

Victoria Junior College
JC 2 Chemistry
Tutorial: Carboxylic Acids & Derivatives

Complete the following tables.

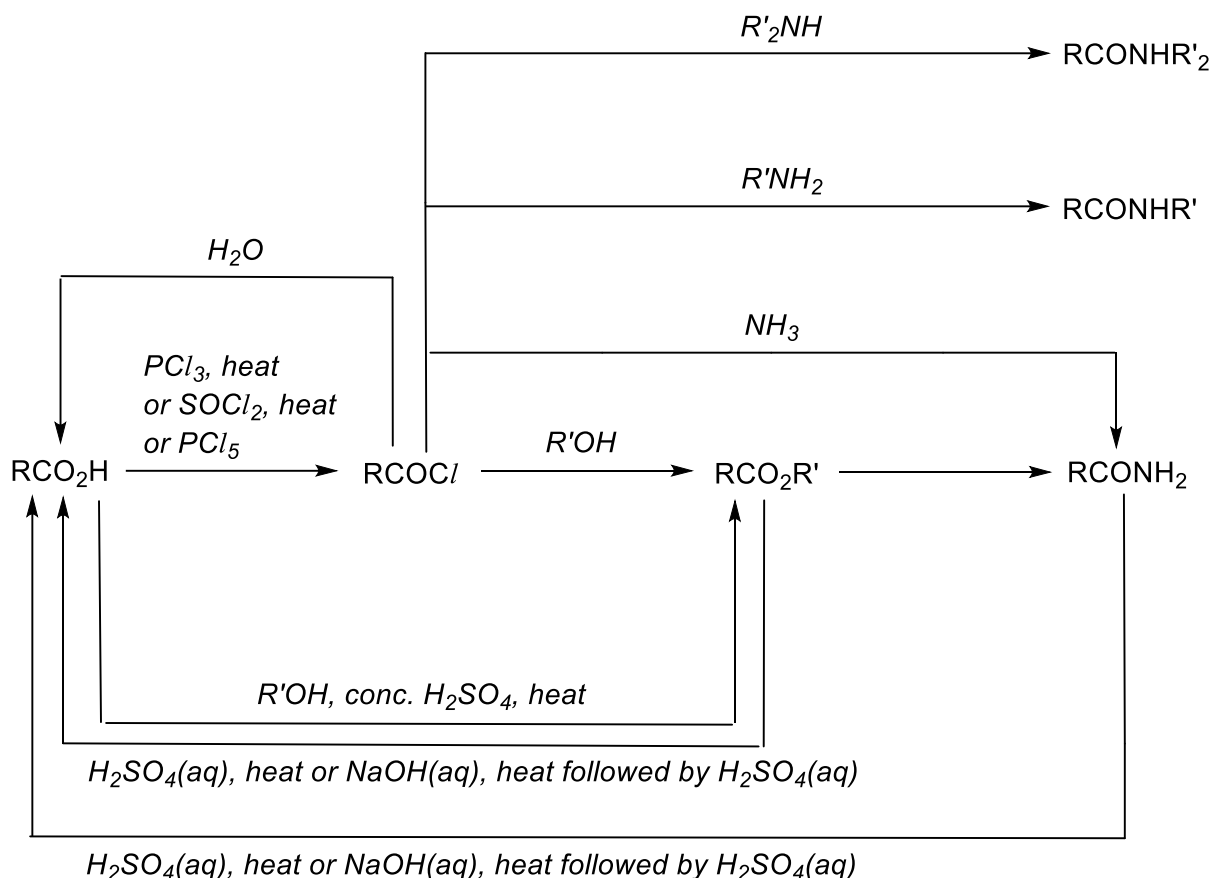
1. Preparation of carboxylic acids

Starting compound	Reagents and conditions	Product
	$\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, heat under reflux OR $\text{KMnO}_4(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, heat	$(\text{CH}_3)_2\text{CHCH}_2\text{CO}_2\text{H}$
$(\text{CH}_3)_2\text{CHCH}_2\text{CHO}$		
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{CN})\text{OH}$		$(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{CO}_2\text{H})\text{OH}$

2. Reactions of carboxylic acids

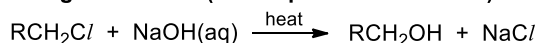
Starting Compound	Reaction Type	Reagents and Conditions	Organic Product [if any]
$(\text{CH}_3)_2\text{C}(\text{OH})\text{CO}_2\text{H}$	redox		
		NaOH	
		Na_2CO_3	
		$\text{HBr}(\text{g})$ heat	
		PCl_3 or SOCl_2 , heat OR PCl_5	
		$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ conc. H_2SO_4 heat	
		CH_3COCl	
	reduction		
	oxidation		

Interconversion of Carboxylic Acids and Acid Derivatives

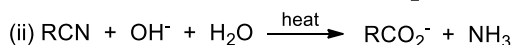
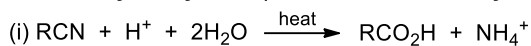


Hydrolysis

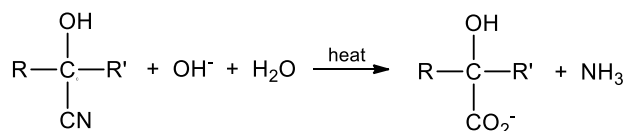
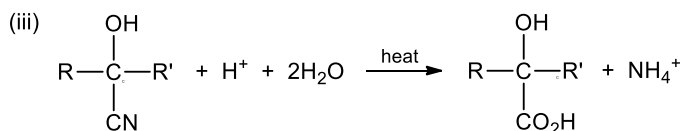
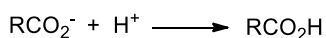
1. Halogenoalkanes (nucleophilic substitution)



2. Nitriles, Cyanohydrins (acidic and alkaline hydrolysis)

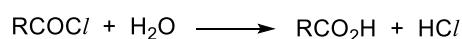


Note: acidification of salt give acid

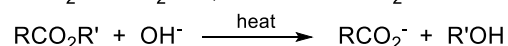
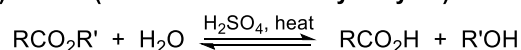


3. Carboxylic Acid Derivatives

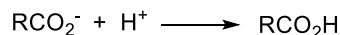
(i) Acyl chlorides (hydrolysis by water)



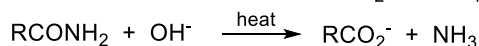
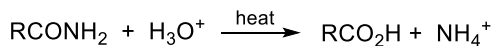
(ii) Esters (acidic and alkaline hydrolysis)



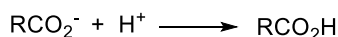
Note: acidification of salt give acid



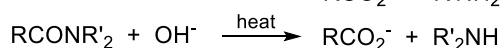
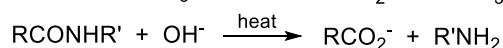
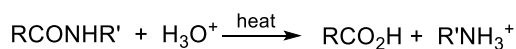
(iii) Amides (acidic and alkaline hydrolysis)



Note: acidification of salt give acid

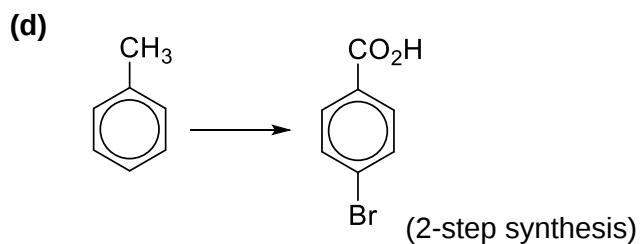
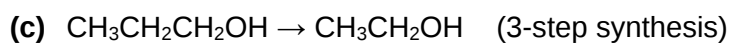
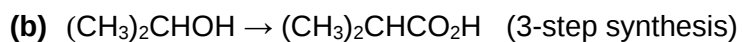
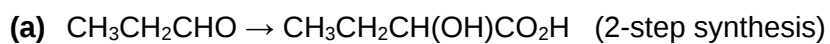


Same reactions for substituted amides

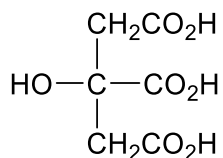


Preparation and Reactions of Carboxylic Acids

1 Devise syntheses of the following compounds from the given starting material. Identify the reagents and conditions at each step and draw the structural formulae of the intermediates.



- 2 Citric acid, which causes the sharp taste of lemon juice, has the following formula.



What reacts completely with 1 mol of citric acid?

- | | | | |
|----------|--------------------------|----------|----------------------------|
| A | 3 mol of PCl_5 | C | 4 mol of Na |
| B | 4 mol of HCl(g) | D | 4 mol of NaOH(aq) |

N13/I/27

- 3 The small hive beetle, which invades colonies of the honeybee, identifies these colonies by detecting the bees' own alarm signal, the pheromone 3-methylbutyl ethanoate.

How may this ester be made in the laboratory?

- A** $(\text{CH}_3)_2\text{CHCH}_2\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{ester} + \text{H}_2\text{O}$
- B** $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CO}_2\text{H} + \text{CH}_3\text{OH} \rightarrow \text{ester} + \text{H}_2\text{O}$
- C** $\text{CH}_3\text{CO}_2\text{H} + (\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OH} \rightarrow \text{ester} + \text{H}_2\text{O}$
- D** $\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH} \rightarrow \text{ester} + \text{H}_2\text{O}$

Modified N10/I/28

Acidity of Carboxylic Acids

- 4 In which sequence is it correctly stated that the value of $\text{p}K_{\text{a}}$ decreases continuously?

- A** $\text{CH}_3\text{CO}_2\text{H} > \text{CCl}_3\text{CO}_2\text{H} > \text{C}_2\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{OH}$
- B** $\text{CCl}_3\text{CO}_2\text{H} > \text{CH}_3\text{CO}_2\text{H} > \text{C}_2\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{OH}$
- C** $\text{C}_2\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{OH} > \text{CH}_3\text{CO}_2\text{H} > \text{CCl}_3\text{CO}_2\text{H}$
- D** $\text{C}_6\text{H}_5\text{OH} > \text{C}_2\text{H}_5\text{OH} > \text{CH}_3\text{CO}_2\text{H} > \text{CCl}_3\text{CO}_2\text{H}$

Preparation and Reactions of Acyl Chlorides

- 5(a)(i)** Draw a displayed formula of benzoyl chloride, $\text{C}_6\text{H}_5\text{COCl}$. Describe a pathway in which it can be synthesised from benzoic acid.

- (ii) Describe three reactions of benzoyl chloride with water, ethanol and methylamine, giving a balanced equation in each case.

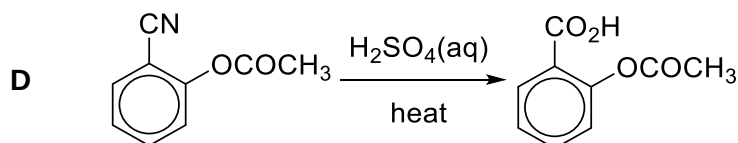
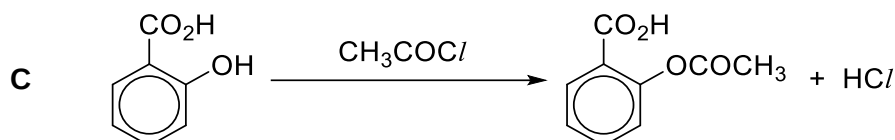
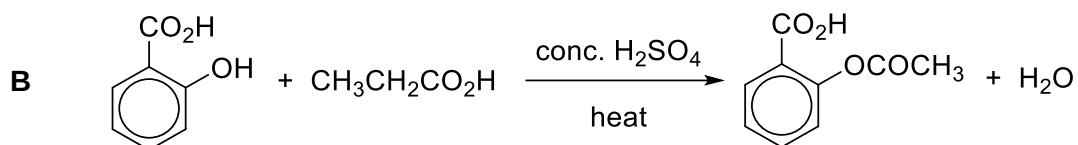
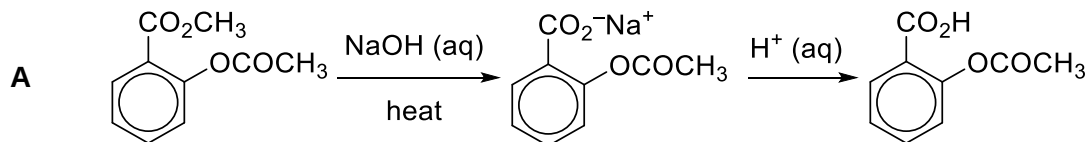
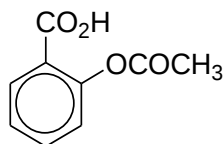
- (b)** State and explain how the ease of hydrolysis of 1-chloropropane differ from that of propanoyl chloride and chlorobenzene. Adapted J94/I/8, N23/I/22

Adapted J94/I/8, N23/I/22

[illegible]

Preparation and Reactions of Esters

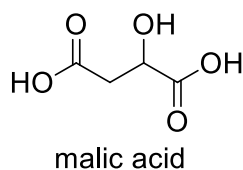
6 Which of the following could be a correct synthesis of aspirin?



N90/I/29

Integrated Questions and Structural Elucidation

7(a) Malic acid occurs in green apples and grapes. It is often added to beverages and confectionery to confer a sour taste.



Malic acid can be dehydrated to give a mixture of two isomeric alkenedioic acids with the molecular formula $C_4H_4O_4$.

(i) Draw the structures of the isomers and state the type of isomerism they show.

(ii) Suggest the reagents and conditions for the dehydration reaction.

.....

(iii) The pK_a values of the two acidic groups in one isomer **J**, are 3.0 and 4.4, whereas in the other isomer, **K**, they are 1.9 and 6.2.

Use the pK_a values to suggest which isomer, **J** or **K**, produces the more stable mono-anion on treatment with 1 mol of NaOH? Explain your answer.

.....

.....

.....

.....

.....

.....

(iv) Draw the displayed formula of the mono-anion produced in (iii), and use your formula to suggest an explanation for why it is more stable than the mono-anion of the other isomer.

.....

.....

.....

.....

.....

.....

Gently heating the anhydrous crystals of one of the isomers **J** or **K** produces a neutral compound **L**, $C_4H_2O_3$, which does not react with sodium metal or give a precipitate with 2,4–dinitrophenylhydrazine.

Compound **L** reacts with ammonia to give a compound **M**, $C_4H_5NO_3$, which gives a salt on reaction with NaOH but not with HCl. Compound **M** decolourises $Br_2(aq)$.

- (b) Suggest structures for compounds **L** and **M**, and identify which isomer, **J** or **K**, produces **L**. Write equations for all reactions, and explain the observations.

When malic acid is heated with acidified $K_2Cr_2O_7$, compound **N** is formed. Heating **N** in an inert solvent for several hours produces **P**, $C_3H_4O_3$ and a gas **Q**. Both **N** and **P** react with 2,4–dinitrophenylhydrazine. Compound **P** also gives a yellow precipitate with aqueous alkaline iodine.

- (c) Suggest structures for **N** and **P**, and use the information given to suggest the identity of gas **Q**.

N12/III/5

- 8 Heating a plant oil under reflux in alkali followed by acidifying the cooled mixture gives an optically active acid **A**, $C_{18}H_{34}O_3$ and glycerol, $HOCH_2CH(OH)CH_2OH$, in the molar ratio of 3:1.

A decolorises an organic solution of bromine. Treatment of **A** with hot acidified potassium manganate(VII) gives **B**, which has the formula $HO_2C(CH_2)_7CO_2H$, and a carboxylic acid **C**, which is optically inactive.

Heating **C** with soda lime causes it to lose its $-CO_2H$ group to give an organic compound **D**, with liberation of carbon dioxide.

On warming with alkaline aqueous iodine, **C** does not give tri-iodomethane. On warming with alkaline aqueous iodine, **D** does give tri-iodomethane, together with the salt of heptanoic acid, $CH_3(CH_2)_5CO_2H$.

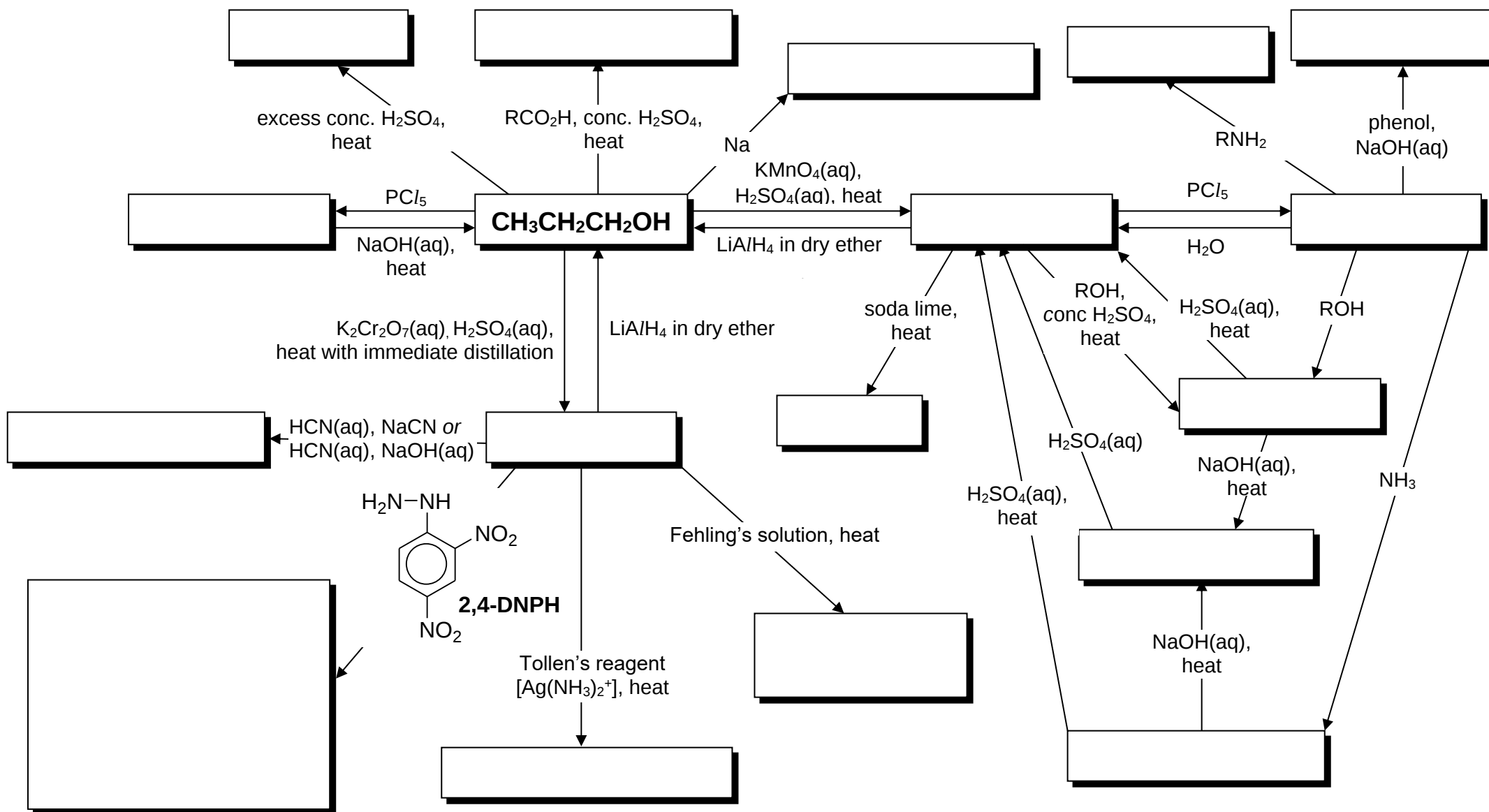
On warming with concentrated sulfuric acid, **A** gives **E**, $C_{18}H_{32}O_2$. Treatment of **E** with hot acidified potassium manganate(VII) gives **B**, heptanoic acid, and other products.

Identify compounds **A**, **C**, **D** and **E**, account for all these observations and suggest a structure for the plant oil.

[High marks can be scored for appropriate chemistry without a complete structure for the plant oil.]

[12]

Reactions of Alcohols, Aldehydes, Carboxylic acids and its derivatives



Victoria Junior College
JC 2 Chemistry
Supplementary Questions: Carboxylic Acids & Derivatives

Preparation and Reactions of Carboxylic Acids

- 1 One of the products from the vigorous hydrolysis of oil of bitter almonds is mandelic acid, $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CO}_2\text{H}$.

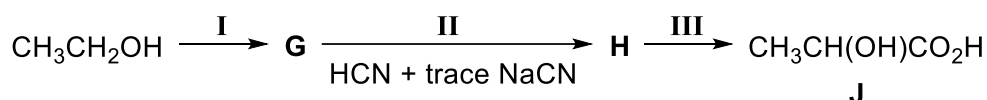
(a) Suggest structural formula for the products of the reaction of mandelic acid, with the following reagents.

- (i) HBr
- (ii) SOCl_2
- (iii) CH_3COCl
- (iv) $\text{C}_2\text{H}_5\text{OH} / \text{H}^+$
- (v) $\text{NaOH}(\text{aq})$

- (b) A sample of mandelic acid isolated from bitter almonds was contaminated with a neutral impurity. A 0.100 g sample of the impure acid required 6.00 cm^3 of $0.100 \text{ mol dm}^{-3}$ NaOH to neutralise it. Calculate the percentage purity of the mandelic acid.

J97/I/8

- 2 Lactic acid (2-hydroxypropanoic acid), **J**, occurs in soured milk. It can be synthesised from ethanol by the following series of reactions.



Compounds **G** and **H** both react with alkaline aqueous iodine. Compound **G** reacts with 2,4-dinitrophenylhydrazine and also with Fehling's solution. Compound **H** reacts with sodium metal.

- (a) Identify **G** and **H**, explaining how the identities you suggest fit in with the test reactions described above.
- (b) Suggest reagents and conditions for reactions **I** and **III**.

N04/III/8(a) either

Acidity of Carboxylic Acids

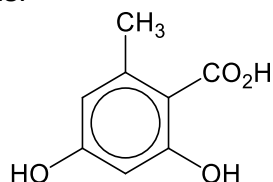
- 3 Explain why ethanoic acid is more acidic than ethanol and why chloroethanoic acid is stronger than ethanoic acid.

How would you expect the acidity of 3-chloropropanoic acid and of fluoroethanoic acid to compare with that of chloroethanoic acid?

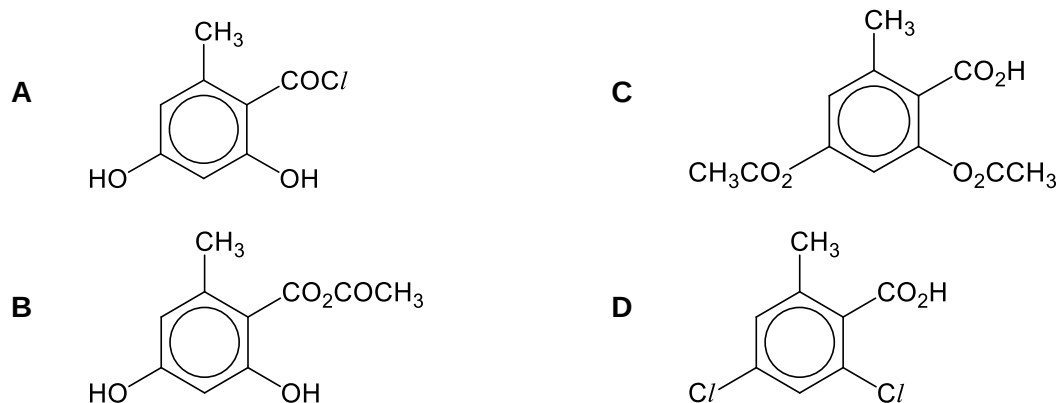
Adapted J96/III/28 and J92/I/10

Preparation and Reactions of Acyl Chlorides

- 4 Orsellinic acid occurs in lichens.



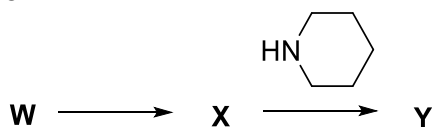
Which formula represents the product of its reactions with ethanoyl chloride?



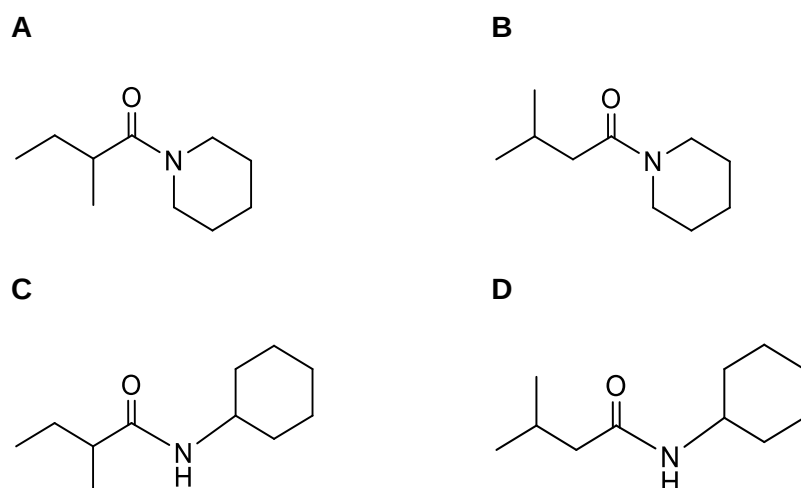
N05/I/27

- 5 The carboxylic acid **W**, $C_5H_{10}O_2$, is produced by *lactobacillus* bacteria during fermentation. Molecules of **W** are chiral. **W** can be converted into compound **X**.

X reacts as shown to form **Y**.



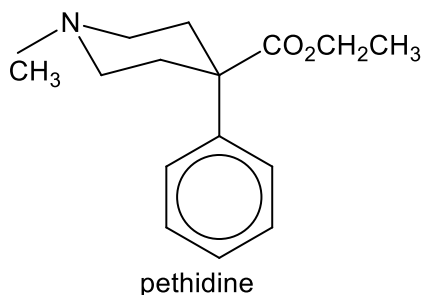
What could be the structure of **Y**?



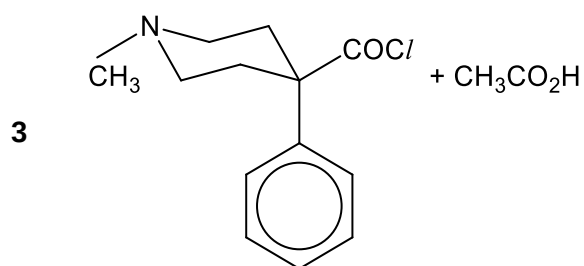
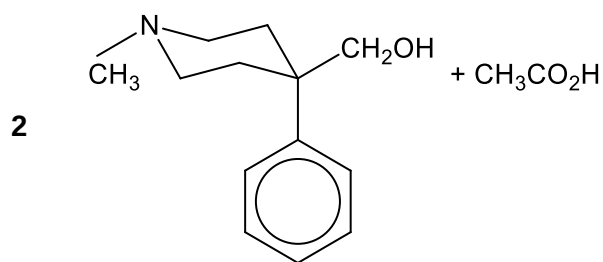
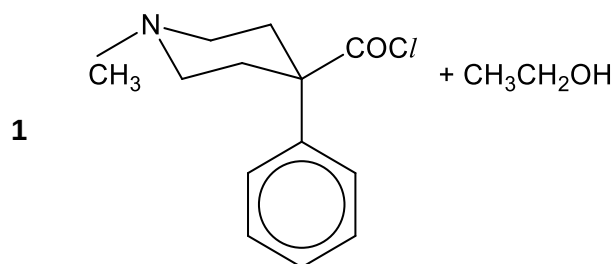
N19/I/23

Preparation and Reactions of Esters

- 6 Pethidine is a narcotic analgesic drug, used as a substitute for morphine in the treatment of acute severe pain.



Which pairs of compounds would produce pethidine when reacted together?



- A 1, 2 and 3 are correct
 B 1 and 2 only are correct
 C 2 and 3 only are correct
 D 1 only is correct

N09/I/39

- 7 An ester **Q** was refluxed with aqueous sodium hydroxide and the resulting mixture then distilled. The distillate gave a positive tri-iodomethane (iodoform) test; the residue in the distillation flask, after acidification, gave a white precipitate.

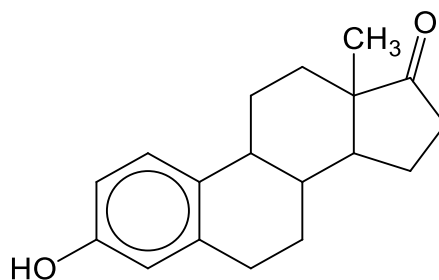
Which of these could be **Q**?

- A $\text{CH}_3\text{CO}_2\text{C}_6\text{H}_5$
 B $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_3$
 C $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_2\text{CH}_3$
 D $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_3$

N10/I/25

Integrated Questions

- 8 The diagram shows the structure of a molecule of the sex hormone oestrone. Which reactions would oestrone be expected to undergo?

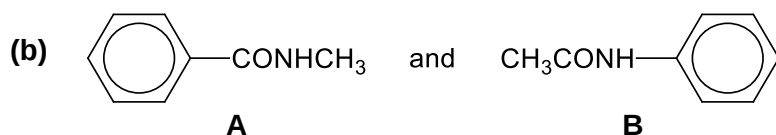
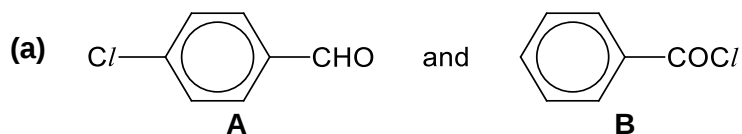


- 1 It gives an orange ppt with 2,4-DNPH reagent.
- 2 It gives hydrogen with metallic sodium.
- 3 It forms an ester with ethanoyl chloride.

- | | | | |
|----------|---------------------------------|----------|---------------------------------|
| A | 1, 2 and 3 are correct | C | 2 and 3 only are correct |
| B | 1 and 2 only are correct | D | 1 only is correct |

N10/I/39

- 9 Suggest methods by which the following compounds could be distinguished from each other by chemical tests. The distinguishing of some of these pairs may rely on a preliminary breaking up of the compounds, and subsequent testing of the reaction products. Do not use spectroscopic techniques.

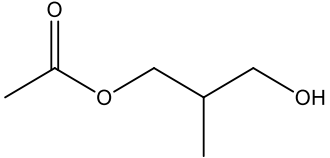


[Do part (b) after completion of topic on Nitrogen Compounds]

N04/III/7(c), (d)

- 10 Suggest structural formulae for the products of the reaction and the reaction types, with the following reagents.

Compound	Type(s) of reaction	Reagents and conditions	Product(s)
		H ₂ (g), Pt	
		KMnO ₄ (aq), NaOH(aq) heat	

		$\text{KMnO}_4(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$ heat	
---	--	--	--