Topic 10.3 : Structural Elucidation in Organic Chemistry

1. HCI/2009/P3/Q3e

A undergoes tri-iodomethane reaction \Rightarrow A contains CH_3CH(OH)- or CH_3CO- group.

From the given molecular formula, **A** is $CH_3CH(OH)CH_2CO_2H$.

A undergoes halogenation (nucleophilic substitution) with PCl_5 to form **B**. A contains –OH and/or – CO_2H groups.

B is CH_3CHC/CH_2COCI .

The -COCl group in **B** undergoes hydrolysis with water to give **C**.

C is CH₃CHC*l*CH₂CO₂H.

C undergoes nucleophilic substitution with KCN, followed by acid hydrolysis to D.

D is $CH_3CH(CO_2H) CH_2CO_2H$.

 ${\bf C}$ undergoes nucleophilic substitution with NH_3 to form ${\bf E}.$

E is $CH_3CH(NH_3^+) CH_2CO_2^-$ (reject the molecular form)

2. DHS/2009/P3/Q2b

The carbon to hydrogen ratio of P is 1:2.

P does not contain benzene ring, but could contain <u>alkene</u> group.

P undergoes <u>electrophilic addition</u> with hydrogen chloride gas to form **Q** and **R** in unequal proportion.

P is an unsymmetrical alkene. Q and R are halogenoalkanes.

Q and **R** undergo <u>nucleophilic substitution</u> with sodium hydroxide to form **S** and **T** respectively.

S and T are <u>alcohols</u>.

S is <u>not oxidized</u> by acidified potassium manganate (VII). **S** is a <u>tertiary alcohol</u>.

T is **<u>oxidized</u>** by acidified potassium manganate (VII) to form **U**.

T is a **primary or secondary alcohol**. U could be **carboxylic acid or ketone**.

U undergoes <u>neutralisation</u> / <u>acid – base reaction</u> with sodium carbonate to liberate carbon dioxide gas.
 U is a carboxylic acid, hence T is a primary alcohol.

P undergoes <u>(strong) oxidation</u> with acidified potassium manganate (VII) to form **V**, $C_5H_{10}O$, <u>which has only one oxygen atom</u>, and carbon dioxide. **P** has a <u>terminal alkene</u> group. **V** is a <u>ketone</u>.

V undergoes <u>condensation</u> with 2,4-dinitrophenylhydrazine to form an orange precipitate.
 V is a ketone / carbonyl compound.

V undergoes <u>reduction</u> with lithium aluminium hydride to form W, which does not exhibit optical activity.

W is a <u>secondary alcohol</u> and is a <u>symmetrical</u> molecule.







3. <u>IJC/2009/P3/Q1f</u>

HA CH3 CH3	J: CH3 CH3	K: CH3 CH2CI	L: CH3 CH3
CH3-C-C-H	$CICH_{-}C - C - H$	сну-с-с-н	CH3-C-C-CI
CH3 CH3	H3C CH3	CH3 CH3	CH3 CH3

4. <u>ACJC/2009/P2/Q4b</u>



5. <u>JJC/2009/P2/Q6c</u>



Ε

- (ii) Excess NH3, heat under reflux in ethanol
- 6. <u>MJC/2009/P3/Q4c</u>
 - (ci) X can be : (accept other logical answers)





(cii)



(ciii) There is 1 alkene double bond that is capable of exhibiting cis-trans isomerism as there are 2 different groups attached to each C atom; no of stereoisomers= <u>2</u>.

7. <u>NJC/2009/P3/Q2e</u>





EXPLANATION OF THE REACTIONS DESCRIBED

[1] M decolourises aqueous bromine due to **electrophilic addition** across the **alkene (C=C)** functional group.

[1] M produces white fumes (of HCl) with PCl_5 due to a **substitution** reaction of the (secondary) **alcohol** functional group.

[1] M produced 3 compounds, N, P and Q with hot acidified potassium manganate (VII) due to **oxidative cleavage** of the (2) **alkene** functional groups present.

[1] N does not undergo **mild oxidation** with Fehling's reagent as it is **not an aldehyde**.

[1] N gives a yellow ppt (of CHI_3) and salt R with aq alkaline iodine due to the (mild) **oxidation** (and cleavage) of the **CH₃COR** group.

[1] P gives an efferve scence (of CO_2) with $Na_2CO_3(s)$ due to a **neutralization** reaction with the **carboxylic acid** functional group.

[1] P gives an orange precipitate with 2,4-DNPH due to **condensation** with the **ketone** functional group.

[1] Q gives an efferve scence (of CO_2) with $Na_2CO_3(s)$ due to a **neutralization** reaction with the **carboxylic acid** functional group.

[1] Q does not give an orange precipitate with 2,4-DNPH due to the **absence of a carbonyl** functional group for **condensation**.

9. <u>RJC/2009/P2/Q4(a),(b)</u>

- (a) Structural/positional isomerism
- (b) Geometric isomerism



cis



trans

10. SAJC/2009/P3/Q4c

Information	Deduction
Stereoisomer A	- contains either an alkene with non-
	identical groups on the same carbon or
	chiral carbon
A reacts with hot acidified potassium	- A undergoes oxidation
manganate(VII) solution	- A contains C=C

B forms a ye	llow precipitate with hot	- B contains <u>CH</u>	<u>3CO-</u>	
alkaline iodine solution.		(do not accept CH ₃ CHOH-)		
Cold alkaline hydrogen cyanide was		- B is a ketone which undergoes		
added to B	and the mixture was	nucleophilic addition with HCN		
reduced to for	m compound C	- C contains an amine functional group		
Compound D	formed white precipitate	- D contains chloroalkane which forms		
with ethanolic	silver nitrate solution.	AgCl		
Compound D	Compound D was reacted with		- D is an alcohol or carboxylic acid	
phosphorous p	pentachloride to form	(do not accept D contains –OH group)		
compound E.		which undergoes nucleophilic		
		substitution / dis	placement reaction to	
		form E which is a an acid chloride.		
Compounds C and E were then reacted		- condensation reaction took place		
to form two compounds \mathbf{F} and \mathbf{G} , with				
identical molecular formula				
$C_7H_{14}O_2NCl.$				
Compound F is neutral.		- F is an amide	or F does not contain	
		phenol/carboxyl	ic acid/amine.	
Compound	Structure	Compound	Structure	
Α	CH ₂ Cl _C _C _C _C _C _C _{H₂CH}	3 D	CH ₂ Cl	
	H CH ₃		0=0	
			HU	
B	CH ₂ CH ₃	E	CH ₂ Cl	
	O=C		c=o	
	5		C	

C	$HO - C - CH_2NH_2$ $ CH_3$ $ CH_3$	F	$HO-C-CH_2NHCOCH_2Cl$ $ CH_3$ $ CH_3$
		G	CH ₂ CH ₃ CH ₂ C/COO-C-CH ₂ NH ₂ CH ₃

11. SAJC/2009/P3/Q5c

Information	Deduction
Both A and B do not react with	- A and B do not have –COOH
Na ₂ CO ₃	
A and B do not give positive test	A and B do not contain any methyl
	ketone CH ₃ CO- or CH ₃ CHOH- group
0.370 g of A reacts with sodium to	Flammable gas – H ₂
form a flammable gas that takes up	No of moles of $A = 0.370/74 = 0.005$
125.8 cm ³ of space at 32.5 °C and 101	mol
kPa.	101000 x 125.8 x 10^{-6} =n x 8.31 x
	(273+32.5)
	No of moles of $H_2 = 0.005$ mol
	- mole ratio of \mathbf{A} : $\mathbf{H}_2 = 1$:1
	- A contains 2 alcohol groups
B does not react with Na	- B does not contain–OH group.

* Alternatively, students can give equations to illustrate the reactions undergone by \mathbf{A} and \mathbf{B}





CHI₃

С

13. <u>TJC/2009/P3/Q1b</u>

• High C:H ratio infers that P is an aromatic compound.



• With anhydrous aluminium chloride P undergoes electrophilic substitution reaction to form Q. As the –OH is an activating group, the substituent will be directed to the ortho or para position.



• **P** undergoes electrophilic substituition as it decolourises aqueous bromine to form white ppt **R**. **R** is 2,4,6-tribromophenol as -OH is a highly activating group.



• Q react with aqueous bromine to form white ppt S, with the same no of bromine atoms per molecule of R. As Q has a C-C double bond, electrophilic addition takes place as well. This implies that 1 Br will be attached to one of the carbons of the C-C double bonds. Thus, only 2 Br will be attached directly to the benzene.



S is optically active because of its chiral carbon. The mirror image of S is non-superimposable.

14. <u>TPJC/2009/P3/Q1d</u>



(i)

A undergoes electrophilic addition with HBr to form **D** and **E**.

A undergoes vigorous oxidation / oxidative cleavage with hot acidified KMnO₄ to form **C**. **C** can undergo neutralization or acid-base reaction with aqueous Na₂CO₃ to liberate CO₂ gas.

B undergoes vigorous oxidation / oxidative cleavage with hot acidified $KMnO_4$ to form CO_2 **B** undergoes electrophilic addition with HBr followed by nucleophilic substitution with aqueous NaOH to form hexan-2,3,5-triol.

(ii) A cannot form cis-trans isomers as it is a cyclic alkene and the trans isomer will result in bond angle strain.

B can form a pair of cis-trans isomers as it has an C=C bond with each carbon bonded to two different groups of atoms.



trans cis hexan-2,3,5-triol has 3 chiral carbons, hence no. of optical isomers = $2^3 = 8$

YJC/2009/P3/Q5c

15.

(c) Structures: (relative positions of the 2 functional groups on the benzene ring is not important)





Any 3 out of the following explanations:

- D has a large <u>hydrophobic</u> group (the benzene ring), ∴does not dissolve in water
- D does not contain <u>phenol and COOH group</u>, ∴does not dissolve in NaOH or
 F contains <u>COOH group</u>, ∴ can dissolve in NaOH
- D contains a C=C double bond, as it undergoes electrophilic addition with chlorine gas to form E.

or equation:



- D contains a <u>benzaldehyde group</u>, .:.does not react with Fehling's solution but reacts with Tollen's reagent
- The <u>benzaldehyde group</u> on **D** is oxidised to <u>COOH group</u>; <u>and</u> the alkene group undergoes oxidative cleavage to form a <u>COOH group</u> with hot acidified KMnO₄ to give **F**.



ACJC/2009/P3/Q4b

16. A has amine group being basic. No reaction with aq Br₂ shows absence of phenylamine. A is a ketone. A has a benzene ring, and is 2,4 directing. A undergoes nucleophilic substitution with aq OH⁻ forming C. C has a primary alcohol forming – COOH confirming by reaction with carbonate. A undergoes elimination.





IJC/2009/P3/Q3a



The ester group in V undergoes hydrolysis when heated with NaOH (aq) to yield compounds W and X.

Compound x undergoes electrophilic substitution with Brz (ago to yield compound Y.

(ii) (ii) Add Iz (aq) in NaOH (aq). Warm compound w gives no observable reaction. Compound 2 gives a yellow precipitate.

IJC/2009/P3/Q5d

18.

(ii) J: К: (0)-сн₂-с́н₃ (0)-CH2 C-CH3

k is a ketone and hence, it can undergo condensation reaction with 2.4. DNPH to give an orange precipitate. k has the structure cHz-c-r and hence, it gives a yellow precipitate when heated with aqueous alkaline Iz. Both J and K are oxidised to \bigcirc -cold when treated with hot acidified

KMn 04.





[1]



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[1] M produces white fumes (of HCl) with PCl_5 due to a substitution reaction of the (secondary) alcohol functional group.

[1] M produced 3 compounds, N, P and Q with hot acidified potassium manganate (VII) due to oxidative cleavage of the (2) alkene functional groups present.

[1] N does not undergo mild oxidation with Fehling's reagent as it is not an aldehyde.

[1] N gives a yellow ppt (of CHI_3) and salt R with aq alkaline iodine due to the (mild) oxidation (and cleavage) of the CH_3COR group.

[1] P gives an effervescence (of CO_2) with $Na_2CO_3(s)$ due to a neutralization reaction with the carboxylic acid functional group.

[1] P gives an orange precipitate with 2,4-DNPH due to condensation with the ketone functional group.

[1] Q gives an effervescence (of CO_2) with $Na_2CO_3(s)$ due to a neutralization reaction with the carboxylic acid functional group.

[1]Q does not give an orange precipitate with 2,4-DNPH due to the absence of a carbonyl functional group for condensation.

RI/2009/P3/Q1c-e

21.

(c) Compound D is



D <u>does not contain –OH nor –COOH</u> since it does not react with sodium. It is a di<u>ester</u> formed when –OH and –COOH groups of one lactic acid molecule reacts with the –COOH and –OH groups respectively of another lactic acid molecule.

(d)(i) E has a <u>chiral centre</u> as it rotates plane-polarised light. E is an <u>aldehyde</u> since it reacts with Fehling's solution to give a reddish brown precipitate.

Amount of hydrogen evolved with sodium per mol of $E = \frac{0.24}{24} \div 0.01 = 1$ mol Hence two displaceable H are present \Rightarrow there are two –OH group.

- (ii) E is an alcohol. The stability of its anion is lower than the stability of the anion of lactic acid as the <u>anion is destabilised by the electron-donating</u> -CH₂CH(OH)CHO group.

Lactic acid is a much stronger acid as its anion forms <u>two equivalent resonance</u> <u>structures with the negative charge on O delocalised over two electronegative O atoms</u>.



(ii) <u>Intramolecular hydrogen-bonding</u> occurs in maleic acid and thus it has lower melting point as there are <u>less sites for inter-molecular hydrogen bonding</u>.





RI/2009/P3/Q5b 22.

(b)	Information	Deduction of structure
	Formula of $G = C_8H_{11}O_3N$	Index of unsaturation
		$= \frac{1}{2}(2x8+2-11+1) = 4$
		(or high C to H ratio)
		\Rightarrow G is likely to contain a benzene ring/ aromatic.
	G rotates plane-polarised light.	G is likely to contain at least one chiral carbon.
	G gives a violet colouration with	G is a phenol with violet colourtion formed by
	neutral FeCl ₃ solution	complex formation.
	G reacts with 2 mol of aq NaOH	There are 2 phenolic-OH group in G, reacting with
		OH ⁻ via acid-base reaction.
	G is insoluble in water but	G is likely to contain an amine group, with $-NH_2$
	dissolves in dil H ₂ SO ₄ .	being protonated by H ⁺ .
	G is oxidised by $K_2Cr_2O_7$ to	G is a secondary alcohol and is oxidised to a
	form a product which reacts	ketone by K ₂ Cr ₂ O ₇ .
	with 2,4–DNPH to give an	
	orange ppt.	
	H is formed by reaction of G	H is formed from G by dehydration, it is likely an
	with Al ₂ O ₃	alkene.
	H reacts with aq Br_2 to form	The product is likely to be a bromohydrin formed
	$C_8H_7O_3NBr_4.$	by electrophilic addition and electrophilic
		substitution into activated benzene ring.
	G reacts with C $\ell CO-COC\ell$ to	The phenol, secondary alcohol and amine reacts

form J which has 3 hexagonal	with $C\ell CO-COC\ell$ via nucleophilic substitution.
rings.	3 hexagonal ring \Rightarrow cyclic esters and amides
	formed with the phenolic -OHs and alcoholic-OH
	and amine on adjacent carbon atoms.

SRJC/2009/P3/Q5a

- 23. (a) G undergoes <u>oxidation</u> with acidified KMnO₄.
 - H undergoes <u>nucleophilic substitution</u> with PCI₅.
 - H is an alcohol or carboxylic acid
 - o J is a halogenoalkane or acyl chloride
 - J undergoes <u>reduction</u> with tin in concentrated hydrochloric acid.
 - o J contains <u>nitrobenzene</u>
 - o K contains phenylamine
 - K reacts with (C₂H₅)₂NCH₂CH₂OH through <u>esterification/nucleophilic</u> substitution/acylation
 - o J must contain acyl chloride
 - H is a <u>carboxylic acid</u>



TPJC/2009/P3/Q4b

24.



A number of other structures are acceptable for **F** & **G**. As long as the structure has the correct functional group, and meets the given molecular formula (ie has a ring), the structure can be accepted. No marks are deducted for highly unstable ring structures such as 3 or 4 member rings.



(ii) F is a [primary/secondary] amide the lone pair of electrons on the N atom are drawn toward the electronegative oxygen atom and are not available for donation.

G is a [primary/secondary] amine and has a lone pair of electrons on the N atom available for donation

TPJC/2009/P3/Q5c 25.

- compound F has high C:H ratio/C:H almost 1, hence likely to be benzene derivatives.
- compound F is insoluble in water but dissolves in NaOH → F is acidic.
- (F undergoes <u>CONDENSATION rx</u> with 2,4-DNPH → F is <u>carbonyl compound</u>.)
- F reacts with Fehling's soln → F is a aliphatic aldehyde.
- F undergoes <u>electrophillic substitution readily</u> with bromine water to form G, which (only has one H of F substituted with Br)→ F is a disubstituted <u>phenol</u>
- F undergoes side chain alkyl gp oxidation with hot H⁺/KMnO₄ to give an acid, H.
- (H, C₈H₆O₅ has one carbon less than F → F has an ethyl side chain)
- H reacts with Na₂CO₃ in 1:1 ratio → H is dibasic acid







