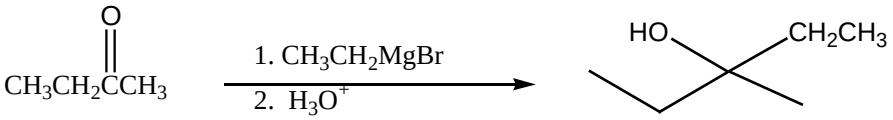
(g) 

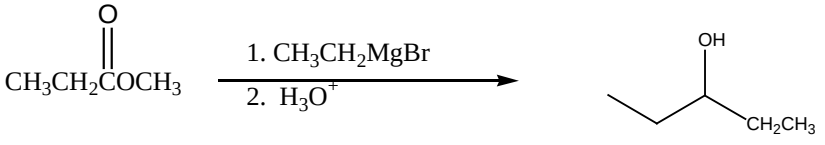


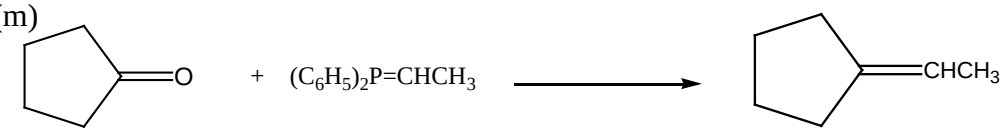
(h) 

(i) 

(j) 

(k) 

(L) 

(m) 

(n) $C_6H_5CH{=}CHCHO + Ph_3P{=}CH_2 \longrightarrow C_6H_5CH{=}CHCH{=}CH_2$

6. Which of the following tertiary alcohols cannot be prepared from the reaction of an ester with excess Grignard reagent?

Ans. (B) (E)

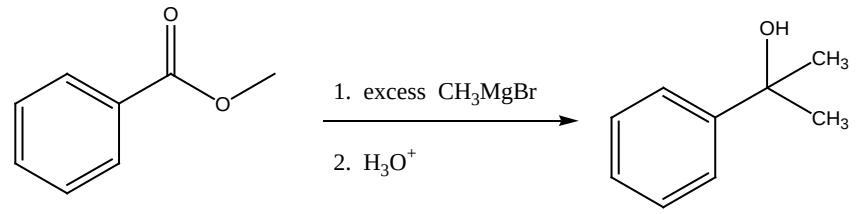
8. How can the following compounds be prepared, starting with a carbonyl compound with one carbon fewer than the desired product?

a. $HCHO \xrightarrow{NaCN} HO{-}CH_2CN \xrightarrow{H_2/Pd} HOCH_2CH_2NH_2$

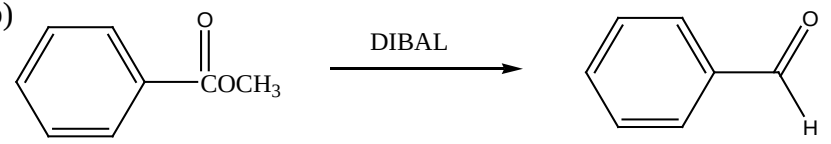
b. $CH_3CHO \xrightarrow{NaCN} CH_3CH(OH)CN \xrightarrow{H_3O^+} CH_3CH(OH)COH$

9. Indicate how the following compounds could be prepared from the given starting materials:

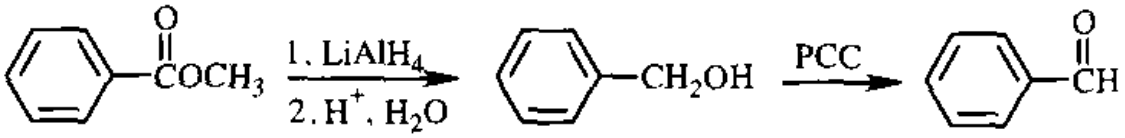
(a)



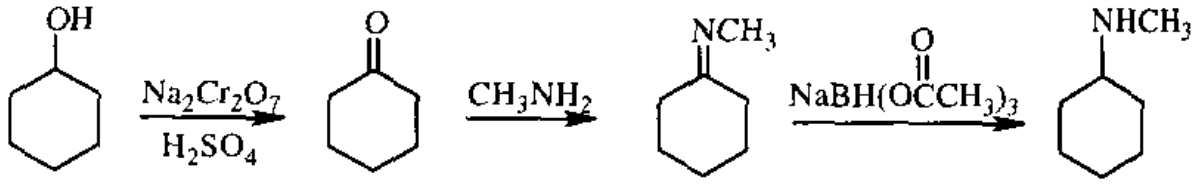
(b)



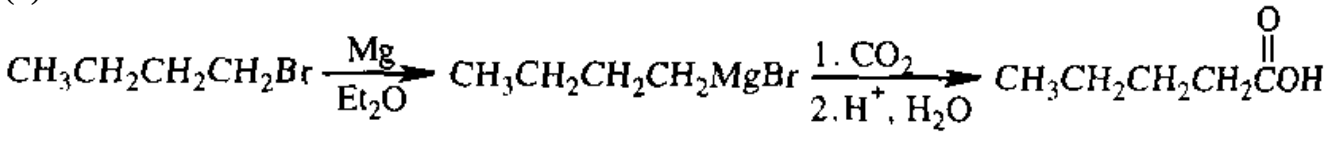
or



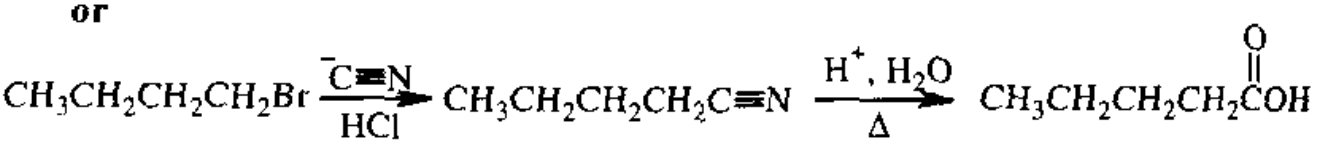
(c)



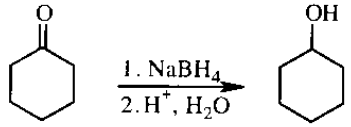
(d)

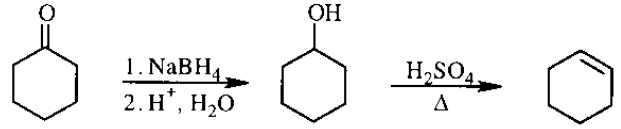


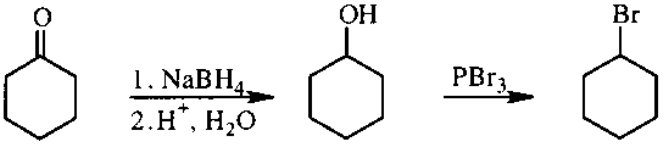
or

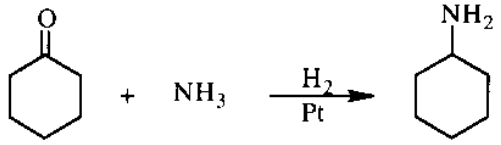


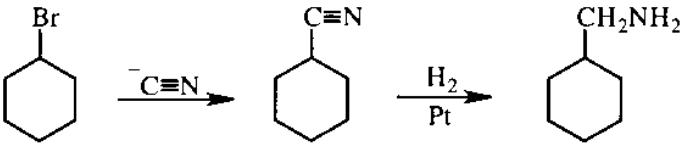
10. Using cyclohexanone as the starting material, describe how wach of the following compounds could be synthesized:

a. 

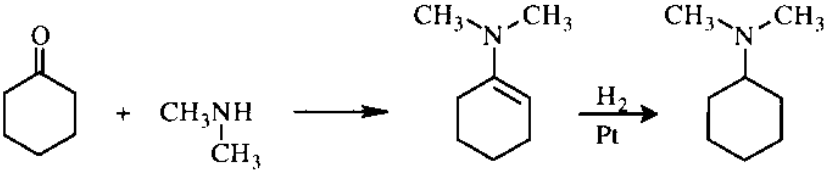
b. 

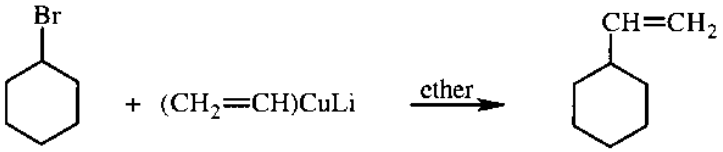
c. 

d. 

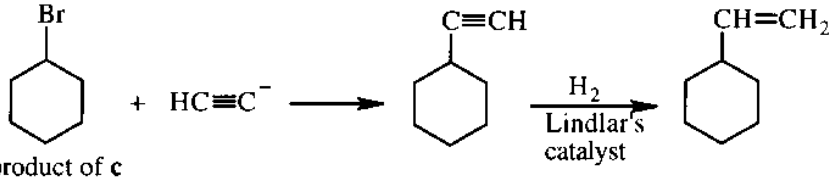
e. 

product of **c**

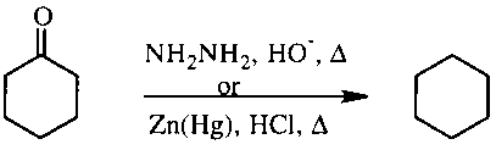
f. 

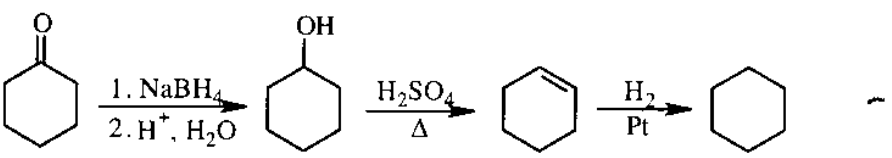
g. 

product of **c**

or 

product of **c**

h. 

or 

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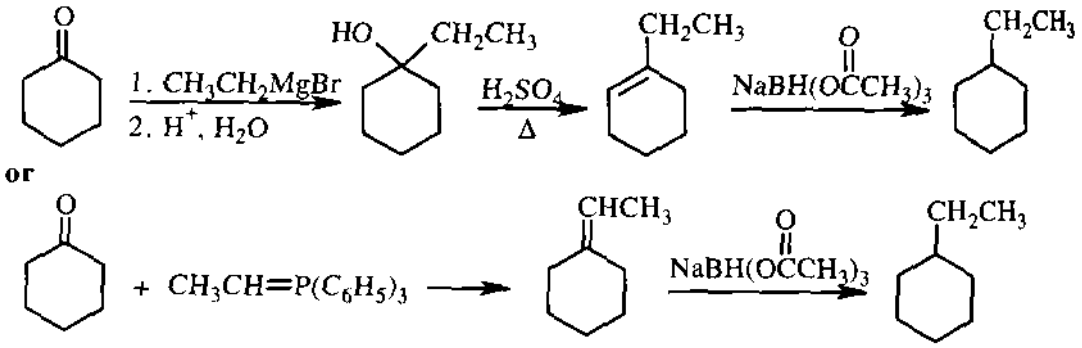
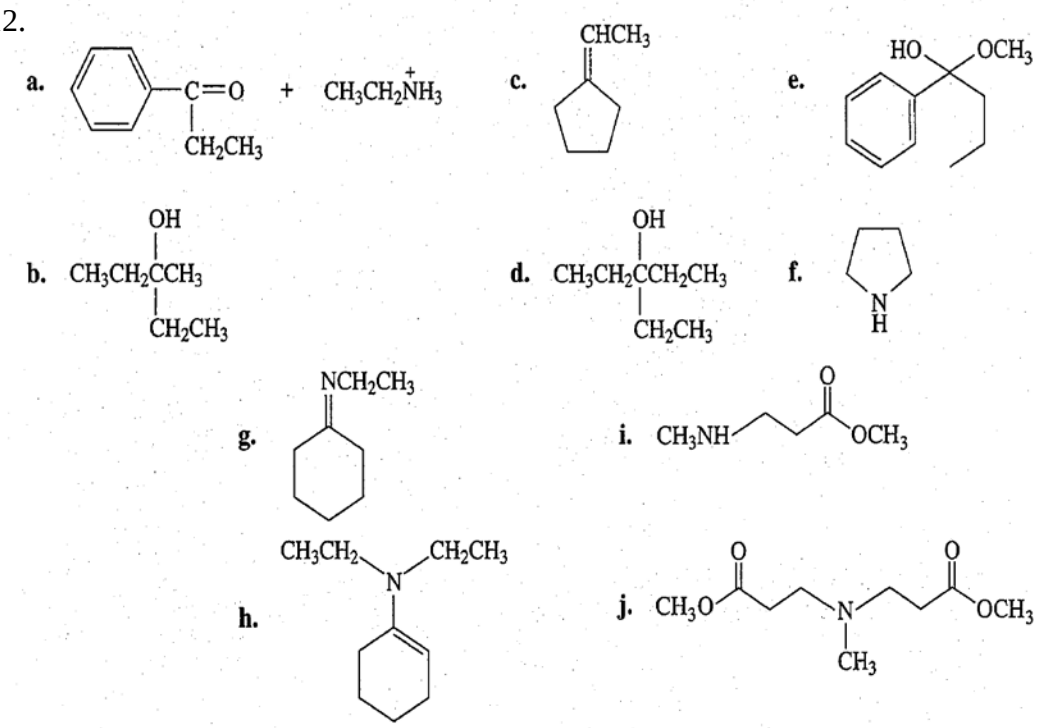


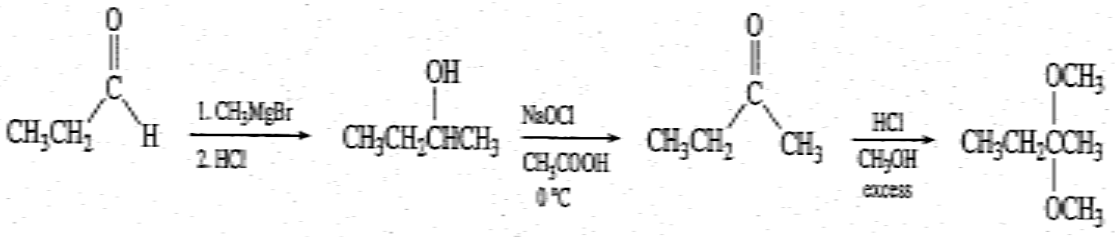
11. Describe a simple chemical test to distinguish phenylacetaldehyde & benzyl alcohol.

2,4-dinitrophyenylhydrazine will react with aldehyde to give a colored product but no reaction with alcohol.

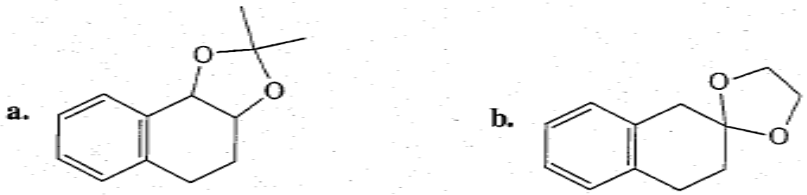
12.



13.



14.



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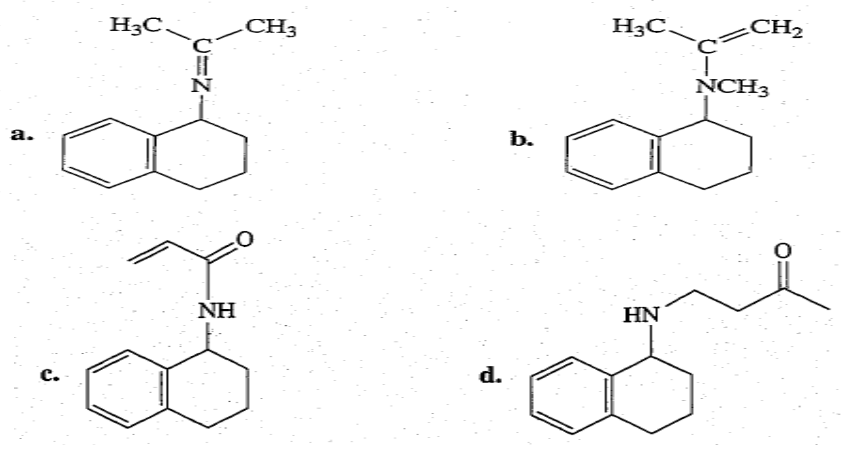
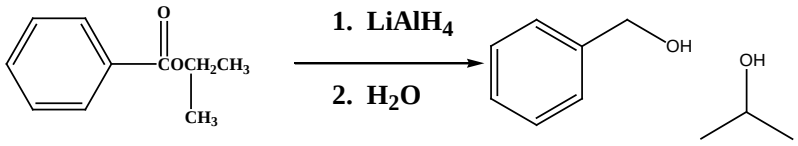


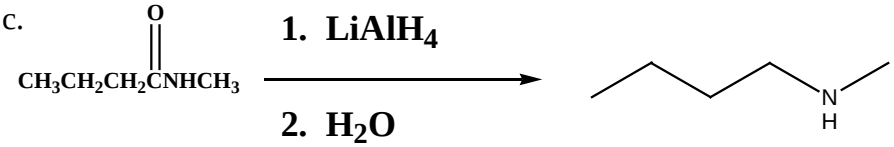
16.

a. $CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[H_2SO_4]{NaCr_2O_7} CH_3CH_2CH_2CH_2CO_2H$

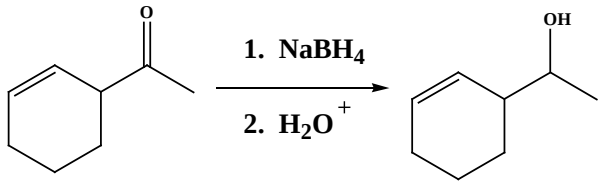
b.



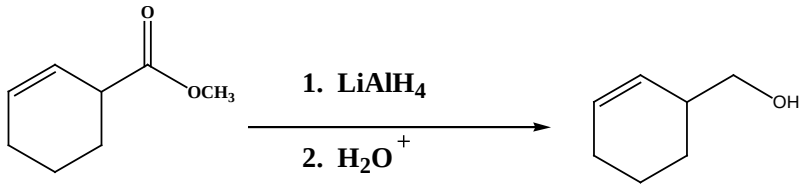
c.



d.



e.



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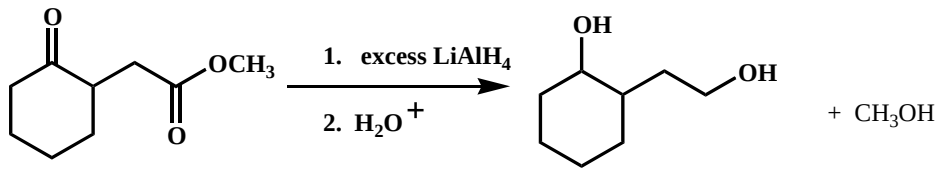
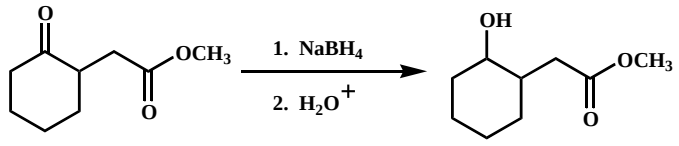
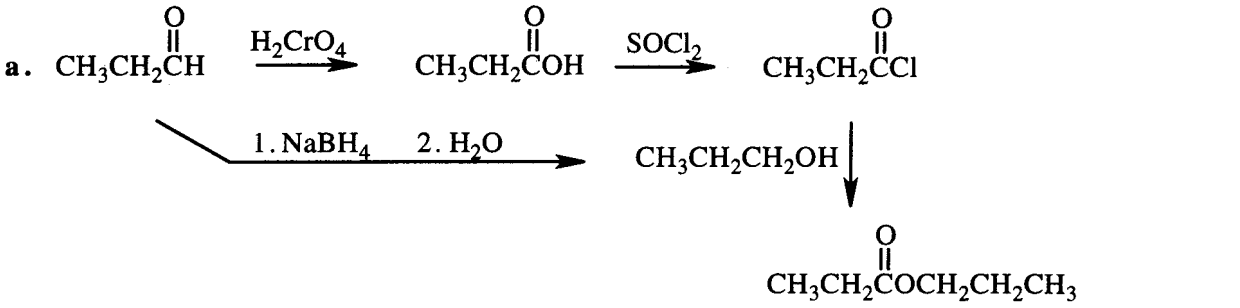
f.

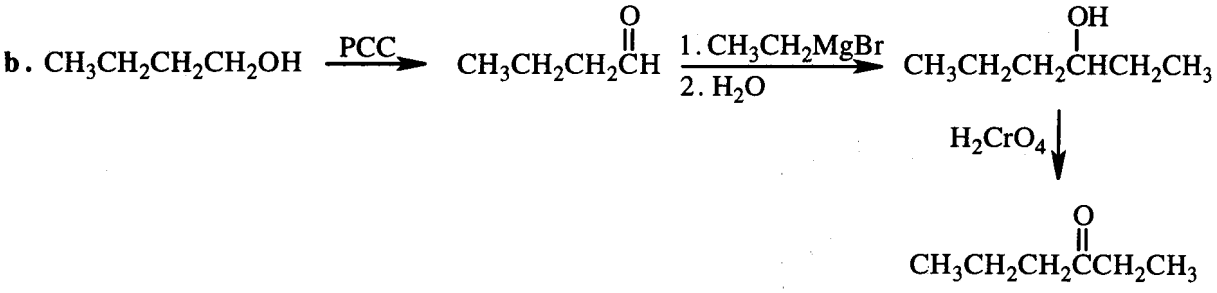


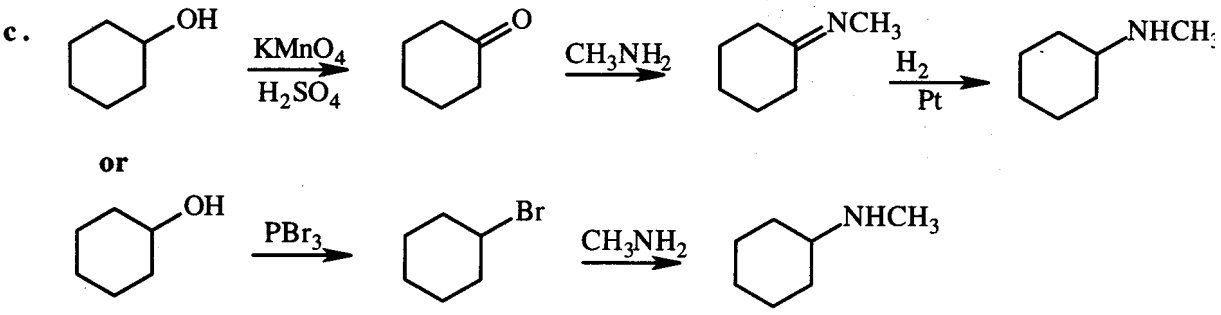
g.

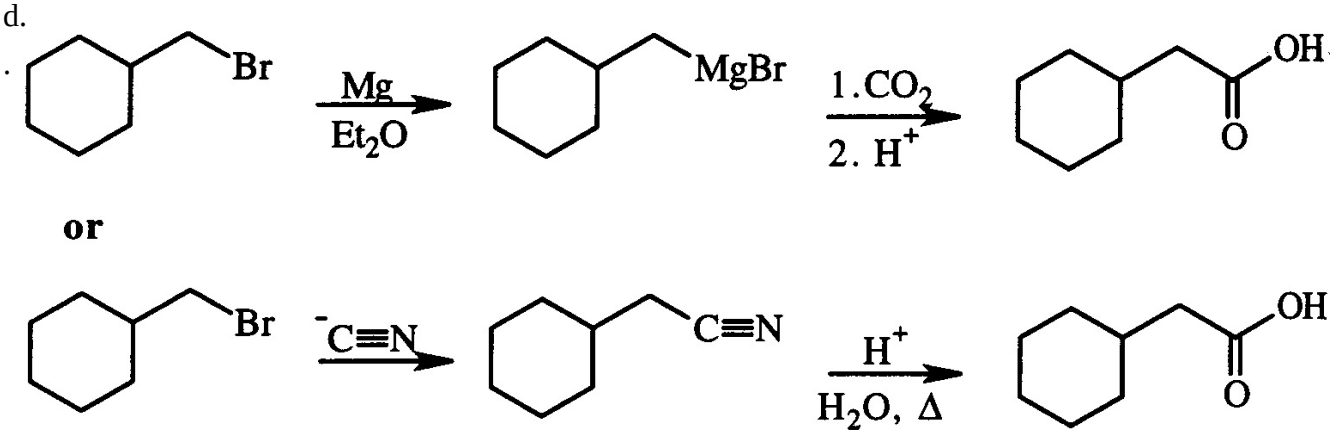


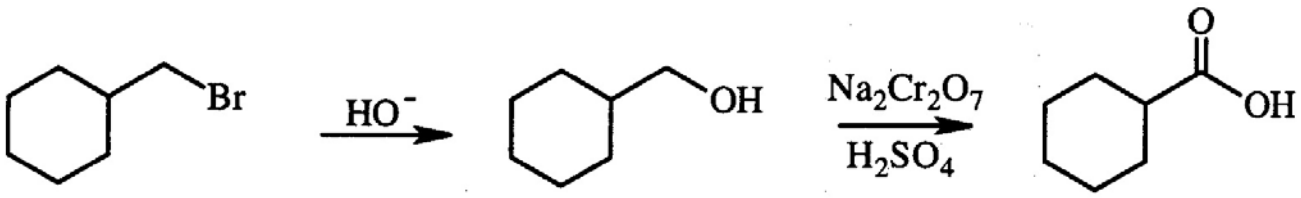
17.

a. 
CH3CH2CH
H2CrO4
CH3CH2COH
SOCl2
CH3CH2CCl
1. NaBH4 2. H2O
CH3CH2CH2OH
CH3CH2COCH2CH2CH3

b. 
CH3CH2CH2CH2OH
PCC
CH3CH2CH2CH
1. CH3CH2MgBr
2. H2O
OH
CH3CH2CH2CHCH2CH3
H2CrO4
CH3CH2CH2CCH2CH3

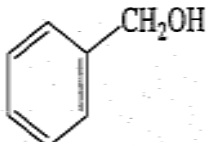
c. 
OH
KMnO4
H2SO4
O
CH3NH2
NCH3
H2
Pt
NHCH3
or
OH
PBr3
Br
CH3NH2
NHCH3

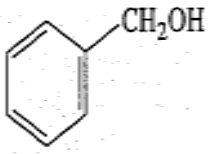
d. 
Br
Mg
Et2O
MgBr
1. CO2
2. H+
OH
O
or
Br
-C≡N
C≡N
H+
H2O, Δ
OH
O

e. 
Br
HO-
OH
Na2Cr2O7
H2SO4
O
OH

18.

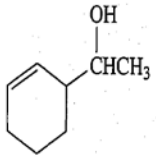
a. $CH_3CH_2CH_2CH_2OH$ + CH_3CH_2OH

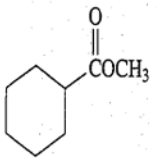
b. 

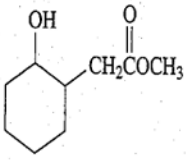
c.  + CH_3OH

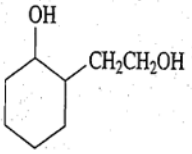
d. $CH_3CH_2CH_2CH_2CH_2OH$

19.

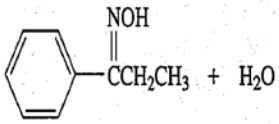
a. 

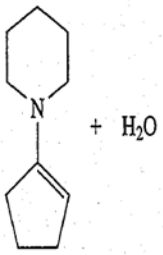
b. 

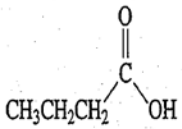
c. 

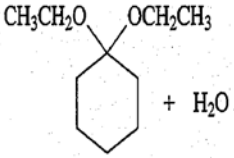
d.  + CH_3OH

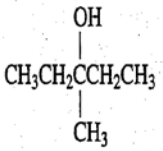
20.

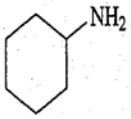
a. 

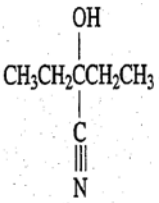
b. 

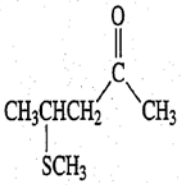
c. 

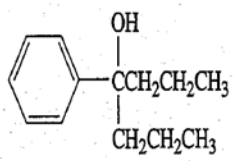
d. 

e. 

f. 

g. 

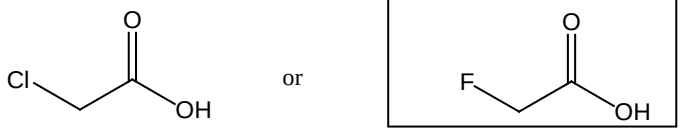
h. 

i. 

Ch 15 Carbonyl (III) Answers

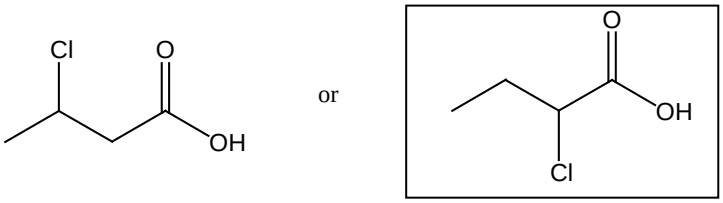
1. Predict which compound in each of the following pairs is more acidic. Give reasons for your choice.

(A)



electronegativity of F > Cl, can stabilize extra electrons

(B)

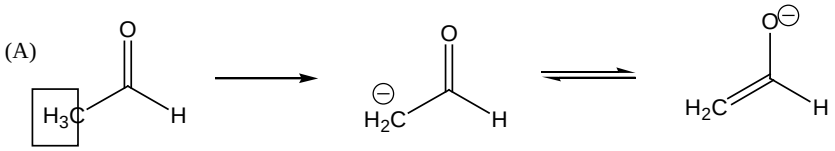


The position of Cl is closer to the carboxylate

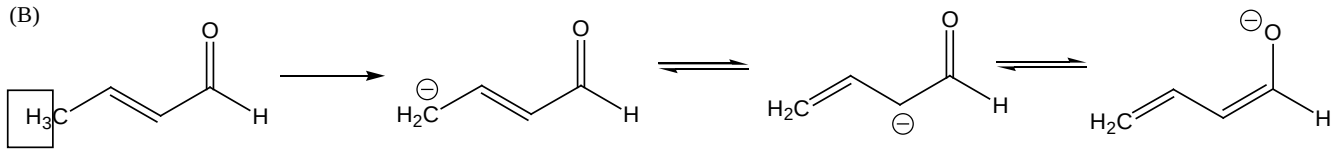
(C) F_3CCOOH is carboxylic acid

2. Identify the most acidic hydrogen atom in the following molecules. draw the significant resonance contributors for the enolate anion generated by deprotonation of each molecule.

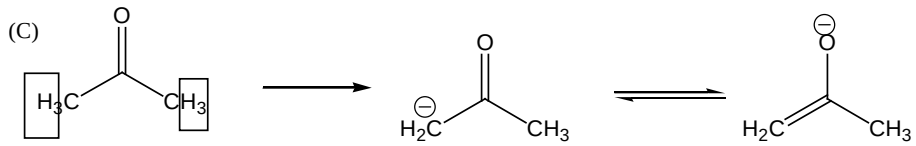
(A)



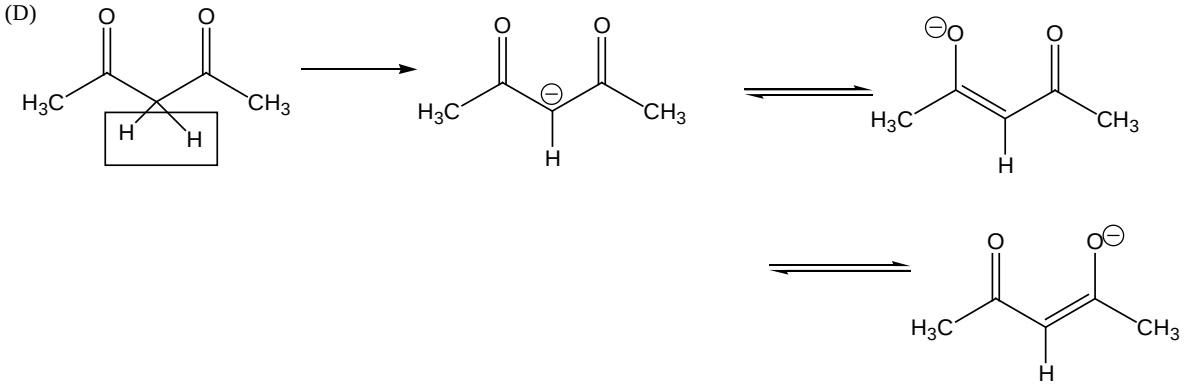
(B)



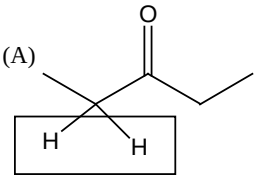
(C)

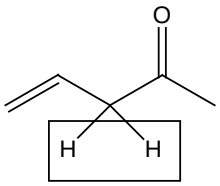


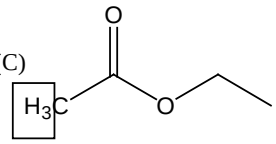
(D)

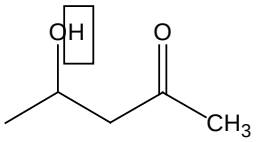


3. Predict which hydrogen is most acidic in each of the following compounds:

(A) 

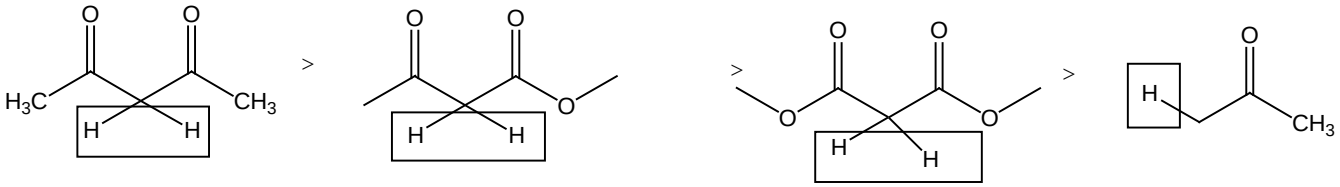
(B) 

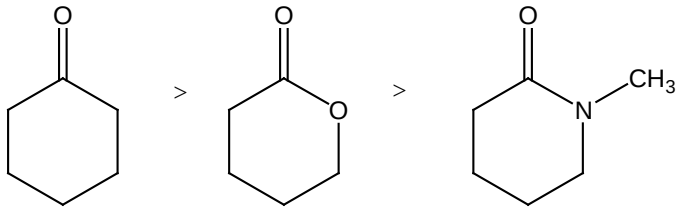
(C) 

(D) 

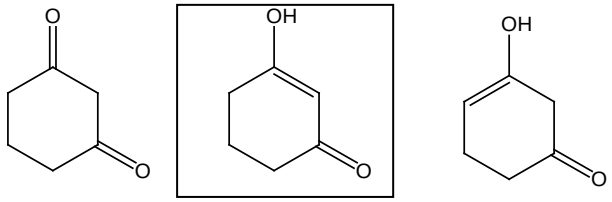
4. List the compounds in each of the following groups in order of decreasing acidity:

(A) $HC\equiv CH$ > $H_2C=CH_2$ > CH_3CH_3

(B) 

(C) 

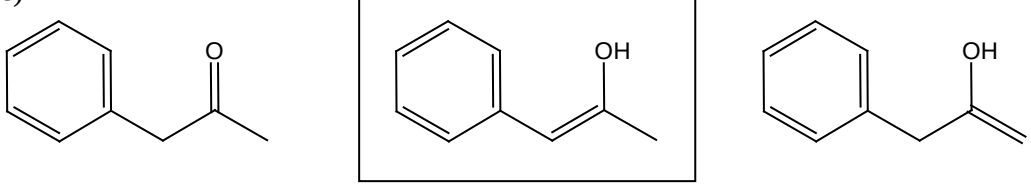
5. Drew the enol tautomers for each of the following compounds. For those compounds that have more than one enol tautomer, indicate which is more stable.

a) 

more stable because the double bonds are conjugated

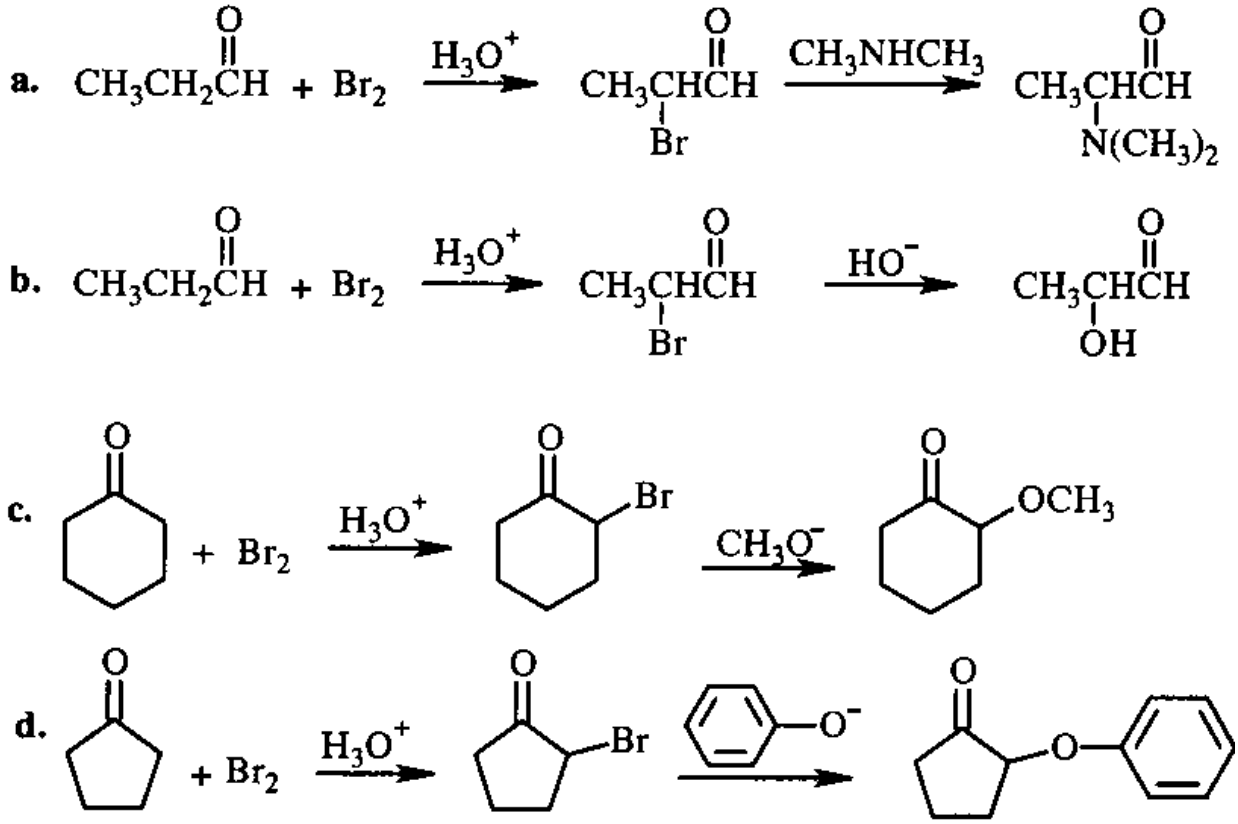
b) 

only one tautomer

c) 

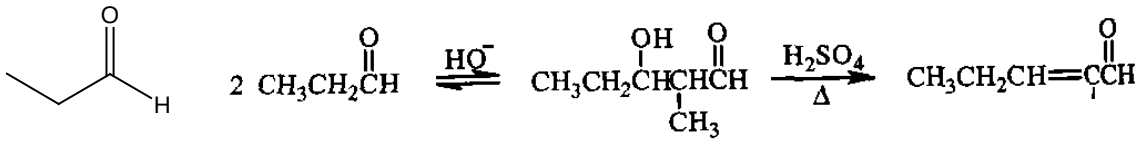
more stable because the double bond is conjugated with benzene

6. How would you prepare the following compounds from the given starting materials?

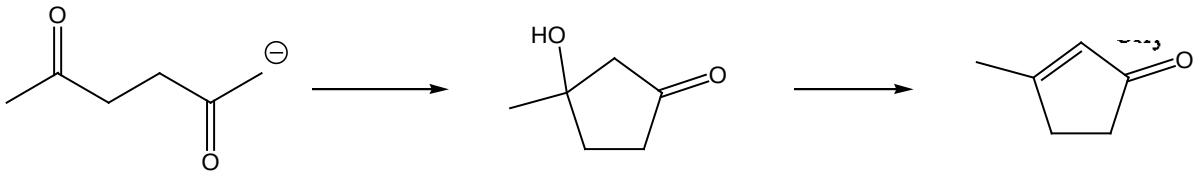


7. Draw the structural formula for the product of the aldol reaction of each compound followed by dehydration.

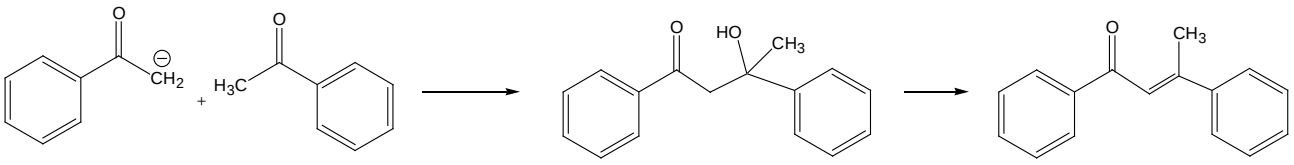
a)



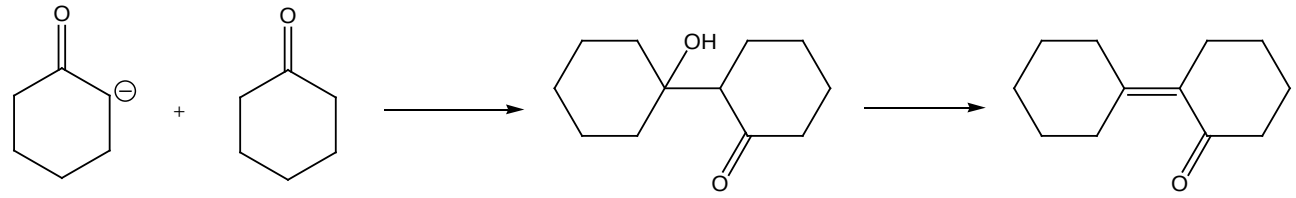
b)



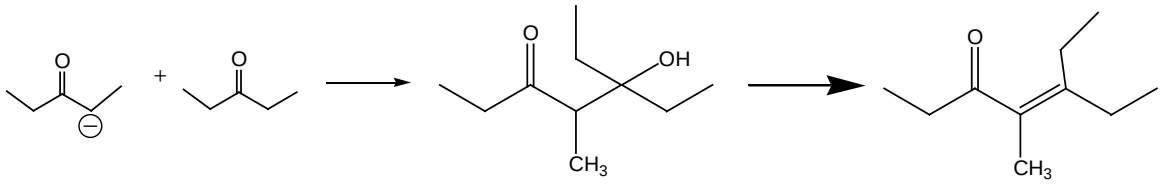
c)



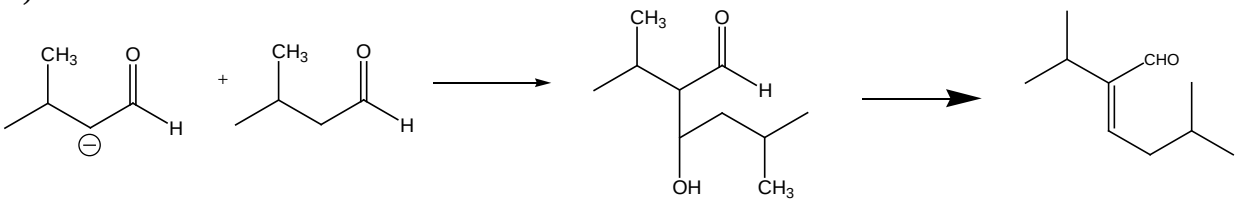
d)



e)

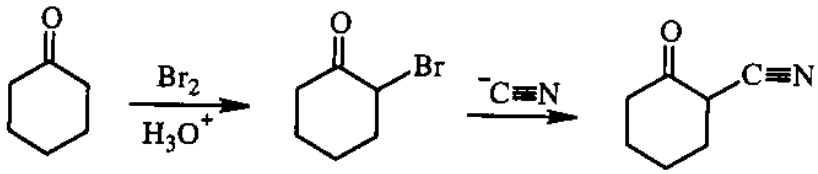


f)

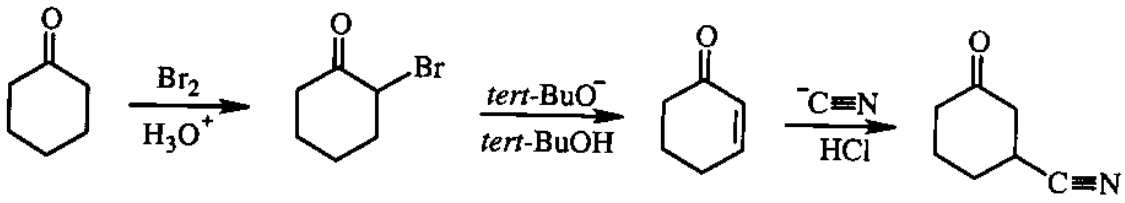


8. How could the following compounds be prepared from cyclohexanone?

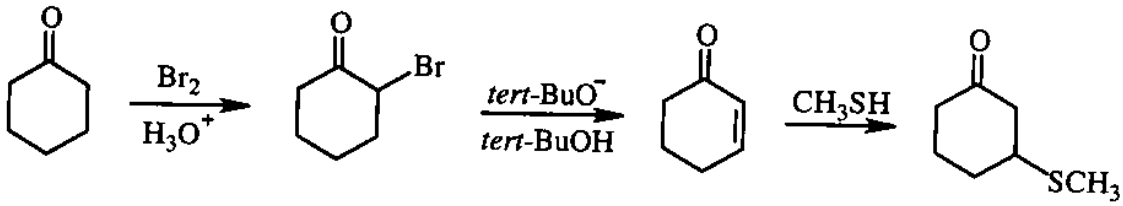
a.



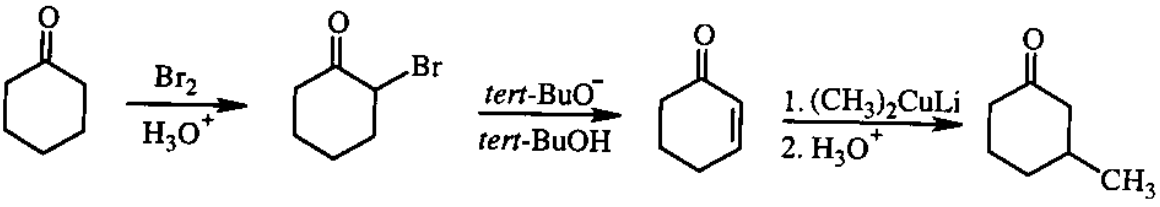
b.



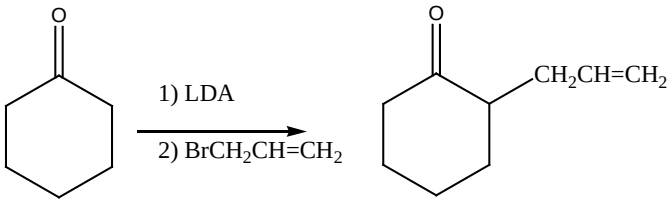
c.



d.

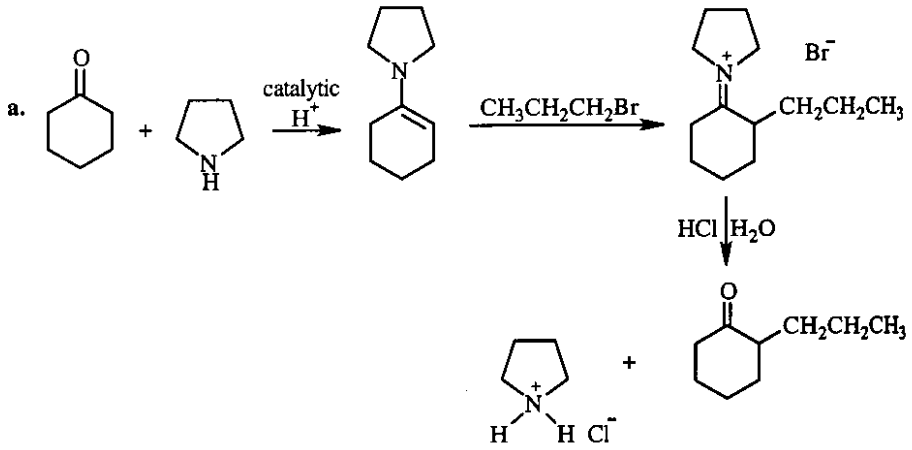


e.

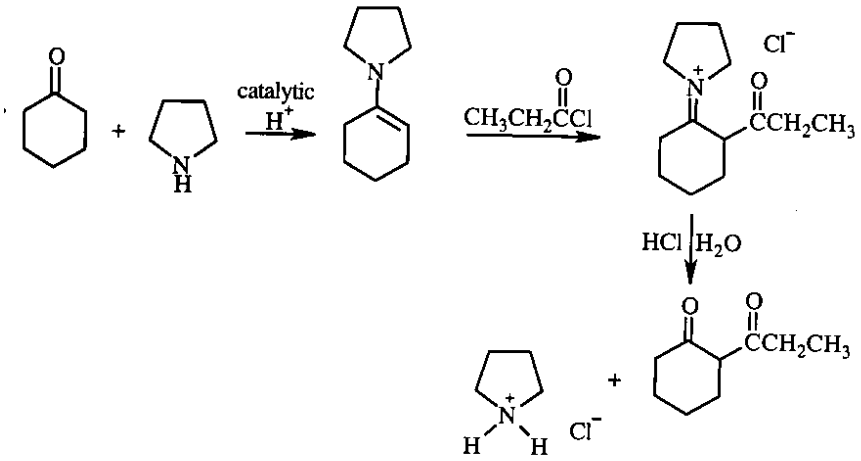


9. Describe how would the following compounds could be prepared using an enamine intermediate?

a)

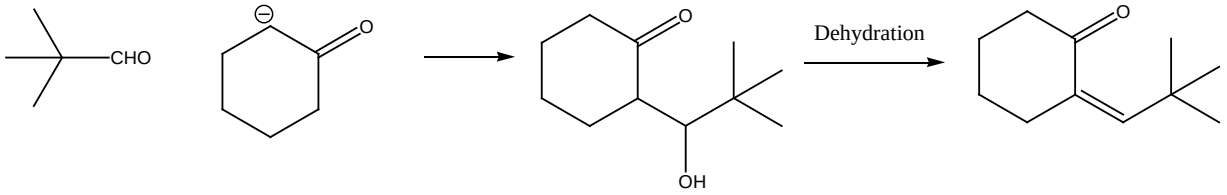


b)

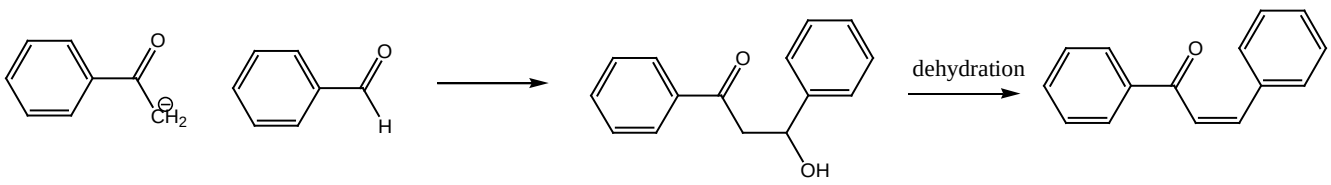


10. Draw the structural formula for the product of each crossed aldol reaction followed by its dehydration.

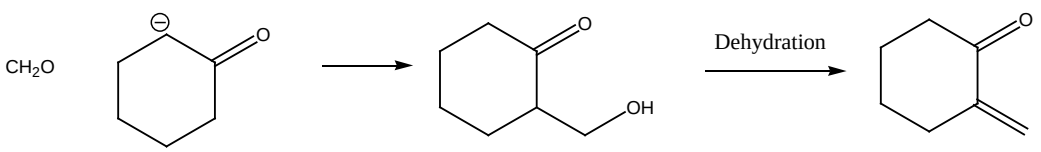
(a)



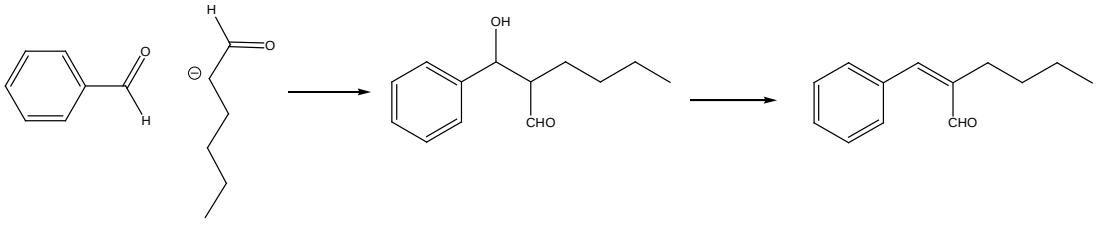
(b)



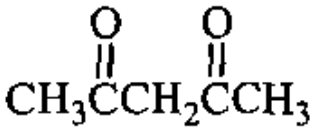
©



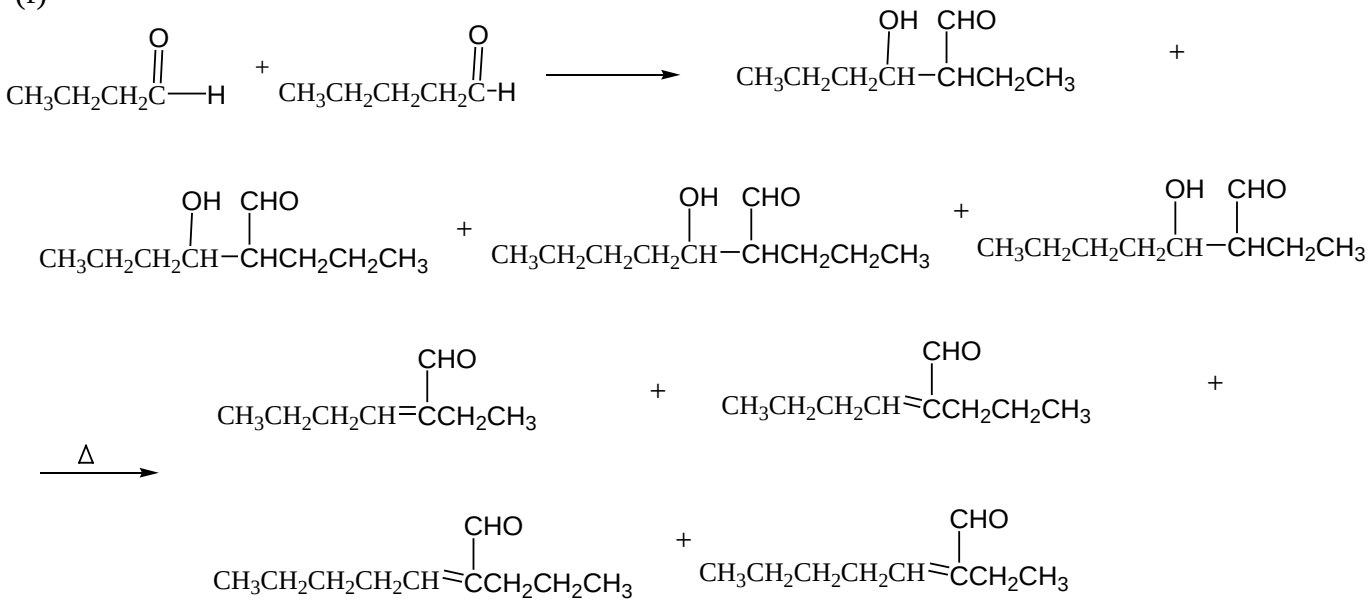
(d)



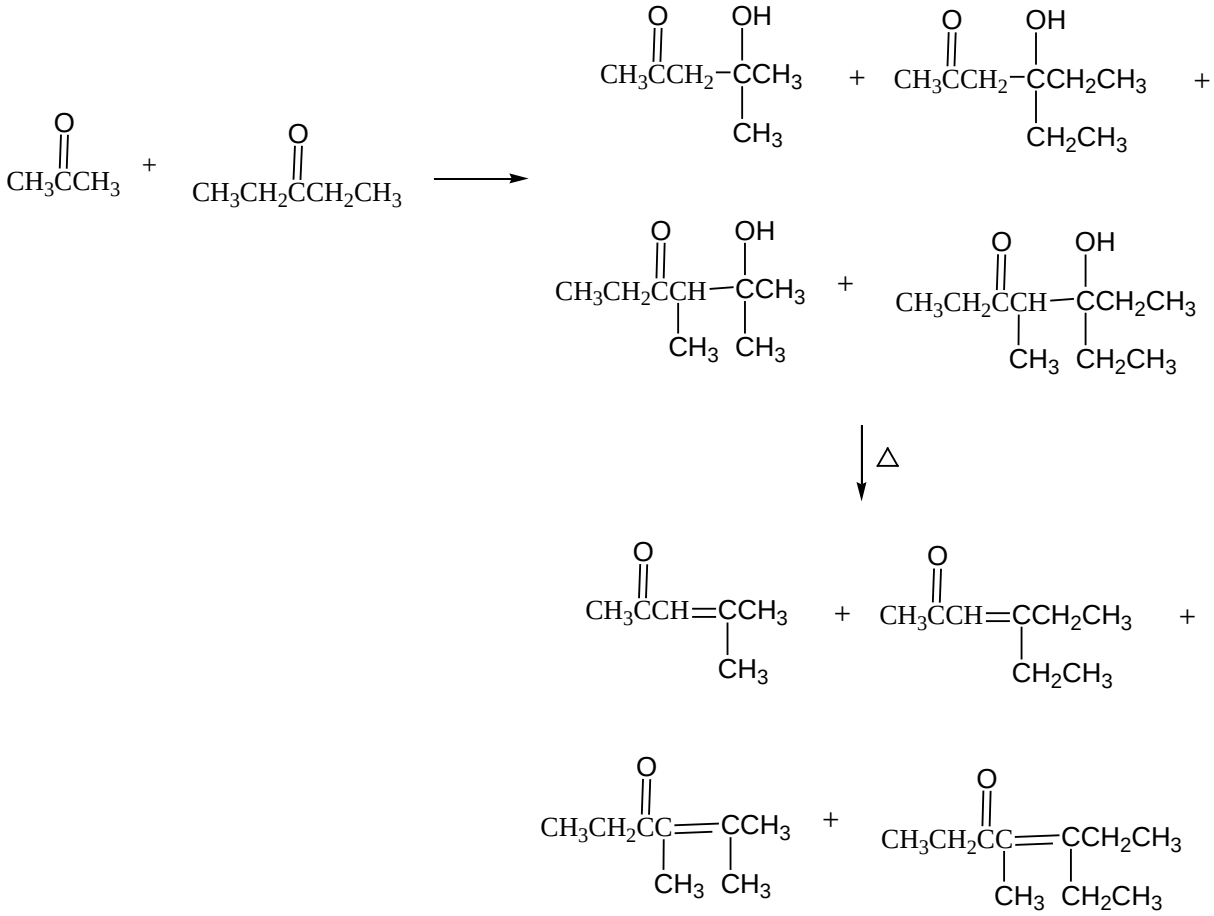
(e)



(f)

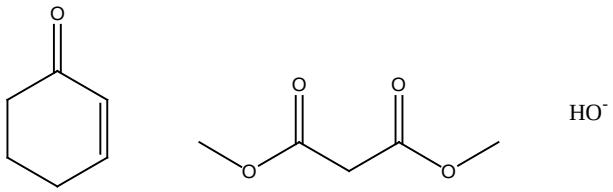


(g)

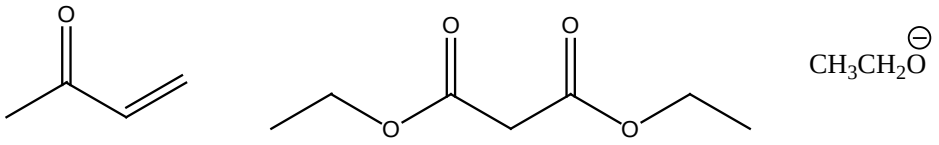


11. How would you prepare the following compounds?

a)

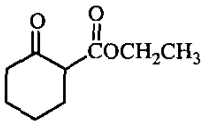


b)

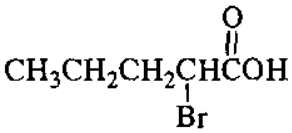


12. Give the products of the following reactions:

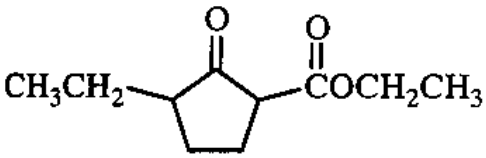
(a)



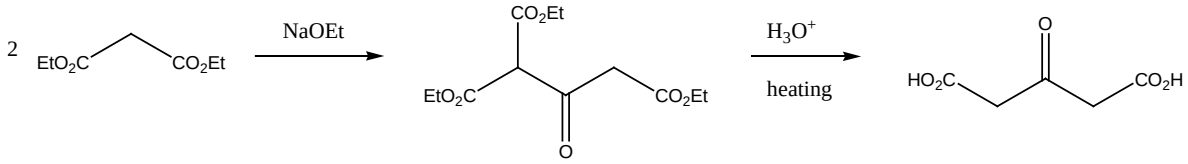
(B)



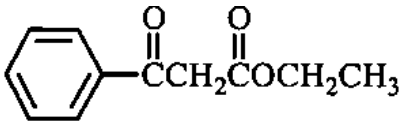
(C)



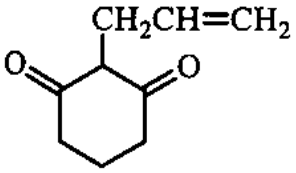
(D)



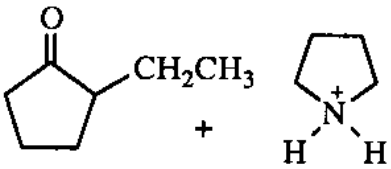
(E)



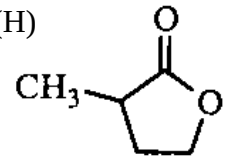
(F)



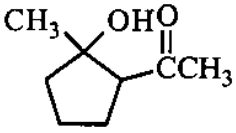
(G)



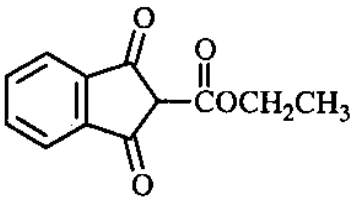
(H)



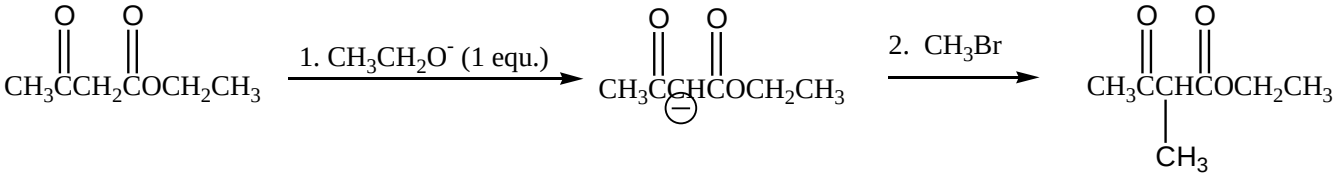
(I)



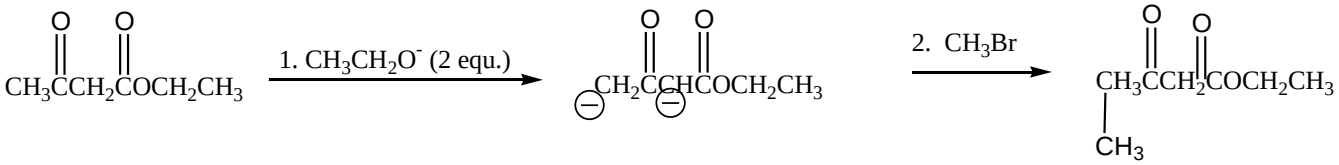
(J)



(k)

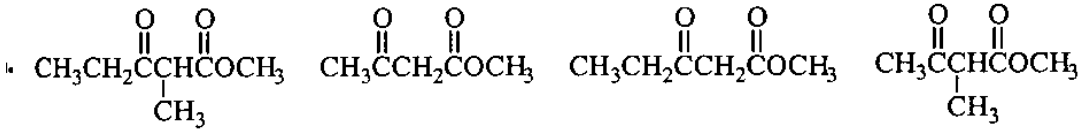


(L)

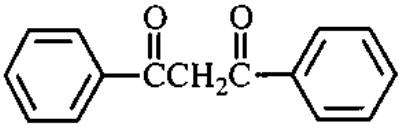


13. Give the product of each of the following reactions:

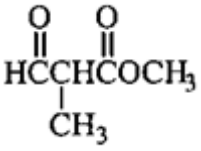
(A)



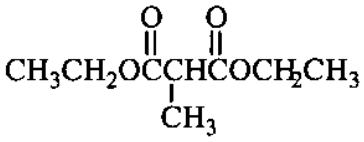
(B)



(C)

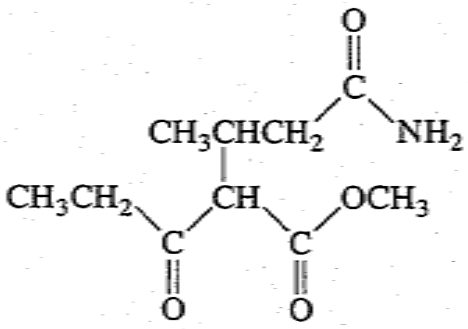


(D)

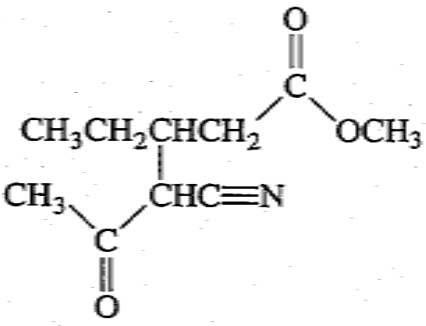


14.

a.

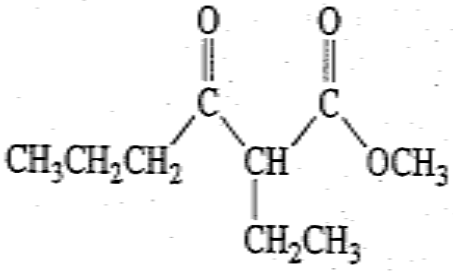


b.

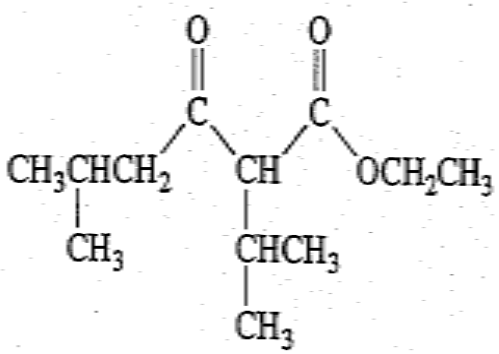


15.

a.

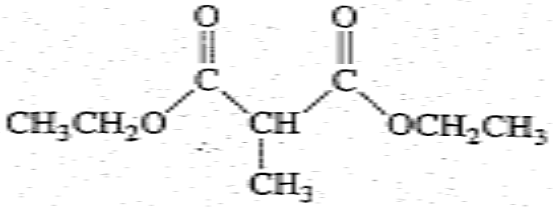


b.

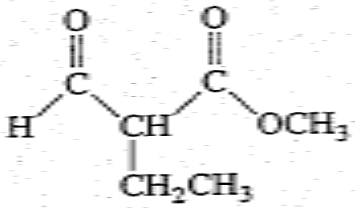


16.

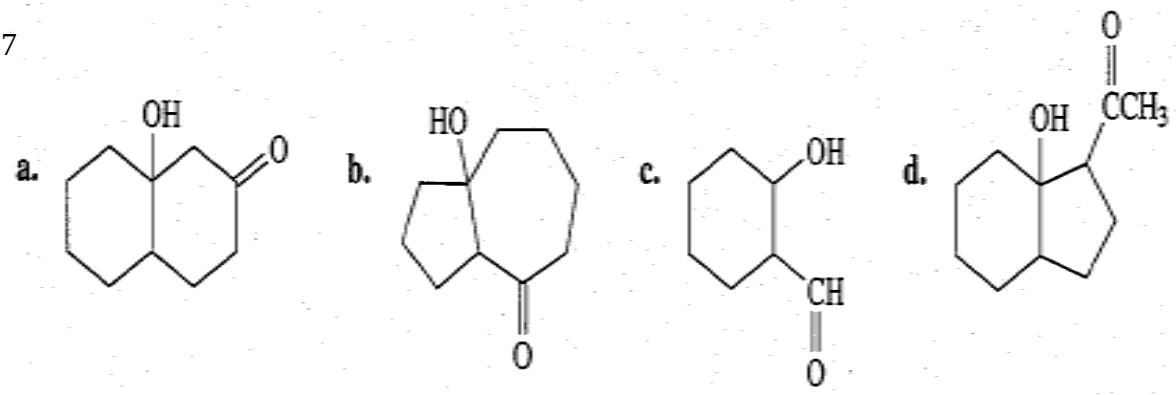
a.



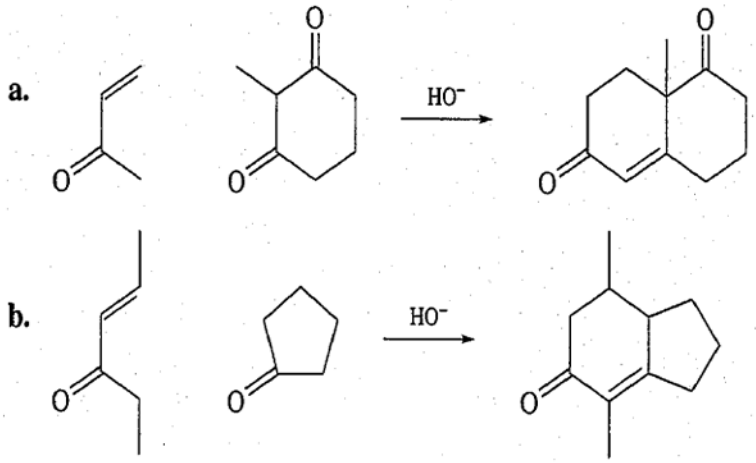
b.



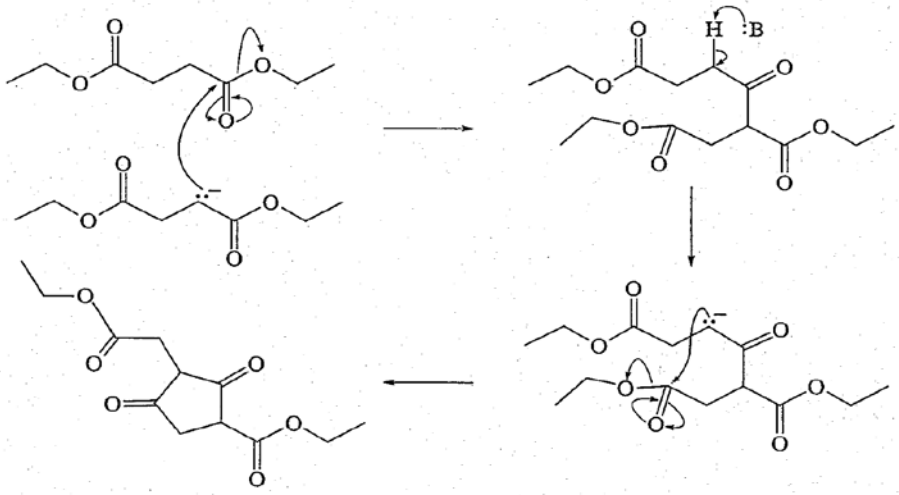
17



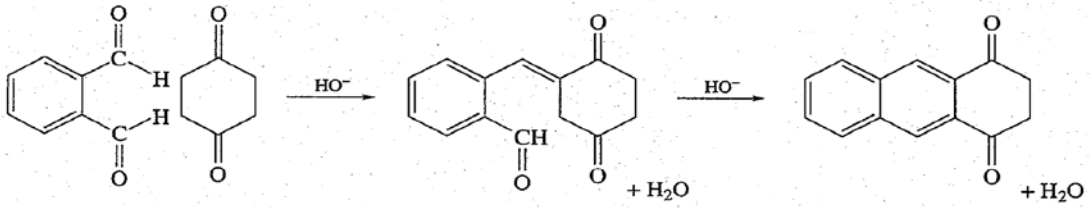
18.



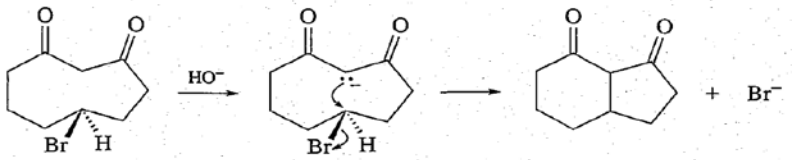
19 **a.** The first reaction is an intermolecular Claisen condensation. An intramolecular condensation reaction forms the final product.



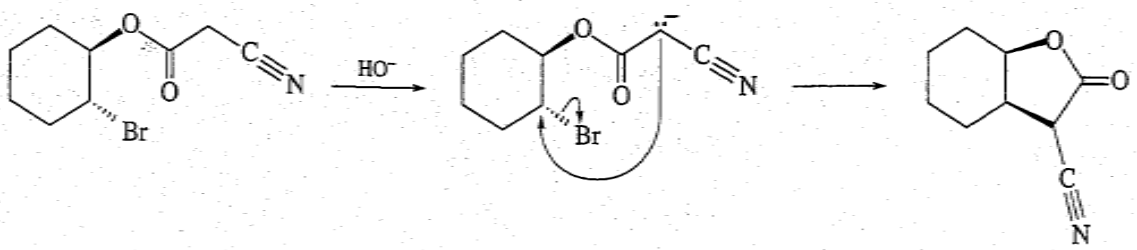
b. The reaction involves two successive aldol condensations.



c. The base removes a proton from the carbon that is flanked by two carbonyl groups; this is followed by an intramolecular S_N2 reaction.



d. A proton is removed from the α-carbon that is flanked by a carbonyl group and a nitrile; then an intramolecular S_N2 reaction occurs.



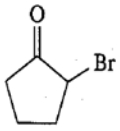
19.

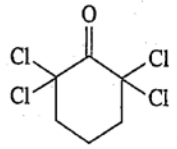
a. $CH_3CH_2C(=O)CH_3 + CO_2$

b. $CH_3CH_2C(Br)(Br)C(=O)H + 2\,Br^-$

c. $CH_3CH_2CH_2CH(CH_2CH_3)C(=O)OCH_3$

d. $CH_3C(=O)CH(CH_2CH_2CH_3)C(=O)CH_3$

e. 

f. 

g. $CH_3CH_2CH_2CH_2C(=O)OH$

Ch 16 Amine Answers

1. Water and diethyl ether are immisible 不互溶 liquids. Charged compounds dissolve in water and uncharged compounds dissolve in ether. $C_6H_{11}COOH$ has a pKa of 4.8 and $C_6H_{11}NH_3^+$ has a pKa of 10.7.

(A) What pH would you make the water layer to cause both compounds to dissolve in water layer?

(B) What pH would you make the water layer to cause $C_6H_{11}COOH$ to dissolve in water layer and the amine to dissolve in the ether layer?

(C) What pH would you make the water layer to cause amine to dissolve in water layer and the acid to dissolve in the ether layer?

Ans.

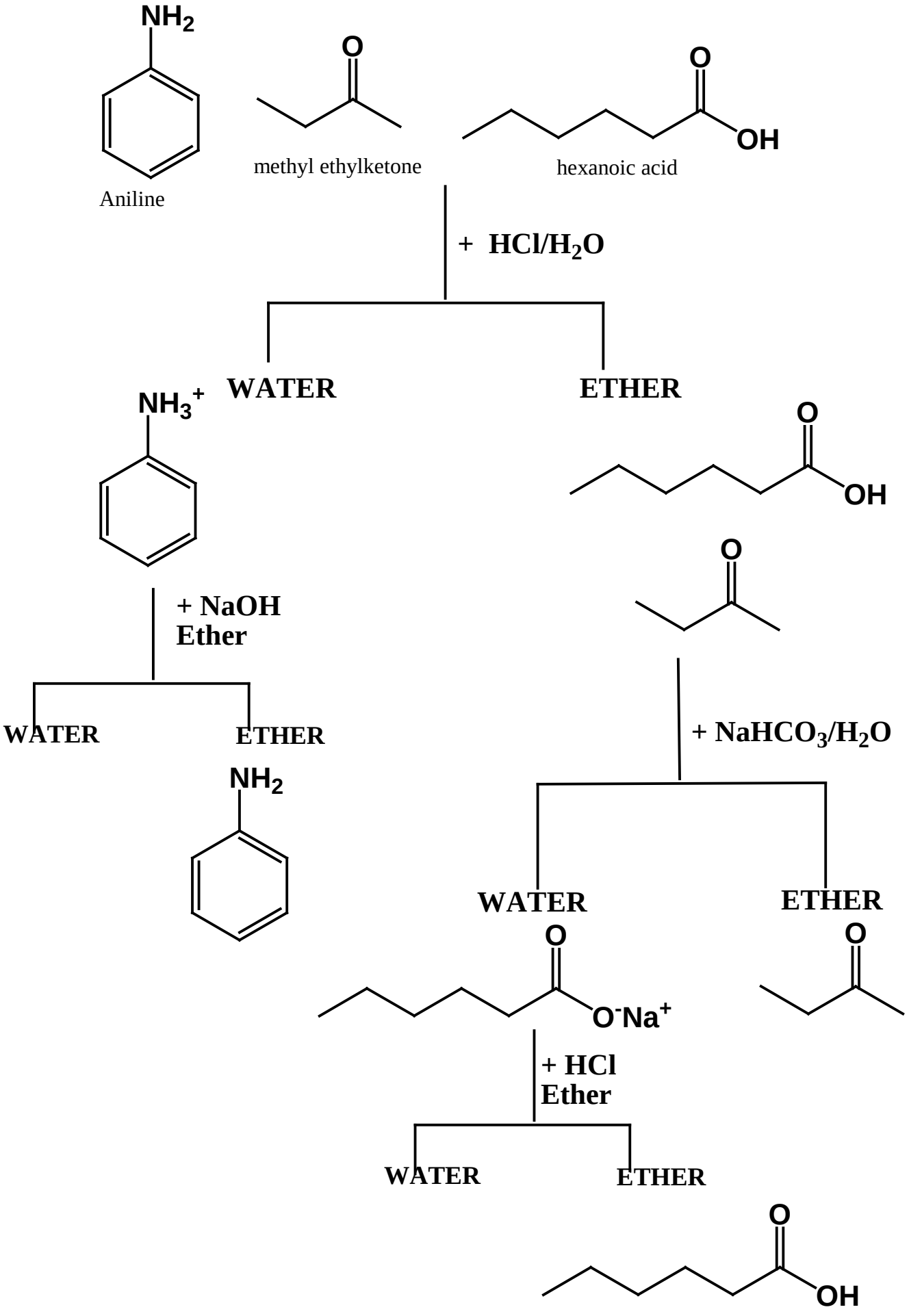
From the Henderson-Hasselbalch equation it can be calculated that in order to obtain a 100: 1 ratio of acidic form:basic form, the pH must be two pH units lower than the pKa of the compound; and in order to obtain a 1 00: 1 ratio of basic form: acidic form, the pH must be two pH units greater than the pKa of the compound.

a. If both compounds are to dissolve in water, they both must be charged. Therefore, the carboxylic acid must be in its basic form, and the aniine must be in its acidic form. To accomplish this, the pH will have to be at least two pH units greater than the pKa of the carboxylic acid and at least two pH units less than the pKa of the ammonium ion. In other words, it must be between pH 6.8 and pH 8.7.

b. For the carboxylic acid to dissolve in water, it must be charged (in its basic form), so the pH will have to be greater than 6.8. For the amine to dissolve in ether, it will have to be neutral (in its basic form), so the pH will have to be greater than 12.7 to have essentially all of it in the neutral fortn. Therefore, the pH of the water layer must be greater than 12.7.

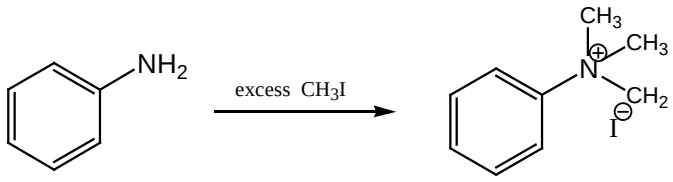
c. To dissolve in ether, the carboxylic acid will have to be neutral, so the pH will have to be less than 2.8 to have essentially all the carboxylic acid in the acidic (neutral) form. To dissolve in water, the amine will have to be charged, so the pH will have to be less than 8.7 to have essentially all the amine in the acidic form. Therefore, the pH of the water layer must be less than 2.8.

2. 請設計一個以不同酸鹼水溶液與有機溶液分配(partition) 方法，於乙醚溶液中含 3 種化合物 (Aniline, methyl ethylketone, hexanoic acid) 之混合物分離。

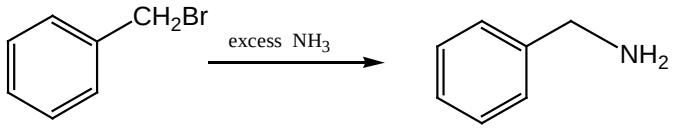


3. Show the product of each of the following reactions:

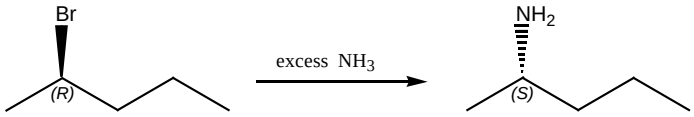
(a) aniline with excess methyl iodide



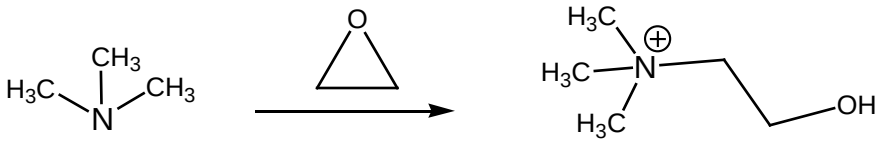
(b) benzyl bromide with excess ammonia



(c) (R)-2-bromopentane with excess ammonia

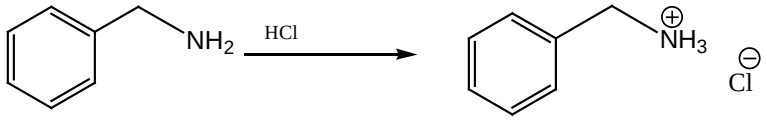


(d) trimethylamine with ethylene oxide

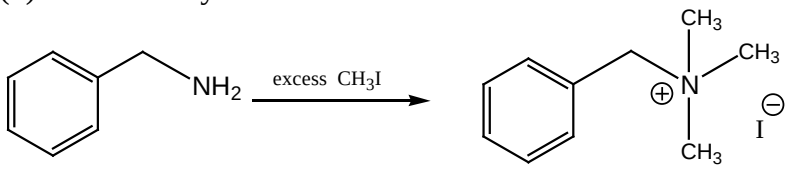


4. Show the product expected from the reaction of benzylamine with each of the following reagents:

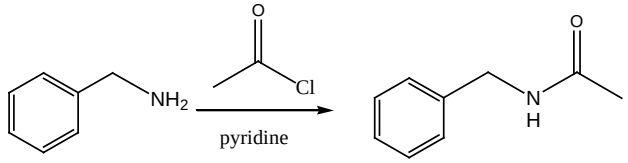
(a) hydrogen chloride



(b) excess methyl iodide

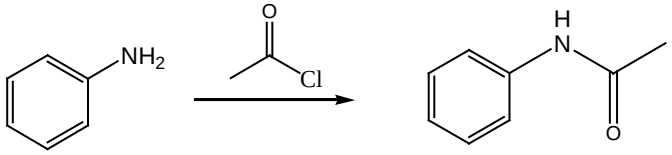


(C) acetyl chloride and pyridine

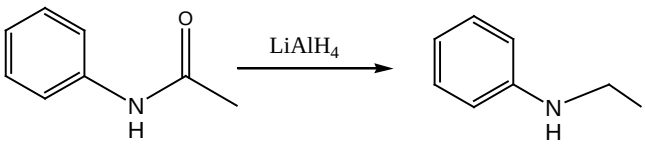


5. Show the product of each of the following reactions:

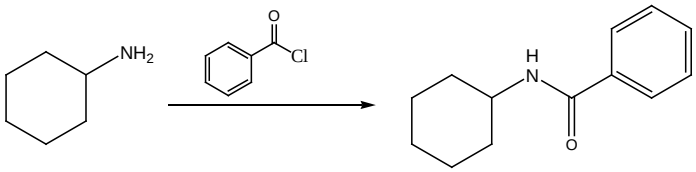
(a) aniline with acetyl chloride and dilute NaOH



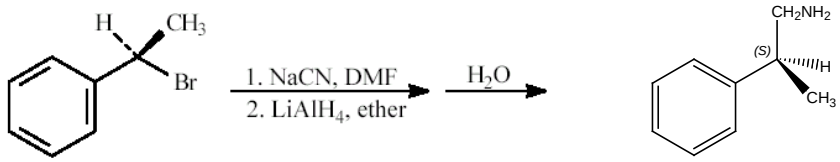
(b) the product of part (a) with LiAIH4



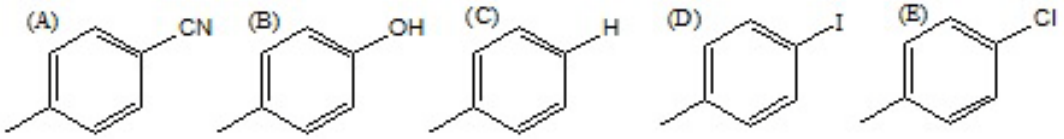
(c) cyclohexylamine with benzoyl chloride (C6H5COCl) and pyridine

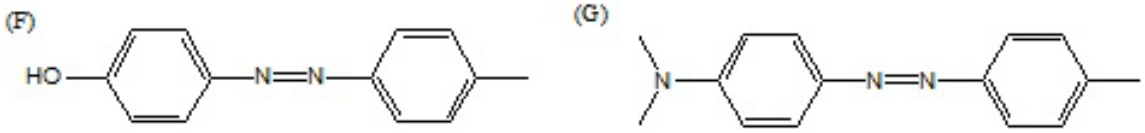


(D)



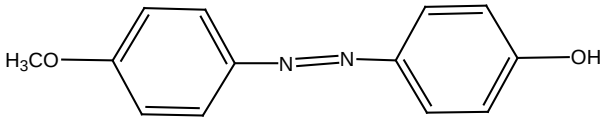
6. Show the products of the reaction of the diazonium salt prepared from p-toluidine (p-methylaniline) with each of the following reagents:



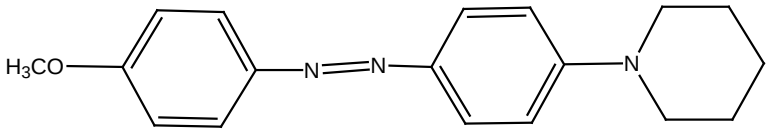


7. Show the product of the reaction of p-methoxyaniline first with sodium nitrite and hydrochloric acid and then with each of the following compounds:

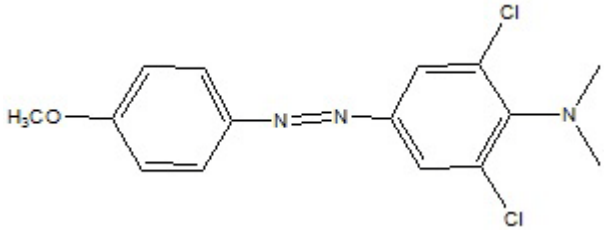
(A) phenol



(b) N-phenylpiperidine



(c) 2,6-dichloro-N,N-dimethylaniline



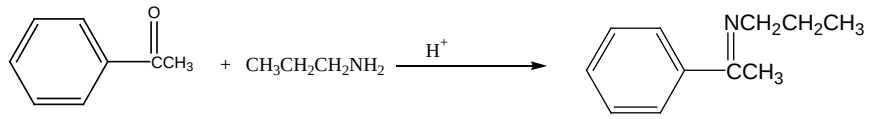
What alkyl bromide would you use in a Garbiel synthesis to prepare each of the following amines?

(a) pentylamine (b) benzylamine (c) isohexylamine (d) cyclohexylamine

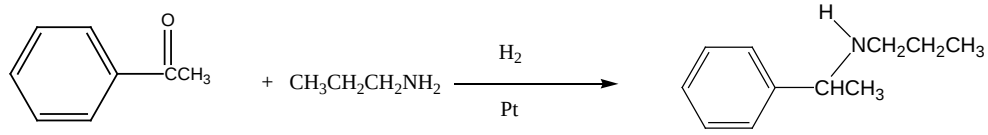
Ans. (a) pentyl bromide (b) benzyl bromide (c) Isohexyl bromide (d) cyclohexyl bromide

8. Show the product of each of the following reactions:

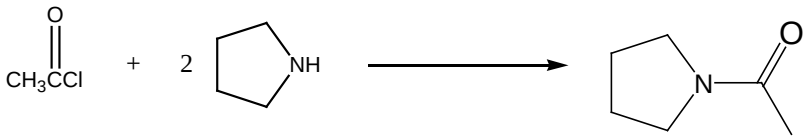
(a)



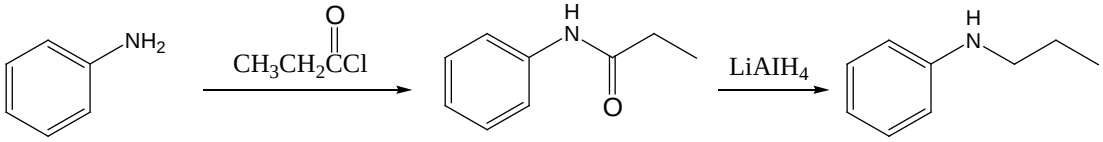
(b)



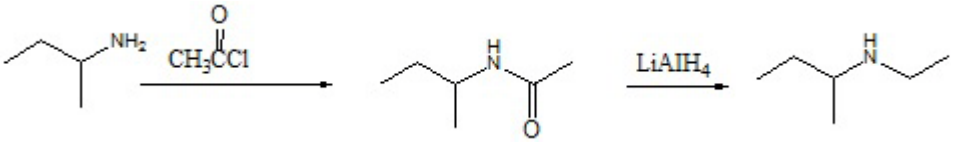
(c)



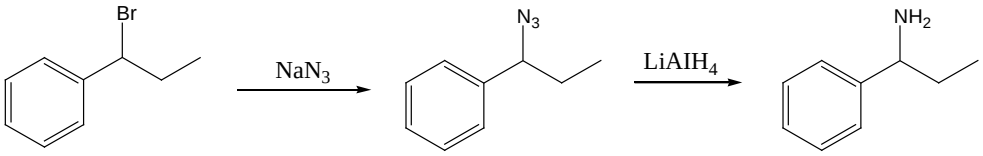
(d) aniline with CH_3CH_2COCl and then $LiAlH_4$



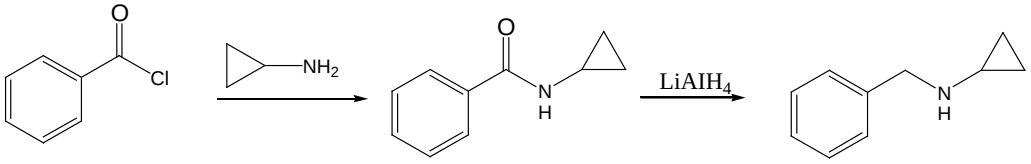
(e) 2-butanamine with acetyl chloride and then LiAlH4



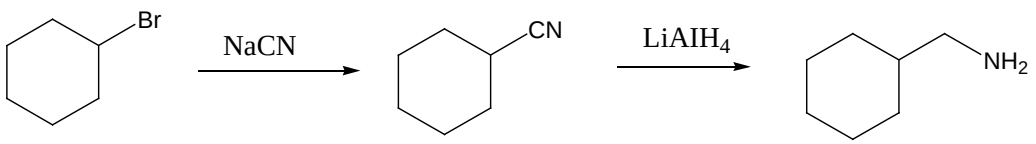
(f) 1-phenyl-l-bromopropane with sodium azide and then LiAlH4



(g) cyclopropylamine with benzoyl chloride and then LiAlH4



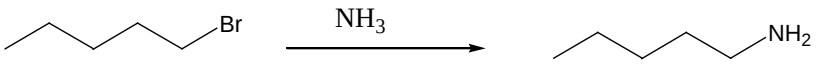
(h) cyclohexyl bromide with sodium cyanide and then LiAlH4



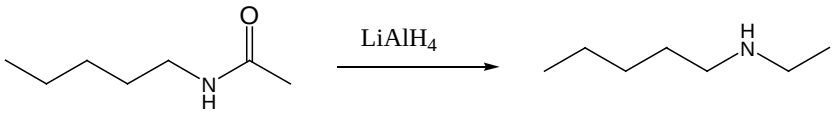
9. Show how to prepare 1-pentanamine using the designated starting materials:

(a) ammonia (b) an amide (c)an alkyl halide + sodium cyanide (d)an alkyl halide + sodium azide

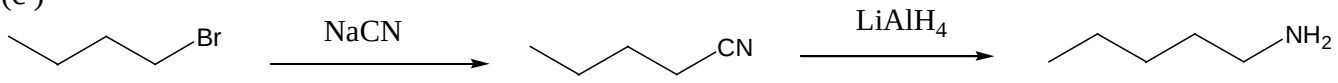
(a)



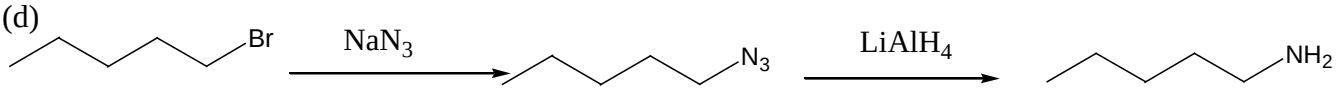
(b)



(c)



(d)



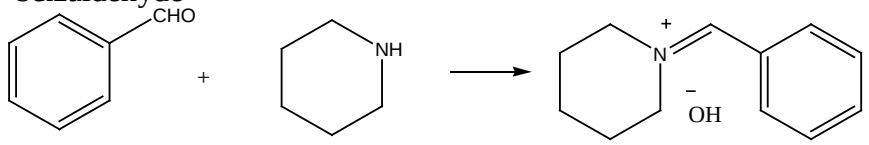
10. What alkyl bromide would you use in a Garbiel synthesis to prepare each of the following amines?

(A). Pentyl bromide (b) Benzyl bromide (c) Isohexyl bromide (d) Cyclohexyl bromide

11. Show the product from the reaction of piperidine with the following compounds:

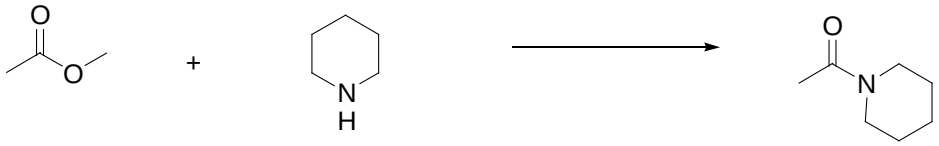
(a) benzaldehyde (b) acetic anhydride (c) methyl acetate (d) acetaldehyde (e) acetyl chloride (f) methyl iodide (1 eq.) (g) methyl iodide (excess) (H) cyclohexanon (I) 1. benzaldehyde, then 2. sodium borohydride. (J) 1. methyl iodide (excess), then 2. Ag2O, heating

(a) benzaldehyde

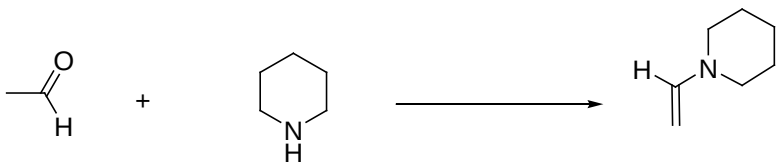


(b) acetic anhydride

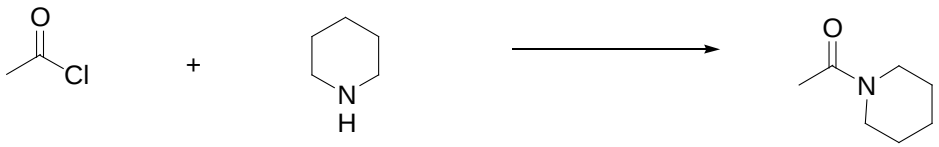
(c) methyl acetate



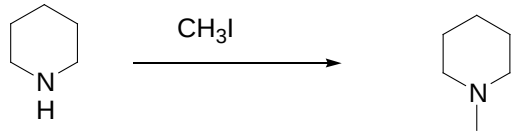
(d) acetaldehyde



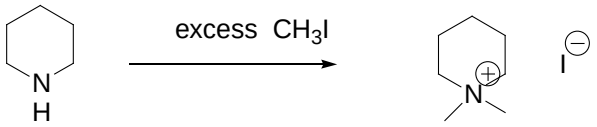
(e) acetyl chloride



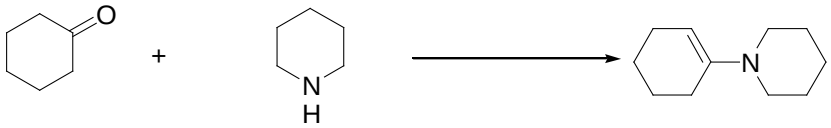
(f) methyl iodide (1 eq.)



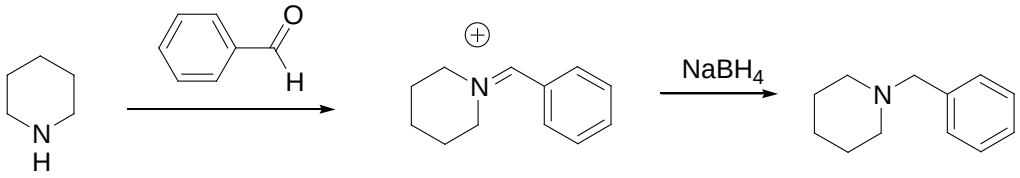
(g) methyl iodide (excess)



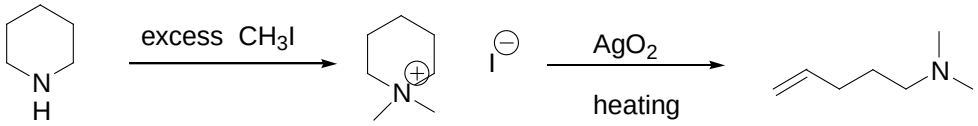
(H) cyclohexanone



(I) 1. benzaldehyde, then 2. sodium borohydride.

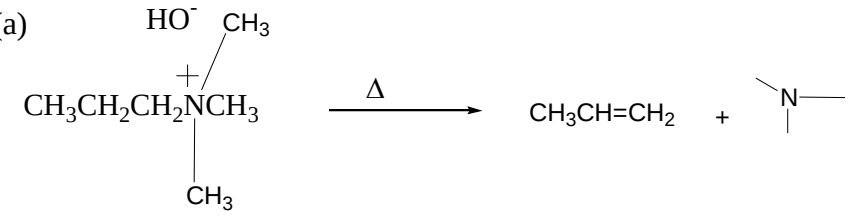


(J) 1. methyl iodide (excess), then 2. Ag2O, heating

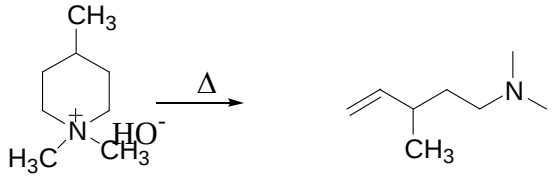


12. Give the products of each of the following reactions:

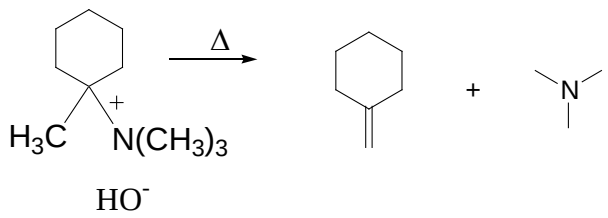
(a)



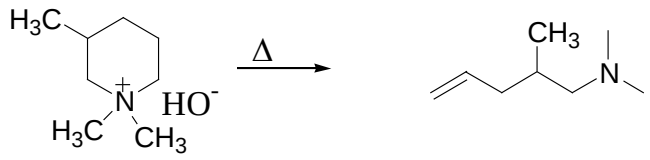
(B)



(C)



(D)

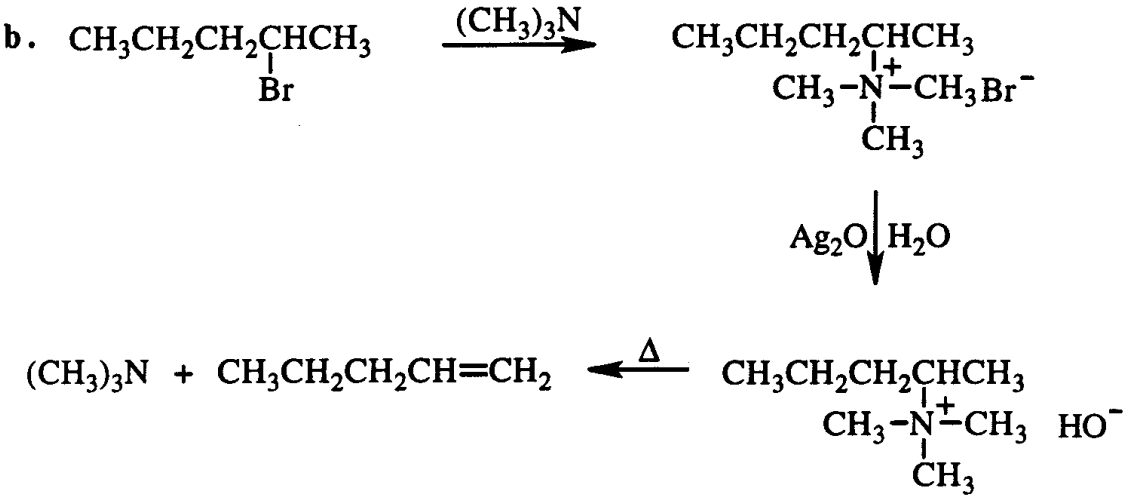


13. Describe a synthesis for each of the following compounds, using the given starting material and any necessary reagents:

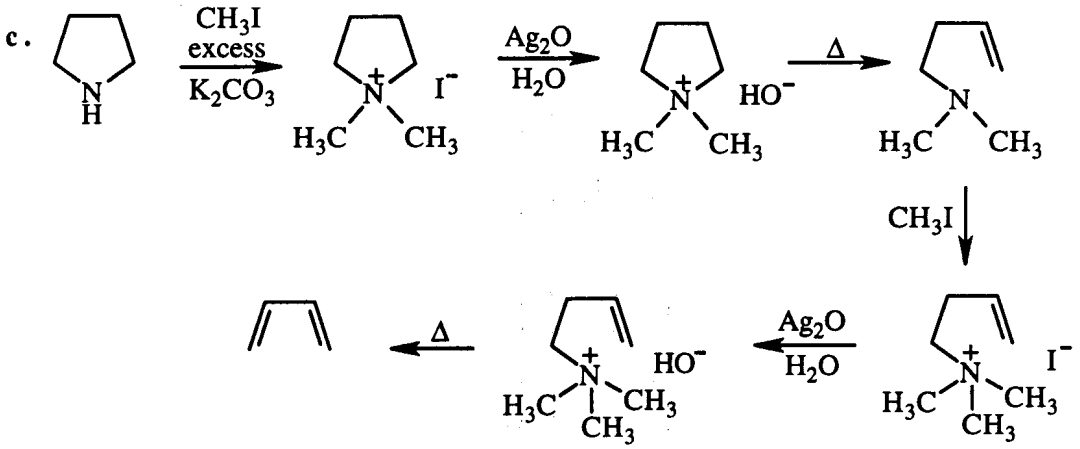
(a)

$CH_3CH_2CH_2CH_2NH_2$ + CH_3I → $CH_3CH_2CH_2CH_2N(CH_3)_3$ + Ag_2O → $CH_3CH_2CH{=}CH2$

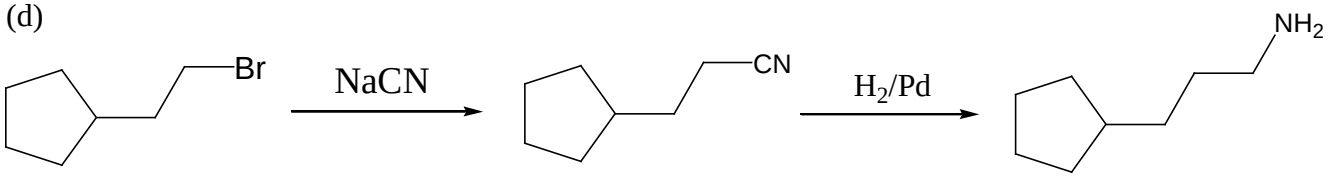
b.



c.

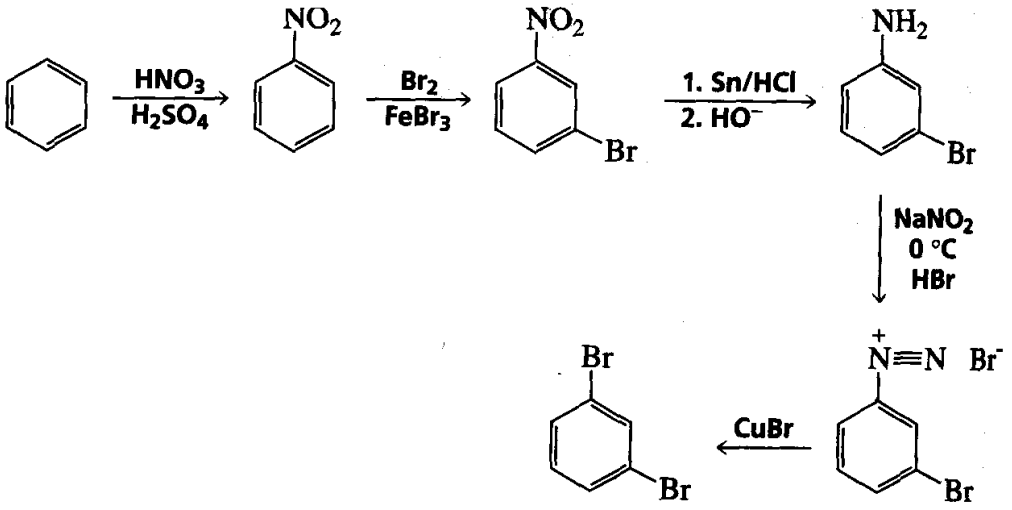


(d)

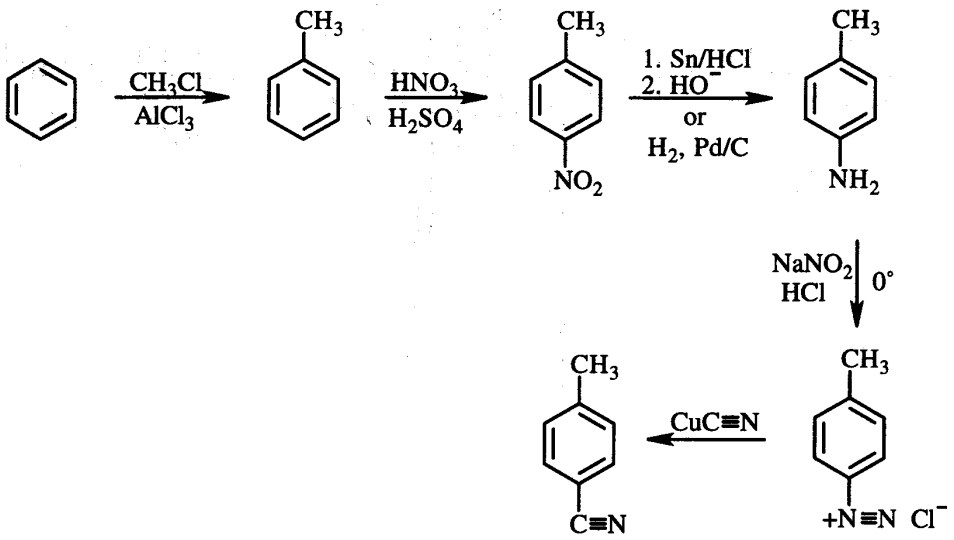


14. Show how the following compounds could be synthesized from benzene:

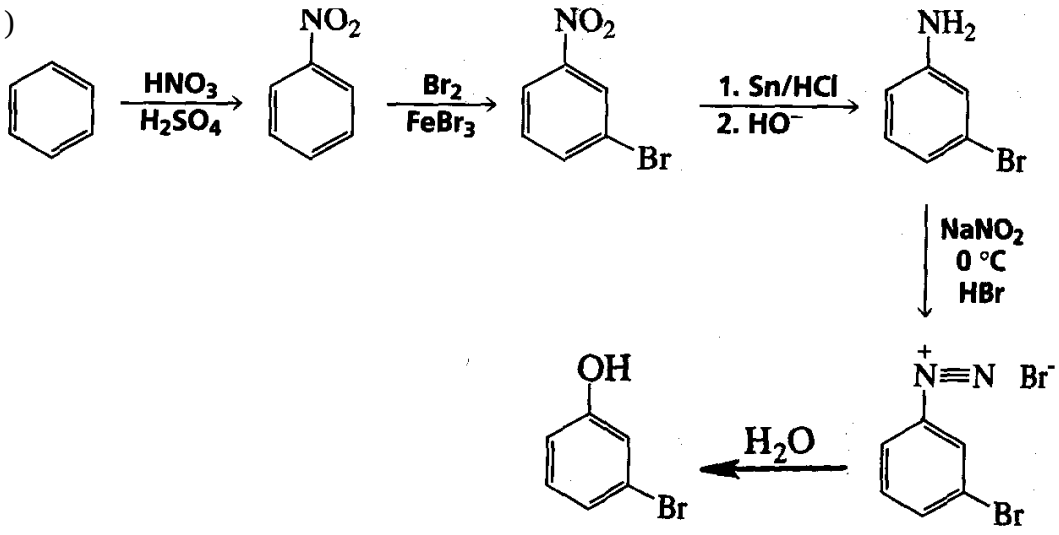
(a)



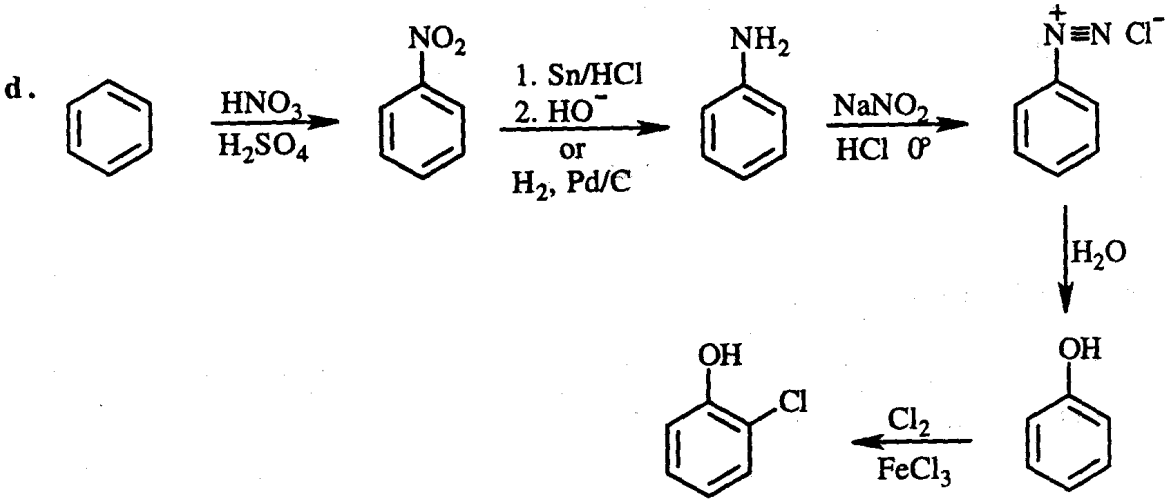
(b)



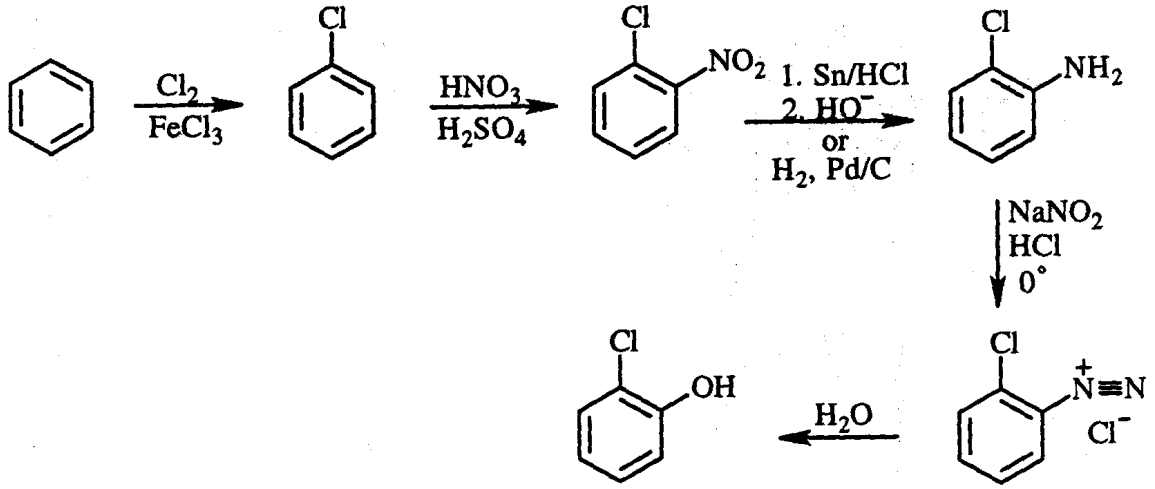
(C)



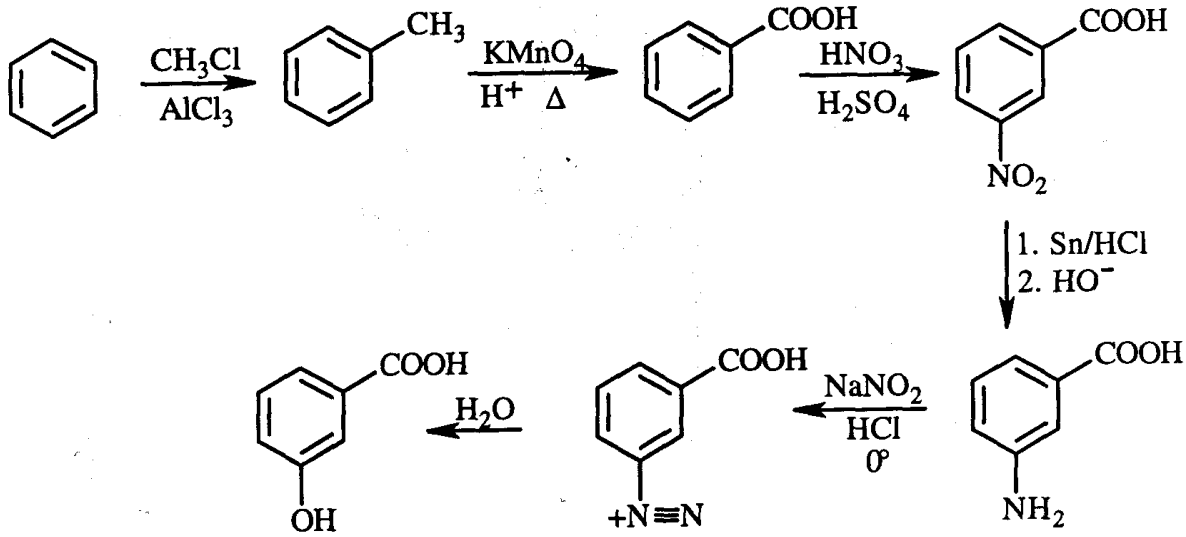
d.


HNO3
H2SO4
NO2
1. Sn/HCl
2. HO−
or
H2, Pd/C
NH2
NaNO2
HCl 0°
+N≡N Cl−
H2O
OH
Cl2
FeCl3
OH
Cl

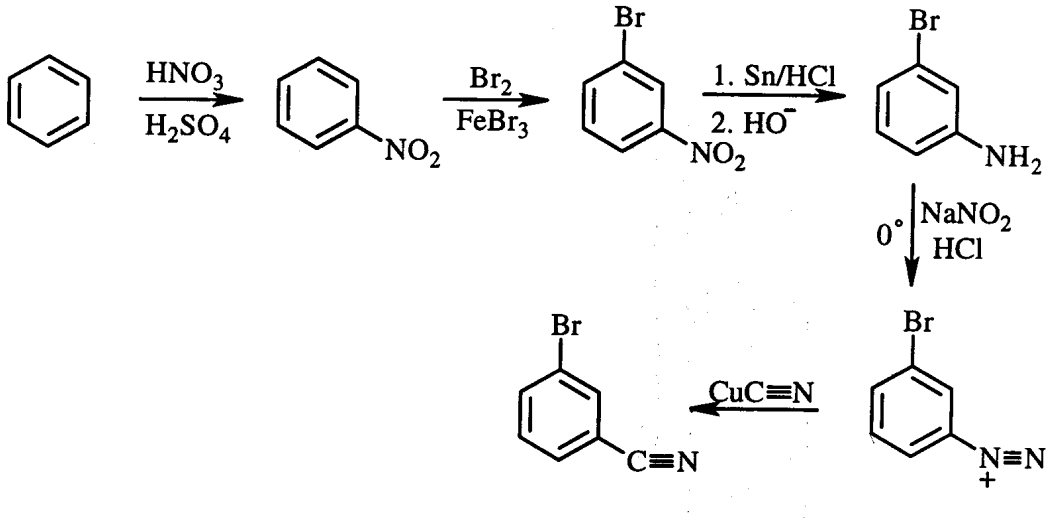
or


Cl2
FeCl3
Cl
HNO3
H2SO4
Cl
NO2
1. Sn/HCl
2. HO−
or
H2, Pd/C
Cl
NH2
NaNO2
HCl
0°
Cl
+N≡N
Cl−
H2O
Cl
OH

(e)


CH3Cl
AlCl3
CH3
KMnO4
H+ Δ
COOH
HNO3
H2SO4
COOH
NO2
1. Sn/HCl
2. HO−
COOH
NH2
NaNO2
HCl
0°
COOH
+N≡N
H2O
COOH
OH

(f)


HNO3
H2SO4
NO2
Br2
FeBr3
Br
NO2
1. Sn/HCl
2. HO−
Br
NH2
0°
NaNO2
HCl
Br
N≡N
+
CuC≡N
Br
C≡N

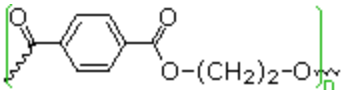
Ch 17 Polymer Answers

1. 我國環保署規定:

「市面上販售之商品凡使用下表所列「應回收容器材質類別」裝填表中所列「裝填物質種類」(含免洗餐具)之各類別業者應負責回收清除、處理該項容器」

塑膠(不含塑膠袋)請你寫出以上每一塑膠之化學結構 general structure formula

(1) 聚乙烯對苯二甲酸酯(PET)



(2) 聚苯乙烯(PS)—發泡 - [CH2-CH(C6H5)]n-

(3) 聚苯乙烯(PS)—未發泡 - [CH2-CH(C6H5)]n-

(3) 聚氯乙烯(PVC) - (CH2-CHCl)n-

(4) 聚乙烯(PE)- (CH2-CH2)n-

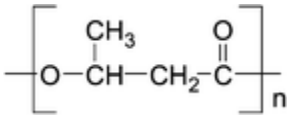
(5) 聚丙烯(PP)- [CH2-CH(CH3)]n-

2. 可以回收重覆再用的聚合物為何

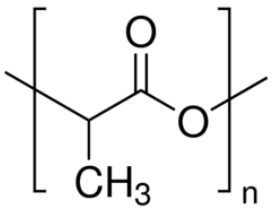
PET PE PVC PP PS PLA

3. 可被生物分解 biodegradable 的聚合物為何

(1) Polyhydroxybutyate PHB



(2) Polylactic acid



Ch 18 UV, Vis & IR spectroscopy

1. 以能量由小至大排列 UV, visible light, IR, X-ray, microwave, radio frequency

radio frequency < microwave < IR < Vis < UV < X-ray

2. 以波長由小至大排列 UV, visible light, IR, X-ray, microwave, radio frequency

X-ray < UV < Vis < IR < microwave < radio frequency

3. UV 分析甚麼？其分析原理為何? .IR 分析甚麼？其分析原理為何?

UV:

分析: Conjugated double bond

原理: Electron excitation

IR:

A. 分析: functional groups

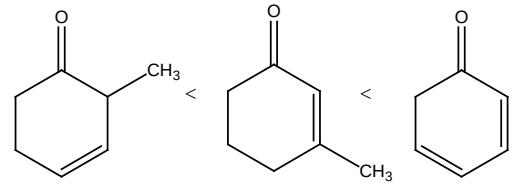
b. 原理: bond vibration, stretching & bending

4. 以下由小至大排列其 λ_{max}

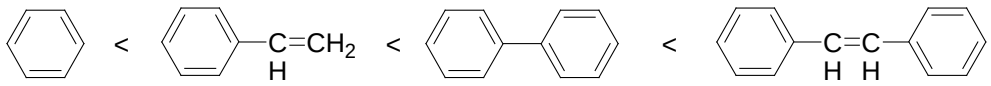
D < C < A < B < E

6. 以下由小至大排列其λmax

A.

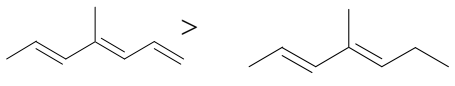


B.

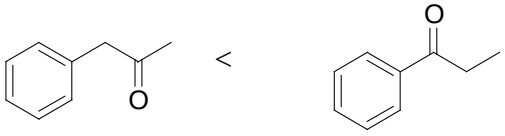


7. How could you distinguish between the compounds in each of the following pairs using UV spectroscopy?

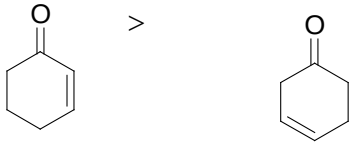
a.



b.



c.

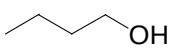
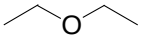


d.

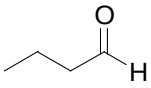
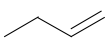
phenol: □max at (pH> 11) > □max (pH+7)

anisol: no change

8. 如何以 IR 圖譜分辨以下每組化合物:

(a)  and 

butanol has broad signal > 3000cm^{-1} ∵ -OH

(b)  and 

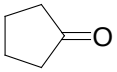
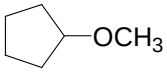
CHO: 2750 cm^{-1} & 2850 cm^{-1}, 1725 cm^{-1}, no > 3000 cm^{-1}

Alkene : 3100-3020 cm^{-1}

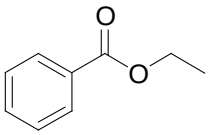
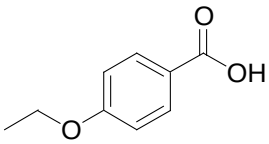
(c)  and 

pentanol has broad signal > 3000cm^{-1} ∵ -OH

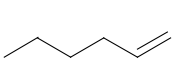
Alkene : 3100-3020 cm^{-1}

(d)  and 

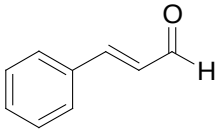
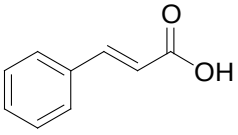
ketone: ~1715 cm^{-1}

(e)  and 

acid: C=O: ~1710 cm^{-1}, OH: >3000 cm^{-1}

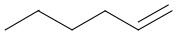
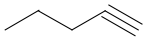
(f)  and 

alkene : 3100-3020 cm^{-1}

(g)  and 

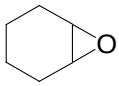
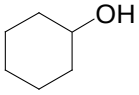
CHO: 2750 cm^{-1} & 2850 cm^{-1}, 1725 cm^{-1}

acid: C=O: ~1710 cm^{-1}, OH: >3000 cm^{-1}

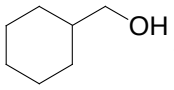
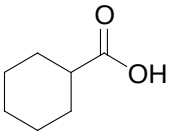
(h)  and 

alkene : 3100-3020 cm^{-1}

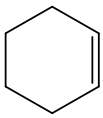
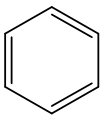
alkyne: ≡C-H: ~3300 cm-1, C≡C: 2150 ㎝$^{-1}$

(i)  and 

hexanol has broad signal > 3000cm^{-1} ∵ -OH

(j)  and 

COOH: C=O 1730-1700 cm^{-1}, broad & intense
Very broad O-H (3400-2400 cm^{-1})

(k)  and 

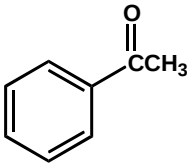
alkene: C=C-H stretching: >3000 cm^{-1}
sharp absorption bands: ~1600 cm^{-1}
benzence: C=C-H stretching: >3000 cm^{-1}
sharp absorption bands: ~1600 cm–1 & 1500–1430 cm^{-1}

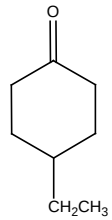
8. A solution of 4-methyl-3-penten-2-one in ethanol shows an absorbance of 0.52 at 236 nm in a cell with a 1 cm light path. Its molar absorptivity in ethanol at that wavelength is 126000.
What is the concentration of the compound?
A = abc
0.52 = 126000 x 1 x c
c = 4.126 x 10^{-6}M

9. Indicate which of the following compounds is responsible for the following spectra
(I)
~2100 cm-1 C=C
~3300 cm-1 C=H
∴ $CH_3CH_2CH_2CH_2C{\equiv}CH$

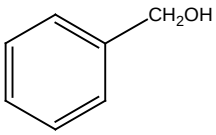
(II)
~1750 cm-1 C=O
no >3000 cm-1 no OH, not acid
no 2700 cm-1 not aldehyde
~1200 cm-1 C-O
$CH_3CH_2C(=O)OCH_2CH_3$

(III)
Broad band ~3300 cm-1 -OH
No ~1600 cm-1 & ~3100 cm-1 not akene
No ~1700 cm-1 not C=O
$CH_3CH_2CH_2CH_2OH$

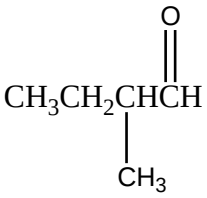
(IV) No Broad band ~3300 cm-1 no -OH
~1685 cm-1 C=O
No ~2700 cm-1 not CHO


(v) 

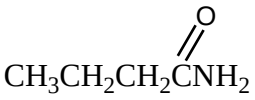
~1700 cm-1 C=O; No >3000 cm-1 not benzene enone~1680 cm-1, No ~2100 cm-1 & ~3300 cm-1, not alkyne

(VI) 

(VII)

(a) 

B. ~3300 cm-1 & ~3200 cm-1 amide (NH_2 stretch); no ~3050 cm-1, not alkene nor benzene



(c) No ~1600 cm-1 & ~1500 cm-1, not benzene, no >3000 cm-1, simple ketone