ACS Review Carboxylic Acid Derivatives Nucleophilic Acyl Substitution

- 1. Which of the following is isopropyl benzoate?
 - A. $C_6H_5CO_2CH(CH_3)_2$
 - B. $C_6H_5CH_2CO_2CH(CH_3)_2$
 - $C. \qquad (CH_3)_2 CHCO_2 C_6 H_5$
 - D. $(CH_3)_2CHCO_2CH_2C_6H_5$
- 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?

```
0 0
              || ||
A) CH<sub>3</sub>COCCH<sub>3</sub>
             0
              Ш
B) CH<sub>3</sub>CCl
             0
             Ш
C) CH<sub>3</sub>COCH<sub>2</sub>CH<sub>3</sub>
              Ο
              Ш
D) CH<sub>3</sub>CNH<sub>2</sub>
          A.
                      А
          Β.
                      В
          C.
                      С
```

D. D

5. The compound shown below is classified as a(an):



- A. lactone
- B. β -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.	I > II > III > IV
ъ	TTTTTTTTTTTTT

- B. IV > III > II > I
- C. I > III > II > IV
- $D. \qquad II > III > IV > I$
- 7. What is the product of the following reactions?



- 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, 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 (°C): 28, 57, 100, 141

	methyl acetate	2-butanol	2-methylbutane	propanoic acid
A)	100°	141°	28°	57°
B)	57°	100°	28°	141°
C)	28°	100°	57°	141°
D)	141°	57°	28°	100°

A. A B. B C. C D. D

10. Which of the following would work best in preparing *tert*-butyl benzoate?

- A. $C_6H_5CO_2H$ plus (CH₃)₃COH with H₂SO₄ catalyst and heat
- B. $C_6H_5CO_2Na$ plus (CH₃)₃CBr and heat
- C. $C_6H_5CONH_2$ plus (CH₃)₃COH and heat
- D. $C_6H_5CO_2H$ plus SOCl₂ followed by (CH₃)₃COH with pyridine
- 11. Saponification and neutralization of ¹⁸O labeled ethyl acetate, as shown below, yields which of the following isotopically labeled products?

 $CH_{3}C^{H_{2}}CH_{2}CH_{3} \qquad \frac{(1) \text{ NaOH, H}_{2}O, \text{ heat}}{(2) \text{ H}_{3}O^{+}}$ $A) CH_{3}COH + CH_{3}CH_{2}OH$ $B) CH_{3}C^{H}OH + CH_{3}CH_{2}OH$ $C) CH_{3}COH + CH_{3}CH_{2}^{H}OH$ 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



- 14. Which one of the following does <u>not</u> react with benzoyl chloride, C_6H_5COC1 ?
 - A. NH_3
 - B. CH₃NH₂
 - C. $(CH_3)_2NH$
 - D. (CH₃)₃N
- 15. Which one of the following is <u>not</u> a good way to make ethyl acetate?
 - A. CH_3CO_2H and CH_3CH_2OH with H_2SO_4 as a catalyst
 - B. CH₃CO₂H and CH₃CH₂OH with NaOH
 - C. CH₃COCl and CH₃CH₂OH with pyridine
 - D. $(CH_3CO)_2O$ and CH_3CH_2OH with H_2SO_4 as a catalyst
- 16. The following tetrahedral intermediate breaks down to:

$$CH_{3}CH_{2} - C - CI$$

$$|$$

$$OCH_{3}$$

- A. propanoyl chloride and CH₃OH
- B. propanoic acid and CH₃Cl
- C. propanal and HCl
- D. methyl propanoate and HCl
- 17. Which one of the following tetrahedral intermediates dissociates to an ester?

$$A) H_{3}C - C - NH_{2}$$
$$OCH_{3}$$
$$B) H_{3}C - C - OCCH_{3}$$
$$H_{3}C - C - OCCH_{3}$$
$$H_{3}C - C - NH_{2}$$
$$CI$$
$$C) H_{3}C - C - NH_{2}$$
$$CI$$
$$D) H_{3}C - C - OCCH_{3}$$
$$OCH_{3}$$
$$A. A$$
$$B. B$$
$$C. C$$
$$D. D$$

18. Which of the following is the product of the addition of water to methyl isocyanate, $CH_3N=C=O$?





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, CH₃NH₃⁺ Cl⁻, when hydrolyzed in aqueous acid solution except one. Which one?



21. Identify the monomer(s) used to make the following polymer.





```
О
                          О
A) HOC(CH<sub>2</sub>)<sub>4</sub>COH and NH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>NH<sub>2</sub>
B) H_2NC(CH_4)CNH_2 and HO(CH_2)_6OH
О
||
С) H<sub>2</sub>N(CH<sub>2</sub>)<sub>5</sub>COH
             0
             Ш
D) NH<sub>2</sub>C(CH<sub>2</sub>)<sub>5</sub>OH
          A.
                      А
          B.
                      В
          C.
                      С
          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

sec-butyl benzoate	<u>2-butanol</u>
A) R	S
B) R	R
C) S	R
D) S	racemic

A.	Α
B.	В
C.	С
D.	D

23. Which of the following compounds, on reaction with aqueous sodium hydroxide, yields sodium butanoate, CH₃CH₂CO₂Na, at the slowest rate?

O \parallel A) (CH₃CH₂CH₂C)₂O O \parallel B) CH₃CH₂CH₂COCH₃

C) $CH_3CH_2CH_2CNH_2$

O || D) CH₃CH₂CH₂COH

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?



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





26. Which of the following is the product of the reaction shown below?



D. D

27. Which one of the following would not give butyl acetate when reacted with 1-butanol?

```
0
      Ш
CH<sub>3</sub>COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
                                           butyl acetate
             0
              Ш
A) CH<sub>3</sub>CCl (with pyridine)
            00
             11 11
B) CH<sub>3</sub>COCCH<sub>3</sub> (with pyridine)
C) CH_3CO_2H (with H_2SO_4)
             0
              Ш
D) CH<sub>3</sub>CH (with H<sub>2</sub>SO<sub>4</sub>)
         A.
                    А
         B.
                    В
                    С
         C.
         D.
                    D
```

28. With the stereochemistry of the starting material shown, identify the stereochemistry of 2-butanol in the following reaction sequence.



30. What is the product of the following reaction sequence?

 $CH_{3}CO_{2}H \xrightarrow{SOCl_{2}} \xrightarrow{2 HN(CH_{3})_{2}}$

```
O
||
A) CH<sub>3</sub>CN(CH<sub>3</sub>)<sub>2</sub>
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OH |B) CH₃CHN(CH₃)₂ C) CH₃CH₂N(CH₃)₂ O |D) CH₃CON(CH₃)₂ A. A B. B

> C. C D. D

31. Identify the product obtained in the hydrolysis of the following cyclic acid anhydride.



32. What is the product of the following reaction?

$$CH_{3}CH_{2}CH_{2}CH_{2}OH \xrightarrow{(CH_{3}C)_{2}O}$$

- A. butanal
- B. butyl acetate
- C. 2-hexanone
- D. ethyl butanoate

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

1. A

31. с 32. в