SHORT ANSWER

Drawing Instructions: Draw structures corresponding to each of the given names.

1. Draw: cis-4-tert-butylecyclohexanol

ANS:

2. Draw: 3-methyl-2-buten-1-ol

ANS:

3. Draw: 2-phenyl-2-propanol

ANS:

4. Draw: glycerol

ANS:

5. Draw: 2, 4, 6-trinitrophenol

ANS:
**IUPAC Naming Instructions:** Provide proper IUPAC names.

6. Name:

\[
\text{HOCH}_2\text{CH}_2\text{OH}
\]

ANS:
(E)-2-ethylbut-2-en-1-ol

7. Name:

\[
\text{HOCH}_2\text{CH}_2\text{OH}
\]

ANS:
1, 2-ethanediol or ethylene glycol

8. Name:

\[
\text{HOCH}_2\text{CH}_2\text{OH}
\]

ANS:
allyl alcohol or 2-propen-1-ol

9. Name:

\[
\text{HOCH}_2\text{CH}_2\text{OH}
\]

ANS:
hydroquinone or p-dihydroxybenzene or 1,4-benzenediol

**Exhibit 17-1**
Rank the following groups of compounds from most acidic (1) to least acidic (4). Place the number corresponding to the compound's relative rank in the blank below the structure.

<table>
<thead>
<tr>
<th>NO₂</th>
<th>CH₂CH₂CH₂CH₂OH</th>
<th>NO₂</th>
<th>CH₂CH₂CH₂CHOH</th>
<th>NO₂</th>
<th>CH₂CH₂CH₂CH₂OH</th>
<th>NO₂</th>
<th>CH₂CH₂CH₂CH₂OH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

10.   ____   ____   ____   ____   ____
11. Explain why nonafluoro-2-methyl-2-propoxide is a much weaker base than tert-butoxide.

ANS:

Nonafluoro-2-methyl-2-propoxide anion is more stable than tert-butoxide anion because the electron-withdrawing fluoride atoms inductively delocalize the negative charge. Since nonafluoro-2-methyl-2-propoxide is more stable than tert-butoxide, it is a weaker base.
Exhibit 17-2
Refer to the data below to answer the following question(s).

$pK_a$s of Some Phenols

<table>
<thead>
<tr>
<th>$Y$</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>−H</td>
<td>9.89</td>
</tr>
<tr>
<td>$m$-NO$_2$</td>
<td>8.28</td>
</tr>
<tr>
<td>$p$-NO$_2$</td>
<td>7.17</td>
</tr>
<tr>
<td>$m$-OCH$_3$</td>
<td>9.65</td>
</tr>
<tr>
<td>$p$-OCH$_3$</td>
<td>10.21</td>
</tr>
</tbody>
</table>

14. Refer to Exhibit 17-2. The weakest acid in the table is:

ANS: $p$-methoxyphenol

15. Refer to Exhibit 17-2. Which of the acids in the Table has the weakest conjugate base?

ANS: $p$-nitrophenol

16. Refer to Exhibit 17-2. How do you account for the difference in acidity between meta and para-nitrophenol?

ANS:
In $m$-nitrophenol, the inductive effect of the electron-withdrawing nitro group helps to stabilize the negative charge on oxygen. However, when the nitro group is para to the oxygen, direct conjugation of the negative charge on oxygen with the nitro group can occur. $p$-Nitrophenolate ion is, thus, more stable than $m$-nitrophenolate ion, and, as a result, forms more readily.
Exhibit 17-3
To answer the following question(s), consider the reaction below:

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\rightarrow
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{CHOH} \\
\end{array}
\]

17. Refer to Exhibit 17-3. The best reagents for accomplishing the above transformation are:

a. 1. OsO₄, pyridine
   2. NaHSO₃, H₂O
b. 1. Hg(OAc)₂, H₂O
   2. NaBH₄
c. 1. RCO₂H, CH₂Cl₂
   2. H₂O⁺
d. 1. BH₃, THF
   2. H₂O₂, OH

ANS: d

d
18. Refer to Exhibit 17-3. The alcohol product is classified as a:

a. 1° alcohol
b. 2° alcohol
c. 3° alcohol
d. 4° alcohol

ANS: b

b

19. Refer to Exhibit 17-3. On the templates provided below, draw both conformations of the alcohol product. Circle the least stable conformation.
ANS:

Exhibit 17-4
To answer the following question(s), consider the reaction below:

21. Refer to Exhibit 17-4. On the structures provided below, draw arrows which account for the complete stepwise mechanism for this reaction.

ANS:
22. Refer to Exhibit 17-4. The dehydration of secondary and tertiary alcohols by reaction with 
POCl₃ in pyridine is an example of:

a. an E1 process  

b. an S_N1 process  

c. an E2 process  

d. an S_N2 process  

ANS: c

23. Refer to Exhibit 17-4. Why is 3-methylcyclohexene the major product of this reaction 
instead of 1-methylcyclohexene?

ANS: In E2 elimination, dehydration proceeds most readily when the two groups to be eliminated have a 
trans-diaxial relationship. In this compound, the only hydrogen with the proper geometric 
relationship to the –OH group is at C₆ so the major product of this reaction is 3-
methylcyclohexene.

24. Acid-catalyzed dehydration of 2,2-dimethylcyclohexanol yields 1,2-dimethylcyclohexene as 
one of the major products. Write the complete stepwise mechanism for this reaction. Show 
all electron flow with arrows and show all intermediate structures.

ANS:
Exhibit 17-5
To answer the following question(s), consider the reaction below:

\[
\begin{align*}
\text{HO} & \quad \text{H} & \quad \text{SOCl}_2 & \quad \text{H} & \quad \text{Cl} & \quad \text{SO}_2 & \quad \text{HCl}
\end{align*}
\]

25. Refer to Exhibit 17-5. Provide the complete IUPAC name for the starting material in this reaction.

ANS:
(R)-2-heptanol

26. Refer to Exhibit 17-5. The starting material can be classified as a:

a. 1° alcohol  
b. 2° alcohol  
c. 3° alcohol  
d. 4° alcohol

ANS: b

27. Refer to Exhibit 17-5. Write the complete stepwise mechanism for the reaction. Show all intermediates and all electron flow with arrows.

ANS:
28. Refer to Exhibit 17-5. The conversion of an alcohol into an alkyl chloride by reaction with \( \text{SOCl}_2 \) is an example of:

a. an E1 process  
b. an \( S_N 1 \) process  
c. an E2 process  
d. an \( S_N 2 \) process  

ANS:  
d

**Exhibit 17-6**  
Consider the Grignard reaction below to answer the following question(s).

![Grignard reaction diagram]

29. Refer to Exhibit 17-6. The electrophile in this reaction is:

ANS:  
B

30. Refer to Exhibit 17-6. The nucleophile in this reaction is:

ANS:  
A

31. Refer to Exhibit 17-6. The alcohol product can be classified as a:

a. 1° alcohol  
b. 2° alcohol  
c. 3° alcohol  
d. 4° alcohol  

ANS:  
c
A highly useful and general method for the synthesis of alcohols is the addition of Grignard reagents to carbonyl compounds. Show what Grignard reagent and what carbonyl compound you would start with to prepare each alcohol below. List all possibilities.

32. ANS:

33. ANS:
34. \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \]
\[ \text{CH}_2\text{CH}_3 \]

ANS:
\[ \text{H} - \text{C} - \text{H} + \text{BrMg} - \text{CHCH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CHCH}_2\text{OH} \]

35. 

ANS:
\[ \text{CH}_3\text{C} = \text{CH} \]
\[ \text{OH} \]

Exhibit 17-8
Give the major organic product(s) of the following reactions or sequences of reactions. Show all relevant stereochemistry.

36. 

ANS:
\[ \text{OH} \]
\[ \text{CrO}_3, \text{H}_2\text{SO}_4, \text{H}_2\text{O}, \text{acetone} \]

\[ \text{OH} \]
\[ \text{OH} \]

\[ \text{OH} \]
\[ \text{CrO}_3, \text{H}_2\text{SO}_4, \text{H}_2\text{O}, \text{acetone} \]

\[ \text{OH} \]
\[ \text{CrO}_3, \text{H}_2\text{SO}_4, \text{H}_2\text{O}, \text{acetone} \]

\[ \text{OH} \]
\[ \text{CrO}_3, \text{H}_2\text{SO}_4, \text{H}_2\text{O}, \text{acetone} \]
Alcohols and Phenols

37. ANS:

38. ANS:

39. ANS:
40. ANS:

\[
\begin{align*}
\text{CH}_3\text{C}\text{CH}_2\text{OH} & \xrightarrow{\text{H}_2\text{O}^+} \text{CH}_3\text{C}==\text{C} \text{CH}_3 \\
\text{CH}_3\text{C}\text{CH}_2\text{OH} & \xrightarrow{\text{H}_2\text{O}^+} \text{CH}_3\text{C}==\text{C} \text{CH}_3
\end{align*}
\]

41. ANS:

\[
\begin{align*}
\text{C}==\text{OCH}_3 + 2 \text{C}==\text{MgBr} & \xrightarrow{1. \text{ether}} \text{C}==\text{OCH}_3 + 2 \text{C}==\text{MgBr} \\
\text{C}==\text{OCH}_3 + 2 \text{C}==\text{MgBr} & \xrightarrow{2. \text{H}_2\text{O}^+} \text{C}==\text{OCH}_3 + 2 \text{C}==\text{MgBr}
\end{align*}
\]

42. ANS:

\[
\begin{align*}
\text{C}==\text{OH} & \xrightarrow{1. \text{LiAlH}_4, \text{ether}} \text{C}==\text{OH} \\
\text{C}==\text{OH} & \xrightarrow{2. \text{H}_2\text{O}^+} \text{C}==\text{OH}
\end{align*}
\]
Alcohols and Phenols

43. Ans:

44. Ans:

45. Ans:

46. Ans:
47. \[
\begin{align*}
\text{ANS:} \quad & \quad \begin{array}{c}
\text{OH} \\
CH_3
\end{array} \\
& \xrightarrow{(KSO_3)_2\text{NO}} \\
& \xrightarrow{\text{H}_2\text{O}} \\
\end{align*}
\]

48. \[
\begin{align*}
\text{ANS:} \quad & \quad \begin{array}{c}
\text{OH} \\
CH_3
\end{array} \\
& + \quad \begin{array}{c}
\text{(CH}_3\text{)}_2\text{C} \\
\text{= CH}_2
\end{array} \\
& \xrightarrow{\text{H}_2\text{SO}_4} \\
\end{align*}
\]

49. \[
\begin{align*}
\text{ANS:} \quad & \quad \begin{array}{c}
\text{OH} \\
\text{(CH}_3\text{)}_3\text{C}
\end{array} \\
& + \quad \begin{array}{c}
\text{CH}_3
\end{array} \\
& \xrightarrow{\text{NaBH}_4} \\
& \text{alcohol}
\end{align*}
\]
Alcohols and Phenols

Exhibit 17-9

Choose the best reagent(s) for carrying out the following conversions from the list provided below. Place the letter of the best choice in the blank to the left of the conversion. Reagents may be used more than once.

a. 1. CH₃MgBr, ether
   2. H₂O⁺

b. 1. PBr₃
   2. NaOH

c. 1. (CH₃)₃SiCl, (CH₃CH₂)₃N
   2. CH₃MgBr, ether
   3. H₂O⁺

d. 1. LiAlH₄, ether
   2. H₂O⁺

b. 1. p-TosCl, pyridine
   2. NaOH

e. 1. CrO₃, H₂SO₄, H₂O

f. NaBH₄, ethanol

1. H₂O⁺

h. Dess–Martin periodinane, CH₂Cl₂

50. _____

ANS: f

51. _____

ANS: g

52. _____

ANS: h
53. \[ \text{HO} \quad \text{CH}_3 \quad \text{HO} \]

ANS: c

54. \[ \text{HO} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{HO} \]

ANS: e

55. Propose a synthesis of Dimestrol starting from \( p \)-methoxypropiophenone as the only source of carbon.

\[
\begin{align*}
\text{H}_3\text{CO} & \quad \text{O} \\
\text{H}_3\text{CO} & \quad \text{NaBH}_4 \\
\text{H}_3\text{CO} & \quad \text{H}_2\text{CO} \\
\text{H}_3\text{CO} & \quad \text{PBr}_3 \\
\text{H}_3\text{CO} & \quad \text{Mg} \\
\text{H}_3\text{CO} & \quad 1. \text{ether} \\
\text{H}_3\text{CO} & \quad 2. \text{H}_2\text{O}^+ \\
\end{align*}
\]

ANS:
56. Outline the synthetic steps necessary to carry out the conversion below. You may use any organic or inorganic reagents you need. Show the structures of all intermediate compounds that would probably be isolated during the course of your synthesis, and show all necessary reagents.

\[
\text{H}_2\text{C} \quad \text{OH} \\
\text{C}_{\text{H}} \quad \text{Br} \\
\text{MgBr} \\
\text{ether} \\
1. \text{ether} \\
2. \text{H}_2\text{O}^+ \\
\text{H}_2\text{C} \quad \text{OH}
\]

ANS:

57. Synthesize the following alcohol starting with cyclohexene and bromocyclopentane as the only organic starting materials. Show all reagents and all intermediates in your synthesis.

\[
\text{Br} \\
\text{from} \\
\text{and}
\]

\[
\text{Br}
\]

18
ANS:

\[
\begin{align*}
&\text{Br} \\
&\text{MgBr} \\
&\text{ether} \\
&\text{1. ether} \\
&\text{2. H}_2\text{O}^+ \\
\end{align*}
\]

**Exhibit 17-10**

Propose structures for alcohols that have the following $^1\text{H}$ NMR spectra.

58. $\text{C}_3\text{H}_8\text{O}$
ANS: isopropyl alcohol (2-propanol), \((\text{CH}_3)_2\text{CHOH}\)

59. \(\text{C}_7\text{H}_8\text{O}\) (neat solution; no solvent)

Spectrum obtained from: SBDSWeb: http://www.aist.go.jp/RIODB/SDBS

ANS: benzyl alcohol

\[
\begin{array}{c}
\text{CH}_2\text{OH} \\
\end{array}
\]