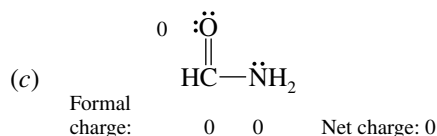
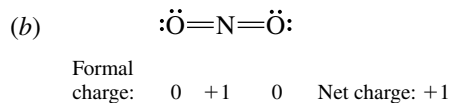
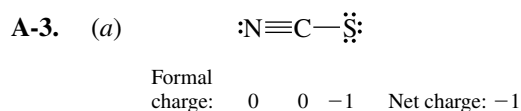
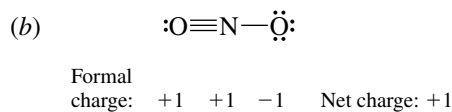
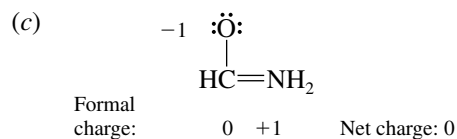
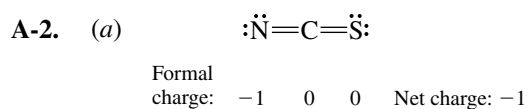
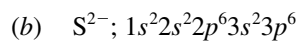
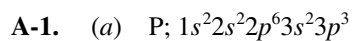


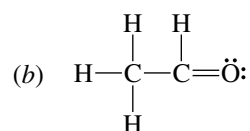
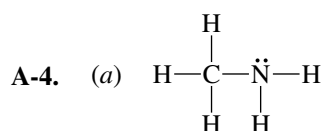
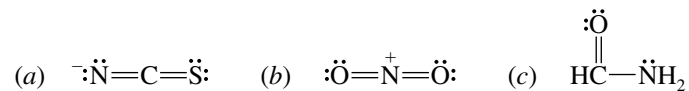
APPENDIX A

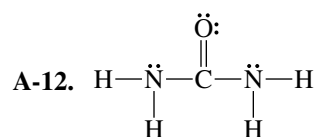
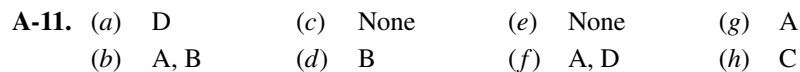
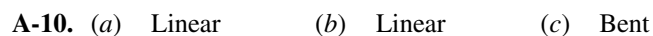
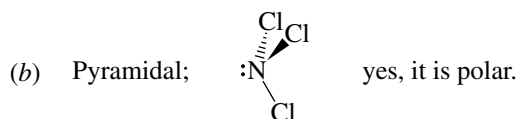
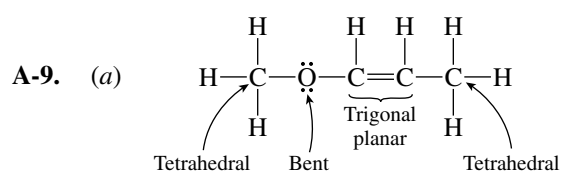
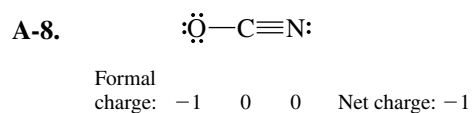
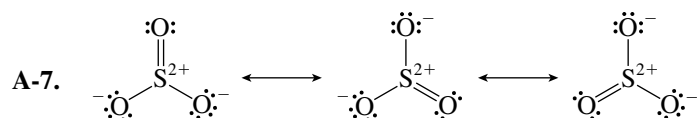
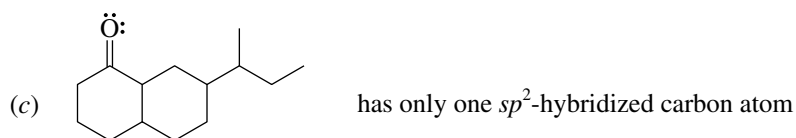
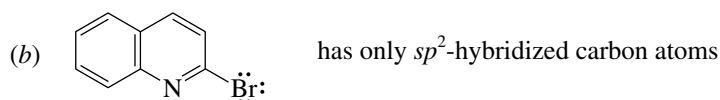
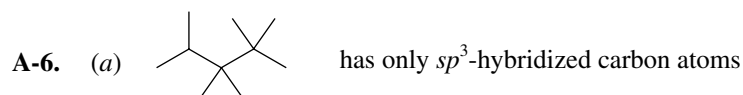
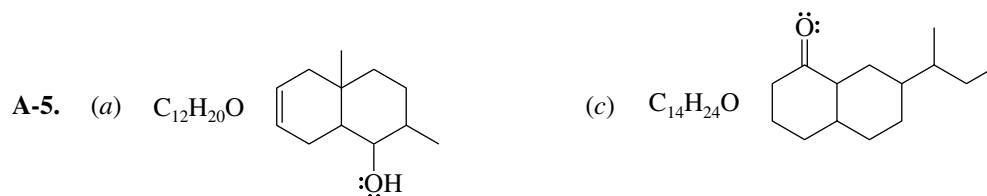
ANSWERS TO THE SELF-TESTS

CHAPTER 1



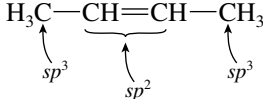
The more stable Lewis structures are



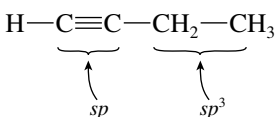


A-13. (a) 11 σ ; 1 π (b) 9 σ ; 2 π (c) 12 σ ; 4 π (d) 13 σ ; 4 π

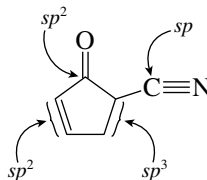
A-14. (a) $\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}_3$ (c) All carbons are sp^2 .



(b) $\text{H}-\text{C}\equiv\text{C}-\text{CH}_2-\text{CH}_3$



(d)



B-1. (b) B-2. (b) B-3. (c) B-4. (d)

B-5. (a) B-6. (b) B-7. (a) B-8. (d)

B-9. (b) B-10. (d) B-11. (b) B-12. (e)

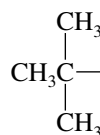
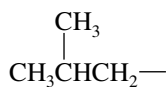
B-13. (d) B-14. (b) B-15. (d)

CHAPTER 2

A-1. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$ $\text{CH}_3\text{CH}_2\text{CHCH}_3$

Common: *n*-Butyl
Systematic: Butyl

sec-Butyl
1-Methylpropyl



Common: Isobutyl
Systematic: 2-Methylpropyl

tert-Butyl
1,1-Dimethylethyl

A-2. (a) 28 (8 C—C; 20 C—H) (b) 27(9 C—C; 18 C—H)

A-3. (a) Oxidized (b) Neither (c) Neither (d) Reduced

A-4. (a) $\begin{array}{c} \text{CH}_3\text{CHCH}_3 \\ | \\ \text{CH}_3\text{CHCHCHCH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$ (b) Six methyl groups, three isopropyl groups

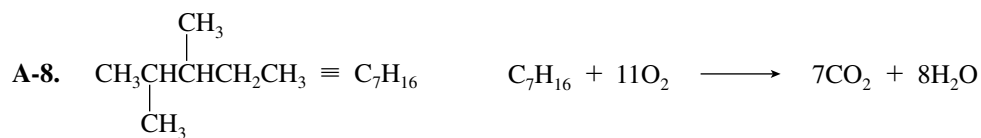
A-5. (a) 3,4-Dimethylheptane (b) (1,2-Dimethylpropyl)cyclohexane

A-6. Primary Secondary Tertiary

(a) 4 3 2

(b) 3 5 3

A-7. (a) 1,3-Dimethylbutyl; secondary
(b) 1,1-Diethylpropyl; tertiary
(c) 2,2-Diethylbutyl; primary



A-9.



Cyclopentane



Methylcyclobutane



Ethylcyclopropane

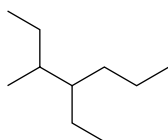


1,1-Dimethylcyclopropane



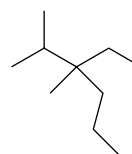
1,2-Dimethylcyclopropane

A-10. (a)



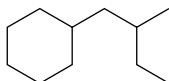
4-Ethyl-3-methylheptane

(c)

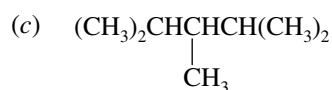


3-Ethyl-2,3-dimethylhexane

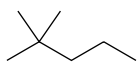
(b)



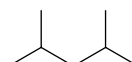
(2-Methylbutyl)cyclohexane

A-11. (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (b) $(\text{CH}_3)_3\text{CC}(\text{CH}_3)_3$ (d) $(\text{CH}_3)_3\text{CC}(\text{CH}_3)_3$

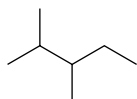
A-12.



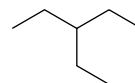
2,2-Dimethylpentane



2,4-Dimethylpentane



2,3-Dimethylpentane



3-Ethylpentane



3,3-Dimethylpentane

A-13. Alcohol, alkene, ester, ketone

A-14. 10,049 kJ/mol

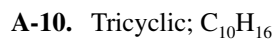
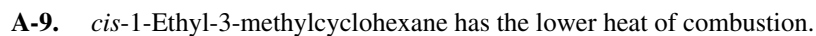
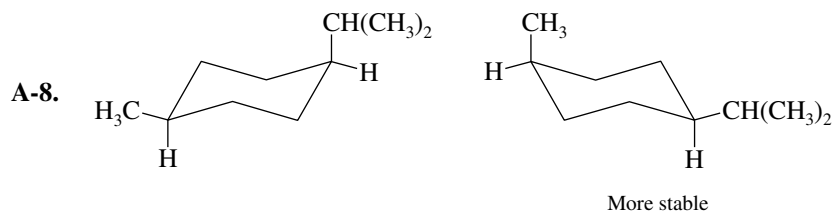
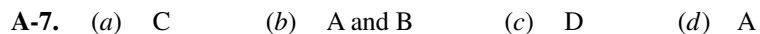
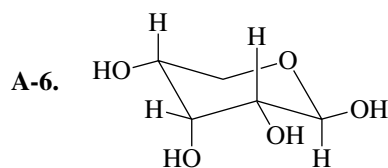
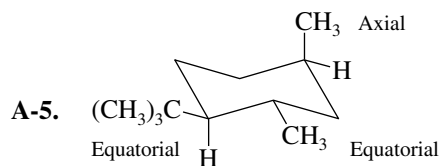
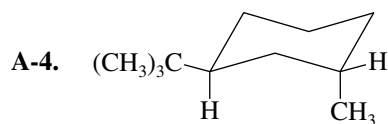
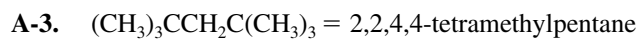
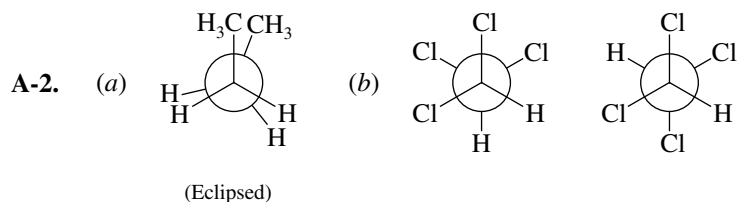
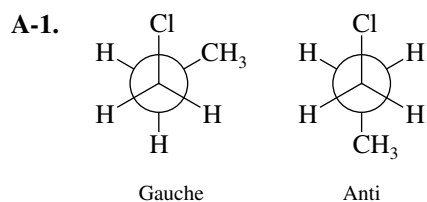
B-1. (a) B-2. (d) B-3. (d) B-4. (c)

B-5. (b) B-6. (a) B-7. (c) B-8. (c)

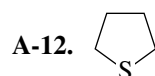
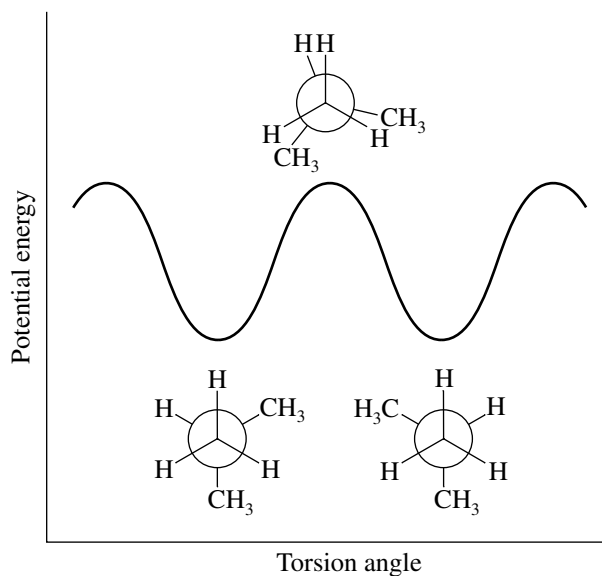
B-9. (a) B-10. (a) B-11. (b) B-12. (e)

B-13. (d) B-14. (d)

CHAPTER 3



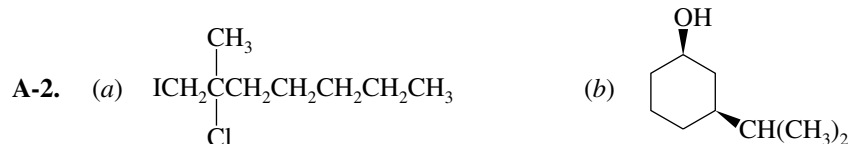
A-11. The form of the curve more closely resembles ethane than butane.



- | | | | | | | | |
|-------|-----|-------|-----|-------|-----|-------|-----|
| B-1. | (d) | B-2. | (b) | B-3. | (c) | B-4. | (a) |
| B-5. | (c) | B-6. | (a) | B-7. | (d) | B-8. | (e) |
| B-9. | (c) | B-10. | (e) | B-11. | (b) | B-12. | (a) |
| B-13. | (d) | B-14. | (b) | | | | |

CHAPTER 4

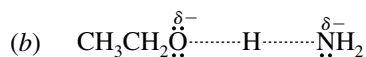
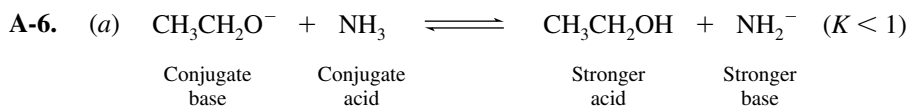
- A-1. (a) *trans*-1-Bromo-3-methylcyclopentane
 (b) 2-Ethyl-4-methyl-1-hexanol



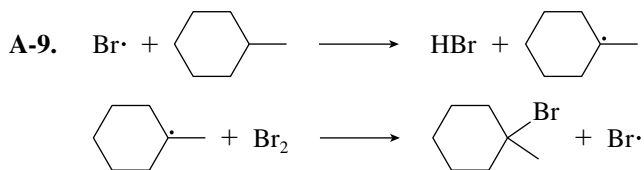
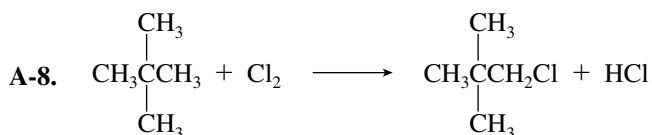
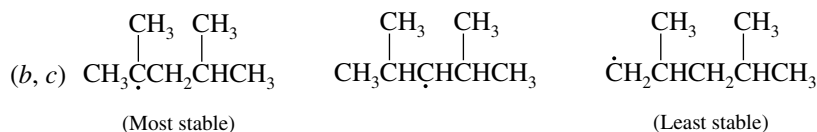
- A-3. (a) **Functional class:** 1-ethyl-3-methylbutyl alcohol
Substitutive: 5-methyl-3-hexanol
 (b) **Functional class:** 1,1,2-trimethylbutyl chloride
Substitutive: 2-chloro-2,3-dimethylpentane

- A-4. Conjugate acid $\text{CH}_3\overset{+}{\text{O}}\text{H}_2$; conjugate base $\text{CH}_3\ddot{\text{O}}:^-$

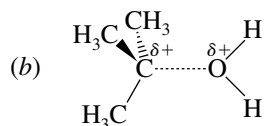
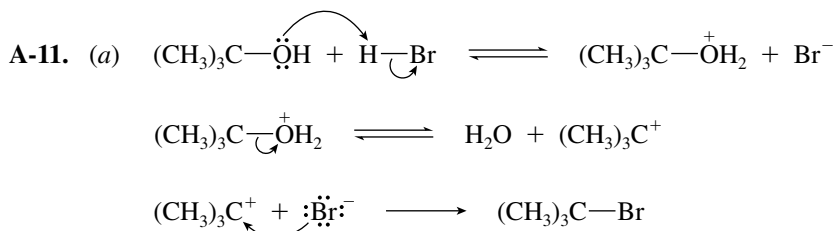




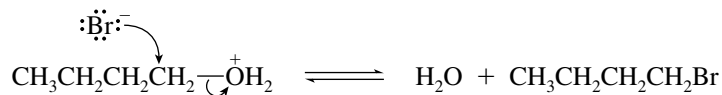
A-7. (a) Three



A-10. $\Delta H^\circ = -57 \text{ kJ } (-13.5 \text{ kcal})$



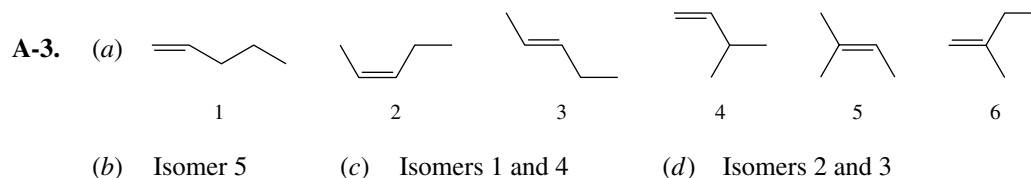
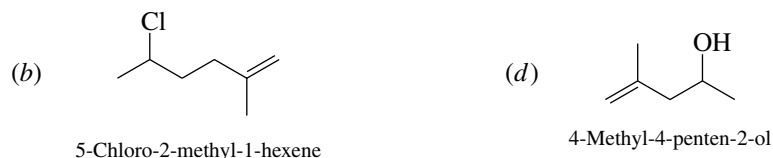
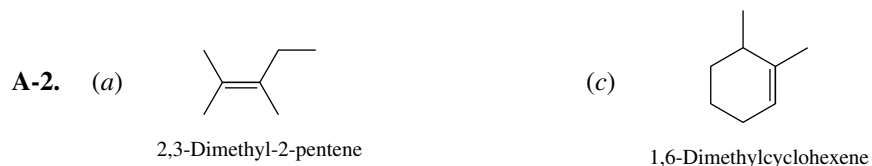
(c) Water is displaced directly from the oxonium ion of 1-butanol by bromide ion. A primary carbocation is not involved.



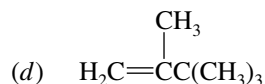
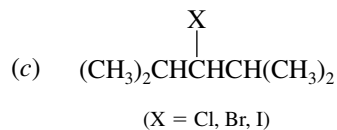
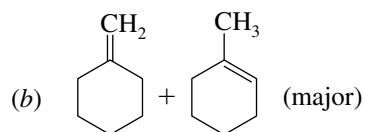
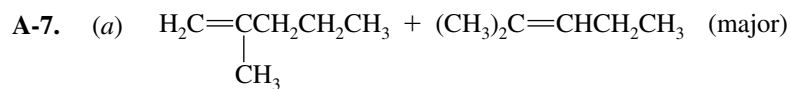
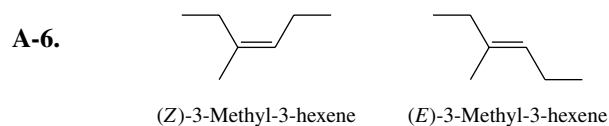
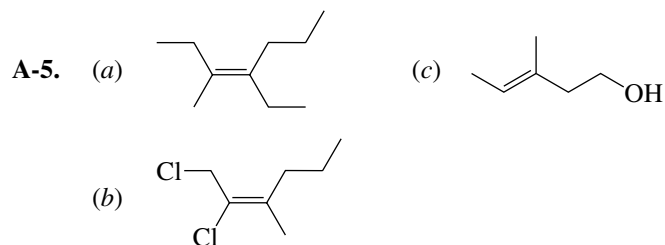
- A-12. (a) 3-Methyl-3-pentanol (c) Fluorine (F_2) (e) Cl_2
 (b) $\text{KOC}(\text{CH}_3)_3$ (d) Ethyl radical, $\text{CH}_3\dot{\text{C}}\text{H}_2$
- B-1. (e) B-2. (c) B-3. (b) B-4. (c)
 B-5. (e) B-6. (c) B-7. (d) B-8. (a)
 B-9. (c) B-10. (d) B-11. (c) B-12. (e)
 B-13. (a) B-14. (c) B-15. (c) B-16. (c)

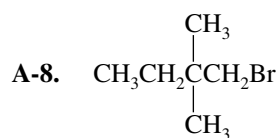
CHAPTER 5

- A-1. (a) 2,4,4-Trimethyl-2-pentene (c) (*E*)-2,7-Dibromo-3-(2-methylpropyl)-2-heptene
 (b) (*E*)-3,5-Dimethyl-4-octene (d) 5-Methyl-4-hexen-3-ol

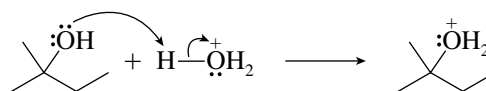


- A-4. Two sp^2 C atoms; four sp^3 C atoms; three sp^2 — sp^3 σ bonds

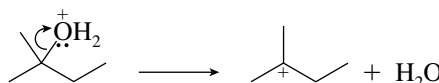




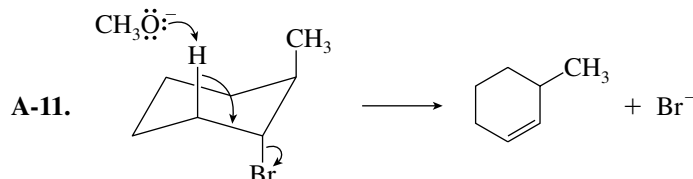
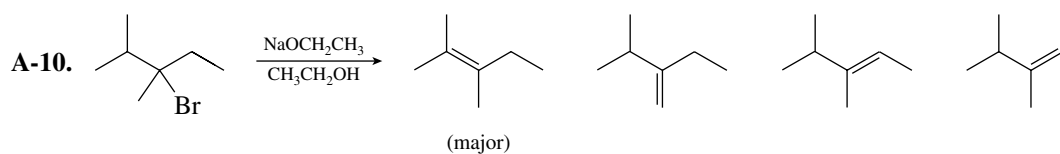
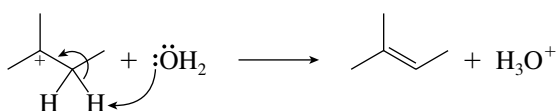
A-9. Step 1: Protonation



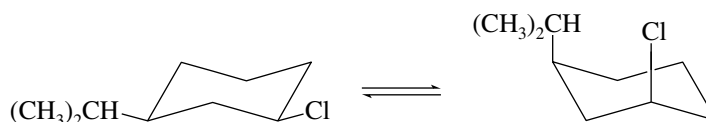
Step 2: Dissociation



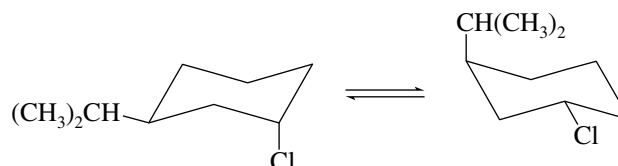
Step 3: Deprotonation



A-12. Cis isomer:

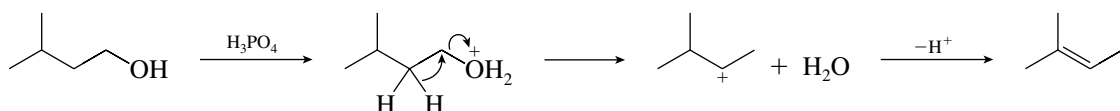


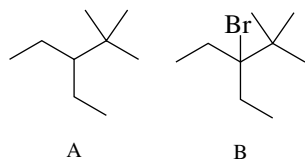
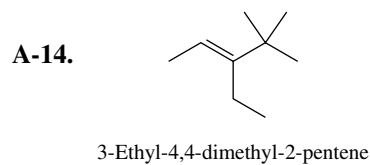
Trans isomer:



The trans isomer will react faster because its most stable conformation (with the isopropyl group equatorial) has an axial Cl able to undergo E2 elimination.

A-13. Rearrangement (hydride migration) occurs to form a more stable carbocation.

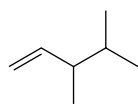




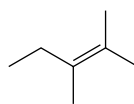
- B-1. (c) B-2. (c) B-3. (d) B-4. (c)
 B-5. (a) B-6. (b) B-7. (a) B-8. (a)
 B-9. (a) B-10. (d) B-11. (b) B-12. (c)
 B-13. (a) B-14. (c) B-15. (a)

CHAPTER 6

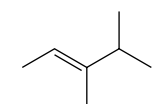
A-1. Five;



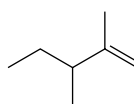
3,4-Dimethyl-1-pentene



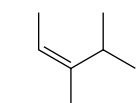
2,3-Dimethyl-2-pentene



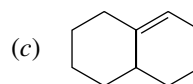
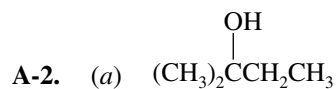
(E)-3,4-Dimethyl-2-pentene



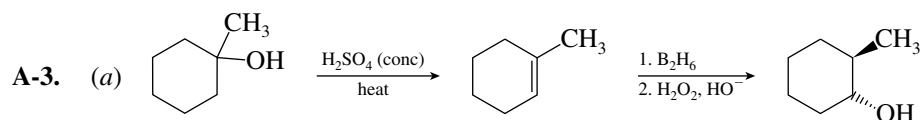
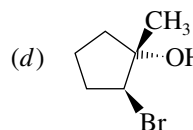
2,3-Dimethyl-1-pentene

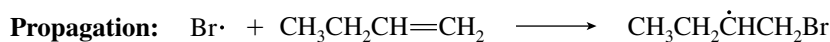
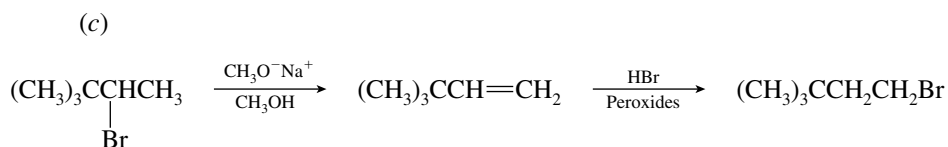
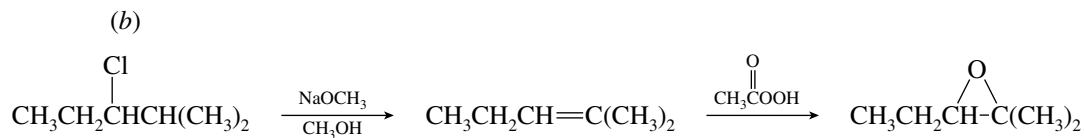


(Z)-3,4-Dimethyl-2-pentene

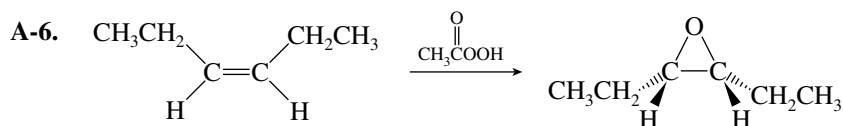
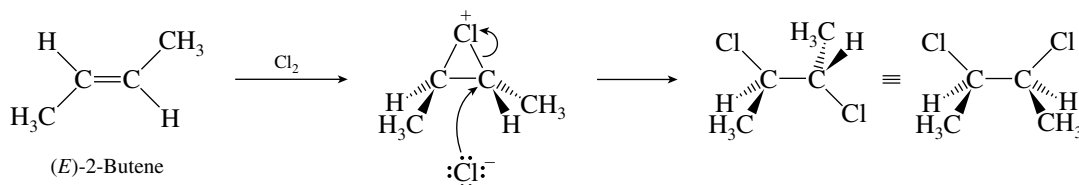


(b) HBr, peroxides

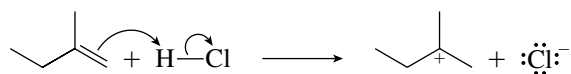




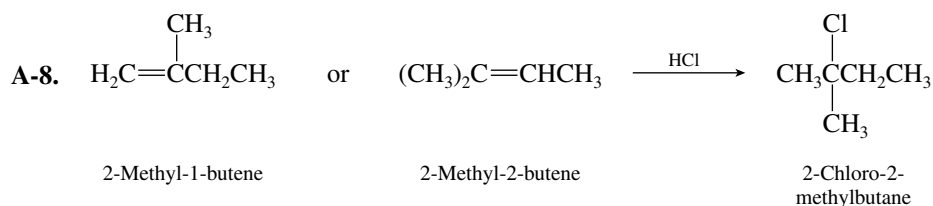
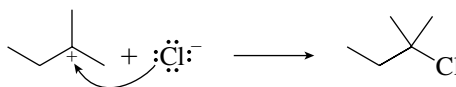
A-5.



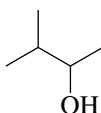
A-7. Step 1: Protonation to form a carbocation

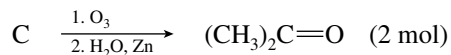
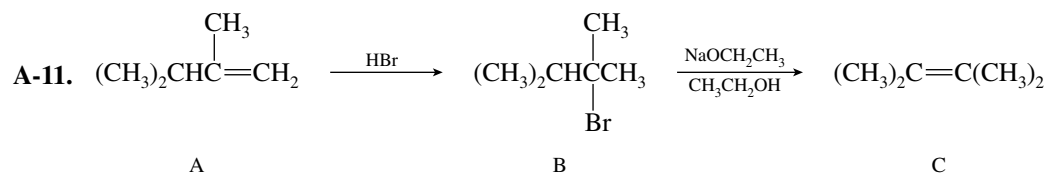
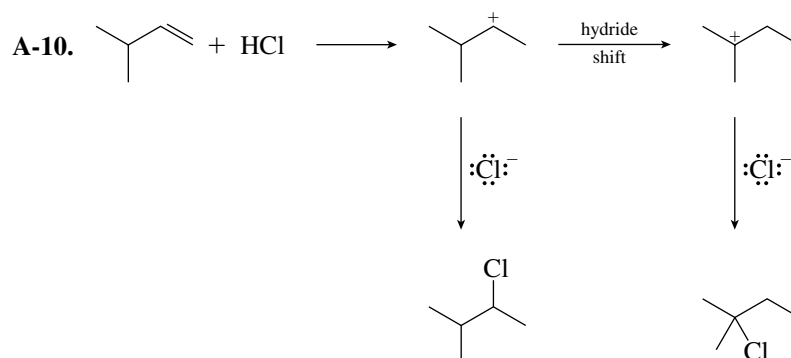


Step 2: Nucleophilic addition of chloride ion



A-9.





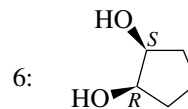
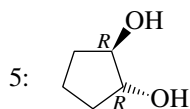
- B-1. (c) B-2. (a) B-3. (c) B-4. (d)
 B-5. (d) B-6. (e) B-7. (b) B-8. (b)
 B-9. (b) B-10. (b) B-11. (a) B-12. (e)
 B-13. (e)

CHAPTER 7

- A-1. (a) 1 and 2, both achiral; identical
 (b) 3 and 4, both chiral; enantiomers
 (c) 5 chiral, 6 achiral (meso); diastereomers
 (d) 7 and 8, both chiral; diastereomers
 (e) 9 and 10, both chiral; diastereomers

A-2. 3: (*R*)-2-Chlorobutane;

4: (*S*)-2-Chlorobutane



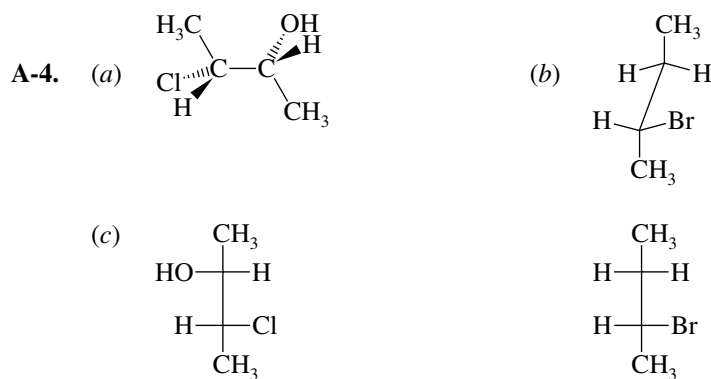
7: (2*S*,3*R*)-2,3-Dibromopentane;

8: (2*R*,3*R*)-2,3-Dibromopentane

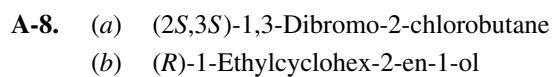
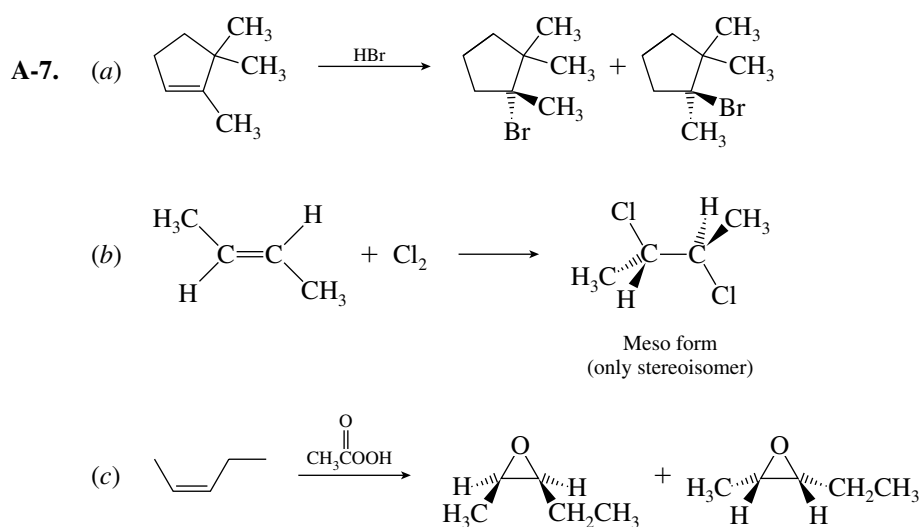
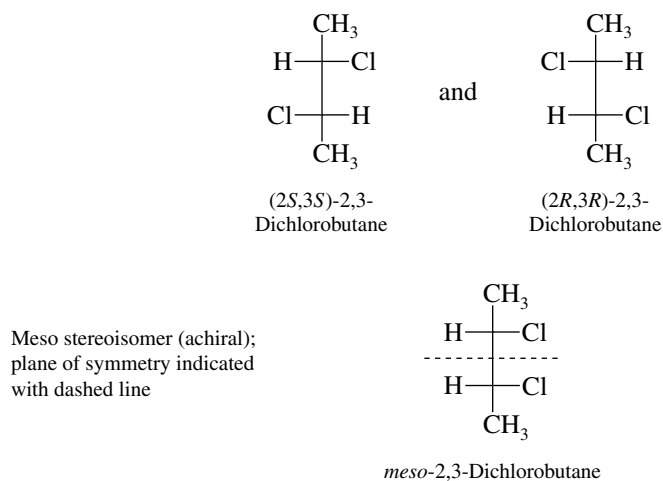
9: (2*E*,5*R*)-5-Chloro-2-hexene;

10: (2*Z*,5*S*)-5-Chloro-2-hexene

- A-3. (a) Three; meso form is possible. (c) Four; no meso form possible.
 (b) Eight; no meso form possible.

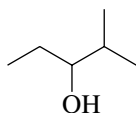


A-5. Chiral stereoisomers:



A-9. Two: (2*R*,3*S*)-2-bromo-3-chlorobutane and (2*S*,3*S*)-2-bromo-3-chlorobutane; they are diastereomers.

A-10.



Racemic mixture

B-1. (c) **B-2.** (c) **B-3.** (b) **B-4.** (d)

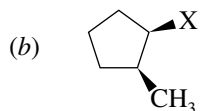
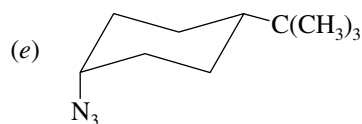
B-5. (b) **B-6.** (c) **B-7.** (d) **B-8.** (d)

B-9. (b) **B-10.** (c) **B-11.** (d) **B-12.** (d)

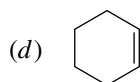
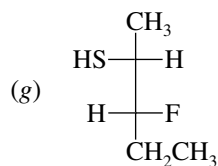
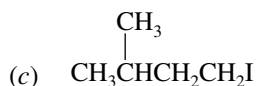
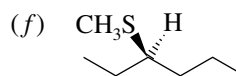
B-13. (e) **B-14.** (b)

CHAPTER 8

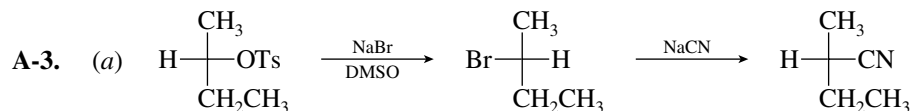
A-1. (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$



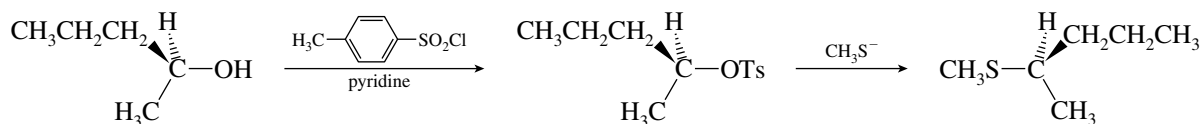
(X = OTs, Br, I)



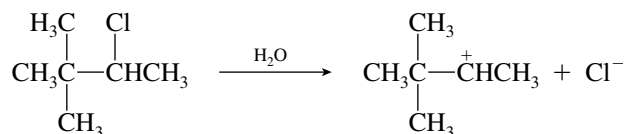
A-2. $(\text{CH}_3)_2\text{CHO}^- \text{Na}^+ + \text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$



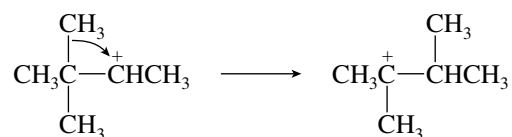
(b)



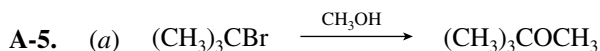
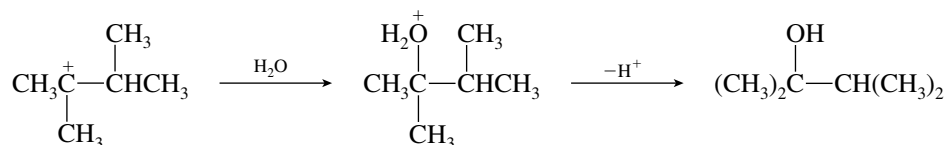
A-4. Step 1: Ionization to form a secondary carbocation



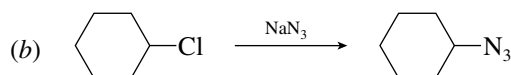
Step 2: Rearrangement by methyl migration to form a more stable tertiary carbocation



Step 3: Capture of the carbocation by water, followed by deprotonation

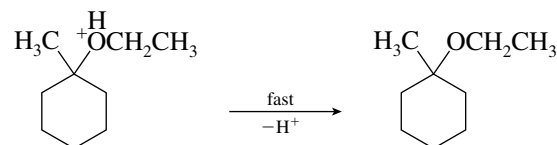
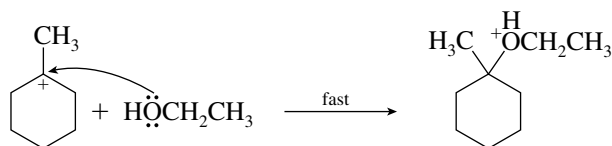
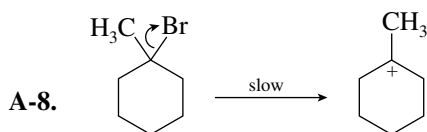
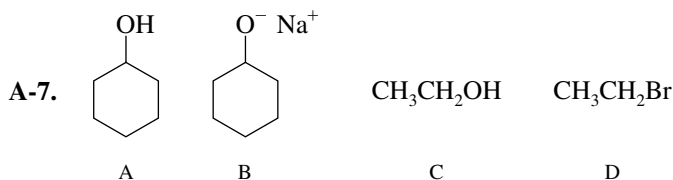


$\text{S}_{\text{N}}1$, unimolecular substitution; rate = $k[(\text{CH}_3)_3\text{CBr}]$

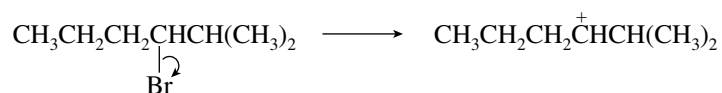


$\text{S}_{\text{N}}2$, bimolecular substitution; rate = $k[\text{C}_6\text{H}_{11}\text{Cl}][\text{NaN}_3]$

- A-6.** (a) Sodium iodide is soluble in acetone, whereas the byproduct of the reaction, sodium bromide, is not. According to Le Chatelier's principle, the reaction will shift in the direction that will replace the component removed from solution, in this case toward product.
- (b) Protic solvents such as water form hydrogen bonds to anionic nucleophiles, thus stabilizing them and decreasing their nucleophilic strength. Aprotic solvents such as DMSO do not solvate anions very strongly, leaving them more able to express their nucleophilic character.



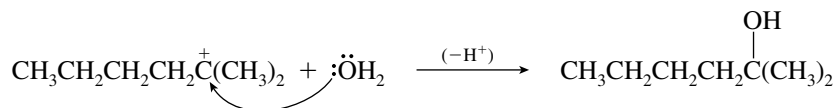
A-9. Dissociation to give a secondary carbocation



Rearrangement by hydride migration to give a tertiary carbocation



Capture of the carbocation by water to give product



- B-1. (b) B-2. (c) B-3. (d) B-4. (c)
 B-5. (d) B-6. (a) B-7. (c) B-8. (d)
 B-9. (c) B-10. (a) B-11. (a) B-12. (c)
 B-13. (c) B-14. (c)

CHAPTER 9

- A-1. (a) 4,5-Dimethyl-2-hexyne (c) 6,6-Dimethylcyclodecyne
 (b) 4-Ethyl-3-propyl-1-heptyne

- A-2. (a) $\text{CH}_3\text{CH}_2\text{CH}_2\overset{\text{Cl}}{\text{C}}=\text{CH}_2$ (e) $(\text{CH}_3)_2\text{CHC}\equiv\text{CH}$

- (b) $\text{CH}_3\text{CH}_2\text{CH}_2\overset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}}\text{CH}_3$ (f) Na, $\text{NH}_3(l)$

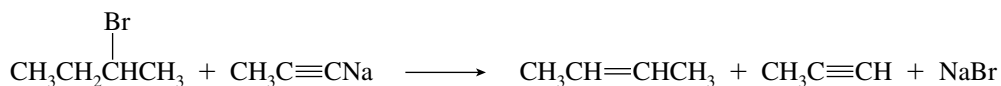
- (c) $\text{H}_2\text{O}, \text{H}_2\text{SO}_4, \text{HgSO}_4$ (g) $\text{H}_3\text{C}-\overset{\text{Cl}}{\text{C}}=\overset{\text{Cl}}{\text{C}}-\text{CH}_2\text{CH}_3$

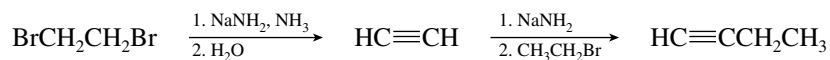
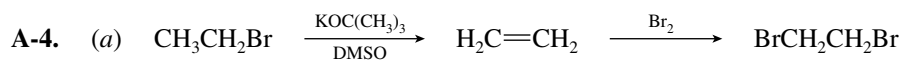
- (d) $\text{H}_3\text{C}-\overset{\text{H}}{\text{C}}=\overset{\text{H}}{\text{C}}-\text{CH}_3$ (h) $\text{CH}_3\text{CH}_2\text{CH}_2\overset{\text{CH}_3}{\text{C}}\text{HCO}_2\text{H} + \text{CH}_3\text{CH}_2\text{CO}_2\text{H}$

A-3. Reaction (2) is effective; the desired product is formed by an $\text{S}_{\text{N}}2$ reaction.



Reaction (1) is not effective, owing to E2 elimination from the secondary bromide.

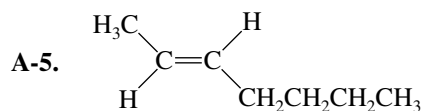
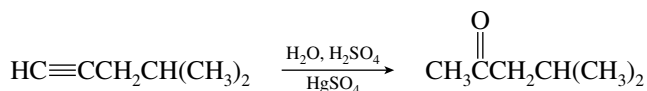
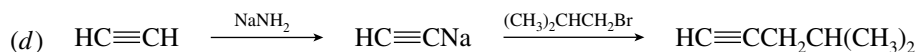
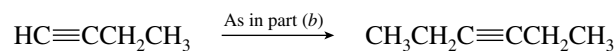
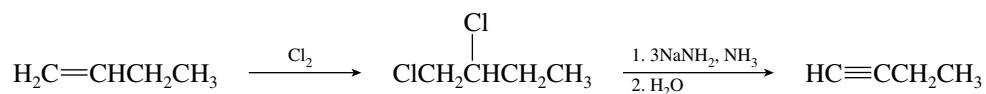




(b)



(c)

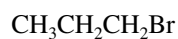
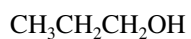


(E)-2-Heptene



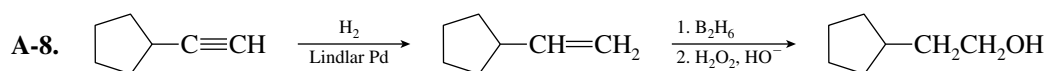
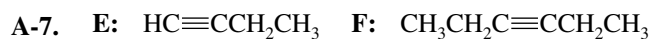
A

B



C

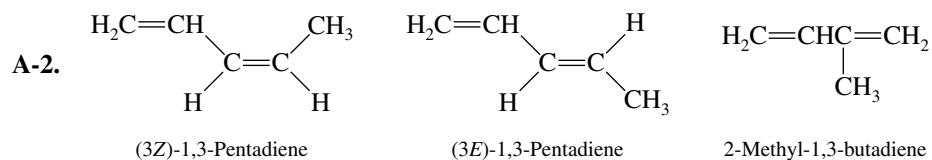
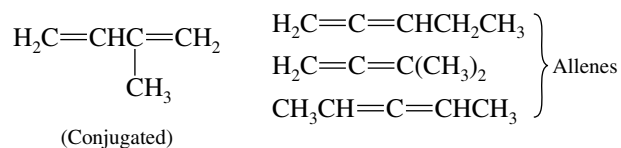
D



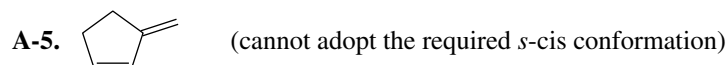
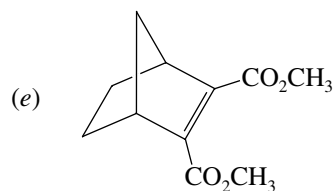
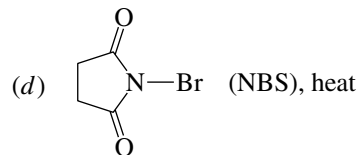
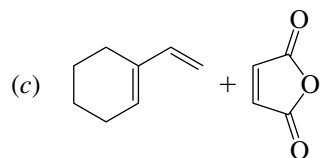
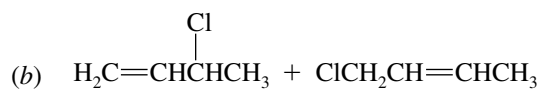
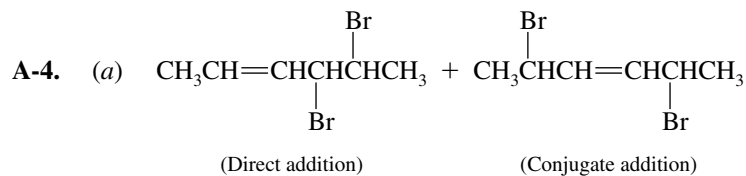
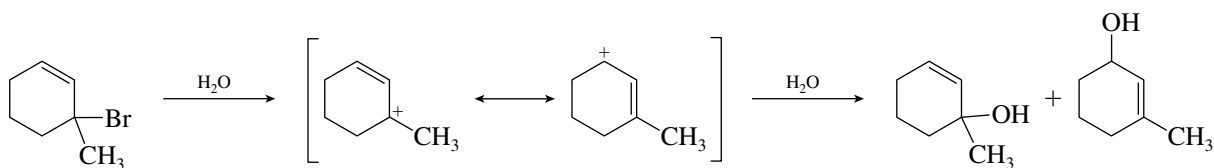
CHAPTER 10

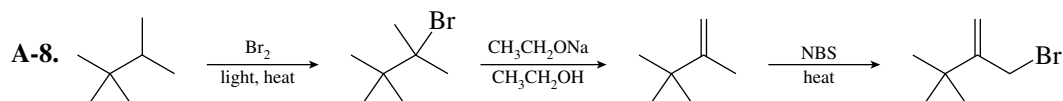
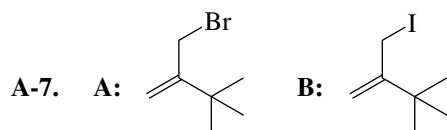
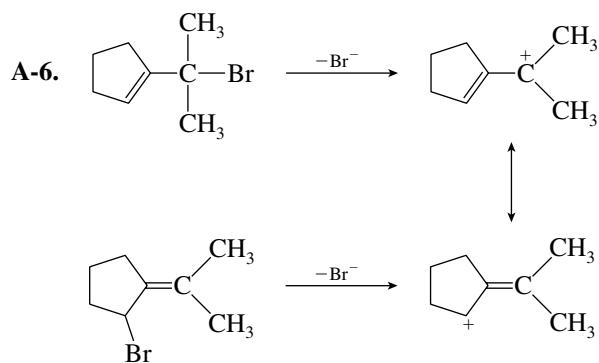


(Conjugated)



A-3.

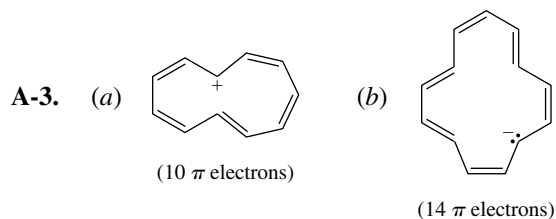
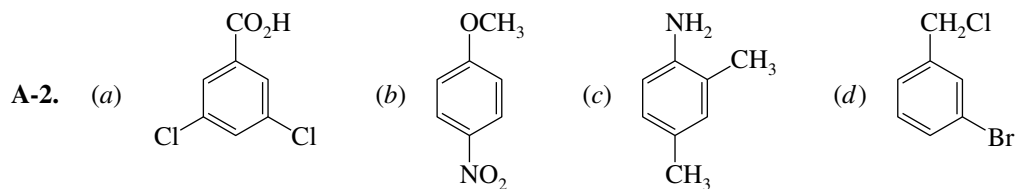




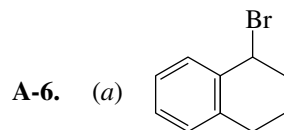
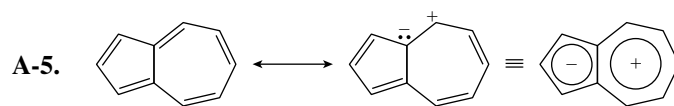
- B-1.** (b) **B-2.** (c) **B-3.** (a) **B-4.** (c)
B-5. (a) **B-6.** (d) **B-7.** (a) **B-8.** (a)
B-9. (a) **B-10.** (d)

CHAPTER 11

- A-1. (a) *m*-Bromotoluene (c) *o*-Chloroacetophenone
 (b) 2-Chloro-3-phenylbutane (d) 2,4-Dinitrophenol

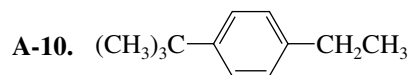
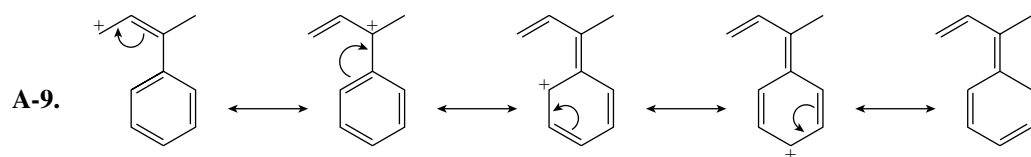
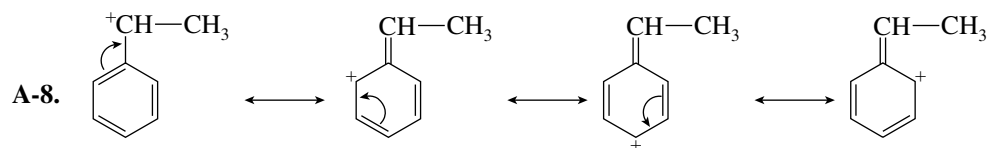
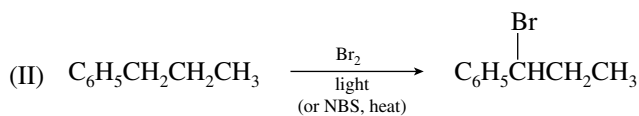
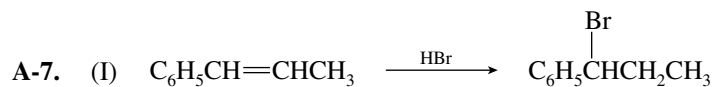
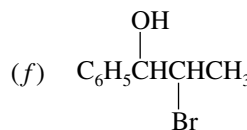
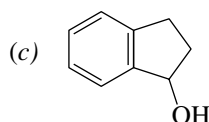
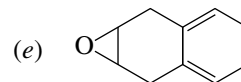


- A-4. (a) Eight π electrons. No, the substance is not aromatic.
 (b) 6 π electrons. Yes, it is aromatic.
 (c) 14 π electrons. Yes, it is aromatic.



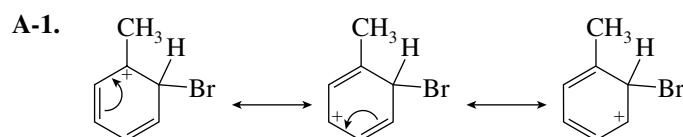
(d) $\text{Na}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4, \text{H}_2\text{O}, \text{heat}$

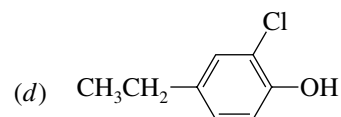
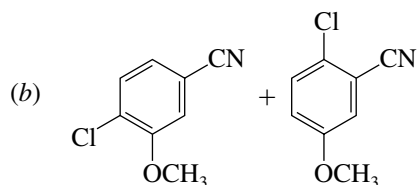
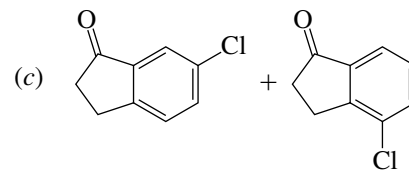
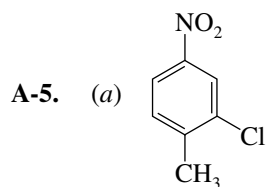
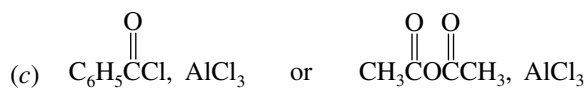
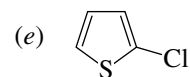
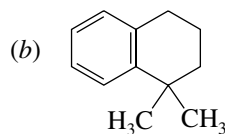
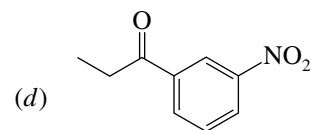
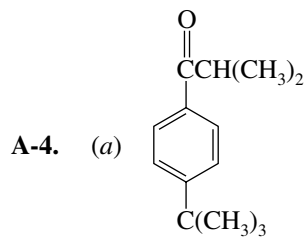
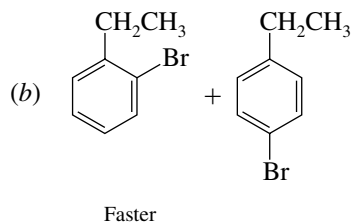
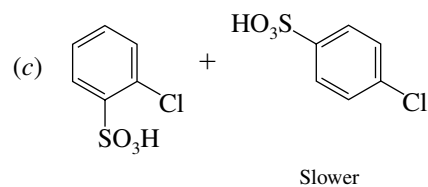
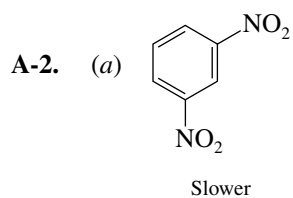
(b) $\text{C}_6\text{H}_5\text{CH}_2\text{X}$ (X = Cl, Br, I, OTs)



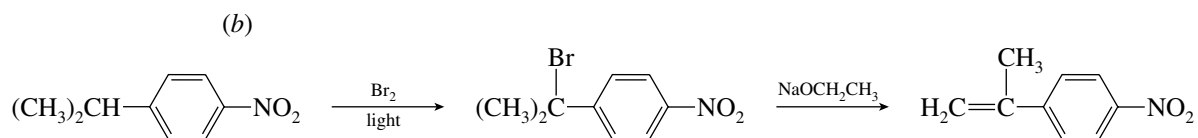
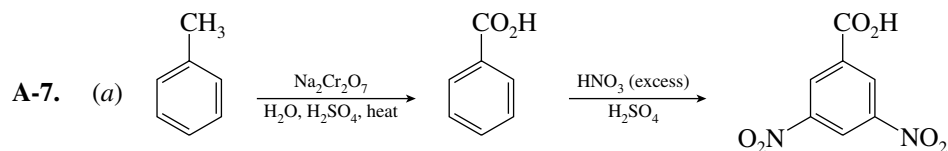
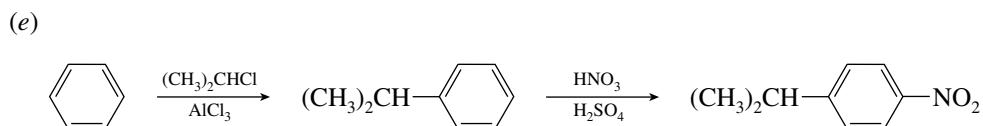
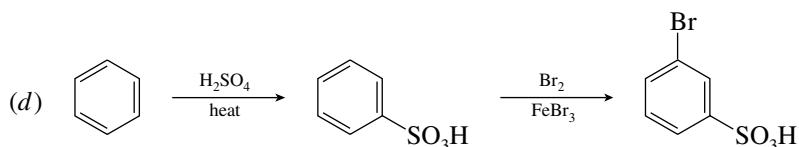
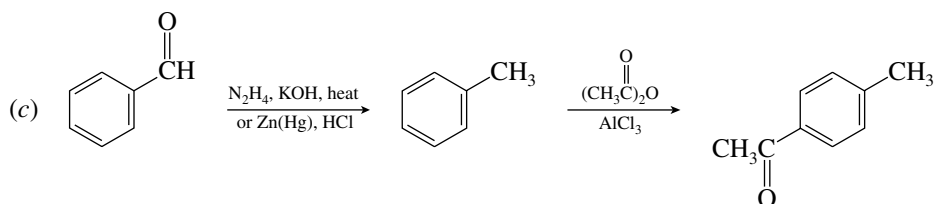
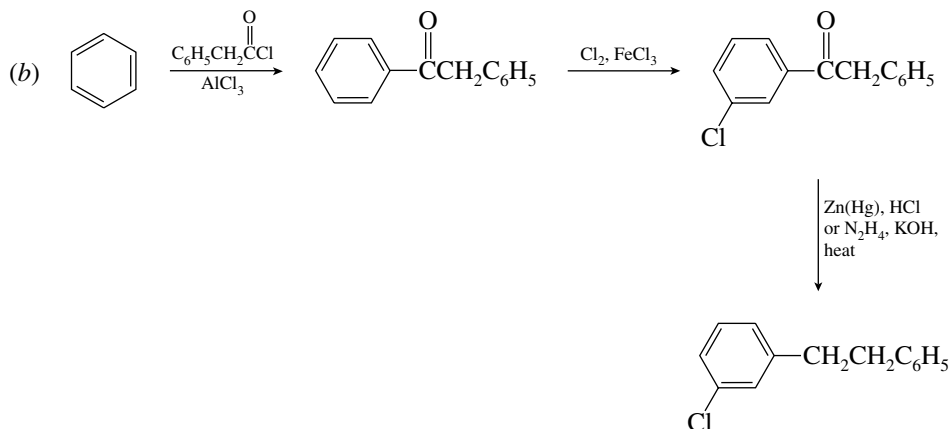
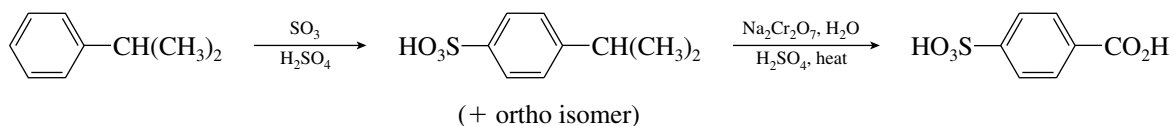
- B-1. (c) B-2. (c) B-3. (a) B-4. (b)
 B-5. (a) B-6. (d) B-7. (b) B-8. (d)
 B-9. (b) B-10. (d) B-11. (a) B-12. (b)
 B-13. (c) B-14. (d) B-15. (c)

CHAPTER 12





A-6. (a)



[Prepared from benzene as in
Problem A-6(e)]

A-6. Pentane: three signals; 2-methylbutane: four signals; 2,2-dimethylpropane: two signals

A-7. 2,3-Dimethylbutane: $(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)_2$

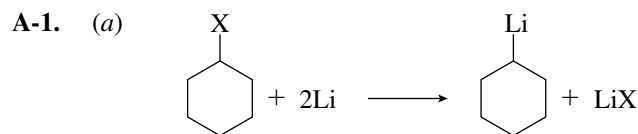
B-1. (d) B-2. (a) B-3. (b) B-4. (b)

B-5. (b) B-6. (a) B-7. (b) B-8. (a)

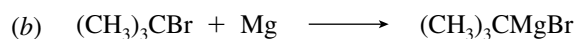
B-9. (c) B-10. (a) B-11. (c) B-12. (c)

B-13. (a) B-14. (a) B-15. (d)

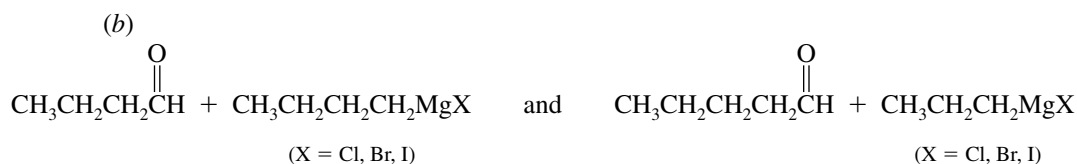
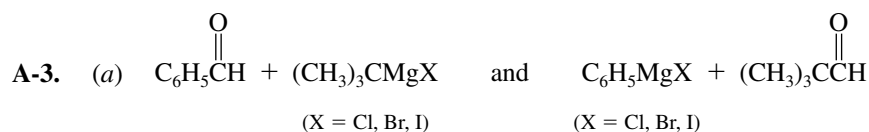
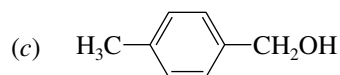
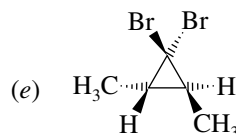
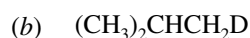
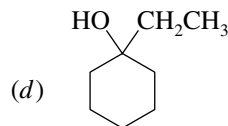
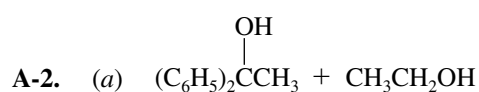
CHAPTER 14



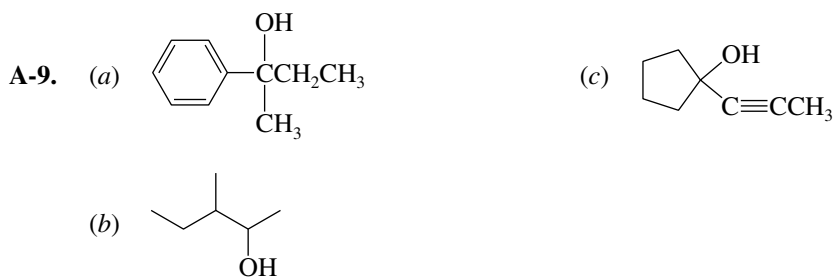
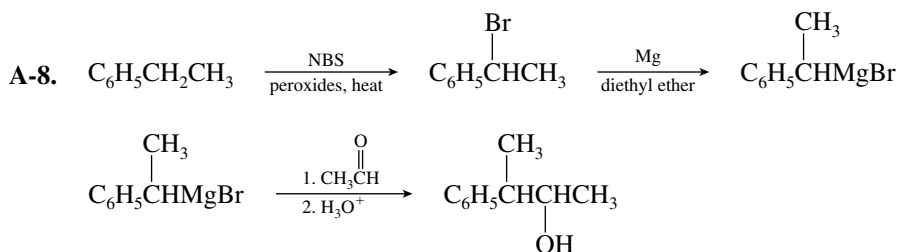
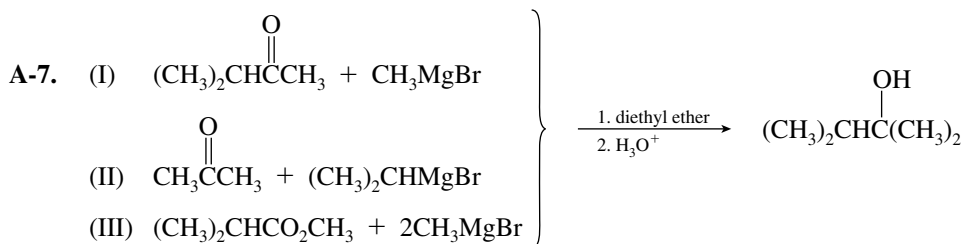
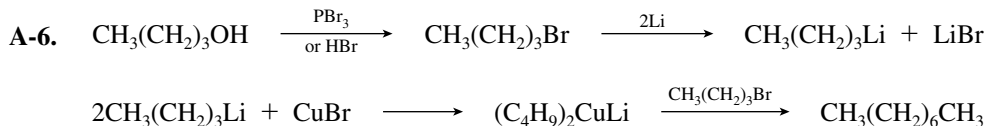
(X = Cl, Br, I)



(X = Cl, Br, I)

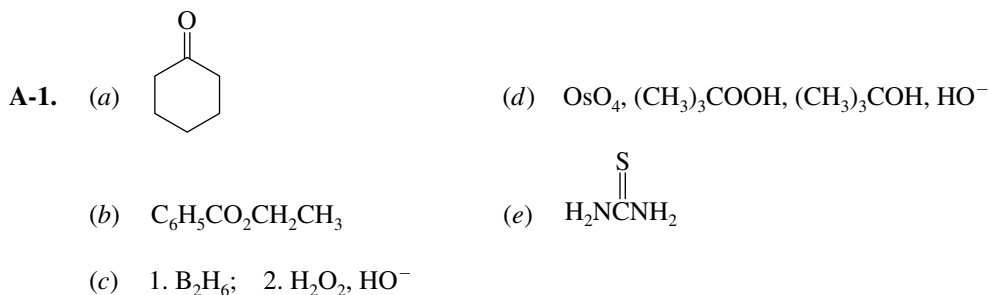


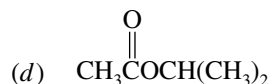
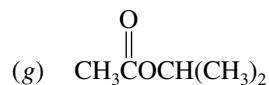
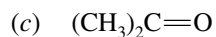
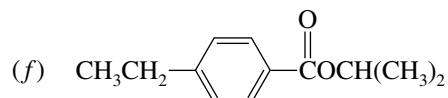
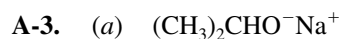
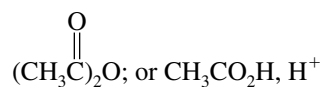
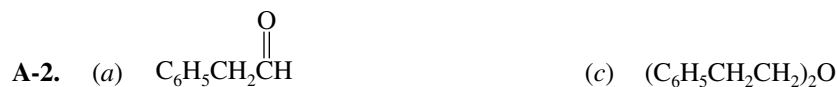
A-5. Solvents A, B, and E are suitable; they are all ethers. Solvents C and F have acidic hydrogens and will react with a Grignard reagent. Solvent D is an ester which will react with a Grignard reagent.



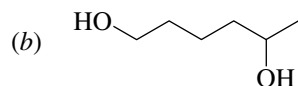
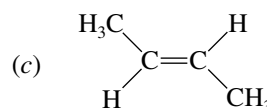
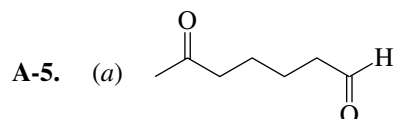
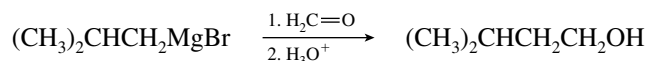
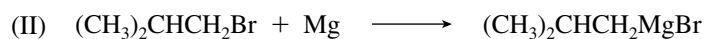
- B-1. (c) B-2. (a) B-3. (d) B-4. (a)
 B-5. (e) B-6. (c) B-7. (b) B-8. (a)
 B-9. (e) B-10. (b) B-11. (b) B-12. (b)

CHAPTER 15





A-4. (I)

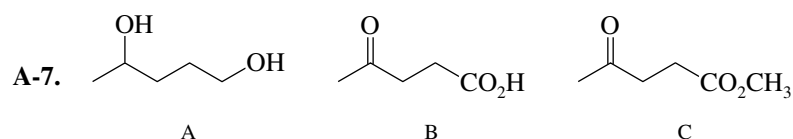


A-6. (a) PCC or PDC in CH_2Cl_2

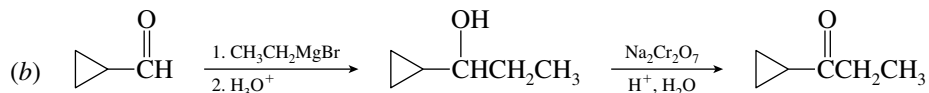
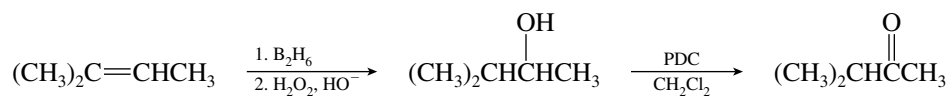
(b) $\text{Na}_2\text{Cr}_2\text{O}_7, \text{H}^+, \text{H}_2\text{O}$, heat

(c) 1. LiAlH_4 ; 2. H_2O

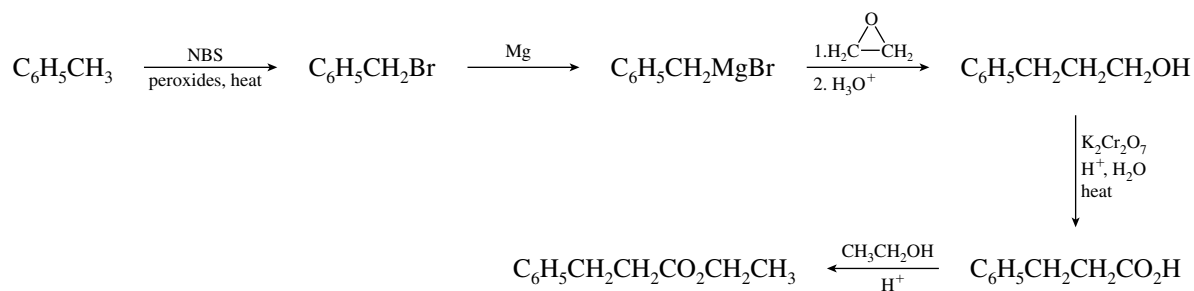
(d) $\text{OsO}_4, (\text{CH}_3)_3\text{COOH}, (\text{CH}_3)_3\text{COH}, \text{HO}^-$



A-8. (a)



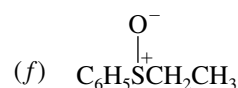
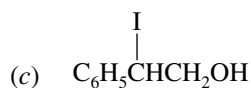
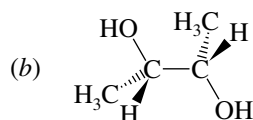
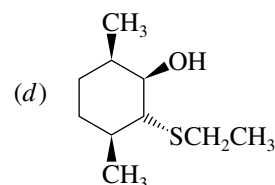
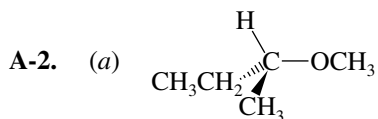
(c)

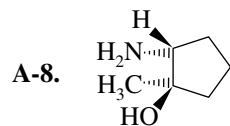
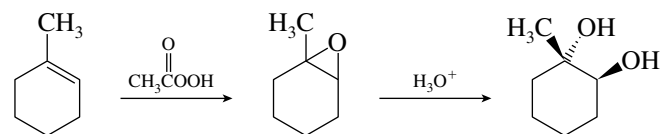
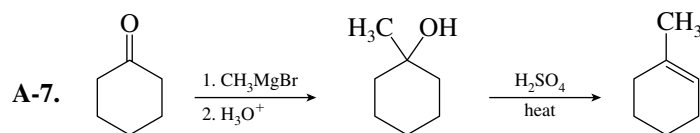
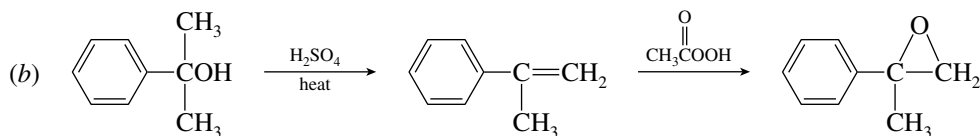
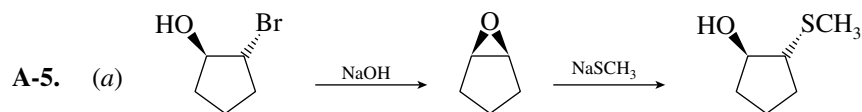
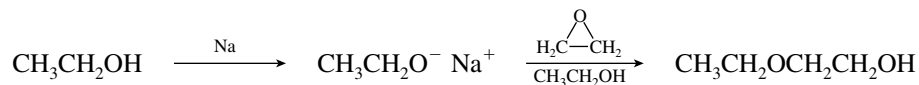
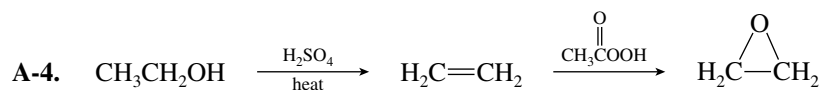
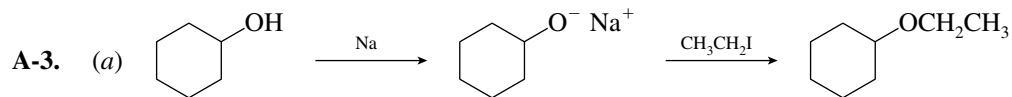


- B-1. (e) B-2. (d) B-3. (c) B-4. (c)
 B-5. (b) B-6. (b) B-7. (a) B-8. (a)
 B-9. (d) B-10. (a) B-11. (b) B-12. (d)
 B-13. (e) B-14. (a) B-15. (c)

CHAPTER 16

- A-1. $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$
Methyl propyl ether
 $\text{CH}_3\text{OCH}(\text{CH}_3)_2$
Isopropyl methyl ether
 $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
Diethyl ether



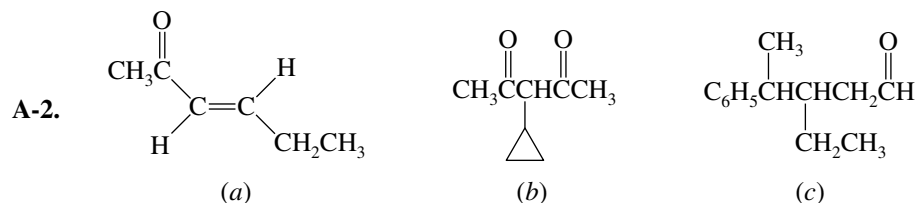


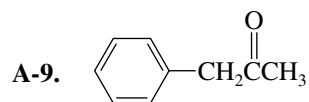
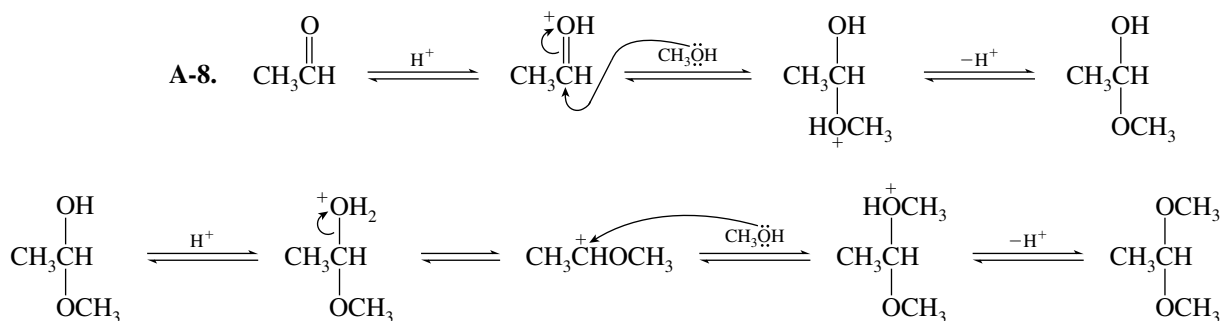
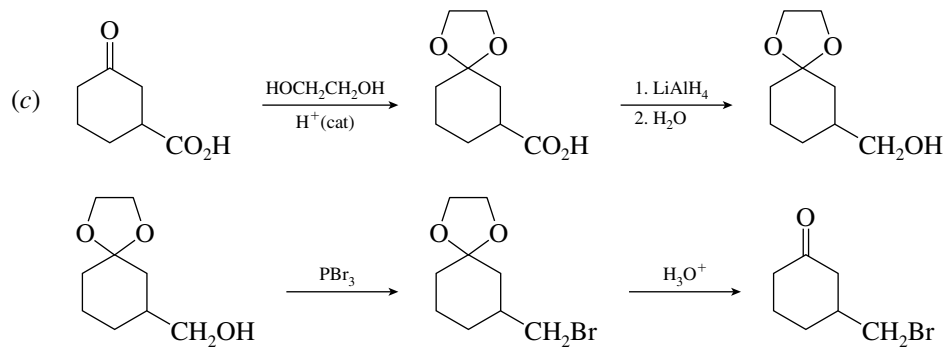
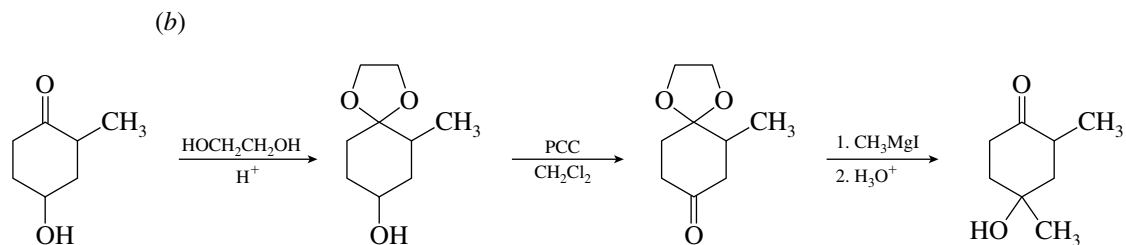
B-1. (a) B-2. (a) B-3. (c) B-4. (d) B-5. (d)

B-6. (e) B-7. (a) B-8. (c) B-9. (d) B-10. (d)

CHAPTER 17

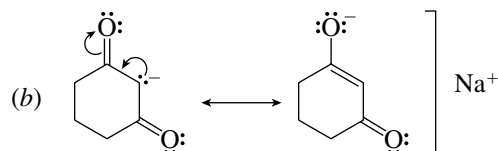
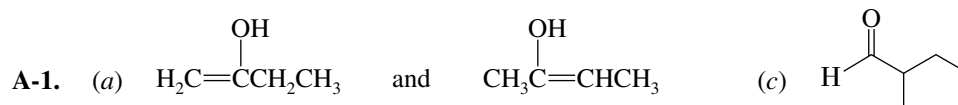
- A-1. (a) 3,4-Dimethylhexanal
 (b) 2,2,5-Trimethylhexan-3-one
 (c) *trans*-4-Bromo-2-methylcyclohexanone
 (d) 5-Methyl-4-hexen-3-one

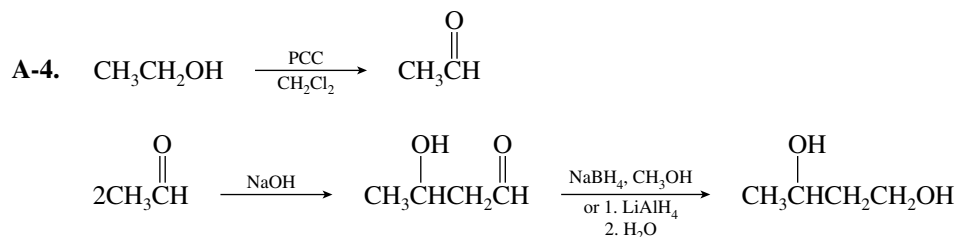
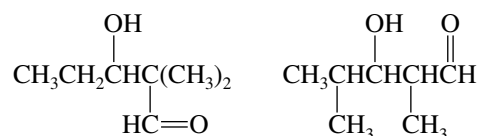
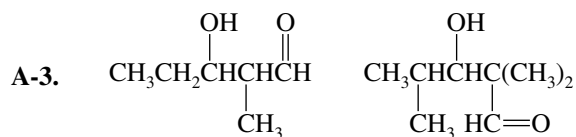
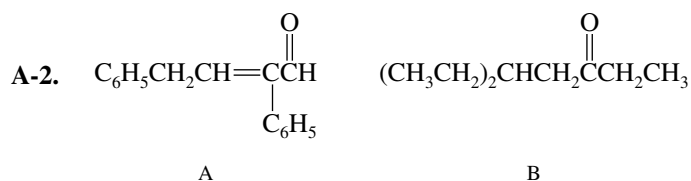




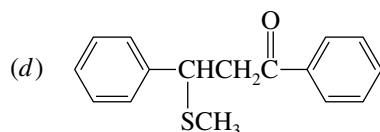
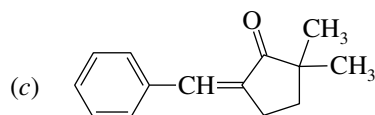
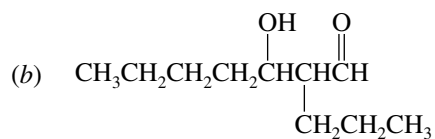
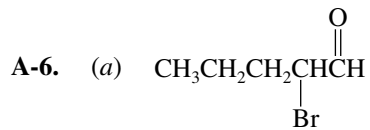
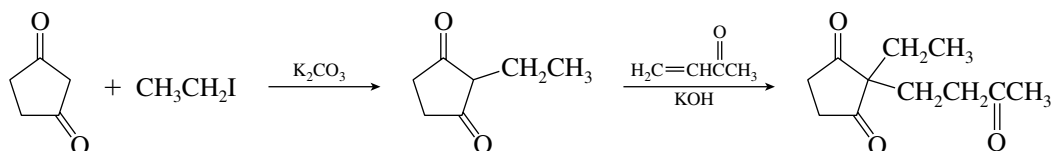
- | | | | |
|------------------|------------------|------------------|------------------|
| B-1. (c) | B-2. (d) | B-3. (a) | B-4. (c) |
| B-5. (b) | B-6. (b) | B-7. (a) | B-8. (b) |
| B-9. (e) | B-10. (c) | B-11. (c) | B-12. (c) |
| B-13. (d) | B-14. (e) | B-15. (a) | B-16. (c) |

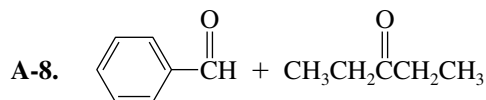
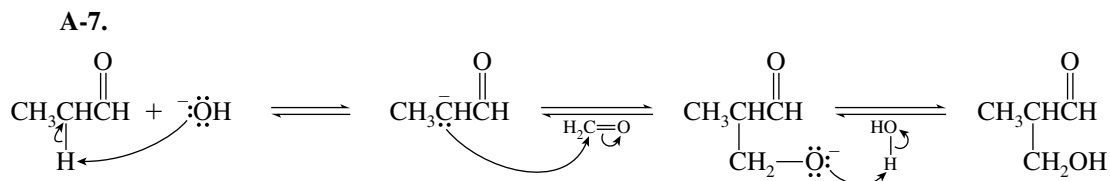
CHAPTER 18





A-5.





B-1. (a) B-2. (c) B-3. (b) B-4. (b)

B-5. (a) B-6. (c) B-7. (c) B-8. (e)

B-9. (c) B-10. (b) B-11. (a) B-12. (a)

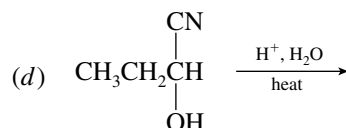
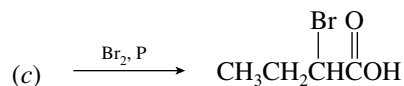
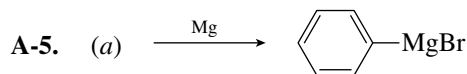
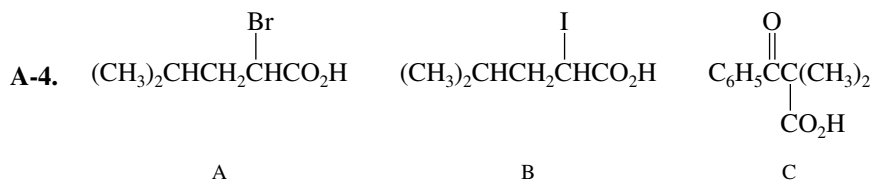
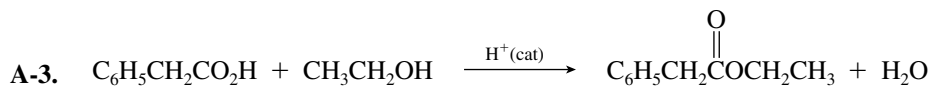
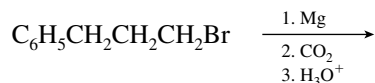
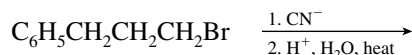
CHAPTER 19

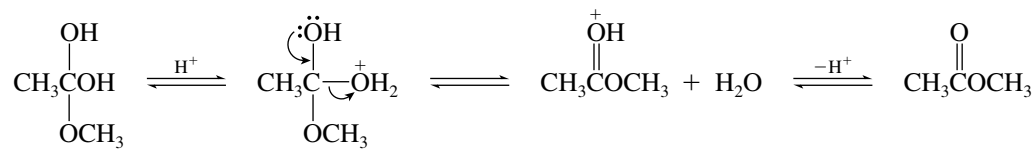
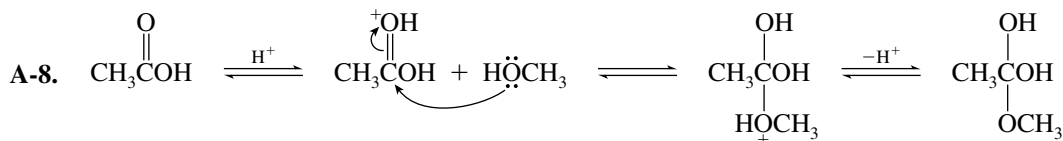
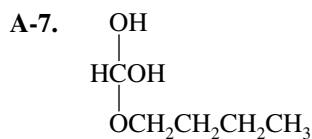
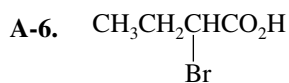
A-1. (a) 4-Methyl-5-phenylhexanoic acid

(b) Cyclohexanecarboxylic acid

(c) 3-Bromo-2-ethylbutanoic acid

A-2. 4-Phenylbutanoic acid is $C_6H_5CH_2CH_2CH_2CO_2H$.





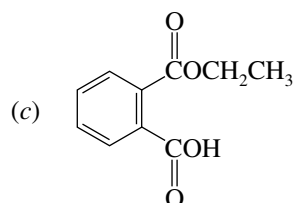
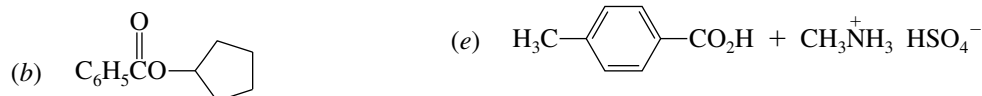
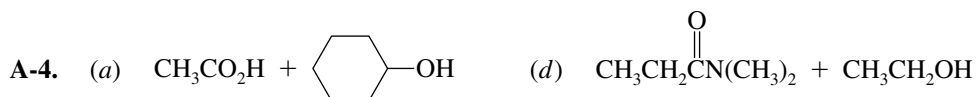
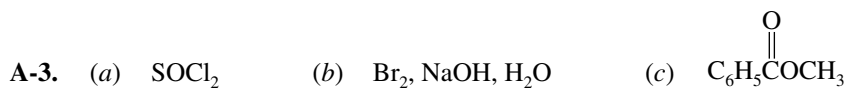
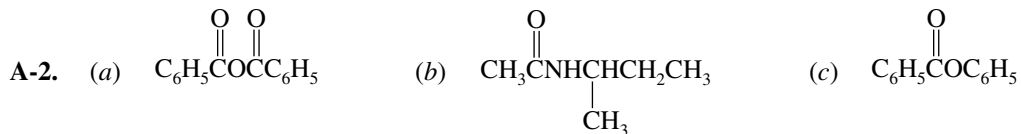
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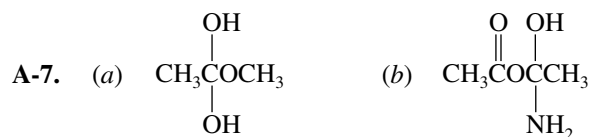
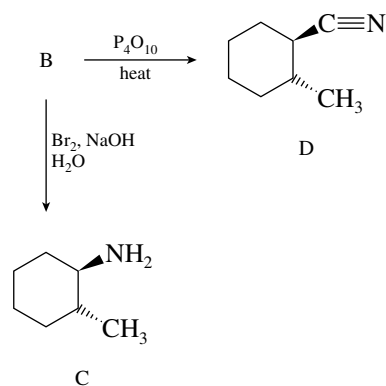
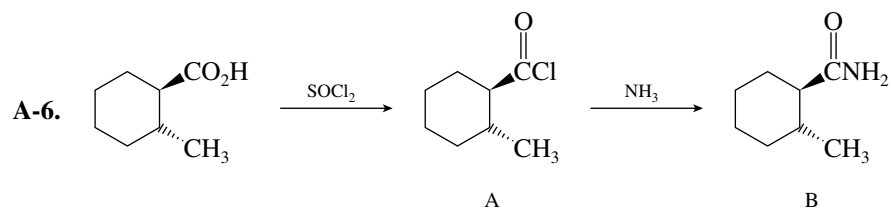
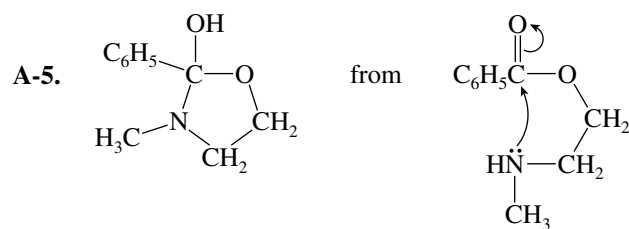
B-5. (c) B-6. (d) B-7. (c) B-8. (d)

B-9. (e) B-10. (c) B-11. (e)

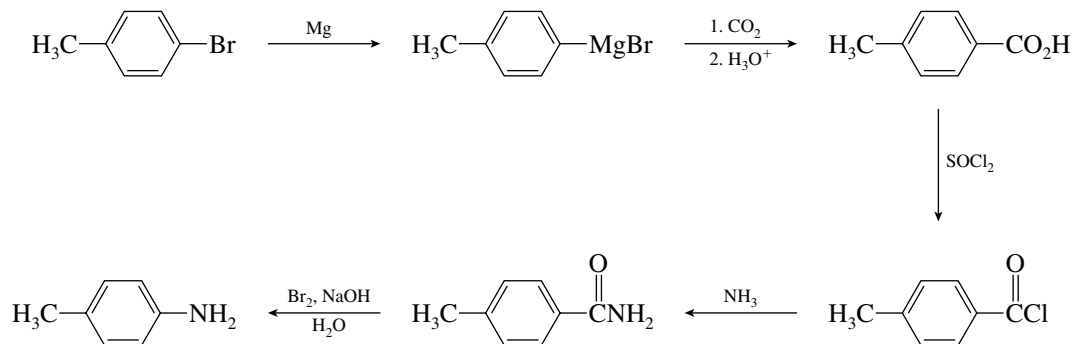
CHAPTER 20

A-1. (a) Propyl butanoate (c) 4-Methylpentanoyl chloride
 (b) *N*-Methylbenzamide

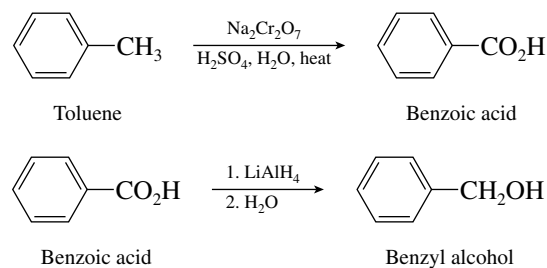


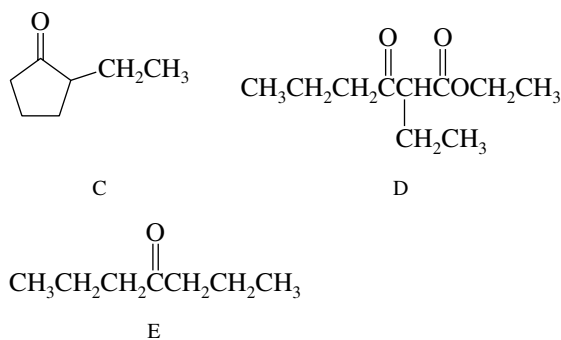


A-8.

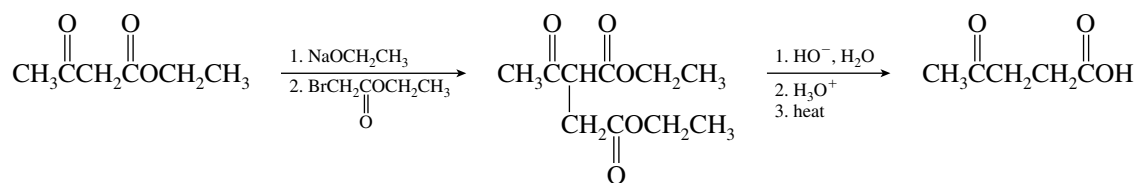


A-9.

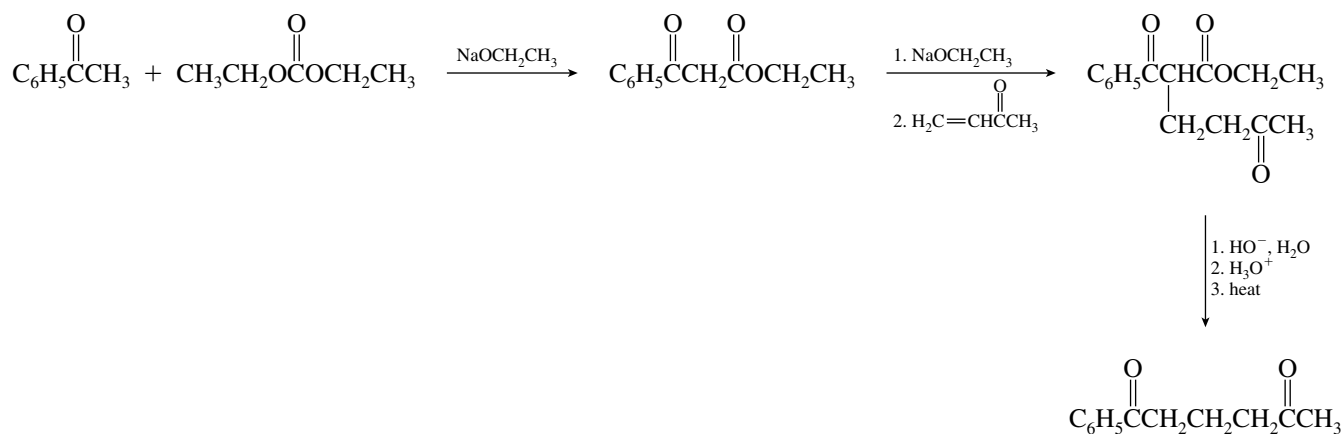




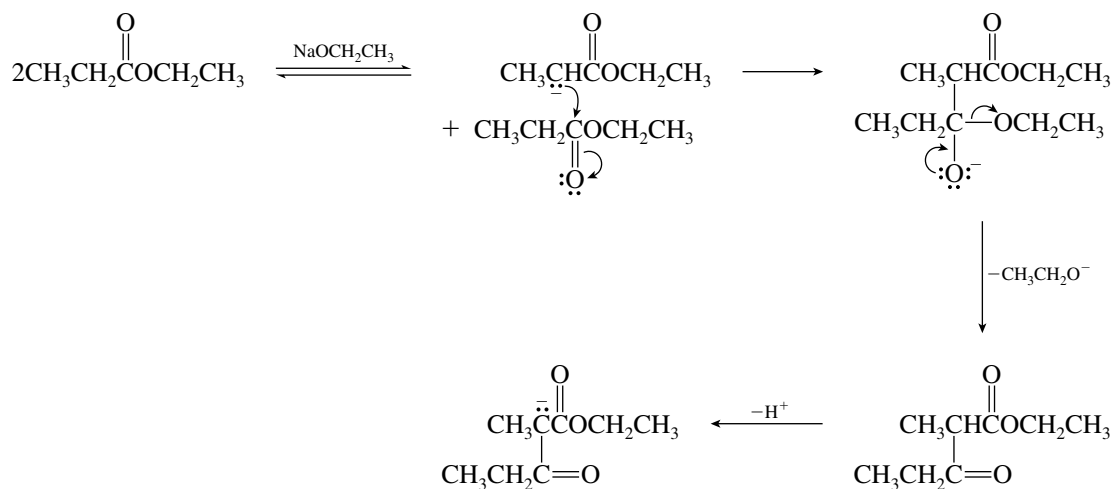
A-3. (a)



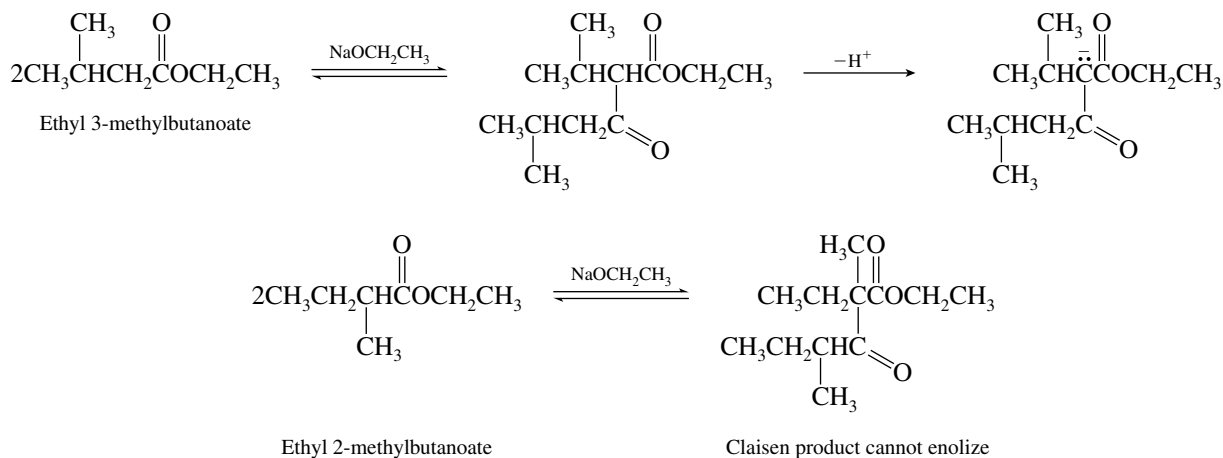
(b)



A-4.



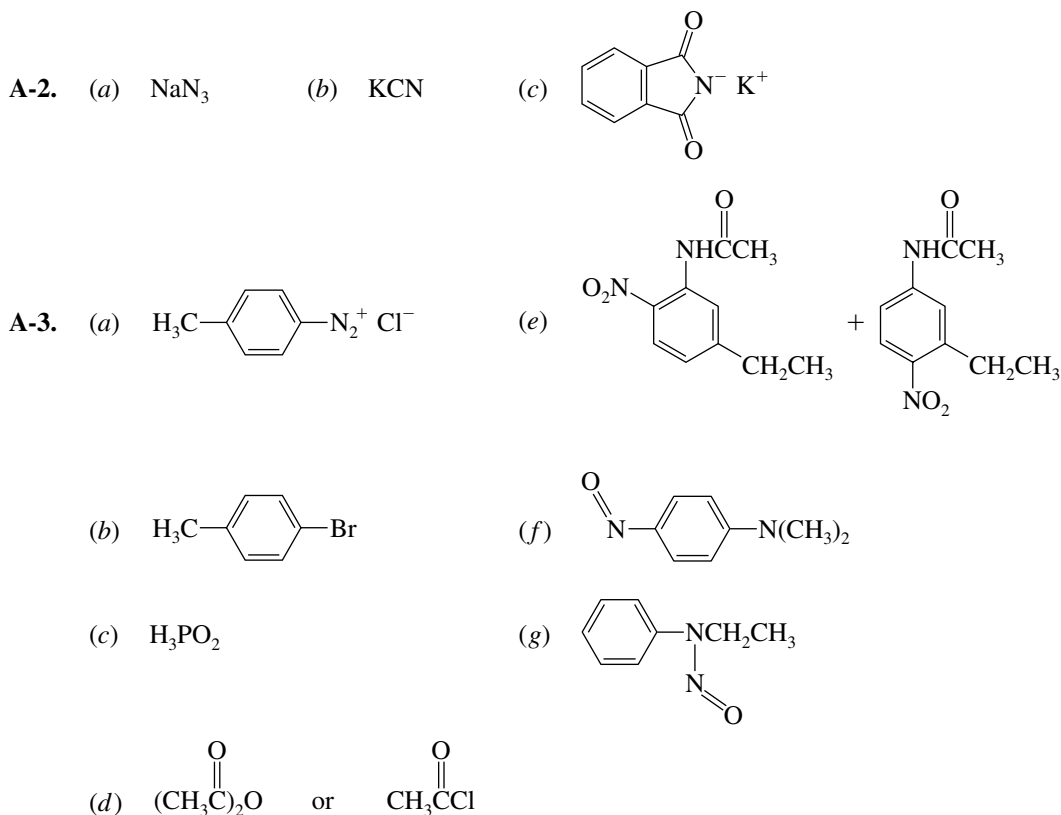
A-5. Enolization of the Claisen condensation product is necessary for completion of the reaction. The condensation product of ethyl 3-methylbutanoate can enolize; the product from condensation of ethyl 2-methylbutanoate cannot.

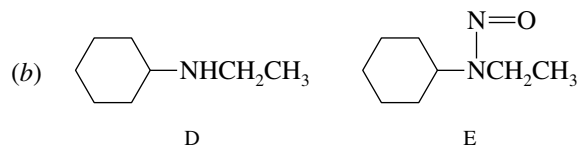
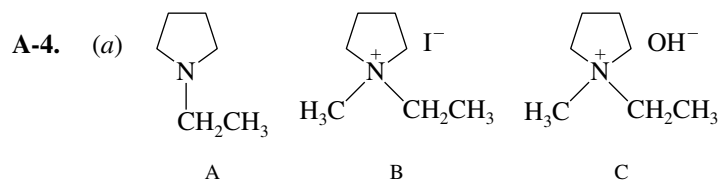


- B-1.** (b) **B-2.** (d) **B-3.** (c) **B-4.** (b)
B-5. (c) **B-6.** (c) **B-7.** (b) **B-8.** (d)

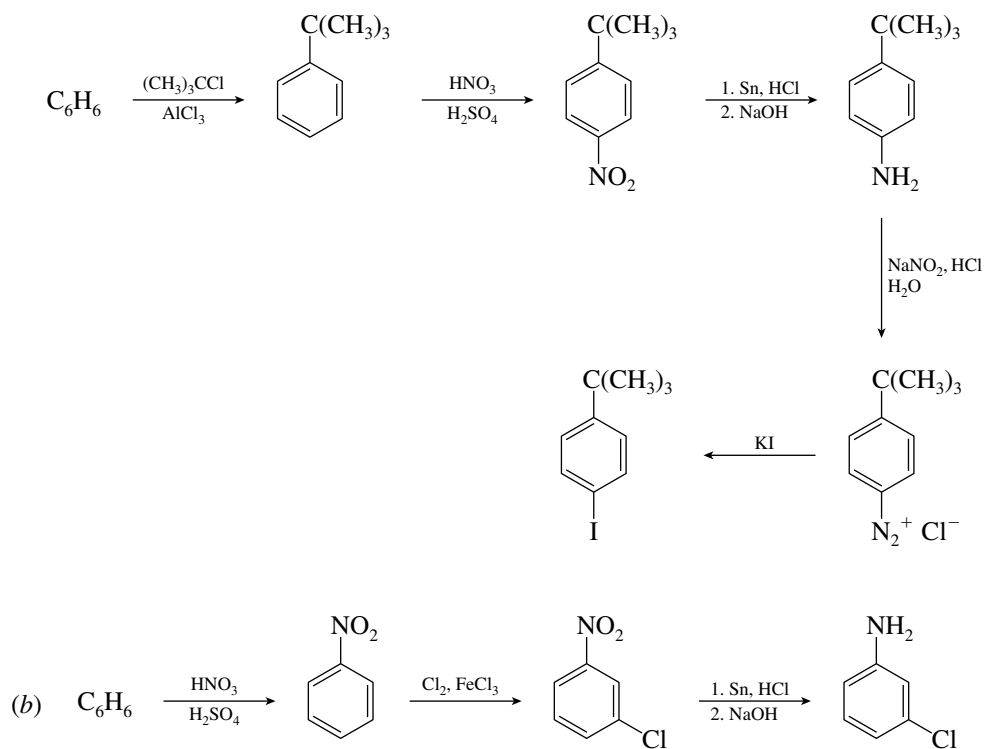
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- A-1.** (a) 1,1-Dimethylpropylamine or 2-methyl-2-butanamine; primary
 (b) *N*-Methylcyclopentylamine or *N*-methylcyclopentanamine; secondary
 (c) *m*-Bromo-*N*-propylaniline; secondary

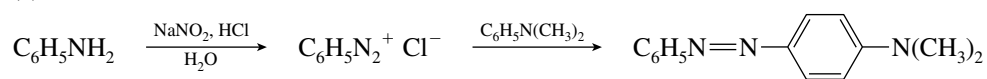




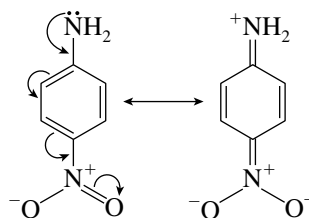
A-5. (a)



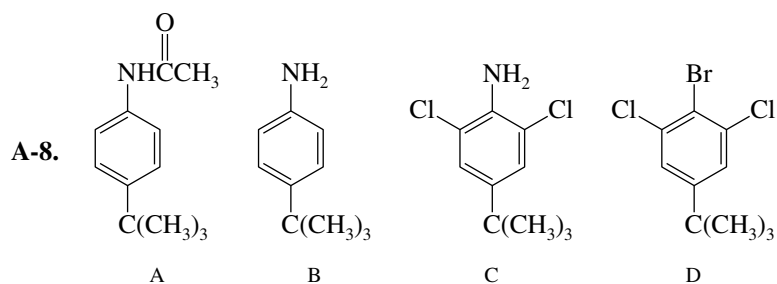
(c)



A-6. In the para isomer, resonance delocalization of the electron pair of the amine nitrogen involves the nitro group.

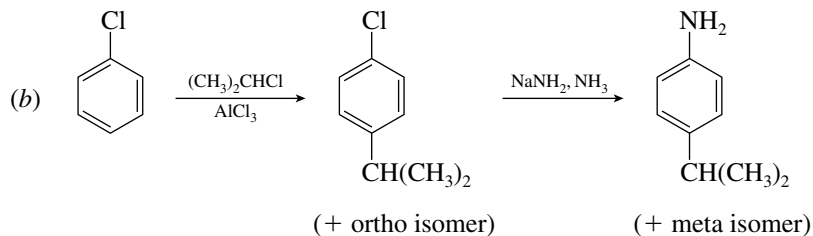
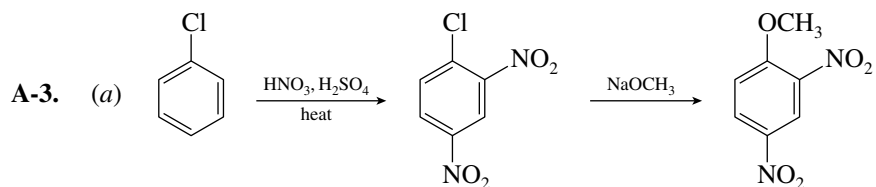
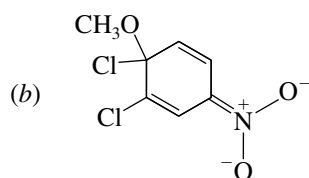
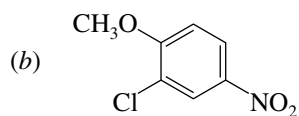
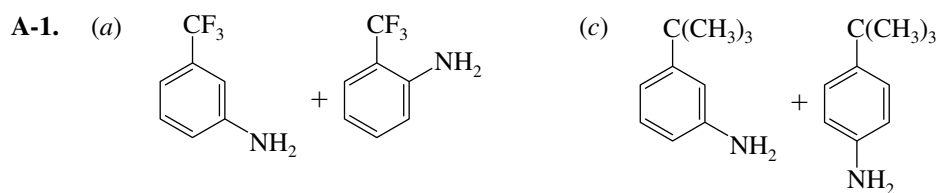


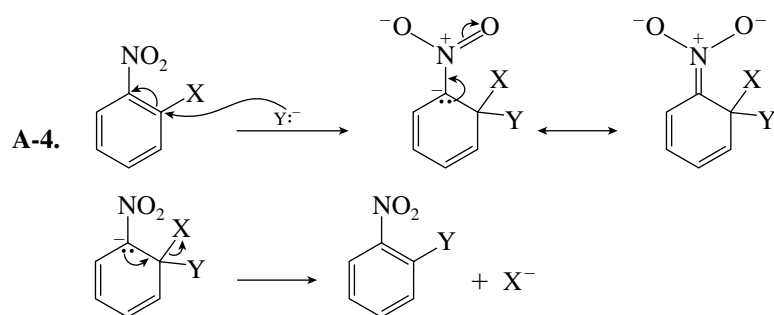
A-7. Strongest base: C, an alkylamine
Weakest base: D, a lactam (cyclic amide)



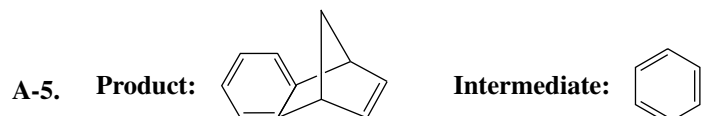
- B-1. (b) B-2. (d) B-3. (c) B-4. (d)
 B-5. (c) B-6. (e) B-7. (d) B-8. (c)
 B-9. (d) B-10. (e) B-11. (c) B-12. (b)
 B-13. (c) B-14. (c)

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The mechanism for para substitution is similar.

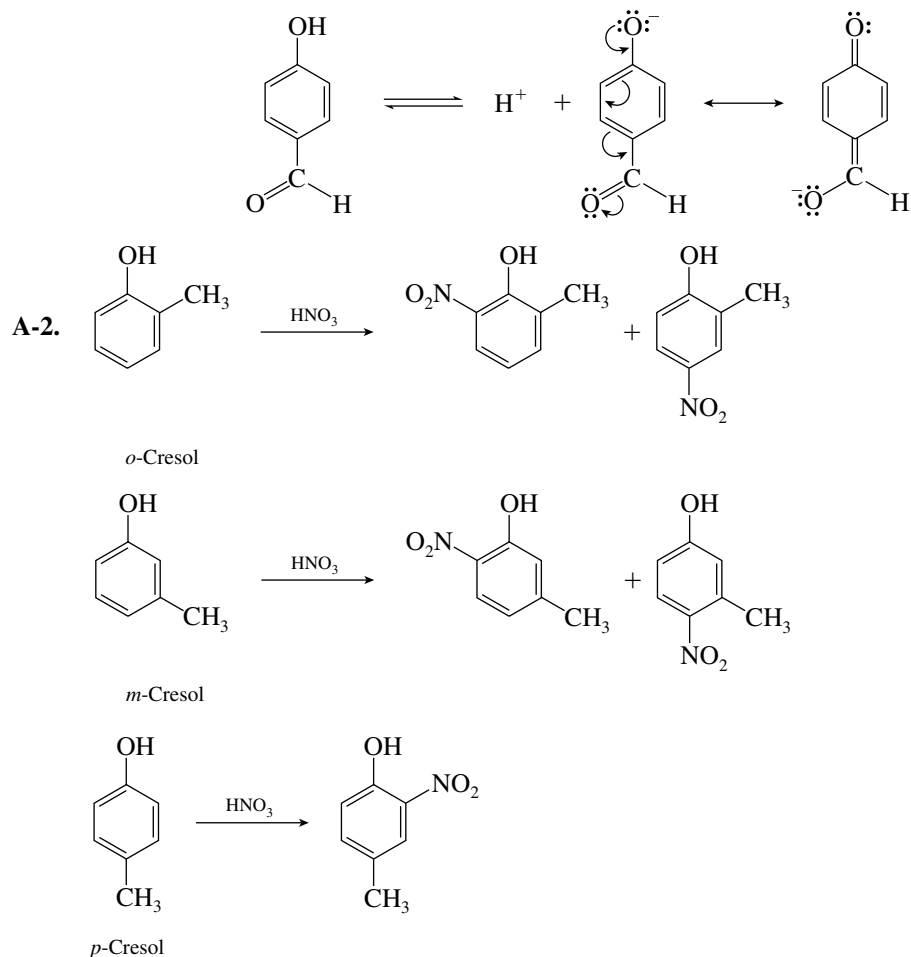


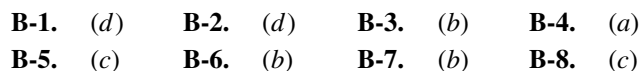
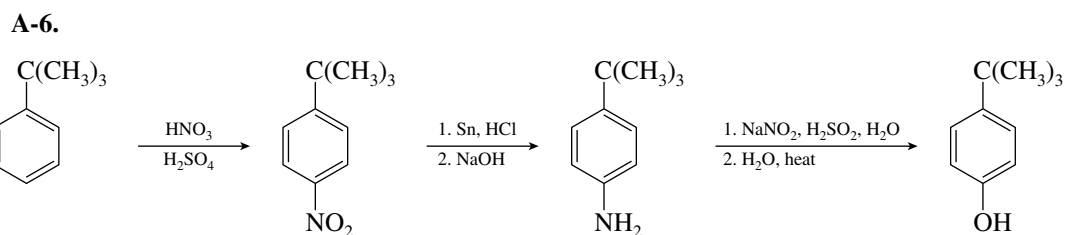
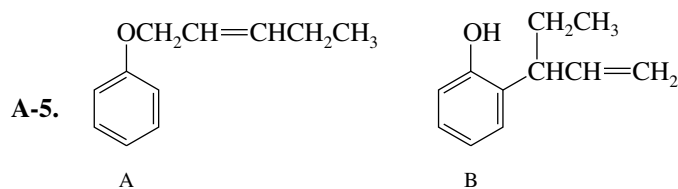
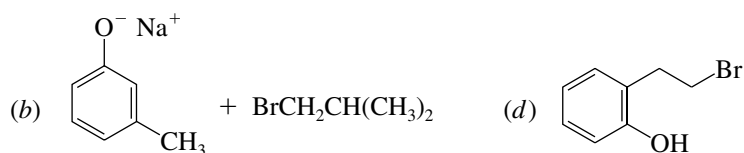
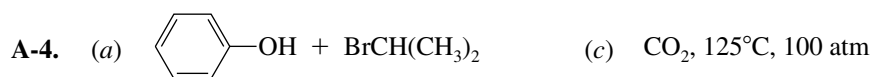
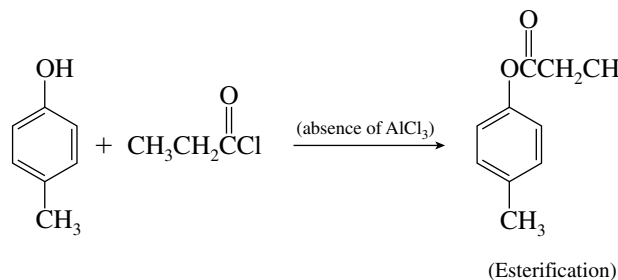
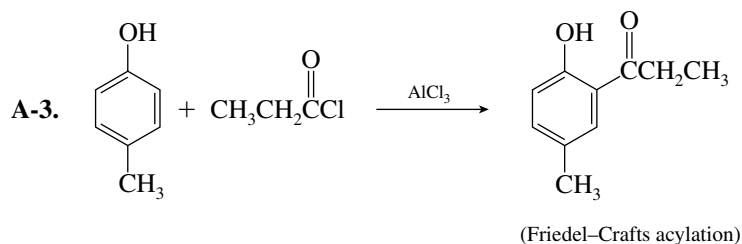
B-1. (a) B-2. (a) B-3. (c) B-4. (d)

B-5. (b) B-6. (a) B-7. (a) B-8. (a)

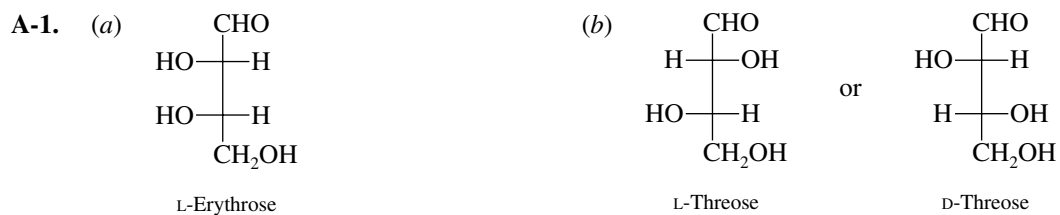
CHAPTER 24

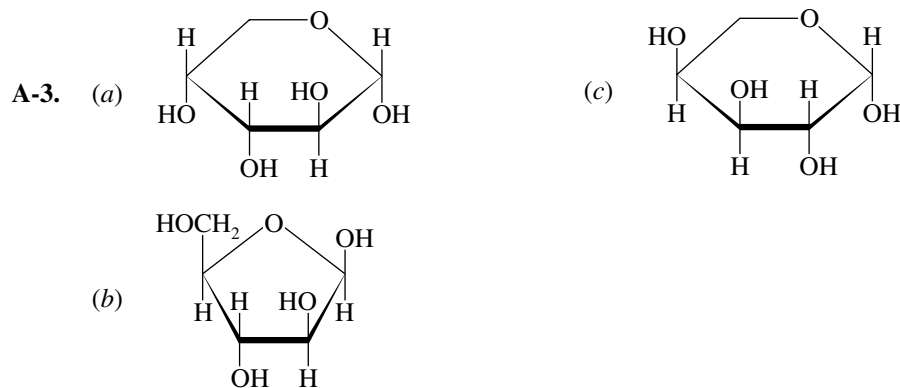
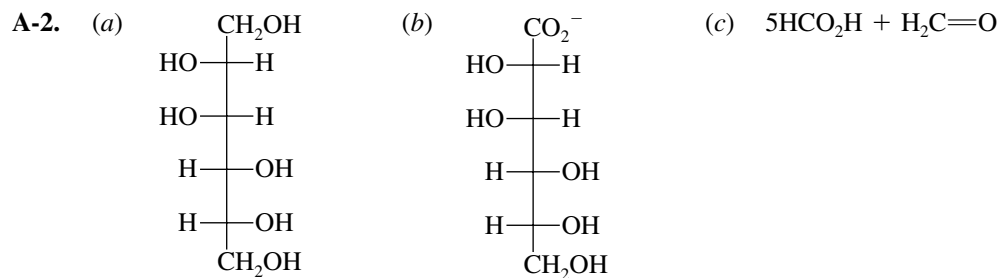
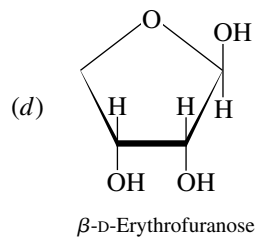
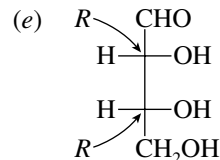
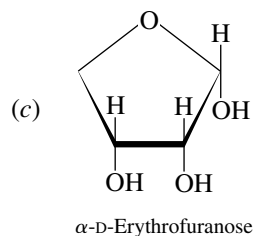
A-1. *p*-Hydroxybenzaldehyde is the stronger acid. The phenoxide anion is stabilized by conjugation with the aldehyde carbonyl.





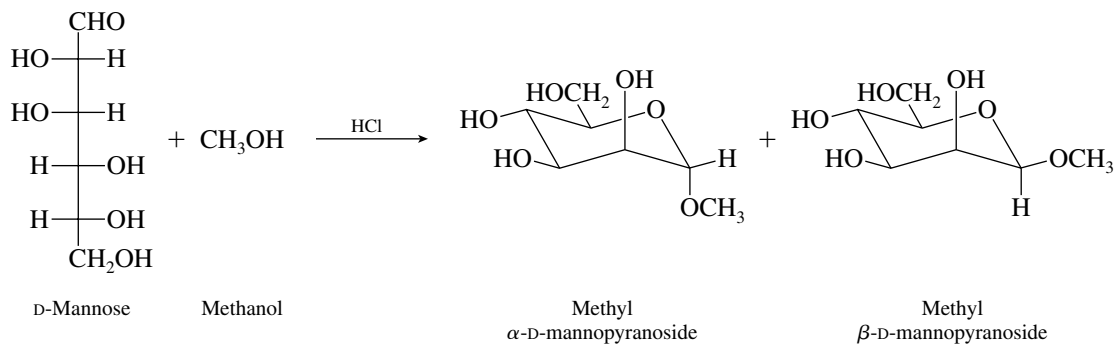
CHAPTER 25





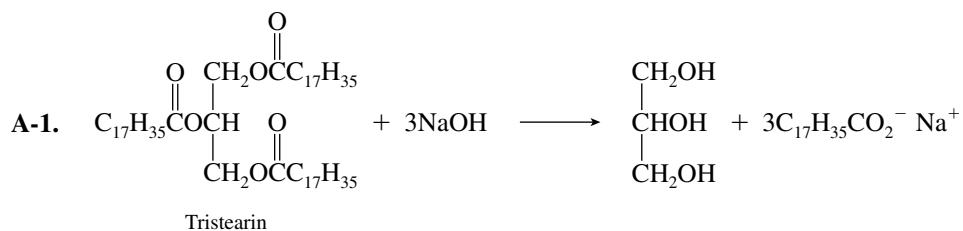
A-4. β -D-Idopyranose (β -pyranose form of D-idose)

A-5. The products are diastereomers.

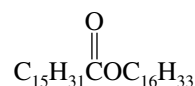


- B-1. (b) B-2. (d) B-3. (b) B-4. (a) B-5. (c)
 B-6. (c) B-7. (a) B-8. (c) B-9. (c) B-10. (c)

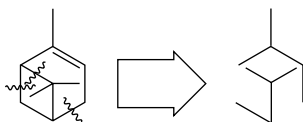
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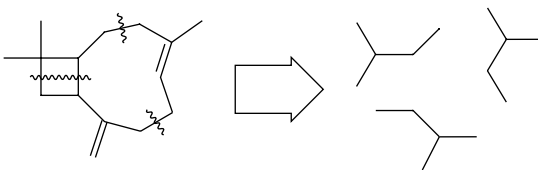
A-2. Fats are triesters of glycerol. A typical example is tristearin, shown in the preceding problem. A wax is usually a mixture of esters in which the alkyl and acyl group each contain 12 or more carbons. An example is hexadecyl hexadecanoate (cetyl palmitate).



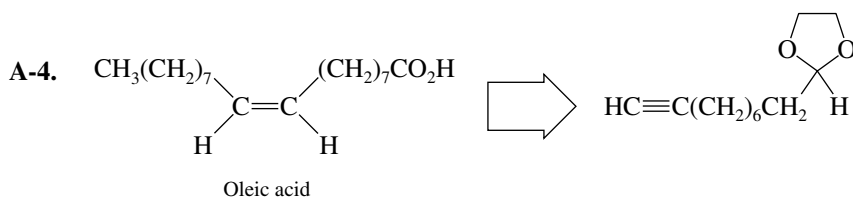
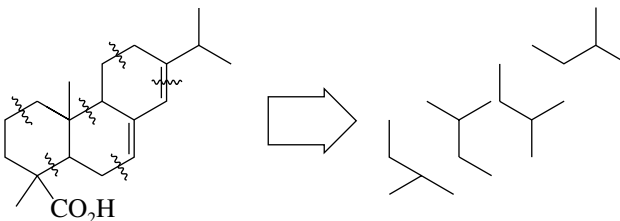
A-3. (a) Monoterpene;

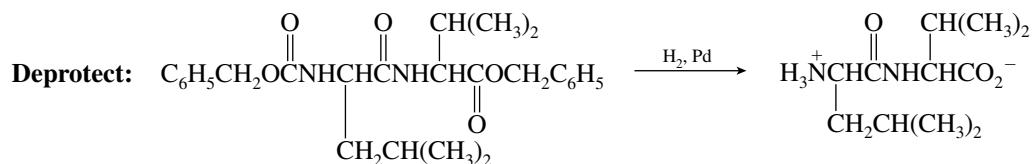
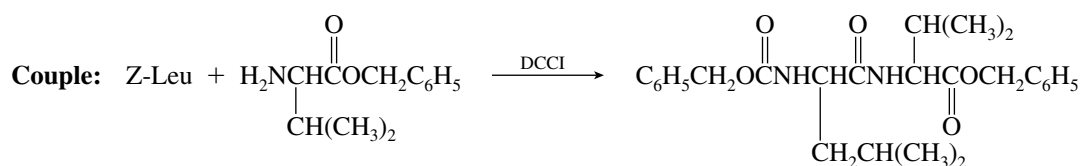
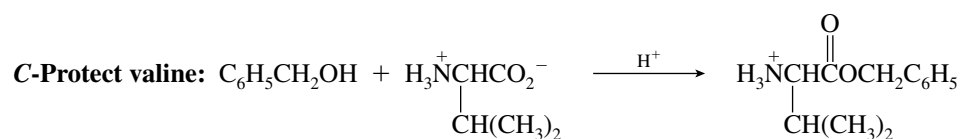
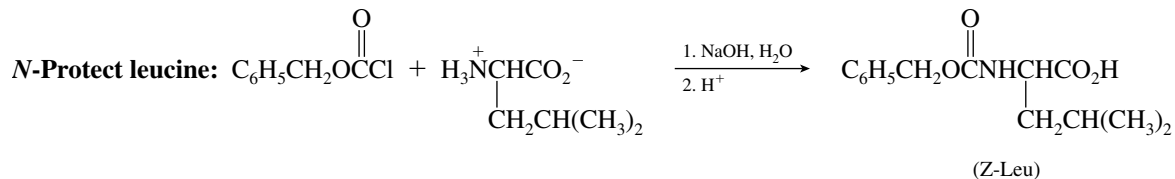
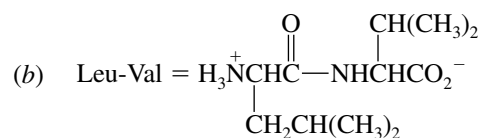


(b) Sesquiterpene;



(c) Diterpene;

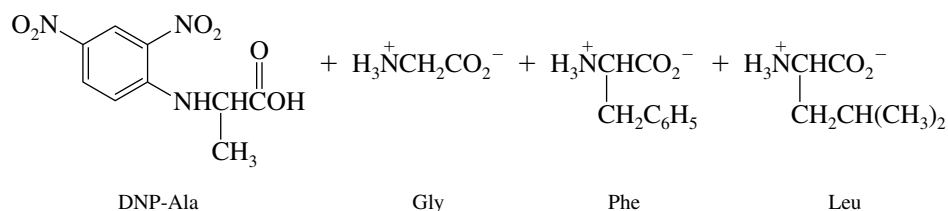


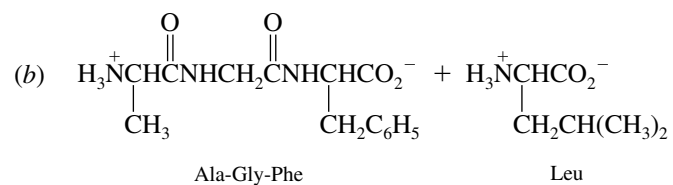


A-4. Leu-Val-Gly-Ala-Phe

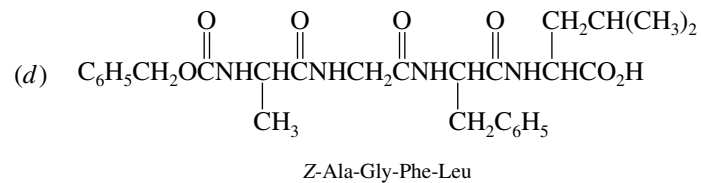
- A-5.** (a) Pentapeptide (c) Serine (e) Ser-Ala-Leu-Phe-Gly
 (b) Four (d) Glycine

A-6. (a)





(c) Same as part *b*; Ala-Gly-Phe + Leu



- B-1.** (c) **B-2.** (c) **B-3.** (a) **B-4.** (d)
B-5. (c) **B-6.** (b) **B-7.** (c) **B-8.** (a)

APPENDIX B

TABLES

Table B-1 Bond Dissociation Energies of Some Representative Compounds*

Bond	Bond dissociation energy, kJ/mol (kcal/mol)	Bond	Bond dissociation energy, kJ/mol (kcal/mol)
Diatomic molecules			
H—H	435 (104)	H—F	568 (136)
F—F	159 (38)	H—Cl	431 (103)
Cl—Cl	242 (58)	H—Br	366 (87.5)
Br—Br	192 (46)	H—I	297 (71)
I—I	150 (36)		
Alkanes			
CH ₃ —H	435 (104)	CH ₃ —CH ₃	368 (88)
CH ₃ CH ₂ —H	410 (98)	CH ₃ CH ₂ —CH ₃	355 (85)
CH ₃ CH ₂ CH ₂ —H	410 (98)	(CH ₃) ₂ CH—CH ₃	351 (84)
(CH ₃) ₂ CH—H	397 (95)	(CH ₃) ₃ C—CH ₃	334 (80)
(CH ₃) ₃ C—H	380 (91)		
Alkyl halides			
CH ₃ —F	451 (108)	(CH ₃) ₂ CH—F	439 (105)
CH ₃ —Cl	349 (83.5)	(CH ₃) ₂ CH—Cl	339 (81)
CH ₃ —Br	293 (70)	(CH ₃) ₂ CH—Br	284 (68)
CH ₃ —I	234 (56)	(CH ₃) ₃ C—Cl	330 (79)
CH ₃ CH ₂ —Cl	338 (81)	(CH ₃) ₃ C—Br	263 (63)
CH ₃ CH ₂ CH ₂ —Cl	343 (82)		
Water and alcohols			
HO—H	497 (119)	CH ₃ CH ₂ —OH	380 (91)
CH ₃ O—H	426 (102)	(CH ₃) ₂ CH—OH	385 (92)
CH ₃ —OH	380 (91)	(CH ₃) ₃ C—OH	380 (91)

*Note: Bond dissociation energies refer to bonds indicated in structural formula for each substance.

Table B-2 Acid Dissociation Constants*

Acid	Formula	Conjugate base	Dissociation constant	pK _a
Hydrogen fluoride	H—F	F^-	3.5×10^{-4}	3.5
Acetic acid	$\text{CH}_3\text{CO}_2\text{—H}$	CH_3CO_2^-	1.8×10^{-5}	4.7
Hydrogen cyanide	H—CN	CN^-	7.2×10^{-10}	9.1
Phenol	$\text{C}_6\text{H}_5\text{O—H}$	$\text{C}_6\text{H}_5\text{O}^-$	1.3×10^{-10}	9.8
Water	HO—H	HO^-	1.8×10^{-16}	15.7
Ethanol	$\text{CH}_3\text{CH}_2\text{O—H}$	$\text{CH}_3\text{CH}_2\text{O}^-$	10^{-16}	16
Alkyne (terminal; R = alkyl)	$\text{RC}\equiv\text{C—H}$	$\text{RC}\equiv\text{C}^-$	10^{-26}	26
Ammonia	$\text{NH}_2\text{—H}$	NH_2^-	10^{-36}	36
Alkene C—H	$\text{RCH}=\text{CH—H}$	$\text{RCH}=\text{CH}^-$	10^{-45}	45
Alkane C—H	$\text{RCH}_2\text{CH}_2\text{—H}$	$\text{RCH}_2\text{CH}_2^-$	10^{-62}	62

*Note: Acid strength decreases from top to bottom of the table; conjugate base strength increases from top to bottom.

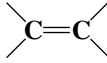

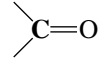
Table B-3 Chemical Shifts of Representative Types of Protons

Type of proton	Chemical shift (δ), ppm*	Type of proton	Chemical shift (δ), ppm*
$\text{H—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{—R}$	0.9–1.8	$\text{H—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{—NR}$	2.2–2.9
$\text{H—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{—C}=\text{C}$	1.6–2.6	$\text{H—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{—Cl}$	3.1–4.1
$\text{H—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$	2.1–2.5	$\text{H—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{—Br}$	2.7–4.1
$\text{H—C}\equiv\text{C—}$	2.5	$\text{H—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{—O}$	3.3–3.7
$\text{H—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{—Ar}$	2.3–2.8	H—NR	1–3 [†]
$\text{H—}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{=}\overset{\text{H}}{\text{C}}\text{—}$	4.5–6.5	H—OR	0.5–5 [†]
H—Ar	6.5–8.5	H—OAr	6–8 [†]
$\text{H—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$	9–10	$\text{H—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$	10–13 [†]

*These are approximate values relative to tetramethylsilane; other groups within the molecule can cause a proton signal to appear outside of the range cited.

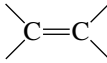
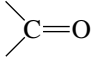
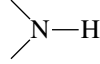
[†] The chemical shifts of protons bonded to nitrogen and oxygen are temperature- and concentration-dependent.

Table B-4 Chemical Shifts of Representative Carbons

Type of carbon	Chemical shift (δ), ppm*	Type of carbon	Chemical shift (δ), ppm*
RCH ₃	0–35		100–150
R ₂ CH ₂	15–40		
R ₃ CH	25–50		110–175
RCH ₂ NH ₂	35–50		
RCH ₂ OH	50–65		190–220
—C≡C—	65–90		

* Approximate values relative to tetramethylsilane.

Table B-5 Infrared Absorption Frequencies of Some Common Structural Units

Structural unit	Frequency, cm ⁻¹	Structural unit	Frequency, cm ⁻¹
Stretching vibrations			
<i>Single bonds</i>		<i>Double bonds</i>	
—O—H (alcohols)	3200–3600		1620–1680
—O—H (carboxylic acids)	2500–3600		
 N—H	3350–3500	Aldehydes and ketones	1710–1750
<i>sp</i> C—H	3310–3320	Carboxylic acids	1700–1725
<i>sp</i> ² C—H	3000–3100	Acid anhydrides	1800–1850 and 1740–1790
<i>sp</i> ³ C—H	2850–2950	Acyl halides	1770–1815
		Esters	1730–1750
<i>sp</i> ² C—O	1200	Amides	1680–1700
<i>sp</i> ³ C—O	1025–1200		
		<i>Triple bonds</i>	
		—C≡C—	2100–2200
		—C≡N	2240–2280
Bending vibrations of diagnostic value			
<i>Alkenes</i>		<i>Substituted derivatives of benzene</i>	
Cis-disubstituted	665–730	Monosubstituted	730–770 and 690–710
Trans-disubstituted	960–980	Ortho-disubstituted	735–770
Trisubstituted	790–840	Meta-disubstituted	750–810 and 680–730
		Para-disubstituted	790–840