Suggested Answers to Carboxylic Acid & Derivatives Tutorial

1(a) Decreasing acid strength:

ethanoic acid > phenol > ethanol

In general, $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

The acidity of a compound depends on the relative stability of its conjugate base anion (A^-). The more stable the conjugate base, the more acidic the compound will be.

In the ethanoate ion ($CH_3CO_2^-$), the negative charge on oxygen is dispersed over the two highly electronegative oxygen atoms resulting in two equivalent resonance structures. Hence, $CH_3CO_2^-$ ion is resonance-stabilised to a larger extent than $C_6H_5O^-$ ion.

In the phenoxide ion ($C_6H_5O^-$), the p-orbital containing the lone pair of electrons on the O atom overlaps with the π-electron cloud of the benzene ring so that the negative charge on O delocalises into the benzene ring. The dispersal of negative charge stabilises $C_6H_5O^-$ ion but this resonance stabilisation is not as great as that in the $CH_3CO_2^-$ ion.

In the ethoxide ion ($CH_3CH_2O^-$), the electron-donating alkyl (ethyl) group intensifies the negative charge on O atom, which destabilises $CH_3CH_2O^-$ ion. Therefore, $CH_3CH_2O^-$ is the least stable.

(b) Decreasing acid strength:

trifluoroethanoic acid > trichloroethanoic acid > chloroethanoic acid > ethanoic acid

In general, $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

The acidity of a compound depends on the relative stability of its conjugate base anion (A^-). The more stable the conjugate base, the more acidic the compound will be.

Compared to CH_3COO^- ion, the CF_3COO^-, CCl_3COO^- and $ClCH_2COO^-$ ions are more stable due to the presence of electron-withdrawing F or Cl group(s) to disperse the negative charge and hence stabilising the anion.

CCl_3COO^- ion is more stable than $ClCH_2COO^-$ ion as it has 2 more electron-withdrawing Cl groups to disperse the negative charge.

Since F is more electronegative than Cl, the F group is more electron-withdrawing than the Cl group and the negative charge is dispersed to a greater extent in CF_3COO^- ion than in CCl_3COO^- ion. Hence CF_3COO^- ion is more stable than CCl_3COO^- ion.

2 Decreasing ease of hydrolysis:

$C_6H_5COCl > C_6H_5CH_2Cl > C_6H_5Cl$

The carbon of the acyl group in C_6H_5COCl has a higher $\delta+$ charge (or is more electron deficient) as it is bonded to two electronegative atoms (O and Cl). The carbon bonded to the chlorine atom in $C_6H_5CH_2Cl$ has lower $\delta+$ charge (or is less electron deficient) as it is bonded to only one electronegative atom (Cl). Hence, C_6H_5COCl can attract nucleophiles more easily and is more susceptible to nucleophilic attack as compared to $C_6H_5CH_2Cl$.

In addition, the carbon of the acyl group in C_6H_5COCl, being sp^2 hybridised and trigonal planar, provides less steric hindrance during nucleophilic attack compared to the carbon bonded to the chlorine atom in $C_6H_5CH_2Cl$, which is sp^3 hybridised and tetrahedral. Thus, C_6H_5COCl undergoes hydrolysis with ease with water (a weak nucleophile) while $C_6H_5CH_2Cl$ requires a stronger nucleophile OH^- under heating.

C_6H_5Cl is the least susceptible to hydrolysis. This is because the p orbital containing the lone pair of electrons on the C*l* atom overlaps with the π electron cloud of the benzene ring, resulting in a lone pair of electrons in the p orbital of C*l* delocalising into the benzene ring. As a result, the C-C*l* bond has partial double bond character. Since the bond is strengthened, the cleavage of this bond (which is necessary during hydrolysis) is made very difficult.

3 **(a)** Test: Add aq Na_2CO_3 (or aq $NaHCO_3$) to each compound in a test-tube.

Observation:	For C_6H_5COOH:	Effervescence observed, CO_2 gas evolved formed white ppt with limewater/aq $Ca(OH)_2$.
	For C_6H_5OH:	No effervescence / no gas is evolved.
Other tests:	Neutral $FeCl_3$(aq):	Violet complex observed for phenol. No violet complex for benzoic acid.
	Or aqueous Br_2:	Phenol decolourises orange Br_2 and a white ppt is formed. No decolourisation of Br_2 and no white ppt for benzoic acid.

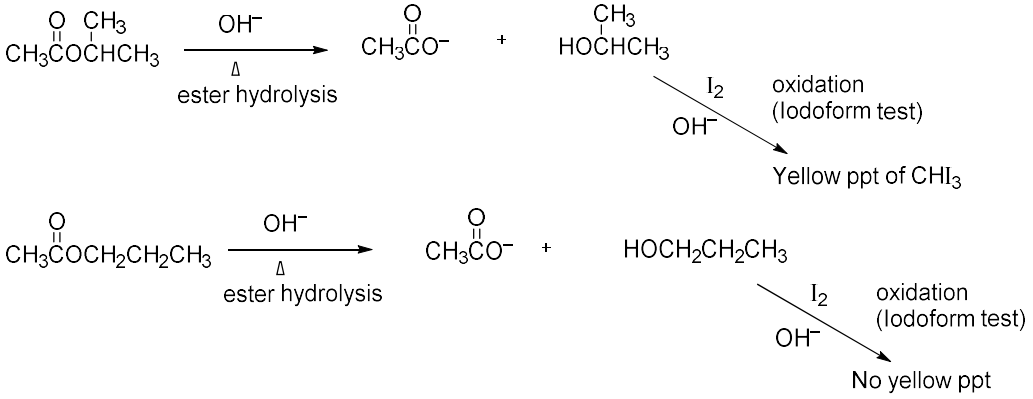
(b) Test: Add aq $AgNO_3$ to each compound in a test-tube.

Observation:	For CH_3CH_2COCl:	White ppt (AgC*l*) formed and white fumes (HC*l*) evolved.
	For $ClCH_2CH_2COOH$:	No white ppt and no white fumes.

Note: Aq. Na_2CO_3 should not be used as a distinguishing test between acid chlorides and carboxylic acids. Acid chlorides such as CH_3CH_2COCl undergo hydrolysis readily in aqueous medium, under room temperature conditions. The products, HC*l* and carboxylic acid, will react with aq. Na_2CO_3 to produce CO_2.

(c) Test: Add NaOH(aq) to each compound in a test-tube and heat in a hot water bath. Then add aq I_2.
OR Add NaOH(aq) and I_2(aq) to each compound in a test-tube and heat in a hot water bath.

Observation:	For $CH_3COOCH(CH_3)_2$:	Yellow ppt of CHI_3
	For $CH_3COOCH_2CH_2CH_3$:	No yellow ppt formed.



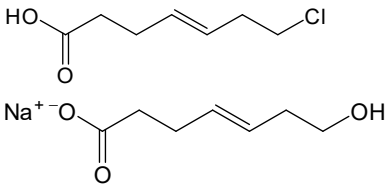
(d) Test: Add 2 drops of aq $KMnO_4$ and aq H_2SO_4 to each compound in a test-tube and heat in a hot water bath.

Observation: For HCOOH: Purple $KMnO_4$ decolourises. Effervescence observed, CO_2 gas evolved formed white ppt with aq limewater/$Ca(OH)_2$.

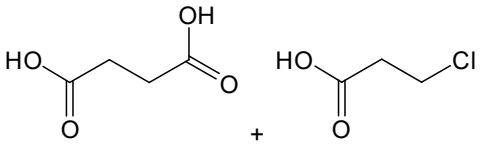
For CH_3COOH: Purple $KMnO_4$ is not decolourised.

Note: HCOOH also gives a positive test with Tollens' reagent & Fehling's solution.

4 **(a)** CH_3OH +

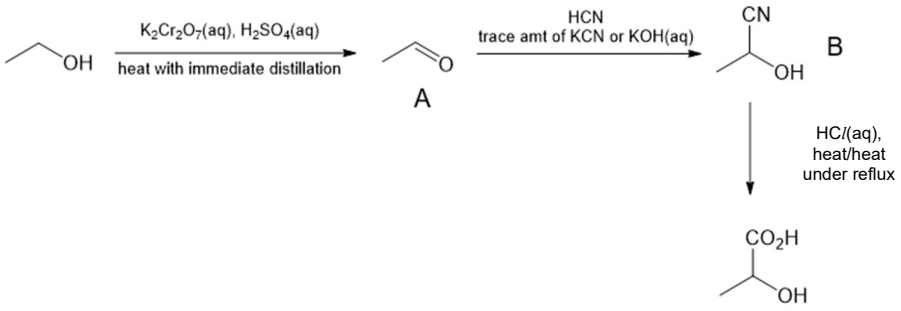


(b) CH_3OH +

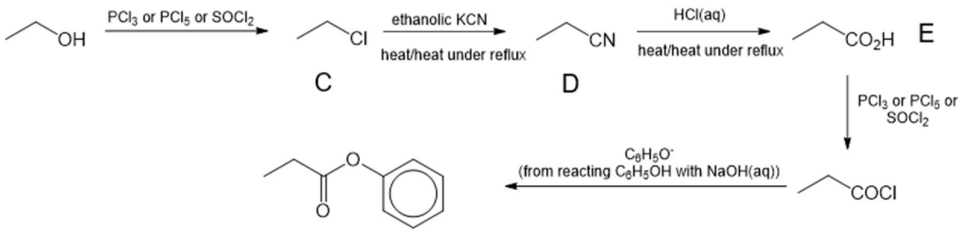


(c) CO_2 +

5 **(a)**



(b)

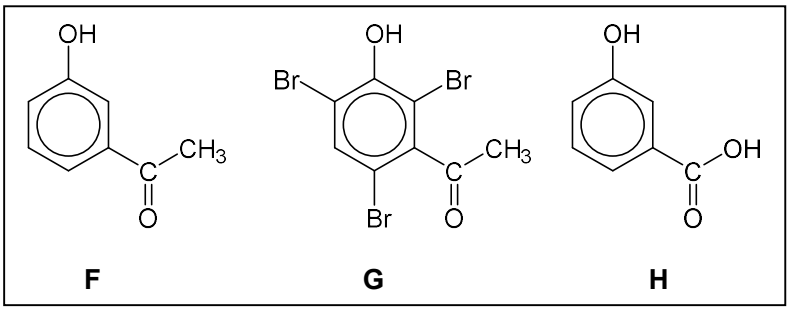


Note: HC*l* with Zn$C l_2$ can also be used for the first step.

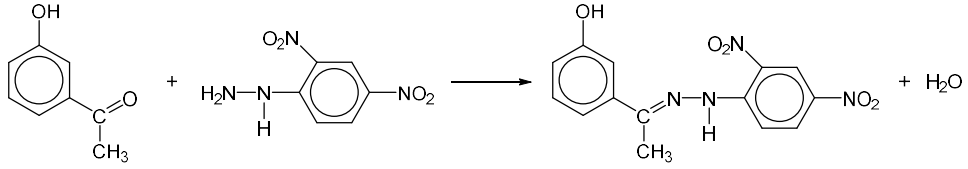
6 **(a)**

Evidence	**Deduction**
F, $C_8H_8O_2$	**F** has a high C:H ratio of 1:1 and > 6 C atoms ➔ **F** likely contains benzene ring
F insoluble in water	➔presence of large non-polar group such as benzene ring in **F**
F dissolves in NaOH(aq)	**F** undergoes acid-base reaction ➔ **F** contains acidic functional group ➔ **F** is either a phenol or a carboxylic acid
F reacts with 2,4-DNPH	**F** undergoes condensation with 2,4-DNPH ➔ **F** is a carbonyl compound

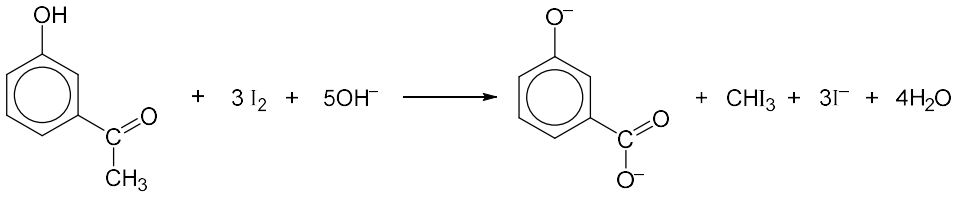
F does not react with Fehling's solution	**F** is <u>not oxidised</u> by Fehling's solution ➔ **F** is <u>not</u> an aliphatic aldehyde ➔ **F** is either an <u>aromatic aldehyde</u> or a <u>ketone</u>
F + $Br_2(aq) \longrightarrow$ **G** ($C_8H_5O_2Br_3$)	**F** undergoes <u>electrophilic substitution</u> with $Br_2(aq)$ ➔ **F** contains a <u>strongly activated</u> benzene ring ➔ **F** is a <u>phenol</u>
G has 3 H atoms substituted with 3 Br atoms	➔ **G** has <u>Br substituted at the 2,4 and 6</u> positions with respect to the phenol OH group.
F + I_2/ $OH^-(aq)$ then $H^+ \longrightarrow$ **H**	**F** <u>undergoes oxidation</u> by alkaline $I_2(aq)$ (positive iodoform test) followed by acid-base reaction to form **H** ➔ **F** is a <u>methyl ketone</u> ➔ **H** is a carboxylic acid with 1 C less than **F**
H dissolves in both NaOH(aq) and $Na_2CO_3(aq)$.	**H** undergoes <u>acid-base</u> reaction with NaOH and Na_2CO_3 ➔ **H** is a <u>carboxylic acid (confirmed)</u>



(b) (i)

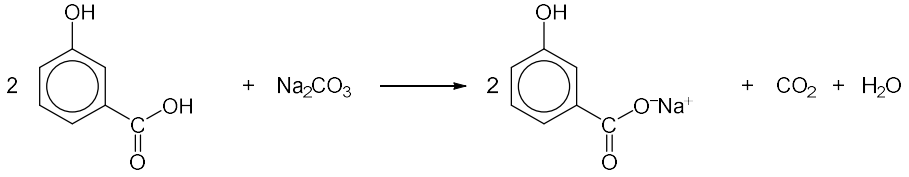


(ii)



Note: An extra mol of OH^- is required to neutralise the acidic phenol group.

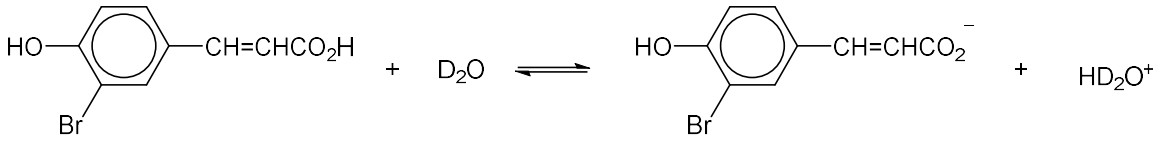
(iii)



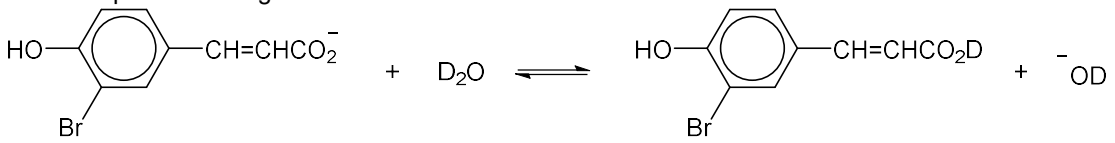
7
Ans: **B (2)**

In D_2O solvent, the phenol and COOH groups can lose H^+ to form the respective conjugate bases.

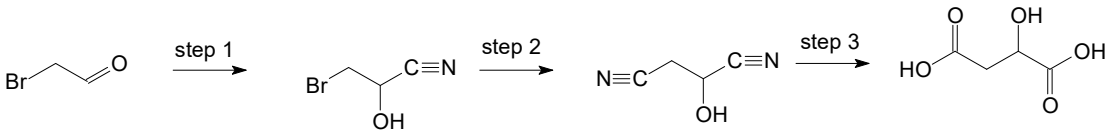
Using the COOH group as an example:



The carboxylate anion can then undergo basic hydrolysis with D_2O to form RCOOD as the deuterated solvent is present in large excess:



8(a)



Step 1: <u>HCN, trace of KCN</u>
Step 2: <u>ethanolic KCN, heat/heat under reflux</u>
Step 3: <u>dilute HC*l*, heat/heat under reflux</u>

[Note : Step 1 and 2 involving cyanide could be carried out in any order]

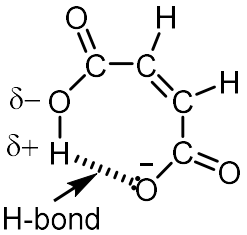
(b) (i) cis-trans isomerism

(ii) excess concentrated H_2SO_4, heat (or Al_2O_3, heat)

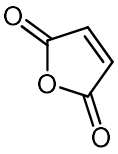
(iii) The pK_a values suggest that **K**, having a low first pK_a coupled with a high second pK_a produces the more stable mono-anion.

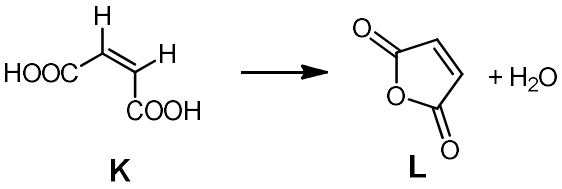
The first pK_a is much lower implying that **K** loses its first proton more readily to form the mono-anion and it is therefore also <u>more difficult for the mono-anion of **K** to accept H^+</u>. The second pK_a is much higher, implying it is <u>more difficult for the mono-anion to lose a 2nd proton, thus mono-anion of **K** more stable.</u>

(iv) The more stable anion is produced from the <u>cis isomer (**K**)</u> as <u>intramolecular hydrogen bonding can exist</u> (shown below) as the oxygen with the negative charge is in <u>close proximity</u> to the H atom of the adjacent COOH group.

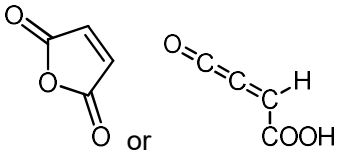
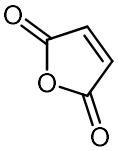


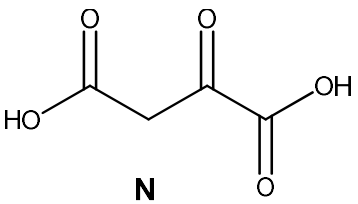
Note:
pK_a (1) of the cis isomer, **K**, should be smaller since the mono-anion is more stable and less likely to accept back H^+ as compared to the trans isomer.
pK_a (2) of the cis isomer, **K**, is larger as it is now more difficult to lose the 2nd proton as it is involved in intramolecular hydrogen bonding.)

(c) **L** is 

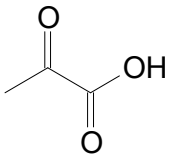


K **L**

Evidence	**Deductions**
J or **K** → **L**, $C_4H_2O_3$	**J/K** ($C_4H_4O_4$) loses a water molecule to form **L** ($C_4H_2O_3$) **L** could be  or
L, $C_4H_2O_3$ is neutral.	**L** is not a carboxylic acid since it is neutral.
L has no reaction with Na.	**L** does not undergo redox with Na. →**L** has no –OH group.
L has no reaction with 2,4-DNPH.	**L** does not undergo condensation with 2,4-DNPH. →**L** is not an aldehyde or ketone. **L** is formed from the condensation reaction between –H of one COOH group and –OH of another COOH group, thus losing one molecule of water. The 2–COOH groups must be in close proximity →hence the isomer is **K**, cis isomer.  **L** is

(d) 

N



P

<u>Gas Q could be CO_2</u>.

Evidence	Deductions
Malic acid, $C_4H_6O_5$ on heating with $K_2Cr_2O_7$ forms **N**.	oxidation of 2° alcohol to ketone with loss of 2H atoms. ➔**N** is a ketone with molecular formula $C_4H_4O_5$
Heating **N** produces **P**, $C_3H_4O_3$ and gas **Q**.	**Gas Q could be CO_2** as difference in molecular formula of **N** and **P** is CO_2.
N and **P** react with 2,4-DNPH.	**N** and **P** undergo condensation reaction with 2,4-DNPH ➔**N** and **P** are carbonyl compounds
P gives yellow ppt with aqueous alkaline iodine.	**P** undergoes oxidation with aqueous alkaline I_2 (positive iodoform test) ➔**P** has $-COCH_3$ group. CHI_3 is the yellow ppt.