

CARBOXYLIC ACIDS AND THEIR DERIVATIVES

A STUDENT SHOULD BE ABLE TO:

1. Give the IUPAC name given the structure, and draw the structure given the name, of carboxylic acids and their metal salts, acyl chlorides, esters, amides, and nitriles. Also, draw the structure given any of the following common names: phthalic, oxalic, malonic, succinic and glutaric acids; formic and acetic acids and their salts, chlorides, esters, and amides; acetic and phthalic anhydrides.
2. Predict the relative physical properties (boiling point, solubility) of carboxylic acids and their derivatives. Compounds containing previously studied functional groups may also be included.
3. Predict the relative acidity and basicity of compounds and ions. Important criteria include:

The normal order of acidity of functional groups is: $\text{RSO}_3\text{H} > \text{RCO}_2\text{H} > \text{ArOH} > \text{H}_2\text{O} > \text{ROH} > \text{RCCH} > \text{RNH}_2 > \text{RH}$.

Within a functional group family, conjugate acids are stronger acids than conjugate bases. That is, $\text{H}_3\text{X}^+ > \text{H}_2\text{X} > \text{HX}^-$.

Within a functional group family, electron-donating (activating) groups give stronger bases, and electron-withdrawing (deactivating) groups give stronger acids. The effect of an electron-withdrawing group depends on its proximity to the carboxylic acid moiety.

The stronger the acid, the weaker its conjugate base (and vice versa).
4. Predict the product of reactions giving rise to carboxylic acids (many of these are review), and the reactions of carboxylic acids and their derivatives, when given starting materials and reaction conditions. Important reactions include:

Acid-base reactions. Stronger acid + stronger base \rightarrow weaker acid + weaker base.
Oxidation of 1° alcohols, aldehydes, alkylbenzenes and alkynes.
Hydrolysis of nitriles.
Reductions with lithium aluminum hydride (LAH).
Carboxylation (carbonation) of Grignard reagents.
Nucleophilic acyl substitution (interconversion of carboxylic acids and their derivatives).
5. Predict and explain experimental results from your knowledge and understanding of nucleophilic acyl substitution mechanisms.
6. Use the reactions of #4 above, plus others learned earlier, to propose syntheses of carboxylic acids and related compounds.
7. Predict and interpret spectra and solubility test results to identify unknown carboxylic acids and their derivatives.

Solubility Tests for Monofunctional Compounds

This section tells you how to predict results for known compounds and use results to classify unknowns. Some are useful as stand-alone tests, but compounds that dissolve in water are soluble in all of the other reagents listed here; follow the whole scheme to get the best possible information. For these tests, “soluble” means “one drop of unknown will dissolve in one mL of solvent”.

Solubility in water

If a compound is soluble in water, it is a compound of about four carbons or less that contains N or O (or it may contain more than one functional group). If the compound contains five or six carbons it may or may not be soluble. If it contains six carbons or more it will be insoluble. If the compound is soluble, the *solution* is then tested with litmus paper.

If the solution turns blue litmus red, the unknown is a carboxylic acid (RCO_2H).

If the solution turns red litmus blue, the unknown is an amine (RNH_2 , R_2NH , or R_3N).

If the solution is neutral to litmus, the unknown includes a neutral O- or N-containing functional group such as alcohol, ether, aldehyde, ketone, ester, or amide.

If the compound is insoluble in water, go on to the next solubility test.

Solubility in 5% NaOH

If the compound is soluble in 5% NaOH but insoluble in water, it is acidic, either a phenol (ArOH) or a carboxylic acid (RCO_2H). This is reaction solubility, not like-dissolves-like solubility; the alkaline test solution reacts with acidic compounds to give ionic, water-soluble products. You must run the water solubility test first for this test to be useful; 5% NaOH is 95% water, and compounds that dissolve in water also dissolve in 5% NaOH because of that.

To distinguish between phenols and carboxylic acids, you can use the NaHCO_3 solubility test (next). If the compound is insoluble in 5% NaOH, go to the 5% HCl solubility test.

Solubility in 5% NaHCO_3

Sodium bicarbonate is weaker as a base than NaOH. NaHCO_3 is an ingredient of some over-the-counter medications that react with excess stomach acid, but NaOH is far too strong a base, and therefore far too dangerous, for that. This is another reaction-solubility test; bicarbonate ion reacts with carboxylic acids but not with phenols to produce water-soluble salts. The reaction also gives carbon dioxide, and these bubbles are visible, making this a useful stand-alone test for carboxylic acids.

Solubility in 5% HCl

This is yet another reaction-solubility test. Basic organic compounds (amines) react with the acid to give water-soluble products. As with the 5% NaOH test, it is necessary to test with water first, for the same reason.

If the compound is insoluble in 5% HCl, go to the next (and last) solubility test.

Solubility in concentrated H_2SO_4

Alkenes, alkynes, and compounds that contain N and O are protonated by this extremely powerful acid, and the products of these reactions dissolve. Concentrated sulfuric acid is approximately 94% acid. Compounds that contain only alkyl groups, halogen atoms, and benzene rings (RH , RX , ArH , ArX) will fail to dissolve.

To best prepare for this module, please work Chapter 21 Skill Builder problems in the textbook.

A STUDENT WHO HAS MASTERED THE OBJECTIVES FOR THIS UNIT SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

1.1 Draw the structure of each of the following compounds.

- a) malonic acid b) acetic anhydride c) sodium formate
- d) acetonitrile e) phthalic anhydride f) dimethyl succinate

1.2 Name each of the following compounds.

- a) $(\text{CH}_3)_3\text{CCH}_2\text{COOH}$ b) $\text{ClCH}_2\text{-C}(=\text{O})\text{-OCH}_2\text{CH}_3$ c) $\text{CH}_3\text{CH}(\text{C}_6\text{H}_5)\text{-C}(=\text{O})\text{-NH}_2$
- d) $\text{C}_6\text{H}_5\text{-C}(=\text{O})\text{-Cl}$ e) $\text{CH}_3\text{CH}_2\text{CH}_2\text{-C}(=\text{O})\text{-N}(\text{CH}_3)\text{CH}_2\text{CH}_3$ f) $\text{C}_4\text{H}_7\text{-C}(=\text{O})\text{-OH}$

2.1 Which of the following compounds has the HIGHEST boiling point?

- A. $\text{C}_6\text{H}_5\text{-C}(=\text{O})\text{-Cl}$ B. $\text{C}_6\text{H}_5\text{-C}(=\text{O})\text{-NH}_2$ C. $\text{C}_6\text{H}_5\text{-C}(=\text{O})\text{-H}$ D. $\text{C}_6\text{H}_5\text{-C}(=\text{O})\text{-CH}_3$

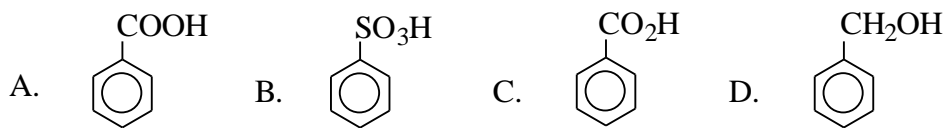
2.2 Which of the following compounds has the LOWEST boiling point?

- A. $\text{CH}_3\text{-C}(=\text{O})\text{-OH}$ B. $\text{CH}_3\text{-C}(=\text{O})\text{-NH}_2$ C. $\text{CH}_3\text{-C}(=\text{O})\text{-Cl}$ D. $\text{CH}_3\text{CH}_2\text{-OH}$

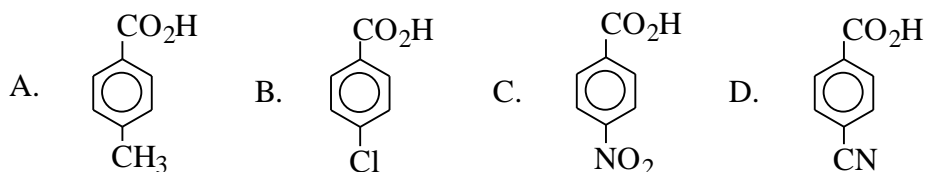
2.3 Which of the following compounds is most soluble in water?

- A. $\text{CH}_3\text{CH}_2\text{COOCH}_3$ B. $\text{CH}_3\text{COOCH}_2\text{CH}_3$
- C. $\text{CH}_3\text{CH}_2\text{COOH}$ D. $\text{CH}_3\text{CH}_2\text{CHO}$

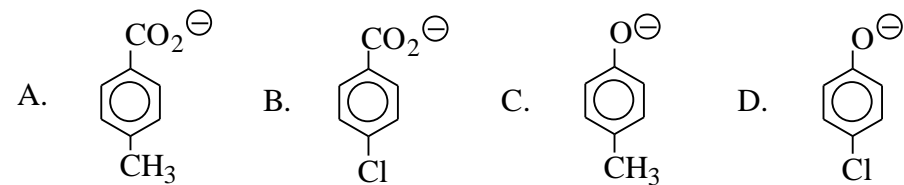
3.1 Which of the following compounds is the strongest acid?



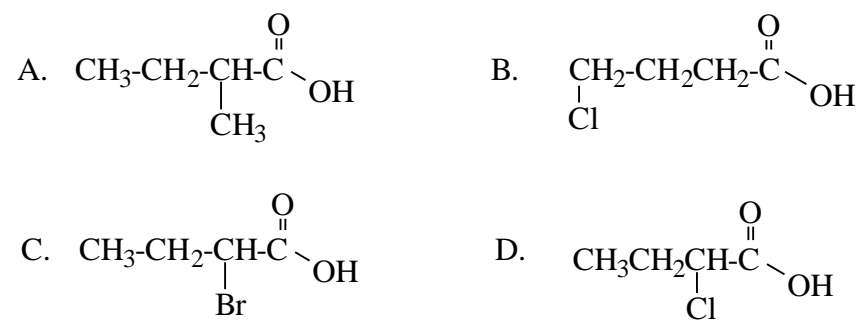
3.2 Which of the following compounds is the weakest acid?



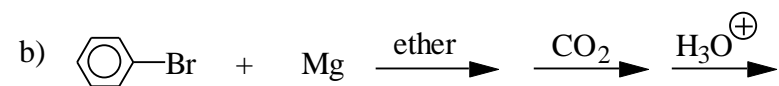
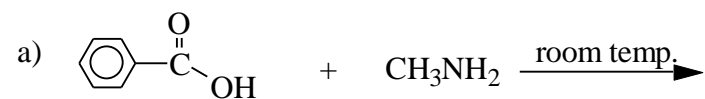
3.3 Which of the following compounds is the weakest base?



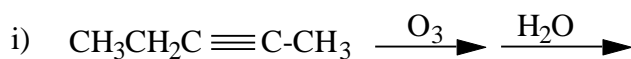
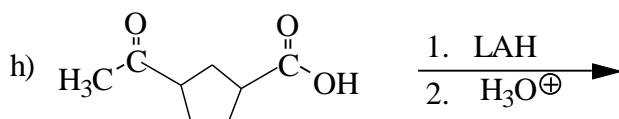
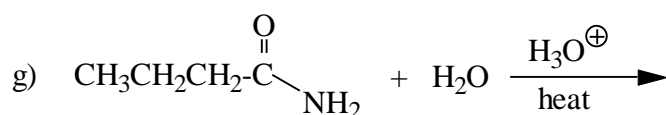
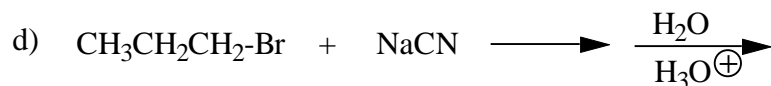
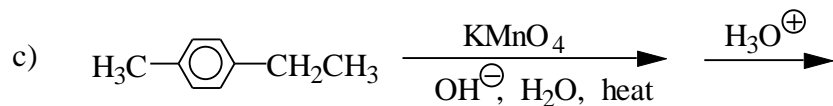
3.4 Which of the following compounds is the strongest acid?



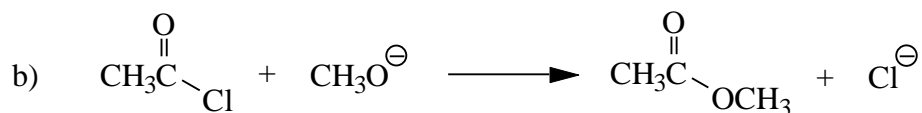
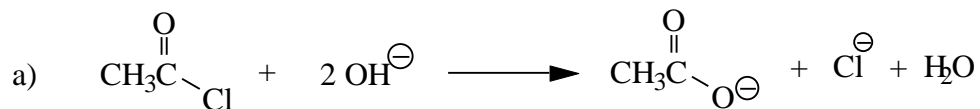
4. Predict the product(s) of each of the following reactions.



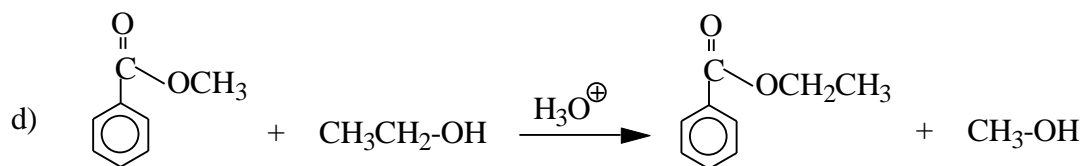
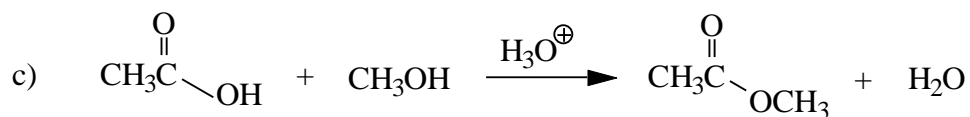
4. Reactions (Continued):



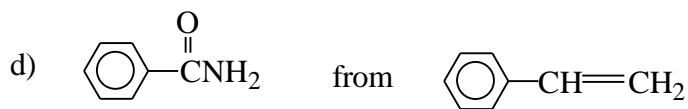
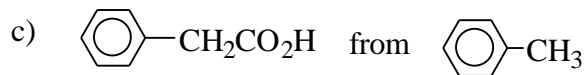
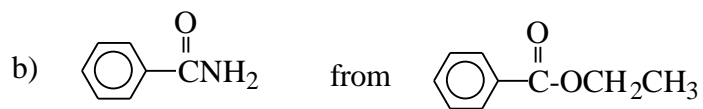
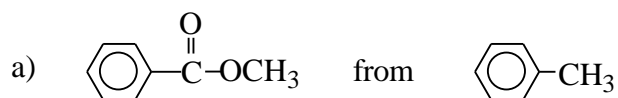
5. Propose a mechanism for each of the following reactions.



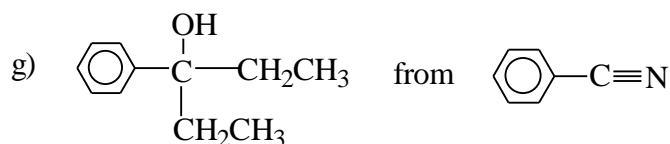
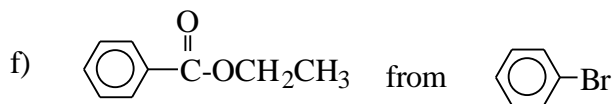
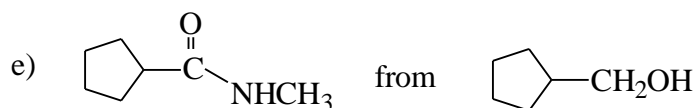
5. Mechanisms (Continued):



6. Propose a synthesis of each of the indicated compounds from the given starting material and any other needed reagents.



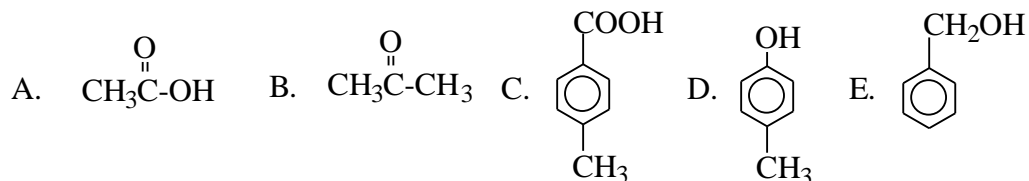
6. Synthesis (Continued):



7.1 For these questions, choose the answer from the list of possible compounds at the end of the section.

- Which of the following compounds has a broad peak in its IR spectrum in the $2500\text{-}3000\text{ cm}^{-1}$ region and gives an aqueous solution that turns blue litmus red?
- Which of them gives a broad, strong absorption peak in its IR spectrum near 3400 cm^{-1} is insoluble in water and 5% NaOH (aq), but is soluble in conc. H_2SO_4 ?
- Which of them is insoluble in water and soluble in both NaOH (aq) and NaHCO_3 (aq)?
- Which of them has only one peak in its proton NMR spectrum?

The possible answers are:



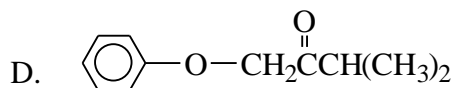
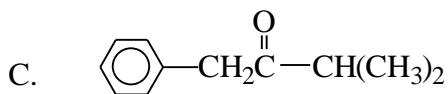
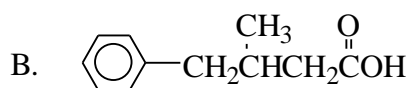
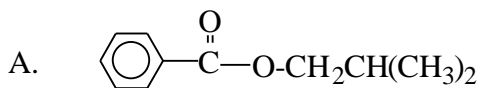
7.2. Identify each of the following unknowns from the given spectroscopic information.

a) $C_4H_8O_3$ **IR spectrum:** broad peak in $2500-3000\text{ cm}^{-1}$ region and a peak at 1715 cm^{-1}

triplet, 1.27 delta, 3H
quartet, 3.66 delta, 2H
singlet, 4.13 delta, 2H
singlet, 10.95 delta, 1H

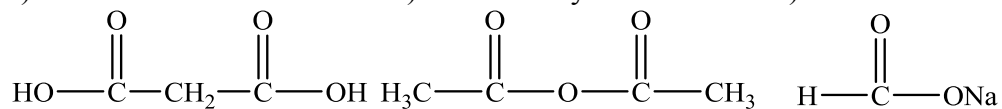
b) An unknown compound having the formula $C_{11}H_{14}O_2$ gave the following proton magnetic resonance spectrum:

doublet, δ 1.4, 6H
multiplet, δ 2.2, 1H
doublet, δ 4.1, 2H
multiplet, δ 7.1, 5H

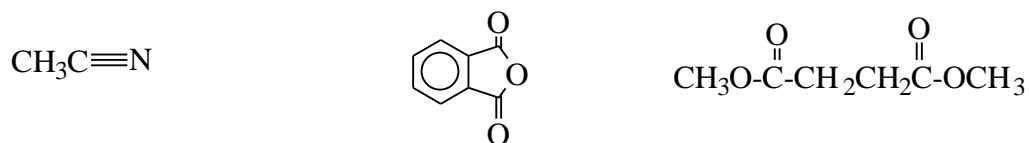


SOLUTIONS TO SAMPLE PROBLEMS:

- 1.1 a) malonic acid b) acetic anhydride c) sodium formate



- d) acetonitrile e) phthalic anhydride f) dimethyl succinate

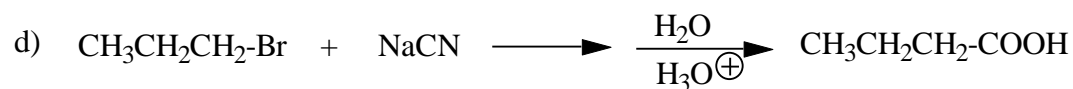
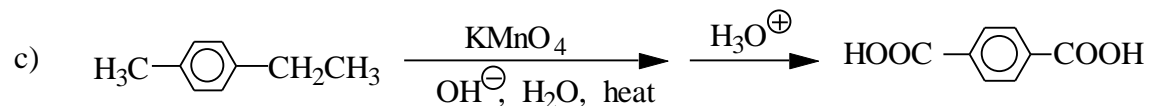
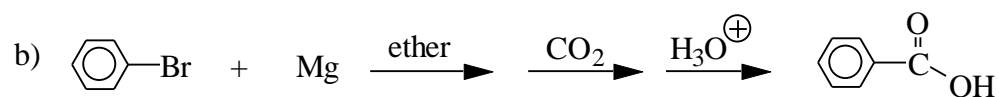
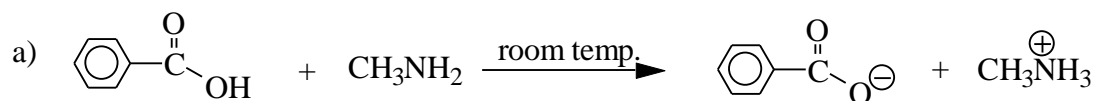


- 1.2 a) 3,3-Dimethylbutanoic acid
 b) Ethyl chloroethanoate (or ethyl chloroacetate)
 c) 2-Phenylpropanamide
 d) Benzoyl chloride
 e) *N*-Ethyl-*N*-methylbutanamide
 f) Cyclobutane carboxylic acid

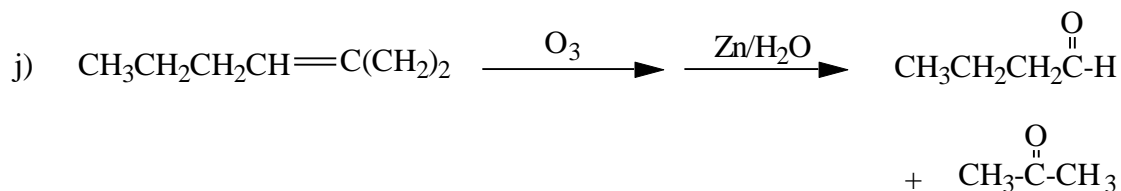
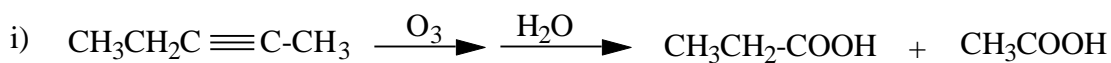
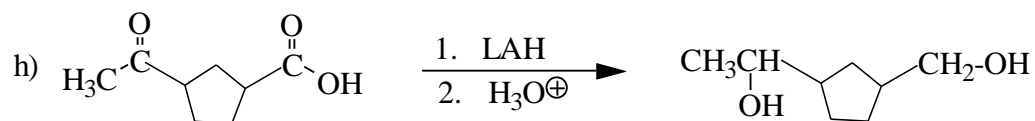
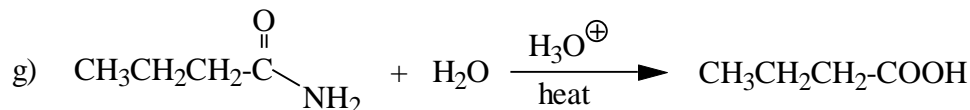
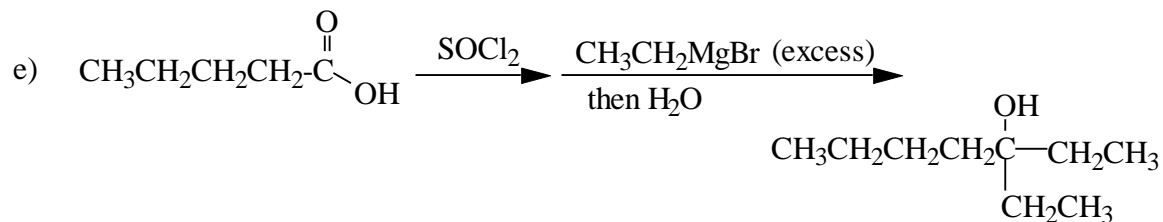
- 2.1 B
 2.2 C
 2.3 C

- 3.1 B
 3.2 A
 3.3 B
 3.4 D

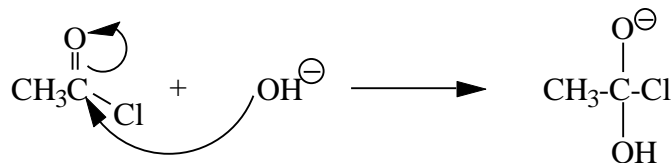
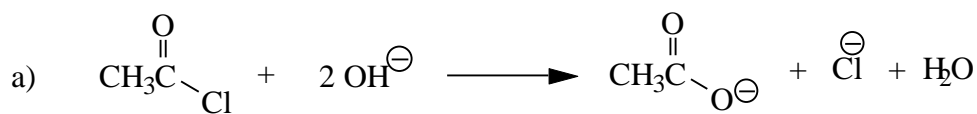
4. Predicting the products of reactions.



4. Predicting the products of reactions. (Continued):



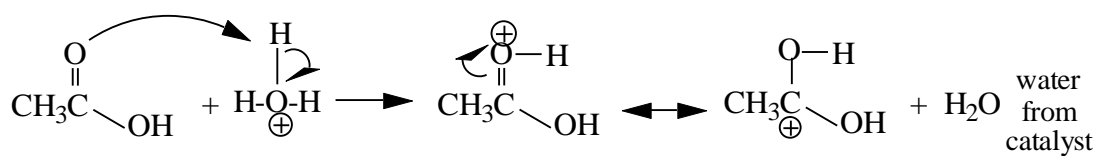
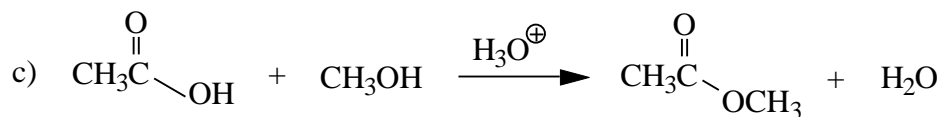
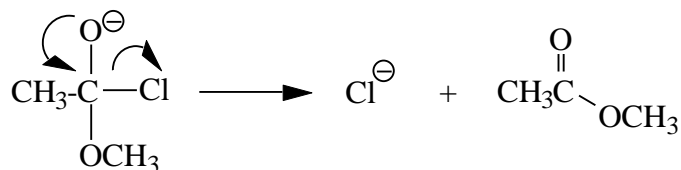
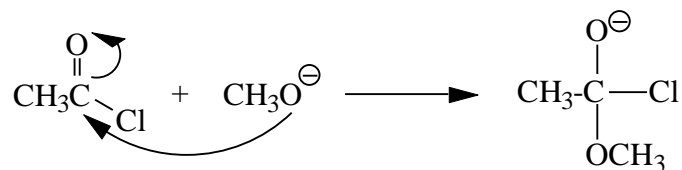
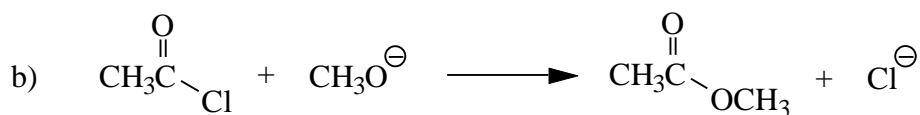
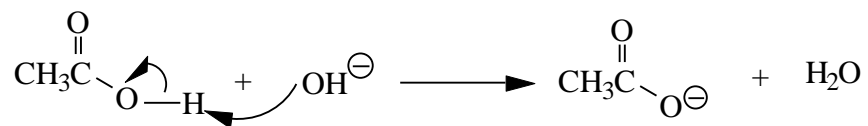
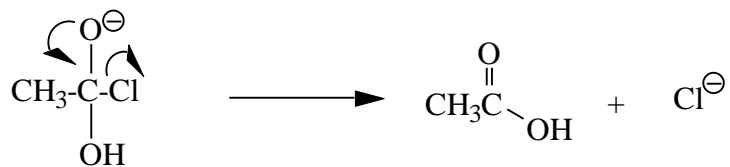
5. Mechanisms:



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5. Mechanisms (Continued):

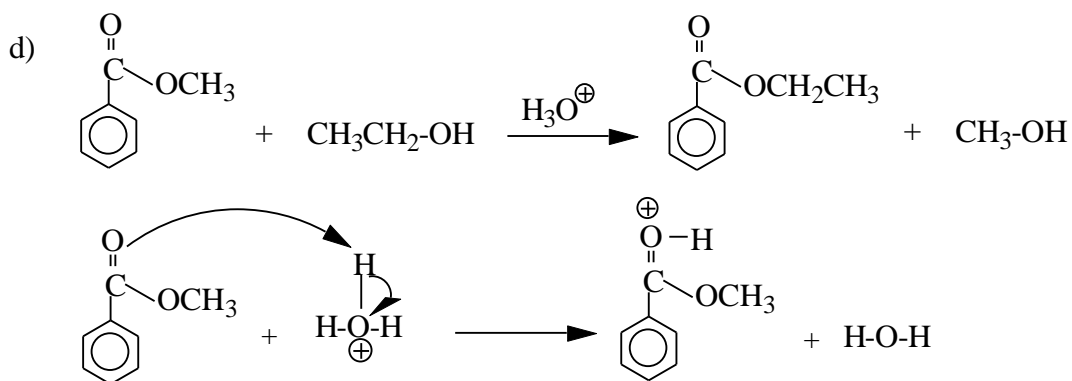
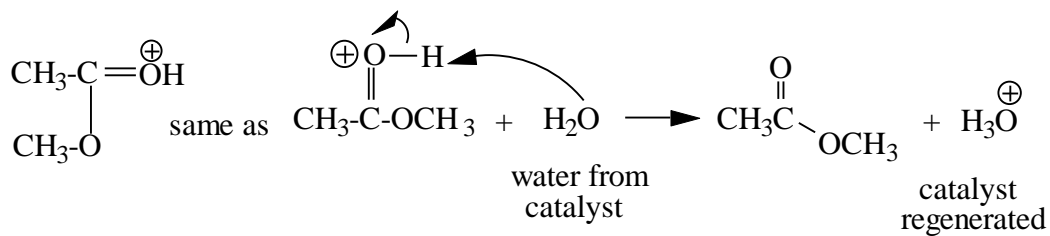
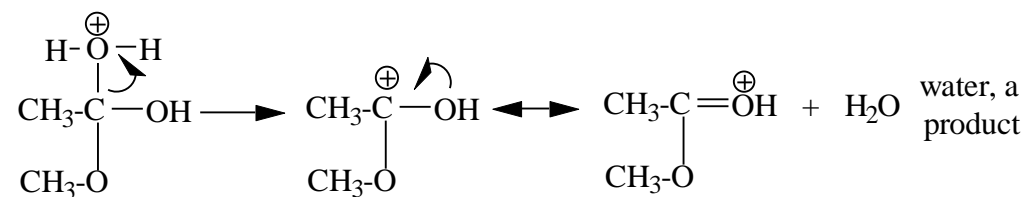
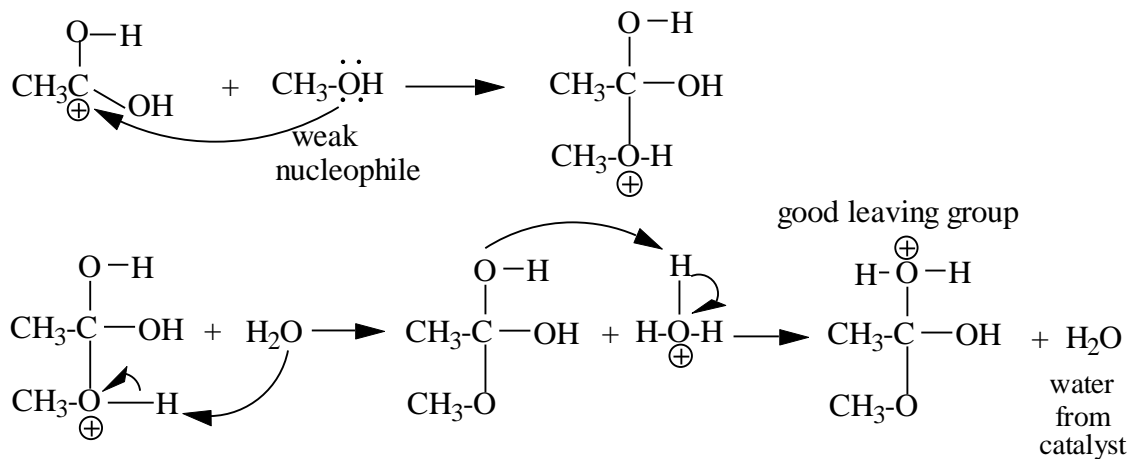
a) (continued)



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5. Mechanisms (Continued):

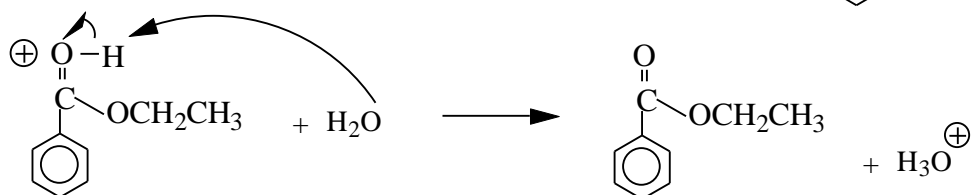
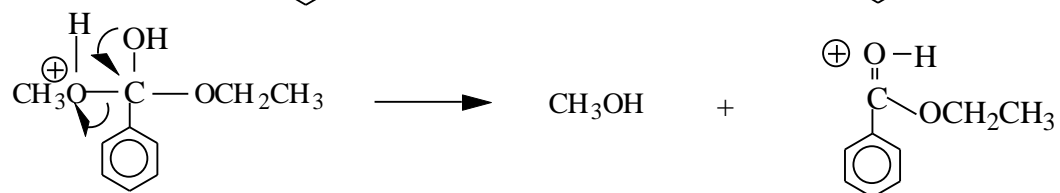
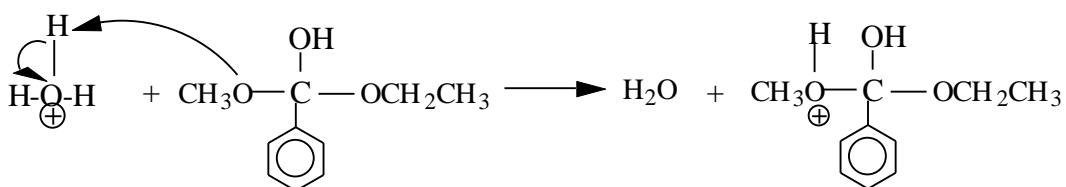
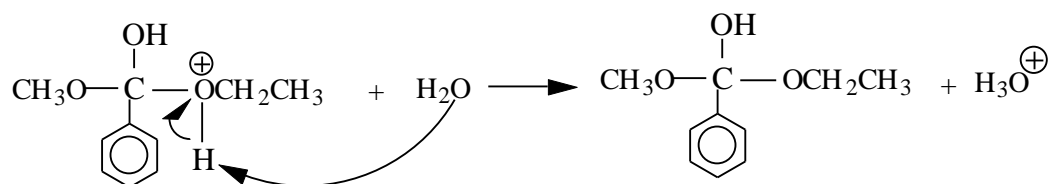
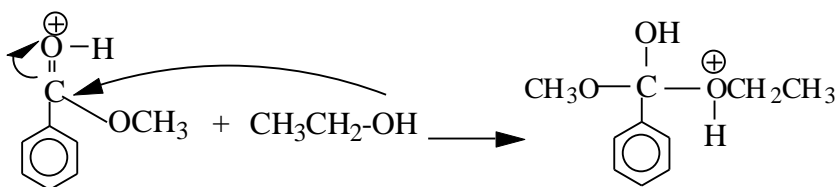
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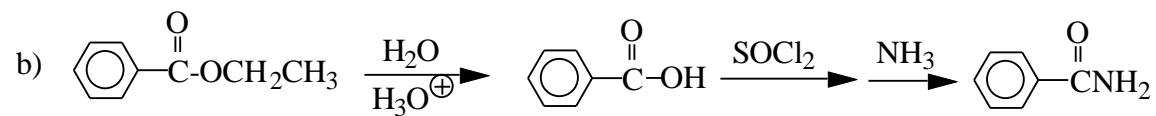
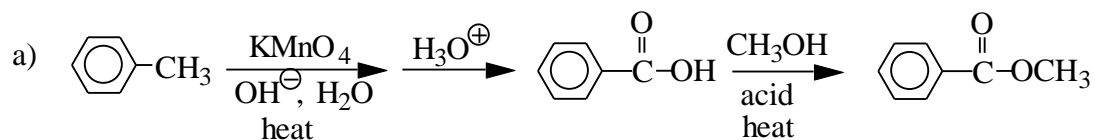
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5. Mechanisms (Continued):

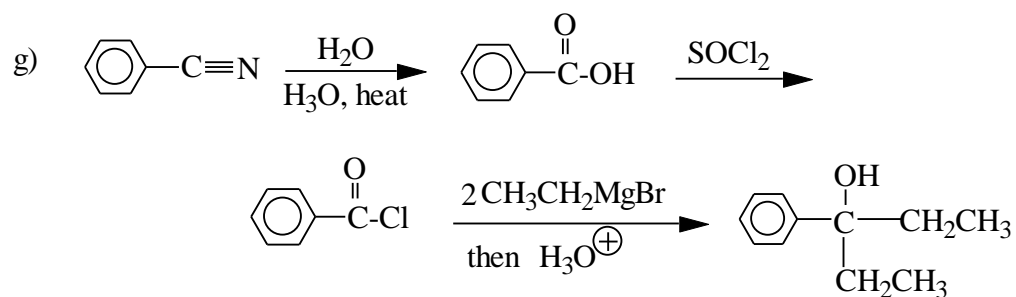
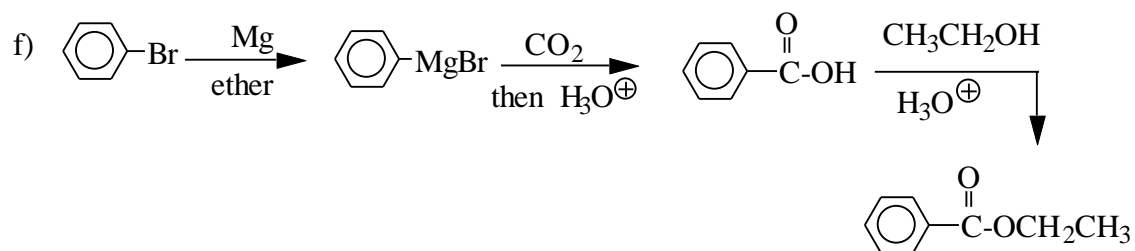
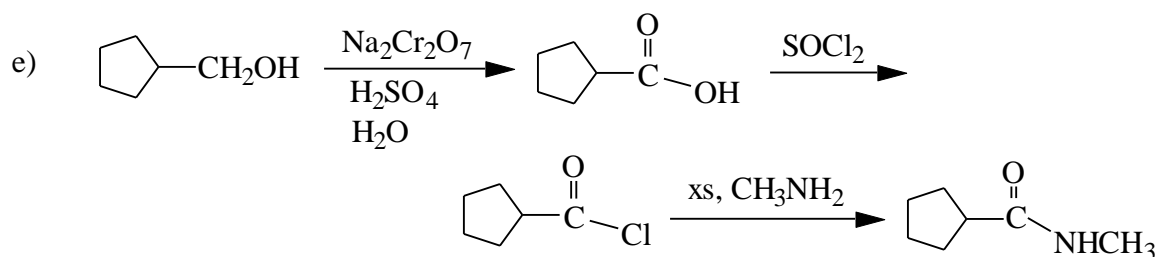
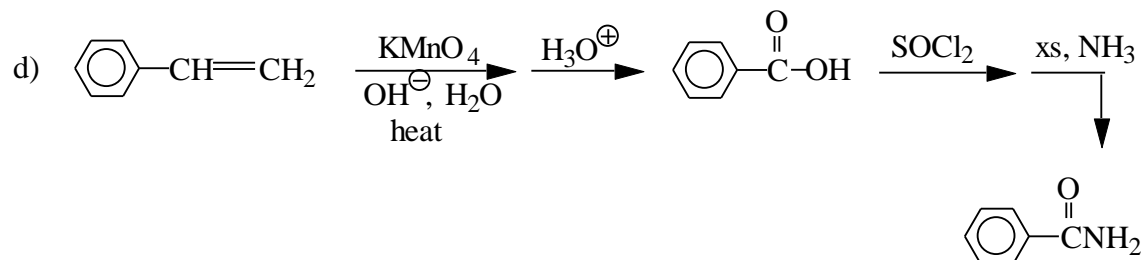
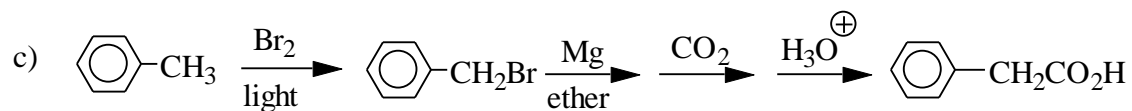
d) Continued



6. Propose a synthesis.

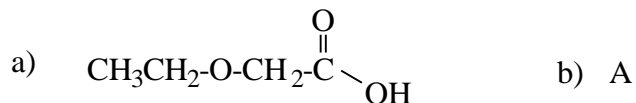


6. Synthesis (Continued):

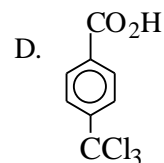
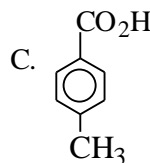
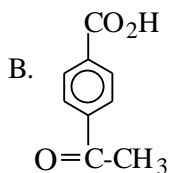
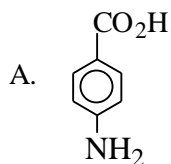


7.1 a) A b) E c) C d) B

7.2



1) Which of the following compounds is the strongest acid?

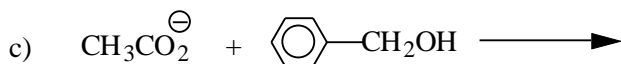
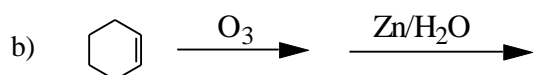
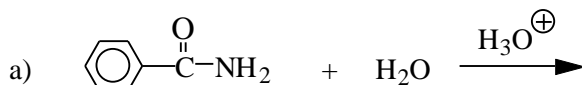


2) **Draw:** Benzyl benzoate

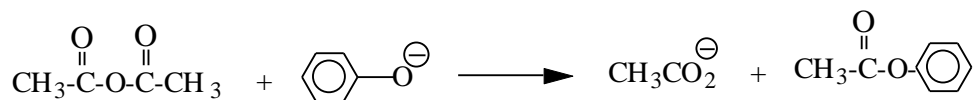
3) **Name:**



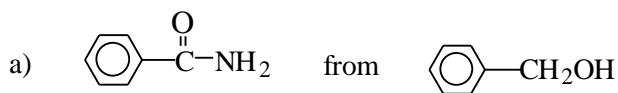
4) Predict the major product(s) (if any) of each of the following reactions.



5) Propose a mechanism for the following reaction.



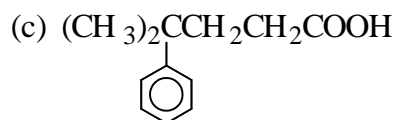
6) Propose syntheses, from the given starting material and any other needed reagents.



1. Nomenclature: Give the name when given the structure or the structure when given the name.

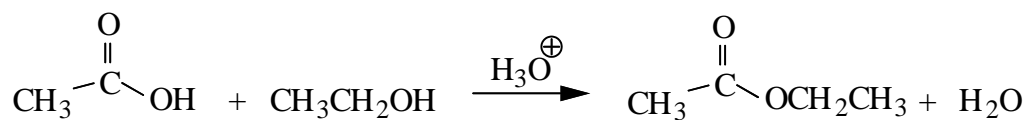
(a) Draw: *N,N*-diethylbenzamide

(b) Draw: benzyl propanoate

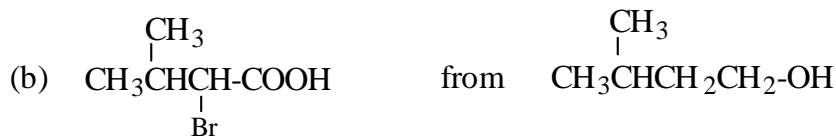
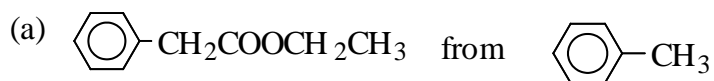


(d) HOOC-COOH

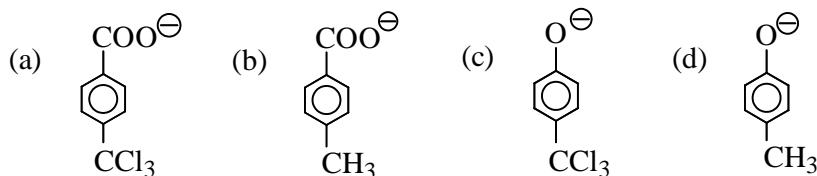
2. Write an acceptable mechanism for the following reaction.



3. Propose a synthesis of the compound indicated, from the given starting material and any other needed reagents.



4. Which of the following is the weakest base?

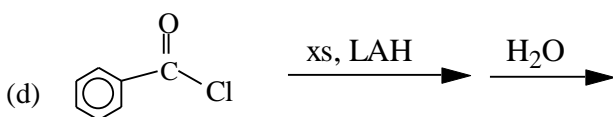
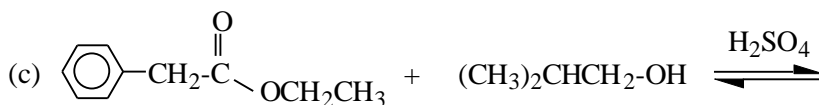
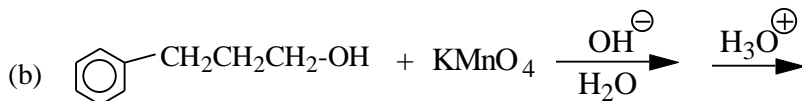
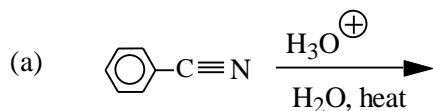


5. Identify the following compound from the given spectroscopic information.

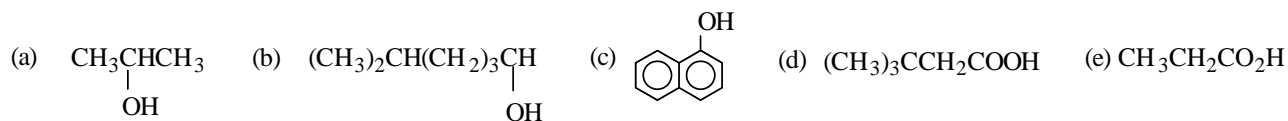
$C_4H_7BrO_2$ **IR Spectrum:** broad peak in $2500-3000\text{ cm}^{-1}$ region and a peak at 1715 cm^{-1}
 1H NMR spectrum;

Triplet	δ 1.08	(3H)
Multiplet	δ 2.07	(2H)
Triplet	δ 4.23	(1H)
Singlet	δ 10.97	(1H)

6. Predict the product(s) (if any) of each of the following reactions.



7. For questions (a) and (b), choose the answers from the list of possible compounds shown below.



(a) Which compound is insoluble in water and 5% NaOH(aq), but is soluble in conc. sulfuric acid?

(b) Which compound is insoluble in water, and soluble in both $NaHCO_3$ (aq) and NaOH?