Exam

Name_____

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

1) Carboxylic acids boil at considerably higher temperatures than do alcohols, ketones, or aldehydes of similar molecular weights. This is because they: 1) _____
   A) form stable hydrogen–bonded dimers.
   B) are hydrophobic.
   C) are more acidic.
   D) have a greater oxygen content.
   E) none of the above.

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

2) Are carboxylic acids of more than 10 carbons more soluble in polar or nonpolar solvents? 2) _____

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

3) Which of the following is the strongest acid? 3) _____
   A) chloroacetic acid
   B) fluoroacetic acid
   C) bromoacetic acid
   D) acetic acid

4) Which of the following is the strongest acid? 4) _____
   A) dichloroacetic acid
   B) trichloroacetic acid
   C) chloroacetic acid
   D) acetic acid

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

5) Draw an acetic acid dimer. Be sure to indicate the hydrogen bonds present. 5) _____

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

6) At pH 4.5, which of the following acids would be most dissociated? 6) _____
   A) octanoic acid ($pK_a = 4.89$)
   B) *p*–nitrobenzoic acid ($pK_a = 3.41$)
   C) acetic acid (ethanoic acid) ($pK_a = 4.74$)
   D) hexanoic acid ($pK_a = 4.88$)
   E) water

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

7) What products result from the reaction of sodium propanoate with hydrobromic acid? 7) _____

ESSAY. Write your answer in the space provided or on a separate sheet of paper.

8) What salt results from the reaction of benzoic acid with potassium hydroxide?

9) Name the salt formed from the reaction of acetic acid with ammonia.

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

10) An unknown compound is insoluble in water but dissolves in sodium bicarbonate with a release of carbon dioxide bubbles. The compound is almost certainly: 10) _____
A) an aldehyde
B) a carboxylic acid
C) an amine
D) an alcohol
E) an alkyl chloride

ESSAY. Write your answer in the space provided or on a separate sheet of paper.

11) Using acid–base extractions, how might you purify a crude sample of benzoic acid?

12) What two features are prominent in the infrared spectrum of a carboxylic acid?

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

13) Where would one expect to find the ^{1}H NMR signal for the carboxyl group's hydrogen in propanoic acid? 13) _____
A) δ 10 – 13 ppm
B) δ 4.1 – 5.6 ppm
C) δ 6.1 – 7.8 ppm
D) δ 8 – 9 ppm
E) δ 9.5 – 10 ppm

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

14) 1–Hexanol reacts with chromic acid to yield what product? 14) _____

ESSAY. Write your answer in the space provided or on a separate sheet of paper.

15) What two alkenes, which contain only one double bond, yield exclusively propanoic acid upon oxidation with hot concentrated $KMnO_4$?

16) 2–Phenylethanol yields what acid upon treatment with cold chromic acid?

17) 2–Phenylethanol yields what acid upon treatment with hot chromic acid or permanganate?

18) Hept–3–yne yields what acids upon treatment with concentrated permanganate of ozone followed by water?

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

19) Carboxylic acids can be made from Grignards by treating the Grignard reagents with: 19) _____
A) esters
B) diborane
C) carbon monoxide
D) carbon dioxide
E) aldehydes

ESSAY. Write your answer in the space provided or on a separate sheet of paper.

20) Suggest a sequence of synthetic steps through which phenylacetic acid can be prepared from toluene via phenylacetonitrile.

21) Suggest a sequence of synthetic steps through which phenylacetic acid can be prepared from toluene and in which Grignard chemistry is employed.

22) Provide a detailed, stepwise mechanism for the reaction of acetyl chloride with methanol to produce methyl acetate and HCl.

23) What are the products of the reaction of benzoic acid with thionyl chloride?

24) What are the products of the reaction of phenylacetic acid with oxalyl chloride?

25) Give a detailed, stepwise mechanism for the Fischer esterification of acetic acid with methanol.

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

26) Which of the following conditions will drive the equilibrium of the Fischer esterification towards ester formation? 26) _____
A) addition of water
B) removal of water as it is formed
C) addition of an inorganic acid as a catalyst
D) addition of alcohol
E) both B and D

27) The methyl ester of a carboxylic acid can be synthesized directly using: 27) _____
A) CH_2N_2 B) $C_2O_2Cl_2$ C) PCl_5 D) $SOCl_2$ E) CH_3NH_2

28) Esters and amides are most easily made by nucleophilic acyl substitution reactions on: 28) _____
A) carboxylic acids
B) alcohols
C) acid chlorides
D) acid anhydrides
E) carboxylates

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

29) Provide a detailed, stepwise mechanism for the methylation of a carboxylic acid with diazomethane. 29) _____

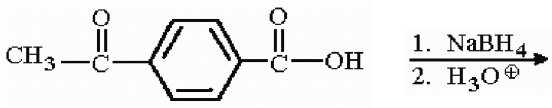
MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

30) The first mechanistic step in the direct reaction of an amine with a carboxylic acid to produce an amide is: 30) _____
A) nucleophilic attack on the carbonyl carbon
B) loss of N_2
C) loss of CO_2
D) loss of H_2O
E) an acid–base reaction

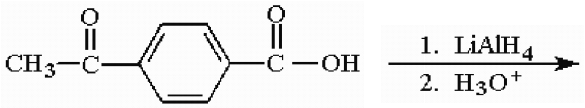
31) Lithium aluminum hydride reduces carboxylic acids to primary alcohols via what intermediate? 31) _____
A) a methyl ester
B) an aldehyde
C) a ketone
D) a secondary alcohol
E) an acid chloride

ESSAY. Write your answer in the space provided or on a separate sheet of paper.

32) Provide the major organic product for the following reaction.



33) Provide the major organic product for the following reaction.



MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

34) LiAl $[OC(CH_3)_3]_3H$ will reduce an acid chloride to an: 34) _____
A) aldehyde B) alcohol C) alkane D) acid E) acetal

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

35) Suggest a sequence of synthetic steps through which *p*–toluic acid can be prepared from toluene. 35) _____

ESSAY. Write your answer in the space provided or on a separate sheet of paper.

36) Suggest a sequence of synthetic steps through which 2–phenylethanol can be prepared from toluene. One of your intermediates must be a carboxylic acid.

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

37) What alkyllithium would react with acetic acid to form 2–butanone? 37) _____

A) phenyllithium
B) vinyllithium
C) ethyllithium
D) propyllithium
E) methyllithium

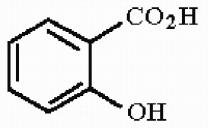
ESSAY. Write your answer in the space provided or on a separate sheet of paper.

38) How does the O–H stretch in the IR spectrum of a carboxylic acid differ from the O–H stretch of an alcohol?

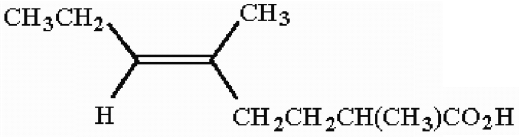
39) Provide the structure of succinic acid.

40) Provide the IUPAC name for $HO_2CCH_2C(CH_3)_2CH_2CH_2CO_2H$.

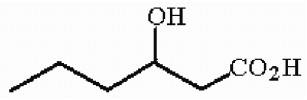
41) Provide the IUPAC name for the compound shown below.



42) Provide the IUPAC name for the compound shown below.



43) Provide the IUPAC name for the compound shown below.



44) Provide the structure of *trans*–1,3–cyclohexanedicarboxylic acid.

45) Provide the structure of pent–3–ynoic acid.

46) Provide the structure of 3–nitrophthalic acid.

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

47) The strongest dichlorobutanoic acid is: 47) _____
A) 4,4–dichlorobutanoic acid
B) 3,3–dichlorobutanoic acid
C) 3,4–dichlorobutanoic acid
D) 2,3–dichlorobutanoic acid
E) 2,2–dichlorobutanoic acid

48) Which of the following compounds is the strongest acid? 48) _____
A) *m*–methylbenzoic acid
B) water
C) *p*–bromobenzoic acid
D) *p*–nitrobenzoic acid
E) *m*–methoxybenzoic acid

49) An acid which could <u>not</u> be prepared by the reaction of an organic halide with cyanide ion followed by acid hydrolysis of the nitrile is: 49) _____
A) $(CH_3)_3CCO_2H$
B) $CH_3(CH_2)_{14}CO_2H$
C) propanoic acid
D) phenylacetic acid
E) acetic acid

50) An acid which could <u>not</u> be prepared from an organic halide by carboxylation of the Grignard reagent is: 50) _____
A) benzoic acid
B) 4–oxocyclohexanecarboxylic acid
C) propanoic acid
D) 2–methylbutanoic acid
E) 2,2–dimethylpropanoic acid

51) The conversion of butanoic acid to 2–pentanone is best accomplished with: 51) _____
A) methyllithium
B) 1. methanol, sulfuric acid; 2. methyllithium
C) 1. sulfuric acid; 2. methanol
D) 1. thionyl chloride; 2. methanol
E) 1. thionyl chloride; 2. methylmagnesium bromide

52) Which of the following reactions involves the formation of a methyl ester from a carboxylic acid? 52) _____
A) reaction with CH_2N_2
B) Hunsdiecker reaction
C) Hell–Volhard–Zelinsky reaction
D) Cope elimination
E) hydroboration with diborane

53) An ether solution of $PhCO_2H$ (A), $PhNH_2$ (B), and $PhCH_3$ (C) is extracted with aqueous NaOH. The ether layer will contain what compound(s) after the extraction? 53) _____
A) A + C B) A only C) A + B D) B + C E) A + B + C

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

54) Provide a detailed, stepwise mechanism to show how PhCHO is formed by the reaction of PhCOCl with LiAlH [O(CH3)3]3. 54) _____

ESSAY. Write your answer in the space provided or on a separate sheet of paper.

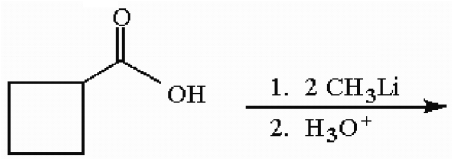
55) Provide the structure of the major organic compound which results when cyclopentanecarboxylic acid is treated with thionyl chloride and the resulting product is treated with LiAlH[OC(CH3)3]3.

56) Deduce a reasonable structure for the compound which exhibits the following spectroscopic data. $C_5H_9ClO_2$: IR: 2700–3400 cm^{-1} (broad), 1710 cm^{-1}; ^1H NMR: _ 1.40 (6H, singlet), 3.60 (2H, singlet), 10.1 (1H, singlet) ppm.

57) Propose a reasonable synthetic route to prepare cyclohexylacetic acid from methylenecyclohexane.

58) Propose a reasonable synthetic route to prepare butanal from butanoic acid.

59) Provide the structure of the major organic product of the reaction sequence shown.



60) Draw a Fischer projection of the product which results when (*R*)–2–bromobutane is treated with the following sequence of reagents: 1. CN^-, 2. H_3O^+, and 3. CH_2N_2.

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

61) The combination of a carbonyl group and a hydroxyl group on the same carbon atom is called a _____ group. 61) _____
A) carbonate
B) urethane
C) carboxylate
D) carboxyl
E) carbamate

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

62) Provide the structure of 3,3–dimethylheptanoic acid. 62) _____

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

63) The common name for pentanedioic acid is: 63) _____
A) pimelic acid
B) succinic acid
C) glutaric acid
D) oxalic acid
E) adipic acid

64) In the propanoate ion,: 64) _____
A) the carbon–oxygen double bond is shorter.
B) the carbon atom bears a –1 charge.
C) one of the oxygen atoms bears a –1 charge.
D) the carbon–oxygen double bond is longer.
E) both the carbon–oxygen bonds are the same length.

65) Which of the following is the strongest acid? 65) _____
A) $(CH_3)_2CHCO_2H$
B) $CH_3OCH_2CO_2H$
C) $O_2NCH_2CO_2H$
D) $CH_3CH_2CO_2H$
E) $PhCH_2CO_2H$

66) In the mass spectrum of pentanoic acid, the base peak occurs at *m*/*z*: 66) _____
A) 73 B) 102 C) 60 D) 101 E) 85

67) What compound is produced when cyclohexene is treated with concentrated $KMnO_4$? 67) _____
A) benzoic acid
B) succinic acid
C) adipic acid
D) hexanoic acid
E) cyclohexanecarboxylic acid

68) What compound is produced when $(CH_3)_2CHCH_2Br$ is subjected to the following sequence of steps: 1. Mg, Et_2O, 2. CO_2, 3. H_3O^+? 68) _____
A) 2–methylpropanoic acid
B) 2–methylhexanoic acid
C) 3–methylbutanoic acid
D) 3–methylpropanoic acid
E) 2–methylbutanoic acid

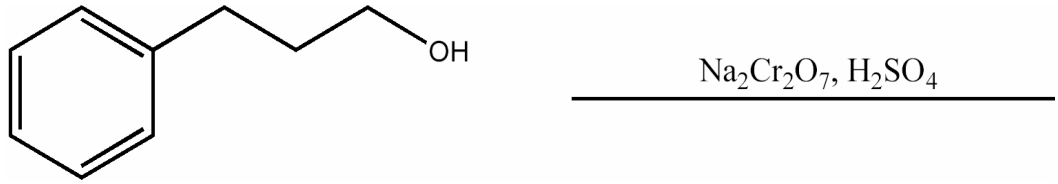
69) Acid chlorides can be prepared from carboxylic acids by treatment with: 69) _____
A) $(COCl)_2$
B) $SOCl_2$
C) KCl
D) both A and B
E) both B and C

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

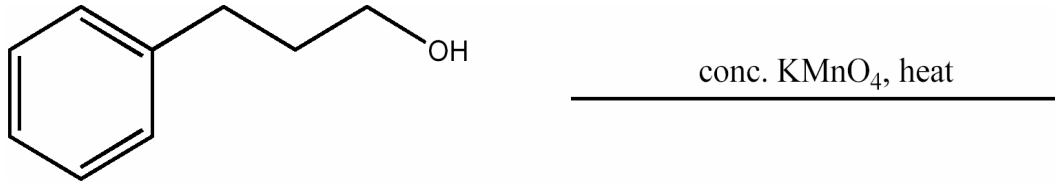
70) How can one prepare ethyl cyclohexyl ketone from cyclohexanecarboxylic acid? 70) _____

71) Provide the structure of glutaric acid. 71) _____

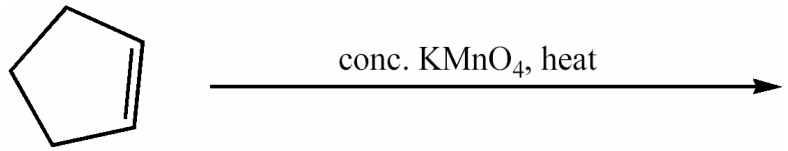
72) Provide the major organic product of the following reaction. 72) _____



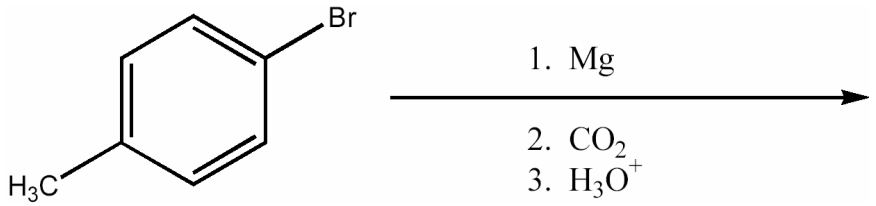
73) Provide the major organic product of the following reaction. 73) _____



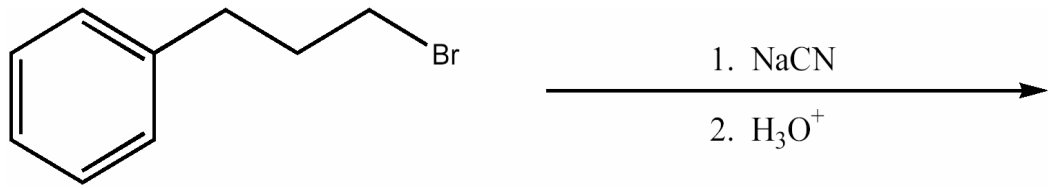
74) Provide the major organic product of the following reaction. 74) _____



75) Provide the major organic product of the following reaction. 75) _____



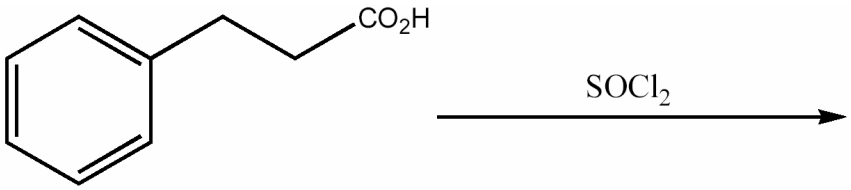
76) Provide the major organic product of the following reaction. 76) _____



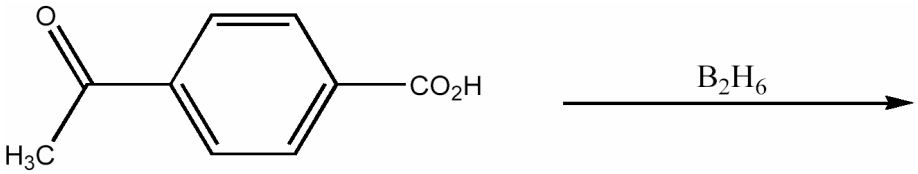
77) Provide the major organic product of the following reaction. 77) _____

$HC(OCH_2CH_3)_3 \xrightarrow{H_3O^+, \text{ heat}}$

78) Provide the major organic product of the following reaction. 78) _____



79) Provide the major organic product of the following reaction. 79) _____



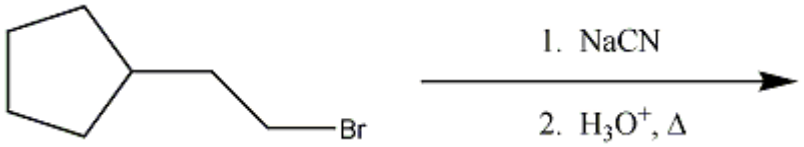
MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

80) Which of the following reagents can be used to convert a carboxylic acid directly into its corresponding acid chloride derivative? 80) _____

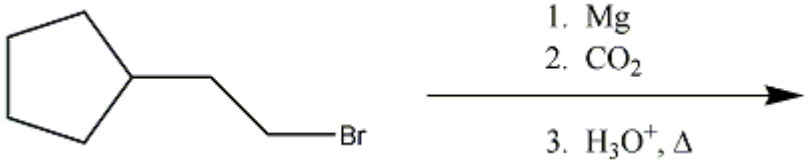
A) HCl B) CH_3COCl C) NaOCl D) CH_3Cl E) $(COCl)_2$

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

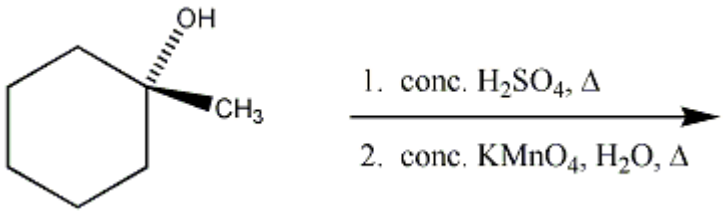
81) Provide the major organic product of the following reaction sequence. 81) _____



82) Provide the major organic product of the following reaction sequence. 82) _____

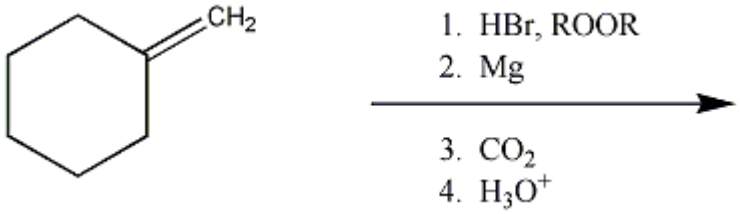


83) Provide the major organic product of the following reaction sequence. 83) _____

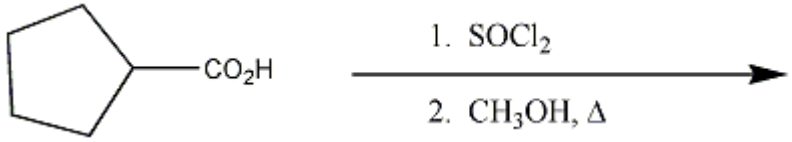


84) Provide the sequence of reagents needed to accomplish the conversion below. 84) _____

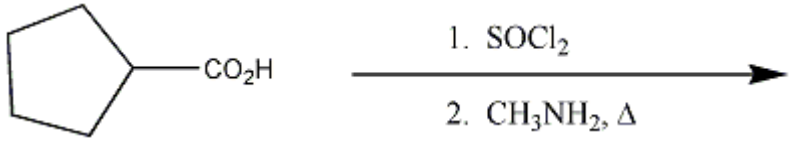
85) Provide the major organic product of the following reaction sequence. 85) _____



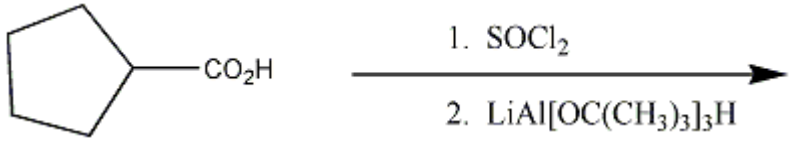
86) Provide the major organic product of the following reaction sequence. 86) _____



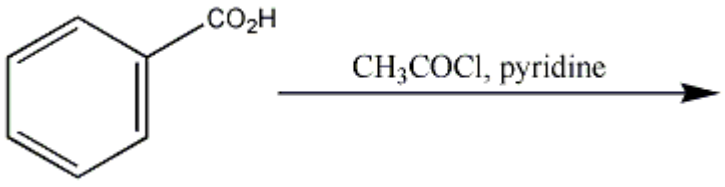
87) Provide the major organic product of the following reaction sequence. 87) _____



88) Provide the major organic product of the following reaction sequence. 88) _____



89) Provide the major organic product of the following reaction sequence. 89) _____



90) Provide the structure of zinc undecanoate, a major component in several athlete's foot medications. 90) _____

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

91) Which of the following statements is true? 91) _____

A) The carbonyl carbon in a carboxylic acid gives a ^{13}C signal in the same region as a carbonyl carbon from an ester or amide in the range of 150 to 180 ppm.
B) The carbonyl carbon in a carboxylic acid does not give a ^{13}C signal in a ^{13}C–NMR spectrum.
C) The carbonyl carbon in a carboxylic acid cannot be distinguished from an aromatic carbon because they both give signals in the range of 110 to 130 ppm.
D) The carbonyl carbon in a carboxylic acid gives a ^{13}C signal in the same region as a carbonyl carbon from a ketone or aldehyde – in the range of 200 ppm.
E) The carbonyl carbon of a carboxylic acid splits a proton signal into a doublet in an H–NMR spectrum.

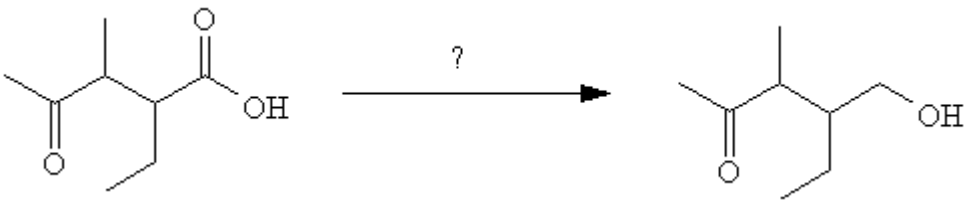
92) After completing the synthesis of 3–methylpentanoic acid, which of the following treatments will neutralize the mineral acids and facilitate the distribution of the organic acid from the organic layer to the aqueous extraction layer? 92) _____

A) Extraction with ether.
B) Extraction with water.
C) Extraction with aqueous NaCl.
D) Extraction with dilute aqueous HCl.
E) Extraction with aqueous $NaHCO_3$.

93) Which of the following statements is true? 93) _____

A) At two pH units above the pKa, the carboxylate ion concentration exceeds the concentration of the carboxylic acid by a 100 to 1 ratio.
B) At two pH units below the pKa the carboxylate ion concentration is equal to the carboxylic acid concentration.
C) At two pH units below the pKa, the carboxylate ion concentration exceeds the concentration of the carboxylic acid by a 2 to 1 ratio.
D) At two pH units below the pKa, the carboxylate ion concentration exceeds the concentration of the carboxylic acid by a 10 to 1 ratio.
E) At two pH units above the pKa, the carboxylate ion concentration exceeds the concentration of the carboxylic acid by a 2 to 1 ratio.

94) Which of the reagents listed below would work best in the following reaction? 94) _____



A) $LiAlH_4$
B) BH_3 –THF
C) $LiAl[(OC(CH_3)_3]_3H$
D) $NaBH_4$
E) none of the above

95) Which sequence of steps below describes the best synthesis of 5–oxohexanoic acid starting with 1–methylcyclopentan–1–ol 95) _____

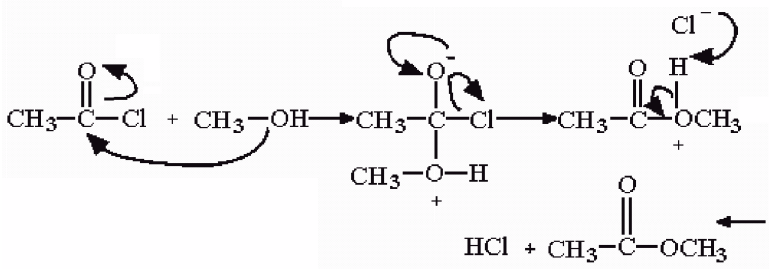
A) 1. Conc. $KMnO_4$
2. Dry gaseous HBr
3. mg/ether
4. CO_2

B) 1. Conc. $KMnO_4$
2. CH_3MgBr/ ether
3. H_3O^+

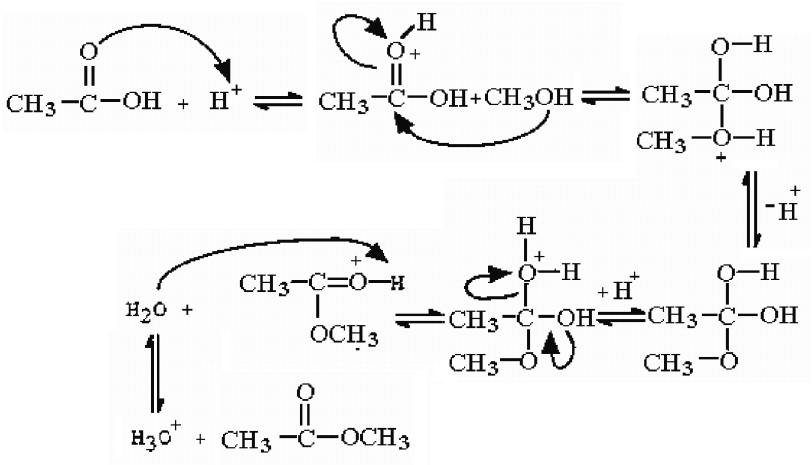
C) 1. H_2SO_4 and heat
2. Conc. $KMnO_4$

D) 1. H_2SO_4 and heat
2. O_3
3. $(CH_3)_2S$
4. PCC

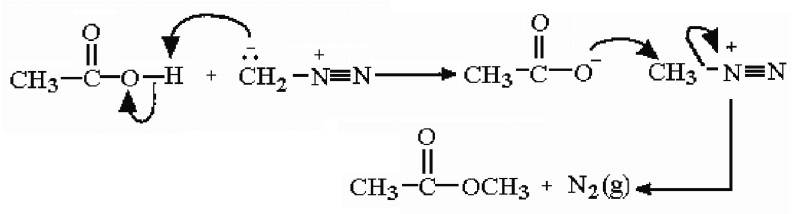
E) 1. H_2SO_4 and heat
2. Conc. $KMnO_4$
3. $LiAlH_4$
4. H_3O^+

1) A
2) nonpolar solvents
3) B
4) B
5) 
6) B
7) propanoic acid and sodium bromide
8) potassium benzoate
9) ammonium acetate
10) B
11) 1. Dissolve sample in ether.
    2. Extract with water to remove water–soluble impurities.
    3. Extract with sodium bicarbonate to separate benzoate from organic impurities.
    4. Acidify aqueous layer and extract benzoic acid into ether.
    5. Dry ether layer, filter to remove drying agent, and evaporate ether to give purified benzoic acid.
12) The carbonyl stretch at ~1710 cm^{-1} and the hydroxyl stretch between 2500 and 3500 cm^{-1}.
13) A
14) Hexanoic acid
15) *E*– and *Z*–hex–3–ene
16) phenylacetic acid
17) benzoic acid
18) propanoic and butanoic acids
19) D
20) 1. Br_2, hν or NBS
    2. NaCN, acetone
    3. H^+, H_2O
21) 1. Br_2, hν or NBS
    2. Mg, ether
    3. CO_2
    4. H^+, H_2O
22) 
23) benzoyl chloride, SO_2(g), and HCl(g)
24) phenylacetyl chloride, HCl (g), CO (g), and CO_2 (g)

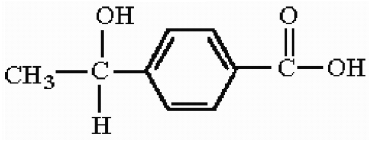
25)



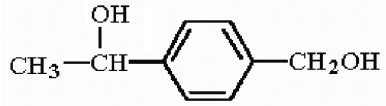
26) E
27) A
28) C
29)



30) E
31) B
32)



33)



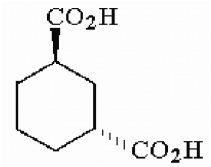
34) A
35) 1. Br_2, $FeBr_3$
2. Mg, ether
3. CO_2
4. H_3O+

36) 1. Br_2, hν or NBS
2. NaCN, acetone
3. H+, H_2O
4. $LiAlH_4$

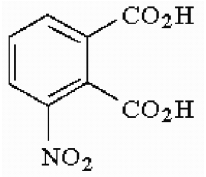
or

1. Br_2, hν or NBS
2. Mg, ether
3. CO_2
4. H+, H_2O
5. $LiAlH_4$

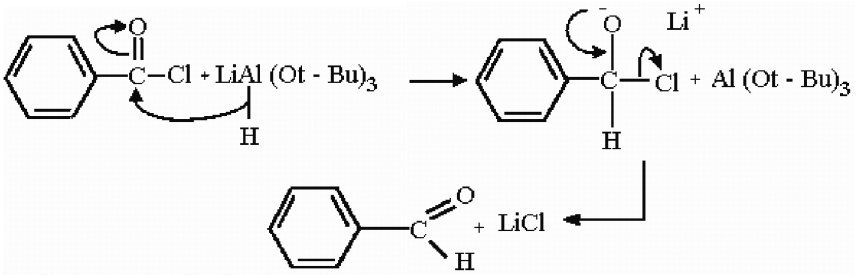
37) C
38) The O–H stretch of a carboxylic acid is broader and shifted to lower wavenumbers.
39) $HO_2C\ CH_2CH_2CO_2H$
40) 3,3–dimethylhexanedioic acid
41) *o*–hydroxybenzoic acid or 2–hydroxybenzoic acid
42) *E*–2,5–dimethyloct–5–enoic acid
43) 3–hydroxyhexanoic acid
44)

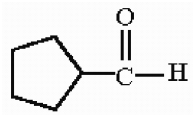


45) $CH_3C{\equiv}CCH_2CO_2H$
46)



47) E
48) D
49) A
50) B
51) A
52) A
53) D
54)



55)


56) $(CH_3)_2CClCH_2CO_2H$

57) 1. HBr, peroxides
2. Mg, ether
3. CO_2
4. H^+, H_2O

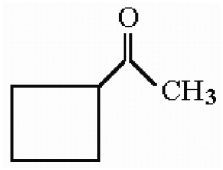
or

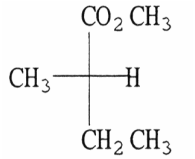
1. HBr, peroxides
2. NaCN, acetone
3. H^+, H_2O

58) 1. $LiAlH_4$
2. PCC

or

1. $SOCl_2$
2. $LiAlH[OC(CH_3)_3]_3$

59)


60)


61) D

62) $CH_3CH_2CH_2CH_2C(CH_3)_2CH_2CO_2H$

63) C

64) E

65) C

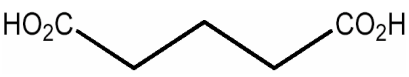
66) C

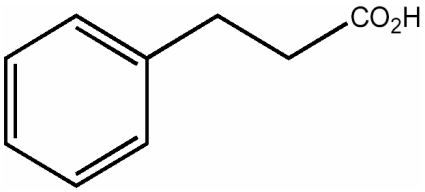
67) C

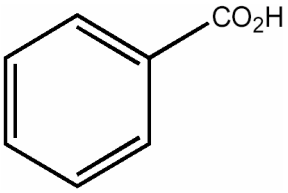
68) C

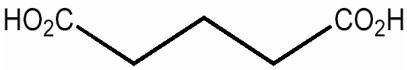
69) D

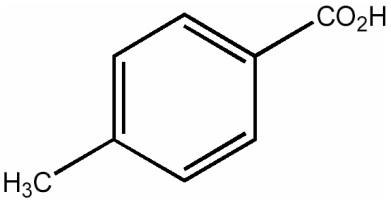
70) 1. CH_3CH_2Li (2 eq.)
2. H_3O^+

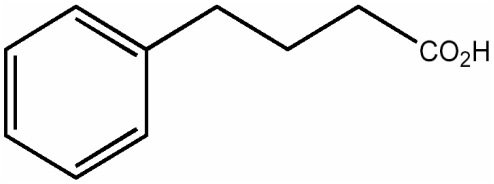
71)


72) 

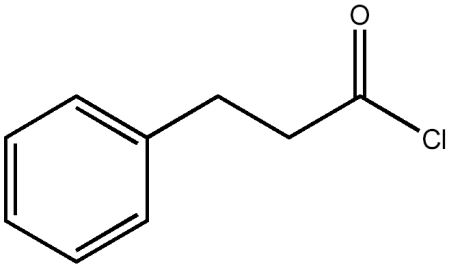
73) 

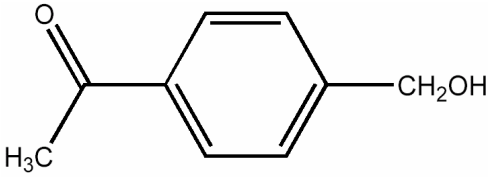
74) 

75) 

76) 

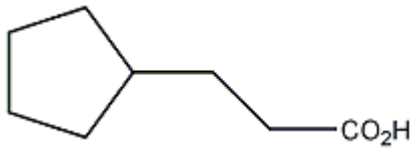
77) HCO_2H + CH_3CH_2OH

78) 

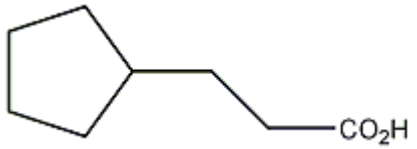
79) 

80) E

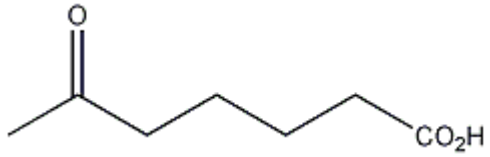
81)



82)

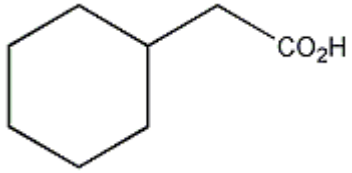


83)

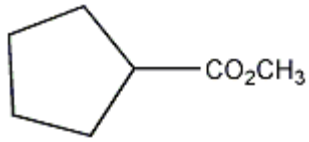


84) 1. BH_3•THF
2. H_2O_2, HO^-
3. $Na_2Cr_2O_7$

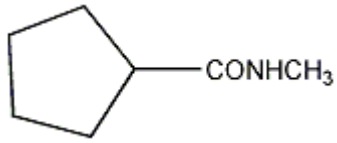
85)



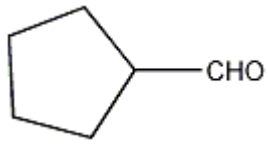
86)



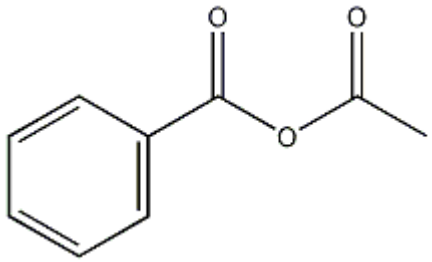
87)



88)



89)



90) $Zn[O_2C(CH_2)_9CH_3]_2$

91) A

92) E

93) A

94) B

95) C