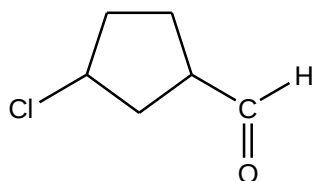
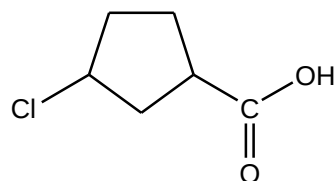
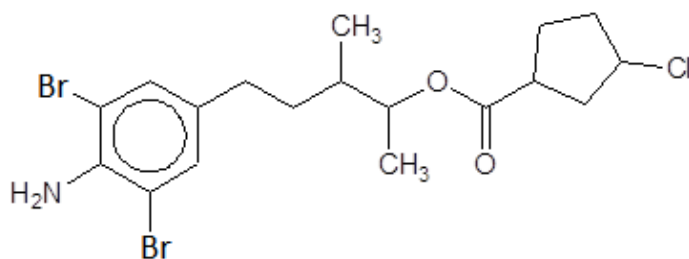
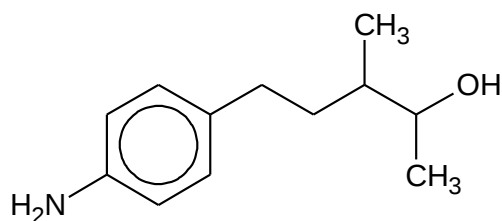
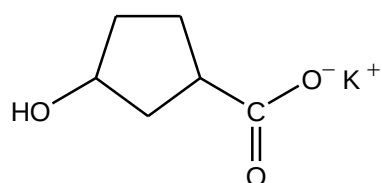
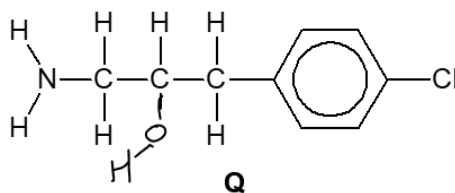
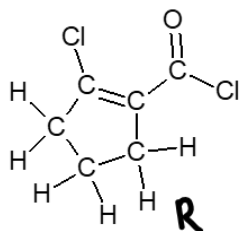


**Worked Solutions to Organic Chemistry Revision Booklet (Structured Questions)****1) Organic Synthesis****1.****(a)****D****E****(b)** Step 2: NaOH(aq); heatStep 3: KMnO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> (aq), heat or K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, H<sub>2</sub>SO<sub>4</sub> (aq), heat**(c)(i)****(ii)**

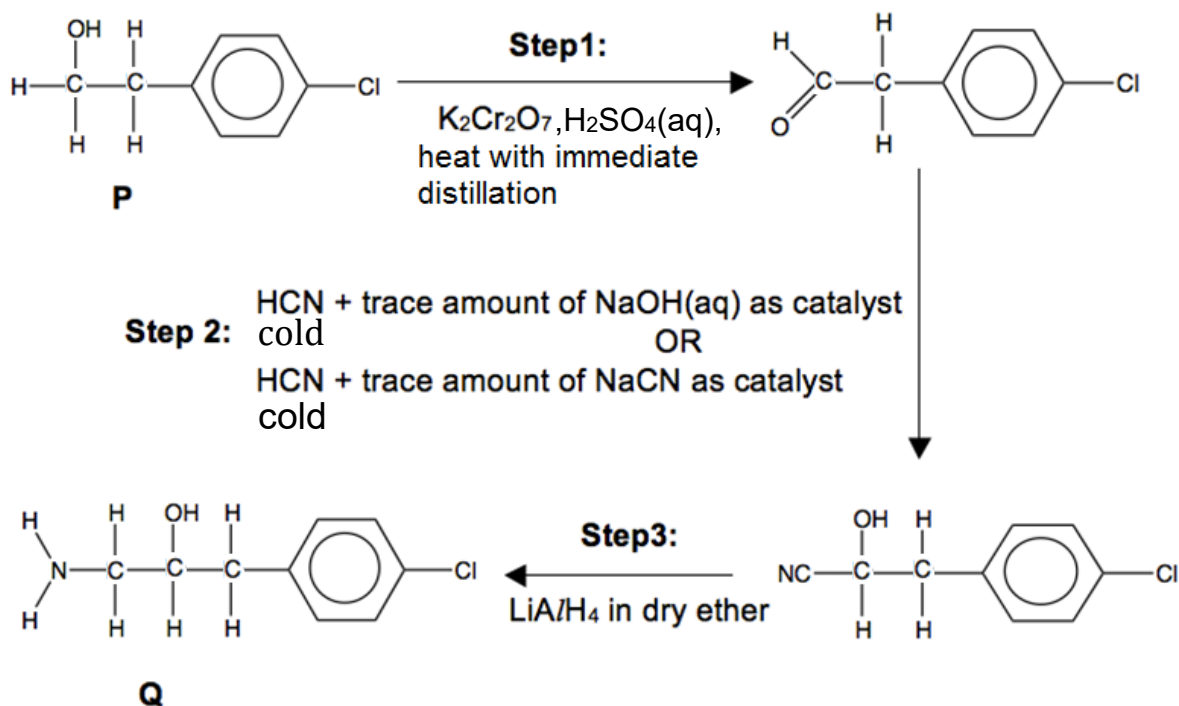
and

**\*remember to check for acid-base reaction after hydrolysis****2.****(a)****\*Hydrolyse the amide, S, to deduce the structures of R and Q.****\*Displayed formula shows all the bonds in the correct shape (i.e. trigonal planar, bent)**

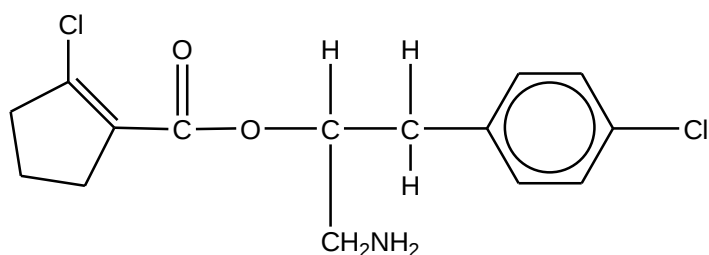
(b) Step 1: Oxidation ( $1^\circ$  alcohol to aldehyde) [controlled oxidation]

Step 2: Nucleophilic addition (of HCN)

Step 3: Reduction (of nitrile)

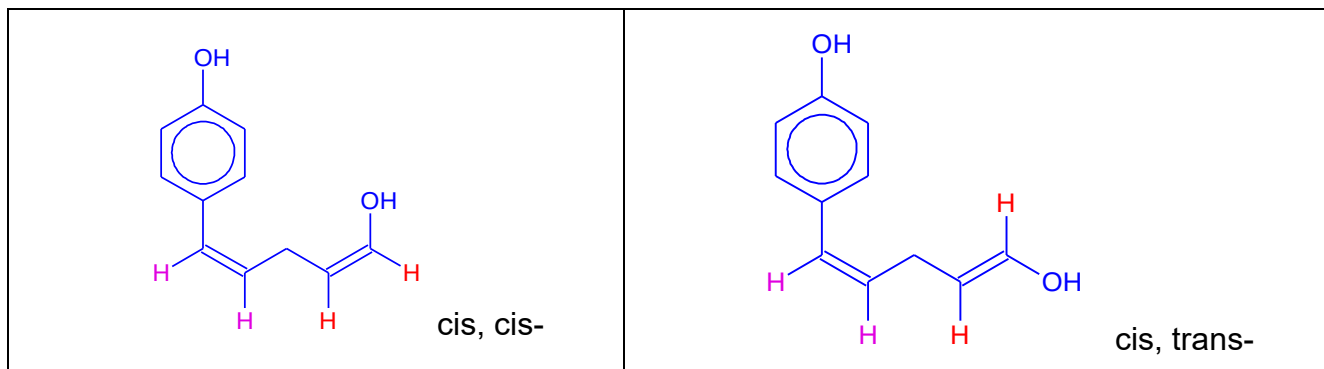


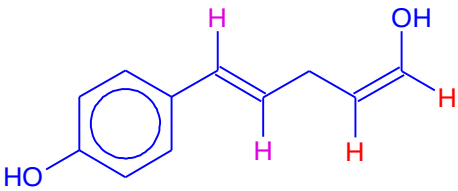
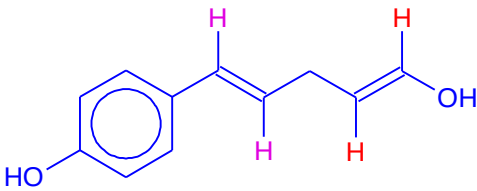
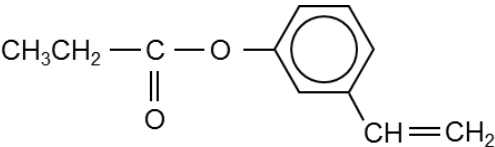
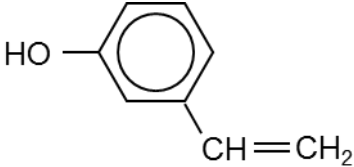
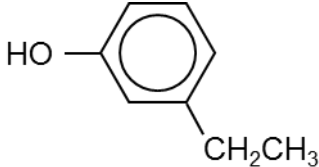
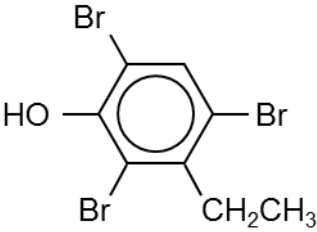
(c)



Acyl chloride, **R**, can undergo condensation reaction with alcohol in **Q** to form an ester.

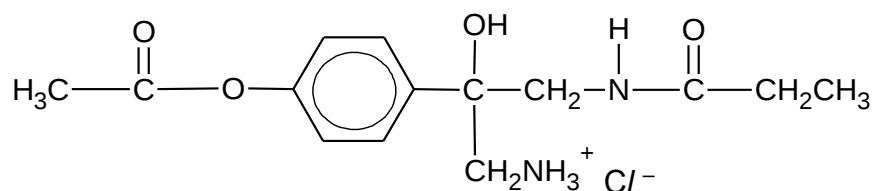
3. (a) cis-trans isomerism



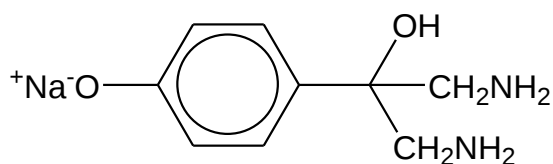
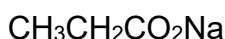
|     |                                                                                                                                                                                                       |                                                                                                                                                                                                    |
|-----|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|     |  <p>trans,cis-</p>                                                                                                   |  <p>trans,trans-</p>                                                                                             |
| (b) |  <p><b>Q</b> (C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>)</p> <p>Ester – undergoes acidic hydrolysis with aq HCl/</p> | <p>CH<sub>3</sub>CH<sub>2</sub>CO<sub>2</sub>H</p> <p><b>R</b> (C<sub>3</sub>H<sub>6</sub>O<sub>2</sub>)</p>                                                                                       |
|     |  <p><b>S</b> (undergoes reduction of alkene to give <b>T</b>)</p>                                                    |  <p><b>T</b> (Phenol undergoes electrophilic substitution with Br<sub>2</sub>(aq) – multiple substitutions)</p> |
|     |  <p><b>U</b> (C<sub>8</sub>H<sub>7</sub>OBr<sub>3</sub>)</p>                                                       |                                                                                                                                                                                                    |

- 4 (i)
1. Primary amine
  2. Tertiary alcohol
  3. amide
  4. ester

- (ii) cold HCl(aq) only acid-base reaction takes place (ester & amide hydrolysis require heat)



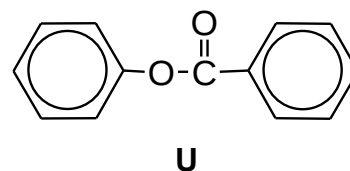
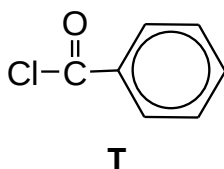
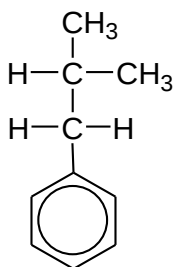
Hot NaOH(aq) alkaline hydrolysis followed by acid-base reaction of the products.



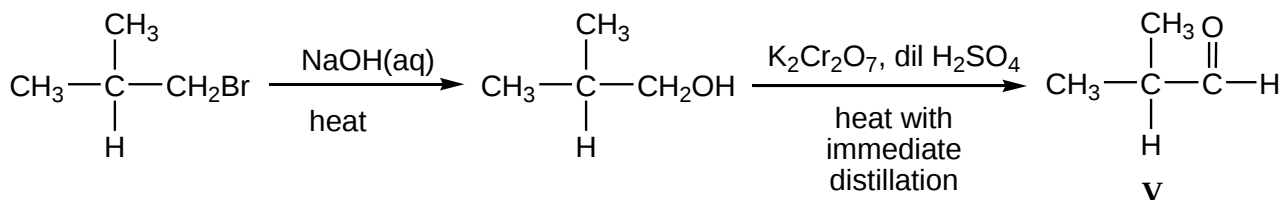
- 5 (i)  $\text{AlBr}_3$  or  $\text{FeBr}_3$  or  $\text{AlCl}_3$  or  $\text{FeCl}_3$ , anhydrous

- (ii) Benzene, although electron rich, is stabilised by resonance. Hence, benzene requires a strong electrophile for the electrophilic attack to take place. The presence of a Lewis acid catalyst (eg.  $\text{AlBr}_3$ ) is necessary for the formation of the strong electrophile,  $(\text{CH}_3)_2\text{CHCH}_2^+$ .

(iii)



- (iv) **V** is an aliphatic aldehyde as it gives a reddish brown ppt with Fehling's solution.

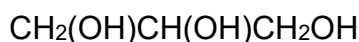
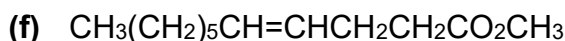


**6 (a)** Condensation (Nucleophilic acyl substitution)**(c)** Methyl ethanoate should be the limiting reagent.

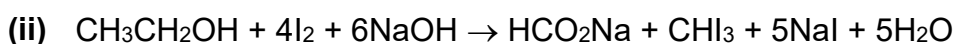
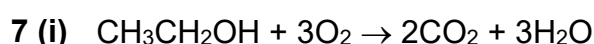
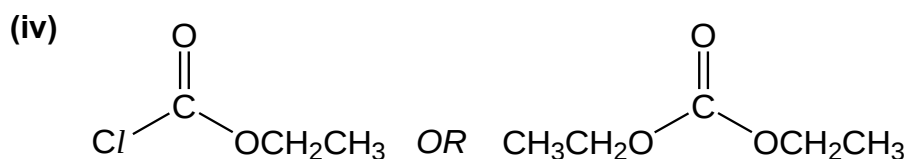
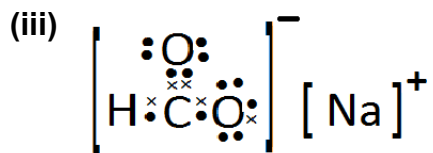
Ethanol should be in excess so that all the methyl ethanoate can be converted.

**(d)** More energy is required to overcome the stronger hydrogen bonds between methanol molecules during boiling than the permanent dipole-dipole interactions between methyl ethanoate molecules, leading to a higher boiling point.

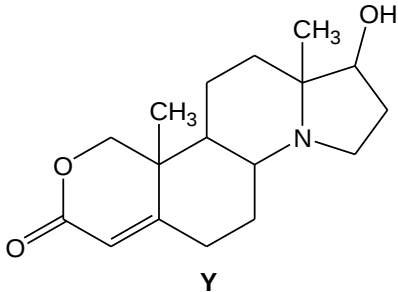
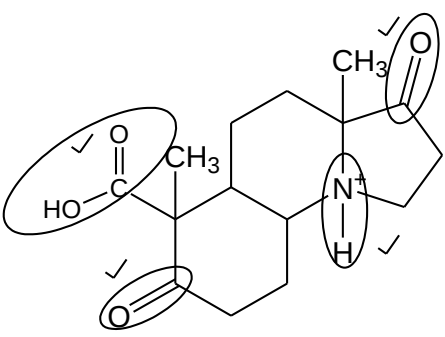
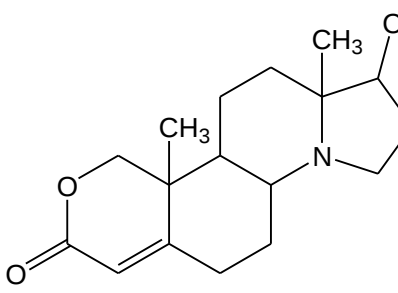
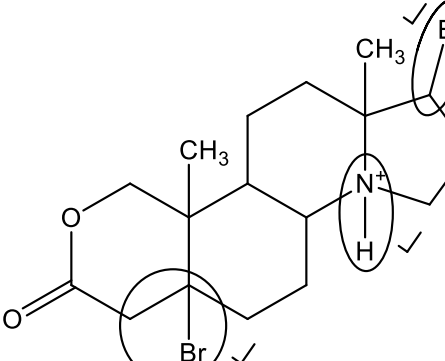
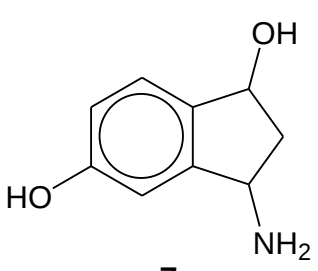
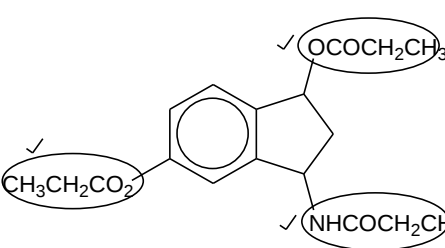
The instantaneous dipole-induced dipole interactions between ethyl ethanoate molecules are stronger than the hydrogen bonds between methanol molecules due to greater ease of distortion of larger electron cloud size of ethyl ethanoate molecules, requiring more energy to overcome during boiling, leading to a higher boiling point.

**(e)** Fractional distillation (particularly used when the boiling points of the liquids are quite similar)**(g)** Amt of HCl reacted =  $1.00 \times 15.20 \times 10^{-3} = 0.0152 \text{ mol}$ Total amt of  $\text{NH}_3$  =  $1.00 \times 25.0 \times 10^{-3} = 0.0250 \text{ mol}$ Amt of  $\text{NH}_3$  that reacted with ester =  $0.0250 - 0.0152 = 0.0098 \text{ mol} = \text{amt of ester}$  $M_r$  of the ester =  $1.00 / 0.0098 = 102.0$ Thus,  $15 + 12 + 32 + 14x + 15 = 102.0$ 

$$x = 2$$

**\*\*No of C atoms decrease by 1.**

8

| compound                                                                                                                        | reagent(s)                                                                                                                                                                                                                                                            | organic product                                                                      |
|---------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
|  <p style="text-align: center;"><b>Y</b></p>   | <p>KMnO<sub>4</sub>, dilute<br/>H<sub>2</sub>SO<sub>4</sub></p> <p>[O] of 2° alcohol,<br/>acid-base<br/>reaction of 3°<br/>amine,<br/>oxidative<br/>cleavage of<br/>alkene,<br/>acidic hydrolysis<br/>of ester followed<br/>by [O] of its 1°<br/>alcohol product)</p> |    |
|  <p style="text-align: center;"><b>Y</b></p>  | <p>HBr(g), heat</p> <p>(N.S. of 2°<br/>alcohol, E.A. of<br/>alkene, acid-base<br/>reaction of 3°<br/>amine)</p>                                                                                                                                                       |   |
|  <p style="text-align: center;"><b>Z</b></p> | <p>propanoyl<br/>bromide</p> <p>(condensation of<br/>phenol, alcohol &amp;<br/>amine with<br/>propanoyl<br/>bromide; yield of<br/>phenyl ester is<br/>enhanced if Na is<br/>used to convert<br/>phenol to<br/>phenoxide first)</p>                                    |  |

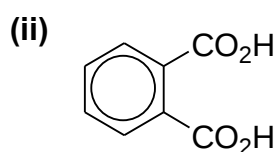
- 9 (i)** Step I: 1. cold concentrated  $\text{H}_2\text{SO}_4$   
2. warm with  $\text{H}_2\text{O}$

Step III:  $\text{HCN}$  with trace amount of  $\text{NaCN}$ , cold

|      |                                                                                   |                                            |
|------|-----------------------------------------------------------------------------------|--------------------------------------------|
| (ii) | $\text{CH}_3\text{COCH}_2\text{CH}_3$ <p style="text-align: center;"><b>B</b></p> | <p style="text-align: right;"><b>E</b></p> |
|------|-----------------------------------------------------------------------------------|--------------------------------------------|

- (iii) The electron deficient C centre in the carbonyl group is  **$\text{sp}^2$  hybridised** / the **geometry about the carbonyl C is trigonal planar**. Hence, there is **equal probability for the  $\text{CN}^-$  nucleophile to attack from either side of the plane containing the  $\text{C}=\text{O}$  bond**, leading to the formation of a pair of enantiomers in a 1:1 ratio.

- 10(i)** **step 1:** acid-metal reaction / redox reaction  
**step 3:** alkaline hydrolysis



Since 1 mol of **X** reacts with exactly 1 mol of sodium carbonate  $\Rightarrow$  1 mol of **X** contained 2  $-\text{COOH}$  groups.

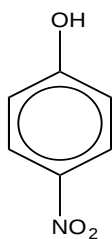
|              |                                             |                                             |
|--------------|---------------------------------------------|---------------------------------------------|
| <b>11(i)</b> | <p style="text-align: center;"><b>A</b></p> | <p style="text-align: center;"><b>B</b></p> |
|              | <p style="text-align: center;"><b>C</b></p> | <p style="text-align: center;"><b>D</b></p> |

- (ii) Step I:  $\text{NaOH(aq)}$ / $\text{KOH(aq)}$ ; heat  
Step II:  $\text{H}_2\text{SO}_4\text{(aq)}$ ,  $\text{K}_2\text{Cr}_2\text{O}_7\text{(aq)}$ ; heat with immediate distillation

Step III: NaOH/KOH in ethanol; heat

Step IV: I<sub>2</sub>, NaOH(aq), warm

12(a)



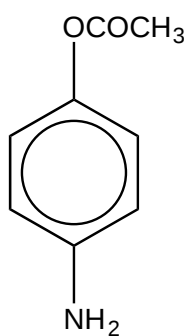
(-NO<sub>2</sub> must be substituted at the 4-position relative to phenol in order form the following products in the given reaction scheme)

(b) Stage 1: **Sn, conc. HCl; heat**

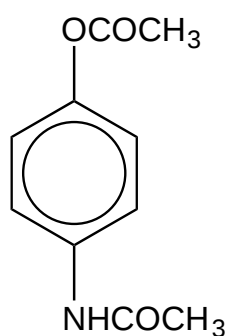
Stage 2: **NaOH(aq)** (to liberate phenylamine)

(c) (i) **CH<sub>3</sub>COCl**

(ii)

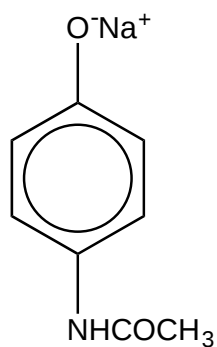


OR



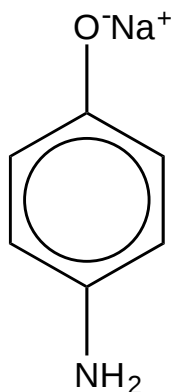
(consider condensation between phenol and acyl chloride)

(d) (i)



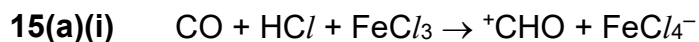
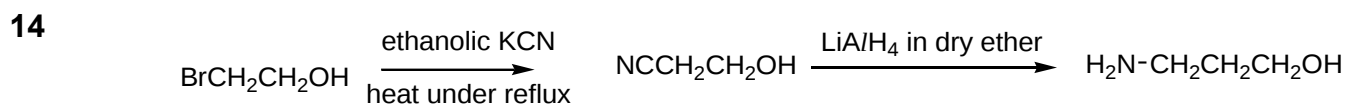
(acid-base reaction of phenol by aq NaOH)

(ii)

and  $\text{CH}_3\text{COO}^-\text{Na}^+$ 

(acid-base reaction of phenol by aq NaOH, alkaline hydrolysis of amide)

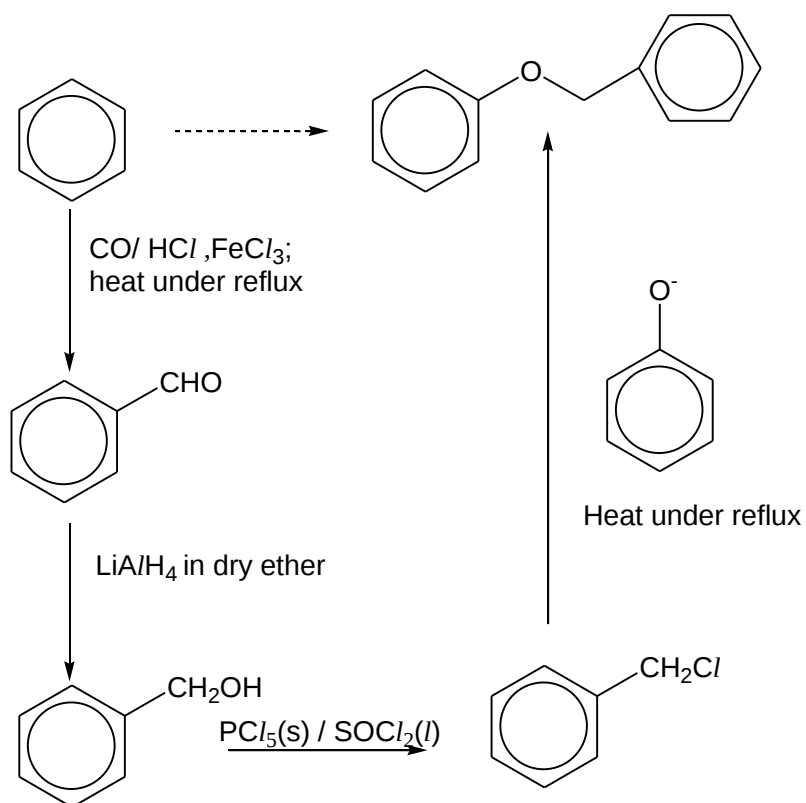
|           |                                                          |                                                         |                                                         |
|-----------|----------------------------------------------------------|---------------------------------------------------------|---------------------------------------------------------|
| <b>13</b> | <b>X</b><br>$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ | <b>Y</b><br>$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ | <b>Z</b><br>$\text{CH}_3\text{CHC}/\text{CO}_2\text{H}$ |
|-----------|----------------------------------------------------------|---------------------------------------------------------|---------------------------------------------------------|

Reagents and conditions for conversion of **Y** to **Z**: limited  $\text{C}/_2(\text{g})$ , uv light

(ii)  $\text{FeCl}_3$  hydrolyses in water to yield  $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$  and  $\text{Cl}^-$  ions / dissolve in water to form  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ .

Fe in  $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$  or Fe in  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  has no more vacant orbitals in the valence shell to accept the lone electron pair from  $\text{Cl}^-$  to generate the strong electrophile.

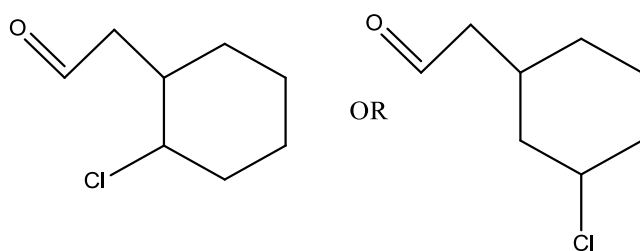
(b)



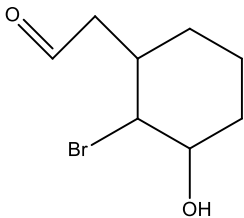
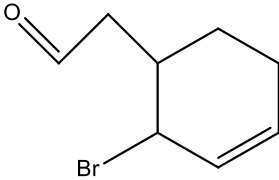
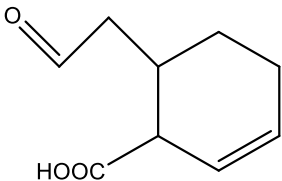
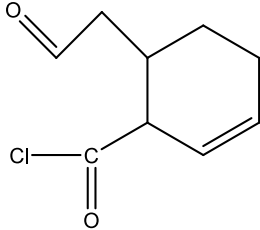
(step 3 requires anhydrous condition; step 4 is N.S where the phenoxide is acting as nucleophile)

16(a)(i)  $\text{HCl}(\text{g}) + \text{BaSO}_4$

(ii)



(E.A. of alkene with  $\text{HCl}$ )

| (b) | Step                                                                                | Reagents and conditions                                                               |
|-----|-------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
|     | I                                                                                   | $\text{Br}_2(\text{aq})$ (E.A. of alkene)                                             |
|     | II                                                                                  | Ethanollic KCN; heat (N.S. of -Br with -CN)                                           |
|     | III                                                                                 | Aqueous $\text{H}_2\text{SO}_4$ ; heat (acidic hydrolysis of nitrile)                 |
|     | IV                                                                                  | Anhydrous $\text{PCl}_5$ or $\text{SOCl}_2$ or $\text{PCl}_3$                         |
|     |  A |  B  |
|     |  C |  D |

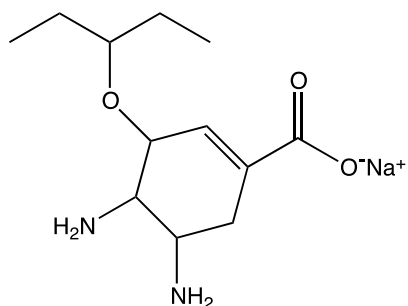
Note: Step1 must be E.A. of  $\text{Br}_2(\text{aq})$  in order for N.S (of -Br by -CN) & elimination (of  $\text{H}_2\text{O}$  by hot alumina) to take place in the subsequent steps)

17(a)(i) Amide, primary amine, ester, alkene

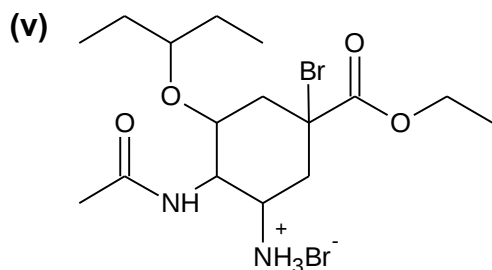
(ii) To increase its solubility (ion-dipole interactions with water) so that it is more easily absorbed by the body.

(iii) Alkaline Hydrolysis

(iv)

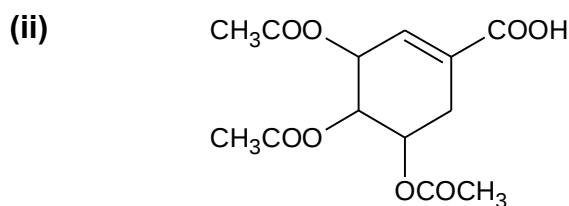


,  $\text{CH}_3\text{COO}^- \text{Na}^+$  and  $\text{CH}_3\text{CH}_2\text{OH}$



**\*\*Acid-base reaction of amine and electrophilic addition of alkene group**

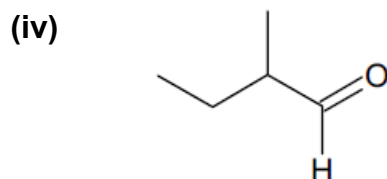
(b)(i) 1635-1690  $\text{cm}^{-1}$  (alkene absorption range)



18 (i) Nucleophile

(ii)  $\text{CH}_2(\text{OH})(\text{NH}_2)$

(iii) HCN



19 (a) Rxn A: Nucleophilic addition

Rxn B: Hydrolysis

(b)(i) No naked flame around / heating should be done with heating mantle / water bath as chemicals are flammable.

Perform experiment in fume cupboard as chemicals are toxic.

(ii) To exclude any trace of water/moisture or to ensure chemicals are dry.

(iii)  $\text{CH}_3\text{CH}_2\text{I} + \text{Mg} \rightarrow \text{CH}_3\text{CH}_2\text{MgI}$

$$\text{amt of Mg} = \text{amt of CH}_3\text{CH}_2\text{I} = \frac{1.50}{24.3} = 0.06173 \text{ mol}$$

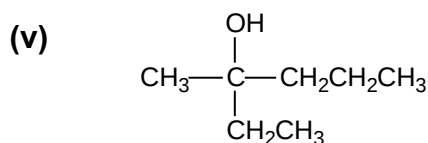
$$\text{Vol of CH}_3\text{CH}_2\text{I} = \frac{\text{mass}}{\text{density}} = \frac{0.06173 \times 156}{1.93} = 4.99 \text{ cm}^3$$

(iv) Amt of grignard reagent produced in step II = 0.06173 mol

$$\text{Amt of pentan-2-one} = \frac{\text{density} \times \text{vol}}{\text{Mr of pentan-2-one}} = \frac{0.814 \times 6.0}{86.0} = 0.0568 \text{ mol}$$

&lt; Amt of grignard reagent

Since pentan-2-one reacts with Grignard reagent in the mole ratio of 1:1, hence Grignard reagent is in excess

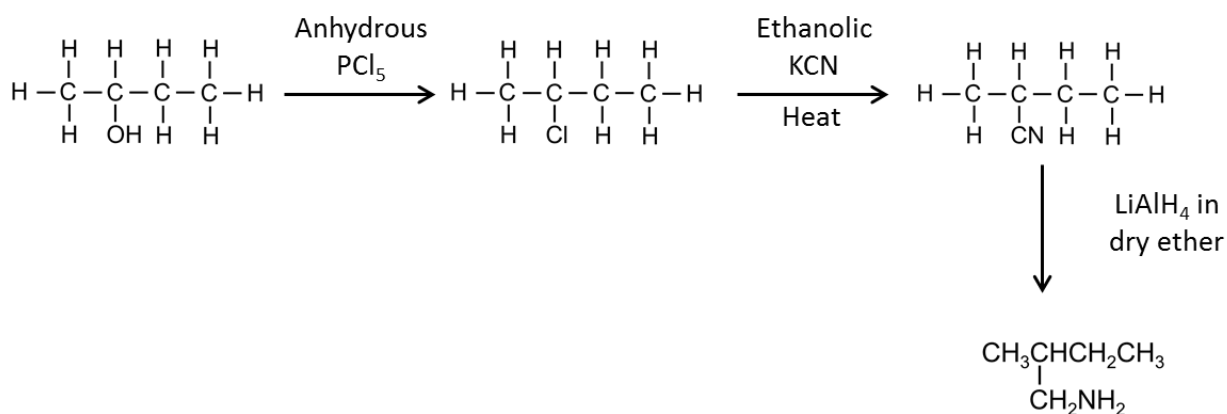


(vii) Ethoxyethane forms an *immiscible layer above* the aqueous layer because of:

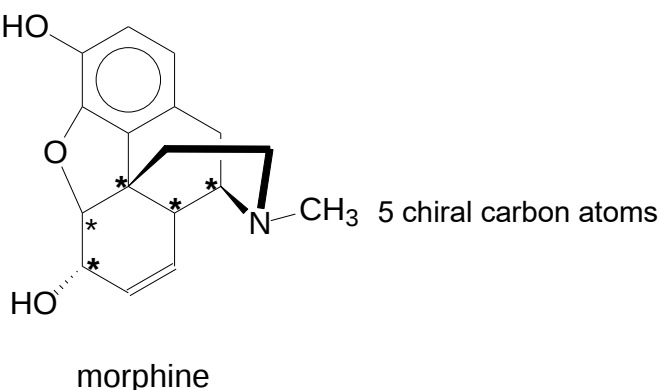
- unfavourable interaction between ethoxyethane and water due to bulky non-polar alkyl chain in ethoxyethane or hydrogen bonds between water molecules and ethoxyethane is weaker than the instantaneous dipole-induced dipole interactions between ethoxyethane molecules due to its bulky non-polar alkyl chain.
- ethoxyethane is less dense than water ( $0.713 \text{ g cm}^{-3}$  as against  $1 \text{ g cm}^{-3}$ )

| (viii) | Chemicals added                       | Impurity removed                                 |
|--------|---------------------------------------|--------------------------------------------------|
|        | 1. water                              | Mg salts e.g. $\text{MgI}_2$ / $\text{Mg(OH)Br}$ |
|        | 2. saturated sodium hydrogencarbonate | $\text{HCl}$                                     |
|        | 3. sodium thiosulfate                 | iodine                                           |
|        | 4. saturated sodium chloride          | $\text{H}_2\text{O}$                             |

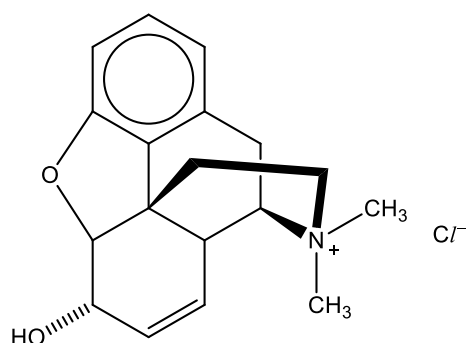
19 (c)



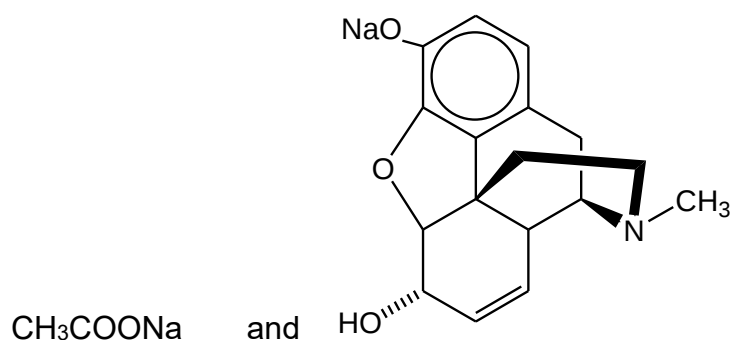
20 (i)



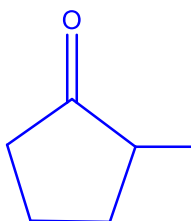
(ii)



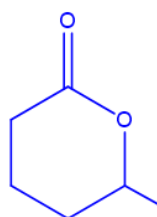
(iii)



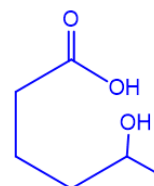
21 L:



M:

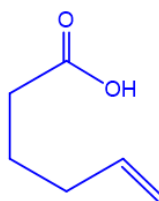
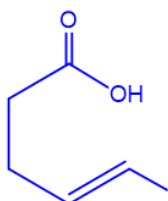


N:



P:

O:



22 (i) Secondary alcohol; alkene

(ii) Step III: KMnO<sub>4</sub>(aq), NaOH(aq); heat (alkaline medium to form -COONa)  
 Step IV: I<sub>2</sub>, NaOH(aq); heat

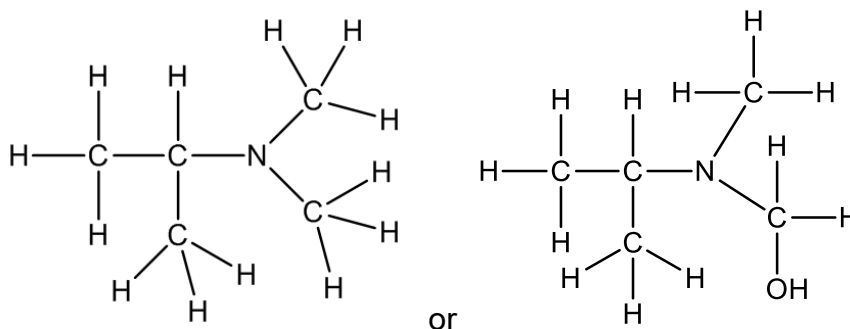
(iii) Secondary alcohol

The secondary alcohol will undergo oxidation in reaction III to form a methyl ketone, which subsequently loses 1 carbon in the iodoform reaction in reaction IV.

23 (i) (lower pK<sub>b</sub> value = stronger base)

The additional **methyl group** on *N*-methylcyclohexylamine is **electron-donating**. Hence it **increases** the **electron density on N atom**, making the lone pair on N more available to accept a  $H^+$ .

(ii)

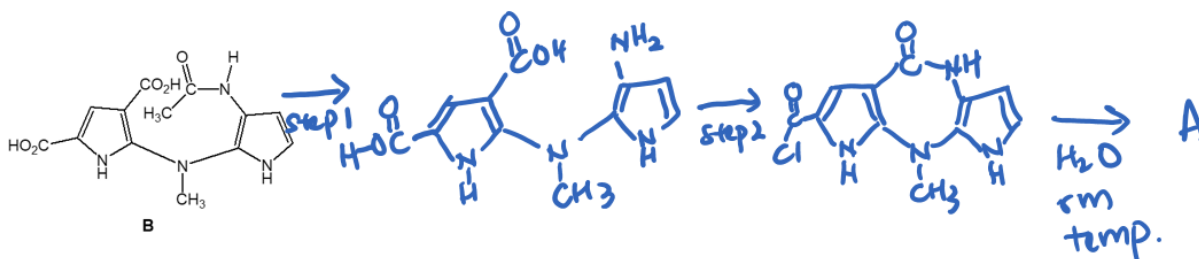


or

(iii) For phenylamine, **lone pair on N is delocalised into** the  $\pi$  electron cloud of **the benzene ring/ electron density at N is reduced via resonance with the adjacent benzene ring**. Hence, the lone pair is less available for donation, and phenylamine acts as a **weak nucleophile**.

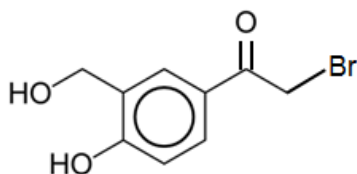
24.

| Step | Reagents and conditions                                                                                                                                   |
|------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1    | dil HCl, (or dil HNO <sub>3</sub> or dil H <sub>2</sub> SO <sub>4</sub> ) heat; followed by dil NaOH (to deprotonate the amine)                           |
| 2    | PCl <sub>5</sub> (s), anhydrous<br>(or PCl <sub>3</sub> , SOCl <sub>2</sub> , anhydrous) (-COOH group becomes -COCl to react with amine via condensation) |
| 3    | Water (hydrolysis of -COCl)                                                                                                                               |



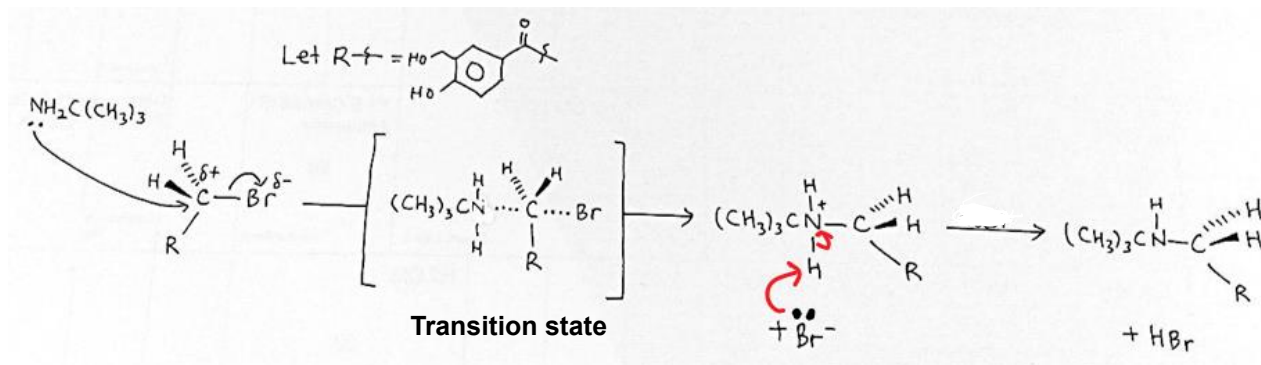
25(a) There is a possibility of many side products as random substitution of hydrogen atoms on any alkyl group found in the compound can occur via free radical substitution..

(b) Nucleophilic substitution

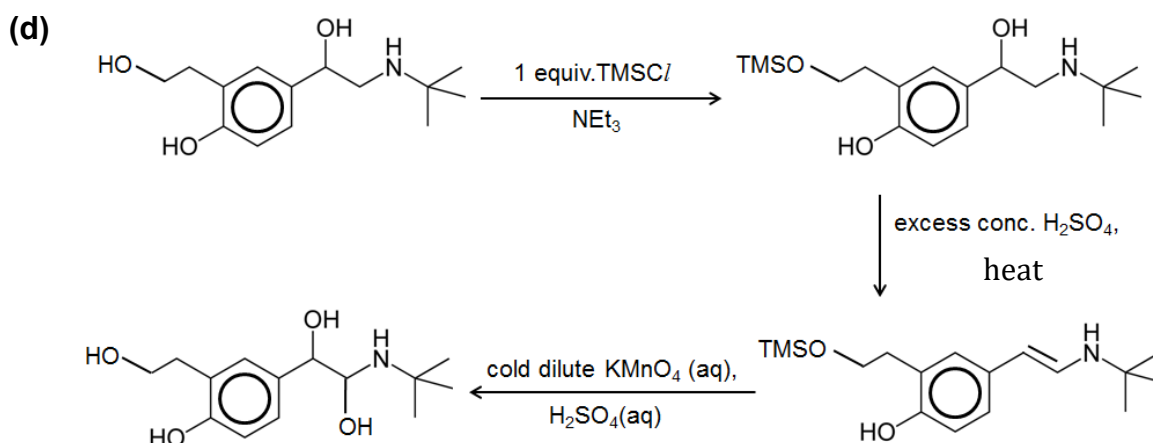


Cannot react via  $S_N1$  mechanism as the carbocation formed will be destabilised by the electron-withdrawing effect of the adjacent  $C=O$ .

Thus, it undergoes the  $S_N2$  mechanism instead.



(c)  $\text{H}^-$  from  $\text{LiAlH}_4$  readily reacts with partial positive H of water.



(for the last step of mild oxidation of alkene, acidic medium is used instead of alkaline medium to prevent the phenol from acid-base reaction to become a phenoxide ion)

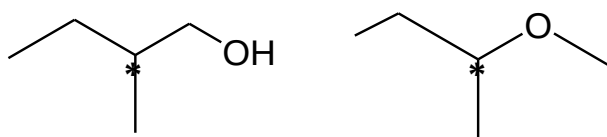
- 26(a)(i) Isopentyl acetate is immiscible with water / does not interact well with water because the energy released from forming **hydrogen bond between isopentyl acetate and water is not sufficient to overcome the instantaneous dipole-induced dipole interactions between isopentyl acetate due to its bulky hydrocarbon chain.**
- (ii) Isopentyl acetate has a larger electron cloud which is more easily distorted causing the instantaneous dipole-induced dipole to be stronger than the hydrogen bonding between isopentyl alcohol molecules. Hence, more energy is required to overcome the intermolecular forces between isopentyl acetate molecules.
- (iii)  $\text{H}_2\text{O}(\text{g})$  can escape, thus shifting the position of equilibrium to the right to partially offset the loss of water, thus forming more ester.
- (iv) To react with the unreacted ethanoic acid.
- (v) To allow  $\text{CO}_2$  to escape, preventing the build-up of pressure in the separating funnel.

|        |                 |                                                    |
|--------|-----------------|----------------------------------------------------|
| (b)(i) | <b>Step I</b>   | Excess concentrated $\text{H}_2\text{SO}_4$ , heat |
|        | <b>Step II</b>  | $\text{NaOH}$ (aq); heat                           |
|        | <b>Step III</b> | Ethanol KCN; heat                                  |
|        | <b>Step IV</b>  | Concentrated $\text{H}_2\text{SO}_4$ ; reflux      |

(ii)

|              |              |              |
|--------------|--------------|--------------|
| <b>Q</b><br> | <b>R</b><br> | <b>S</b><br> |
| <b>T</b><br> | <b>U</b><br> | <b>V</b><br> |

(iii)

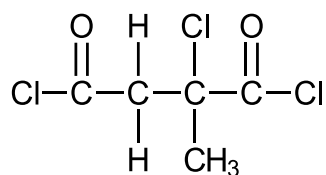
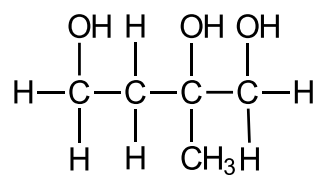
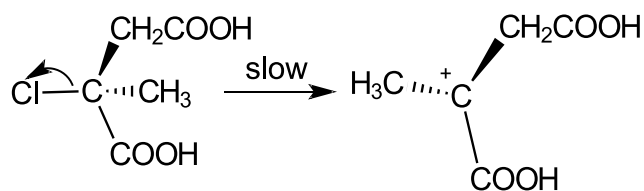
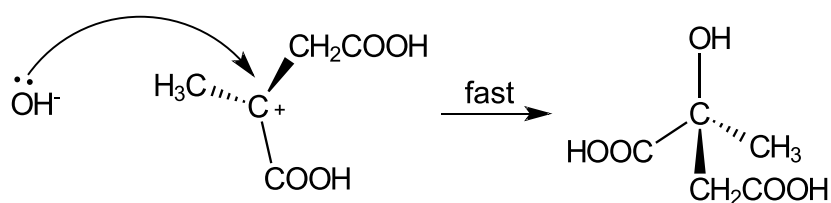


27(a)(i) Carboxylic acid and tertiary alcohol

(ii)

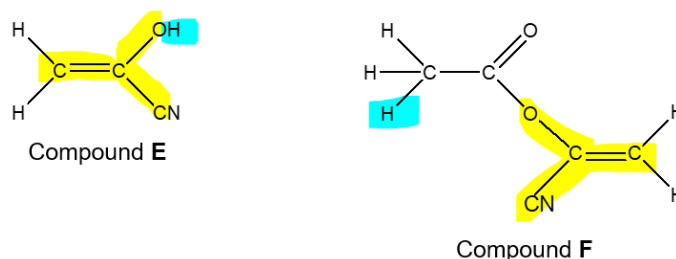
|           | Reagents and Conditions                                                                                                       |
|-----------|-------------------------------------------------------------------------------------------------------------------------------|
| Stage I   | $\text{HCl(g)}$ , room temperature                                                                                            |
| Stage II  | $\text{NaOH(aq)}$ , heat, followed by $\text{H}_2\text{SO}_4\text{(aq)}$<br>(to protonate $-\text{COO}^-$ to $-\text{COOH}$ ) |
| Stage III | $\text{PCl}_5\text{(s)}$ , anhydrous                                                                                          |

(iii)

**K****L**(iv) Name of mechanism: Nucleophilic substitution ( $\text{S}_{\text{N}}1$ )**Step 1:****Step 2:**

- (v) Citramalic acid formed from Stage II is a racemic mixture, hence it is optically inactive. The nucleophile,  $\text{OH}^-$  ion, can attack from either the top or bottom of the trigonal planar carbocation with equal probabilities, resulting in the formation of equal amount of each enantiomer. Effect on plane-polarised light is equal but opposite by each enantiomer, hence net zero optical activity.

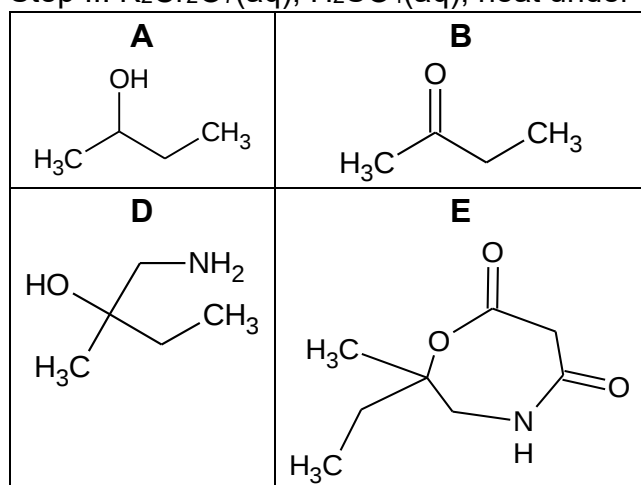
28



(in step 2,  $-\text{OH}$  of compound E act as nucleophile to attack the electron-deficient C in  $\text{C}=\text{O}$  of ketene)

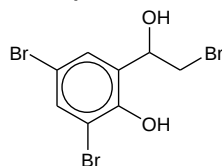
- 29 (a) Step I: cold conc  $\text{H}_2\text{SO}_4$  followed by  $\text{H}_2\text{O}$  and warm  
 Step II:  $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ ,  $\text{H}_2\text{SO}_4(\text{aq})$ , heat under reflux OR  $\text{H}_2\text{SO}_4(\text{aq})$ ,  $\text{KMnO}_4(\text{aq})$ , heat

(b)



- (c) The attacking nucleophile,  $^-\text{CN}$ , can approach the trigonal planar carbonyl C from the top or bottom of the plane with equal probability hence resulting in a racemic mixture.

- 30 Step I: Electrophilic substitution of phenol with  $\text{Br}_2(\text{aq})$  will also take place to produce the



product as the lone pair of electrons on O in phenol group delocalises into benzene ring, hence making benzene ring more electron rich & susceptible towards attack by electrophile, hence multiple substitutions.

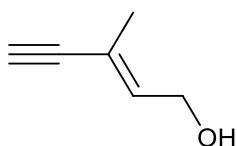
Step II: Nucleophilic substitution requires nucleophile ( $-\text{CN}$ ) which is in very low concentration as  $\text{HCN}$  is a weak acid & only dissociates partially.

Alternative method: Heat with ethanolic  $\text{KCN}/\text{NaCN}$

Step V: Esterification between  $-\text{CO}_2\text{H}$  and phenol group cannot take place under such conditions. The lone pair of electrons on O in phenol group is not nucleophilic enough to attack the  $-\text{CO}_2\text{H}$  as it is delocalized into the benzene ring.

Alternative method: Add anhydrous  $\text{PCl}_5$  /  $\text{SOCl}_2$  to convert  $-\text{COOH}$  to  $-\text{COCl}$  and use  $\text{NaOH}$  to convert phenol to phenoxide.

31 (i)



(ii) Reduction

(iii) Palladium is a heterogeneous catalyst in this reaction. the presence of partially filled  $d$  orbitals allow the reactants to be adsorbed on the metal surface, weakening the existing bond. The product molecules desorb at the end of reaction, making the active sites available for other reactant.

(iv)  $\text{H}_2/\text{Ni}$  will cause all the double bonds (and triple bond) to be reduced.

32 I: Methanol  $\rightarrow$  Methanal

Reagents and conditions:  $\text{K}_2\text{Cr}_2\text{O}_7$ , dil.  $\text{H}_2\text{SO}_4$ , heat with distillation

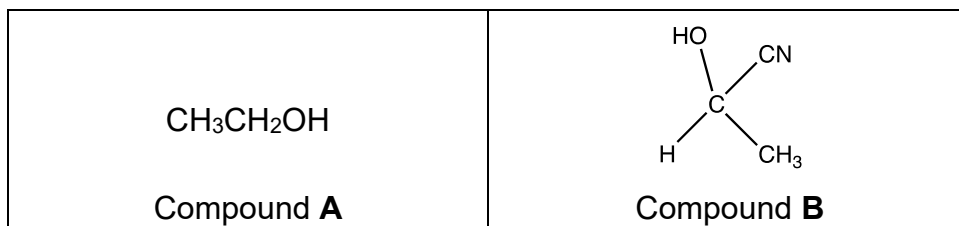
II: Methanol  $\rightarrow$  Methanoic acid

Reagents and conditions:  $\text{K}_2\text{Cr}_2\text{O}_7$ , dil.  $\text{H}_2\text{SO}_4$ , heat under reflux (cannot use  $\text{KMnO}_4$ , dil.  $\text{H}_2\text{SO}_4$ , heat,  $\text{HCOOH}$  will be oxidized to  $\text{CO}_2$ , see III below)

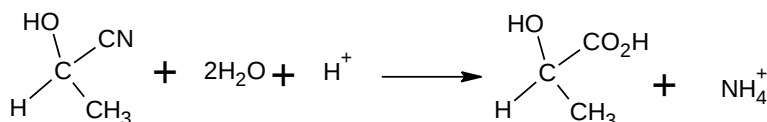
III: Methanol  $\rightarrow$  Carbon dioxide

Reagents and conditions:  $\text{KMnO}_4$ , dil.  $\text{H}_2\text{SO}_4$ , heat under reflux

33 (i)

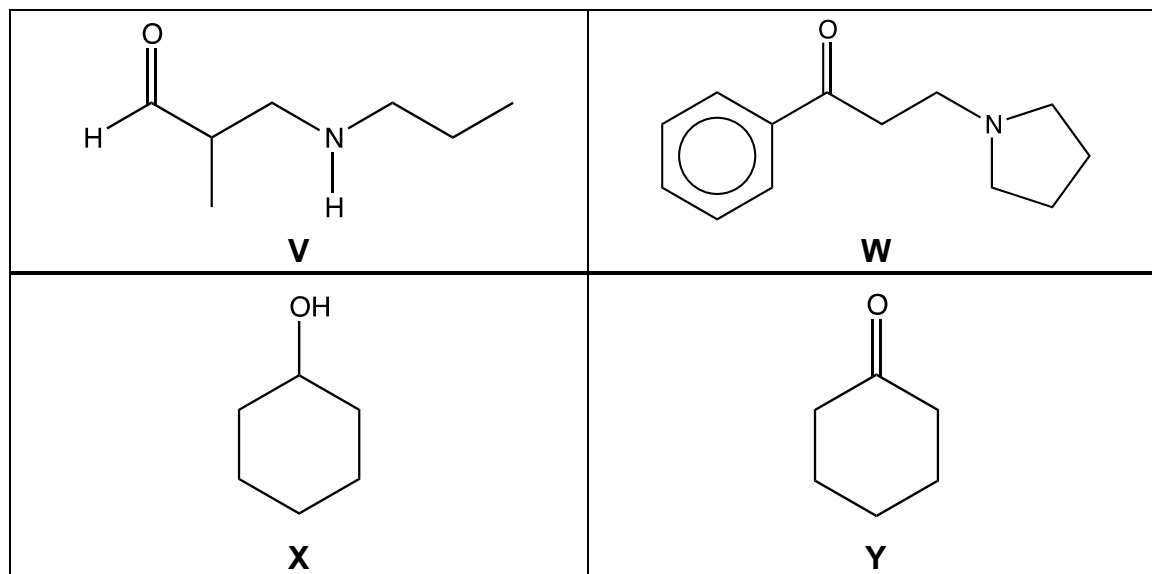
(ii) Reagents and conditions: NaOH(aq); heat(iii) Type of reaction: **Acidic Hydrolysis**

Balanced equation:

(iv) Carbonyl carbon is trigonal planar and the  $^-\text{CN}$  nucleophile can attack the carbonyl carbon from top and bottom of the plane with equal probability, forming equal amount of each optical isomers, resulting in a racemic mixture.

In bacteria fermentation, the nucleophilic attack can only take place from one side since enzyme has specific reaction site, thus only 1 optical isomer is formed.

34 (a)

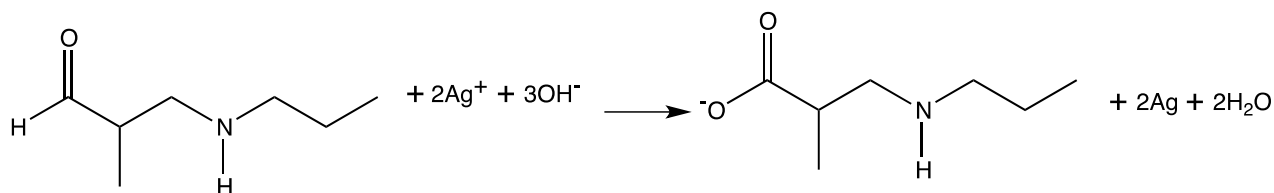


(b)(ii) I Aqueous NaOH, heat;

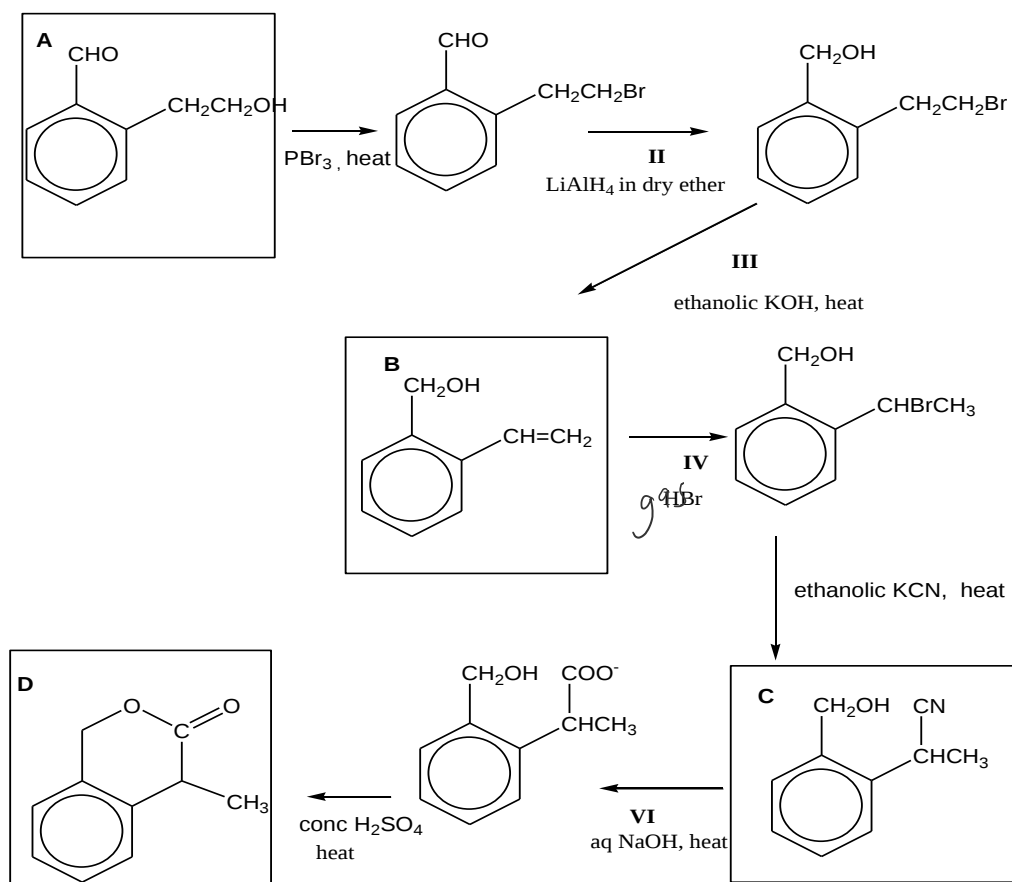
II  $\text{KMnO}_4(\text{aq})$ ,  $\text{H}_2\text{SO}_4(\text{aq})$ , heat or  $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ ,  $\text{H}_2\text{SO}_4(\text{aq})$ , heat(c)(i) White ppt: AgCl, Complex:  $[\text{Ag}(\text{NH}_3)_2]^+$ 

(ii) Z is Tollen's reagent.

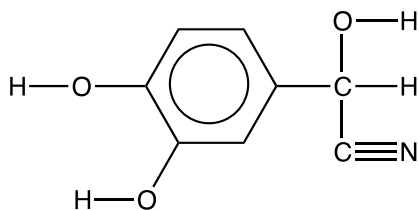
V will give a V gives a silver mirror. W will not give a silver mirror.



35

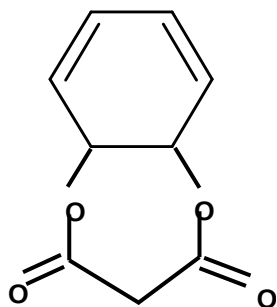


36 (i)

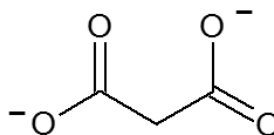
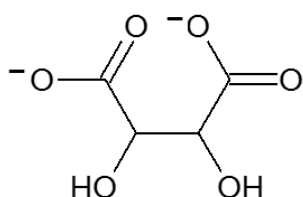
(ii) Step I:  $\text{HCN}$ , trace amount of  $\text{NaCN}$ , coldStep II:  $\text{LiAlH}_4$  in dry ether or  $\text{H}_2$ ,  $\text{Pt}$ Step III:  $\text{CH}_3\text{Br}$ ; heat (Nucleophilic Substitution)

37 (i)  $\text{LiAlH}_4$  in dry ether, room temperature OR  $\text{NaBH}_4$  in ethanol

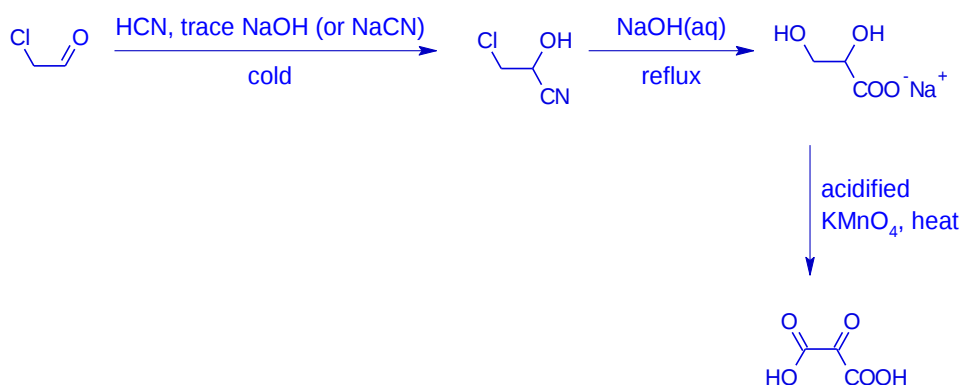
(ii) B:



D & E:



(iii)



(iv)

The  $\delta^+$  carbon atom in is bonded to 2 very electronegative atoms (O and Cl), thus making the carbon atom highly electron-deficient ( $\delta^+$ ).

Whereas the  $\delta^+$  carbon atom is less electron-deficient as it is only bonded to one electronegative atom (Cl).

Since the more electron deficient ( $\delta^+$ ) the carbon atom, the easier it is for hydrolysis to occur,

thus it is easier for to undergo hydrolysis as compared to .

## 2) Distinguishing Test

**1** Reagent(s) & conditions: **aqueous Br<sub>2</sub>**

Observations: For **B**: **White precipitate** is formed and **orange Br<sub>2</sub> is decolourised.**

For **A**: No white precipitate and orange aq Br<sub>2</sub> not decolourised.

**2 (i)** Add dilute sulfuric acid and KMnO<sub>4</sub> to separate test tubes of the esters and warm.

Only methyl ethanoate would decolorise purple KMnO<sub>4</sub> and effervescence (gas gives white precipitate with limewater)

**\*\*hydrolysis of the ester takes place first, it is the alcohol product that gives the positive observation.**

**(ii)** Add NaOH(aq) and I<sub>2</sub> to separate test tubes of the esters and warm.

If a yellow precipitate is observed, ethyl ethanoate is present.

**\*\*hydrolysis of the ester takes place first, it is the alcohol product that gives the positive observation.**

**3** Add **NaOH(aq)** to each compound and **heat**. Then **cool** and **acidify** each mixture with **HNO<sub>3</sub>(aq)**, followed by adding **AgNO<sub>3</sub>(aq)**.

Observation: CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>Cl gave a **white ppt** of AgCl, but no ppt with CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>OH.

Alternative:

Tests which gave a positive observation with the alcohol:

Na metal. Effervescence observed with CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>OH (gas that extinguishes a lighted splint with a 'pop' sound) but no effervescence observed with CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>Cl.

K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>(aq), H<sub>2</sub>SO<sub>4</sub>(aq); heat. CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>OH turned orange dichromate(VI) to green, but orange remains with CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>Cl.

KMnO<sub>4</sub>(aq), H<sub>2</sub>SO<sub>4</sub>(aq); heat. CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>OH decolourised purple KMnO<sub>4</sub>, but purple remains with CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>Cl.

Anhydrous PCl<sub>5</sub> or SOCl<sub>2</sub>; CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>OH gave white fumes of HCl, but no white fumes with CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>Cl.

**4** warm with H<sub>2</sub>SO<sub>4</sub>(aq), KMnO<sub>4</sub> and test the gas evolved with limewater.

But-1-ene would turn purple KMnO<sub>4</sub> colourless and gives effervescence (a gas that forms a white ppt with limewater) while but-2-ene would turn purple KMnO<sub>4</sub> colourless but no effervescence.

**5** Aqueous NaOH; heat. Acidify with excess dilute HNO<sub>3</sub>, followed by adding aqueous AgNO<sub>3</sub>.

Cream precipitate of AgBr would be observed for BrCH<sub>2</sub>CH<sub>2</sub>OH but no precipitate would be observed with HOCH<sub>2</sub>CH<sub>2</sub>OH.

**6** **Reagent/condition:** H<sub>2</sub>SO<sub>4</sub>(aq), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, heat

**Expected observation:** orange acidified dichromate(VI) turns green with *Shikimic* acid while orange remains with **R**.

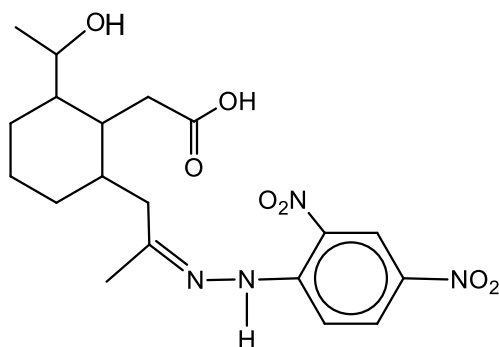
**7** Neutral  $\text{FeCl}_3(\text{aq})$  **\*\* exclusive test for phenol and its derivatives**

Morphine: Violet complex observed

Codeine: No violet complex observed

**8** Test: 2,4-dinitrophenylhydrazine

Observations: orange ppt formed for **U** and no orange ppt for **T**



**9** Test: warm with  $\text{HCl}(\text{aq})$ , followed by neutral  $\text{FeCl}_3(\text{aq})$ .

Observations: Aspirin gives a violet colouration while **X** does not.

**OR**

Test: warm with  $\text{HCl}(\text{aq})$ , followed by  $\text{Br}_2(\text{aq})$ .

Observations: orange  $\text{Br}_2$  decolourises for aspirin but not for **X**.

**\*\*warming with  $\text{HCl}$  allows the ester to undergo hydrolysis, positive observation is for the phenol obtained**

**10** **Reagents and conditions:**  $\text{NaOH}(\text{aq})$ ; heat, test for gas with moist red litmus paper

**Observations:** Red litmus turns blue for asparagine. Red litmus remains for tryptophan.

**OR**

**Reagents and conditions:** Bromine in  $\text{CCl}_4$  (in the dark) / aqueous bromine

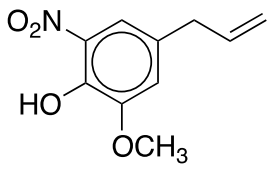
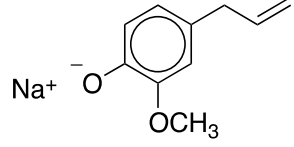
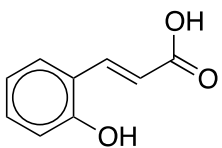
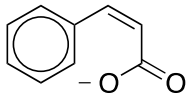
**Observations:** Tryptophan: orange red bromine turns colourless / orange aq bromine turns colourless. Asparagine: orange red or orange solution remains.

**OR**

**Reagents and conditions:**  $\text{H}_2\text{SO}_4(\text{aq})$ ,  $\text{KMnO}_4$ ; warm

**Observations:** Purple turns colourless for tryptophan. Purple remains for asparagine.

11

| reagent                               | A, B, C or D | structural formula of the organic product                                           |
|---------------------------------------|--------------|-------------------------------------------------------------------------------------|
| dilute $\text{HNO}_3$                 | D            |  |
| Na                                    | D            |  |
| dilute $\text{H}_2\text{SO}_4$ ; heat | A            |  |
| Fehling's reagent                     | B            |  |

12

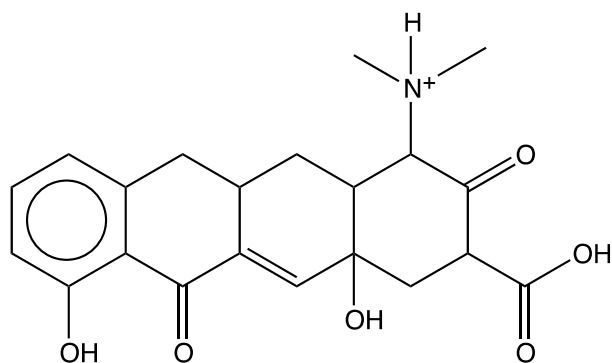
Any one of the following tests and observations:

1) Add  $\text{Na}_2\text{CO}_3(\text{aq})$

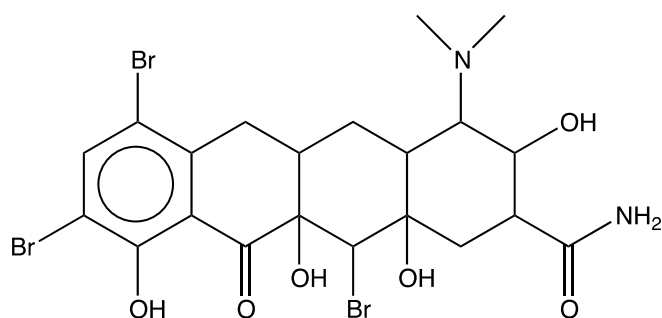
Observation: Effervescence of  $\text{CO}_2$  that formed white precipitate with limewater observed for ibuprofen but no effervescence evolved for 2-methylpropylbenzene.

2) Add  $\text{PCl}_5(\text{s})$  or  $\text{SOCl}_2(\text{l})$  anhydrous

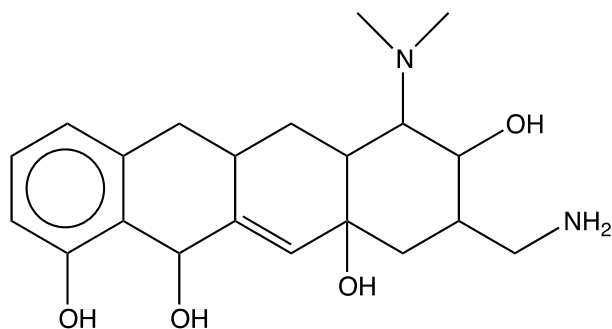
Observation: White fumes of  $\text{HCl}$  observed for ibuprofen but no fumes evolved for 2-methylpropylbenzene.

**13(i)**

(oxidation of 2° alcohol)

**(ii)**

(Electrophilic Substitution of phenol, Electrophilic addition of alkene)

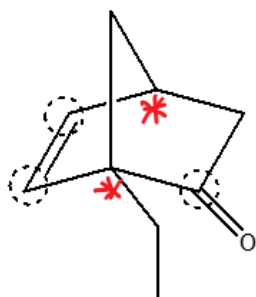
**(iii)**

(Reduction of amide into amine)

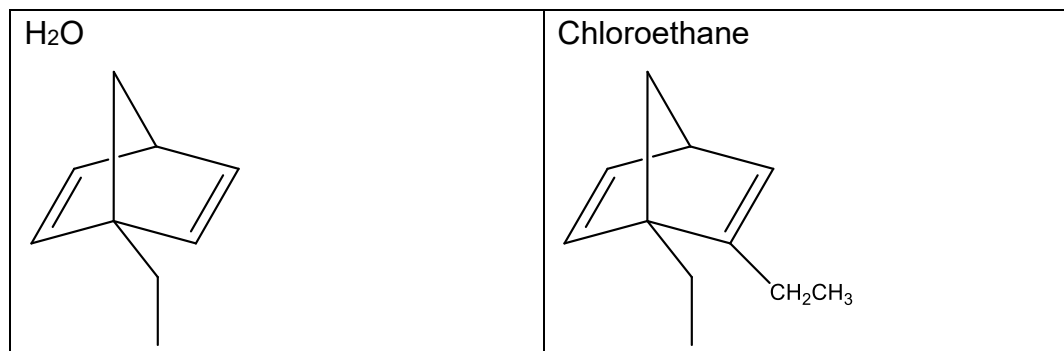
- iv)** Reagents and condition: cold dilute alkaline KMnO<sub>4</sub>(aq)  
**M** will decolourise purple KMnO<sub>4</sub>, brown ppt of MnO<sub>2</sub> forms  
**N** will not decolourise purple KMnO<sub>4</sub>.

14(i) Number of chiral centers = 2

(ii)



(iii)



(iv)

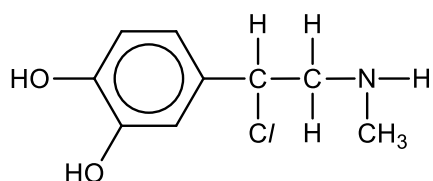
Reagents and conditions: KMnO<sub>4</sub>, aq. H<sub>2</sub>SO<sub>4</sub>; warm

Observations: S decolourise purple KMnO<sub>4</sub> but purple KMnO<sub>4</sub> remains in R

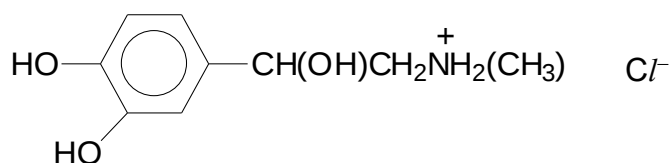
\*K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> accepted

**Note: Hydrolysis of the ester followed by reaction with the alcohol produced.**

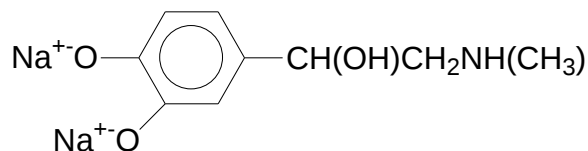
15(ai)



(ii)



(iii)



(b)

Test: Warm both compounds with NaOH(aq) separately

Observations: For compound **Z**, alkaline gas liberated turning moist red litmus paper blue. For adrenaline, moist red litmus paper remains.

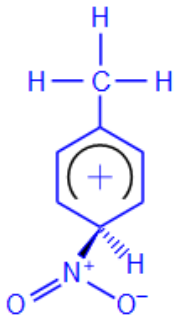
Test: Add PCl<sub>5</sub>(s) to both compounds separately

Observations: For adrenaline, copious white fumes of HCl will be observed. For the compound **Z**, no white fumes will be observed.

- 16** Reagent and condition:  $I_2(aq)$ ,  $NaOH(aq)$ , warm  
Observations for **C**: Yellow ppt of  $CHI_3$  formed.  
Observations for **D**: No yellow ppt of  $CHI_3$  formed.

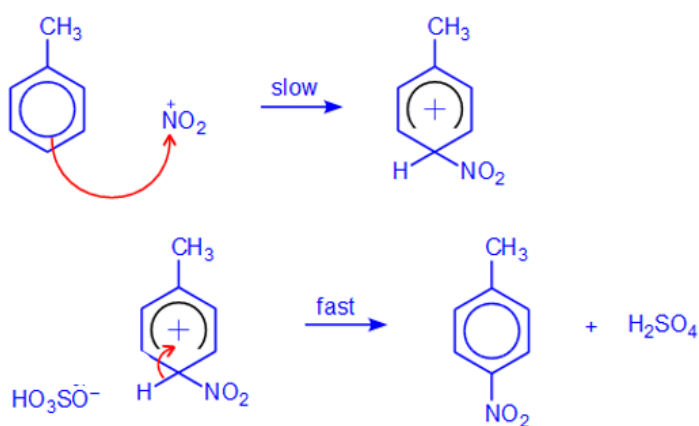
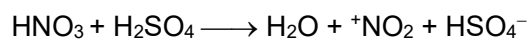
**\*\*the warm aq NaOH cause hydrolysis of ester and the Iodoform test positive for the methyl carbinol group)**

**3) Reaction Mechanism****1 (a)**

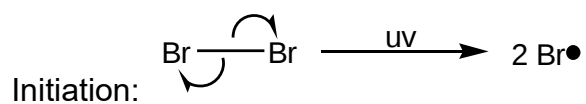
| <i>isomer V</i>                                                                   | <i>organic intermediate X</i>                                                       |
|-----------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
|  |  |

**(b)** Electrophilic substitution

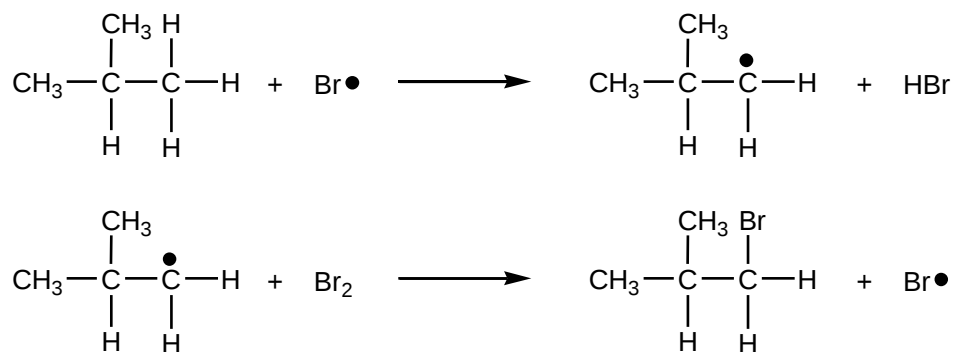
Mechanism:

**2 (i)** Limited  $\text{Br}_2$  (or excess 2-methylpropane) and ultraviolet light

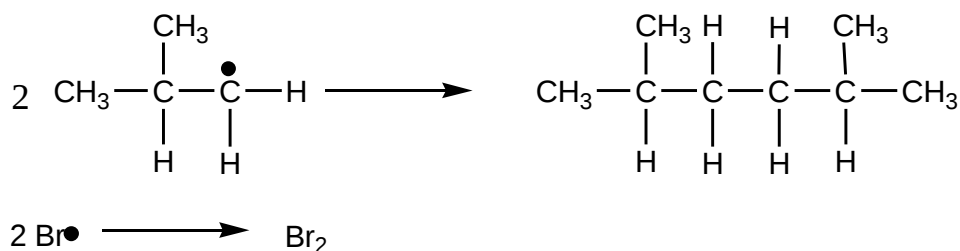
Free radical substitution



Propagation:



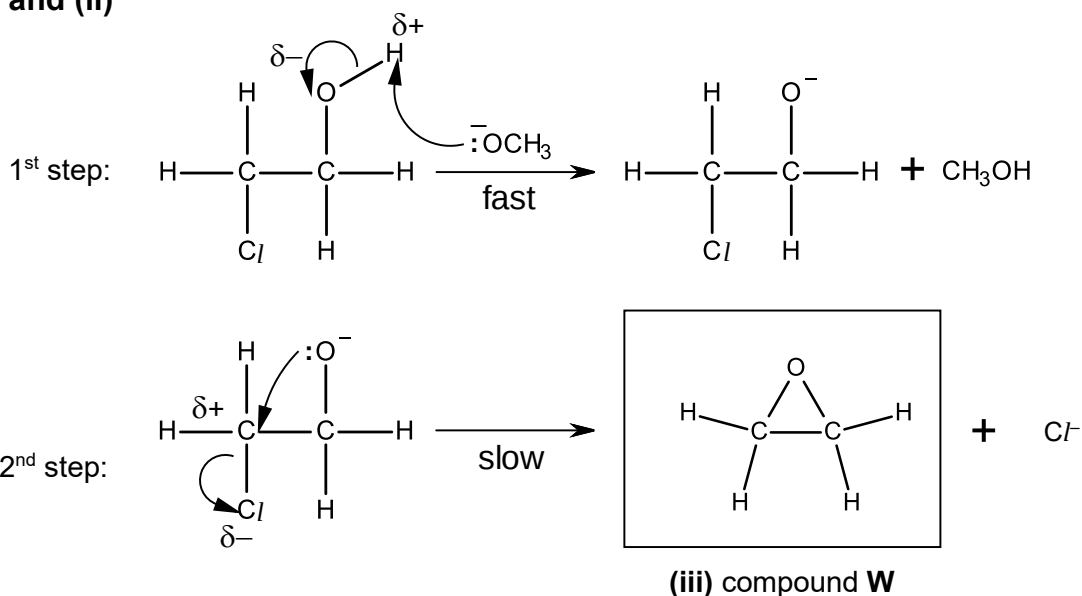
Termination:



- (iii) There are 9 primary H atoms available for substitution to form 1-bromo-2-methylpropane compared to 1 tertiary H atom to form 2-bromo-2-methylpropane. By equal probability of substitution, expected ratio of 1-bromo-2-methylpropane: 2-bromo-2-methylpropane is 9 : 1.

However, a tertiary radical,  $\bullet\text{C}(\text{CH}_3)_3$ , is more stable than a primary radical,  $\bullet\text{CH}_2\text{CH}(\text{CH}_3)_2$ . The 3 electron-donating alkyl group reduces the electron deficiency of the alkyl radical to a greater extent. Thus more tertiary radicals are formed, giving rise to more 2-bromo-2-methylpropane than expected. & thus the observed percentages.

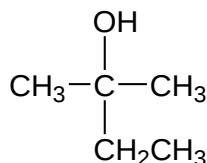
### 3 (i) and (ii)



**4(a)(i)** Nucleophilic addition**(ii)** Hydrolysis

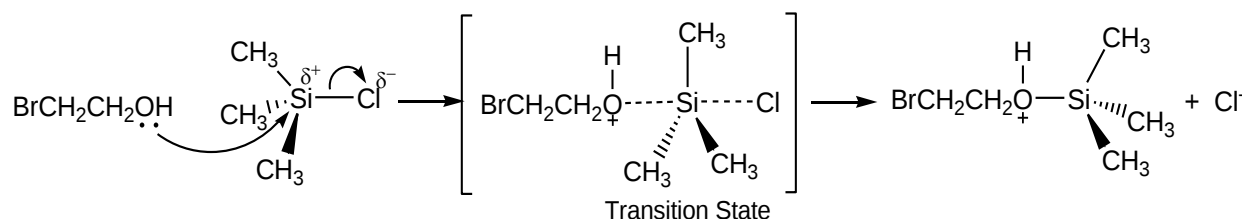
- (iii)** There is trigonal planar arrangement about the carbonyl carbon which can be attacked by  $\text{CH}_3\text{CH}_2^-$  nucleophile (from  $\text{CH}_3\text{CH}_2\text{MgBr}$ ) either from the top or bottom of the plane with equal probability.

This leads to the formation of 1:1 ratio of the two enantiomers.

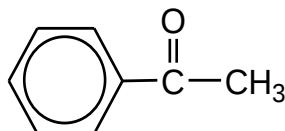
**(iv)**

- (b)** The Grignard reagent cannot be prepared as it would react with the ketone group in the same molecule.

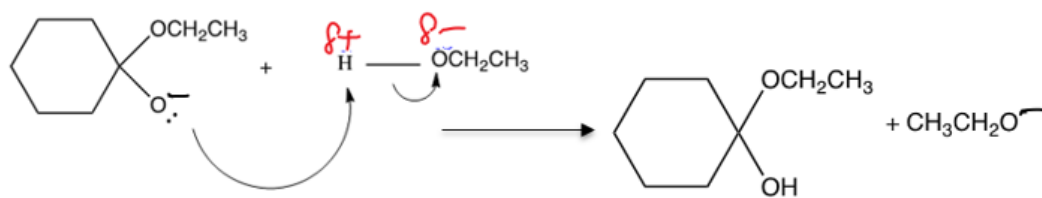
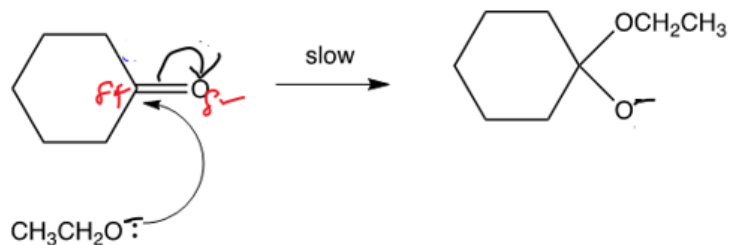
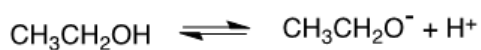
- (c)(i)** Nucleophile approaches the electron deficient C atom from the side opposite to the Cl atom (in chlorotrimethylsilane). Inversion of configuration takes place.



- (ii)** Silicon is larger than carbon. More space for the three methyl substituents thus poses less steric hindrance to the incoming nucleophile.

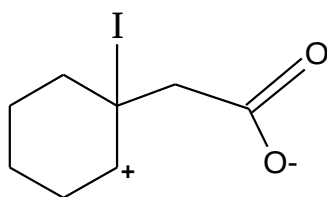
**(iii)****5 (a)** Nucleophilic addition

- (b)**  $\text{OH}^-$  will react with ethanol to generate a stronger nucleophile  $\text{CH}_3\text{CH}_2\text{O}^-$ .

**(c)** Nucleophilic addition**(d)**

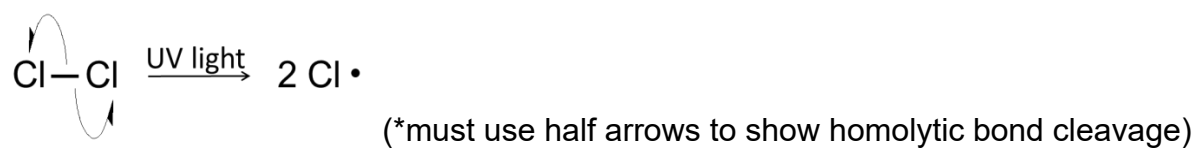
Calcium chloride is a drying agent, which help to remove water. Hence the position equilibrium will shift right to increase the yield of the product.

- 6 **R** undergoes electrophilic addition with iodine and acid-base reaction in alkaline medium to form

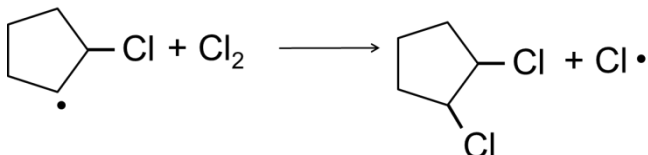
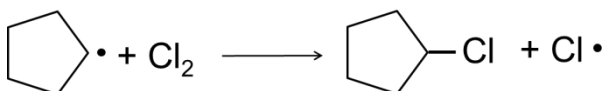
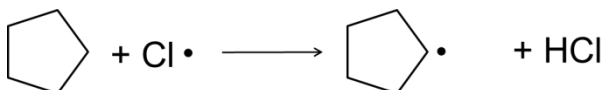


- 7 Free Radical Substitution

Initiation:

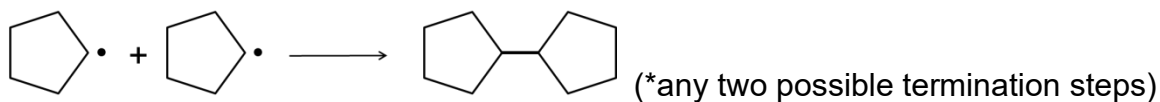
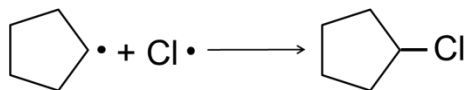
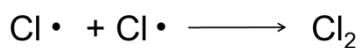


Propagation:

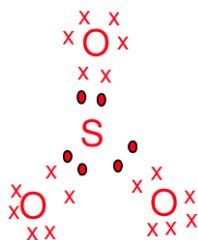


(\*must show formation of  $\text{C}_5\text{H}_8\text{Cl}_2$ )

Termination:



8 (i)

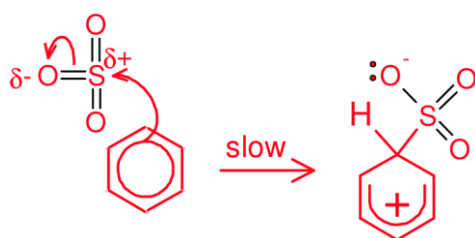


(ii) Electrophile

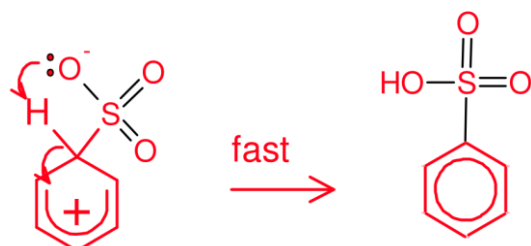
The three oxygen atoms are more electronegative than the sulfur and so draw electrons towards themselves. The sulfur atom is electron deficient and is attacked by the benzene ring.

(iii) Electrophilic Substitution

**Step 2: Formation of the sigma complex (Slow step)**

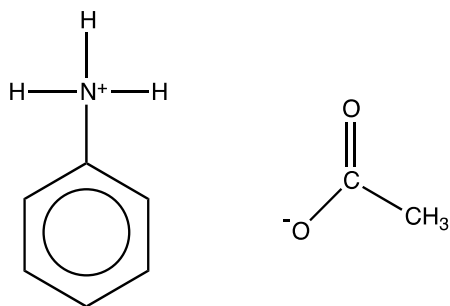


**Step 3: Loss of proton to form the substitution product**



(iv) Sulfanic acid forms zwitterions (intramolecular acid base reaction), hence the strong ionic bonds between oppositely charged ions give rise to the high melting point.

9(a)(i)



(ii) The amine will form ion-dipole interactions with water molecules.

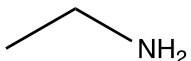
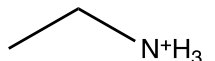
The acid will form hydrogen bonds with water molecules.

Due to the favourable solute-solvent interaction, both products are soluble in water (still

together in the aqueous medium), hence separation is not possible.

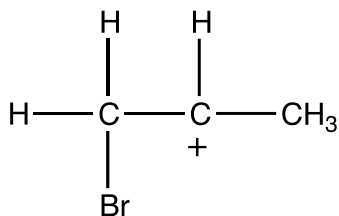
- (iii) Add NaOH to hydrolysis products until moist litmus paper turns blue. Shake the reaction mixture with water in the separating funnel to isolate the acid in the aqueous medium, leaving behind the amine.

Phenylamine exist in liquid state and it is not miscible with the aqueous layer due to the presence of bulky non-polar benzene ring.

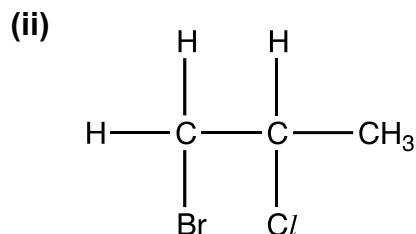
- (b) Under acidic conditions,   $\text{NH}_2$  is protonated to .

The lone pair on the nitrogen is not available for the nucleophilic substitution to form the quaternary amine salt.

- (c)(i) Propene undergoes an electrophilic addition reaction with  $\text{Br}_2(\text{aq})$  in conc. NaCl. The secondary carbocation is more stable than the primary carbocation as it has one more electron donating alkyl groups to disperse the positive charge of the carbocation.

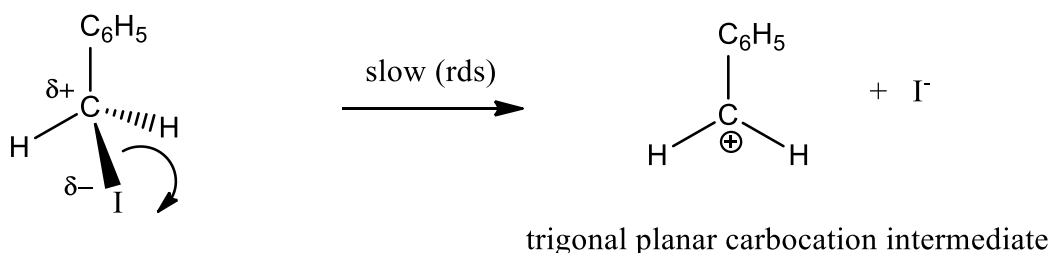
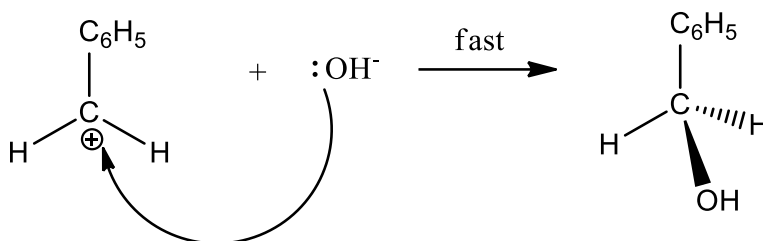


There is a high concentration of  $\text{Cl}^-$ , thus it will form a bond with the carbocation.



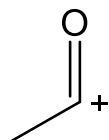
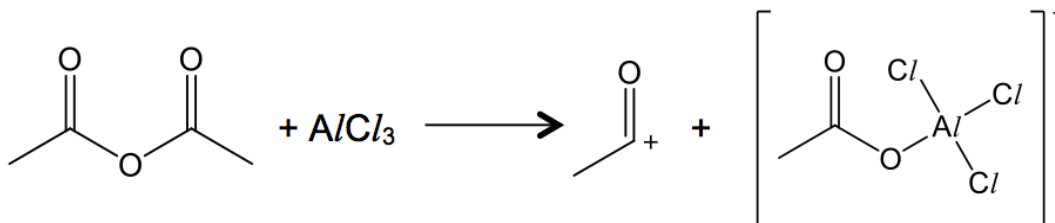
**10 (i) Mechanism: Nucleophilic Substitution ( $S_N1$ )**

Step 1: Formation of carbocation

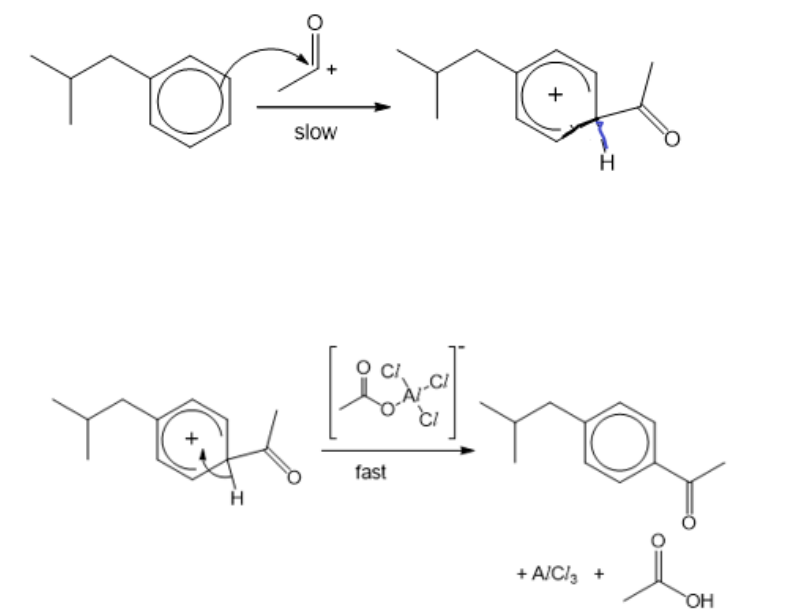
Step 2: Attack of  $\text{OH}^-$  nucleophile

- (ii) The  $\text{C}_6\text{H}_5\text{CH}_2^+$  carbocation is resonance-stabilised as the  $\pi$  electron from benzene ring can delocalise into the empty  $p$  orbital of the carbocation dispersing the positive charge of the carbocation.

For  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{I}$ , the carbocation formed is a primary carbocation and it is not resonance-stabilised. Hence, the reaction proceeds by  $S_N2$  mechanism instead.

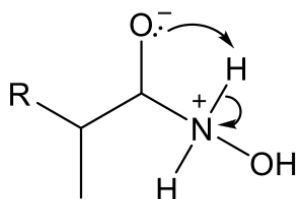
**11(a)(i)****(ii)**

(iii)



(b) The carbon is  $\text{sp}^3$  hybridised. Optimum bond angle for  $\text{sp}^3$  C is  $109.5^\circ$ , to minimise repulsion between bond pairs. However, the  $60^\circ$  bond angle in the three-membered ring result in significant repulsion between bond pairs thus result in instability.

(c)



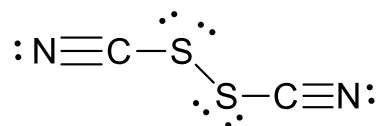
- (d)(i) The solubility of ibuprofen lysine salt is higher so it is more easily absorbed by the body.
- (ii) The non-polar part of ibuprofen makes it difficult to penetrate the polar inner layer of the skin. When mixed with the more polar propan-2-ol, the mixture becomes sufficiently polar to penetrate the inner layer of the skin.

12(a)(i)



sp

(ii)

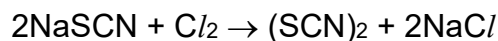
bent shape at sulfur (bond angle of  $105^\circ$ )

linear at CN

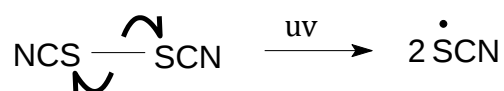
Lone pairs on N

Lone pairs on S

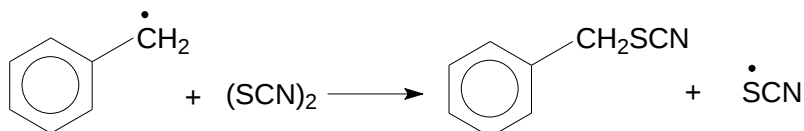
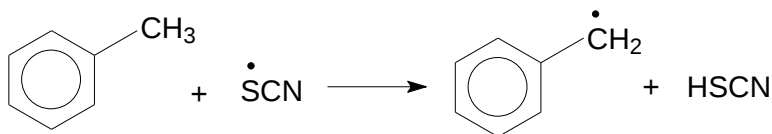
(iii) Thiocyanogen can be synthesised by reacting sodium thiocyanate, NaSCN, with chlorine gas. Write an equation for the formation of thiocyanogen.



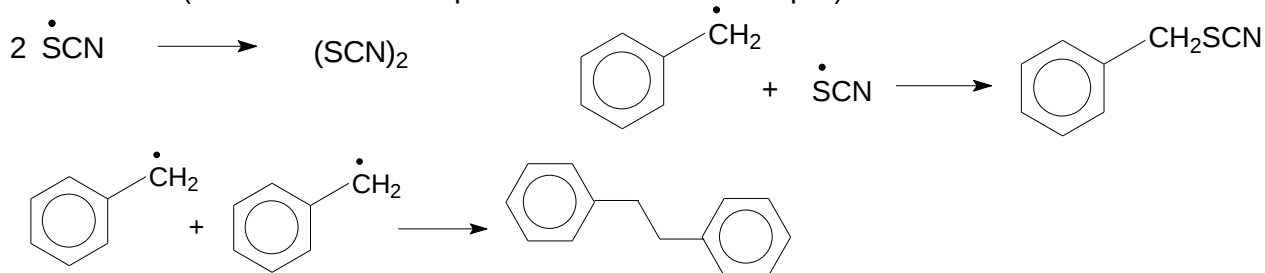
(b)(i) Initiation

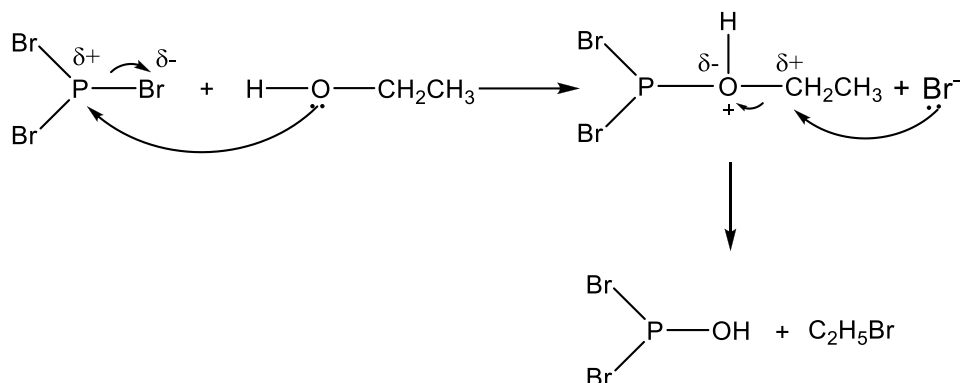


Propagation



Termination (Write down all the possible termination steps.)

(ii) Delocalisation of electrons  $\cdot\text{S}-\text{C}\equiv\text{N}$  in produced at the initiation step allows  $\text{S}=\text{C}=\dot{\text{N}}$  to be formed, resulting in such a side product.

**13 (i) Nucleophilic substitution****(ii)**

**(iii)** To form  $\text{C}(\text{CH}_3)_3\text{Br}$  would require the starting alcohol to be a tertiary alcohol. The bulky R groups makes it difficult for the nucleophile to approach the partial positive P in  $\text{PBr}_3$ .

**(iv)**  $\text{CH}_3\text{COBr}$

**14 (i)** Step 1:  $\text{LiAlH}_4$  in dry ether

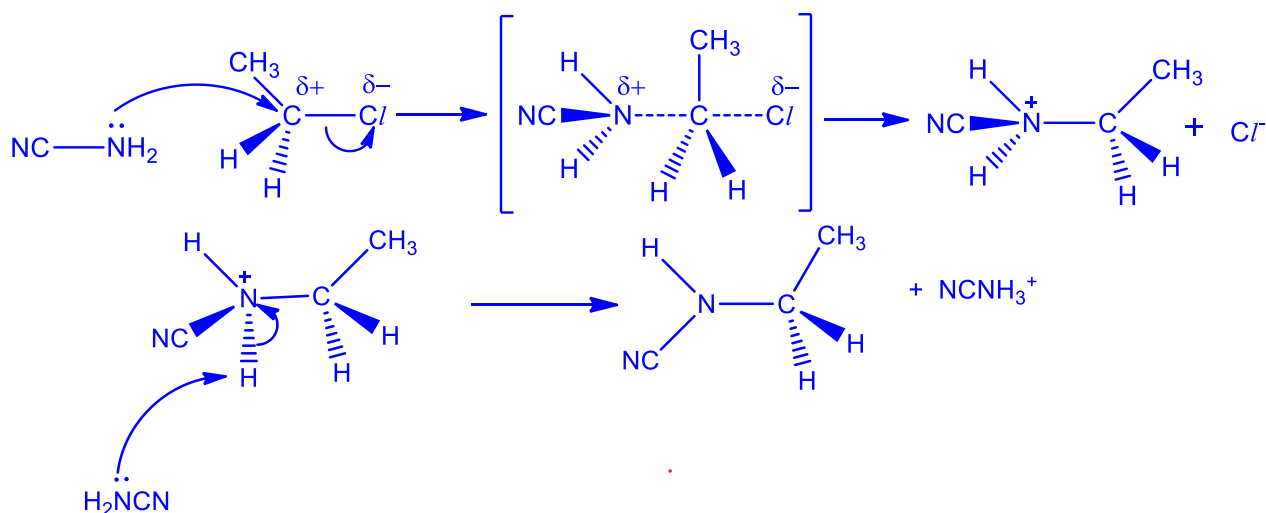
Step 2:  $\text{NaOH}$  in ethanol; heat

**(ii)** **B** undergoes hydrolysis less easily than **A**.

This is because in **B**, the  $\text{C}-\text{C}/$  bond has partial double bond character due to the overlap of the p-orbital of  $\text{C}/$  with the p-orbitals of  $\text{C}=\text{C}$ , resulting in delocalisation of electrons. Thus the  $\text{C}-\text{C}/$  bond in **B** is much stronger than  $\text{C}-\text{C}/$  in **A**, and is harder to hydrolyse.

**15 (i)**

Mechanism: Nucleophilic substitution reaction ( $\text{S}_{\text{N}}2$ )



**(ii)** Nucleophile and Base

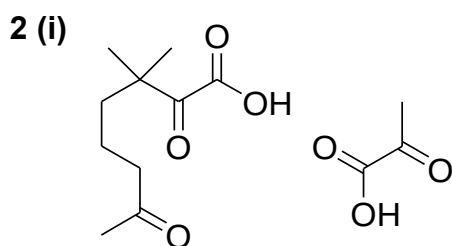
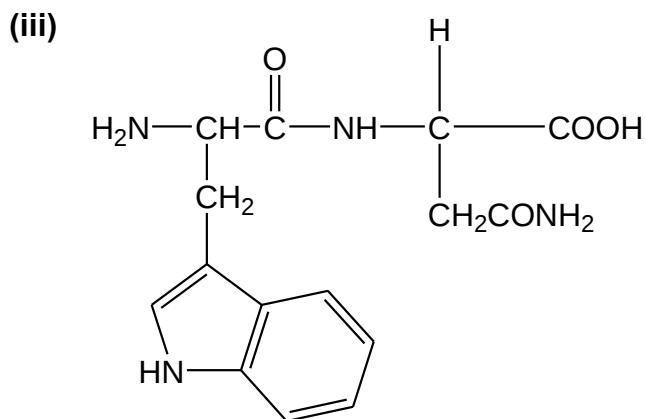
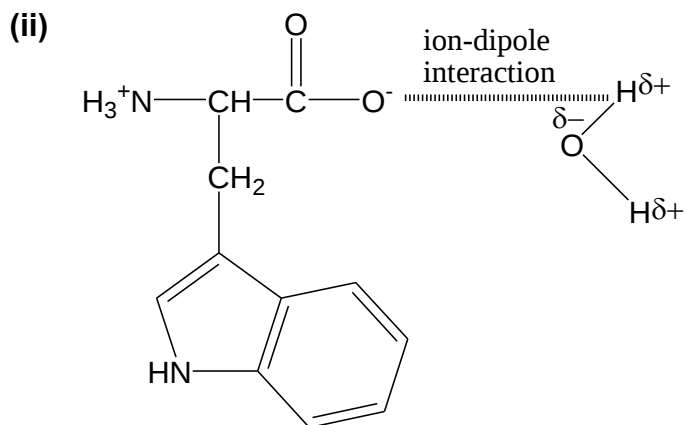
(iii) Excess  $\text{CH}_3\text{CH}_2\text{Cl}$

- (b) The p-orbital of the chlorine atoms overlap with the  $\pi$  electron cloud of the benzene rings. The lone pair of electrons on each  $\text{Cl}$  atom is delocalised into the benzene rings. This results in the  $\text{C}-\text{Cl}$  bond having a partial double-bond character which makes the  $\text{C}-\text{Cl}$  bond stronger and less ready to undergo reaction.

The  $\text{C}$  of the  $\text{C}-\text{Cl}$  bond also has a lower partial positive charge and is less susceptible to nucleophilic attacks. The  $\pi$ -electron cloud of the benzene ring will repel the lone pair of electrons of an incoming nucleophile, rendering attack of the nucleophile difficult.

**4) Amino Acids & Proteins**

- 1 (i) It exists as a giant ionic lattice in its zwitterion form. Energy at room temperature is insufficient to break the strong electrostatic forces of attraction between oppositely charged ions, hence exists as solid.

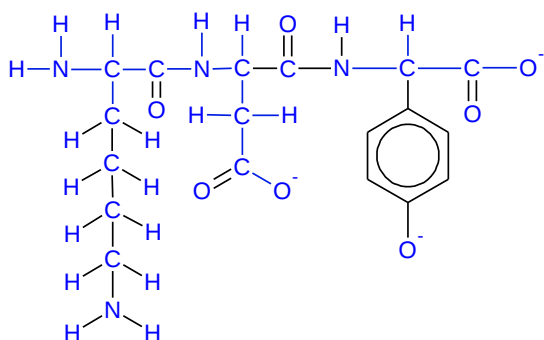


- (ii) BCO is an enzyme and has a very specific action, in this case, to cleave only one of the C=C bond. There are many other C=C double bonds in  $\beta$ -carotene, which will all be cleaved using acidified  $\text{KMnO}_4$  in the laboratory.

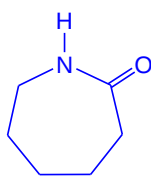
3(a) 7

- (b)(i) Nonapeptide: Tyr-Lys-Asp-Tyr-Lys-Asp-Tyr-Asp-Val

(ii)

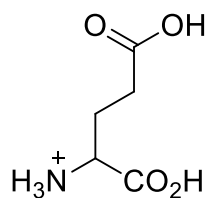
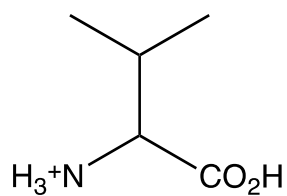


(c)



4 (i) circle the phenol group

(ii)



**5) Kinetics of Organic Reactions**

- 1 (i) Let the rate equation be:  $\text{rate} = k[\text{CH}_3\text{SNa}]^a[\text{CH}_2\text{C}/\text{CH}_2\text{OH}]^b$ .

Comparing Expt 1 and 2,  $[\text{CH}_3\text{SNa}] \times 1.5$ , the relative rate  $\times 1.5$

The order of reaction with respect to  $[\text{CH}_3\text{SNa}]$  is 1.

Hence,  $a = 1$

Comparing experiment 2 and 3,

$$\frac{16}{9} = \frac{k(0.200)^1(0.200)^b}{k(0.150)^1(0.150)^b} \quad \text{Hence, } b = 1.$$

The order of reaction with respect to  $\text{CH}_2\text{C}/\text{CH}_2\text{OH}$  .....1.....

rate equation:  **$\text{rate} = k[\text{CH}_3\text{SNa}][\text{CH}_2\text{C}/\text{CH}_2\text{OH}]$** ,  $k$  = rate constant

OR  **$\text{rate} = k[\text{CH}_3\text{S}^-][\text{CH}_2\text{C}/\text{CH}_2\text{OH}]$**

- (ii)  $\text{CH}_3\text{S}^-$

- (iii) The intermolecular forces between DMSO molecules are permanent dipole-dipole interactions. Since there is no hydrogen bonding between DMSO molecules, DMSO is **unable to stabilise/solvate anions by forming ion-dipole interactions**.

- (iv) The rate of this  $\text{S}_{\text{N}}2$  nucleophilic substitution reaction varies according to the equation:  $\text{rate} = k[\text{CH}_3\text{S}^-][\text{CH}_2\text{C}/\text{CH}_2\text{OH}]$ . Both the nucleophile and the organic molecule are involved in the slow step. Ethanol has hydrogen bonding and the molecules can form ion-dipole interactions with the nucleophile. The lone pair on the nucleophile is less available.

Since DMSO does not solvate the  $\text{CH}_3\text{S}^-$  nucleophile, the lone pair on the nucleophile is **more available to attack the  $\text{CH}_2\text{C}/\text{CH}_2\text{OH}$  molecule**. As a result, the reaction proceeds much faster in DMSO than in ethanol.

- 2 (a) Step 1: Nucleophilic addition

Step 2: Elimination

- (b)(i)  $p$ : 0

From experiment 1, the graph of  $[\text{U}]$  against time is a straight line with constant gradient. The rate of reaction is independent of  $[\text{U}]$ . Hence, reaction is 0 order with respect to **U**.

$q$ : 1

From experiment 1, when [methanal] doubled, the magnitude for the gradient is also

doubled. Hence, reaction is first order with respect to methanal.

*r*: 1

From experiment 2, the graph of [amine] against time shows a constant half-life of 50 min. Hence, reaction is first order with respect to amine.

*s*: 1

From experiment 3, the graph of [H<sup>+</sup>] against time shows a constant half-life of 50 min. Hence, reaction is first order with respect to H<sup>+</sup>.

**(b)(ii)** Rate-determining step: Step 1

Explanation: The rate equation is  $\text{Rate} = k[\text{methanal}][\text{amine}][\text{H}^+]$

In step 1, there are one molecule of methanal reacting with one molecule of amine and H<sup>+</sup> ion, which corresponds to the rate equation as the concentrations of methanol, amine and H<sup>+</sup> are raised to the power of 1 respectively.

**(b)(iii)** The rate determining step involves collision of three particles. The probability of effective collision between the three particles with energy greater or equal to activation energy in the correct orientation is low and hence such a reaction is unusual.

**(iv)** Half-life from experiment 2 = 50 min

$$\text{rate} = k [\text{methanal}] [\text{amine}] [\text{H}^+]$$

since [methanal] and [H<sup>+</sup>] is in large excess,

$$\rightarrow \text{rate} = k' [\text{amine}], \text{ where } k' = k [\text{methanal}][\text{H}^+]$$

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[\text{methanal}] [\text{H}^+]}$$

$$50 = \frac{\ln 2}{k(0.12)(0.12)}$$

$$k = 0.9627$$

$$= 0.963 \text{ mol}^{-2} \text{ dm}^6 \text{ min}^{-1}$$

**(c)(i)** In experiments 4 to 6, the amines used are the same but the carbonyl compound have decreasing number of electron donating alkyl groups bonded to the C=O group. Electron donating alkyl groups makes the carbonyl carbon atom less electron-deficient and less susceptible to nucleophilic attack. Therefore, propanone has two electron donating groups around the carbonyl carbon and reacts the slowest followed by ethanal and methanal which reacts the fastest.

or

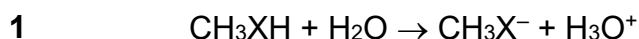
From experiments 4 to 6, the amines used are the same but the number of alkyl groups bonded to the C=O group decrease from two to zero, causing a decrease in steric hindrance to the incoming nucleophile.

Hence, the attacking nucleophile is able to approach carbonyl carbon of methanal in experiment 6 more readily than that of aldehyde and ketone in experiment 5 and 4 respectively. Thus, the initial rate increases.

- (ii) From experiments 6 to 8, the same carbonyl compound (methanal) was used, but the number of electron donating alkyl groups bonded to the nitrogen atom of amine group decrease from two to zero causing a decrease in electron density around the nitrogen atom. The lone pair on N becomes less available and therefore ammonia reacts much slower while secondary amine reacts the fastest.

Thus, the initial rate decreases from experiment 6 to 8.

## 6) Acidity and Basicity of Organic Compounds



S has larger atomic radius than O. Thus S-H bond length is larger and thus weaker than O-H bond.  $\text{CH}_3\text{S-H}$  undergoes greater acid dissociation, and has a smaller  $\text{p}K_a$  value, than methanol.

2  $\text{pH} = 2.04 \Rightarrow [\text{H}^+] = 9.12 \times 10^{-3} \text{ mol dm}^{-3}$

(a)  $K_a = [\text{H}^+]^2 \div \text{conc of acid} = (9.12 \times 10^{-3})^2 \div 0.100 = 8.32 \times 10^{-4} \text{ mol dm}^{-3}$   
value of  $K_a = 8.32 \times 10^{-4}$

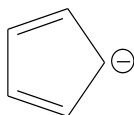
- (b) Propanoic acid having a smaller  $K_a$  is a weaker acid than lactic acid. Hence more energy is needed to help dissociate the weaker acid into ions.

Thus, the reaction of propanoic acid with  $\text{NaOH(aq)}$  will be less exothermic.

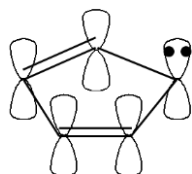
3 Type of reaction: Elimination

(a) Reagents and conditions: Ethanolic KOH; heat

(b)



The negative charge of the conjugate base is dispersed via resonance. This is due to continuous overlap of p-orbitals of all the carbon in the 5 membered ring. As the conjugate base is relatively stable, the C-H in cyclopentadiene is more acidic than expected.



**4(a)** Secondary amine, tertiary amine, amide, alkene and carboxylic acid

**(b)(i)**  $sp^2$  hybrid orbital

**(ii)**  $N_c > N_b > N_d$

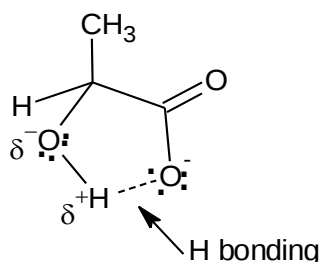
Comparing  $N_c$  and  $N_b$ , there is a carboxylic acid group on the carbon adjacent to  $N_b$ . Carboxylic acid group is an electron withdrawing group and will decrease the availability of lone pair of electrons on  $N_b$  for donation. Therefore,  $N_c$  is more basic than  $N_b$ .

Lone pair of electrons on  $N_d$  is unavailable for donation due to significant delocalization to adjacent  $C=O$ .

**(c)(i)** Compound A exists as zwitterions and are held together by strong ionic bonds in a giant ionic lattice. A large amount of heat energy is needed to overcome the strong ionic bonds.

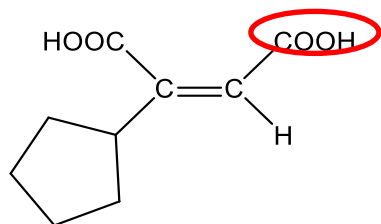
**(ii)** There is a large reservoir of zwitterions. The positively charged amine salt is acidic and will neutralize the small amount of added  $OH^-$  and maintains pH.

**5** Intramolecular hydrogen bond is possible in lactate ion between the carboxylate ion and the protonic H in  $-OH$ .



**6**

**(i)**

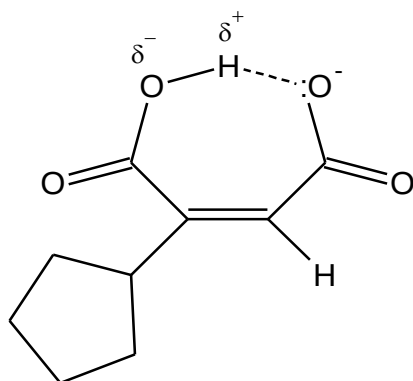


It is further from the electron donating cyclopentane group which intensifies the negative charge & hence destabilises the carboxylate

anion.

(ii) Cis-trans isomerism / geometric isomerism

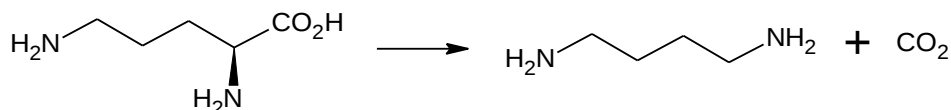
(iii)



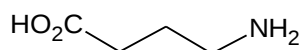
The conjugate base formed after 1<sup>st</sup> acid dissociation is stabilised by intra hydrogen bonding of the carboxylate group with –OH, making the 1<sup>st</sup> acid dissociation more favourable. However, it makes the H from the 2<sup>nd</sup> carboxylic acid significantly less acidic since energy is required to overcome intramolecular H-bonding. Thus the large difference in  $K_a$  values.

7 (i) Gaseous by-product:  $\text{CO}_2$

Equation (stereochemistry not required):



(ii) Structure:



Name: 4-aminobutanoic acid

(iii)  $K_b$  is a measure of the strength/ basicity of a weak base.

OR

$$K_b \text{ of a weak base, B} = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

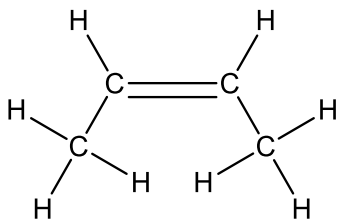
(iv)  $K_b$ :  $\alpha\text{-NH}_2$  of L-ornithine <  $\text{R-NH}_2$  of L-ornithine

$\alpha\text{-NH}_2$  of L-ornithine is closer to the electron-withdrawing  $\text{-CO}_2\text{H/ -CO}_2^-$  group which decreases the availability of the lone pair of electrons on N atom of  $\alpha\text{-NH}_2$ . Hence,  $\alpha\text{-NH}_2$  is a weaker base than  $\text{R-NH}_2$  of L-ornithine.

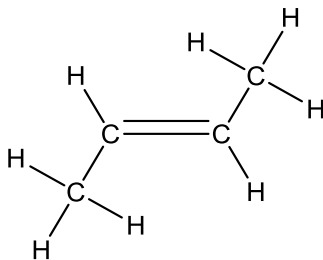
## 7) Isomerism

1 (i) Geometric isomerism / *cis-trans* isomerism

(ii)

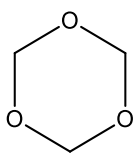


Cis-but-2-ene



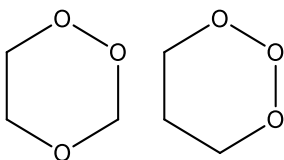
trans-but-2-ene

2 (i)



structure must be highly symmetrical with only one type of H for FRS to form only one mono-bromo product.

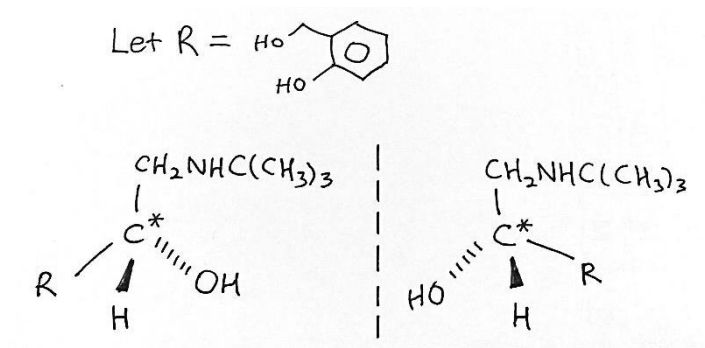
(ii)



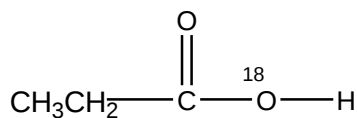
(iii) Weak O–O bond due to  
**repulsion of lone pairs of electrons on adjacent O atoms** OR  
**repulsion of two  $\delta^-$  charges on adjacent O atoms.**

3 (a) Primary alcohol, secondary alcohol, phenol, secondary amine

(b) Optical isomerism

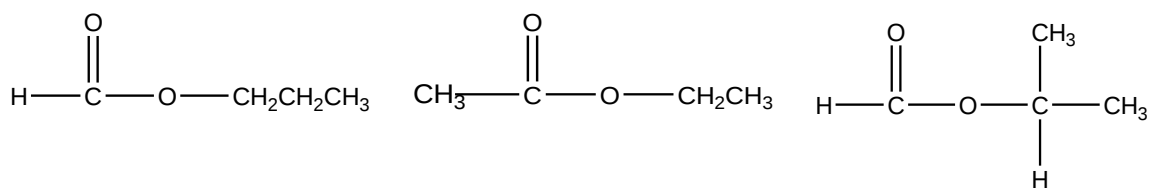


4 (i)



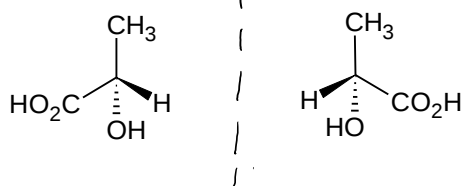
**CH<sub>3</sub>OH**

(ii)



- 5 Geometric isomerism / cis-trans isomerism, arises when there is restricted rotation about the double bond and the two groups on each C of the restricted bond must not be identical.

## 6 Optical isomerism



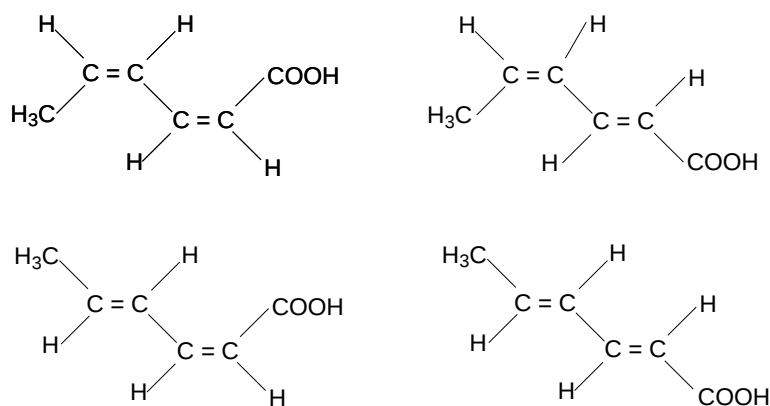
- 7(i) C3-C4 bond is stronger.

C1-C2 bond:  $sp^3 - sp^2$  overlap

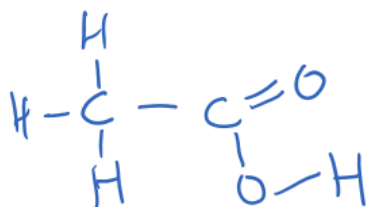
C3-C4 bond:  $sp^2 - sp^2$  overlap

As the  $sp^2$  hybrid orbitals of C3 and C4 contains greater s-character, there is more efficient orbital overlap leading to a stronger bond.

(ii)



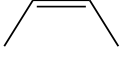
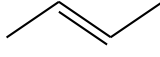
(iii)

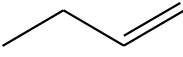
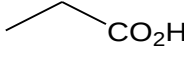


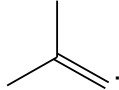
**8) Organic Structural Elucidation**

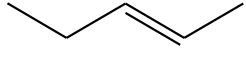
1 **A**,  $C_nH_{2n}$ , an alkene

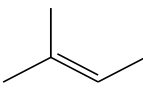
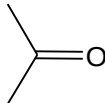
2 **B**,  $C_nH_{2n}$ , a cycloalkane

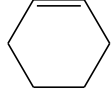
3 **C**,  $C_4H_8$ ,  $CH_3CH=CHCH_3$ ; cis-but-2-ene,  and trans-but-2-ene,   
(symmetrical since only one organic product is obtained after oxidative cleavage)

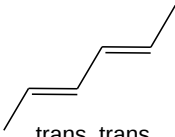
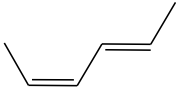
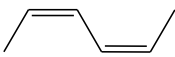
4 **D**,  $C_4H_8$ , , **E**,  (D is terminal alkene since  $CO_2$  is formed after oxidative cleavage)

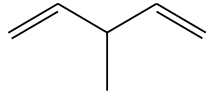
5 **F**,  $C_4H_8$ , ; **G**, 

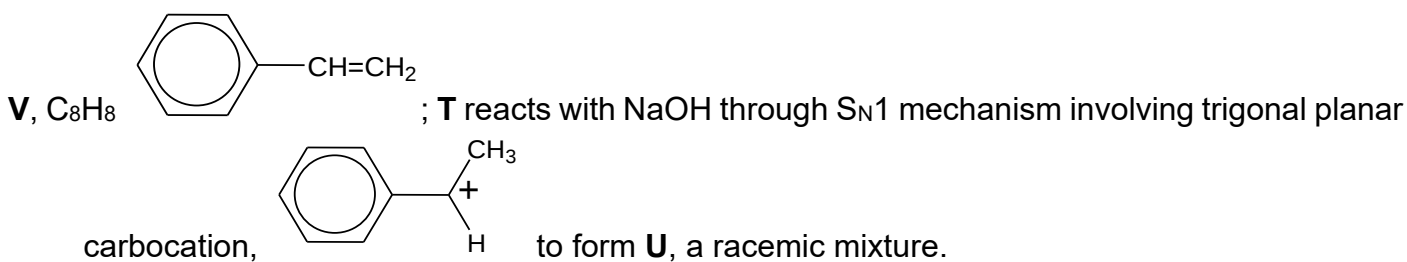
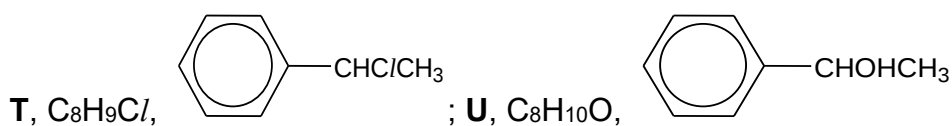
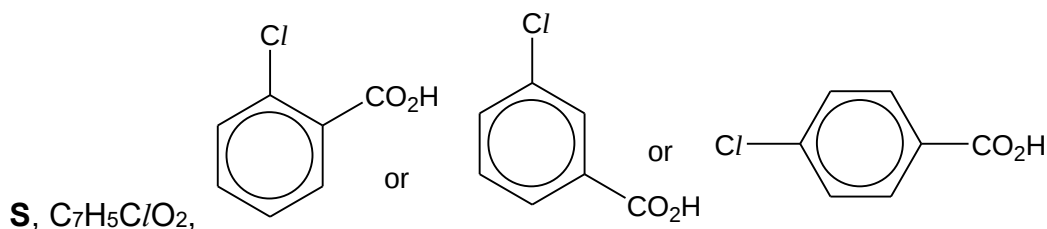
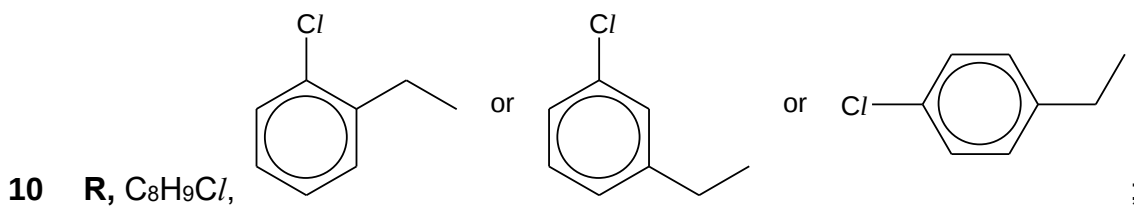
6 **H**,  $C_5H_{10}$ , ; **K**,  $C_3H_6O_2$  is  $CH_3CH_2CO_2H$ ; **L**,  $C_2H_4O_2$  is  $CH_3CO_2H$

**J**,  $C_5H_{10}$ , ; **L**,  $C_2H_4O_2$  is  $CH_3CO_2H$ ; **M**,  $C_3H_6O$ , 

7 **N**,  $C_6H_{10}$ ,  (note: 2 degree of unsaturation, since it only reacts with 1 mol of  $Br_2$ , it must have only 1 double bond, and therefore 1 ring)

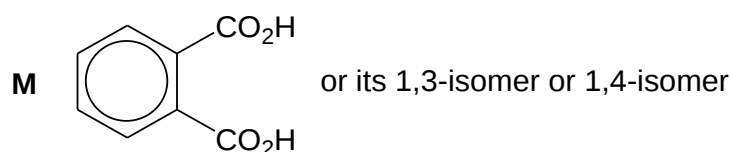
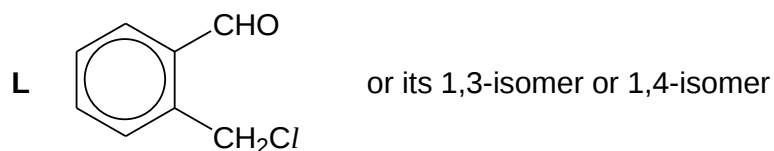
8 **P**,  $C_6H_{10}$ ,  $CH_3CH=CHCH=CHCH_3$ ;  trans, trans     cis, trans same as trans, cis     cis, cis

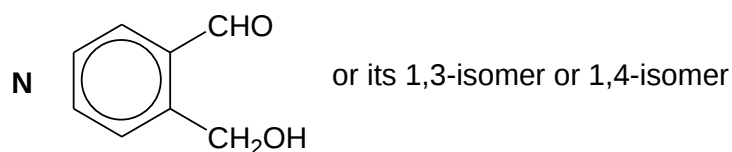
9 **Q**,  $C_6H_{10}$ , 



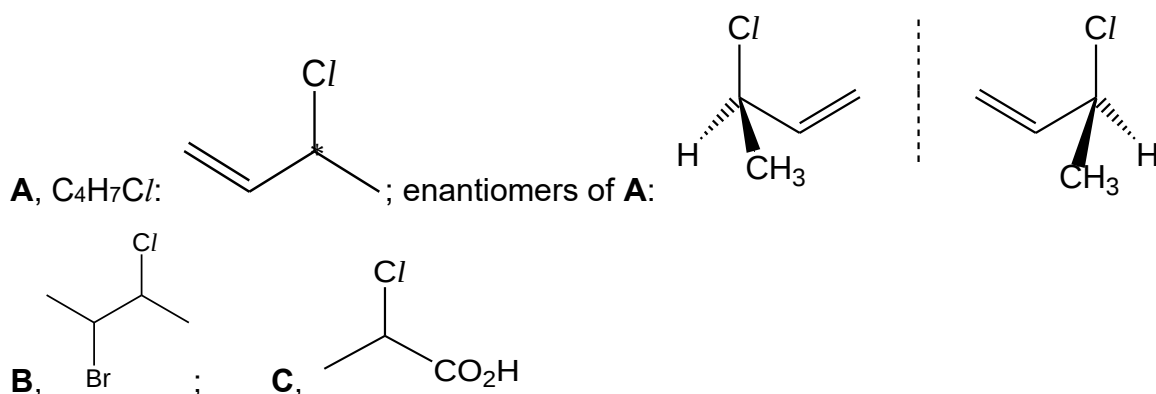
11 **L**,  $C_8H_7OC$ :

- $\frac{C}{H}$  ratio  $\sim 1 \Rightarrow$  has benzene ring
- undergoes side-chain oxidation with acidified  $KMnO_4$  to form **M**, diacid (has 4 O's)  $\Rightarrow$  two alkyl substituent present.
- undergoes condensation with 2,4-DNPH & mild oxidation with Tollen's reagent  $\Rightarrow$  benzaldehyde since the 2 side chain is 1 C each.
- undergoes nucleophilic substitution with NaOH(aq) to form **N** and liberate chloride ions

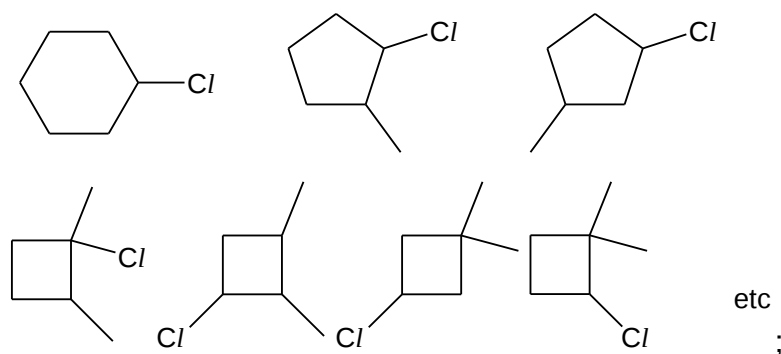


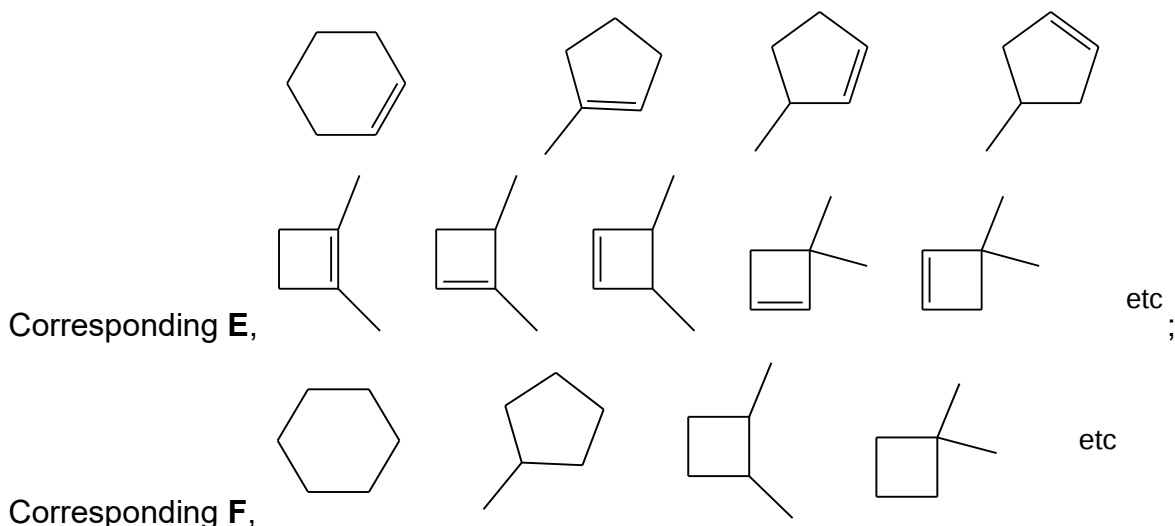
**12(a) A, C<sub>4</sub>H<sub>7</sub>Cl:**

- has a chiral C with 4 different atoms or groups of atoms attached
- C:H ratio  $\approx 1:2$  & reacts with HBr (1 : 1 ratio) (electrophilic addition)  $\Rightarrow$  has 1 C=C bond
- undergoes oxidative cleavage with acidified KMnO<sub>4</sub> to give CO<sub>2</sub> & acid **C**  $\Rightarrow$  has terminal C=C bond

**(b) MF of D: C<sub>6</sub>H<sub>11</sub>Cl,****D, C<sub>6</sub>H<sub>11</sub>Cl:**

- C:H ratio  $\approx 1:2$  & does not react with bromine  $\Rightarrow$  NO C=C bond / has a ring
- undergoes elimination with alc KOH to form alkene **E**, C<sub>6</sub>H<sub>10</sub>
- is reduced by H<sub>2</sub> to an alkane **F**

**D, any one:**

**13 B: C<sub>9</sub>H<sub>10</sub>:**

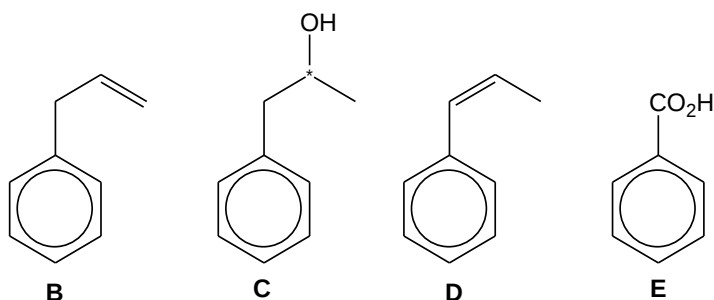
- C:H ratio ~ 1:1  $\Rightarrow$  has benzene ring
- decolourised Br<sub>2</sub> (electrophilic addition)  $\Rightarrow$  has C=C bond
- undergoes oxidative cleavage to give CO<sub>2</sub>  $\Rightarrow$  has terminal C=C bond / =CH<sub>2</sub>
- undergoes hydration (electrophilic addition) with steam to give a racemic mixture of alcohol **C**, C<sub>9</sub>H<sub>12</sub>O (Markovnikov's rule)

**C, C<sub>9</sub>H<sub>12</sub>O:**

- is dehydrated by hot Al<sub>2</sub>O<sub>3</sub> to form **D**, C<sub>9</sub>H<sub>10</sub>, alkene or with C=C bond (isomer of **B**) (Saytzeff's rule)

**D, C<sub>9</sub>H<sub>10</sub>:**

- undergoes oxidative cleavage to form CH<sub>3</sub>CO<sub>2</sub>H and **E**, C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>, benzoic acid

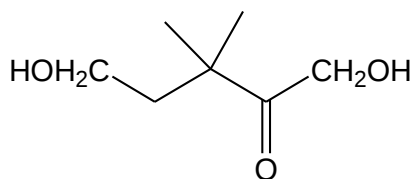
**14 P, C<sub>10</sub>H<sub>14</sub>O:**

- C:H ratio ~ 1:1  $\Rightarrow$  has benzene ring
- Decolourised aq Br<sub>2</sub> (electrophilic addition) to form **Q**, C<sub>10</sub>H<sub>14</sub>OBr<sub>4</sub>  $\Rightarrow$  has 2 C=C bond
- Insoluble in NaOH(aq)  $\Rightarrow$  not phenol / alcohol
- Can be oxidised by Tollen's reagent  $\Rightarrow$  has -CHO group
- Undergoes oxidative cleavage with acidified KMnO<sub>4</sub> to form **R**, C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>, and **S**, C<sub>7</sub>H<sub>10</sub>O<sub>5</sub>

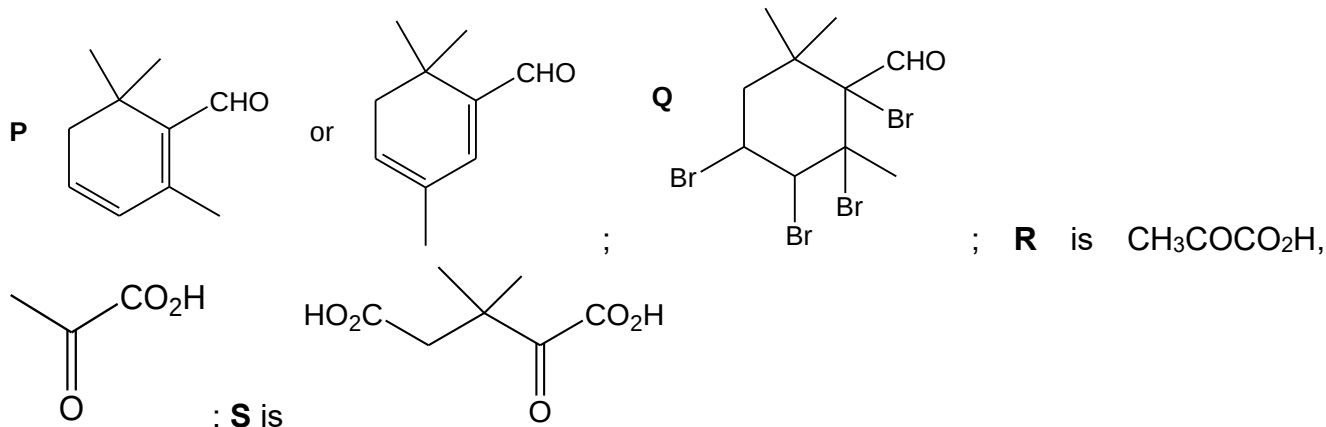
**R, C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>:**

- Forms yellow CHI<sub>3</sub> with aq I<sub>2</sub>/OH<sup>-</sup>  $\Rightarrow$  has CH<sub>3</sub>CO- group

**S**,  $C_7H_{10}O_5$ ,



- Is reduced by  $LiAlH_4$  to form

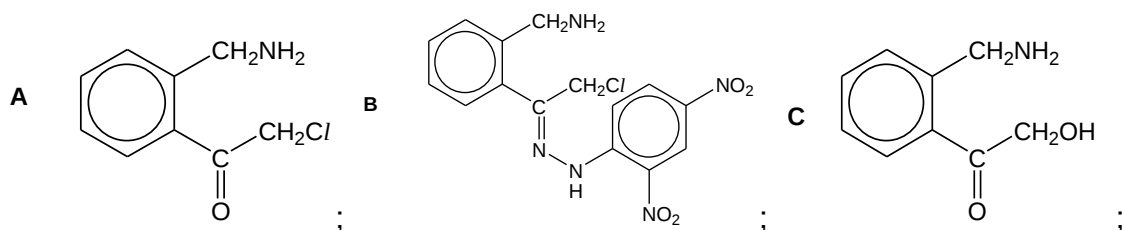


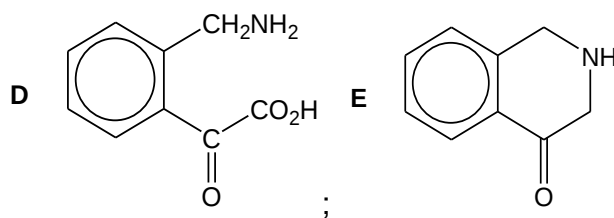
**15 A**,  $C_9H_{10}NOCl$ :

- C:H ratio  $\approx 1:1 \Rightarrow$  has benzene ring
- basic  $\Rightarrow$  has amino group
- undergoes condensation with 2,4-dinitrophenylhydrazine to form **B** & does not react with Tollen's reagent  $\Rightarrow$  **A** is ketone
- no reaction with aq bromine  $\Rightarrow$  no C=C bond or not phenolic
- undergoes electrophilic substitution with 2 mol bromine in  $FeBr_3 \Rightarrow$  is 1,2- or 1,4-disubstituted
- undergoes nucleophilic substitution &/or hydrolysis with hot  $NaOH(aq)$  to form **C**,  $C_9H_{11}NO_2 \Rightarrow$  Cl not directly attached to benzene ring & **C** has -OH group
- undergoes nucleophilic substitution in a sealed tube (loss of HCl from amino and Cl groups) to form **E**,  $C_9H_9NO$  (amine)

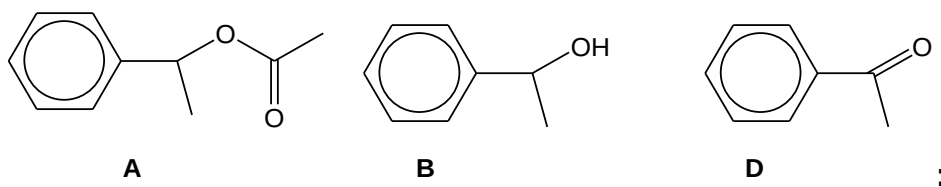
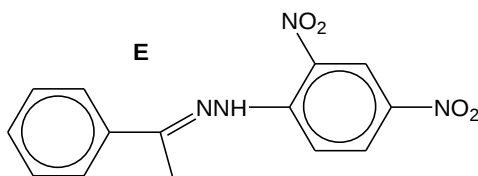
**C**,  $C_9H_{11}NO_2$ :

- is oxidised by acidified  $K_2Cr_2O_7$  to **D** (with 1 -CO<sub>2</sub>H group as 0.10 mol **D** reacts with 0.05 mol aq sodium carbonate)  $\Rightarrow$  **C** is 1° alcohol or has -CH<sub>2</sub>OH group



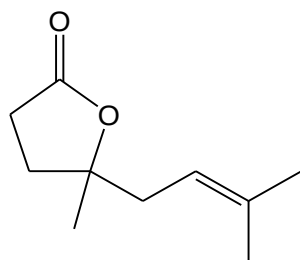
**16 A, C<sub>10</sub>H<sub>12</sub>O<sub>2</sub>:**

- C:H ratio ~ 1:1  $\Rightarrow$  has benzene ring
- is neutral with 2O's & is hydrolysed by hot hydrochloric acid to form **B** and **C**  $\Rightarrow$  **A** is ester  
**B**, C<sub>8</sub>H<sub>10</sub>O (alcohol, pdt of hydrolysis of ester)"
- has CH<sub>3</sub>CH(OH)- group which forms CHI<sub>3</sub> with aq alkaline iodine
- oxidised by acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to form **D**, C<sub>8</sub>H<sub>8</sub>O  $\Rightarrow$  **B** is 2° alcohol & **D** a ketone (1 O)  
**D**, C<sub>8</sub>H<sub>8</sub>O, ketone – undergoes condensation with 2,4-dinitrophenylhydrazine to form hydrazine **E**.

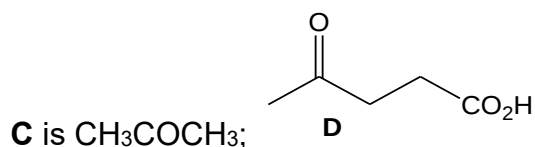
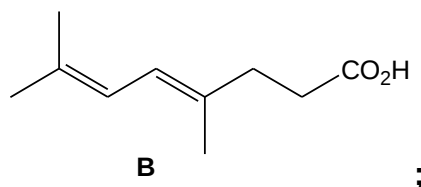
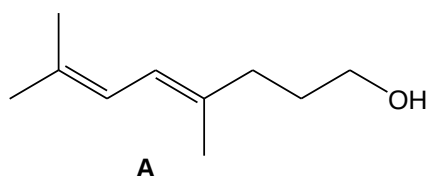
**C** is CH<sub>3</sub>CO<sub>2</sub>H**17 A, C<sub>10</sub>H<sub>18</sub>O:**

- C: H ratio ~ 1: 2  $\Rightarrow$  aliphatic with 2 C=C bonds or 1 C=C bond + 1 ring or 2 rings / no benzene ring
- undergoes redox reaction with Na(s)  $\Rightarrow$  **A** has –OH, alcohol / phenol
- can be oxidised by acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to **B**, C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>  $\Rightarrow$  **A** is a 1° alcohol, **B** is carboxylic acid (2 O's)
- 1 mol **A** reacted with 2 mol bromine (electrophilic addition)  $\Rightarrow$  **A** has 2 C=C bonds
- undergoes oxidative cleavage with hot acidified KMnO<sub>4</sub> to give 3 pdts: **C**, C<sub>3</sub>H<sub>6</sub>O, **D**, C<sub>5</sub>H<sub>8</sub>O<sub>3</sub>, and effervescence of CO<sub>2</sub> (from C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>); total no of C = 10)
- C** and **D**: undergo mild oxidation with aq I<sub>2</sub>/ NaOH to form CHI<sub>3</sub>  $\Rightarrow$  each has CH<sub>3</sub>CO- group (NOT CH<sub>3</sub>C(OH)H- group as both are pdts of oxidative cleavage)
- B**, C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>:

- undergoes electrophilic addition with steam to form alcohol; then undergoes self-condensation



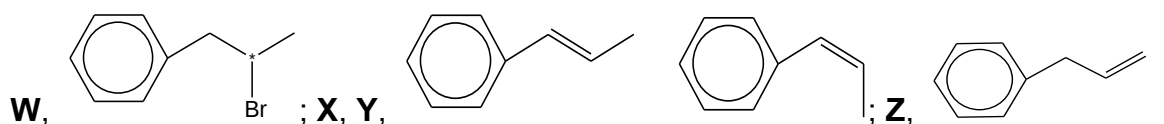
to form cyclic ester, **F**,



### 18(a)W:

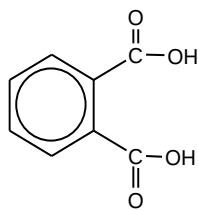
- is optically active RBr has chiral C
- undergoes elimination with hot concentrated alc NaOH to form 3 isomeric alkenes, **X**, **Y** and **Z**, where **Z** is minor pdt (Saytzeff's rule)

Both **X** and **Y** react with bromine to form 1,2-dibromo-1-phenylpropane, whereas **Z** with the same reagent gives 2,3-dibromo-1-phenylpropane

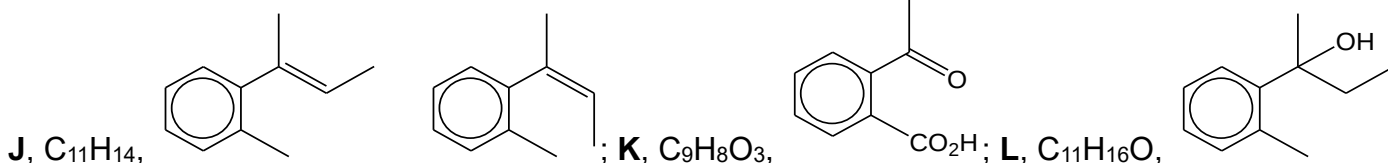


### 19 J, $\text{C}_{11}\text{H}_{14}$ :

- C:H ratio  $\sim 1:1 \Rightarrow$  has benzene ring
  - exhibits cis-trans isomerism; no chiral C  $\Rightarrow$  alkene / has C=C bond
  - undergoes oxidative cleavage with hot acidified  $\text{KMnO}_4$  to form **K**,  $\text{C}_9\text{H}_8\text{O}_3$ , with 1  $-\text{CO}_2\text{H}$  and 1 ketone functional groups
  - reacts with steam (electrophilic addition) to form **L**,  $\text{C}_{11}\text{H}_{16}\text{O}$  with a chiral C (Markovnikov's addition)
- K**,  $\text{C}_9\text{H}_8\text{O}_3$ , undergoes a stepping-down reaction (Triiodomethane test, followed by acidification) to



form

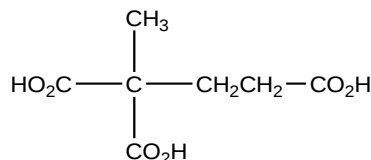
**20 A**,  $C_8H_{12}$ :

-  $\frac{C}{H}$  ratio  $\sim \frac{1}{2} \Rightarrow$  alkene with 3 C=C bonds / 2 C=C bonds + 1 ring / 1 C=C bond with 2 rings

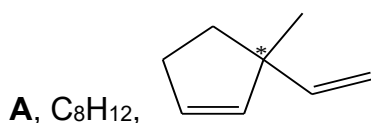
- is chiral

- is oxidatively cleaved by hot acidified  $KMnO_4$  to form:

$\Rightarrow$  **A** has terminal C=C bond /  $=CH_2$



with only 7 C's

**21 P**,  $C_{18}H_{20}$ :

- C:H ratio  $\sim 1:1 \Rightarrow$  has benzene ring(s)

- exists in 2 isomeric forms (likely cis-trans)

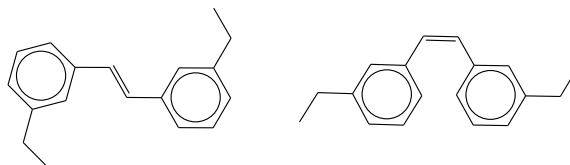
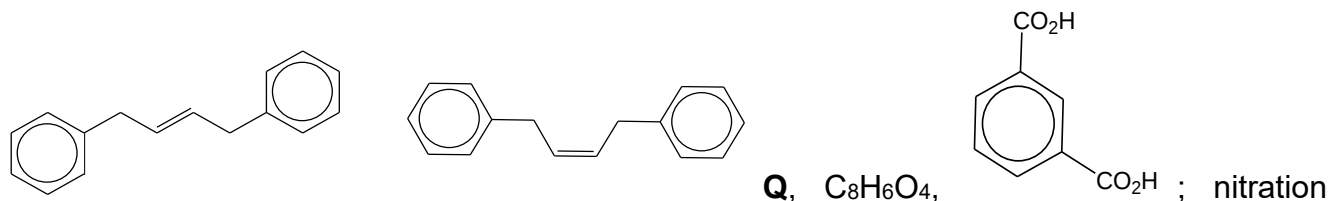
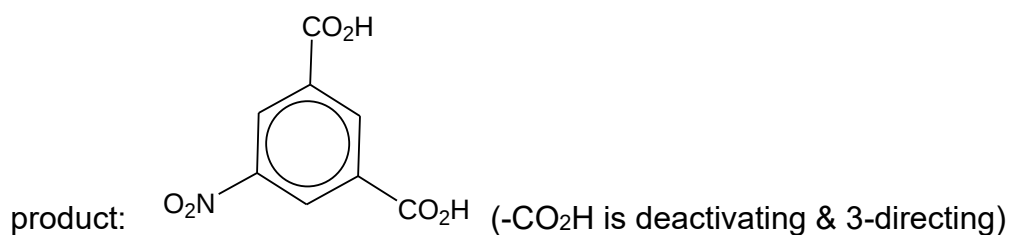
- 1 mol reacts with 1 mol  $Br_2(l)$  (electrophilic addition)  $\Rightarrow$  has 1 C=C bond

- undergoes oxidative cleavage / side-chain oxidation with acidified  $KMnO_4$  to form **Q**,  $C_8H_6O_4$ , &  $CO_2 \Rightarrow$  1 mol **P** gives 2 mol each of **Q** and  $CO_2$

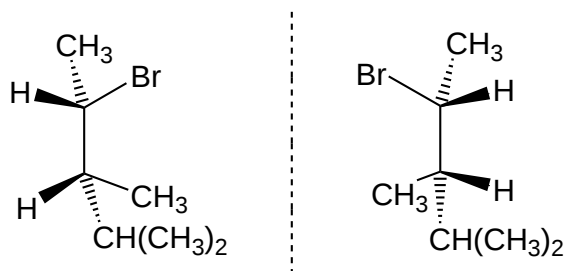
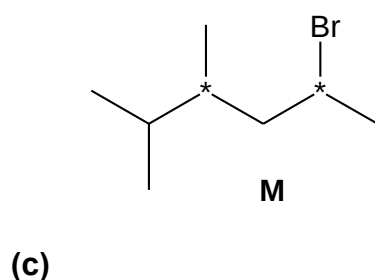
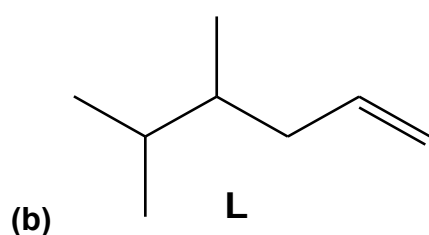
**Q**,  $C_8H_6O_4$ :

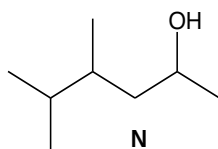
- 1 mol is neutralised by 2 mol NaOH  $\Rightarrow$  dicarboxylic acid / has 2  $-CO_2H$  groups

- Undergoes electrophilic substitution (nitration) with conc  $HNO_3$  + conc  $H_2SO_4$  to give only 1 mono-substituted product  $\Rightarrow$  1,3-dicarboxylic acid

**P:****either****or****Q**,  $\text{C}_8\text{H}_6\text{O}_4$ , ; nitration**22 (a) L**,  $\text{C}_8\text{H}_{16}$ :

- C:H ratio  $\sim 1:2 \Rightarrow$  NO benzene ring
- 1 mol reacts with 1 mol  $\text{Br}_2(l) \Rightarrow$  has 1 C=C bond
- undergoes oxidative cleavage with acidified  $\text{KMnO}_4$  to form carbon dioxide & 3,4-dimethylpentanoic acid  $\Rightarrow$  has terminal C=C bond / has  $=\text{CH}_2$  group
- undergoes electrophilic addition with HBr to form optically active **M**,  $\text{C}_8\text{H}_{17}\text{Br}$

**M**,  $\text{C}_8\text{H}_{17}\text{Br}$  reacted with hot  $\text{NaOH(aq)}$  through nucleophilic substitution to form **N**,  $\text{C}_8\text{H}_{18}\text{O}$ 



(d) NaOH(aq); heat;

23 **A**, C<sub>4</sub>H<sub>8</sub>O:

- C:H ratio = 1:2  $\Rightarrow$  has 1 C=C **or** C=O bond
  - undergoes oxidative cleavage with hot acidified KMnO<sub>4</sub> to form **B**, C<sub>3</sub>H<sub>4</sub>O<sub>4</sub>, with effervescence  $\Rightarrow$  has terminal C=C bond / =CH<sub>2</sub> group
  - reacts with aq bromine (electrophilic addition) to form **C**, C<sub>4</sub>H<sub>9</sub>O<sub>2</sub>Br  $\Rightarrow$  **A** has 1 C=C bond
  - reacts with phosphorus pentachloride to form **D**, C<sub>4</sub>H<sub>7</sub>Cl, chloroalkane  $\Rightarrow$  **A** has -OH group
- B**, C<sub>3</sub>H<sub>4</sub>O<sub>4</sub>:

- 1 mol neutralised by 2 mol NaOH  $\Rightarrow$  **B** has 2 -CO<sub>2</sub>H & **A** is 1° alcohol

Both **A** and **C** can be oxidised by acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>  $\Rightarrow$  **A** & **C** both have 1° alcohol group

**A**: CH<sub>2</sub>=CHCH<sub>2</sub>CH<sub>2</sub>OH      **B**: HO<sub>2</sub>CCH<sub>2</sub>CO<sub>2</sub>H      **C**: CH<sub>2</sub>BrCH(OH)CH<sub>2</sub>CH<sub>2</sub>OH

**D**: CH<sub>2</sub>=CHCH<sub>2</sub>CH<sub>2</sub>Cl

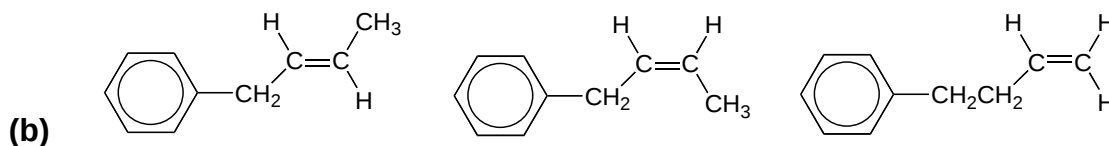
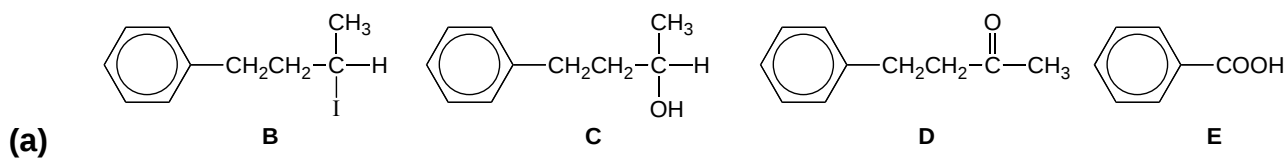
24 **B**, C<sub>10</sub>H<sub>13</sub>I:

- C:H ratio  $\sim$  1:1  $\Rightarrow$  has benzene ring
- undergoes nucleophilic substitution with KOH(aq) to give **C**, C<sub>10</sub>H<sub>14</sub>O  $\Rightarrow$  **B** is iodoalkane & **C**, an alcohol

**C**, C<sub>10</sub>H<sub>14</sub>O:

- oxidised by acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to form **D**, C<sub>10</sub>H<sub>12</sub>O (ketone; 1 O)  $\Rightarrow$  **C** is 2° alcohol
- undergoes oxidative cleavage with hot acidified KMnO<sub>4</sub> to give **E**, C<sub>7</sub>H<sub>6</sub>O<sub>2</sub> (benzoic acid)  $\Rightarrow$  **C** has 1 side chain on benzene ring

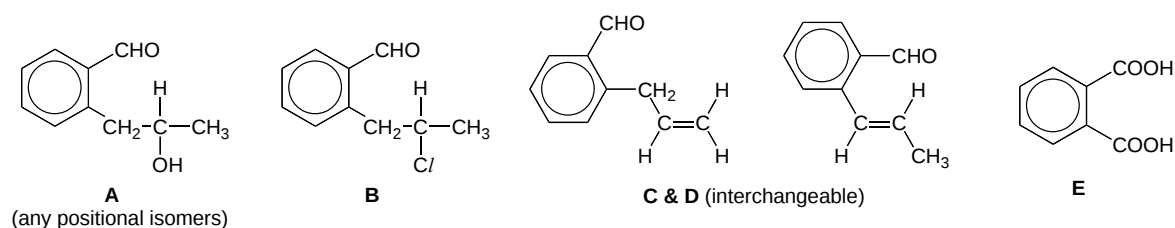
Both **C** and **D** undergo positive triiodomethane test  $\Rightarrow$  **C** has CH<sub>3</sub>CH(OH)- group & **D** has CH<sub>3</sub>CO- group



**25 A** ( $C_{10}H_{12}O_2$ ):

- C:H ratio  $\sim 1:1 \Rightarrow$  has benzene ring
- optically active  $\Rightarrow$  chiral C
- oxidised by Tollen's reagent  $\Rightarrow$  has  $-CHO$  aldehyde
- reacts positively with aq  $I_2 / NaOH \Rightarrow$  has  $CH_3CH(OH)-$  or  $CH_3CO-$  group
- reacts with phosphorus pentachloride to form **B**  $\Rightarrow$  **A** has alcohol group; **B** is alkyl chloride
- dehydrated by excess hot conc sulfuric acid to give **C** and **D** (alkenes)

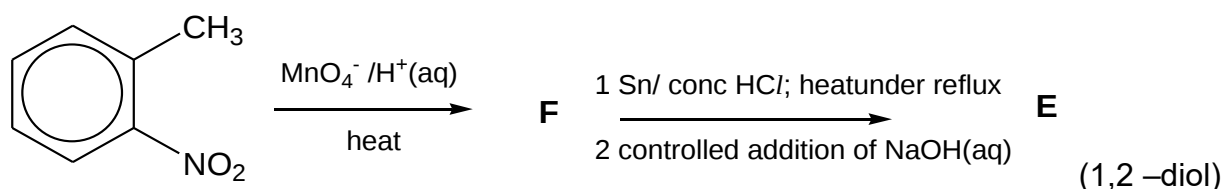
**A, B, C** or **D**: separately undergo side-chain oxidation &/or oxidative cleavage with hot acidified  $KMnO_4$  to form **E** ( $C_8H_6O_4$ , benzene-1,2-dicarboxylic acid)

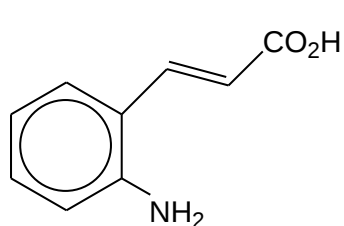
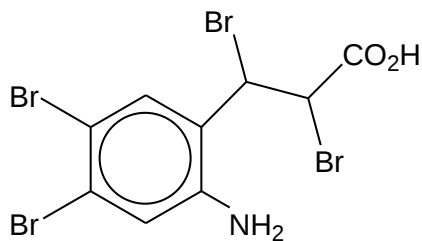
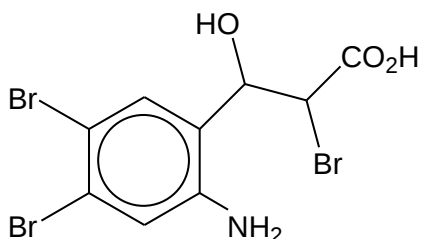
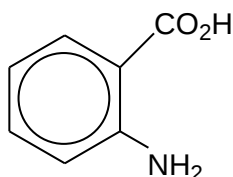
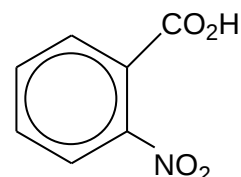
**26 B**,  $C_9H_9NO_2$ :

- C:H ratio =  $1:1 \Rightarrow$  has benzene ring
- forms zwitterions in aqueous solution which conducts electricity  $\Rightarrow$  is amino acid / has  $-NH-$  and  $-CO_2H$  group
- reacts with aq  $Na_2CO_3$  to give  $CO_2 \Rightarrow$  has  $-CO_2H$  group
- reacts with aq  $Br_2$  (electrophilic substitution and electrophilic addition) to give **C**,  $C_9H_7Br_4NO_2$ , and **D**,  $C_9H_8Br_3NO_3 \Rightarrow$  is phenyl amine + 1 C=C bond (2 Br from electrophilic substitution, 2 Br from electrophilic addition for **C**) & is 1,2- or 1,4-disubstituted
- 1 mol reacts with hot acidified  $KMnO_4$  through oxidative cleavage & / or side-chain oxidation to give 2 mol  $CO_2$  & neutralisation of resultant solution gives **E**,  $C_7H_7O_2N$

**E**,  $C_7H_7O_2N$ :

- soluble in  $NaOH(aq)$  and  $HCl(aq) \Rightarrow$  has both basic and acidic groups
- is synthesised by:



**B****C****D****E****F**

**27 H**,  $C_5H_{10}O_2$ , formula for ester and carboxylic acid or 2  $-OH$  groups + 1  $C=C$  bond

**H**,  $C_5H_{10}O_2$ , forms **I**,  $C_5H_6O_4$ , when heated under reflux with acidified  $K_2Cr_2O_7$

- **H** is oxidised to **I**;

- **H** has two  $1^\circ$  alcohol groups; **I** is a dioic acid / has 2  $-CO_2H$  groups

**H** decolourised aq  $Br_2$  to form **J**,  $C_5H_{11}O_3Br$

- **H** undergoes electrophilic addition; **J** has  $Br$  &  $OH$  on adjacent  $C$ 's

**H** reacts with hot acidified  $KMnO_4$  to form **M**,  $C_3H_4O_4$  (only organic product)

**H** undergoes oxidative cleavage and lost 2  $C$  as  $CO_2$ ; **H** has  $=CHCH_2OH$  group

- From given synthetic route

**M** is  $HO_2CCH_2CO_2H$

**H**:  $HOCH_2CH_2CH=CHCH_2OH$

**I**:  $HO_2CCH_2CH=CHCO_2H$

**J**:  $HOCH_2CH_2CHBrCH(OH)CH_2OH$

**K**:  $HOCH_2CH_2Cl$

**L**:  $HOCH_2CH_2CN$

**28 P** ( $C_5H_{10}Cl_2$ )

- reacts with  $NaOH(aq)$  to give **Q**

**Q:**

- gives yellow ppt with aq  $I_2/NaOH$

- forms **R** ( $C_5H_{10}O_2$ ) with hot acidified  $K_2Cr_2O_7$

**R:**

- reacts with  $Na(s)$  to give  $H_2$  (redox reaction)

- reacts with  $HCN$  and trace  $NaOH$  (nucleophilic addition) to give **S**

**S:**

- is reduced to **T** which reacted with chloromethane to **U** ( $C_7H_{17}O_2N$ )

- **P** is a chloroalkane (no double bonds), undergoes hydrolysis to form **Q** with 2  $-OH$  groups

**Q**

- has  $CH_3CH(OH)-$  group; forms  $CHI_3$  and carboxylic salt **R**

- either has two  $2^\circ$  alcohol groups and is oxidised to **R** (diketone)

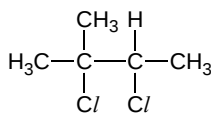
- or has one  $2^\circ$  and one  $3^\circ$  alcohol groups and is oxidised to **R** (ketone + alcohol)

**R** has  $-OH$  group

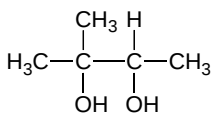
**R** has carbonyl group (ketone);

**S** is a cyanohydrin ( $-CH(OH)CN$ )

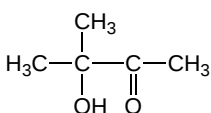
**T**:  $1^\circ$  amine ( $-CH_2NH_2$ ), undergoes nucleophilic substitution with  $CH_3Cl$



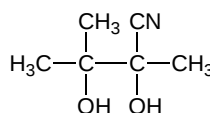
**P**



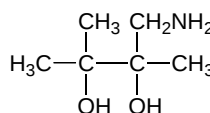
**Q**



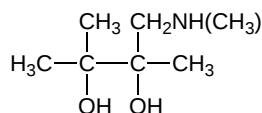
**R**



**S**



**T**



**U**

**29 (a)**

**A**,  $C_9H_{11}Br$ :

- C:H ratio  $\sim 1:1 \Rightarrow$  has benzene ring

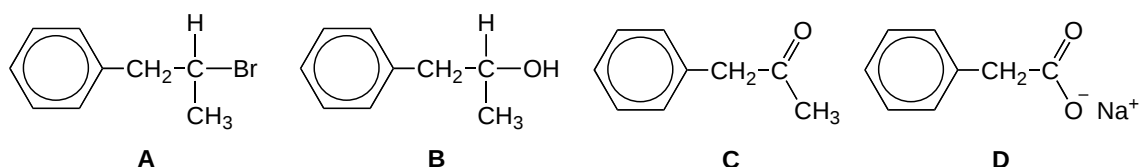
- Undergoes nucleophilic substitution with hot aq  $KOH$  to form **B**,  $C_9H_{12}O \Rightarrow$  **A** is bromoalkane; **B** is alcohol

**B**,  $C_9H_{12}O$ :

- oxidised by acidified  $K_2Cr_2O_7$  to give **C**,  $C_9H_{10}O \Rightarrow$  **B** is  $2^\circ$  alcohol; **C** is ketone (1 O)

- undergoes positive triiodomethane test to give **D**,  $C_8H_7O_2Na$  and  $CHI_3$  (yellow ppt)  $\Rightarrow$  **B** has  $CH_3CH(OH)-$  group; **D** is salt of  $RCO_2^-$

- undergoes side-chain oxidation with hot acidified  $KMnO_4$  to give **E**,  $C_7H_6O_2 \Rightarrow$  **B** has a side chain of 2 C's (ethyl group) attached directly to benzene ring; **B** must be benzoic acid

**(b)**

Why benzoic acid is more acidic than phenylmethanol:

–ve charge of  $\text{CO}_2^-$  can delocalize over the entire groups; this helps to disperse electron density and hence stabilises the conjugate base.

For phenylmethanol, the adjacent electron donating alkyl group intensifies electron density on  $\text{O}^-$  and hence destabilises the conjugate base.

**30 (a)**

**P**,  $\text{C}_9\text{H}_8\text{O}_2$ :

C:H ratio  $\sim 1:1 \Rightarrow$  has benzene ring

oxidised by Tollen's reagent  $\Rightarrow$  has  $\text{CHO}$  group

undergoes positive test with aq  $\text{I}_2/\text{NaOH}$  to give  $\text{CHI}_3$  (yellow ppt)  $\Rightarrow$  **P** has  $\text{CH}_3\text{CH}(\text{OH})-$  or  $\text{CH}_3\text{CO}-$  group

reduced by lithium aluminium hydride to form **Q**,  $\text{C}_9\text{H}_{12}\text{O}_2 \Rightarrow$  **P** has 2 carbonyl functional groups (coz **Q** has 4H's added)

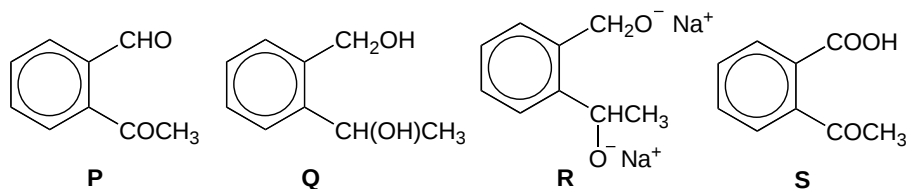
undergoes side-chain oxidation / oxidative cleavage with acidified  $\text{KMnO}_4$  to form **S**,  $\text{C}_9\text{H}_8\text{O}_3$

**Q**,  $\text{C}_9\text{H}_{12}\text{O}_2$ :

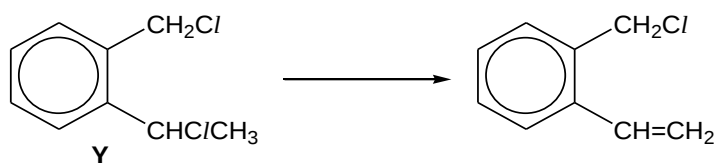
inert to aq  $\text{Na}_2\text{CO}_3 \Rightarrow$  not carboxylic acid

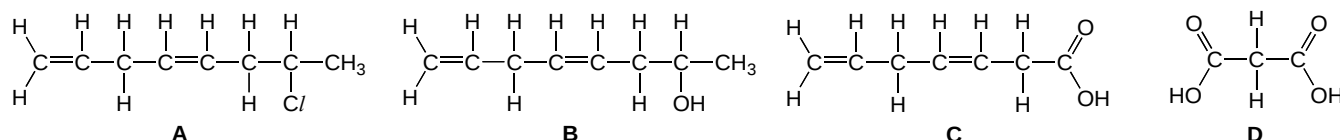
reacts with  $\text{Na(s)}$  (redox reaction) to form **R**,  $\text{C}_9\text{H}_{10}\text{O}_2\text{Na}_2$ , with strong effervescence of  $\text{H}_2 \Rightarrow$  **Q** has 2  $\text{OH}$  or alcohol groups

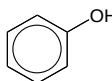
can be obtained by reacting **Y** with hot  $\text{NaOH(aq)} \Rightarrow$  **Q** is

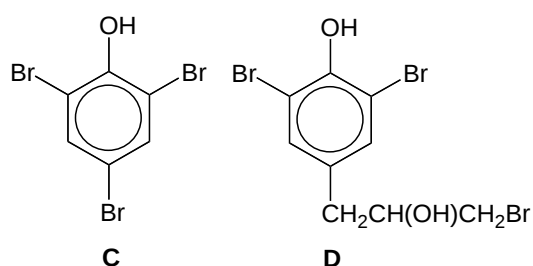
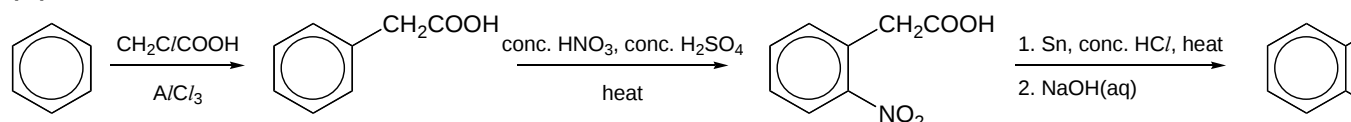


**(b)** **Y** undergoes elimination to give alkene and nucleophilic substitution to give alcohol.



**31 (a)****A**,  $C_8H_{13}Cl$ :-C:H ratio  $\sim 1:2 \Rightarrow$  NO benzene ring / is aliphatic (chloroalkane)- optically active  $\Rightarrow$  **A** has chiral C- undergoes nucleophilic substitution with hot NaOH(aq) to form **B**,  $C_8H_{14}O \Rightarrow$  **A** is aliphatic (chloroalkane); **B** has alcohol functional group**B**,  $C_8H_{14}O$ :- undergoes electrophilic addition with 2 mol  $Br_2 \Rightarrow$  has 2 C=C bonds- undergoes positive test with aq  $I_2$ / NaOH  $\Rightarrow$  has  $CH_3CH(OH)-$  group and **C**,  $C_7H_{10}O_2$  is carboxylic acid- undergoes oxidative cleavage with hot acidified  $KMnO_4$  to gives **D**,  $C_3H_4O_4$  and  $CH_3COCH_2CO_2H$  and  $CO_2 \Rightarrow$  **B** has 1 C=C bond between C3 and C4 and 1  $=CH_2$  groupTri-iodomethane,  $CHI_3$ **(b)****32 A**,  $C_6H_6O$ :-C:H ratio = 1:1 with 1 O  $\Rightarrow$  is phenol- reacts with 3-chloropropene in aluminium chloride (electrophilic substitution) to form **B**,  $C_9H_{10}O$ **A**, **B**:- decolourise aq bromine (electrophilic substitution & /or electrophilic addition) to form white precipitates **C** and **D**, respectively  $\Rightarrow$  presence of phenol or C=C bond**C**, **D**: have same no of Br per molecule; **D** is optically active (has chiral C)

**(a)(i)**  ; Electrophilic Substitution

**(a)(ii)****(b)**

Can also undergo the following sequence:

1. Nitration 2. Reduction 3. Friedel-craft acylation 4. Salt formation.

### 33 T (neutral)

- MF:  $C_4H_5O_3$

- is hydrolysed by hot  $NaOH(aq)$  to form **U**,  $C_2H_6O_2$  & sodium ethanoate  $\Rightarrow$  **T** is an ester & **U** is a diol (2O's; saturated)

**U**,  $C_2H_6O_2$ :

- mono-substitution of -OH group with  $HCl$  forms **V**,  $C_2H_5OCl$ , which undergoes nucleophilic substitution with alc  $KCN$  to form **W**,  $C_3H_5ON$  (nitrile)

**W**,  $C_3H_5ON$ :

- undergoes hydrolysis with hot acid to form optically inactive **X**,  $C_3H_6O_3$ ; which undergoes self-condensation to form **Y**,  $C_3H_4O_2$  (cyclic ester)

- oxidation of **X** gives solid **Z**,  $C_3H_4O_4$  (dicarboxylic acid) and hence soluble in water

**T**:  $CH_2OHCH_2O_2CCH_3$

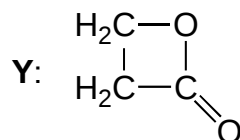
**U**:  $CH_2OHCH_2OH$

**V**:  $CH_2OHCH_2Cl$

**W**:  $CH_2OHCH_2CN$

**X**:  $CH_2OHCH_2COOH$

**Z**:  $HOOCCH_2COOH$



### 34 P, $C_{16}H_{30}O_4$ :

-C:H ratio  $\sim 1:2 \Rightarrow$  no benzene ring

- insoluble in both water and dilute  $NaOH(aq) \Rightarrow$  NO -OH or  $-CO_2H$  group

- is hydrolysed by acid to form **Q**,  $C_6H_{14}O$  & **R**,  $C_4H_6O_4 \Rightarrow$  has ester group

**Q**,  $C_6H_{14}O$ :

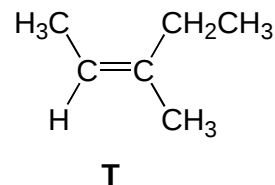
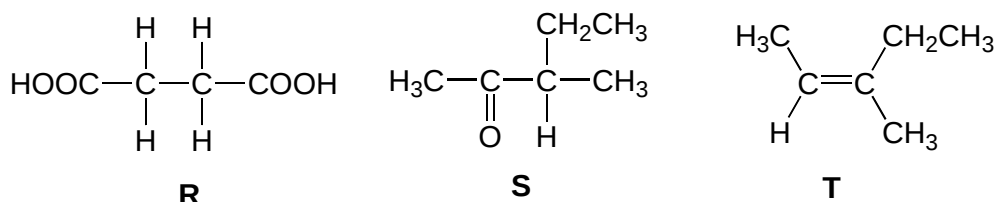
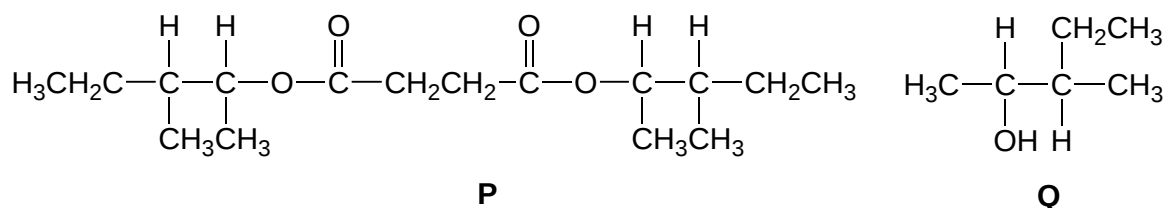
- rotates plane of plane-polarised light  $\Rightarrow$  has chiral C

- is oxidised by hot acidified  $KMnO_4$  to give **S**,  $C_6H_{12}O$ , which give yellow ppt with aq  $I_2/NaOH \Rightarrow$  **Q** is  $2^\circ$  alcohol with  $CH_3CH(OH)-$  group & **S** has  $CH_3CO-$  group

- dehydrated by  $Al_2O_3$  to give alkene **T**,  $C_6H_{12}$ , which upon vigorous oxidation give butanone as a pdt  $\Rightarrow$  **T** must be  $CH_3CH_2CH(CH_3)=CHCH_3$

**R**,  $C_4H_6O_4$ :

- synthesised from 1,2-di-iodoethane with hot ethanolic  $NaCN$  followed by warming with dilute sulfuric acid  $\Rightarrow$  **R** must be  $HO_2CCH_2CH_2CO_2H$

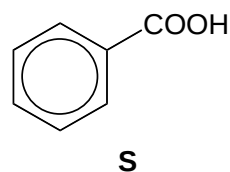
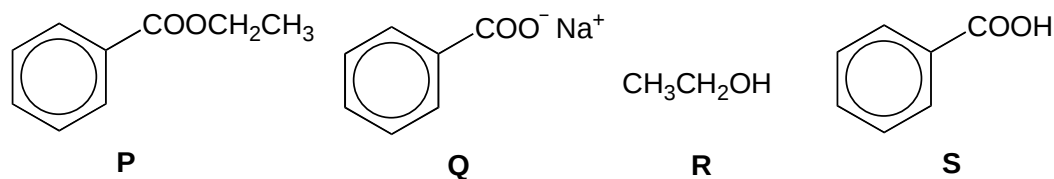


**35 P** (mono-substituted aromatic):

- hydrolysed by hot NaOH(aq) to give **Q** & **R**, which upon acidification gives **S**, C<sub>7</sub>H<sub>6</sub>O<sub>2</sub> (benzoic acid) ⇒ **P** has ester group

**R** (neutral and can be distilled over)

- is ethanol reacts with sodium (redox) and is oxidised to ethanoic acid by acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>



**36 C**, C<sub>10</sub>H<sub>9</sub>NO

- C:H ratio ~ 1:1 ⇒ has benzene ring

- neutral & not very soluble (slowly dissolves) in water ⇒ has amide (1 O and 1 N) / -CN and -OH groups

- hydrolysed by hot dilute sulfuric acid to form **D** (soluble in both NaOH(aq) & aq Na<sub>2</sub>CO<sub>3</sub>) ⇒ **D** is carboxylic acid

- obtained by heating **E**, C<sub>9</sub>H<sub>9</sub>Cl/O with alc KCN (NS) ⇒ **E** is chloroalkane (Cl on side alkyl chain, not on benzene ring)

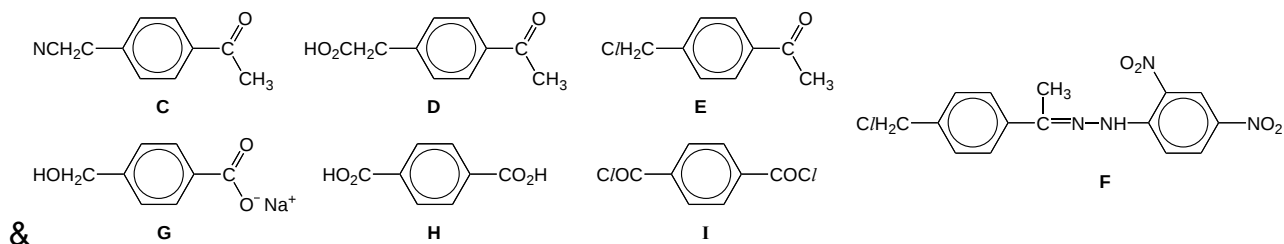
**E**:

- no reaction with Tollen's reagent; reacts with 2,4-DNPH to give orange ppt ⇒ **E** is ketone, **F**, a hydrazone

- reacts positively with warm aq I<sub>2</sub>/NaOH ⇒ **E** has CH<sub>3</sub>CO- group & **G**, salt of carboxylic acid  
Side-chain of **G** is oxidised by hot acidified KMnO<sub>4</sub> & **H** is formed.

**H:**

- reacts with 2 mol  $\text{PCl}_5$  to give **I**,  $\text{C}_8\text{H}_4\text{Cl}_2\text{O}_2 \Rightarrow$  **H** has 2  $-\text{CO}_2\text{H}$ ; **I** has 2  $-\text{CO}_2\text{Cl}$



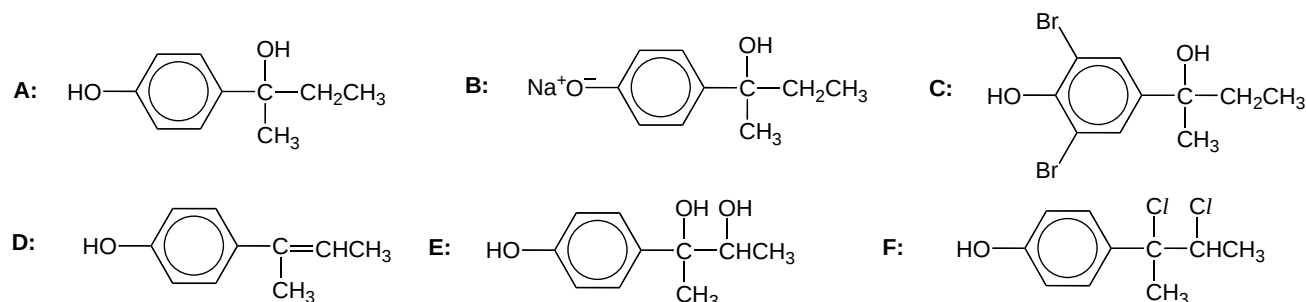
&amp;

**37 A** ( $\text{C}_{10}\text{H}_{14}\text{O}_2$ ):

- C:H ratio  $\sim 1:1 \Rightarrow$  has benzene ring
- optically active; NO reaction with aq  $\text{Na}_2\text{CO}_3 \Rightarrow$  has chiral C and not carboxylic acid (could be phenol)
- neutralised slowly by  $\text{NaOH(aq)}$  to form **B** (water soluble)  $\Rightarrow$  weak acidic group (phenol likely)
- reacts with  $\text{HBr}$  (substitution) but not acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  (cannot be oxidised)  $\Rightarrow$   $3^\circ$  alcohol
- reacts with aq bromine (electrophilic addition + electrophilic substitution) to form **C** ( $\text{C}_{10}\text{H}_{12}\text{O}_2\text{Br}_2$ ) – 2 H substituted  $\Rightarrow$  1,2 or 1,4 di-substituted benzene ring
- dehydrated by conc sulfuric acid to form **D** ( $\text{C}_{10}\text{H}_{12}\text{O}$ ), cis-trans isomers  $\Rightarrow$   $-\text{OH}$  with a H on adjacent C

**D** ( $\text{C}_{10}\text{H}_{12}\text{O}$ ) undergoes mild oxidation with cold, dilute aq alkaline  $\text{KMnO}_4$  to **E** ( $\text{C}_{10}\text{H}_{14}\text{O}_3$ , diol)  $\Rightarrow$  **D** has 1  $\text{C}=\text{C}$  bond

**E** ( $\text{C}_{10}\text{H}_{14}\text{O}_3$ ) reacts with phosphorous pentachloride to give **F** ( $\text{C}_{10}\text{H}_{12}\text{OCl}_2$ )  $\Rightarrow$  has 2  $-\text{OH}$  groups

**38 A**,  $\text{C}_{10}\text{H}_{13}\text{Br}$ :

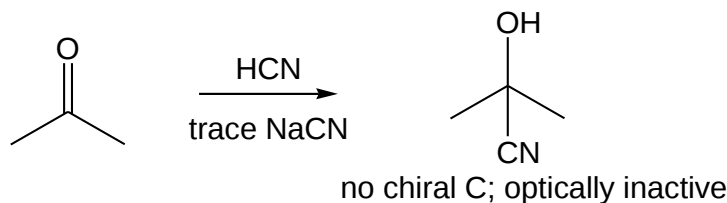
- C:H ratio  $\sim 1:1 \Rightarrow$  has benzene ring
- undergoes elimination with hot ethanolic  $\text{NaOH}$  to give only **B**,  $\text{C}_{10}\text{H}_{12} \Rightarrow$  **A**, bromoalkanes; **B**, alkene has  $\text{C}=\text{C}$  bond

**B**,  $\text{C}_{10}\text{H}_{12}$ :

- oxidised to benzaldehyde and **C**,  $\text{C}_3\text{H}_6\text{O}$

**C**,  $\text{C}_3\text{H}_6\text{O}$ :

- undergoes nucleophilic addition with HCN to give **D**,  $C_4H_7NO$  (optically active; has chiral C)  
 $\Rightarrow$  **C** is propanal (not propanone) as otherwise **D** will not be optically active:

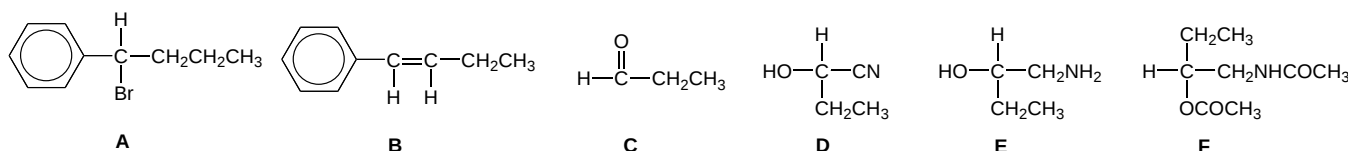


**D**,  $C_4H_7NO$ :

- reduced by lithium aluminium hydride to **E**,  $C_4H_{11}N$  ( $1^\circ$  amine)  $\Rightarrow$  **D** is nitrile & is reduced to  $1^\circ$  amine

**E**,  $C_4H_{11}NO$ :

- 1 mol reacts with 2 mol ethanoyl chloride to give **F**,  $C_8H_{15}NO_3 \Rightarrow$  **E** has 1 amine and 1 alcohol groups per molecule; **F**, has ester and amide groups



### 39 **G**, $C_{10}H_{11}O_2Br$ :

- C:H ratio  $\sim 1:1 \Rightarrow$  has benzene ring
- no reaction with aq  $Na_2CO_3$ , hydrolysed slowly by hot  $NaOH(aq)$  to form phenyl methanol and **H**,  $C_3H_5O_3Na$  (salt of acid)  $\Rightarrow$  **G** is an ester

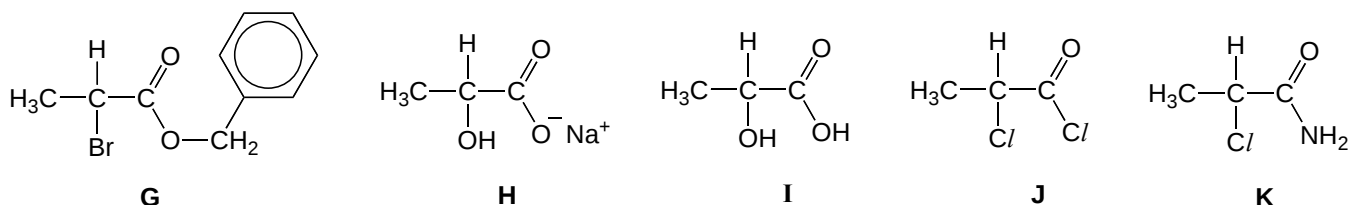
**H**,  $C_3H_5O_3Na$ :

- gives  $H_2$  with  $Na(s)$  (redox reaction) and reacts with alkaline aq  $I_2$  to form ppt  $\Rightarrow$  **H** has  $CH_3CH(OH)-$  group
- acidification gives **I**,  $C_3H_6O_3 \Rightarrow$  **I** has  $-CO_2H$

**I**,  $C_3H_6O_3$ :

- reacts with phosphorus pentachloride to give **J**,  $C_3H_4Cl_2O \Rightarrow$  **I** has 2  $-OH$  groups

**J** reacts with ammonia to give **K**,  $C_3H_6ONCl \Rightarrow$  **J** is acid chloride & **K** is amide



### 40 **X** (diacid):

- MF:  $C_4H_6O_5$
- undergoes condensation with ethanol/ conc sulfuric acid to give **Y**,  $C_8H_{14}O_5$  (diester; added



**42 T, C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>N:**

- optically active  $\Rightarrow$  has chiral C
- reacts with  $\text{PCl}_5$  to give white fumes & **U**  $\Rightarrow$  **T** has  $-\text{OH}$  **U**:
- gives  $\text{NH}_3$  & **V** with hot  $\text{NaOH(aq)} \Rightarrow$  **U** & **T**; each has amide linkage; **V** is salt of acid

**W, C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>:**

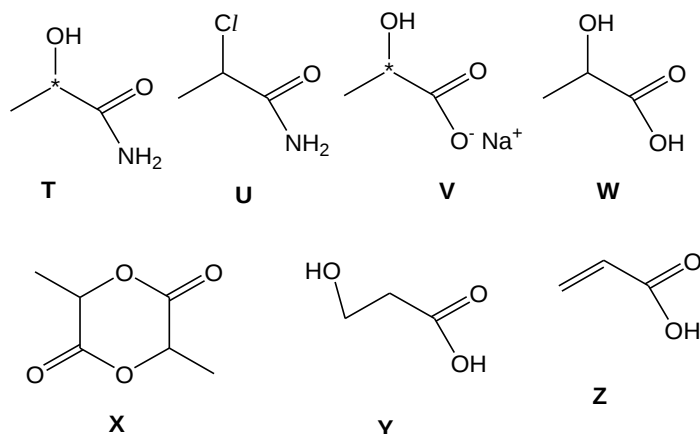
- from acidification of **V**

**W, C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>:**

- undergoes condensation in conc sulfuric acid to form cyclic diester, **X**, C<sub>6</sub>H<sub>8</sub>O<sub>4</sub>

**Y C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>:**

- isomer of **W** (optically inactive)
- dehydrated to **Z**, C<sub>3</sub>H<sub>4</sub>O<sub>2</sub>

**43 A, C<sub>5</sub>H<sub>9</sub>O<sub>2</sub> (M<sub>r</sub> 136.5):**

readily dissolves in  $\text{NaOH(aq)}$  at room temperature  $\Rightarrow$  has acidic  $-\text{CO}_2\text{H}$

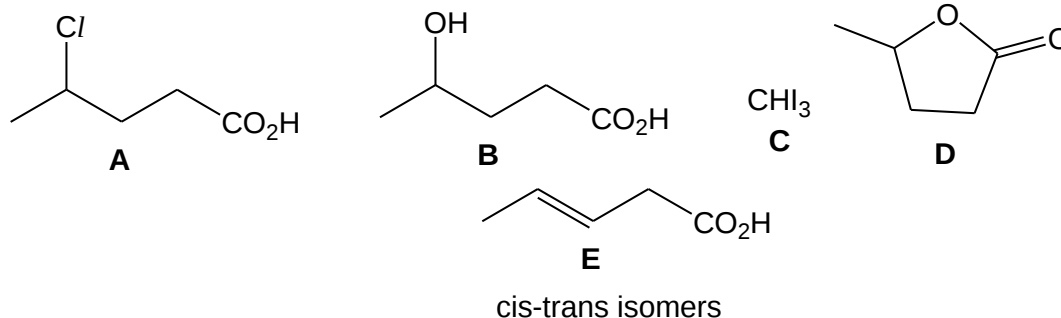
reacts with hot  $\text{NaOH(aq)}$  (nucleophilic substitution), followed by acidification to give **B**, C<sub>5</sub>H<sub>10</sub>O<sub>3</sub>

**B, C<sub>5</sub>H<sub>10</sub>O<sub>3</sub>:**

- reacts positively with warm aq  $\text{I}_2/\text{NaOH}$  to give yellow ppt, **C**,  $\text{CHI}_3 \Rightarrow$  **B** has  $-\text{CH(OH)CH}_3$
- reacts with hot conc sulfuric acid to form **D** (ester; sweet smelling) and **E**, C<sub>5</sub>H<sub>8</sub>O<sub>2</sub> (alkene; exhibit cis-trans isomerism)

**E C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>:**

- 1 mol reacts with 1 mol  $\text{Br}_2 \Rightarrow$  has 1  $\text{C}=\text{C}$  bond
- undergoes oxidative cleavage with hot, acidified  $\text{KMnO}_4$  to give **F**, C<sub>3</sub>H<sub>4</sub>O<sub>4</sub>  $\Rightarrow$  **E** has  $\text{C}=\text{C}$  between C<sub>2</sub> and C<sub>3</sub>

**44 G, C<sub>10</sub>H<sub>18</sub>O:**

- no reaction with 2,4-dinitrophenylhydrazine reagent; can be reduced by H<sub>2</sub>/ Pd to **H**, C<sub>10</sub>H<sub>17</sub>O ⇒ **G** has C=C bond
- reacts with ethanoyl chloride to give **J**, C<sub>12</sub>H<sub>20</sub>O<sub>2</sub> (condensation; ester); cannot be oxidised by acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> ⇒ **G** has 3° alcohol group
- oxidised by cold acidified KMnO<sub>4</sub> to give **K**, C<sub>10</sub>H<sub>22</sub>O<sub>5</sub> ⇒ has 2 C=C bonds (4 –OH added)
- dehydrated by conc sulfuric acid to give **L** and **M** (both C<sub>10</sub>H<sub>16</sub>; alkene)

**L:**

- undergoes oxidative cleavage with hot acidified KMnO<sub>4</sub> to give **N**, C<sub>3</sub>H<sub>4</sub>O<sub>3</sub>, **P**, C<sub>3</sub>H<sub>4</sub>O<sub>4</sub>, and **Q**, C<sub>3</sub>H<sub>6</sub>O and CO<sub>2</sub> ⇒ has 2 C=C bond & 1 =CH<sub>2</sub> group

**N and Q:**

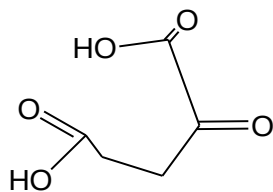
- both give yellow precipitate with aq I<sub>2</sub>/ NaOH ⇒ each has CH<sub>3</sub>CO– group

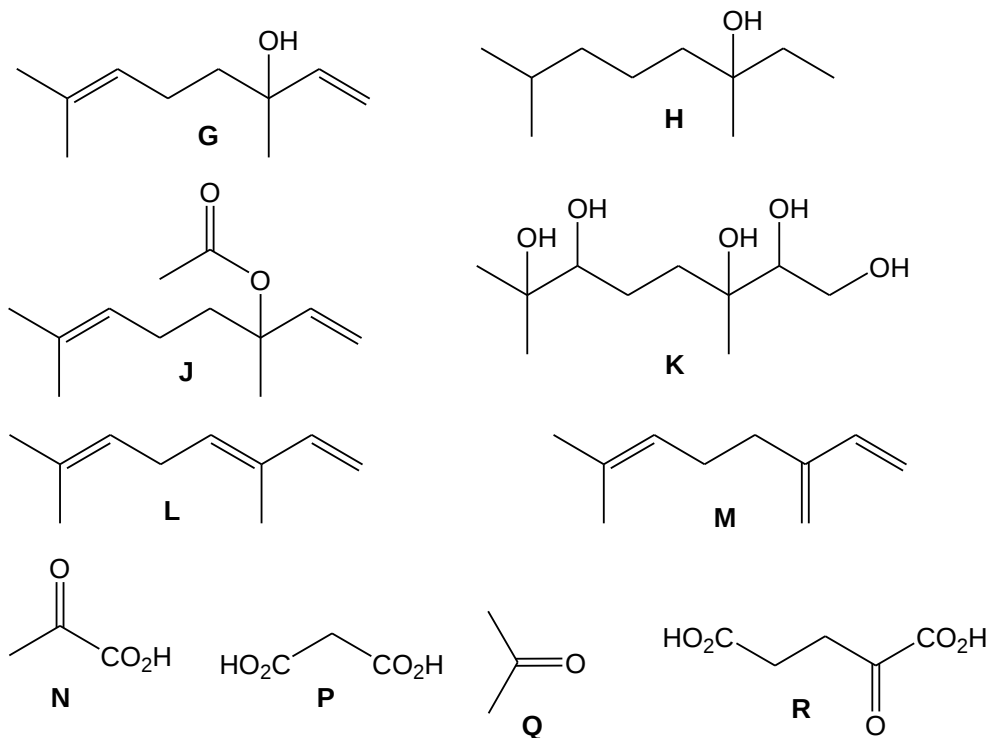
**P, C<sub>3</sub>H<sub>4</sub>O<sub>4</sub>:**

- 0.104 g neutralised by 20.00 cm<sup>3</sup> of 0.10 mol dm<sup>-3</sup> NaOH ⇒ has 2 –CO<sub>2</sub>H (diacid)

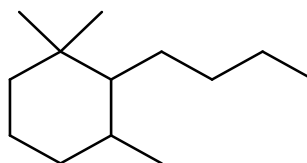
**M, C<sub>10</sub>H<sub>16</sub>:**

- is oxidatively cleaved by hot conc acidified KMnO<sub>4</sub> to give **Q** and **R**, C<sub>5</sub>H<sub>6</sub>O<sub>5</sub> ⇒ **M** has 2 C=CH<sub>2</sub> groups

**R:** can be obtained from **S** by careful oxidation with hot concentrated acidified KMnO<sub>4</sub> ⇒ **R** is



45 **C, D** ( $C_{13}H_{22}$ ) & **E** ( $C_{13}H_{20}$ ):



- each reacts with  $H_2/Ni$  to give  $C_{13}H_{26}$ ,

**C**: exists as a pair of enantiomers  $\Rightarrow$  has chiral C

**D, E** - no optical activity  $\Rightarrow$  no chiral C

**C, D**: 1 mol each reacts with 2 mol  $Br_2 \Rightarrow$  each has 2  $C=C$  bonds

- undergo oxidative cleavage with acidified  $KMnO_4$  to give ethanoic acid as 1 of 2 organic products

**E**: 1 mol reacts with 3 mol  $Br_2$  (electrophilic addition)  $\Rightarrow$  has 3  $C=C$  bonds

**C** - undergoes oxidative cleavage with acidified  $KMnO_4$  to give **F**,  $C_{10}H_{16}O_3$ ,

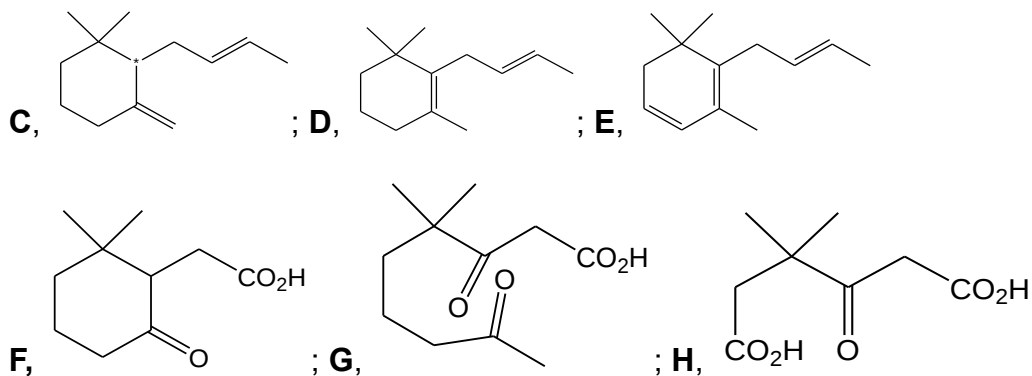
**D** - undergoes oxidative cleavage with acidified  $KMnO_4$  to give **G**,  $C_{11}H_{18}O_4$

**E** - undergoes oxidative cleavage with acidified  $KMnO_4$  to give ethanoic acid,  $CH_3COCO_2H$  and **H**,  $C_8H_{12}O_5$ .

**F** and **G**:

- react with  $NaOH$  in 1 : 1 ratio  $\Rightarrow$  each has 1  $-CO_2H$  group

**H**,  $C_8H_{12}O_5$  - 1 mol neutralised by 2 mol  $NaOH \Rightarrow$  is diacid

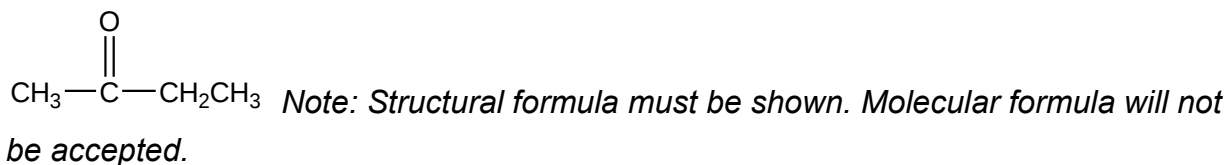


**46** Volume of CO<sub>2</sub> = 8.2 – 3.4 = 4.8 dm<sup>3</sup>

$$\text{Number of moles of CO}_2 = \frac{4.8}{24} = 0.200 \text{ mol}$$

$$\text{Number of moles of C in 1 mole of X} = 0.2/0.05 = 4 \text{ mol}$$

$$n = 4$$



**47**  
**(a)**

|                    | C    | H   | O    | S    |
|--------------------|------|-----|------|------|
| Percentage by mass | 51.2 | 7.7 | 13.7 | 27.4 |
| Mole ratio         | 4.3  | 7.7 | 0.86 | 0.85 |
| Simplest ratio     | 5    | 9   | 1    | 1    |

$$\text{Empirical formula} = \text{C}_5\text{H}_9\text{OS}$$

**(b)** Using the ideal gas equation,  $pV = nRT = (m/M_r)RT$

$$M_r = (mRT)/pV$$

$$= [0.219 \times 8.31 \times (95 + 273)] / (150 \times 10^3 \times 38.2 \times 10^{-6}) = 116.9$$

**48 (i)**  $(101\ 000) (282 \times 10^{-6}) = (1/M_r) (8.31) (200 + 273)$

$M_r = 138$

**(ii)**

|                       | <b>C</b> | <b>H</b> | <b>O</b> |
|-----------------------|----------|----------|----------|
|                       | 60.8     | 4.4      | 34.8     |
|                       | 5.06     | 4.4      | 2.18     |
|                       | 2.32     | 2.0      | 1        |
| <b>Simplest ratio</b> | <b>7</b> | <b>6</b> | <b>3</b> |

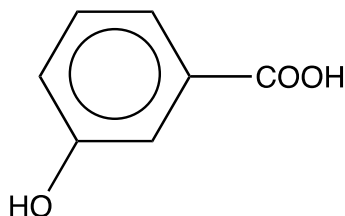
Empirical formula of **D** is **C<sub>7</sub>H<sub>6</sub>O<sub>3</sub>**

Molecular formula of **D**: **C<sub>7</sub>H<sub>6</sub>O<sub>3</sub>**

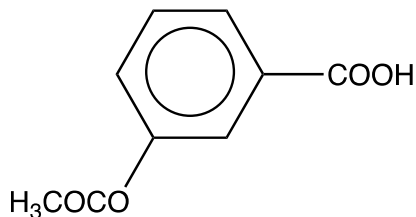
**(iii)** Carboxylic acid and phenol

**(iv)** Molecular formula of **E**: C<sub>7</sub>H<sub>3</sub>O<sub>3</sub>Br<sub>3</sub>

**(v)**



**(vi)**



**49) F and K** undergoes **strong oxidation** with KMnO<sub>4</sub> to give **G** and **H**

→ Since there is a decrease in no of C atoms after oxidation, both F and K must contain **alkenes**.

**F** liberates four mole of carbon dioxide

→ **F** contains (terminal) **alkenes**.

**F** undergoes **redox** with Na metal

→  $0.10\text{mol} \equiv 1.2\text{dm}^3 \equiv 1\text{H}_2 \equiv 1\text{ROH}$

→ **F** contains only 1 **alcohol**.

**F does not undergo strong oxidation** with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

→ **F** contains a **tertiary alcohol**.

**F** undergoes **elimination** with excess concentrated sulfuric acid to give **I**, C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>

→ **F** contains an **alcohol**.

I further oxidises to give J,  $C_3H_2O_5$ , and an inorganic by-product

→ I contains 4 **carboxylic acid** and  **$CO_2$**  is the by-product

H undergoes **mild oxidation** with iodoform

→ H contains a **terminal methyl ketone**

(since it is an [O] product, it cannot be a methyl carbinol)

H dissolves in aqueous sodium hydroxide.

→ H contains an **acidic group** (i.e.  $-COOH$ )

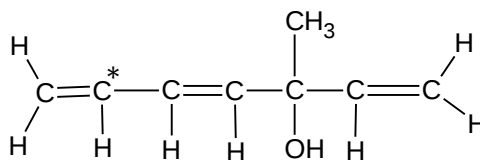
L is an oxidised product

→ L contains a **tricarboxylic acid** and the inorganic product is  **$CO_2$** .

|          |          |          |
|----------|----------|----------|
|          |          |          |
| <b>G</b> | <b>I</b> | <b>J</b> |
|          |          |          |
| <b>K</b> | <b>H</b> | <b>L</b> |

**Note : methyl group can be on any position**

(ii) F:



**Enantiomerism:**

F has **no plane of symmetry**. OR

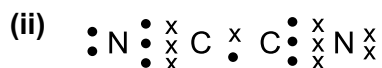
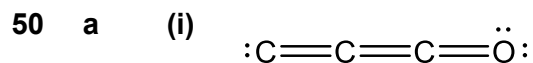
F **rotates plane polarised light**. OR

F has a pair of **non-superimposable images**.

**Cis-trans:**

**Restricted rotation about C=C OR****two different substituents about each C on C=C**

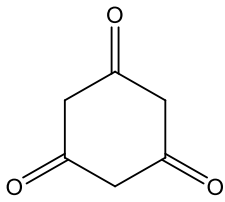
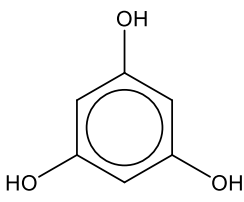
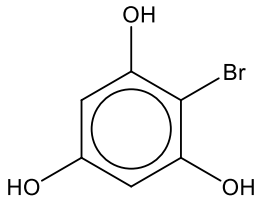
(iii) no of enantiomers present = 4



b

| Information/Reaction                                                                                              | Deduction                                                       |
|-------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------|
| X/Y has <u>C:H</u> ratio of 1:1                                                                                   | X/Y might contain a <u>benzene ring</u> .                       |
| X does not undergo <u>electrophilic substitution</u> nor <u>electrophilic addition</u> with Br <sub>2</sub> (aq)  | X does not contain a phenol nor a C=C.                          |
| X undergoes <u>condensation</u> with 2,4-DNPH but does not undergo <u>oxidation</u> with Tollens' reagent.        | X is a <u>ketone</u> .                                          |
| X undergoes <u>free-radical substitution</u> with Br <sub>2</sub> to give only one monobromo compound.            | X is <u>highly symmetrical</u> .                                |
| Y undergoes <u>electrophilic substitution</u> with HNO <sub>3</sub> (aq) to give only one mono-nitrated compound. | Y is a <u>phenol</u> .<br>Y is also <u>highly symmetrical</u> . |

**Structures:**

|                                                                                     |                                                                                     |                                                                                       |
|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
|  |  |  |
| <b>X</b>                                                                            | <b>Y</b>                                                                            | <b>Z</b>                                                                              |