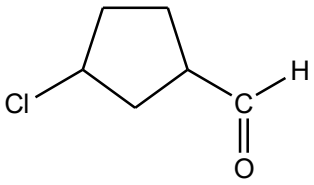
Worked Solutions to Organic Chemistry Revision Booklet (Structured Questions)

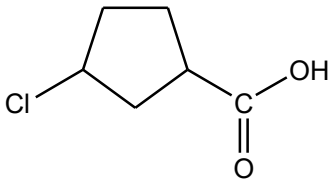
1) Organic Synthesis

1.

(a)



D

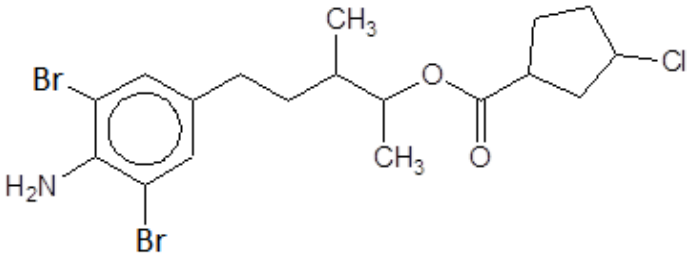


E

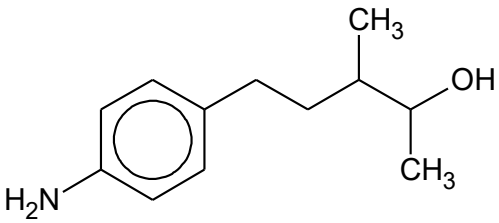
(b) Step **2**: NaOH(aq); heat

Step **3**: $KMnO_4$,H_2SO_4 (aq), heat or $K_2Cr_2O_7$, H_2SO_4 (aq), heat

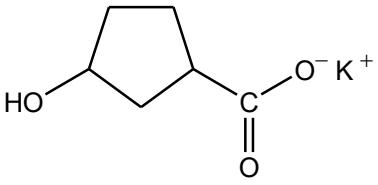
(c)(i)



(ii)



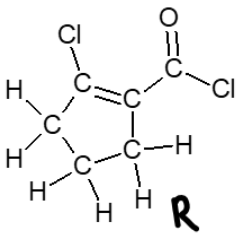
and



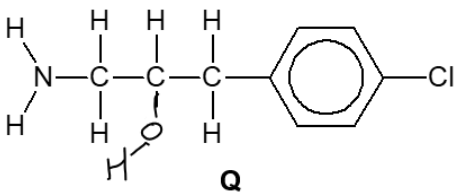
*remember to check for acid-base reaction after hydrolysis

2.

(a)



R



Q

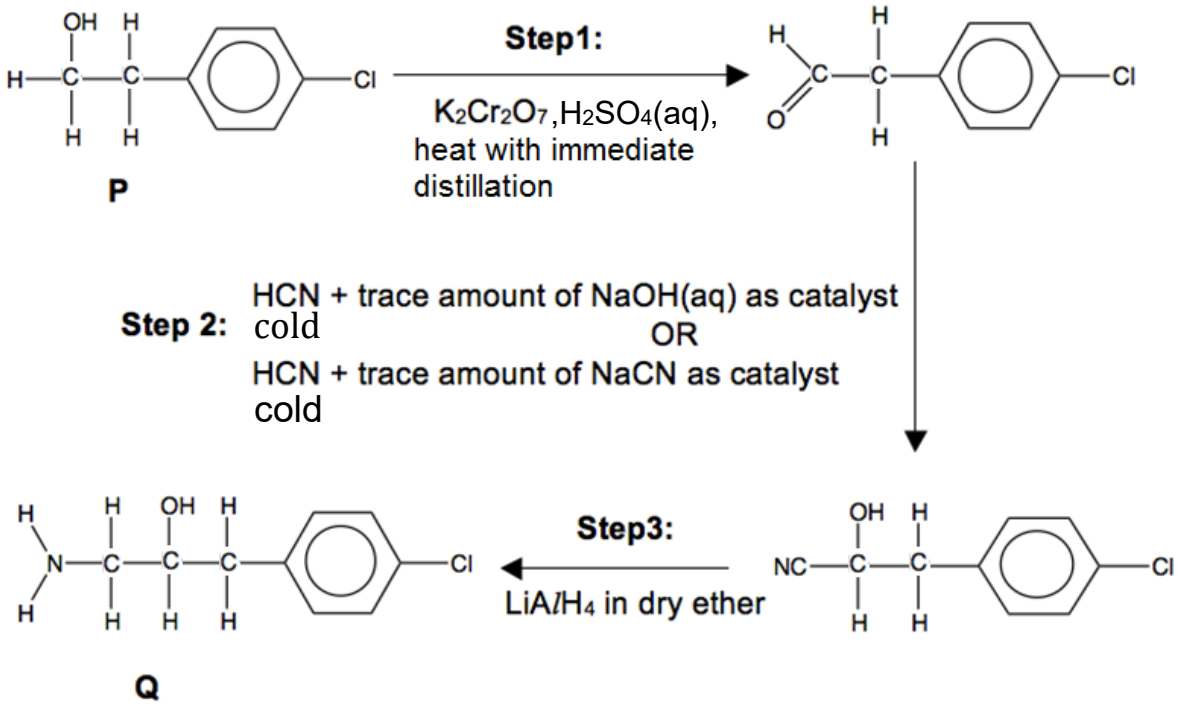
*Hydrolyse the amide, **S**, to deduce the structures of **R** and **Q**.

*Displayed formula shows all the bonds in the correct shape (i.e. trigonal planar, bent)

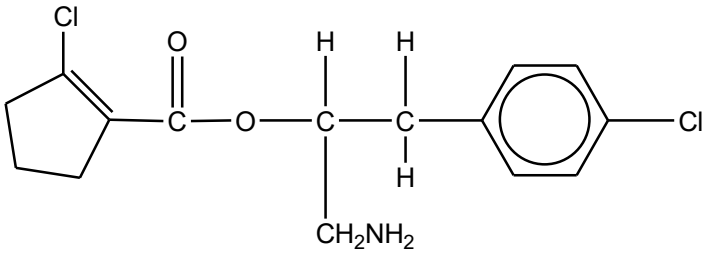
(b) Step **1**: Oxidation (of 1° alcohol to aldehyde) [controlled oxidation]

Step **2**: Nucleophilic addition (of HCN)

Step **3**: Reduction (of nitrile)

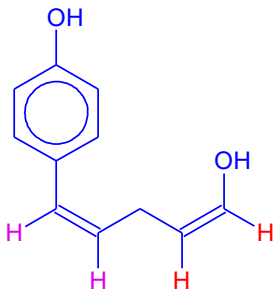
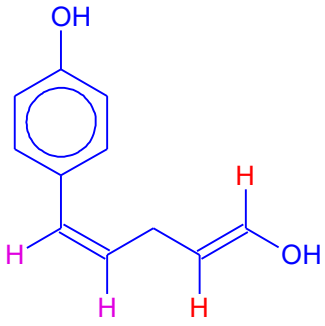


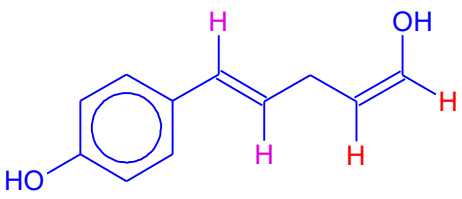
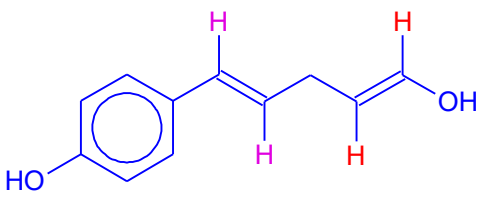
(c)



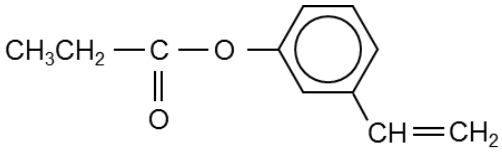
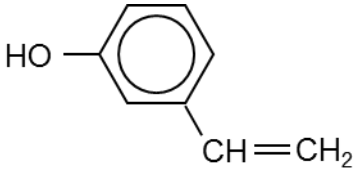
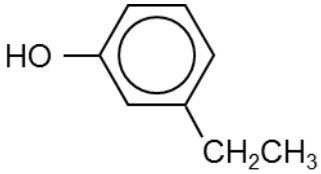
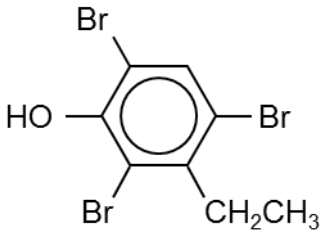
Acyl chloride, **R**, can undergo **<u>condensation</u>** reaction with alcohol in **Q** to form an **<u>ester</u>.**

3. (a) cis-trans isomerism

 cis, cis-	 cis, trans-

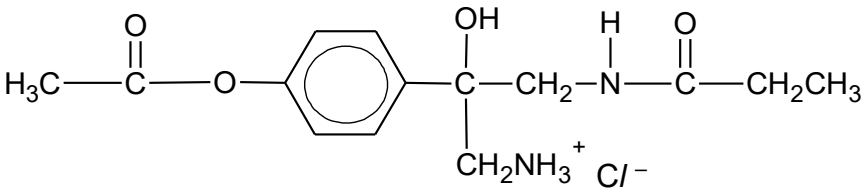
 trans,cis-	 trans,trans-

(b)

 **Q** ($C_{11}H_{12}O_2$) Ester – undergoes acidic hydrolysis with aq HC*l*	$CH_3CH_2CO_2H$ **R** ($C_3H_6O_2$)
 **S** (undergoes reduction of alkene to give **T**)	 **T** (Phenol undergoes electrophilic substitution with Br_2(aq) – multiple substitutions)
 **U** ($C_8H_7OBr_3$)	

4 (i) 1. *primary* amine (Need to state the type of amine to award mark)
2. *tertiary* alcohol (Need to state the type of alcohol to award mark)
3. amide
4. ester

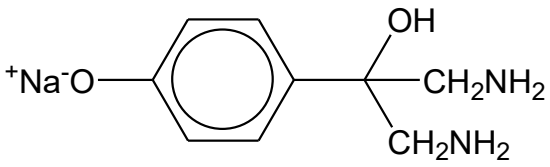
(ii) cold HC*l*(aq): only acid-base reaction takes place (ester & amide hydrolysis require heat)



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

CH_3CO_2Na

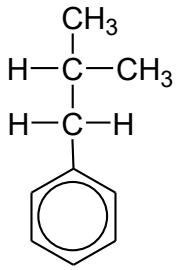
$CH_3CH_2CO_2Na$



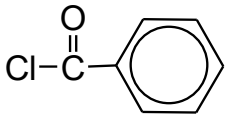
5 (i) A*l*Br_3 or $FeBr_3$ or A*l*$C\!l_3$ or $FeC\!l_3$, anhydrous

(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. A*l*Br_3) is necessary for the formation of the strong electrophile, $(CH_3)_2CHCH_2^+$.

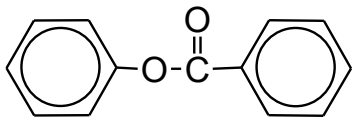
(iii)



S

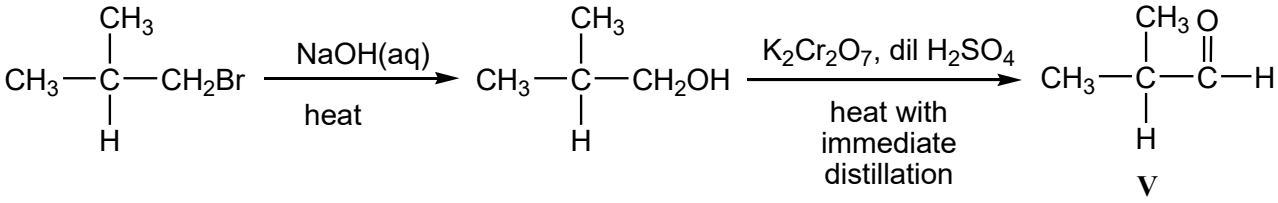


T



U

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



V

6 (a) Condensation (Nucleophilic acyl substitution)

(b) $CH_3CO_2CH_3 + CH_3CH_2OH \rightarrow CH_3CO_2CH_2CH_3 + CH_3OH$

To arrive the answer, follow the equation given: $RCO_2R' + R''OH \rightarrow RCO_2R'' + R'OH$

(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)

(f) $CH_3(CH_2)_5CH=CHCH_2CH_2CO_2CH_3$

$CH_2(OH)CH(OH)CH_2OH$

(g) Amt of HC*l* reacted = $1.00 \times 15.20 \times 10^{-3} = 0.0152$ mol

Total amt of $NH_3 = 1.00 \times 25.0 \times 10^{-3} = 0.0250$ mol

Amt of NH_3 that reacted with ester = 0.0250 – 0.0152 = 0.0098 mol = amt of ester

M_r of the ester = 1.00 / 0.0098 = 102.0

Thus, $15 + 12 + 32 + 14x + 15 = 102.0$

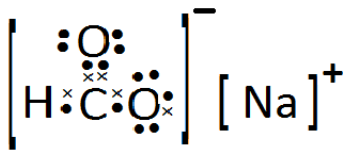
$x = 2$

7 (i) $CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

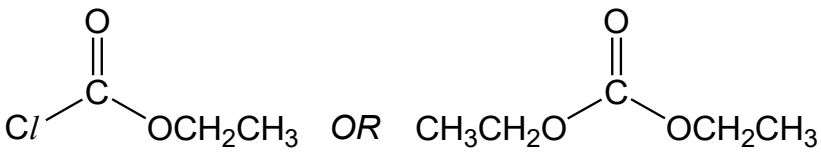
(ii) $CH_3CH_2OH + 4I_2 + 6NaOH \rightarrow HCO_2Na + CHI_3 + 5NaI + 5H_2O$

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

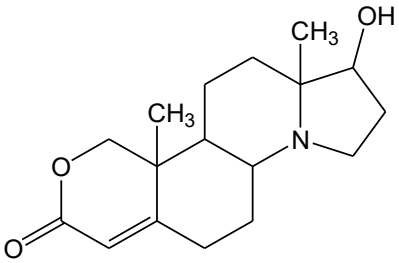
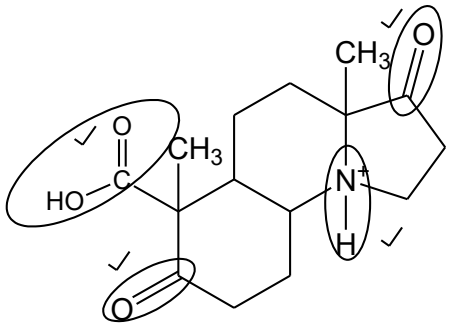
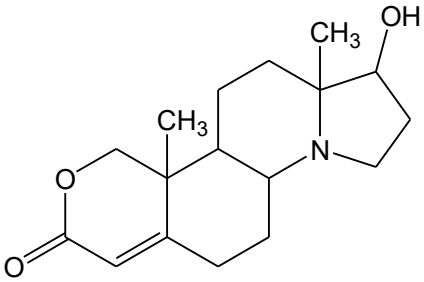
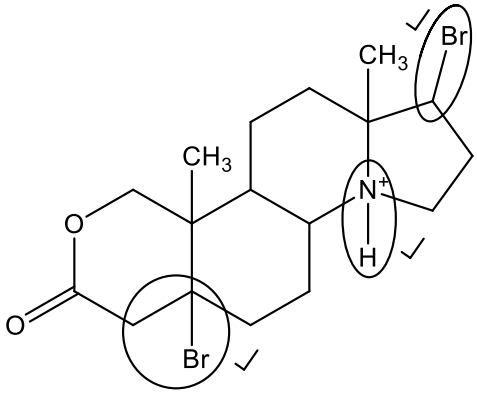
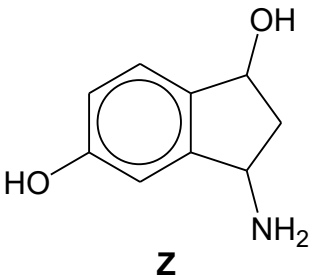
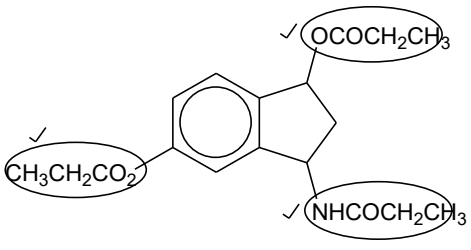
(iii)



(iv)



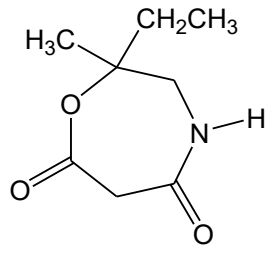
8

compound	reagent(s)	organic product
 **Y**	$KMnO_4$, dilute H_2SO_4 [O] of 2º alcohol, acid-base reaction of 3 º amine, oxidative cleavage of alkene, acidic hydrolysis of ester followed by [O] of its 1 º alcohol product)	
 **Y**	HBr(g), heat (N.S. of 2º alcohol, E.A. of alkene, acid-base reaction of 3º amine)	
 **Z**	propanoyl bromide (condensation of phenol, alcohol & amine with propanoyl bromide; yield of phenyl ester is enhanced if Na is used to convert phenol to phenoxide first)	

9 (i) Step **I**: H_3PO_4 catalyst, $H_2O(g)$

Step **III**: HCN with trace amount of NaCN or NaOH, cold

(ii)

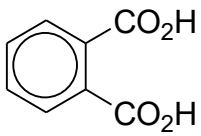
$CH_3COCH_2CH_3$ **B**	CH_2NH_2 / $CH_3CCH_2CH_3$ / OH **D**	 **E**

(iii) The electron deficient C centre in the carbonyl group is **sp^2 hybridised / the geometry about the carbonyl C is trigonal planar**. Hence, there is **equal probability for the $^-$CN** nucleophile to attack from **either side of the plane containing the C=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

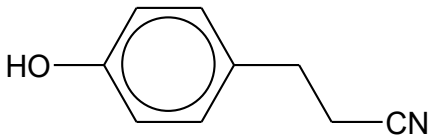
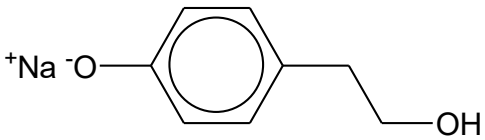
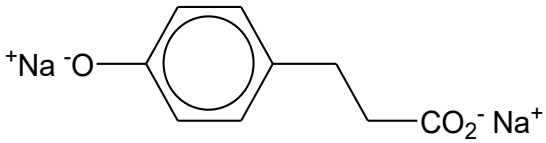
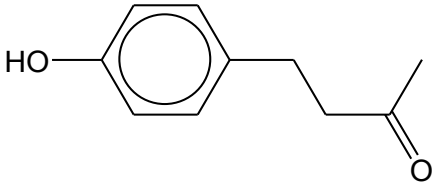
step 3: alkaline hydrolysis

(ii)



Since 1 mol of **X** reacts with exactly 1 mol of sodium carbonate => 1 mol of **X** contained 2 -COOH groups.

11(i)

 **A**	 **B**
 **C**	 **D**

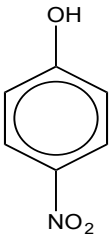
(ii) Step **I**: NaOH(aq)/KOH(aq); heat

Step **II**: H_2SO_4(aq), $K_2Cr_2O_7$(aq); heat with immediate distillation

Step **III**: NaOH/KOH in ethanol; heat

Step **IV**: I_2, NaOH(aq), warm

12(a)



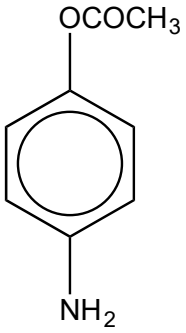
(-NO_2 must be substituted at the 4-position relative to phenol in order form the following products in the given reaction scheme)

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

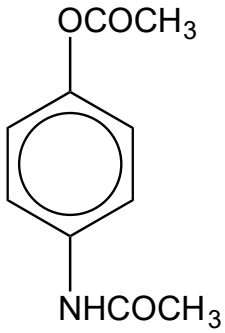
Stage 2: **NaOH(aq)** (to liberate phenylamine)

(c) (i) **CH_3COCl**

(ii)

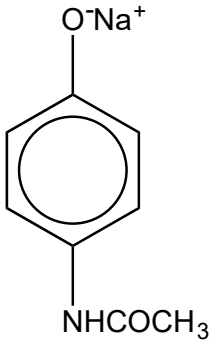


OR



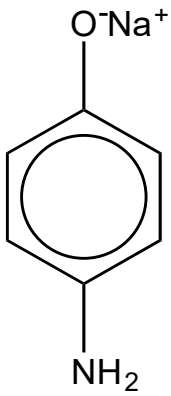
(consider condensation between phenol and acyl chloride)

(d) (i)



(acid-base reaction of phenol by aq NaOH)

(ii)



and $CH_3COO^-Na^+$

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

13

X	Y	Z
$CH_3CH_2CH_2OH$	**$CH_3CH_2CO_2H$**	**CH_3CHCl/CO_2H**

Reagents and conditions for conversion of **Y** to **Z**: limited **Cl_2(g), uv light**

14

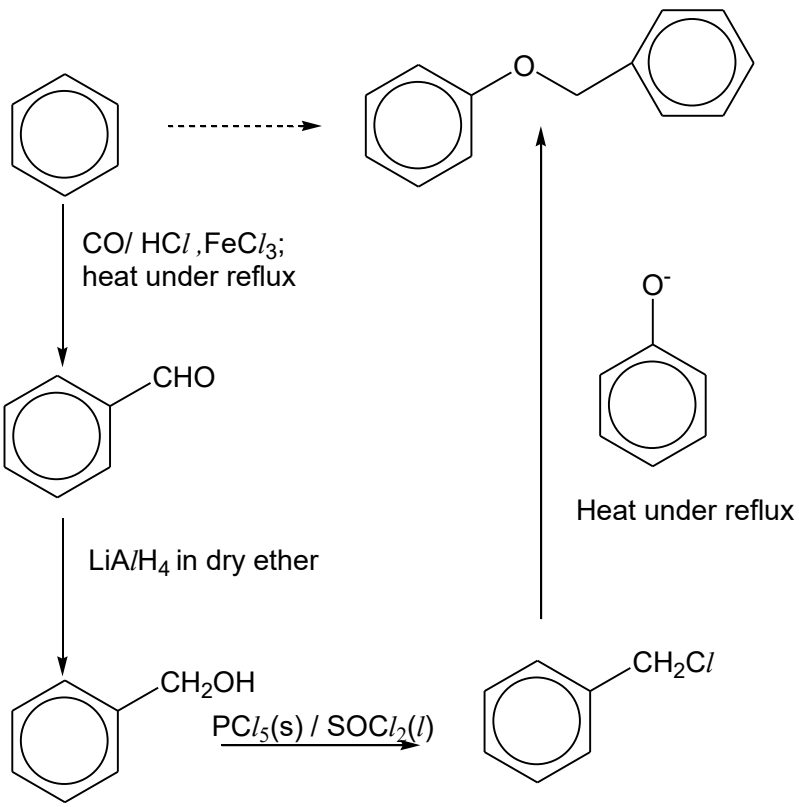
$$BrCH_2CH_2OH \xrightarrow[\text{heat under reflux}]{\text{ethanolic KCN}} NCCH_2CH_2OH \xrightarrow{LiAlH_4 \text{ in dry ether}} H_2N\text{-}CH_2CH_2CH_2OH$$

15(a)(i) $CO + HCl + FeCl_3 \rightarrow {}^+CHO + FeCl_4^-$

(ii) $FeCl_3$ hydrolyses in water to yield $[Fe(H_2O)_5(OH)]^{2+}$ and Cl^- ions /$FeCl_3$dissolve in water to form $[Fe(H_2O)_6]^{3+}$.

Fe in $[Fe(H_2O)_5(OH)]^{2+}$ or Fe in $[Fe(H_2O)_6]^{3+}$ has no more vacant orbitals in the valence shell to accept the lone electron pair from Cl^- to generate the strong electrophile.

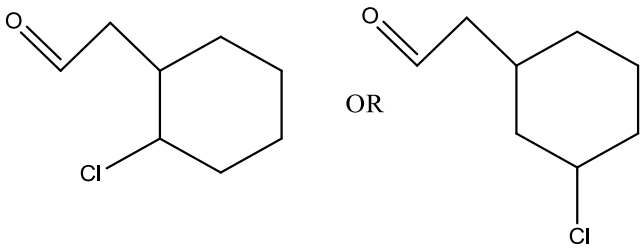
(b)



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

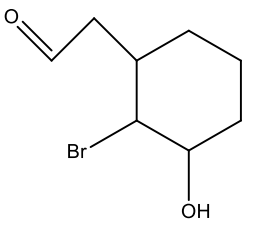
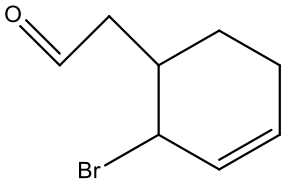
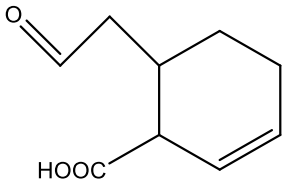
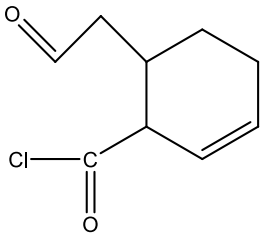
16(a)(i) HCl (g) + $BaSO_4$

(ii)



(E.A. of alkene with HCl)

(b)

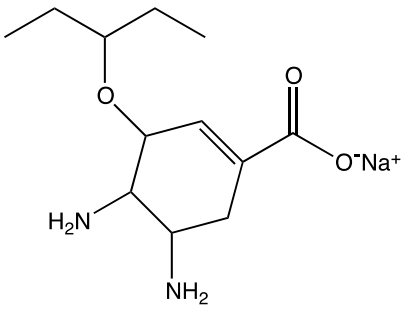
Step	Reagents and conditions
I	Br_2(aq) (E.A. of alkene)
II	Ethanolic KCN; heat (N.S. of -Br with -CN)
III	Aqueous H_2SO_4; heat (acidic hydrolysis of nitrile)
IV	Anhydrous PCl_5 or $SOCl_2$ or PCl_3
 A	 B
 C	 D

Note: Step1 must be E.A. of Br_2(aq) in order for N.S (of -Br by -CN) & elimination (of H_2O by hot alumina) to take place in the subsequent steps)

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

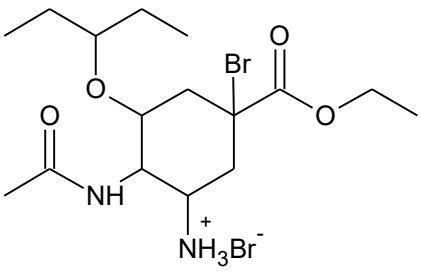
(ii) To increase its solubility (ion-dipole interactions with water) so that it is more easily absorbed by the body.

(iii) Alkaline Hydrolysis

(iv) 

, $CH_3COO^-Na^+$ and CH_3CH_2OH

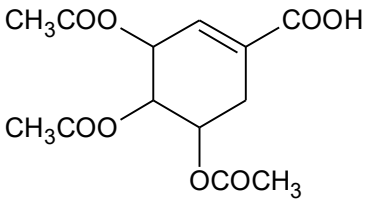
(v)



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

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

(ii)

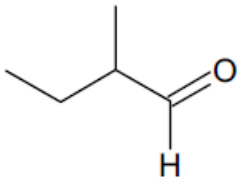


18 (i) Nucleophile

(ii) $CH_2(OH)(NH_2)$

(iii) HCN

(iv)



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) $CH_3CH_2I + Mg \rightarrow CH_3CH_2MgI$

$$amt\ of\ Mg\ = amt\ of\ CH_3CH_2I\ = \frac{1.50}{24.3} = 0.06173\ mol$$

$$Vol\ of\ CH_3CH_2I = \frac{mass}{density} = \frac{0.06173 \times 156}{1.93} = 4.99\ cm^3$$

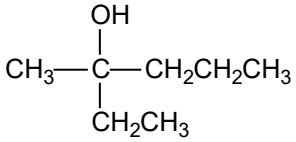
(iv) Amt of grignard reagent produced in step II = 0.06173 mol

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

< 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

(v)



(vi) CH_3CH_3 (ethane)

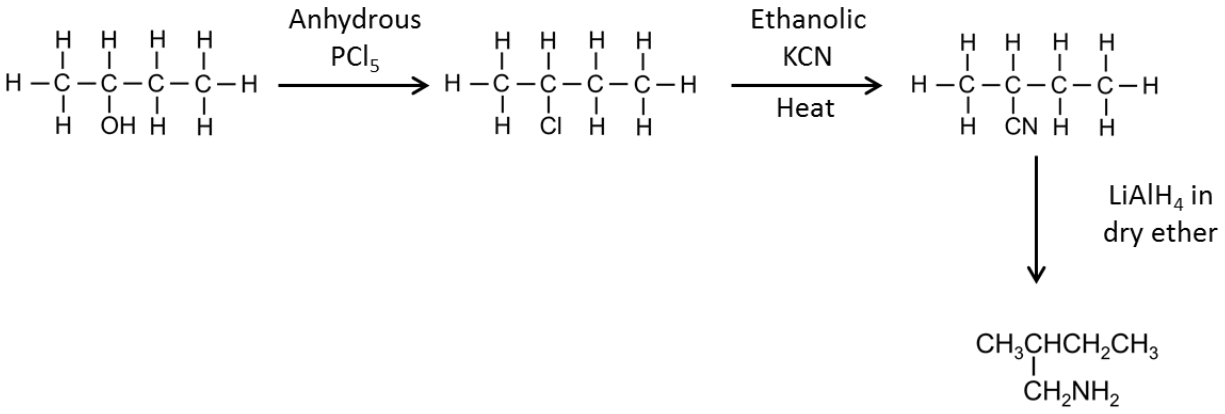
(vii) Ethoxyethane forms an *immiscilble layer above* the aqueous layer because of:

- 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 g cm^{-3} as against 1 g cm^{-3})

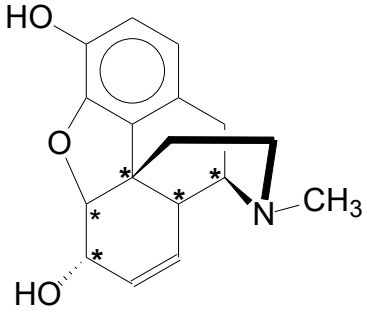
(viii)

Chemicals added	Impurity removed
1. water	Mg salts e.g. MgI_2 / Mg(OH)Br
2. saturated sodium hydrogencarbonate	HC*l*
3. sodium thiosulfate	iodine
4. saturated sodium chloride	H_2O

19 (c)



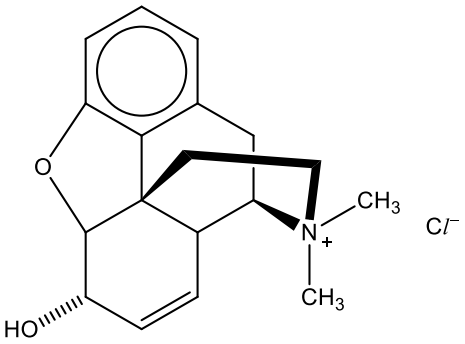
20 (i)



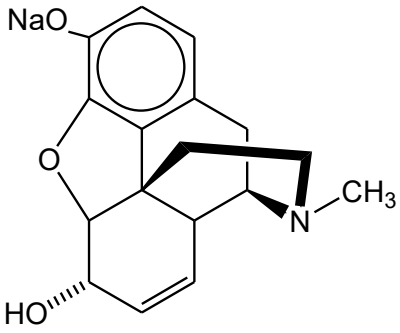
5 chiral carbon atoms

morphine

(ii)

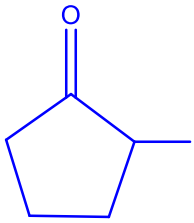


(iii)

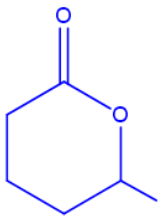


CH_3COONa and

21 **L:**



M:



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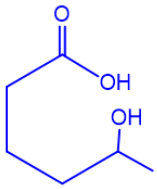

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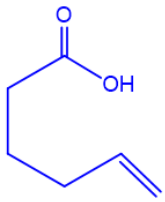
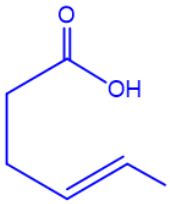


O:



22 (i) Secondary alcohol; alkene

(ii) Step **III**: $KMnO_4$(aq), NaOH(aq); heat (alkaline medium to form -COONa)
Step **IV**: I_2, NaOH(aq); heat

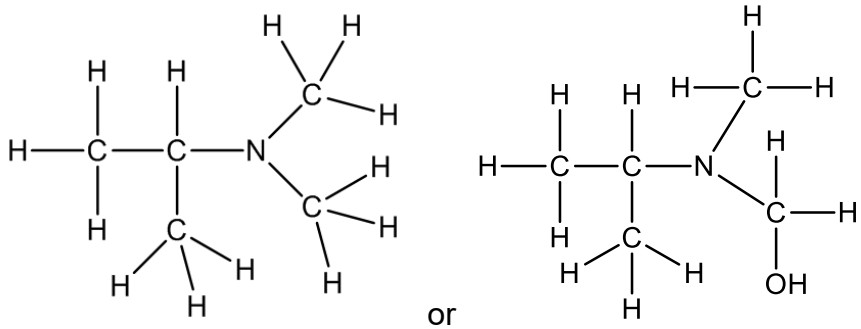
(iii) Secondary **alcohol**

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_b 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)

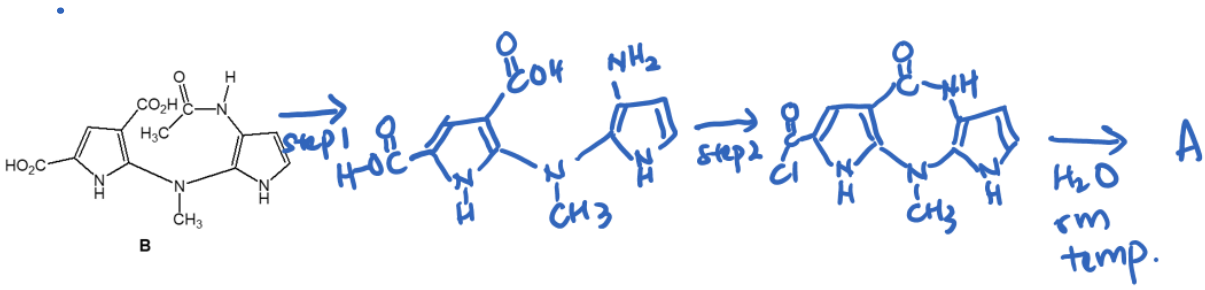


or

(iii) For phenylamine, **lone pair on N is delocalised into** the π 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**.

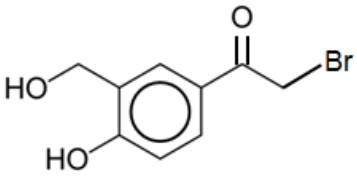
24.

Step	Reagents and conditions
1	dil HC*l*, (or dil HNO_3 or dil H_2SO_4) heat; followed by dil NaOH (to deprotonate the amine)
2	PCl_5(s), anhydrous (or PCl_3 , $SOCl_2$, anhydrous) (-COOH group becomes -COCl to react with amine via condensation)
3	Water (hydrolysis of -COCl)

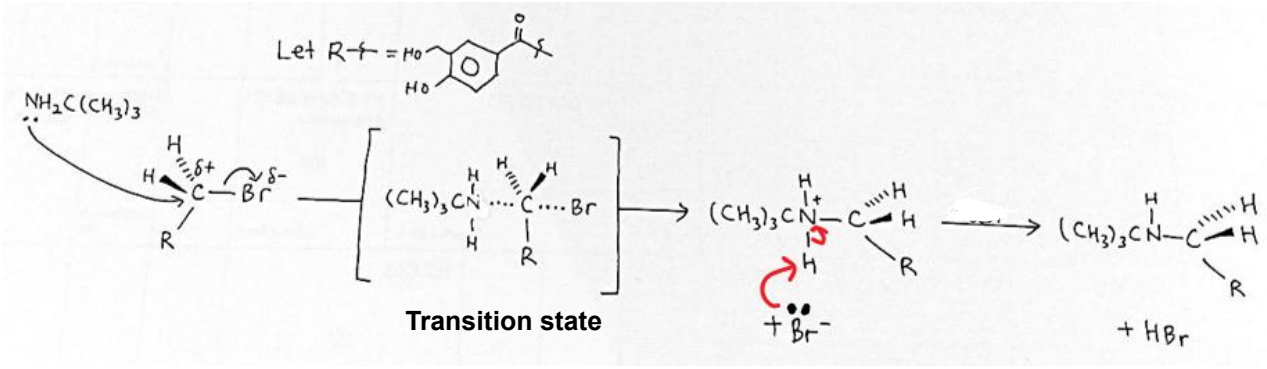


25(a) There is a possibility of many side products as random substitution of hydrogen atoms on any alkyl group found in the compound can occur via free radical substitution..

(b) Nucleophilic substitution

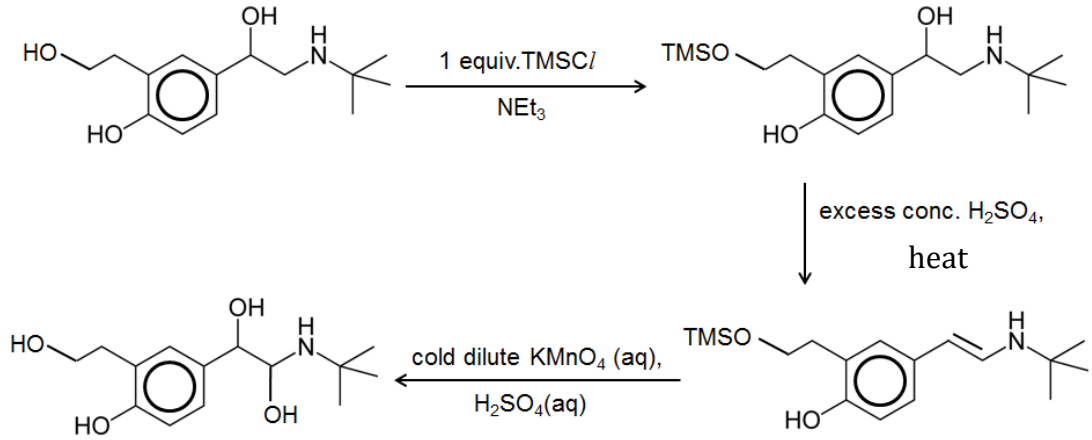


Cannot react via S_N1 mechanism as the carbocation formed will be destabilised by the electron-withdrawing effect of the adjacent C=O.
Thus, it undergoes the S_N2 mechanism instead.



(c) H^- from $LiAlH_4$ readily reacts with partial positive H of water.

(d)



(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) $H_2O(g)$ can escape, thus shifting the position of equilibrium to the right to partially offset the loss of water, thus forming more ester.

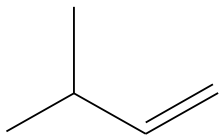
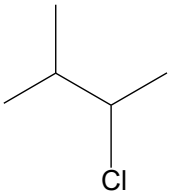
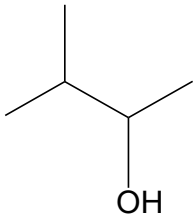
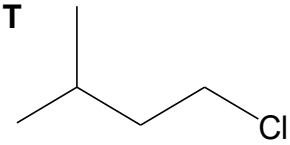
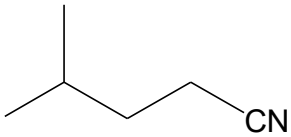
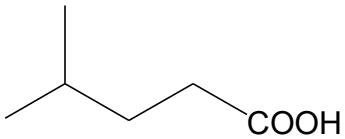
(iv) To react with the unreacted ethanoic acid.

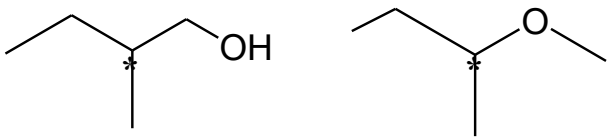
(v) To allow CO_2 to escape, preventing the build-up of pressure in the separating funnel.

(b)(i)

Step I	concentrated H_3PO_4, heat
Step II	NaOH (aq); heat
Step III	Ethanolic KCN; heat
Step IV	H_2SO_4(aq); heat

(ii)

Q 	**R** 	**S** 
T 	**U** 	**V** 

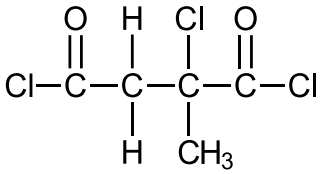
(iii) 

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

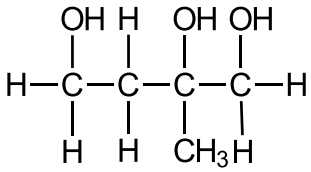
(ii)

	Reagents and Conditions
Stage **I**	HC*l*(g), room temperature
Stage **II**	NaOH(aq), heat, followed by H_2SO_4(aq) (to protonate $-COO^-$ to $-COOH$)
Stage **III**	PCl_5(s), anhydrous

(iii)



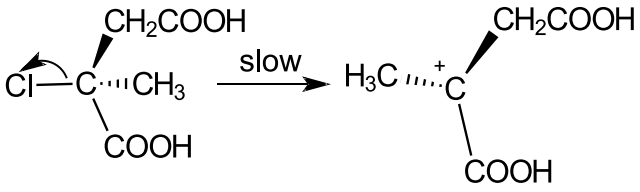
K



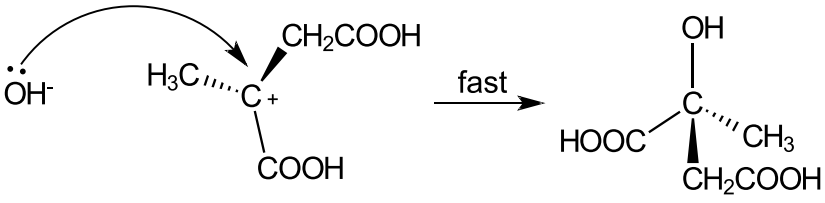
L

(iv) Name of mechanism: Nucleophilic substitution (S_N1)

Step 1:

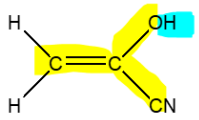


Step 2:

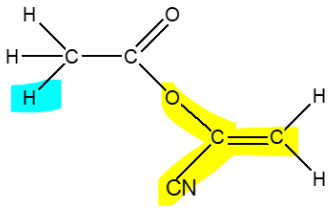


(v) Citramalic acid formed from Stage II is a racemic mixture, hence it is optically inactive.
The nucleophile, OH^- ion, can attack from either the top or bottom of the trigonal planar carbocation with equal probabilities, resulting in the formation of equal amount of each enantiomer.
Effect on plane-polarised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

28



Compound **E**

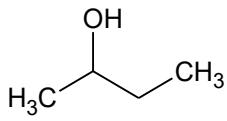
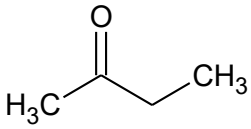
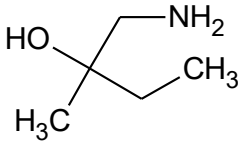
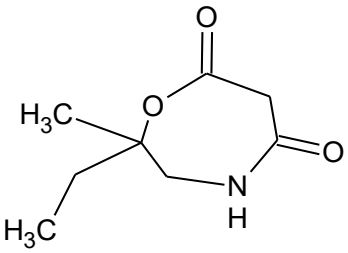


Compound **F**

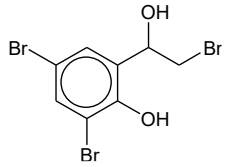
(in step 2, -OH of compound E act as nucleophile to attack the electron-deficient C in C=O of ketene)

29 (a) Step I: $H_2O(g)$, H_3PO_4 catalyst
Step II: $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat under reflux OR $H_2SO_4(aq)$, $KMnO_4(aq)$, heat

(b)

A 	**B** 
D 	**E** 

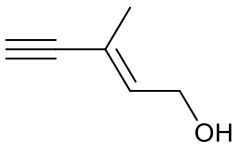
(c) The attacking nucleophile, ^-CN, can approach the trigonal planar carbonyl C from the top or bottom of the plane with equal probability hence resulting in a racemic mixture.

30 Step I: Electrophilic substitution of phenol with Br_2(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 ($^-$CN) which is in very low concentration as HCN is a weak acid & only dissociates partially.
Alternative method: Heat with ethanolic KCN/NaCN

Step V: Esterification between $–CO_2H$ 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 $–CO_2H$ as it is delocalized into the benzene ring.
Alternative method: Add anhydrous PCl_5 / $SOCl_2$ to convert -COOH to -COCl and use NaOH to convert phenol to phenoxide.

31 (i) 

(ii) Reduction

(iii) Palladium is a <u>heterogeneous catalyst</u> in this reaction. <u>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.</u>

(iv) H_2/Ni will cause <u>all the double bonds</u> (and triple bond) <u>to be reduced.</u>

32 **I:** Methanol → Methanal

Reagents and conditions: **$K_2Cr_2O_7$, dil. H_2SO_4, heat with distillation**

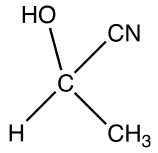
II: Methanol → Methanoic acid

Reagents and conditions: **$K_2Cr_2O_7$, dil. H_2SO_4, heat under reflux (cannot use $KMnO_4$, dil. H_2SO_4, heat, HCOOH will be oxidized to CO_2, see III below)**

III: Methanol → Carbon dioxide

Reagents and conditions: **$KMnO_4$, dil. H_2SO_4, heat under reflux**

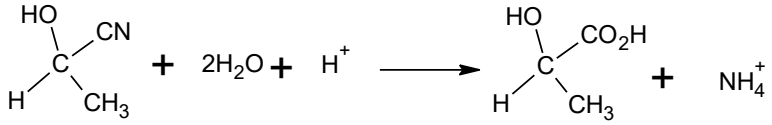
33 (i)

CH_3CH_2OH Compound **A**	 Compound **B**

(ii) Reagents and conditions: NaOH(aq); heat

(iii) Type of reaction: **Acidic Hydrolysis**

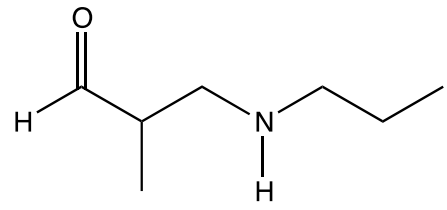
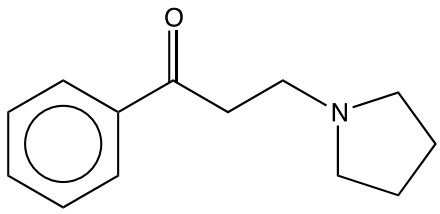
Balanced equation:



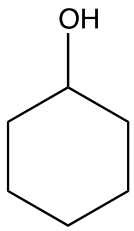
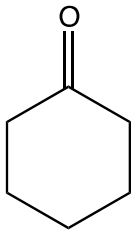
(iv) Carbonyl carbon is trigonal planar and the ^{-}CN nucleophile can attack the carbonyl carbon from top and bottom of the plane with equal probability, forming equal amount of each optical isomers, resulting in a racemic mixture.

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)

 **V**	 **W**

(b)(i)

 **X**	 **Y**

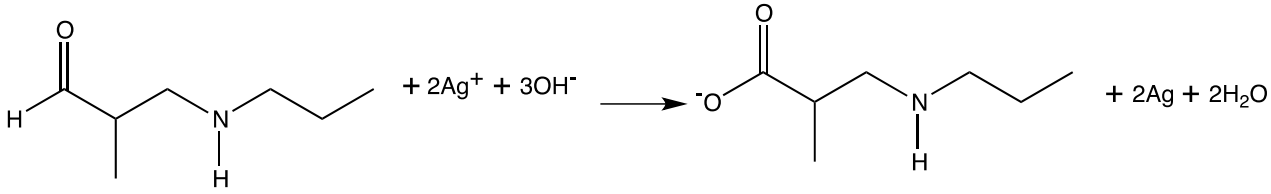
(b)(ii) **I** Aqueous NaOH, heat;

II $KMnO_4(aq)$, $H_2SO_4(aq)$, heat or $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat

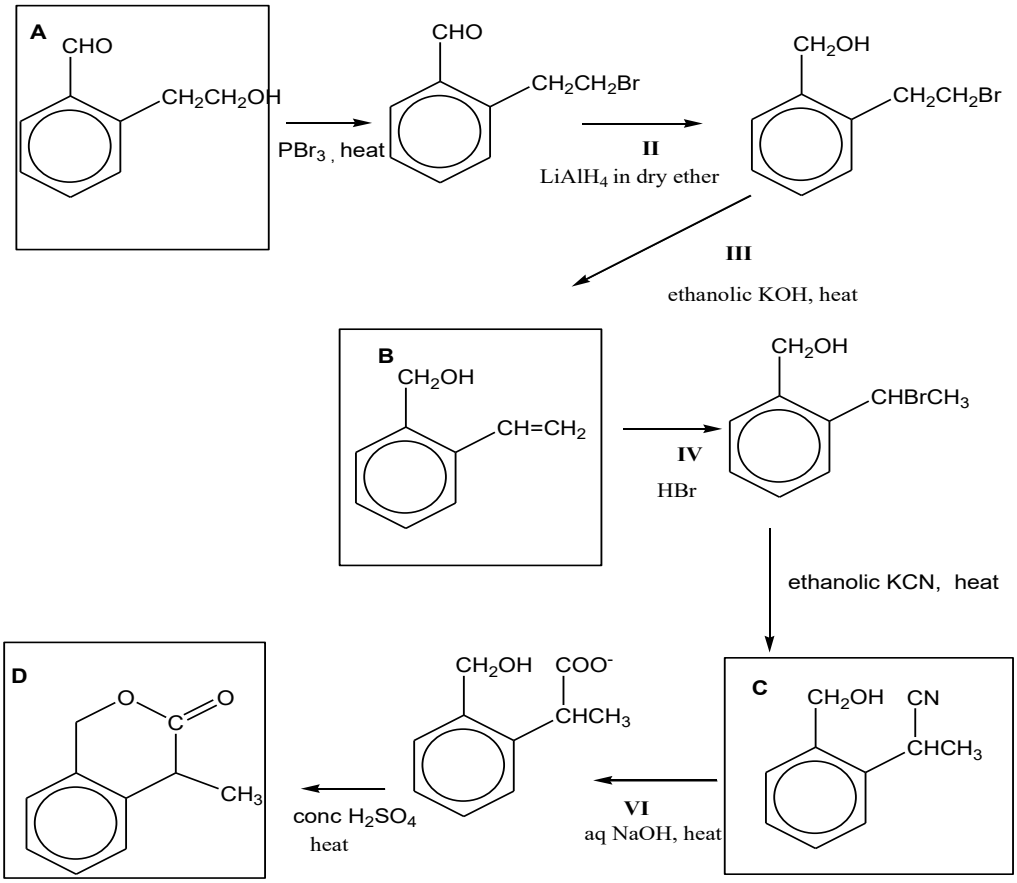
(c)(i) White ppt: AgCl, Complex: $[Ag(NH_3)_2]^+$

(ii) **Z** is Tollen's reagent.

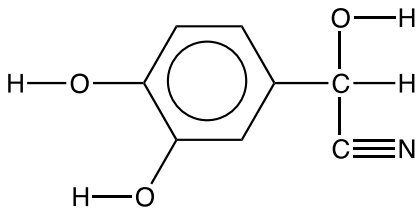
V will give a **V** gives a silver mirror. **W** will not give a silver mirror.



35



36 (i)



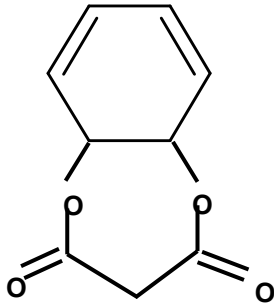
(ii) Step **I**: HCN, trace amount of NaCN, cold

Step **II**: LiA/H_4 in dry ether or H_2, Ni

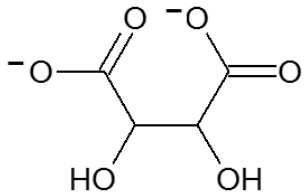
Step **III**: CH_3Br; heat (Nucleophilic Substitution)

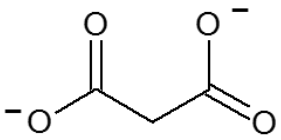
37 **(i)** $LiAlH_4$ in dry ether, room temperature

(ii) **B:**

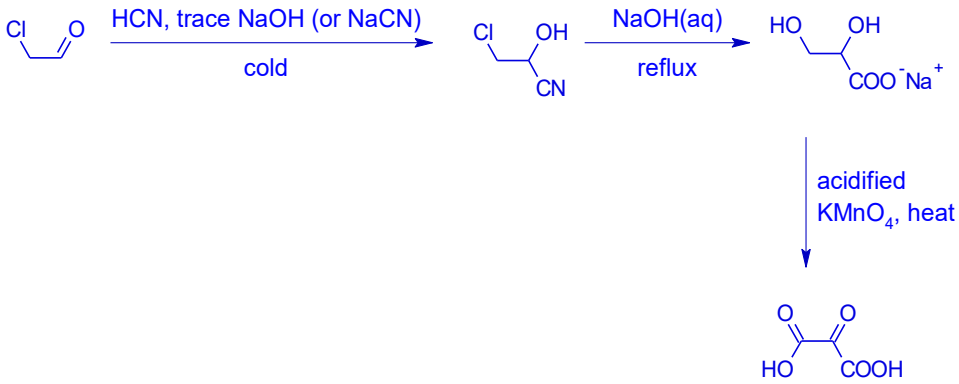


D & E:

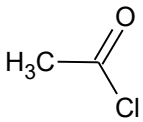


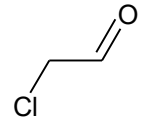


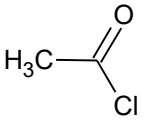
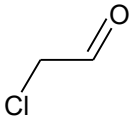
(iii)



(iv)

The δ+ carbon atom in  is bonded to 2 very electronegative atoms (O and C*l*), thus making the carbon atom highly electron-deficient (δ+).

Whereas the δ+ carbon atom is less electron-deficient  as it is only bonded to one electronegative atom (C*l*).

Since the <u>more electron deficient</u> (δ+) the carbon atom, the <u>easier</u> 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_2**

Observations: For **B**: **White precipitate** is formed and **orange Br_2 is decolourised.**

For **A**: No white precipitate and orange aq Br_2 not decolourised.

2 (i) Add dilute sulfuric acid and $KMnO_4$ to separate test tubes of the esters and warm.

Only methyl ethanoate would decolorise purple $KMnO_4$ 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_2 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_3(aq)**, followed by adding **$AgNO_3$(aq)**.

Observation: $CH_3SCH_2CH_2Cl$ gave a **white ppt** of AgCl, but no ppt with $CH_3SCH_2CH_2OH$.

Alternative:

Tests which gave a positive observation with the alcohol:

Na metal. Effervescence observed with $CH_3SCH_2CH_2OH$ (gas that extinguishes a lighted splint with a 'pop' sound) but no effervescence observed with $CH_3SCH_2CH_2Cl$.

$K_2Cr_2O_7$(aq), H_2SO_4(aq); heat. $CH_3SCH_2CH_2OH$ turned orange dichromate(VI) to green, but orange remains with $CH_3SCH_2CH_2Cl$.

$KMnO_4$(aq), H_2SO_4(aq); heat. $CH_3SCH_2CH_2OH$ decolourised purple $KMnO_4$, but purple remains with $CH_3SCH_2CH_2Cl$.

Anhydrous PCl_5 or $SOCl_2$; $CH_3SCH_2CH_2OH$ gave white fumes of HCl, but no white fumes with $CH_3SCH_2CH_2Cl$.

4 warm with H_2SO_4(aq), $KMnO_4$ and test the gas evolved with limewater.

But-1-ene would turn purple $KMnO_4$ colourless and gives effervescence (a gas that forms a white ppt with limewater) while but-2-ene would turn purple $KMnO_4$ colourless but no effervescence.

5 Aqueous NaOH; heat. Acidify with *excess* dilute HNO_3, followed by adding aqueous $AgNO_3$.

Cream precipitate of AgBr would be observed for $BrCH_2CH_2OH$ but no precipitate would be observed with $HOCH_2CH_2OH$.

6 **Reagent/condition:** H_2SO_4(aq), $K_2Cr_2O_7$, heat

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

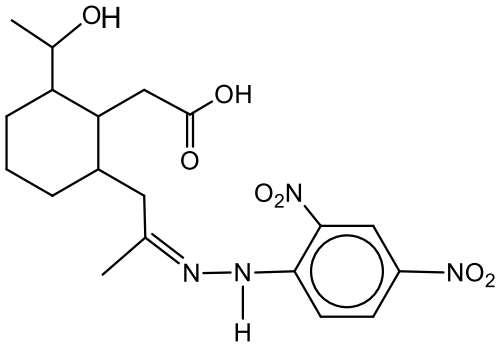
7 $Br_2(aq)$ ** exclusive test for phenol and its derivatives

Morphine: orange solution decolourised and white ppt formed

Codeine: orange solution remains

8 Test: 2,4-dinitrophenylhydrazine

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



9 Test: warm with HC*l*(aq), followed by $Br_2(aq)$.

Observations: orange Br_2 decolourises for aspirin but not for **X**.

**warming with HC*l* allows the ester to undergo hydrolysis, positive observation is for the phenol obtained

10 **Reagents and conditions:** NaOH(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 CCl_4 (in the dark) / aqueous bromine

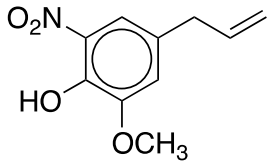
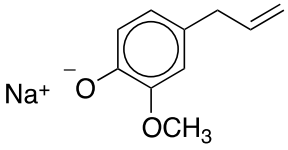
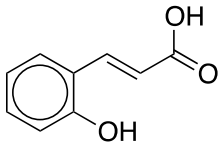
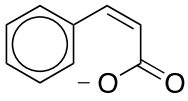
Observations: Tryptophan: orange red bromine turns colourless / orange aq bromine turns colourless. Asparagine: orange red or orange solution remains.

OR

Reagents and conditions: $H_2SO_4(aq)$, $KMnO_4$; 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 HNO_3	D	
Na	D	
dilute H_2SO_4; heat	A	
Fehling's reagent, warm	B	

12 Any one of the following tests and observations:

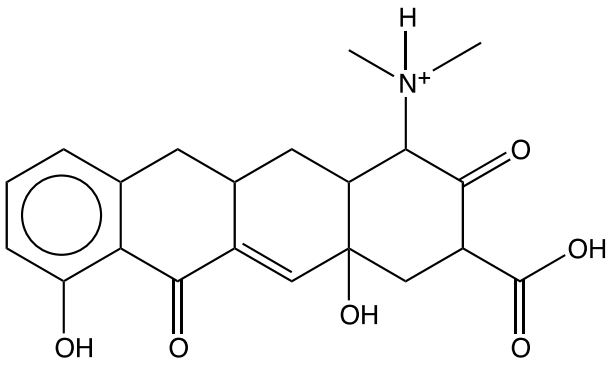
1) Add Na_2CO_3(aq)

Observation: Effervescence of CO_2 that formed white precipitate with limewater observed for ibuprofen but no effervescence evolved for 2-methylpropylbenzene.

2) Add PCl_5(s) or $SOCl_2$(l) anhydrous

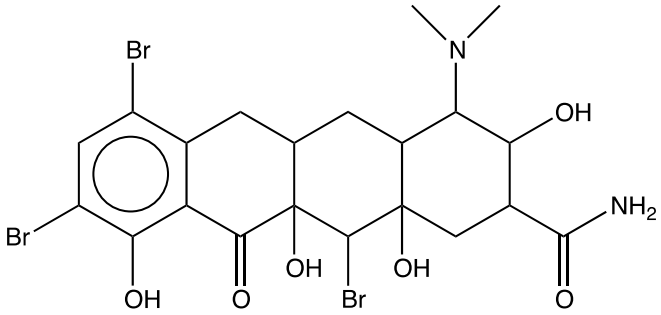
Observation: White fumes of HCl observed for ibuprofen but no fumes evolved for 2-methylpropylbenzene.

13(i)



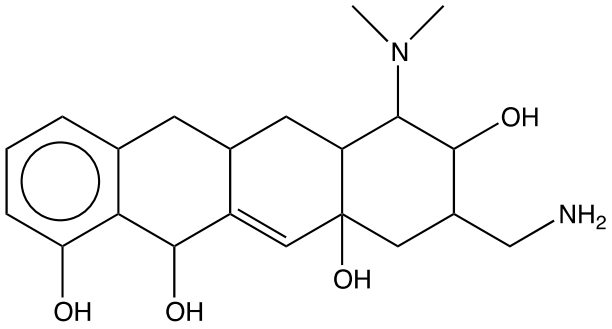
(oxidation of 2º alcohol)

(ii)



(Electrophilic Substitution of phenol, Electrophilic addition of alkene)

(iii)

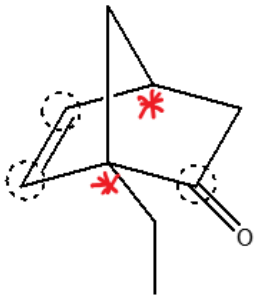


(Reduction of amide into amine)

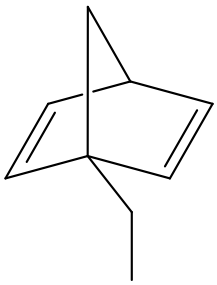
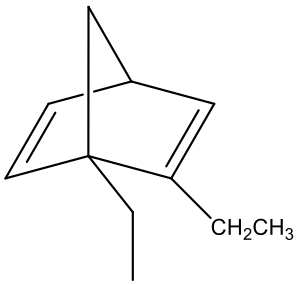
iv) Reagents and condition: cold dilute alkaline $KMnO_4$(aq)
M will decolourise purple $KMnO_4$, brown ppt of MnO_2 forms
N will not decolourise purple $KMnO_4$.

14(i) Number of chiral centers = 2

(ii)

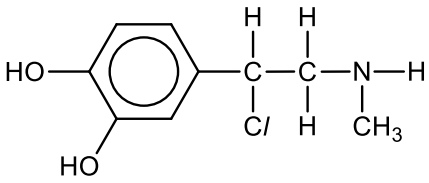


(iii)

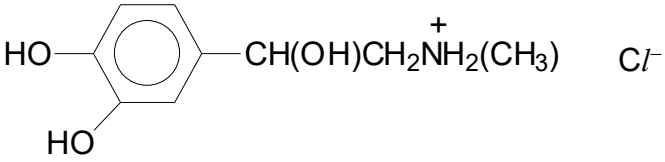
H_2O	Chloroethane
	

(iv) Reagents and conditions: $KMnO_4$, aq. H_2SO_4; warm
Observations: S decolourise purple $KMnO_4$ but purple $KMnO_4$ remains in R
*$K_2Cr_2O_7$ accepted
Note: Hydrolysis of the ester followed by reaction with the alcohol produced.

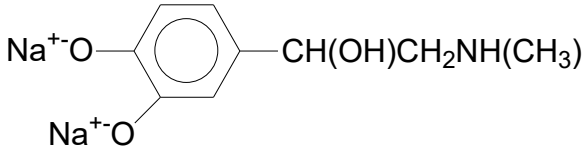
15(ai)



(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_5(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

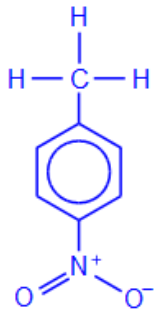
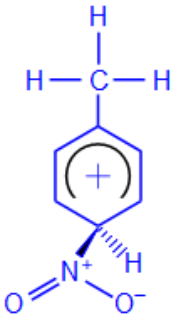
Observations for **C**: Yellow ppt of CHI_3 formed.

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

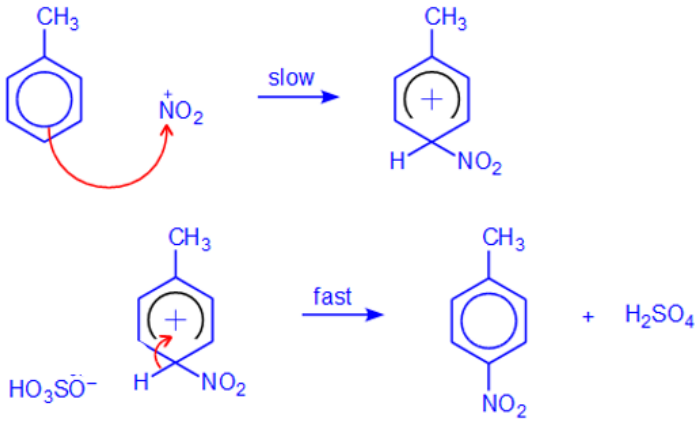
1 (a)

isomer **V**	*organic intermediate* **X**
	

(b) Electrophilic substitution

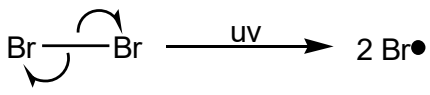
Mechanism:

$HNO_3 + H_2SO_4 \longrightarrow H_2O + {}^{+}NO_2 + HSO_4^-$

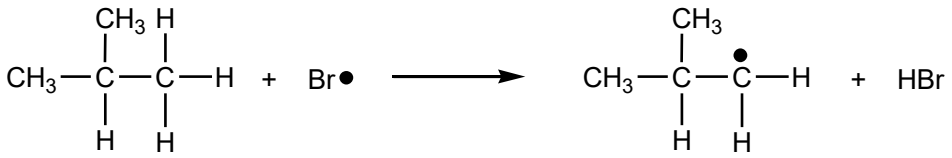


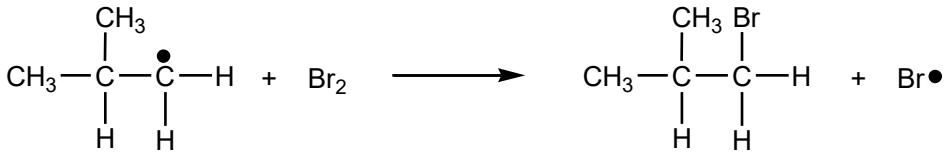
2 (i) Limited Br_2 (or excess 2-methylpropane) and ultraviolet light

Free radical substitution

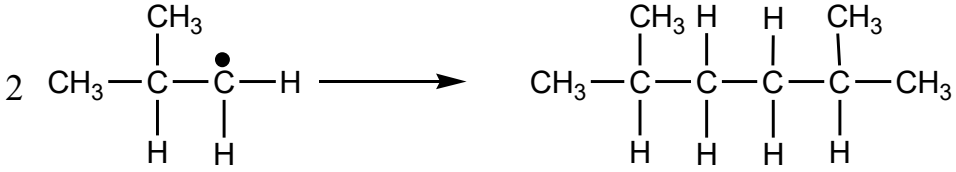
Initiation: 

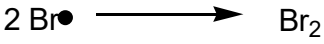
Propagation:





Termination:

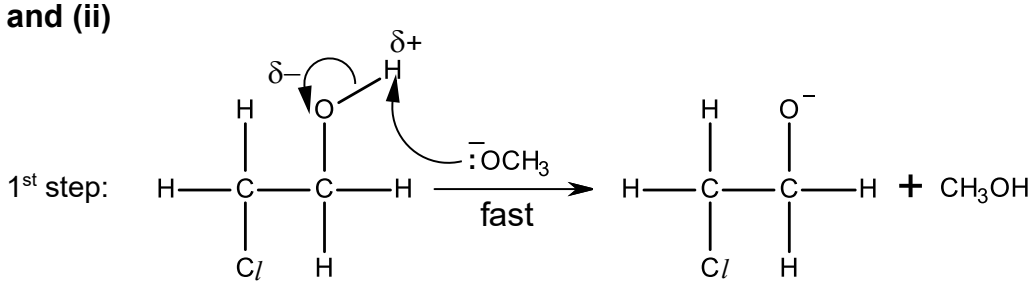


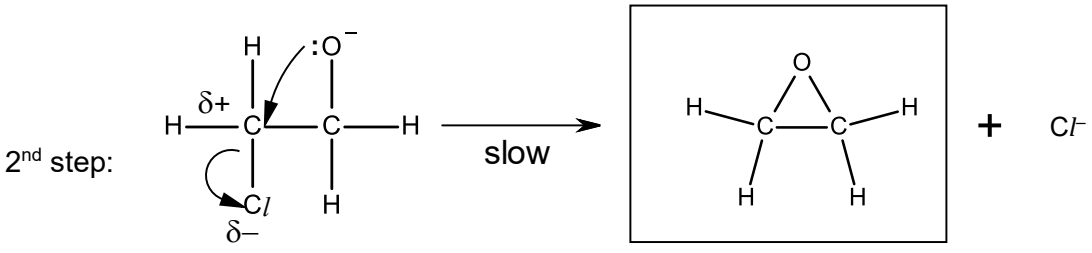


(iii) There are 9 primary H atoms available for substitution to form 1-bromo-2-methylpropane compared to 1 tertiary H atom to form 2-bromo-2-methylpropane.By equal probability of substitution, expected ratio of 1-bromo-2-methylpropane: 2-bromo-2-methylpropane is 9 : 1.

However, a tertiary radical, $\bullet C(CH_3)_3$, is more stable than a primary radical, $\bullet CH_2CH(CH_3)_2$. 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)





(iii) compound **W**

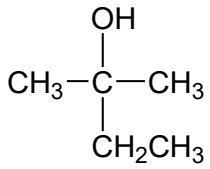
4(a)(i) Nucleophilic addition

(ii) Hydrolysis

(iii) There is <u>trigonal planar arrangement about the carbonyl carbon</u> which can be attacked by $CH_3CH_2^-$ nucleophile (from CH_3CH_2MgBr) either from the <u>top or bottom of the plane</u> with <u>equal probability</u>.

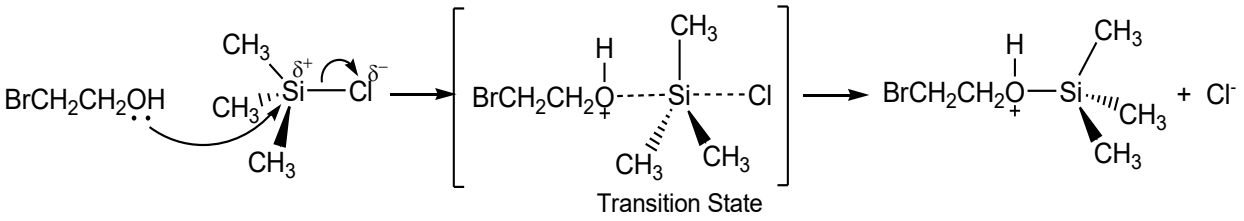
This leads to the formation of <u>1:1 ratio of the two enantiomers.</u>

(iv)



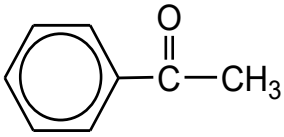
(b) The Grignard reagent cannot be prepared as it would react with the ketone group in the same molecule.

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



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

(iii)



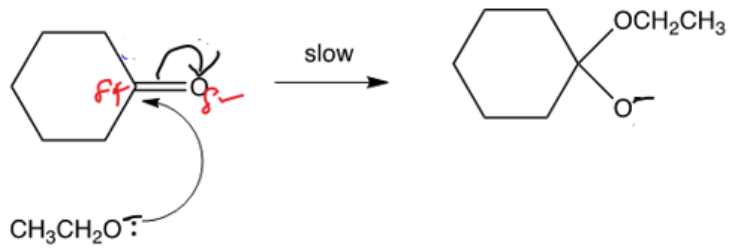
5 (a) Nucleophilic addition

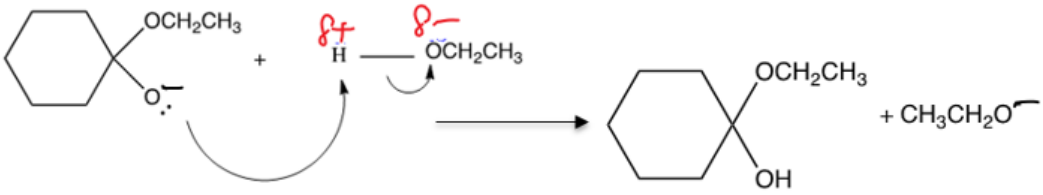
(b) OH^- will react with ethanol to generate a stronger nucleophile $CH_3CH_2O^-$.

(c) Nucleophilic addition

$CH_3CH_2OH + OH^- \longrightarrow CH_3CH_2O^- + H_2O$

$CH_3CH_2OH \rightleftharpoons CH_3CH_2O^- + H^+$

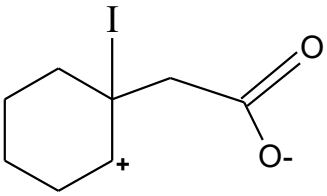




(d)

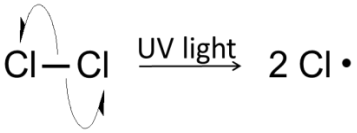
Calcium chloride is a drying agent, which help to remove water. Hence the position equilibrium will shift right to increase the yield of the product.

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



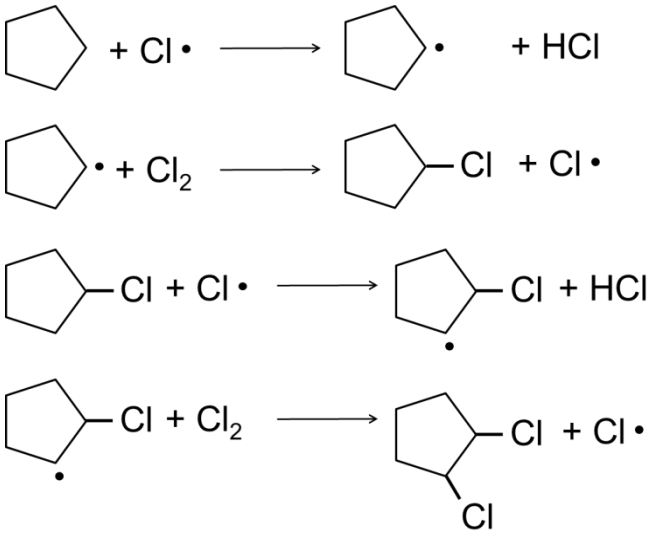
7 Free Radical Substitution

Initiation:



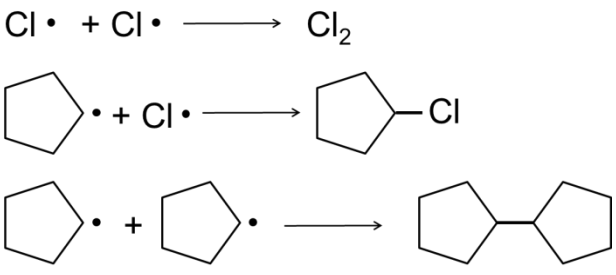
(*must use half arrows to show homolytic bond cleavage)

Propagation:



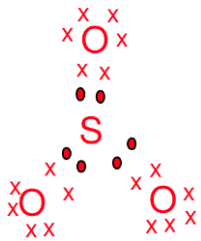
(*must show formation of $C_5H_8Cl_2$)

Termination:



(*any two possible termination steps)

8 (i)

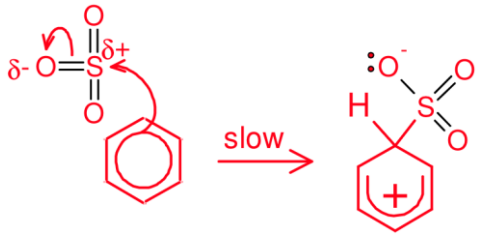


(ii) Electrophile

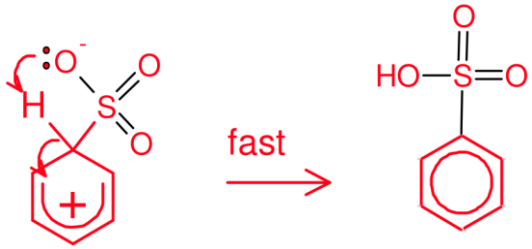
The three oxygen atoms are more electronegative than the sulfur and so draw electrons towards themselves. The sulfur atom is electron deficient and is attacked by the benzene ring.

(iii) Electrophilic Substitution

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

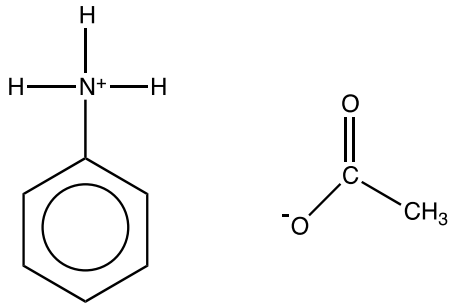


Step 3: Loss of proton to form the substitution product



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

9(a)(i)



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

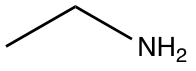
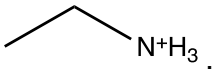
The acid will form hydrogen bonds with water molecules.

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

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

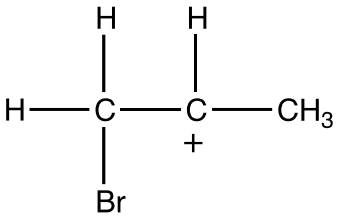
(iii) Add NaOH to hydrolysis products until moist litmus paper turns blue. Shake the reaction mixture with water in the separating funnel to isolate the acid in the aqueous medium, leaving behind the amine.

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,  is protonated to  .

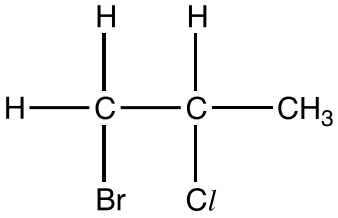
The lone pair on the nitrogen is not available for the nucleophilic substitution to form the quarternary amine salt.

(c)(i) Propene undergoes an electrophilic addition reaction with Br_2(aq) in conc. NaC*l*. The secondary carbocation is more stable than the primary carbocation as it has one more electron donating alkyl groups to disperse the postive charge of the carbocation.



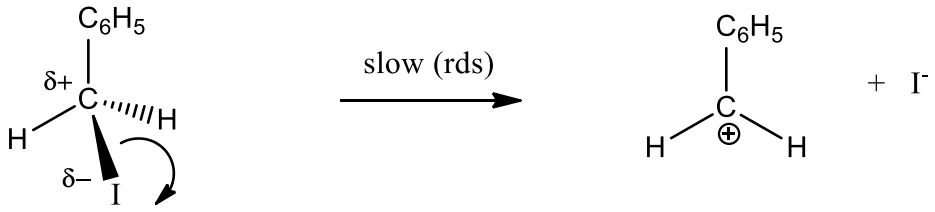
There is a high concentration of Cl^-, thus it will form a bond with the carbocation.

(ii)



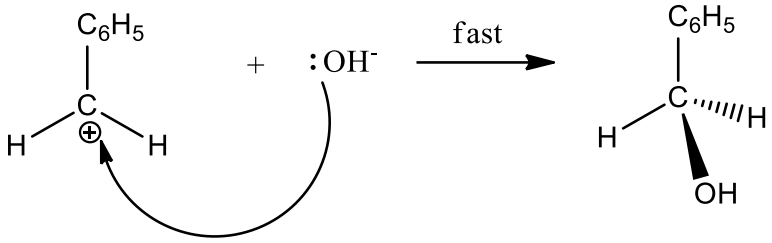
10 (i) Mechanism: Nucleophilic Substitution (S_N1)

Step 1: Formation of carbocation



trigonal planar carbocation intermediate

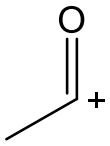
Step 2: Attack of OH^- nucleophile



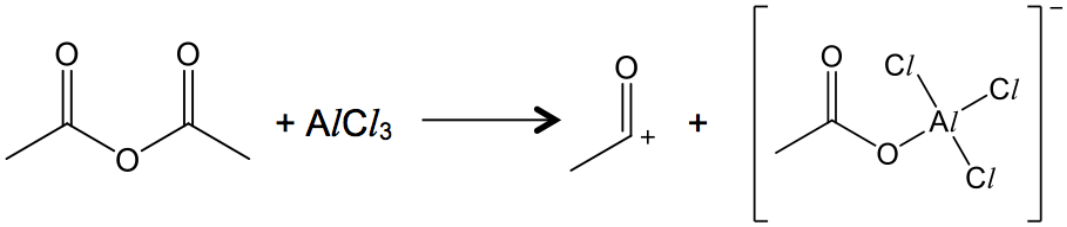
(ii) The **$C_6H_5CH_2^+$ carbocation** is **resonance-stabilised** as the **π electron from benzene ring can delocalise into the empty *p* orbital of the carbocation** dispersing the positive charge of the carbocation.

For $C_6H_5CH_2CH_2I$, the carbocation formed is a primary carbocation and it is not resonance-stabilised. Hence, the reaction proceeds by S_N2 mechanism instead.

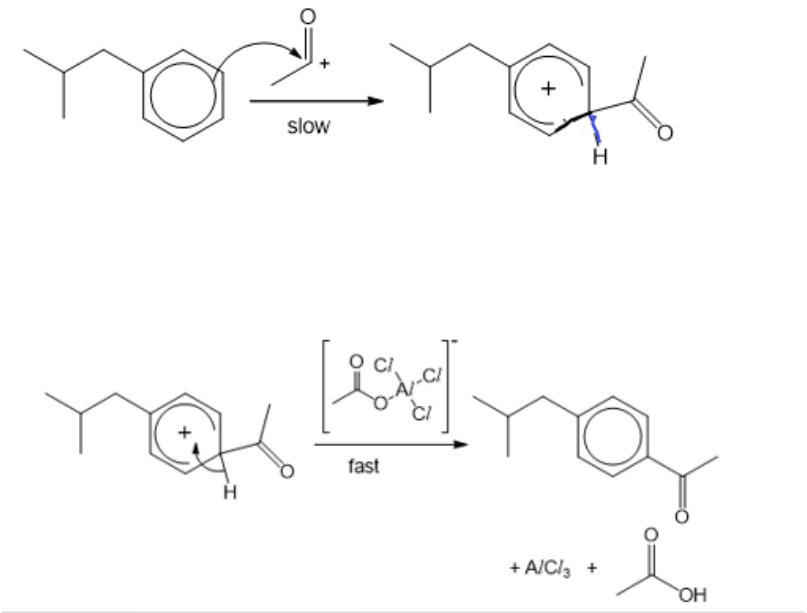
11(a)(i)



(ii)

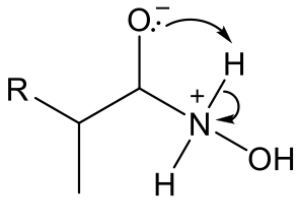


(iii)



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

(c)

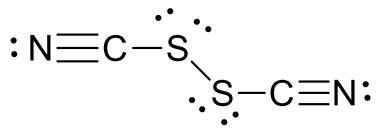


(d)(i) The solubility of ibuprofen lysine salt is higher so it is more easily absorbed by the body.

(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^o)

linear at CN

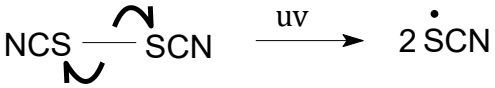
Lone pairs on N

Lone pairs on S

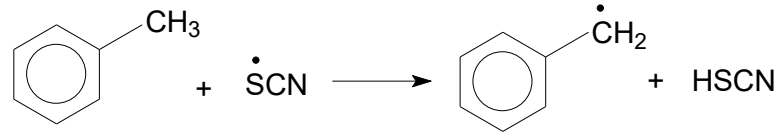
(iii) Thiocyanogen can be synthesised by reacting sodium thiocyanate, NaSCN, with chlorine gas. Write an equation for the formation of thiocyanogen.

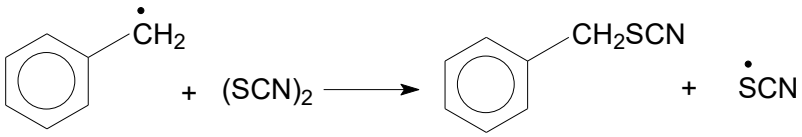
$2NaSCN + Cl_2 \rightarrow (SCN)_2 + 2NaCl$

(b)(i) Initiation

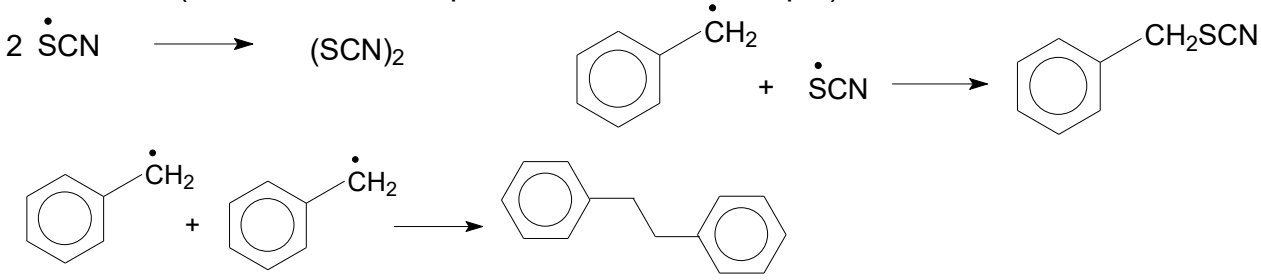


Propagation





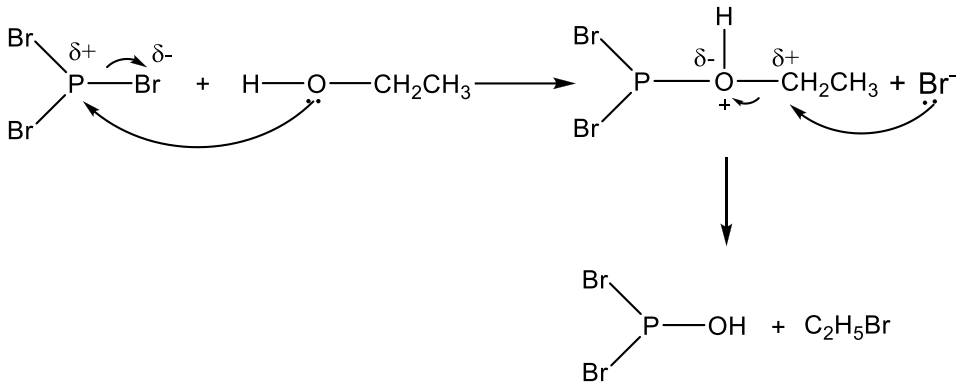
Termination (Write down all the possible termination steps.)



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

13 (i) Nucleophilic substitution

(ii)



(iii) To form $C(CH_3)_3Br$ 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 PBr_3.

(iv) CH_3COBr

14 (i) Step 1: $LiAlH_4$ in dry ether

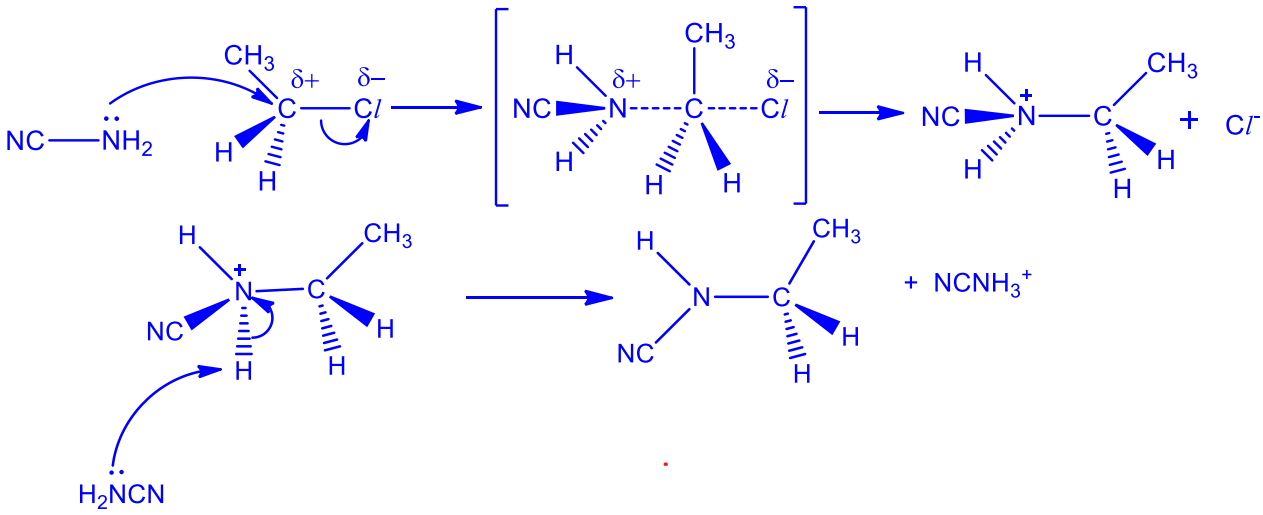
Step 2: NaOH in ethanol; heat

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

This is because in **B**, the C–C*l* bond has <u>partial double bond character</u> due to the <u>overlap of the p-orbital of C*l* with the p-orbitals of C=C, resulting in delocalisation of electrons.</u> Thus the C–C*l* bond in **B** is much stronger than C–C*l* in **A**, and is harder to hydrolyse.

15 (i)

Mechanism: Nucleophilic substitution reaction (S_N2)



(ii) Nucleophile and Base

(iii) Excess CH_3CH_2Cl

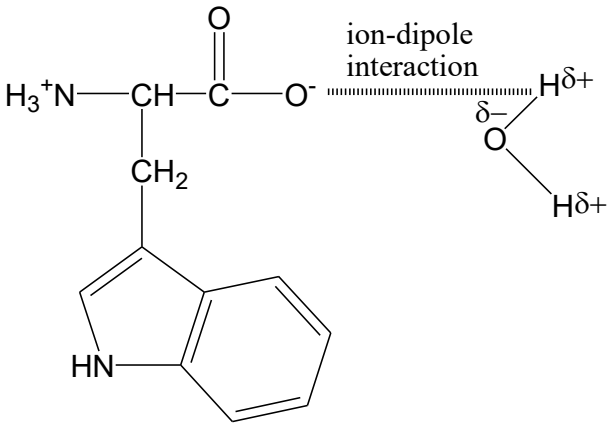
(b) The p-orbital of the chlorine atoms overlap with the π electron cloud of the benzene rings. The lone pair of electrons on each C*l* atom is delocalised into the benzene rings. This results in the C–C*l* bond having a partial double-bond character which makes the C–C*l* bond stronger and less ready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

The C of the C–C*l* bond also has a lower partial positive charge and is less susceptible to nucleophilic attacks. The π-electron cloud of the benzene ring will repel the lone pair of electrons of an incoming nucleophile, rendering attack of the nucleophile difficult.

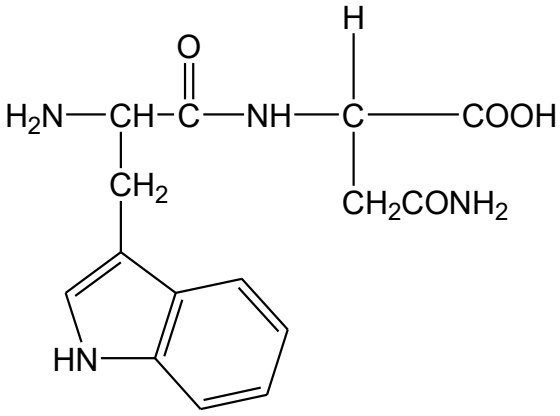
4) Amino Acids & Proteins

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.

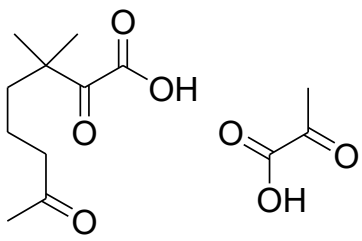
(ii)



(iii)



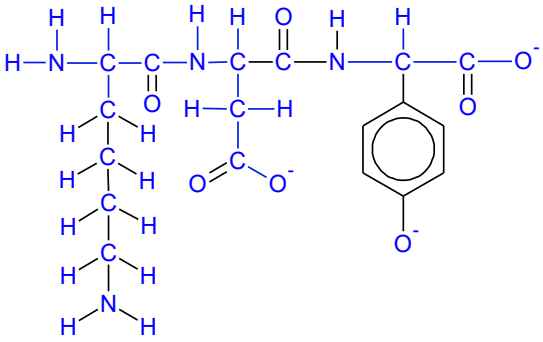
2 (i)



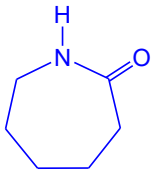
(ii) BCO is an enzyme and has a very specific action, in this case, to cleave only one of the C=C bond. There are many other C=C double bonds in *β*-carotene, which will all be cleaved using acidified $KMnO_4$ in the laboratory.

3(a) 7

(b)

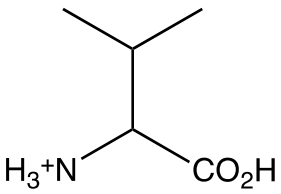


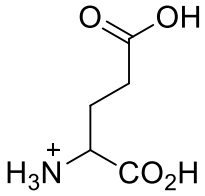
(c)



4 (i) circle the phenol group

(ii)





5) Kinetics of Organic Reactions

1 (i) Let the rate equation be: rate = $k[CH_3SNa]^a[CH_2ClCH_2OH]^b$.

Comparing Expt 1 and 2, $[CH_3SNa]$ x 1.5, the relative rate x 1.5

The order of reaction with respect to [CH3SNa] is 1.

Hence, a = 1

Comparing experiment 2 and 3,

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

The order of reaction with respect to CH_2ClCH_2OH ……**1**……

rate equation: **rate = *k*[CH_3SNa][CH_2ClCH_2OH]**, *k* = rate constant

OR **rate = *k*[CH_3S^-][CH_2ClCH_2OH]**

(ii) CH_3S^-

(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 S_N2 nucleophilic substitution reaction varies according to the equation: rate = $k[CH_3S^-]$ $[CH_2ClCH_2OH]$. 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 CH_3S^- nucleophile, the lone pair on the nucleophile is **more available to attack the CH_2ClCH_2OH 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 [**U**] against time is a straight line with constant gradient

The rate of reaction is independent of [**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 $[H^+]$ against time shows a constant half-life of 50 min. Hence, reaction is first order with respect to H^+.

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

Explanation: The rate equation is Rate = k[methanal][amine][H^+]

In step 1, there are one molecule of methanal reacting with one molecule of amine and H^+ ion, which corresponds to the rate equation as the concentrations of methanol, amine and H^+ 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

rate = k [methanal] [amine] [H^+]

since [methanal] and [H^+] is in large excess,

➔ rate = k' [amine], where k' = k [methanal][H^+]

$$t_{½} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[\text{methanal}]\,[H^+]}$$

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

$$k = 0.9627$$

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

(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

1 $CH_3XH + H_2O \rightarrow CH_3X^- + H_3O^+$

S has larger atomic radius than O. Thus S-H bond length is larger and thus weaker than O-H bond. CH_3S-H undergoes greater acid dissociation, and has a smaller pK_a value, than methanol.

2

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

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

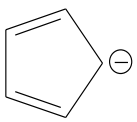
Thus, the reaction of propanoic acid with NaOH(aq) will be less exothermic.

3

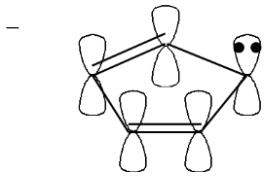
(a) Type of reaction: Elimination

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) **$N_c > N_b > N_d$**

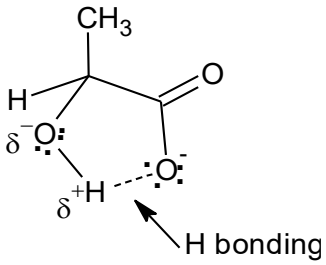
Comparing N_c and N_b, there is a carboxylic acid group one the carbon adjacent to N_b. Carboxylic acid group is electron withdrawing group and will decrease the availability of lone of pair of electrons on N_b for donation. Therefore, N_c is more basic than N_b.

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.

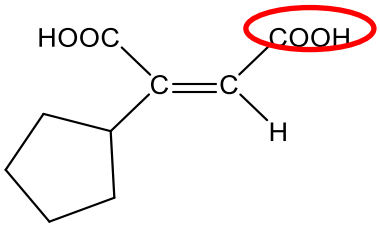
(ii) There is a large reservoir of zwitterions. The positively charged amine salt is acidic and will neutralize the small amount of added OH^- and maintains pH.

5 <u>Intramolecular hydrogen bond</u> is possible in lactate ion between the carboxylate ion and the protonic H in –OH.



6

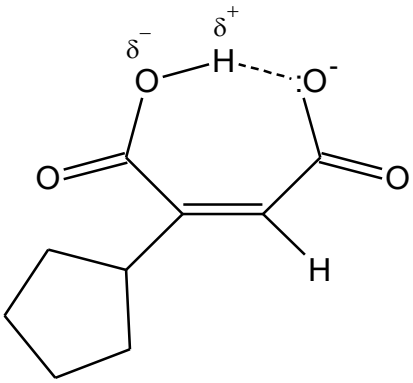
(i)



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

(ii) Cis-trans isomerism / geometric isomerism

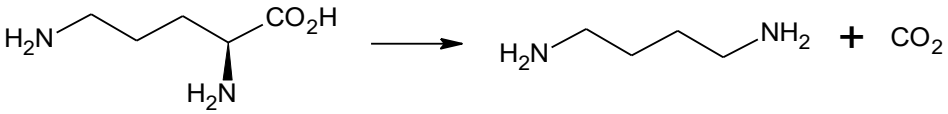
(iii)



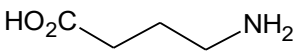
The conjugate base formed after 1st acid dissociation is stabilised by intra hydrogen bonding of the carboxylate group with –OH, making the 1st acid dissociation more favourable. However, it makes the H from the 2nd carboxylic acid significantly less acidic since energy is required to overcome intramolecular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

7 **(i)** Gaseous by-product: 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 of a weak base, B = $\frac{[BH^+][OH^-]}{[B]}$

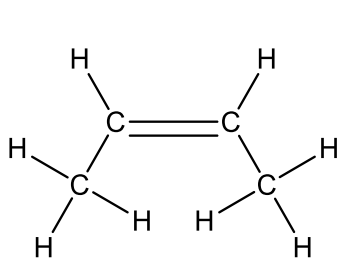
(iv) K_b: α-NH_2 of L-ornithine < R-NH_2 of L-ornithine

α-NH_2 of L-ornithine is closer to the electron-withdrawing –CO_2H/ –CO_2^- group which decreases the availability of the lone pair of electrons on N atom of α-NH_2. Hence, α-NH_2 is a weaker base than R-NH_2 of L-ornithine.

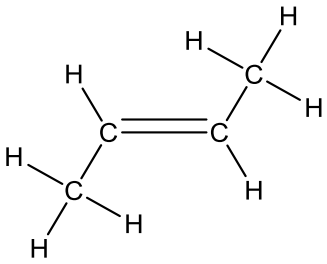
7) Isomerism

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

(ii)

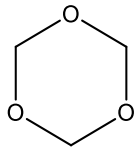


Cis-but-2-ene



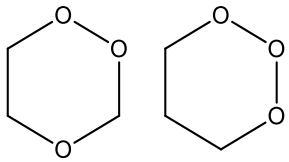
trans-but-2-ene

2 (i)



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

(ii)



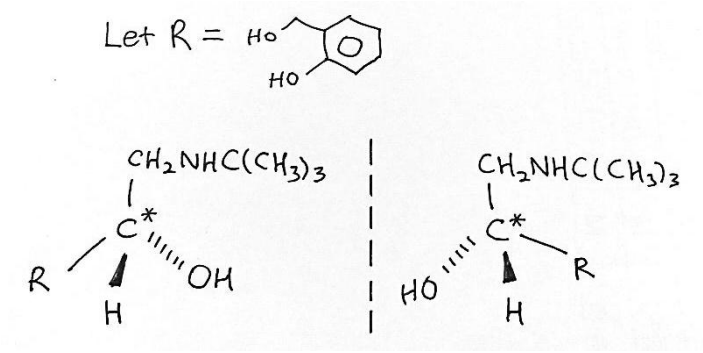
(iii) Weak O–O bond due to

repulsion of lone pairs of electrons on adjacent O atoms OR

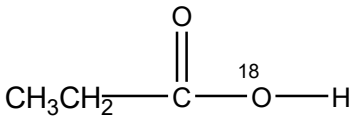
repulsion of two δ– charges on adjacent O atoms.

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

(b) Optical isomerism

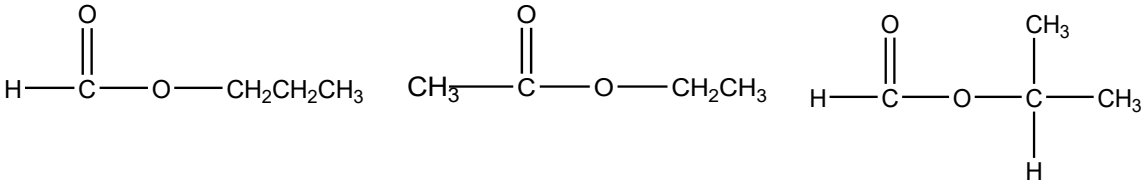


4 (i)



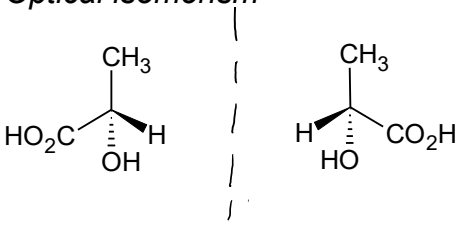
CH$_3$OH

(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*



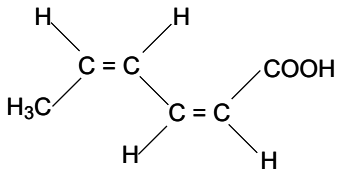
7(i) C3-C4 bond is stronger.

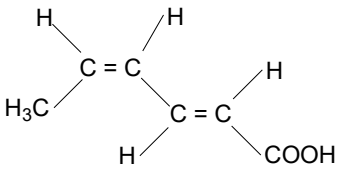
C1–C2 bond: $sp^3 – sp^2$ overlap

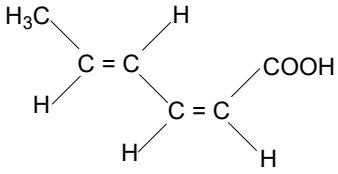
C3–C4 bond: $sp^2 – sp^2$ overlap

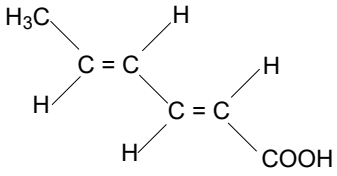
As the sp^2 hybrid orbitals of C3 and C4 contains greater s-character, there is more efficient orbital overlap leading to a stronger bond.

(ii)

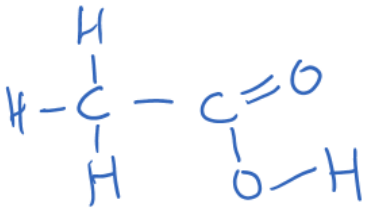

H
H
C = C
COOH
H3C
C = C
H
H


H
H
C = C
H
H3C
C = C
H
COOH


H3C
H
C = C
COOH
H
C = C
H
H


H3C
H
C = C
H
H
C = C
H
COOH

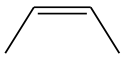
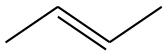
(iii)

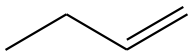
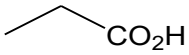

H
H
C
C
O
H
O
H

8) Organic Structural Elucidation

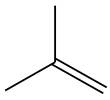
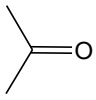
1 **A**, C_nH_{2n}, an alkene

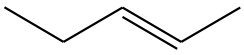
2 **B**, C_nH_{2n}, a cycloalkane

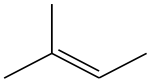
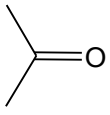
3 **C**, C_4H_8, $CH_3CH=CHCH_3$; cis-but-2-ene,  and trans-but-2-ene, 
(symmetrical since only one organic product is obtained after oxidative cleavage)

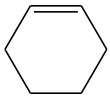
4 **D**, C_4H_8,  , **E**, 

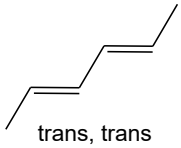
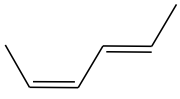
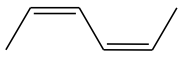
(D is terminal alkene since CO_2 is formed after oxidative cleavage)

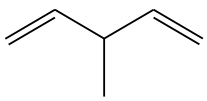
5 **F**, C_4H_8,  ; **G**, 

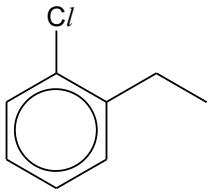
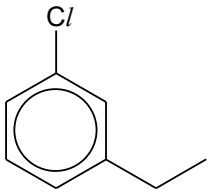
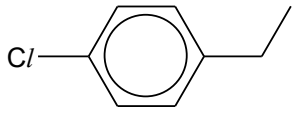
6 **H**, C_5H_{10},  ; **K**, $C_3H_6O_2$ is $CH_3CH_2CO_2H$; **L**, $C_2H_4O_2$ is CH_3CO_2H

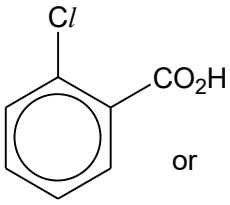
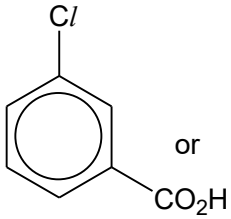
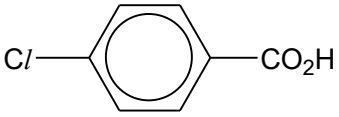
J , C_5H_{10},  ; **L** , $C_2H_4O_2$ is CH_3CO_2H; **M**, C_3H_6O, 

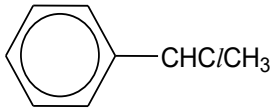
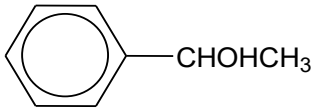
7 **N**, C_6H_{10}, 
(note: 2 degree of unsaturation, since it only reacts with 1 mol of Br2, it must have only 1 double bond, and therefore 1 ring)

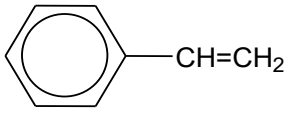
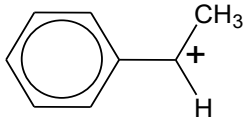
8 **P**, C_6H_{10}, $CH_3CH=CHCH=CHCH_3$; 
trans, trans 
cis, trans same as trans, cis 
cis, cis

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

10 **R,** C_8H_9Cl,  or  or  ;

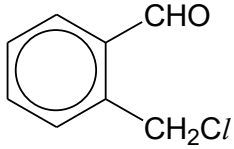
S, $C_7H_5ClO_2$,  or  or 

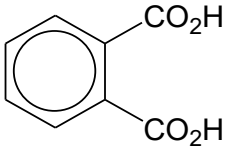
T, C_8H_9Cl,  ; **U**, $C_8H_{10}O$, 

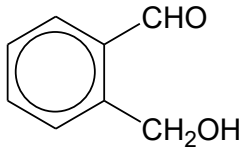
V, C_8H_8  ; **T** reacts with NaOH through S_N1 mechanism involving trigonal planar carbocation,  to form **U**, a racemic mixture.

11 **L**, C_8H_7OCl:

- $\frac{C}{H}$ ratio ~ 1 $\Rightarrow$ has benzene ring
- undergoes side-chain oxidation with acidified $KMnO_4$ to form **M**, diacid (has 4 O's)=> 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

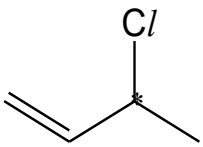
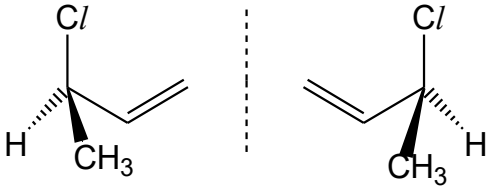
L  or its 1,3-isomer or 1,4-isomer ;

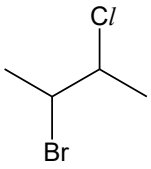
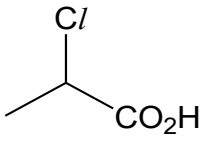
M  or its 1,3-isomer or 1,4-isomer ;

N  or its 1,3-isomer or 1,4-isomer

12(a) A, C_4H_7Cl:

- has a chiral C with 4 different atoms or groups of atoms attached
- C:H ratio ≈ 1:2 & reacts with HBr (1 : 1 ratio) (electrophilic addition) ⇒ has 1 C=C bond
- undergoes oxidative cleavage with acidified $KMnO_4$ to give CO_2 & acid **C** ⇒ has terminal C=C bond

A, C_4H_7Cl:  ; enantiomers of **A**: 

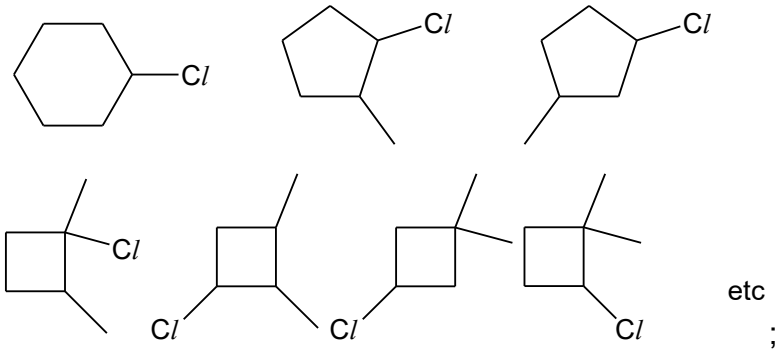
B,  ; **C**, 

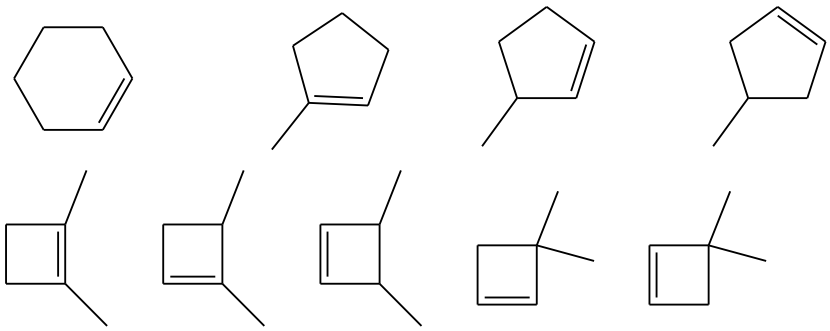
(b) MF of **D**: $C_6H_{11}Cl$,

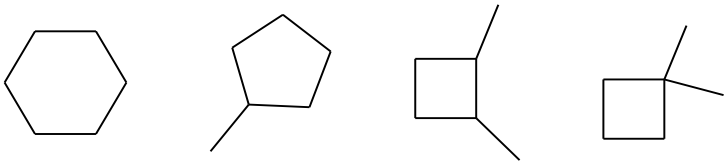
D, $C_6H_{11}Cl$:

- C:H ratio ≈ 1: 2 & does not react with bromine ⇒ NO C=C bond / has a ring
- undergoes elimination with alc KOH to form alkene **E**, C_6H_{10}
- is reduced by H_2 to an alkane **F**

D, any one:

 etc ;

Corresponding **E**,  etc ;

Corresponding **F**,  etc

13 **B:** C_9H_{10}:

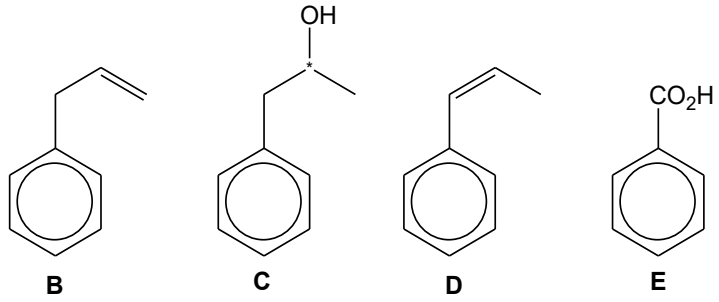
- C:H ratio ~ 1:1 ⇒ has benzene ring
- decolourised Br_2 (electrophilic addition) ⇒ has C=C bond
- undergoes oxidative cleavage to give CO_2 ⇒ has terminal C=C bond / $=CH_2$
- undergoes hydration (electrophilic addition) with steam to give a racemic mixture of alcohol **C**, C $C_9H_{12}O$ (Markovnokov's rule)

C, $C_9H_{12}O$:

- is dehydrated by hot Al_2O_3 to form **D**, C_9H_{10}, alkene or with C=C bond (isomer of **B**) (Saytzeff's rule)

D, C_9H_{10}:

- undergoes oxidative cleavage to form CH_3CO_2H and **E**, $C_7H_6O_2$, benzoic acid



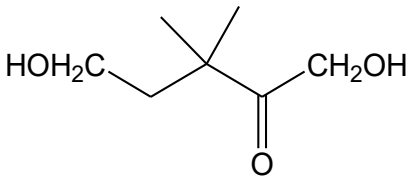
14 **P**, $C_{10}H_{14}O$:

- C:H ratio ~ 1:1 ⇒ has benzene ring
- Decolourised aq Br_2 (electrophilic addition)to form **Q**, $C_{10}H_{14}OBr_4$ ⇒ has 2 C=C bond
- Insoluble in NaOH(aq) ⇒ not phenol /alcohol
- Can be oxidised by Tollen's reagent ⇒ has –CHO group
- Undergoes oxidative cleavage with acidified $KMnO_4$ to form **R**, $C_3H_4O_3$, and **S**, $C_7H_{10}O_5$

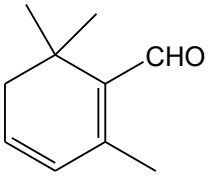
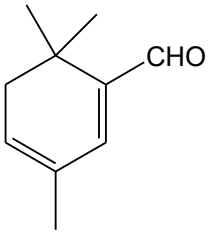
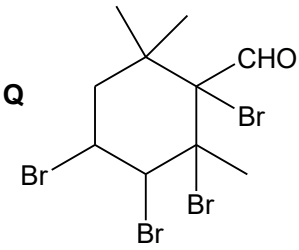
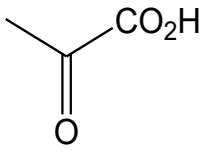
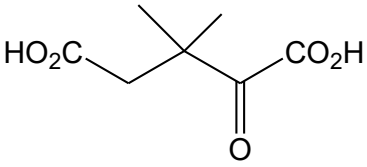
R, $C_3H_4O_3$:

- Forms yellow CHI_3 with aq I_2/OH^- ⇒ has CH_3CO- group

S, $C_7H_{10}O_5$,



- Is reduced by $LiAlH_4$ to form

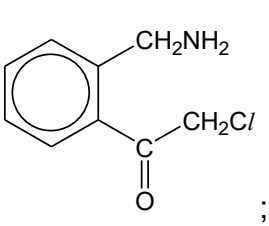
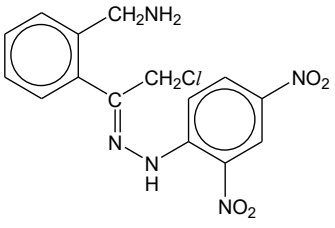
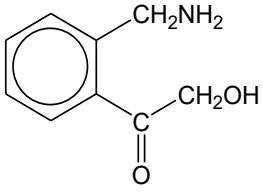
P  or  ; **Q**  ; **R** is CH_3COCO_2H,  ; **S** is 

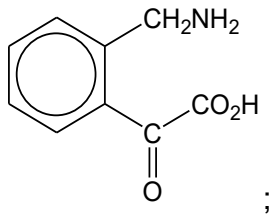
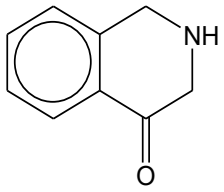
15 **A**, $C_9H_{10}NOCl$:

- C:H ratio ≈ 1:1 ⇒ has benzene ring
- basic ⇒ has amino group
- undergoes condensation with 2,4-dinitrophenylhydrazine to form **B** & does not react with Tollen's' reagent ⇒ **A** is ketone
- no reaction with aq bromine ⇒ no C=C bond or not phenolic
- undergoes electrophilic substitution with 2 mol bromine in $FeBr_3$ ⇒ is 1,2- or 1,4-disubstituted
- undergoes nucleophilic substitution &/or hydrolysis with hot NaOH(aq) to form **C**, $C_9H_{11}NO_2$ ⇒ C*l* not directly attached to benzene ring & **C** has –OH group
- undergoes nucleophilic substitution in a sealed tube (loss of HC*l* from amino and C*l* 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 $–CO_2H$ group as 0.10 mol **D** reacts with 0.05 mol aq sodium carbonate) ⇒ C is 1° alcohol or has $–CH_2OH$ group

A  ; **B**  ; **C**  ;

D  **E**  ;

16 **A**, $C_{10}H_{12}O_2$:

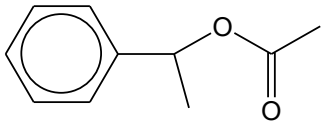
- C:H ratio ~ 1:1 ⇒ has benzene ring

- is neutral with 2O's & is hydrolysed by hot hydrochloric acid to form **B** and **C** ⇒ **A** is ester

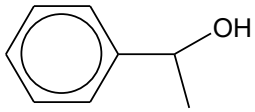
B, $C_8H_{10}O$ (alcohol, pdt of hydrolysis of ester)"

- has $CH_3CH(OH)$- group which forms CHI_3 with aq alkaline iodine
- oxidised by acidified $K_2Cr_2O_7$ to form **D**, C_8H_8O ⇒ **B** is 2° alcohol & **D** a ketone (1 O)

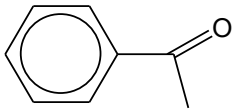
D, C_8H_8O, ketone **–** undergoes condensation with 2,4-dinitrophenylhydrazine to form hydrazine **E**.



A

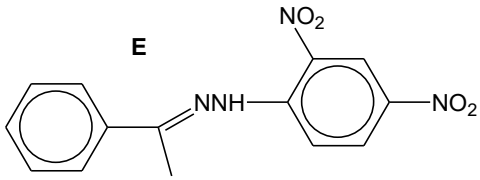


B



D ;

C is CH_3CO_2H

E 

17 **A**, $C_{10}H_{18}O$:

- C: H ratio ~ 1: 2 ⇒ 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) ⇒ **A** has –OH, alcohol / phenol

- can be oxidised by acidified $K_2Cr_2O_7$ to **B**, $C_{10}H_{16}O_2$ ⇒ **A** is a 1° alcohol, **B** is carboxylic acid (2 O's)

- 1 mol **A** reacted with 2 mol bromine (electrophilic addition) ⇒ **A** has 2 C=C bonds

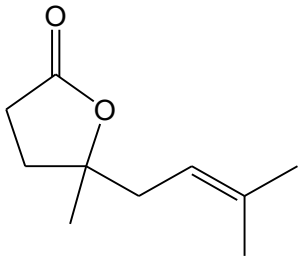
- undergoes oxidative cleavage with hot acidified $KMnO_4$ to give 3 pdts: **C**, C_3H_6O, **D**, $C_5H_8O_3$, and effervescence of CO_2 (from $C_2H_2O_4$); total no of C = 10)

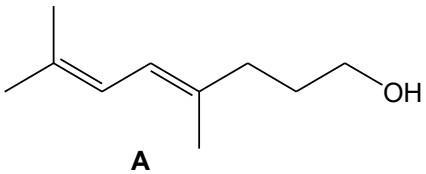
C and **D**: undergo mild oxidation with aq I_2/ NaOH to form CHI_3 ⇒ each has CH_3CO- group (NOT $CH_3C(OH)H$– group as both are pdts of oxidative cleavage)

B, $C_{10}H_{16}O_2$:

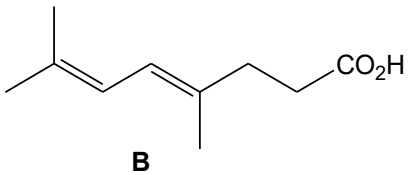
- undergoes electrophilic addition with steam to form alcohol; then undergoes self-condensation

to form cyclic ester, **F**,

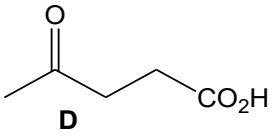




A



B ;

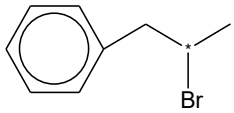
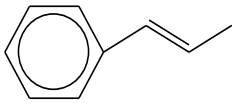
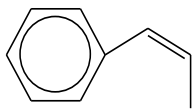
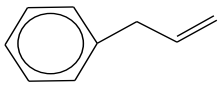
C is CH_3COCH_3; 

D

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

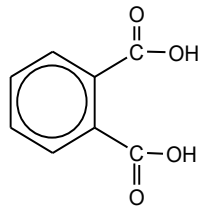
W,  ; **X**, **Y**,   ; **Z**,  ;

19 **J**, $C_{11}H_{14}$:

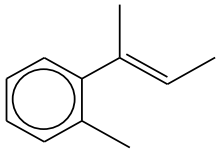
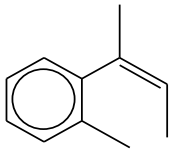
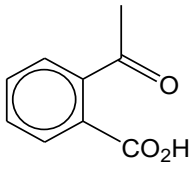
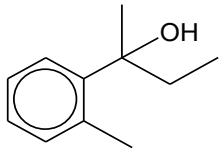
- C:H ratio ~ 1:1 ⇒ has benzene ring
- exhibits cis-trans isomerism; no chiral C ⇒ alkene / has C=C bond

- undergoes oxidative cleavage with hot acidified $KMnO_4$ to form **K**, $C_9H_8O_3$, with 1 $–CO_2H$ and 1 ketone functional groups
- reacts with steam (electrophilic addition) to form **L**, $C_{11}H_{16}O$ with a chiral C (Markovnikov's addition)

K, $C_9H_8O_3$, undergoes a stepping-down reaction (Triiodomethane test, followed by acidification) to



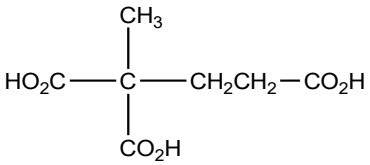
form

J, $C_{11}H_{14}$,  ;  ; **K**, $C_9H_8O_3$,  ; **L**, $C_{11}H_{16}O$, 

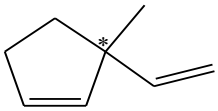
20 **A**, C_8H_{12}:

- $\frac{C}{H}$ ratio ~ ½ ⇒ 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:  with only 7 C's

⇒ **A** has terminal C=C bond / $=CH_2$

A, C_8H_{12}, 

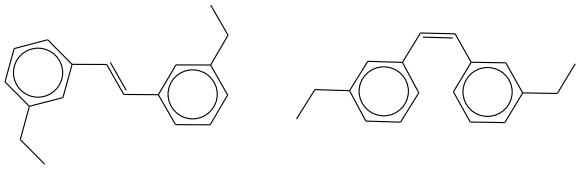
21 **P**, $C_{18}H_{20}$:

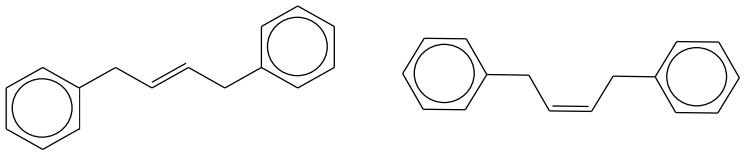
- C:H ratio ~ 1:1 ⇒ has benzene ring(s)
- exists in 2 isomeric forms (likely cis-trans)
- 1 mol reacts with 1 mol $Br_2(l)$ (electrophilic addition) ⇒ has 1 C=C bond
- undergoes oxidative cleavage / side-chain oxidation with acidified $KMnO_4$ to form **Q**, $C_8H_6O_4$, & CO_2 ⇒ 1 mol **P** gives 2 mol each of **Q** and CO_2

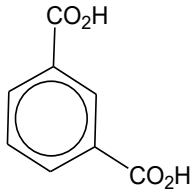
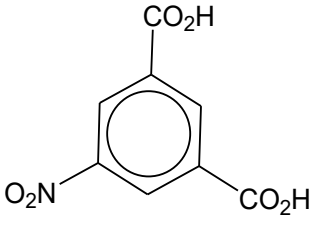
Q, $C_8H_6O_4$:

- 1 mol is neutralised by 2 mol NaOH ⇒ 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 ⇒ 1,3-dicarboxylic acid

P:

either  or

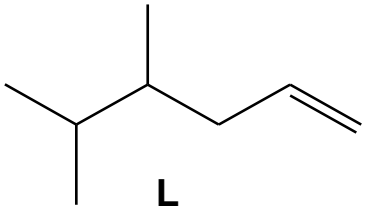


Q, $C_8H_6O_4$,  ; nitration product:  (-CO_2H is deactivating & 3-directing)

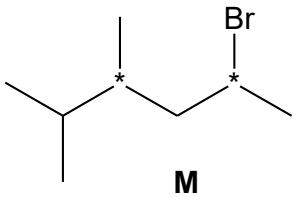
22 **(a) L**, C_8H_{16}:

- C:H ratio ~ 1:2 ⇒ NO benzene ring
- 1 mol reacts with 1 mol $Br_2(l)$ ⇒ has 1 C=C bond
- undergoes oxidative cleavage with acidified $KMnO_4$ to form carbon dioxide & 3,4-dimethylpentanoic acid ⇒ has terminal C=C bond / has $=CH_2$ group
- undergoes electrophilic addition with HBr to form optically active **M**, $C_8H_{17}Br$

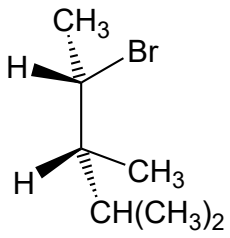
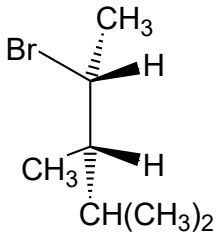
M, $C_8H_{17}Br$ reacted with hot NaOH(aq) through nucleophilic substitution to form **N**, $C_8H_{18}O$

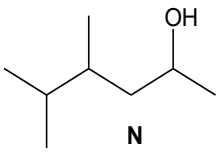
(b) 

L



M

(c)  



N

(d) NaOH(aq); heat;

23 **A,** C_4H_8O:

- C:H ratio =1:2 ⇒ has 1 C=C **or** C=O bond

- undergoes oxidative cleavage with hot acidified $KMnO_4$ to form **B**, $C_3H_4O_4$, with effervescence ⇒ has terminal C=C bond / $=CH_2$ group

- reacts with aq bromine (electrophilic addition) to form **C**, $C_4H_9O_2Br$ ⇒ **A** has 1 C=C bond

- reacts with phosphorus pentachloride to form **D**, C_4H_7Cl, chloroalkane ⇒ **A** has –OH group

B, $C_3H_4O_4$:

- 1 mol neutralised by 2 mol NaOH ⇒ **B** has 2 $-CO_2H$ & **A** is 1° alcohol

Both **A** and **C** can be oxidised by acidified $K_2Cr_2O_7$ ⇒ **A** & **C** both have 1° alcohol group

A: $CH_2=CHCH_2CH_2OH$ **B:** $HO_2CCH_2CO_2H$ **C:** $CH_2BrCH(OH)CH_2CH_2OH$

D: $CH_2=CHCH_2CH_2Cl$

24 **B**, $C_{10}H_{13}I$:

- C:H ratio ~ 1:1 ⇒ has benzene ring

- undergoes nucleophilic substitution with KOH(aq) to give **C**, $C_{10}H_{14}O$ ⇒ **B** is iodoalkane & **C**, an alcohol

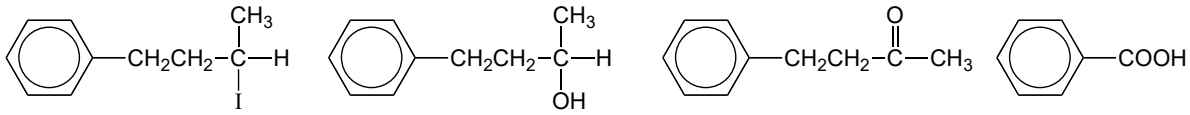
C, $C_{10}H_{14}O$:

- oxidised by acidified $K_2Cr_2O_7$ to form **D**, $C_{10}H_{12}O$ (ketone; 1 O) ⇒ **C** is 2° alcohol

- undergoes oxidative cleavage with hot acidified $KMnO_4$ to give **E**, $C_7H_6O_2$ (benzoic acid) ⇒ **C** has 1 side chain on benzene ring

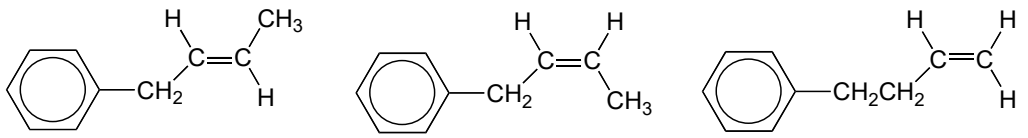
Both **C** and **D** undergo positive triiodomethane test ⇒ **C** has $CH_3CH(OH)$- group & **D** has CH_3CO- group

(a)



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

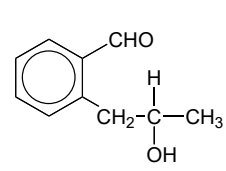
(b)



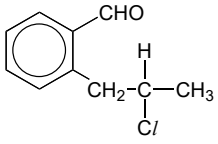
25 **A** ($C_{10}H_{12}O_2$):

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

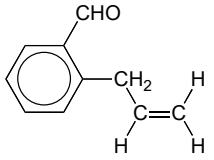
A, **B, C** or **D**: separately undergo side-chain oxidation &/or oxidative cleavage with hot acidified $KMnO_4$ to form **E** ($C_8H_6O_4$, benzene-1,2-dicarboxylic acid)

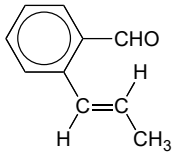


A
(any positional isomers)

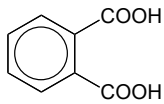


B





C & D (interchangeable)



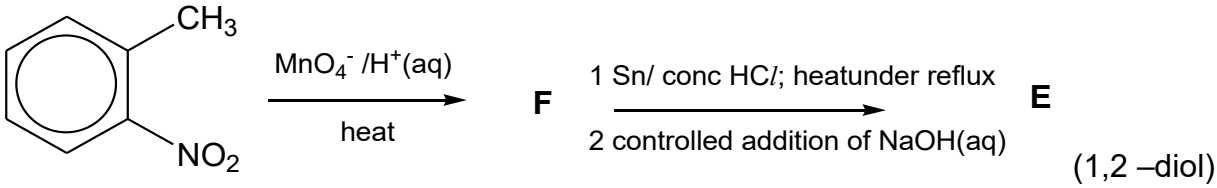
E

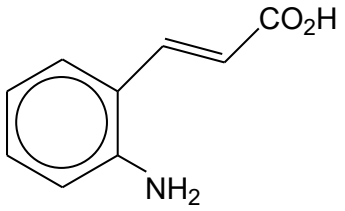
26 **B,** $C_9H_9NO_2$**:**

- C:H ratio = 1:1 ⇒ has benzene ring
- forms zwitterions in aqueous solution which conducts electricity ⇒ is amino acid / has –NH- and $–CO_2H$ group
- reacts with aq Na_2CO_3 to give CO_2 ⇒ has $–CO_2H$ group
- reacts with aq Br_2 (electrophilic substitution and electrophilic addition) to give **C,** $C_9H_7Br_4NO_2$**,** and **D**, $C_9H_8Br_3NO_3$ ⇒ 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-disusbtituted
- 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**, $C_7H_7O_2N$

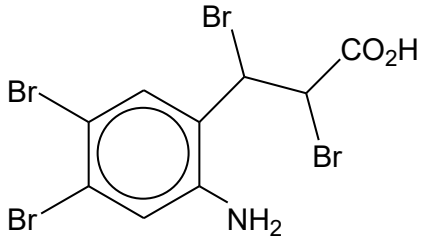
E, $C_7H_7O_2N$:

- soluble in NaOH(aq) and HC*l* (aq) ⇒ has both basic and acidic groups
- is synthesised by:

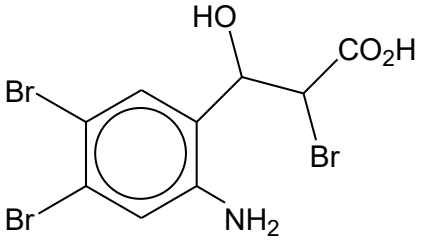




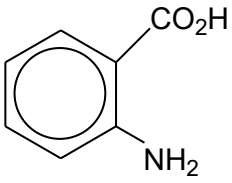
B



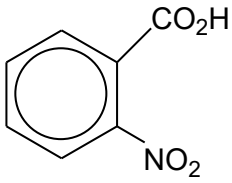
C



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° 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 $HO_2CCH_2CO_2H$

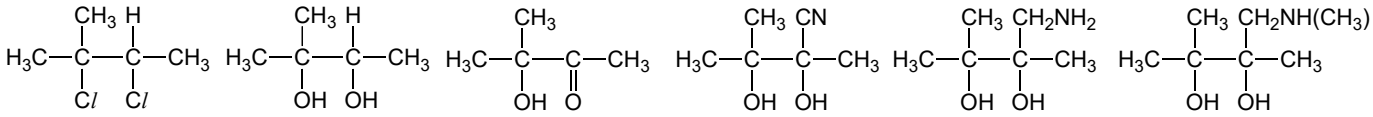
H: $HOCH_2CH_2CH=CHCH_2OH$ **I**: $HO_2CCH_2CH=CHCO_2H$

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**	- **P** is a chloroalkane (no double bonds), undergoes hydrolysis to form **Q** with 2 –OH groups
Q:	**Q**
- gives yellow ppt with aq I_2/ NaOH	- has $CH_3CH(OH)$- group; forms CHI_3 and carboxylic salt **R**
- forms **R** ($C_5H_{10}O_2$) with hot acidified $K_2Cr_2O_7$	- either has two 2° alcohol groups and is oxidised to **R** (diketone) - or has one 2° and one 3° alcohol groups and is oxidised to **R** (ketone + alcohol)
R:	
- reacts with Na(s) to give H_2 (redox reaction)	**R** has –OH group
- reacts with HCN and trace NaOH (nucleophilic addition) to give **S**	**R** has carbonyl group (ketone); **S** is a cynohydrin (-CH(OH)CN)
S:	
- is reduced to **T** which reacted with chloromethane to **U** ($C_7H_{17}O_2N$)	**T**: 1° amine ($-CH_2NH_2$), undergoes nucleophilic substitution with CH_3Cl



29 **(a)**

A, $C_9H_{11}Br$:

- C:H ratio ~ 1:1 ⇒ has benzene ring

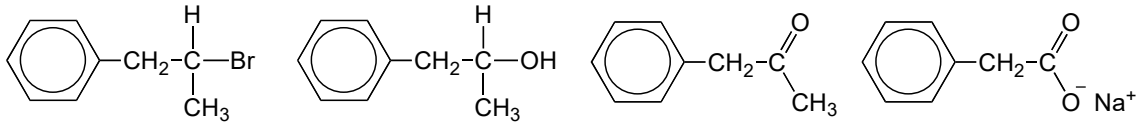
- Undergoes nucleophilic substitution with hot aq KOH to form **B**, $C_9H_{12}O$ ⇒ **A** is bromoalkane; **B** is alcohol

B, $C_9H_{12}O$:

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

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

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



A **B** **C** **D**

(b)

Why benzoic acid is more acidic than phenylmethanol:

–ve charge of $–CO_2^-$ 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 O^- and hence destabilises the conjugate base.

30 (a)

P, $C_9H_8O_2$:

C:H ratio ~ 1:1 ⇒ has benzene ring
oxidised by Tollen's reagent ⇒ has –CHO group

undergoes positive test with aq I_2/ NaOH to give CHI_3 (yellow ppt) ⇒ **P** has $CH_3CH(OH)–$ or $CH_3CO–$ group

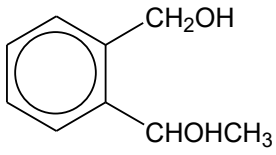
reduced by lithium aluminium hydride to form **Q**, $C_9H_{12}O_2$ ⇒ **P** has 2 carbonyl functional groups (coz **Q** has 4H's added)

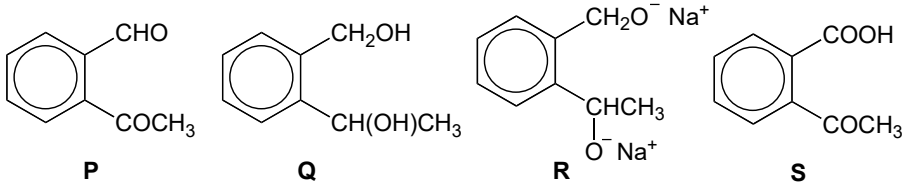
undergoes side-chain oxidation / oxidative cleavage with acidified $KMnO_4$ to form **S**, $C_9H_8O_3$

Q, $C_9H_{12}O_2$:

inert to aq Na_2CO_3 ⇒ not carboxylic acid

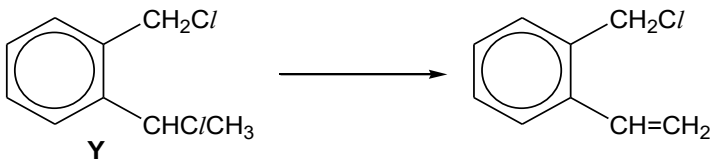
reacts with Na(s) (redox reaction) to form **R**, $C_9H_{10}O_2Na_2$, with strong effervescence of H_2 ⇒ **Q** has 2 –OH or alcohol groups

can be obtained by reacting **Y** with hot NaOH(aq) ⇒ **Q** is 



P **Q** **R** **S**

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



Y

31 (a)

A, $C_8H_{13}Cl$:

-C:H ratio ~ 1:2 ⇒ NO benzene ring / is aliphatic (chloroalkane)

- optically active ⇒ **A** has chiral C

- undergoes nucleophilic substitution with hot NaOH(aq) to form **B**, $C_8H_{14}O$ ⇒ **A** is aliphatic (chloroalkane); **B** has alcohol functional group

B, $C_8H_{14}O$:

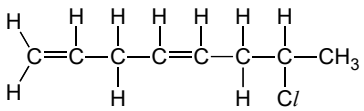
- undergoes electrophilic addition with 2 mol Br_2 ⇒ has 2 C=C bonds

- undergoes positive test with aq I_2/ NaOH ⇒ has $CH_3CH(OH)$– group and **C**, $C_7H_{10}O_2$ is carboxylic acid

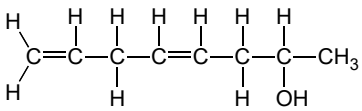
- undergoes oxidative cleavage with hot acidified $KMnO_4$ to gives **D**, $C_3H_4O_4$ and $CH_3COCH_2CO_2H$ and CO_2 ⇒ **B** has 1 C=C bond between C3 and C4 and 1 $=CH_2$ group

Tri-iodomethane, CHI_3

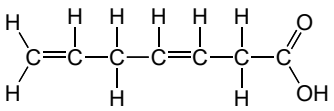
(b)



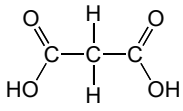
A



B



C



D

32 **A**, C_6H_6O:

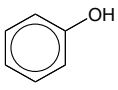
-C:H ratio = 1:1 with 1 O ⇒ is phenol

- reacts with 3-chloropropene in aluminium chloride (electrophilic substitution) to form **B**, $C_9H_{10}O$

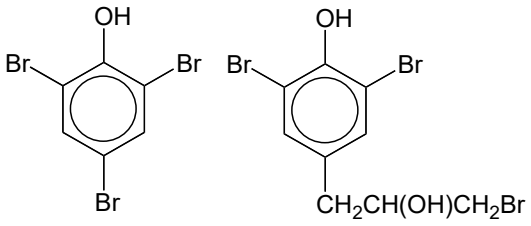
A, **B**:

- decolourise aq bromine (electrophilic substitution & /or electrophilic addition) to form white precipitates **C** and **D**, respectively ⇒ presence of phenol or C=C bond

C, **D**: have same no of Br per molecule; **D** is optically active (has chiral C)

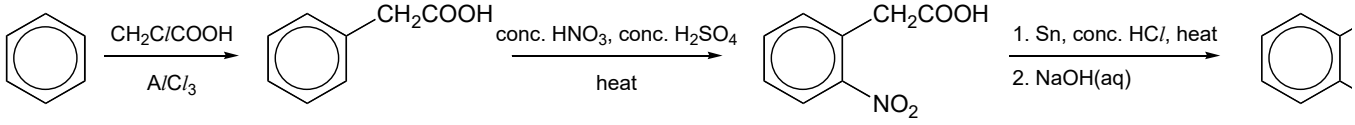
(a)(I) **A**  ; Electrophilic Substitution

(a)(ii)



C **D**

(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 ⇒ **T** is an ester & **U** is a diol (2O's; saturated)

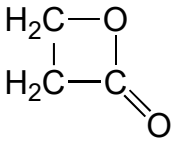
U, $C_2H_6O_2$:

- mono-substitution of -OH group with HC*l* 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 **Y**: 

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 ~ 1:2 ⇒ no benzene ring

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

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

Q, $C_6H_{14}O$:

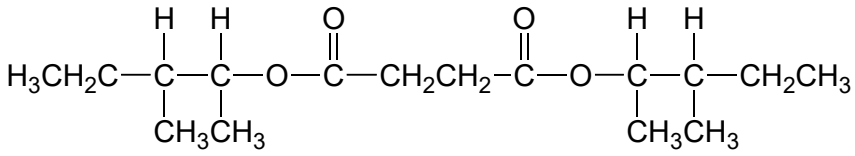
- rotates plane of plane-polarised light ⇒ has chiral C

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

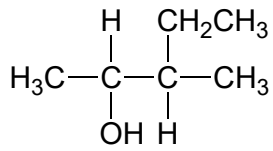
- dehydrated by Al_2O_3 to give alkene **T**, C_6H_{12}, which upon vigorous oxidation give butanone as a pdt ⇒ **T** must be $CH_3CH_2CH(CH_3)=CHCH_3$

R, $C_4H_6O_4$:

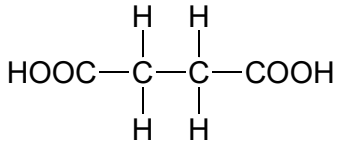
- synthesised from 1,2-di-iodoethane with hot ethanolic NaCN followed by warming with dilute sulfuric acid ⇒ **R** must be $HO_2CCH_2CH_2CO_2H$



P



Q



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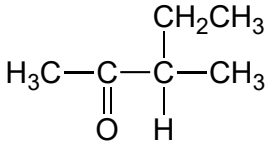

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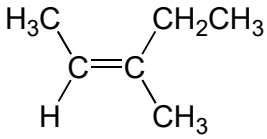


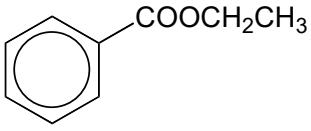
T

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

- hydrolysed by hot NaOH(aq) to give **Q** & **R**, which upon acidification gives **S**, $C_7H_6O_2$ (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 $K_2Cr_2O_7$



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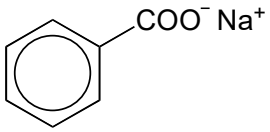

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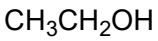

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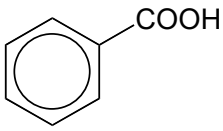


S

36 **C**, $C_{10}H_9NO$

- 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_2CO_3) ⇒ **D** is carboxylic acid

- obtained by heating **E**, C_9H_9ClO with alc KCN (NS) ⇒ **E** is chloroalkane (C*l* on side alkyl chain, not on benzene ring)

E:

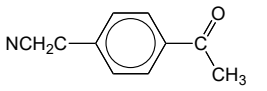
- no reaction with Tollen's' reagent; reacts with 2,4-DNPH to give orange ppt ⇒ **E** is ketone, **F**, a hydrazone

- reacts positively with warm aq I_2/ NaOH ⇒ **E** has CH_3CO- group & **G**, salt of carboxylic acid

Side-chain of **G** is oxidised by hot acidified $KMnO_4$ & **H** is formed.

H:

- reacts with 2 mol PCl_5 to give **I**, $C_8H_4Cl_2O_2$ ⇒ **H** has 2 $–CO_2H$; **I** has 2 $–CO_2Cl$



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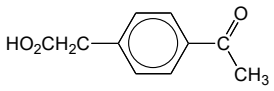
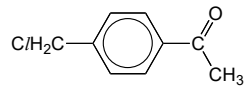


D



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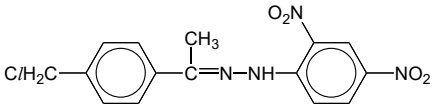

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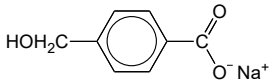


G

H

I

&

37 **A** ($C_{10}H_{14}O_2$):

- C:H ratio ~ 1:1 ⇒ has benzene ring

- optically active; NO reaction with aq Na_2CO_3 ⇒ has chiral C and not carboxylic acid (could be phenol)

- neutralised slowly by NaOH(aq) to form **B** (water soluble) ⇒ weak acidic group (phenol likely)

- reacts with HBr (substitution) but not acidified $K_2Cr_2O_7$ (cannot be oxidised) ⇒ 3º alcohol

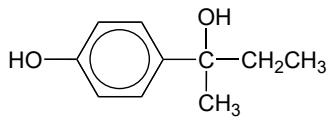
- reacts with aq bromine (electrophilic addition + electrophilic substitution) to form **C** ($C_{10}H_{12}O_2Br_2$) – 2 H substituted ⇒ 1,2 or 1,4 di-substituted benzene ring

- dehydrated by conc sulfuric acid to form **D** ($C_{10}H_{12}O$), cis-trans isomers ⇒ -OH with a H on adjacent C

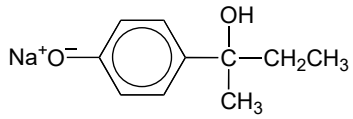
D ($C_{10}H_{12}O$) undergoes mild oxidation with cold, dilute aq alkaline $KMnO_4$ to **E** ($C_{10}H_{14}O_3$, diol) ⇒ **D** has 1 C=C bond

E ($C_{10}H_{14}O_3$) reacts with phosphorous pentachloride to give **F** ($C_{10}H_{12}OCl_2$) ⇒ has 2 –OH groups

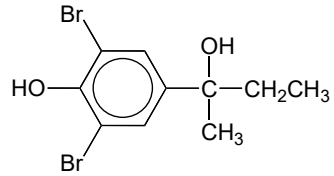
A:



B:



C:



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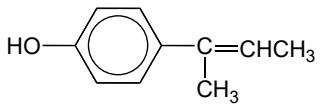
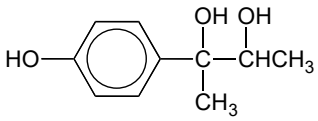


E:



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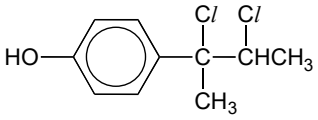


A, $C_{10}H_{13}Br$:

-C:H ratio ~ 1:1 ⇒ has benzene ring

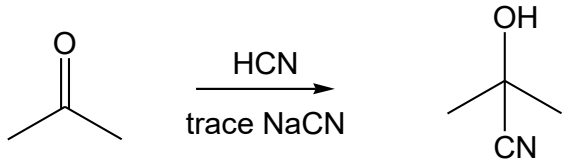
- undergoes elimination with hot ethanolic NaOH to give only **B**, $C_{10}H_{12}$ ⇒ **A**, bromoalkanes; **B**, alkene has C=C bond

B, $C_{10}H_{12}$**:**

- oxidised to benzaldehyde and **C**, C_3H_6O

C, C_3H_6O:

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



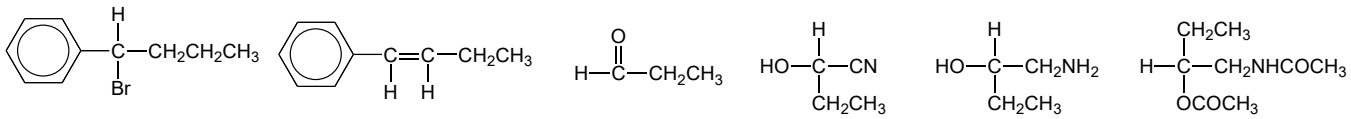
no chiral C; optically inactive

D, C_4H_7NO:

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

E, $C_4H_{11}NO$:

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



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

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

-C:H ratio ~ 1:1 ⇒ 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) ⇒ **G** is an ester

H, $C_3H_5O_3Na$:

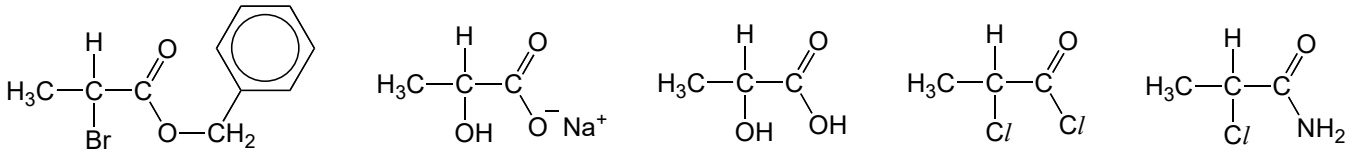
- gives H_2 with Na(s) (redox reaction) and reacts with alkaline aq I_2 to form ppt ⇒ **H** has $CH_3CH(OH)$- group

- acidification gives **I**, $C_3H_6O_3$ ⇒ **I** has $-CO_2H$

I, $C_3H_6O_3$:

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

J reacts with ammonia to give **K**, C_3H_6ONCl ⇒ **J** is acid chloride & **K** is amide



G **H** **I** **J** **K**

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

4C's)

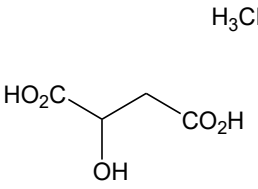
Y, $C_8H_{14}O_5$:

- gives H_2 with Na(s) (redox); oxidised by acidified $K_2Cr_2O_7$ to **Z** ⇒ **Y** has 1° or 2° alcohol group or -CHO

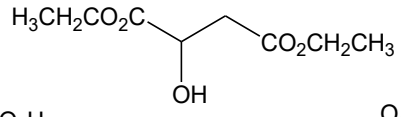
Z:

- undergoes condensation with 2,4-dinitrophenylhydrazine, no reaction with Fehling's and Tollen's reagents ⇒ **Z** is ketone; **Y** has 2° alcohol group

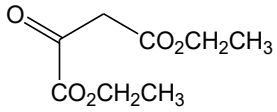
(a) $C_4H_6O_5$



X



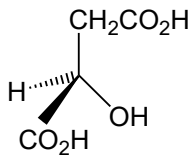
Y

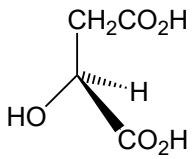


Z

(b)

(c) optical isomerism:





41 **P**, $C_5H_9ClO_2$:

- sparingly soluble in water; readily soluble in NaOH(aq) (neutralisation) ⇒ **P** has $–CO_2H$ group

- hydrolysed by hot NaOH(aq) through nucleophilic substitution; acidified to **Q**, $C_5H_{10}O_3$ ⇒ **Q** has alcohol group

Q, $C_5H_{10}O_3$:

- gives yellow ppt when warmed with aq I_2/ NaOH ⇒ **Q** has $–CH(OH)CH_3$

- reacted with hot conc sulfuric acid to form **R** (ester; condensation) and reacts with hot phosphoric acid to form **S**, $C_5H_8O_2$ (alkene; dehydration)

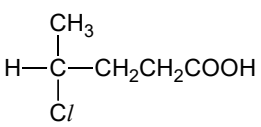
S, $C_5H_8O_2$**:**

- reacts with aq bromine (electrophilic addition) to give $CH_3CHBrCH(OH)CH_2CO_2H$

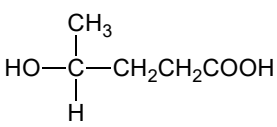
- undergoes oxidatively cleavage with acidified $KMnO_4$ to **T**, $C_3H_4O_4$ & ethanoic acid

T, $C_3H_4O_4$:

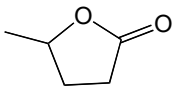
- 1 mol **T** liberates 1 mol carbon dioxide with aq Na_2CO_3



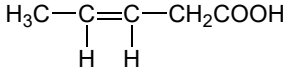
P



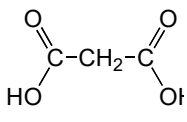
Q



R



S



T

42 **T**, $C_3H_7O_2N$:

- optically active ⇒ has chiral C
- reacts with PCl_5 to give white fumes & **U** ⇒ **T** has –OH **U**:
- gives NH_3 & **V** with hot NaOH(aq) ⇒ **U** & **T**; each has amide linkage; **V** is salt of acid

W, $C_3H_6O_3$:

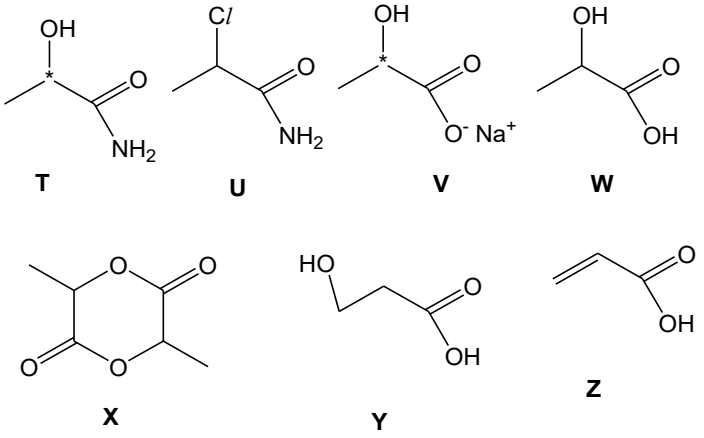
- from acidification of **V**

W, $C_3H_6O_3$:

- undergoes condensation in conc sulfuric acid to form cyclic diester, **X**, $C_6H_8O_4$

Y $C_3H_6O_3$:

- isomer of **W** (optically inactive)
- dehydrated to **Z**, $C_3H_4O_2$



43 **A**, $C_5H_9ClO_2$ (M_r 136.5):

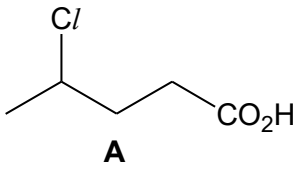
readily dissolves in NaOH(aq) at room temperature ⇒ has acidic $–CO_2H$
reacts with hot NaOH(aq) (nucleophilic substitution), followed by acidification to give **B**, $C_5H_{10}O_3$

B, $C_5H_{10}O_3$:

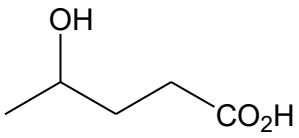
- reacts positively with warm aq I_2/ NaOH to give yellow ppt, **C**, CHI_3 ⇒ **B** has $–CH(OH)CH_3$
- reacts with hot conc sulfuric acid to form **D** (ester; sweet smelling) and **E**, $C_5H_8O_2$ (alkene; exhibit cis-trans isomerism)

E $C_5H_8O_2$:

- 1 mol reacts with 1 mol Br_2 ⇒ has 1 C=C bond
- undergoes oxidative cleavage with hot, acidified $KMnO_4$ to give **F**, $C_3H_4O_4$ ⇒ **E** has C=C between C_2 and C_3



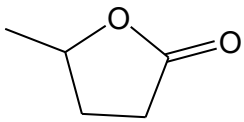
A



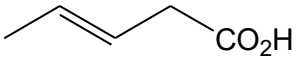
B

CHI_3

C



D



E

cis-trans isomers

44 **G**, $C_{10}H_{18}O$:

- no reaction with 2,4-dinitrophenylhydrazine reagent; can be reduced by H_2/ Pd to **H**, $C_{10}H_{17}O$ $\Rightarrow$ **G** has C=C bond

- reacts with ethanoyl chloride to give **J**, $C_{12}H_{20}O_2$ (condensation; ester); cannot be oxidised by acidified $K_2Cr_2O_7$ $\Rightarrow$ **G** has 3^o alcohol group

- oxidised by cold acidified $KMnO_4$ to give **K**, $C_{10}H_{22}O_5$ $\Rightarrow$ has 2 C=C bonds (4 –OH added)

- dehydrated by conc sulfuric acid to give **L** and **M** (both $C_{10}H_{16}$; alkene)

L:

- undergoes oxidative cleavage with hot acidified $KMnO_4$ to give **N**, $C_3H_4O_3$, **P**, $C_3H_4O_4$, and **Q**, C_3H_6O and CO_2 $\Rightarrow$ has 2 C=C bond & 1 $=CH_2$ group

N and **Q**:

- both give yellow precipitate with aq I_2/ NaOH $\Rightarrow$ each has $CH_3CO–$ group

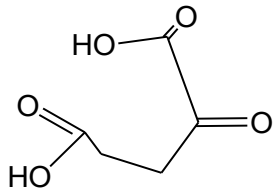
P, $C_3H_4O_4$:

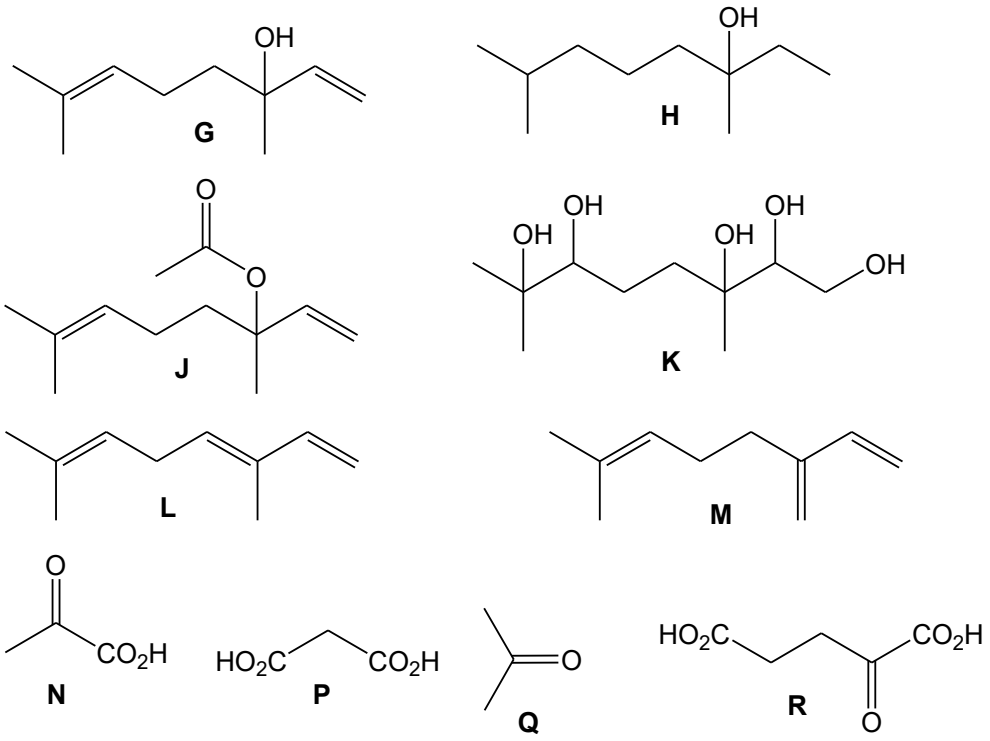
- 0.104 g neutralised by 20.00 cm^3 of 0.10 mol dm^{-3} NaOH $\Rightarrow$ has 2 $–CO_2H$ (diacid)

M, $C_{10}H_{16}$:

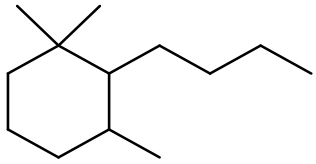
- is oxidatively cleaved by hot conc acidified $KMnO_4$ to give **Q** and **R**, $C_5H_6O_5$ $\Rightarrow$ **M** has 2 $C=CH_2$ groups

R: can be obtained from **S** by careful oxidation with hot concentrated acidified $KMnO_4$ $\Rightarrow$ **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 ⇒ has chiral C

D, **E** - no optical activity ⇒ no chiral C

C, **D**: 1 mol each reacts with 2 mol Br_2 ⇒ 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) ⇒ has 3 C=C bonds

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

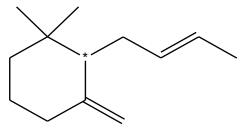
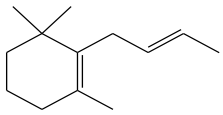
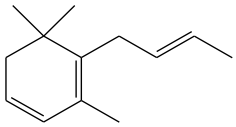
D - undergoes oxidative cleavage with acidified $KMnO_4$ to give **G**, $C_{11}H_{18}O_4$

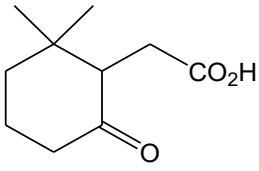
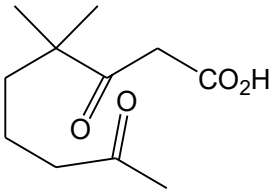
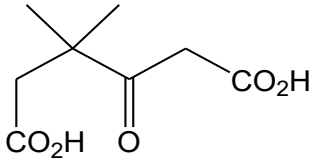
E - undergoes oxidative cleavage with acidified $KMnO_4$ to give ethanoic acid, CH_3COCO_2H and **H**, $C_8H_{12}O_5$.

F and **G**:

- react with NaOH in 1 : 1 ratio ⇒ each has 1 $–CO_2H$ group

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

C,  ; **D**,  ; **E**, 

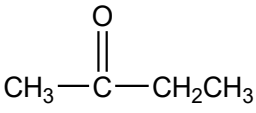
F,  ; **G**,  ; **H**, 

46 Volume of CO_2 = 8.2 – 3.4 = 4.8 dm^3

Number of moles of CO_2 = $\frac{4.8}{24}$ = 0.200 mol

Number of moles of C in 1 mole of X = 0.2/0.05 = 4 mol

n = 4

 *Note: Structural formula must be shown. Molecular formula will not be accepted.*

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

Empirical formula = C_5H_9OS

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

M_r = (mRT)/pV

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

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

M_r = 138

(ii)

	C	**H**	**O**
	60.8	4.4	34.8
	5.06	4.4	2.18
	2.32	2.0	1
Simplest ratio	7	6	3

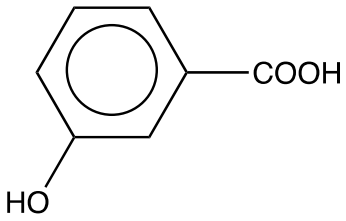
Empirical formula of **D is $C_7H_6O_3$**

Molecular formula of **D**: **$C_7H_6O_3$**

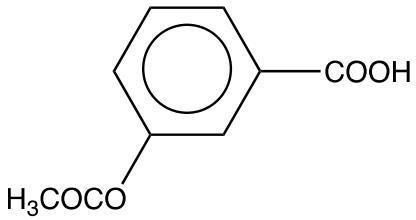
(iii) Carboxylic acid and phenol

(iv) Molecular formula of **E**: $C_7H_3O_3Br_3$

(v)



(vi)



49) F and **K** undergoes **strong oxidation** with $KMnO_4$ 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

➔ 0.10mol ≡ 1.2dm^3 ≡ 1H_2 ≡ 1ROH

➔ **F** contains only 1 **alcohol.**

F does not undergo strong oxidation with $K_2Cr_2O_7$

➔ **F** contains a **tertiary alcohol.**

F undergoes **elimination** with concentrated phosphoric sulfuric acid to give **I**, $C_4H_4O_4$

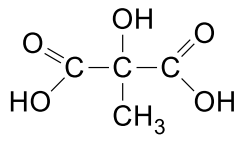
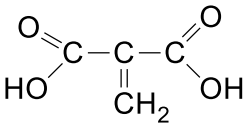
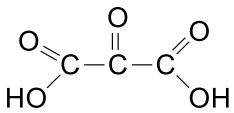
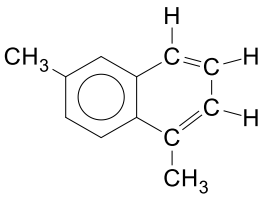
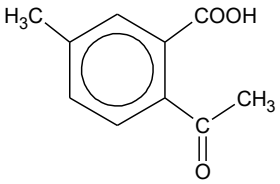
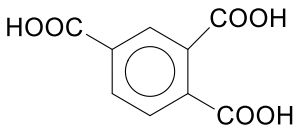
➔ **F** contains an **alcohol.**

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)

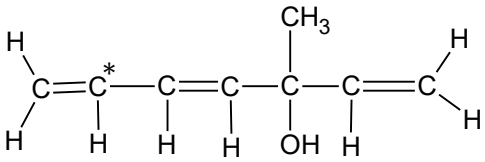
H dissolves in aqueous sodium hydroxide.
→ **H** contains an **acidic group** (i.e. – COOH)

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

		
G	**I**	**J**
		
K	**H**	**L**

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.**

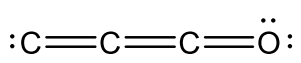
Cis-trans:

Restricted rotation about C=C OR

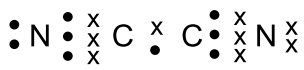
two different substituents about each C on C=C

(iii) no of enantiomers present = **4**

50 a (i)



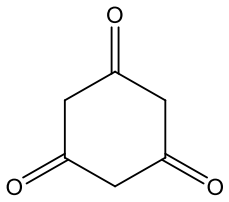
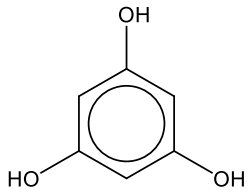
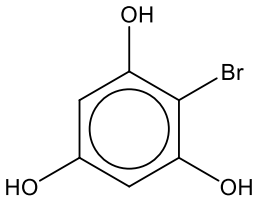
(ii)



b

Information/Reaction	**Deduction**
X/Y has C:H ratio of 1:1	**X/Y** might contain a benzene ring.
X does not undergo electrophilic substitution nor electrophilic addition with Br_2(aq)	**X** does not contain a phenol nor a C=C.
X undergoes condensation with 2,4-DNPH but does not undergo oxidation with Tollens' reagent.	**X** is a ketone.
X undergoes free-radical substitution with Br_2 to give only one monobromo compound.	**X** is highly symmetrical.
Y undergoes electrophilic substitution with HNO_3(aq) to give only one mono-nitrated compound.	**Y** is a phenol. **Y** is also highly symmetrical.

Structures:

		
X	**Y**	**Z**