## ACS Review Carboxylic Acid Derivatives Nucleophilic Acyl Substitution

1. Which of the following is isopropyl benzoate?
A. $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CO}_{2} \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}$
B. $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{CH}\left(\mathrm{CH}_{3}\right)_{2}$
C. $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCO}_{2} \mathrm{C}_{6} \mathrm{H}_{5}$
D. $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{CHCO}_{2} \mathrm{CH}_{2} \mathrm{C}_{6} \mathrm{H}_{5}$
2. What is the name of the following compound?

A. 2-chlorohexyl ethanoate
B. 1-chlorohexyl ethanoate
C. ethyl 2-chlorohexanoate
D. ethyl 1-chlorohexanoate
3. What is the name of the compound shown below?

A. 2-bromo- N -methylpentamide
B. 2-bromo(methylamino)pentamide
C. methylamino 2-bromopentamide
D. methyl 2-bromopentamide
4. Which of the following has the fastest rate of hydrolysis to give acetic acid?
A)

B) $\mathbf{C H}_{3} \mathrm{CCl}$
C) $\mathrm{CH}_{3} \mathrm{COCH}_{2} \mathrm{CH}_{3}$
D) $\mathrm{CH}_{3} \stackrel{\mathrm{O}}{\mathrm{C}} \mathrm{CH}_{2}$
A. A
B. B
C. C
D. D
5. The compound shown below is classified as a(an):

A. lactone
B. $\beta$-ketoester
C. diketone
D. carboxylic acid anhydride
6. Rank the following in order of decreasing rate of hydrolysis.
I. acetyl chloride
II. acetic anhydride
III. ethyl acetate
IV. acetamide
A. $\quad$ I $>$ II $>$ III $>$ IV
B. $\quad$ IV $>$ III $>$ II $>$ I
C. $\quad$ I $>$ III $>$ II $>$ IV
D. $\quad$ II $>$ III $>$ IV $>$ I
7. What is the product of the following reactions?

B)

C)

D)

A. A
B. B
C. C
D. D
8. How are reactions between aldehydes and nucleophiles fundamentally different than reactions between acyl chlorides and nucleophiles?
A. Aldehydes are readily oxidized by nucleophiles to carboxylic acids.
B. Acyl chlorides have a leaving group, $\mathrm{Cl}^{-}$, whereas aldehydes do not.
C. Aldehydes do not form tetrahedral intermediates with nucleophiles.
D. Acyl chlorides readily form enol tautomers.
9. The compounds shown below have similar molecular weights but significantly different boiling points. Match the compound with its boiling point.

Boiling points $\left({ }^{\circ} \mathrm{C}\right): 28,57,100,141$

|  | methyl acetate |  |  | 2-butanol |  |
| :--- | :--- | :--- | :--- | :--- | :--- |
| 2-methylbutane |  | propanoic acid |  |  |  |
| A) | $100^{\circ}$ | $141^{\circ}$ | $28^{\circ}$ | $57^{\circ}$ |  |
| B) | $57^{\circ}$ | $100^{\circ}$ | $28^{\circ}$ | $141^{\circ}$ |  |
| C) | $28^{\circ}$ | $100^{\circ}$ | $57^{\circ}$ | $141^{\circ}$ |  |
| D) | $141^{\circ}$ | $57^{\circ}$ | $28^{\circ}$ | $100^{\circ}$ |  |

A. A
B. B
C. C
D. D
10. Which of the following would work best in preparing tert-butyl benzoate?
A. $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CO}_{2} \mathrm{H}$ plus $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{COH}$ with $\mathrm{H}_{2} \mathrm{SO}_{4}$ catalyst and heat
B. $\quad \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CO}_{2} \mathrm{Na}$ plus $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{CBr}$ and heat
C. $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CONH}_{2}$ plus $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{COH}$ and heat
D. $\quad \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CO}_{2} \mathrm{H}$ plus $\mathrm{SOCl}_{2}$ followed by $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{COH}$ with pyridine
11. Saponification and neutralization of ${ }^{18} \mathrm{O}$ labeled ethyl acetate, as shown below, yields which of the following isotopically labeled products?

A)

A) $\mathrm{CH}_{3} \mathrm{COH}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$
B)

C) $\mathrm{CH}_{3} \stackrel{\mathrm{O}}{\mathrm{O}} \mathrm{OHH}+\mathrm{CH}_{3} \mathrm{CH}_{2}{ }^{18} \mathrm{OH}$
A. A
B. B
C. C
D. approximately equal amounts of A and B
12. What is the relationship between the following two structures?

A. resonance forms
B. stereoisomers
C. constitutional isomers
D. tautomers
13. What are the products of the following reaction?

A. trans-2-methylcyclohexanol and sodium acetate
B. cis-2-methylcyclohexanol and sodium acetate

D.

14. Which one of the following does not react with benzoyl chloride, $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COCl}$ ?
A. $\quad \mathrm{NH}_{3}$
B. $\mathrm{CH}_{3} \mathrm{NH}_{2}$
C. $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{NH}$
D. $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{~N}$
15. Which one of the following is not a good way to make ethyl acetate?
A. $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$ and $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$ with $\mathrm{H}_{2} \mathrm{SO}_{4}$ as a catalyst
B. $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$ and $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$ with NaOH
C. $\quad \mathrm{CH}_{3} \mathrm{COCl}$ and $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$ with pyridine
D. $\left(\mathrm{CH}_{3} \mathrm{CO}\right)_{2} \mathrm{O}$ and $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$ with $\mathrm{H}_{2} \mathrm{SO}_{4}$ as a catalyst
16. The following tetrahedral intermediate breaks down to:

A. propanoyl chloride and $\mathrm{CH}_{3} \mathrm{OH}$
B. propanoic acid and $\mathrm{CH}_{3} \mathrm{Cl}$
C. propanal and HCl
D. methyl propanoate and HCl
17. Which one of the following tetrahedral intermediates dissociates to an ester?
A)

B)

C)

D)

A. A
B. B
C. C
D. D
18. Which of the following is the product of the addition of water to methyl isocyanate, $\mathrm{CH}_{3} \mathrm{~N}=\mathrm{C}=\mathrm{O}$ ?
A) $\mathrm{H}_{3} \mathrm{C}_{\substack{\mathrm{N} \\ \mathrm{H}}}^{\stackrel{\mathrm{O}}{\mathrm{OH}} \mathrm{OH} \text {, }}$
B)

C)


A. A
B. B
C. C
D. D
19. What is the product of the following reaction sequence?

A. 2-methyl-1-pentanol
B. 2-bromo-3-methylpentanoic acid
C. 2-methylpentanoic acid
D. 4-hydroxyhexanoic acid
20. Each of the following gives methylammonium chloride, $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+} \mathrm{Cl}^{-}$, when hydrolyzed in aqueous acid solution except one. Which one?

A)



B)
C)
D)
A. A
B. B
C. C
D. D
21. Identify the monomer(s) used to make the following polymer.


Nylon
A) $\mathrm{HOC}\left(\mathrm{CH}_{2}\right)_{4} \mathrm{COH}$ and $\mathrm{NH}_{2}\left(\mathrm{CH}_{2}\right)_{6} \mathrm{NH}_{2}$
B) $\stackrel{\mathrm{O}}{\substack{\mathrm{O} \\ \mathrm{H}_{2} \mathrm{~N} \\ \mathrm{C} \\\left(\mathrm{CH}_{4}\right) \\ \text { ) } \\ \mathrm{CNH}} 2}$ and $\mathrm{HO}\left(\mathrm{CH}_{2}\right)_{6} \mathrm{OH}$
C) $\stackrel{\stackrel{\mathrm{O}}{\mathrm{O}} \mathrm{H}_{2} \mathrm{~N}\left(\mathrm{CH}_{2}\right)_{5} \mathrm{COH}}{ }$
D) $\mathrm{NH}_{2} \stackrel{\mathrm{O}}{\mathrm{C}}\left(\mathrm{CH}_{2}\right)_{5} \mathrm{OH}$
A. A
B. B
C. C
D. D
22. Identify the stereochemistries of sec-butyl benzoate and 2-butanol in the following reaction sequence. (Assume that the reaction sequence shown follows the customary mechanisms for bimolecular nucleophilic substitution and nucleophilic acyl substitution.)


| sec-butyl benzoate |  | 2-butanol |
| :--- | :--- | :--- |
| A) $R$ |  | $S$ |
| B) $R$ | $R$ |  |
| C) $S$ | $R$ |  |
| D) $S$ | racemic |  |

A. A
B. B
C. C
D. D
23. Which of the following compounds, on reaction with aqueous sodium hydroxide, yields sodium butanoate, $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{Na}$, at the slowest rate?
A)

B) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{COCH}_{3}$
C) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CNH}_{2}$
D) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \stackrel{\mathrm{O}}{\mathrm{CO}}$
A. A
B. B
C. C
D. D
24. Which of the following is the tetrahedral intermediate formed in the reaction of a thioester with ammonia?

A)

B)

C)


D)

A. A
B. B
C. C
D. D
25. Which of the following best represents a mechanistic step in the acid-catalyzed hydrolysis of acetonitrile?

B)

C) $\mathrm{H}_{3} \mathrm{C}-\mathrm{C}=\mathrm{N}:$

D) $\mathrm{H}_{3} \mathrm{C}-\mathrm{C} \equiv \mathrm{N}$ :

A. A
B. B
C. C
D. D
26. Which of the following is the product of the reaction shown below?

A)

B)

C)

D)

A. A
B. B
C. C
D. $D$
27. Which one of the following would not give butyl acetate when reacted with 1-butanol?
$\stackrel{\mathrm{O}}{\mathrm{O}} \underset{\mathrm{CH}_{3} \mathrm{COCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3} \quad \text { butyl acetate }}{ }$
A) $\mathrm{CH}_{3} \stackrel{\|}{\mathrm{CCl}}$ (with pyridine)
B) $\underset{\substack{\mathrm{O} \\ \mathrm{O} \\ \mathrm{O} \\ \mathrm{COCCH}}}{ }$
C) $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$ (with $\mathrm{H}_{2} \mathrm{SO}_{4}$ )
D) $\stackrel{\mathrm{O}}{\mathrm{O}} \mathrm{CH}_{3} \mathrm{C} H\left(\right.$ with $\left.\mathrm{H}_{2} \mathrm{SO}_{4}\right)$
A. A
B. B
C. C
D. D
28. With the stereochemistry of the starting material shown, identify the stereochemistry of 2-butanol in the following reaction sequence.

(S enantiomer)
A. (S)-2-butanol
B. (R)-2-butanol
C. racemic 2-butanol
D. meso-2-butanol
29. Which one of the following reagents converts a carboxylic acid to an acyl chloride as shown below?

A. HCl
B. $\mathrm{NaCl}, \mathrm{H}_{2} \mathrm{O}$
C. $\quad \mathrm{SOCl}_{2}$
D. $\quad \mathrm{Cl}_{2}$
30. What is the product of the following reaction sequence?
$\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H} \xrightarrow{\mathrm{SOCl}_{2}} \xrightarrow{2 \mathrm{HN}\left(\mathrm{CH}_{3}\right)_{2}}$
A)

B) $\mathrm{CH}_{3} \stackrel{\mathrm{OH}}{\mathrm{CH}} \mathrm{CHN}\left(\mathrm{CH}_{3}\right)_{2}$
C) $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{~N}\left(\mathrm{CH}_{3}\right)_{2}$
D) $\mathrm{CH}_{3} \mathrm{CON}\left(\mathrm{CH}_{3}\right)_{2}$
A. A
B. B
C. C
D. D
31. Identify the product obtained in the hydrolysis of the following cyclic acid anhydride.

A. $\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH}$
B. $\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{H}$
C. $\mathrm{HO}_{2} \mathrm{CCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{H}$
D. $\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}=\mathrm{O}$
32. What is the product of the following reaction?
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OH} \xrightarrow{\stackrel{\mathrm{O}}{\mathrm{I}}} \xrightarrow{\left(\mathrm{CH}_{3}\right)_{2} \mathrm{O}}$
A. butanal
B. butyl acetate
C. 2-hexanone
D. ethyl butanoate

## ACS Review Carboxylic Acid Derivatives Nucleophilic Acyl Substitution KEY

1. A
2. C
3. A
4. B
5. D
6. A
7. A
8. в
9. в
10. D
11. C
12. A
13. B
14. D
15. B
16. D
17. D
18. A
19. C
20. в
21. A
22. B
23. C
24. A
25. B
26. D
27. D
28. A
29. C
30. A
31. C
32. в
