SHORT ANSWER

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

1. Draw: 2,2,2-trichloroethanal (chloral)

ANS:

2. Draw: benzophenone

ANS:

3. Draw: trans-3-isopropylecyclohexanecarbaldehyde

ANS:

4. Draw: 5,5-dimethyl-1,3-cyclohexanedione (dimedone)

ANS:
5. Draw: 2-cyclohexenone

ANS:

6. What is the correct structure for 2-hydroxyacetophenone?

a.  

b.  

c.  

d.  

ANS:

c

IUPAC Naming Instructions: Provide proper IUPAC names.

7. Name:

ANS:

\textit{m}-nitrobenzaldehyde

8. Name:

ANS:

4,8-dimethyl-7-nonen-2-one
9. Name:

\[
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{O} \\
\end{array}
\]

ANS: 1-phenyl-2-propanone

10. Name:

\[
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{O} \\
\end{array}
\]

ANS: \textit{cis}-1,3-cyclopentanedicarbaldehyde

11. Name:

\[
\begin{array}{c}
\text{O} \\
\text{H} \\
\end{array}
\]

ANS: 5-oxoheptanal

**Exhibit 19-1**
Consider the reaction below to answer the following question(s):

\[
\begin{array}{c}
\text{O} \\
\text{H}_2\text{O} \\
\end{array} \xrightarrow{\text{base catalyst}} \begin{array}{c}
\text{O} \\
\text{H} \\
\end{array}
\]

12. Refer to Exhibit 19-1. Write the complete stepwise mechanism for the reaction shown above. Show all intermediate structures and all electron flow with arrows.

ANS:

\[
\begin{array}{c}
\text{O} \xrightarrow{\text{OH}} \text{O} \\
\end{array} \xrightarrow{\text{H} \text{OH}} \begin{array}{c}
\text{O} \\
\text{H} \\
\end{array} \xrightarrow{\text{OH}} \text{O}
\]

\[
\begin{array}{c}
\text{O} \xrightarrow{\text{OH}} \text{O} \\
\end{array} \xrightarrow{\text{H} \text{OH}} \begin{array}{c}
\text{O} \\
\text{H} \\
\end{array} \xrightarrow{\text{OH}} \text{O}
\]

\[
\begin{array}{c}
\text{O} \xrightarrow{\text{OH}} \text{O} \\
\end{array} \xrightarrow{\text{H} \text{OH}} \begin{array}{c}
\text{O} \\
\text{H} \\
\end{array} \xrightarrow{\text{OH}} \text{O}
\]

\[
\begin{array}{c}
\text{O} \xrightarrow{\text{OH}} \text{O} \\
\end{array} \xrightarrow{\text{H} \text{OH}} \begin{array}{c}
\text{O} \\
\text{H} \\
\end{array} \xrightarrow{\text{OH}} \text{O}
\]

\[
\begin{array}{c}
\text{O} \xrightarrow{\text{OH}} \text{O} \\
\end{array} \xrightarrow{\text{H} \text{OH}} \begin{array}{c}
\text{O} \\
\text{H} \\
\end{array} \xrightarrow{\text{OH}} \text{O}
\]

\[
\begin{array}{c}
\text{O} \xrightarrow{\text{OH}} \text{O} \\
\end{array} \xrightarrow{\text{H} \text{OH}} \begin{array}{c}
\text{O} \\
\text{H} \\
\end{array} \xrightarrow{\text{OH}} \text{O}
\]

\[
\begin{array}{c}
\text{O} \xrightarrow{\text{OH}} \text{O} \\
\end{array} \xrightarrow{\text{H} \text{OH}} \begin{array}{c}
\text{O} \\
\text{H} \\
\end{array} \xrightarrow{\text{OH}} \text{O}
\]

\[
\begin{array}{c}
\text{O} \xrightarrow{\text{OH}} \text{O} \\
\end{array} \xrightarrow{\text{H} \text{OH}} \begin{array}{c}
\text{O} \\
\text{H} \\
\end{array} \xrightarrow{\text{OH}} \text{O}
\]

\[
\begin{array}{c}
\text{O} \xrightarrow{\text{OH}} \text{O} \\
\end{array} \xrightarrow{\text{H} \text{OH}} \begin{array}{c}
\text{O} \\
\text{H} \\
\end{array} \xrightarrow{\text{OH}} \text{O}
\]

\[
\begin{array}{c}
\text{O} \xrightarrow{\text{OH}} \text{O} \\
\end{array} \xrightarrow{\text{H} \text{OH}} \begin{array}{c}
\text{O} \\
\text{H} \\
\end{array} \xrightarrow{\text{OH}} \text{O}
\]

\[
\begin{array}{c}
\text{O} \xrightarrow{\text{OH}} \text{O} \\
\end{array} \xrightarrow{\text{H} \text{OH}} \begin{array}{c}
\text{O} \\
\text{H} \\
\end{array} \xrightarrow{\text{OH}} \text{O}
\]

\[
\begin{array}{c}
\text{O} \xrightarrow{\text{OH}} \text{O} \\
\end{array} \xrightarrow{\text{H} \text{OH}} \begin{array}{c}
\text{O} \\
\text{H} \\
\end{array} \xrightarrow{\text{OH}} \text{O}
\]

\[
\begin{array}{c}
\text{O} \xrightarrow{\text{OH}} \text{O} \\
\end{array} \xrightarrow{\text{H} \text{OH}} \begin{array}{c}
\text{O} \\
\text{H} \\
\end{array} \xrightarrow{\text{OH}} \text{O}
\]

\[
\begin{array}{c}
\text{O} \xrightarrow{\text{OH}} \text{O} \\
\end{array} \xrightarrow{\text{H} \text{OH}} \begin{array}{c}
\text{O} \\
\text{H} \\
\end{array} \xrightarrow{\text{OH}} \text{O}
\]

\[
\begin{array}{c}
\text{O} \xrightarrow{\text{OH}} \text{O} \\
\end{array} \xrightarrow{\text{H} \text{OH}} \begin{array}{c}
\text{O} \\
\text{H} \\
\end{array} \xrightarrow{\text{OH}} \text{O}
\]

\[
\begin{array}{c}
\text{O} \xrightarrow{\text{OH}} \text{O} \\
\end{array} \xrightarrow{\text{H} \text{OH}} \begin{array}{c}
\text{O} \\
\text{H} \\
\end{array} \xrightarrow{\text{OH}} \text{O}
\]
13. Refer to Exhibit 19-1. The substance formed on addition of water to an aldehyde or ketone is called a hydrate or a/an:

a. vicinal diol  
b. geminal diol  
c. acetal  
d. ketal

ANS: b

14. Refer to Exhibit 19-1. The exact position of the equilibrium between ketones/aldehydes and their hydrates depends on the structure of the carbonyl compound. Although the equilibrium favors the carbonyl compound in most cases, cyclopropanone forms a stable hydrate. Explain this phenomenon based on the structures of cyclopropanone and its hydrate.

ANS: The carbonyl carbon in cyclopropane is highly strained because the preferred bond angle for an \( sp^2 \)-hybridized carbon is 120° but the real angle is 60°. This angle strain is somewhat relieved when cyclopropanone is hydrated—the preferred bond angle for an \( sp^3 \)-hybridized carbon is about 109.5°. Going from \( sp^2 \) to \( sp^3 \) hybridization relieves angle strain by about 10°. Thus, the hydrate of cyclopropane is more stable than the carbonyl form, and the equilibrium lies to the right in this reaction.

15. Refer to Exhibit 19-1. Many nucleophilic addition reactions of aldehydes and ketones are catalyzed by acid or base. Bases catalyze hydration by:

a. making the carbonyl group more electrophilic  
b. shifting the equilibrium of the reaction  
c. making the carbonyl group less electrophilic  
d. converting the water to hydroxide ion, a much better nucleophile

ANS: d

16. This question was omitted on the printed copy. This placeholder question is here to maintain the numbering system integrity between the printed copy and ExamView. Therefore, it has been marked "do not use on test" in ExamView's question information dialog. As a result, this placeholder question is automatically prevented from being chosen as a test question.

ANS: Answer not provided.
17. Enamines formed from the cyclic secondary amine pyrrolidine are important intermediates in the synthesis of 1,5-diketones.

\[
\text{Cyclohexanone} + \text{Pyrrolidine} \underset{\text{HOAc}}{\xrightarrow{\text{H}^+ \text{transfer}}} \text{Enamine} + \text{H}_2\text{O}
\]

On the structures provided below, draw arrows showing electron flow for the reaction mechanism for the acetic acid-catalyzed formation of an enamine from cyclohexanone and pyrrolidine.

ANS:

\[
\text{Cyclohexanone} + \text{Pyrrolidine} \underset{\text{HOAc}}{\xrightarrow{\text{H}^+ \text{transfer}}} \text{Enamine} + \text{H}_2\text{O}
\]
Exhibit 19-2
Consider the data below to answer the following question(s).

Cyanohydrins are important intermediates in the synthesis of $\alpha$-hydroxycarboxylic acids from ketones and aldehydes. The nitrile functional group can be hydrolyzed by aqueous acid to yield a carboxylic acid. Nitriles can also be hydrolyzed to carboxylic acids using aqueous base. Unfortunately, when a cyanohydrin is treated with aqueous base the original carbonyl compound is isolated.

18. Refer to Exhibit 19-2. The reaction of an aldehyde with hydrogen cyanide is an example of _____ reaction.
   a. a nucleophilic substitution
   b. an electrophilic addition
   c. an electrophilic substitution
   d. a nucleophilic addition

ANS: d

19. Refer to Exhibit 19-2. Identify the electrophile in the reaction of benzaldehyde with hydrogen cyanide.

ANS: The benzaldehyde is the electrophile in this reaction.

20. Refer to Exhibit 19-2. The reaction of benzaldehyde with hydrogen cyanide is catalyzed by the addition of a small amount of KCN. Write the complete reaction mechanism for the KCN-catalyzed reaction. Show all electron flow with arrows and show all intermediate structures.
Refer to Exhibit 19-2. Formulate a reasonable mechanism for the reaction of the cyanohydrin of benzaldehyde, shown above, with aqueous NaOH. Show all intermediate structures and all electron flow with arrows.

In the Wittig reaction, a phosphorus ylide adds to a ketone or aldehyde to yield an alkene. Write the complete stepwise mechanism for the Wittig reaction shown below. Show all intermediate structures and all electron flow with arrows.
23. Refer to Exhibit 19-3. The nucleophile in this reaction is:

ANS: B

24. Refer to Exhibit 19-3. The catalyst in this reaction is:

ANS: C

25. Refer to Exhibit 19-3. The product of this reaction is called:

a. an ylide
b. an acetal
c. a gem diol
d. a hydrate

ANS: b
26. Refer to Exhibit 19-3. Write the complete stepwise mechanism for this reaction. Show all electron flow with arrows and show all intermediate structures.

ANS:

![Mechanism Diagram]

**Exhibit 19-4**

α,β-Unsaturated aldehydes and ketones can undergo reaction with nucleophiles at the β carbon, as shown below.

\[
\text{\begin{align*}
\text{C} & \text{C} \\
\text{+} & \text{Nu} \rightarrow \text{C} & \text{C} \\
\text{H} & \text{Nu}
\end{align*}}
\]

27. Refer to Exhibit 19-4. Draw a resonance form for the unsaturated carbonyl that accounts for this reactivity.

ANS:

![Resonance Form Diagram]
28. Refer to Exhibit 19-4. This reaction is called _____ reaction.

a. a 1,2-conjugate addition.
b. an electrophilic addition.
c. a direct addition
d. a 1,2-addition.

ANS: a

Exhibit 19-5
Give the major organic product(s) for each of the following reactions or sequences of reactions. Show all relevant stereochemistry.

29. 

ANS:

30. 

ANS:
31. **ANS:**

32. **ANS:**

33. **ANS:**
34. \[ \text{H}_2\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_2\text{O}^+ \]

\[ \text{ANS:} \quad \text{H}_2\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_3\text{C} \quad \text{H}_2\text{O}^+ \]

35. \[ \text{ANS:} \quad \text{H}_2\text{NNH}_2 \quad \text{KOH, DMSO} \]

36. \[ \text{ANS:} \quad \text{H}_2\text{NNH}_2 \quad \text{KOH, DMSO} \]

36. \[ \text{ANS:} \quad \text{H}_2\text{NNH}_2 \quad \text{KOH, DMSO} \]
37. \[
\text{CH}_3\text{(CH}_2\text{)}_{10}\text{COCH}_3 \xrightarrow{1. \text{DIBAH, toluene}} \text{CH}_3\text{(CH}_2\text{)}_{10}\text{CH}
\]  
\[
\text{CH}_3\text{(CH}_2\text{)}_{10}\text{COCH}_3 \xrightarrow{2. \text{H}_3\text{O}^+} \text{CH}_3\text{(CH}_2\text{)}_{10}\text{CH}
\]

ANS:

38. \[
\text{1. O}_3 \quad \text{2. Zn, H}_3\text{O}^+
\]

ANS:

39. \[
\text{H}_3\text{C} - \text{C} - \text{CH} = \text{CH}_2 + \text{HN(CH}_2\text{CH}_3\text{)}_2 \xrightarrow{\text{ethanol}}
\]

ANS:

40. \[
\text{Br}
\]

ANS:
41. \[
\text{H}_2\text{C}-\text{C}-\text{H} + \text{MgBr}
\]
\[
\text{1. ether} \\
\text{2. H}_2\text{O}^+
\]

ANS:

42.

a. LiAlH₄, THF
b. NaBH₄, ethanol
c. 1. DIBAH, toluene
   2. H₃O⁺
d. All of the above work well

ANS: c

43.

a. LiAlH₄, ether
b. NaBH₄, ethanol
c. CrO₃, pyridine
d. H₂/Pd

ANS: b
44. a. 1. PhMgBr, ether 
   2. $\text{H}_3\text{O}^+$

b. 1. PhCH$_2$MgBr, ether 
   2. $\text{H}_3\text{O}^+$

c. (C$_6$H$_5$)$_3$P=CHC$_6$H$_5$, THF

d. Li(C$_6$H$_5$)$_2$Cu, ether

ANS: d

45.

a. 1. PhMgBr, ether 
   2. $\text{H}_3\text{O}^+$

b. 1. PhCH$_2$MgBr, ether 
   2. $\text{H}_3\text{O}^+$

c. (C$_6$H$_5$)$_3$P=CHC$_6$H$_5$, THF

d. Li(C$_6$H$_5$)$_2$Cu, ether

ANS: c

46. a. NaBH$_4$, ethanol

b. CH$_2$PPh$_3$

c. NaOH, H$_2$O

d. All of the above

ANS: a
Exhibit 19-7
Show how the Wittig reaction might be used to prepare each of the following alkenes. Identify the alkyl halide and the carbonyl components that would be used in each synthesis.

47. ANS:

48. ANS:

Exhibit 19-8
Show how the following conversions might be accomplished. Show all reagents and all intermediate structures. More than one step may be required.

49. ANS:
50. \[ \text{ANS:} \]

51. \[ \text{ANS:} \]

52. \[ \text{ANS:} \]
Exhibit 19-9
Consider the data below to answer the following question(s).

C₇H₁₄O

IR: 1715 cm⁻¹
MS: M⁺ at m/z = 114, α-cleavage fragment at m/z = 71, McLafferty rearrangement fragment at m/z = 86.
¹H NMR: 0.92 δ (6H, triplet), 1.59 δ (4H, multiplet), 2.36 δ (4H, triplet)

53. Refer to Exhibit 19-9. Calculate the degree of unsaturation for this compound.

ANS:
The base formula for C₇H₁₄O is C₇H₁₄. The formula for the saturated compound is C₇H₁₆, so the compound has one degree of unsaturation.

54. Refer to Exhibit 19-9. What functional group is indicated by the IR data?

ANS:
Absorption at 1715 cm⁻¹ in the infrared spectrum indicates the presence of a carbonyl compound, most probably a ketone.

55. Refer to Exhibit 19-9. Interpret the mass spectral data.

ANS:
A fragment at m/z = 71 indicates a loss of 43, or a propyl group, from α-cleavage. A fragment at m/z = 86 indicates a loss of 28, or ethylene, from McLafferty rearrangement (transfer of a hydrogen atom from the gamma carbon to the carbonyl oxygen with concomitant breaking of the bond between the alpha and beta carbon).
56. Refer to Exhibit 19-9. Interpret the $^1$H NMR data.

ANS:
The $^1$H NMR indicates that there are only three different kinds of hydrogen in the molecule. The 6H triplet is due to two equivalent CH$_3$ groups next to two equivalent CH$_2$ groups, the 4H triplet is due to two equivalent CH$_2$ groups next to two other equivalent CH$_2$ groups, shifted by a C=O, and the 4H multiplet is two equivalent CH$_2$ groups between a CH$_2$ and a CH$_3$.

57. Refer to Exhibit 19-9. Propose a structure consistent with the spectral data presented above.

ANS:
4-heptanone, CH$_3$CH$_2$CH$_2$COCH$_2$CH$_2$CH$_3$

**Exhibit 19-10**

Consider the data below to answer the following question(s).

C$_7$H$_{14}$O
IR: 1715 cm$^{-1}$
MS: M$^+$ at m/z = 114, $\alpha$-cleavage fragment at m/z = 71, no McLafferty rearrangement fragment

$^1$H NMR:

![NMR spectrum](image)

Spectrum obtained from: SDBSWeb: http://www.aist.go.jp/RIODB/SDBS
58. Refer to Exhibit 19-10. Interpret the mass spectral data for this compound.

ANS:
A fragment at \( m/z = 71 \) indicates a loss of 43, or a propyl group, from \( \alpha \)-cleavage. The absence of a McLafferty rearrangement fragment means that there is no hydrogen atom on a gamma carbon, so the propyl group must be isopropyl, and not \( n \)-propyl.

59. Refer to Exhibit 19-10. Interpret the \(^1\)H NMR spectrum.

ANS:
The \(^1\)H NMR spectrum indicates that there are only two kinds of hydrogen in this compound. The 12H doublet (one adjacent H) is most likely four equivalent methyl groups of two equivalent isopropyl groups. The 2H multiplet (many adjacent H) is consistent with two equivalent hydrogens of two isopropyl groups, too. The multiplet is shifted to about 2.77 by the adjacent C=O.

60. Refer to Exhibit 19-10. Propose a structure for this compound.

ANS:
2,4-dimethyl-3-pentanone, \((\text{CH}_3)_2\text{CHCOCH(\text{CH}_3)}_2\)

61. Name the following compound. Atoms other than carbon and hydrogen are labeled.

ANS:
1-chloro-3-methyl-2-butanone
**MULTIPLE CHOICE**

1. Which of the labeled peaks would allow the distinction of an aldehyde from a ketone based on this spectrum?

   - a. 1
   - b. 2
   - c. 3
   - d. 4

   **ANS: B**

2. Which of the labeled peaks would allow the distinction of an aldehyde from a ketone based on this spectrum?

   - a. 1
   - b. 2
   - c. 3
   - d. 4
   - e. 5
   - f. This is not the spectrum of an aldehyde.

   **ANS: A**
3. Based only on the spectrum below, what is inferred about the compound used to produce the spectrum?

![Spectrum Image]

a. aromatic  
b. aldehyde  
c. para disubstituted  
d. ethyl substituent  
e. All of the above are evident from the spectrum.

ANS: E

4. Consider the following structure. Atoms other than carbon and hydrogen are labeled.

![Structure Image]

Oxidation of this compound yields:

a.  

b.  

c.  

22
d. No reaction

ANS: D

5. Which of the following reagents could be used to convert 3-cyclopentyl-2-methylpropanal to the following substance? Atoms other than carbon and hydrogen are labeled.

a. CrO$_3$  

b. O$_3$  

c. DIBAH  

d. LiAlH$_4$

ANS: A

6. The following substance is heated in the presence of aqueous NaOH. Atoms other than carbon and hydrogen are labeled.

The product of the reaction is:

a. 

\[
\text{CH}_2\text{OH}  
\]
Aldehydes and Ketones: Nucleophilic Addition Reactions

b. \(\text{O} = \text{C} - \text{OH}\)
\[
\begin{array}{c}
\text{CH}_3 \\
\end{array}
\]
c. \(\text{CH}_2\text{OH}\)
\[
\begin{array}{c}
\text{CH}_3 \\
\end{array}
\]
d. both b and c
e. all of the above

ANS: D

7. If the following substance were treated with HCN followed by aqueous acid and heat,

\[\text{structure image}\]

which of the following would be produced? Atoms other than carbon and hydrogen are labeled.

a. \(\text{HO}\)\(\text{-C} - \text{C} - \text{H} - \text{H} - \text{NH}_2\)
\[
\begin{array}{c}
\text{CH}_3 \\
\end{array}
\]
b. 
\[
\begin{array}{c}
\text{HO} - C - C = N \\
\text{CH}_3
\end{array}
\]

c. 
\[
\begin{array}{c}
\text{HO} - C - C \text{O} - \text{OH} \\
\text{CH}_3
\end{array}
\]
d. both b and c
e. all of the above

ANS: C

8. Which of the following functional groups does not contain a carbonyl group?
   a. ester
   b. carboxylic acid
   c. ketone
   d. phenol

ANS: D

9. Which of the following is not a characteristic of a carbonyl group?
   a. \(sp^2\) hybridized carbon atom
   b. planar geometry about the carbonyl bond
   c. carbonyl carbon atom is electrophilic
   d. carbonyl oxygen atom is nucleophilic
   e. weakly polarized carbon to oxygen bond
   f. All are characteristics of the carbonyl group

ANS: E

10. Consider similar R groups in the following types of carbonyl compounds. In which type(s) of compound is a negative charge on the acyl group not stabilized to function as a leaving group in a nucleophile substitution reactions?
   a. acid chloride
   b. acid anhydride
   c. ester
   d. aldehyde
   e. a and b
Aldehydes and Ketones: Nucleophilic Addition Reactions

f. a, b and c

g. a, b, c, and d

ANS: D

11. Of the types of reactions that characterize carbonyl groups, how is the following reaction classified?

\[
\begin{array}{c}
\text{O} \\
\text{R} \\
\text{C} \\
\text{E} \\
\text{R'} \\
\text{R''} \\
\end{array}
\quad \text{E}^+ \quad \begin{array}{c}
\text{O} \\
\text{R} \\
\text{C} \\
\text{E} \\
\text{R'} \\
\text{R''} \\
\end{array}
\]

a. nucleophilic addition  b. nucleophilic acyl substitution  c. \(\alpha\) substitution  d. carbonyl condensation

ANS: C