## Organic Chemistry, 5e (Bruice) Chapter 17: Carbonyl Compounds II

1) Which of the following compounds is an aldehyde?



2) Which of the following compounds is a ketone?



3) What is the common name for the following compound?



4) Which of the following compounds is acetone?



5) What is the IUPAC name for the following compound?

O  

$$\parallel$$
  
CH<sub>3</sub>CHCH<sub>2</sub>-C-H  
 $\parallel$   
Br  
A) 2-bromobutanal  
B)  $\alpha$ -bromobutanal  
C) 3-bromobutanal  
D)  $\beta$ -bromobutyraldehyde  
E) 3-bromobutanone  
Answer: C  
Type: MC  
Section: 17-1

6) Which of the following compounds is benzaldehyde?



7) What is the IUPAC name for the following compound?

O || CH<sub>3</sub>CCHCH<sub>2</sub>CHCl | CH<sub>3</sub> CH<sub>3</sub> A) 5-chloro-3-methylhexanone B) 1-chloro-1,3-dimethyl-4-pentanone C) 5-chloro-3,5-dimethyl-2-pentanone D) 5-chloro-3-methyl-2-hexanone E) 2-chloro-4-methyl-5-hexanone Answer: D Type: MC Section: 17-1

8) Which of the following is cyclohexanone?



- 9) Provide the proper IUPAC name for PhCH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>CHO. Answer: 4-methyl-5-phenylpentanal Type: SA Section: 17-1
- 10) Provide the proper IUPAC name for CH<sub>3</sub>CHOHCH<sub>2</sub>COCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>. Answer: 2-hydroxy-6,6-dimethyl-4-octanone Type: SA Section: 17-1
- 11) Provide the IUPAC name for the organic compound below.



Answer: ethyl 5-oxopentanoate Type: SA Section: 17-1

12) Provide the IUPAC name for the organic compound below.



Answer: 3-ethyl-4-methylhexanal Type: SA Section: 17-1

13) Provide the IUPAC name for the organic compound below.



Answer: 3-hydroxycyclopentanone Type: SA Section: 17-1

14) Provide the systematic name of the compound below.



Answer: 2-chloro-5-methylheptanal Type: SA Section: 17-1

15) Provide the systematic name of the compound below.

Answer: (Z)-5-methyl-4-hepten-3-one Type: SA Section: 17-1

16) Would you expect the carbonyl carbon of benzaldehyde to be more or less electrophilic than that of acetaldehyde? Explain using resonance structures.

Answer: The carbonyl carbon of benzldehyde would be less electrophilic. Delocalization reduces its partial positive charge as seen in the resonance forms below.



Section: 17-2

- 17) Which carbonyl is more susceptible to nucleophilic attack, that of cyclohexanone or that of hexanal? Provide two reasons for your choice.
  - Answer: Hexanal. The partial positive charge on the carbonyl carbon causes carbonyl compounds to be attacked by nucleophiles. Because a hydrogen is electron-withdrawing relative to an alkyl group, an aldehyde has a greater partial positive charge on its carbonyl carbon and is thus more susceptible to nucleophilic attack. Steric factors also contribute to the greater reactivity of an aldehyde. Because the hydrogen attached to the carbonyl carbon of an aldehyde is smaller than the alkyl group attached to the carbonyl carbon of a ketone, the carbonyl carbon of an aldehyde is more accessible to nucleophilic attack.

Type: SA Section: 17-2

18) List the following carbonyl compounds in order of decreasing reactivity toward nucleophiles: ester, acid chloride, amide, aldehyde, ketone.

Answer: acid chloride > aldehyde > ketone > ester > amide Type: SA Section: 17-2

- 19) Which of the following characterizes the reactions of aldehydes and ketones?
  - A) electrophilic addition
  - B) electrophilic substitution
  - C) nucleophilic acyl substitution
  - D) nucleophilic addition; free radical addition

Answer: D

Type: MC Section: 17-3

- 20) Why do aldehydes undergo nucleophilic addition reactions while esters undergo nucleophilic acyl substitution reactions?
  - A) The carbonyl carbon of an ester is more electrophilic than that of an aldehyde.
  - B) Aldehydes are more sterically hindered than esters.
  - C) Once the nucleophile adds to an aldehyde, the tetrahedral intermediate is too sterically hindered to eliminate one of the attached groups.
  - D) The ester carbonyl carbon is sp3 hybridized while the aldehyde carbonyl carbon is sp2 hybridized.
  - E) Once the nucleophile adds to an aldehyde, neither H- nor R- can be eliminated since they are strongly basic.

Answer: E Type: MC Section: 17-3

21) What is the major product when (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>Br is subjected to the following reaction

sequence: 1. Mg, ether 2. CO<sub>2</sub> 3. H<sub>3</sub>O+?

A) 3-methyl-1-butanol
B) 2-methyl-2-butanol
C) 4-methyl-1-pentanol
D) 4-methylpentanoic acid
Answer: D
Type: MC
Section: 17-4

22) Which of the following reactions can be used to prepare 3-methyl-3-hexanol,



23) What is/are the <u>major</u> product(s) of the following reaction?

?

CH<sub>3</sub>MgBr + HOCH<sub>2</sub>CH 
$$\longrightarrow$$
  
A)  
 $O$   
 $HO-CH_2CCH_3 + HMgBr$   
B)  
 $OMgBr$   
 $HO-CH_2CH$   
 $U$   
 $CH_3$   
C)  
 $CH_4 + BrMgOCH_2CH$   
D)  
 $O$   
 $BrMgCH_2CH + CH_3OH$   
E)  
 $O$   
 $CH_3MgBr + HOCH_2CH  $\longrightarrow$  ?  
Answer: C  
Type: MC  
Section: 17-4$ 

24) Which of the following reactions can be used to prepare:



25) Which of the following alcohols can be prepared by the reaction of methyl formate with excess Grignard reagent?

A) 1-pentanol
B) 2-pentanol
C) 3-pentanol
D) 2-methyl-2-pentanol
E) 3-methyl-3-pentanol
Answer: C
Type: MC
Section: 17-4

26) Complete the following reaction sequence by supplying the missing information:



27) Give three different sets of reagents (a carbonyl compound and a Grignard reagent) that could be used to prepare the following compound.



- 28) What reagent can be used to convert benzophenone into triphenylmethanol? Answer: PhMgBr followed by hydrolysis Type: SA Section: 17-4
- 29) Propose a synthesis of 4-phenyl-2-butanol from 3-phenylpropanal. Answer: 1) CH<sub>3</sub>MgBr

2) H<sub>3</sub>O+ Type: SA Section: 17-4 30) What two distinct combinations of Grignard reagent and aldehyde could be used to prepare the alcohol below?



Answer: phenyl magnesium bromide + butanal **and** propyl magnesium bromide + benzaldehyde Type: SA Section: 17-4

31) Provide the major organic product of the following.



32) Beginning with sodium acetylide (NaCCH), propose a three-step synthesis of hexanal. Answer: 1) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br

2) Sia<sub>2</sub>BH 3) H<sub>2</sub>O<sub>2</sub>, NaOH Type: SA

Section: 17-5

33) Propose a synthesis of 3-methyl-4-heptyn-3-ol from 1-butyne. Answer: 1) NaNH<sub>2</sub>

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2) CH<sub>3</sub>COCH<sub>2</sub>CH<sub>3</sub>
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3) H3O+

Type: SA Section: 17-5

34) Propose a sequence of steps to convert propyne to 4-heptanol.

Answer: 1) NaNH<sub>2</sub>

- 2) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHO
- 3) H<sub>2</sub> (excess), Pt

Type: SA Section: 17-5 35) Which of the following reactions is the best method for preparing acetaldehyde?



36) What is the major product of the following reaction?



37) Which of the following reagents can be used to reduce acetaldehyde to ethyl alcohol?

- A) 1. LiAlH<sub>4</sub>/2. H<sub>3</sub>O+ B) 1. NaBH<sub>4</sub>/2. H<sub>3</sub>O+ C) H<sub>2</sub>/Pt D) A and D E) A, B, and C Answer: E Type: MC Section: 17-6
- 38) Diisobutylaluminum hydride (DIBALH) can be used to carry out which of the following conversions?A) ester to aldehyde
  - B) carboxylic acid to ester
  - C) 2 alcohol to ketone
  - D) aldehyde to carboxylic acid
  - E) ester to ketone

Answer: A Type: MC

Section: 17-6

39) Provide the major organic product which results when (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>COCl is treated with DIBAH.

Answer: (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CHO Type: SA Section: 17-6 40) Provide the major organic product of the following.



41) Provide the major organic product(s) of the reaction below.



42) Provide the major organic product(s) of the reaction below.



43) Which of the following is the best method for preparing lactic acid from acetaldehyde?



44) Which of the sequences works best to accomplish the following conversion?



45) Provide the structure of the cyanohydrin that results when cyclopentanone reacts with HCN. Answer:



Type: SA Section: 17-7 46) Provide the major organic product(s) of the reaction below.



47) Provide the major organic product(s) of the reaction below.



- 48) What class of organic compounds results when cyclopentanone reacts with ethylamine in the presence of trace acid?
  - A) cyanohydrin
  - B) semicarbazone
  - C) imine
  - D) enamine
  - E) oxime
  - Answer: C
  - Type: MC Section: 17-8

49) When the carbonyl group of a neutral ketone is protonated,

- A) the resulting species becomes more electrophilic.
- B) the resulting species is activated toward nucleophilic attack.
- C) subsequent nucleophilic attack on the resulting species is said to occur under acid-catalyzed conditions.
- D) the resulting species has a positive charge.
- E) all of the above

Answer: E Type: MC Section: 17-8 50) Which of the following amines will react with cyclopentanone to form an enamine?
A) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>
B) (CH<sub>3</sub>)<sub>3</sub>N
C) pyridine
D) (CH<sub>3</sub>)<sub>3</sub>CNH<sub>2</sub>
E) none of the above
Answer: E
Type: MC
Section: 17-8

## 51) Which of the following compounds is a hydrazone?



52) What is the major organic product of the following reaction?



53) Which of the following is an enamine?



54) What is the major organic product of the following reaction?



55) What is the major organic product of the following reaction?



56) Provide the major organic product(s) of the reaction below.



57) Provide the major organic product(s) of the reaction below.



58) Provide the structure of cyclohexanone oxime. Answer:



59) Draw the two major resonance forms of the cation which results when cyclohexanone's carbonyl group is protonated.



60) Conversion of aldehydes and ketones to imines is an acid-catalyzed process. Explain why this conversion is actually hindered by the presence of too much acid.

Answer: At very low pH, much more of the amine is protonated and can no longer function as a nucleophile.

Type: SA Section: 17-8

61) Provide a detailed, stepwise mechanism for the acid-catalyzed condensation reaction between benzaldehyde and methylamine.

Answer:



62) Provide a detailed, stepwise mechanism for the acid-catalyzed condensation reaction between cyclohexanone and  $H_2NOH$ .

Answer:



63) Provide the major organic product of the reaction of aniline with 3-pentanone. Answer:



Type: SA Section: 17-8

64) Propose a plausible mechanism that would explain the following conversions:



Answer:



Type: SA Section: 17-8

65) Which would be more appropriate as the reduction in the following sequence, a Clemmensen or a Wolff-Kishner? Explain.



Answer: Wolff-Kishner. The acidic conditions of the Clemmensen would remove the protecting group causing reduction of the aldehyde as well.

Type: SA Section: 17-8

66) Provide the major organic product of the following.



67) Provide the structure of the hydrate of cyclopentanone. Answer:



## 68) The compound:

## о || HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH

can form a hemiacetal by reacting with itself in solution. What is the structure of this hemiacetal?



- 69) Provide the structure of the diethyl acetal of butanal. Answer: CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> Type: SA Section: 17-10
- 70) Provide a detailed, stepwise mechanism for the acid-catalyzed reaction of 2-butanone with ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH) to produce an acetal.

Answer:





72) What is the major product of the following reaction?



73) What sequence of reactions would best accomplish the following conversion?



74) Propose a sequence of steps to carry out the following conversion.



75) Propose a sequence of steps to carry out the following conversion:



Section: 17-11

76) What carbonyl compound and what phosphonium ylide are required for the synthesis of the following alkene?

D) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>MgBr + CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHO E) CH<sub>3</sub>CH<sub>2</sub>CH=PPh<sub>3</sub> + CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CHO Answer: A Type: MC Section: 17-13

78) Give the products obtained from the following Wittig reaction. Show both stereoisomers.



- 79) Provide the sequence of reagents by which a phosphonium ylide can be prepared from 1bromobutane.
  - Answer: 1) Ph<sub>3</sub>P 2) butyllithium Type: SA Section: 17-13
- 80) Provide the major organic product(s) of the reaction below.



81) Which enantiomer is formed from attack of a methyl Grignard reagent on the si face of benzaldehyde?



82) When camphor undergoes nucleophilic attack by CH<sub>3</sub>CH<sub>2</sub>MgBr, the major product is the one in which the Grignard reagent has added *endo*. Explain the stereoselectivity observed. Which face of the carbonyl carbon, *re* or *si*, was attacked?



Answer: The Grignard reagent attacked the more sterically accessible *si* face of the carbonyl carbon. Type: SA Section: 17-14

83) What reagent(s) would you use to accomplish the following conversion?



A) CH<sub>3</sub>Br; H<sub>3</sub>O+
B) CH<sub>3</sub>MgBr; H<sub>3</sub>O+
C) (CH<sub>3</sub>)<sub>2</sub>CuLi; H<sub>3</sub>O+
D) CH<sub>3</sub>Br; LiAlH<sub>4</sub>; H<sub>3</sub>O+
E) LiAlH<sub>4</sub>; CH<sub>3</sub>MgBr; H<sub>3</sub>O+
Answer: B
Type: MC
Section: 17-16

84) What reagent(s) would you use to accomplish the following conversion?



A) CH<sub>3</sub>Br; H<sub>3</sub>O+
B) CH<sub>3</sub>MgBr; H<sub>3</sub>O+
C) (CH<sub>3</sub>)<sub>2</sub>CuLi; H<sub>3</sub>O+
D) CH<sub>3</sub>Br; LiAlH<sub>4</sub>; H<sub>3</sub>O+
E) LiAlH<sub>4</sub>; CH<sub>3</sub>MgBr; H<sub>3</sub>O+
Answer: C
Type: MC
Section: 17-16

- 85) In carbon NMR, the carbon atom of the carbonyl group in aldehydes and ketones has a chemical shift of about:
  - A) 20 ppm.
    B) 40 ppm.
    C) 60 ppm.
    D) 120 ppm.
    E) 200 ppm.
    Answer: E
    Type: MC
    Section: 99
- 86) In the proton NMR spectra of aldehydes and ketones, the protons bonded to carbons adjacent to the carbonyl group typically fall into which of the chemical shift ranges below?
  - A) 1.0-2.0 ppm B) 2.0-3.0 ppm C) 4.0-4.5 ppm D) 7.0-8.0 ppm E) 9.0-10.0 ppm Answer: B Type: MC Section: 99
- 87) Propose an IR frequency that would distinguish between the following compounds:



Answer: Compound I shows a C-H peak for the aldehyde at ~2700 cm<sup>-1</sup>, while compound II shows a peak at ~1380 cm<sup>-1</sup> for CH<sub>3</sub>.

Type: SA Section: 99

88) Identify the compound whose molecular formula and proton NMR spectra are given below:

C<sub>15</sub>H<sub>14</sub>O; a) triplet, at 2.1 ppm (2H) b) triplet, at 2.4 ppm (2H) c) multiplet, at 7.9 - 7.2 ppm (10H) Answer:



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Type: SA
Section: 99
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89) An unknown compound (A),  $C_{10}H_{12}O$ , gave the following proton NMR data: (a) triplet, at 1.0 ppm (3H) (b) quartet, at 2.4 ppm (2H) (c) singlet, at 3.7 ppm (2H) (d) multiplet, at 7.2 ppm (5H) Propose a structure for (A) Answer: (d) (c) (b) (a) (CH<sub>2</sub>CCH<sub>2</sub>CCH<sub>2</sub>CH<sub>3</sub>

90) By which single-step process can benzene be readily converted into acetophenone? Answer: CH<sub>3</sub>COCl, AlCl<sub>3</sub> - a Friedel-Crafts acylation reaction Type: SA

Section: 99

Type: SA Section: 99