Nanyang Junior College

J2 H2 Chemistry Revision Programme 2020

CSI:

CHEMISTRY SURE IMPROVE

[redacted]

Organic Chemistry

1. Intro to Organic Chemistry, Alkanes & Alkenes
2. Arenes
3. Halogen Derivatives
4. Hydroxy Compounds
5. Carbonyl Compounds
6. Carboxylic Acids & Derivatives
7. Nitrogen Compounds
8. Synthesis, Distinguishing Test, Elucidation

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H2 Chemistry Revision Worksheet

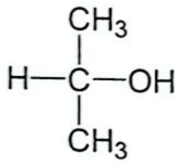
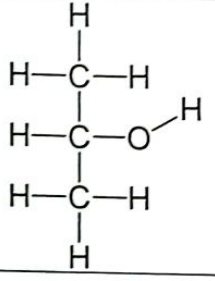
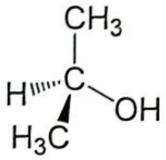
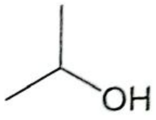
Topics: Introduction to Organic Chemistry / Alkanes / Alkenes

Introduction to Organic Chemistry

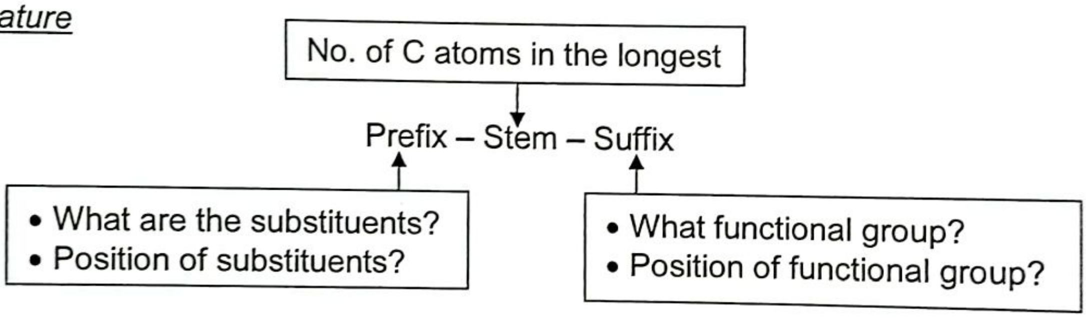
Organic Formulae

Be familiar with the terms used in the question.

Using the $CH(CH_3)_2OH$ as an example,

Structural formula	Displayed formula	Spatial (3D) formula	Skeletal formula
 $H-\underset{CH_3}{\overset{CH_3}{C}}-OH$			

Nomenclature



No. of C atoms in the longest

Prefix – Stem – Suffix

- What are the substituents?
- Position of substituents?

- What functional group?
- Position of functional group?

<table>
<tr><td>Step 1:</td><td>Identify the number of carbon atoms in the longest unbranched chain.
<table>
<tr><th>No. of C atoms</th><th>Stem Name</th></tr>
<tr><td>1</td><td>Meth-</td></tr>
<tr><td>2</td><td>Eth-</td></tr>
<tr><td>3</td><td>Prop-</td></tr>
<tr><td>…</td><td>… (look at notes pg 4)</td></tr>
</table>
Add the word “cyclo” in from of the alkane name if it is a cyclic alkane.</td></tr>
<tr><td>Step 2:</td><td>Identify the main functional group present. When more than one functional group is present in an organic molecule, the suffix indicates the functional group with the highest priority of naming.
(Look at notes pg 5 for functional group priority)</td></tr>
<tr><td>Step 3:</td><td>• Deduce the number of and type of substituents in the parent chain.
• The prefix consists of a number and the name of the substituent separated by a hyphen.
• If there are similar substituents in the molecule, prefixes are used (i.e. 2 similar substituents = di, 3 similar substituents = tri, 4 similar substituents = tetra, etc.
• Give the substituent numbers, which indicates the carbon it is attached to. Remember to give the smallest number to the substituents as possible.</td></tr>
</table>

Isomerism

The existence of different compounds (isomers) with the same molecular formulae but different structural or spatial formulae.

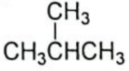
Two main types: Structural isomerism and Stereoisomerism

(1) Structural isomerism

(a) Chain isomerism

Same functional group but the arrangements of the C atoms are different

e.g. $CH_3CH_2CH_2CH_3$ &

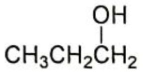


$CH_3CH(CH_3)CH_3$

(b) Positional isomerism

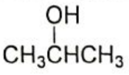
Same functional group attached to different C atoms

e.g.



$CH_3CH_2CH_2OH$

&

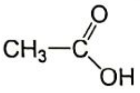


$CH_3CH(OH)CH_3$

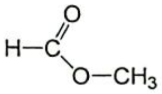
(c) Functional group isomerism

Different functional group

e.g.



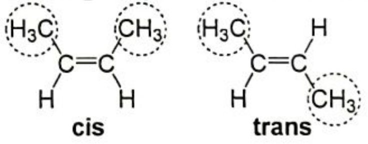
&



(2) Stereoisomerism

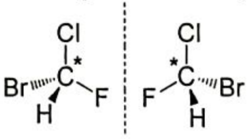
(a) Cis-trans isomerism

Occurs as there is restricted rotation about the C=C double bond due to π-bond. There must be two different groups on each carbon of the double bond.



(b) Enantiomerism

Occurs when there is a chiral carbon, the two optical isomers (enantiomers) are non-superimposable mirror images and no plane, axis or centre of symmetry.



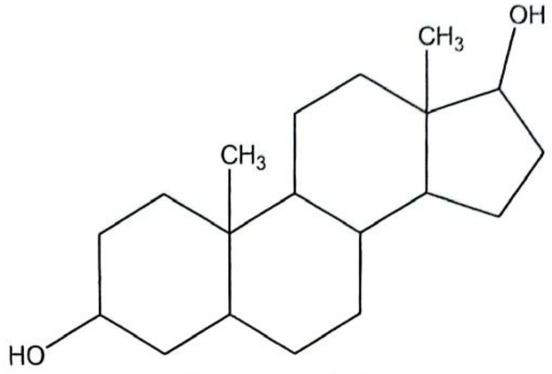
Total number of stereoisomers = 2^n

where n = number of chiral centres + number of C=C bond that can form cis-trans isomerism.

When identifying the no. of isomers (including structural isomers):

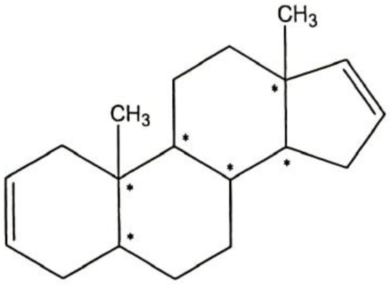
1. Work out the structural isomer.
2. Using formula, 2^n, find the number of stereoisomers for that structure.
3. Sum up all possible stereoisomers from all structural isomers.

Example 1

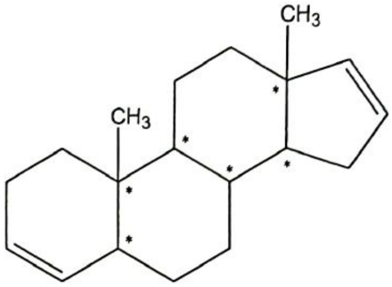


Compound **A**

How many possible isomers, including stereoisomers, can be obtained when **A** is heated with excess concentrated sulfuric acid?



number of stereoisomers = 2^6

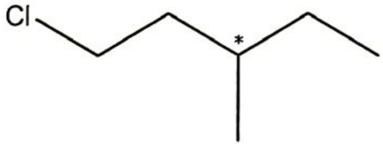


number of stereoisomers = 2^6

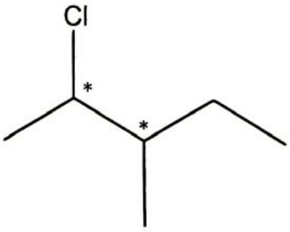
Total number of stereoisomers = $2^6 + 2^6 = 128$

Example 2

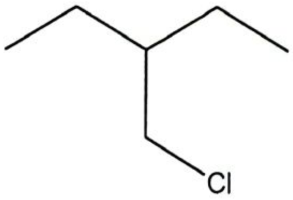
3-methylpentane can undergo reaction with chlorine to form monosubstituted compounds that are optically active. How many possible isomers, including stereoisomers, can be formed in the reaction?



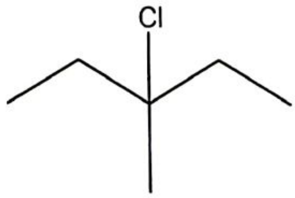
number of isomers = 2^1



number of isomers = 2^2



number of isomers = 2^0



number of isomers = 2^0

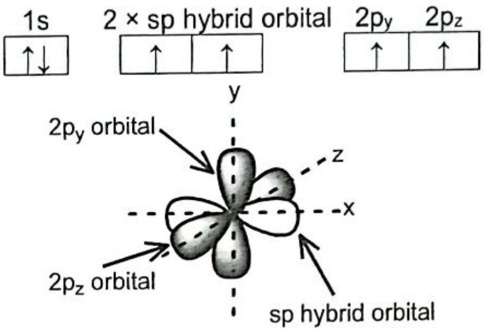
Total number of isomers = $2^1 + 2^2 + 2^0 + 2^0 = 8$

Hybridisation

There are three different types of carbon hybridisation, sp, sp^2 and sp^3.

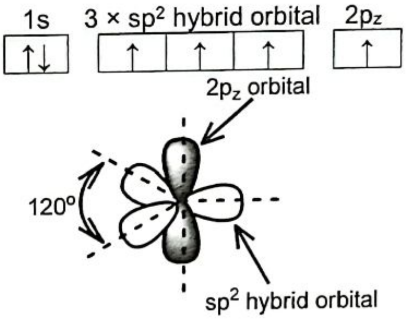
Shape of one hybridised orbital: 

(a) sp hybridisation



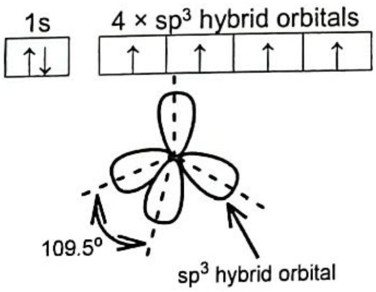
Geometry: linear
Bond angle: 180°
How to identify: 2 atoms directly bonded to C

(b) sp^2 hybridisation



Geometry: trigonal planar
Bond angle: 120°
How to identify: 3 atoms directly bonded to C

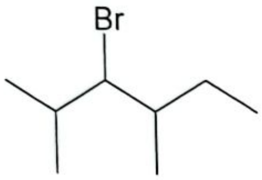
(c) sp^3 hybridisation



Geometry: tetrahedral
Bond angle: 109.5°
How to identify: 4 atoms directly bonded to C

Questions

1 What is the IUPAC name of the following compound?



A 3-bromo-2,4-dimethylhexane

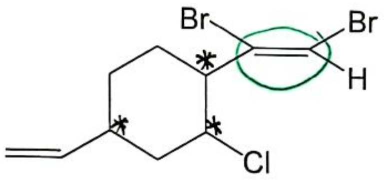
B 2,4-dimethyl-3-bromohexane

C 3-bromo-4-ethyl-2-methylpentane

D 3-bromo-2-ethyl-4-methylpentane

A ✓

2 Compound **W** has the following structure:

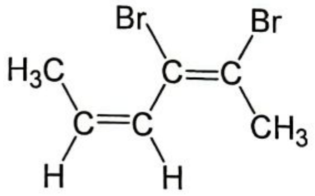


What is the total number of stereoisomers possible for this molecule?

A	4	**C**	16
B	8	**D**	32

8 ✗ C

3 Compound **X** has the following structure:

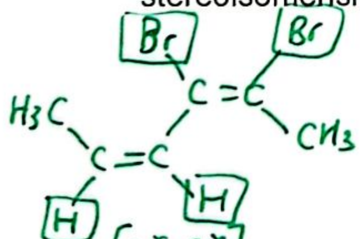


$\rightarrow 2^2 = 4$

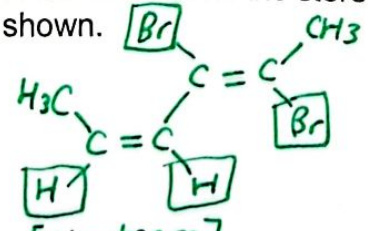
(a) What is the total number of stereoisomers possible for this molecule?

The 2 double bonds can form cis-trans isomerism $\rightarrow n = 2$

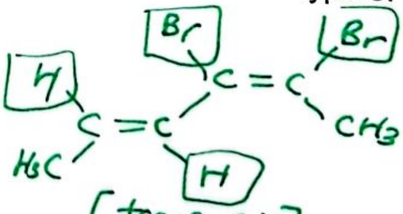
(b) Draw the structural formulae of all the stereoisomers of **X**. Name the type of stereoisomerism shown.



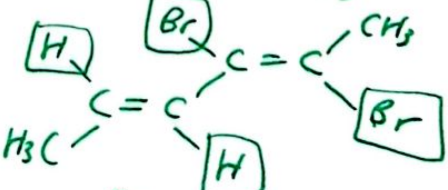
[cis-cis]



[cis-trans]



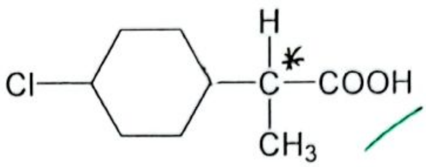
[trans-cis]



[trans-trans]

Type of isomerism: cis-trans isomerism

5 Compound **Y** has the following structure:

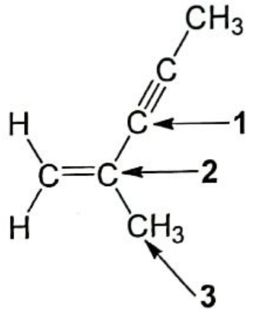


(a) Label an asterisk (*) at the chiral centre(s) in the molecule above.

(b) Draw the enantiomers of compound **Y**.

(c) State how the enantiomers drawn in (b) can be distinguished from each other.

6 Compound **Z** has the following structure:

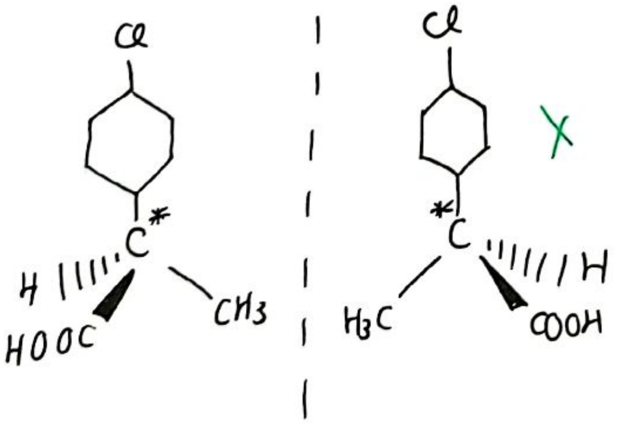


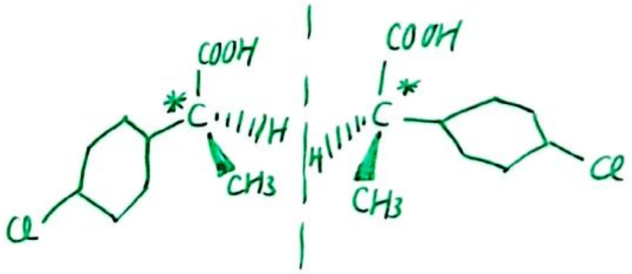
What of the hybridisation of the carbon labeled **1**, **2** and **3**?

	Carbon 1	Carbon 2	Carbon 3
A	sp^2	sp	sp^3
B	sp^2	sp^3	sp
C	sp^3	sp^2	sp
D	sp	sp^2	sp^3

D

5b)





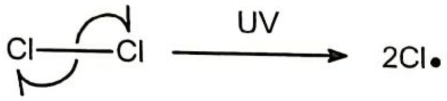
5c) They rotate plane-polarised light in opposite directions, but with the same magnitude of angle of rotation.

Alkanes

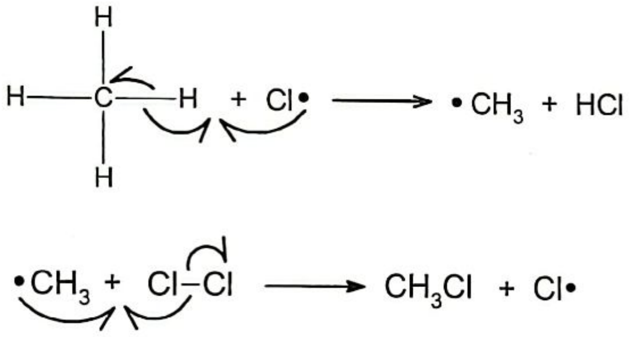
S/N	Reactants	Reagents and Conditions	Products	Type of Reaction / Remarks
1	CH_4	$\xrightarrow{\text{Excess } O_2}$	$CO_2 + 2H_2O$	Combustion
2	Excess CH_4	$\xrightarrow[\text{uv light}]{\text{Limited } X_2 \text{ (X = Cl or Br)}}$	$CH_3X + HX$	Free-radical Substitution Observations: Greenish yellow Cl_2 decolourises Reddish brown Br_2 decolourises

Free-radical Substitution Mechanism

Step 1: Initiation

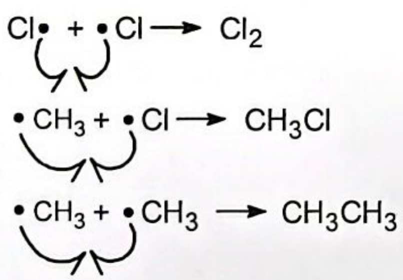


Step 2: Propagation



Connect ball & stick

Step 3: Termination



Connect the dots.

Environmental Concern of Hydrocarbons as Fuels

Pollutants	Formation in car engine	Environmental/ Health Impact	Reaction for removal in catalytic converter
Carbon monoxide	Incomplete combustion of fuel	Combines irreversibly with haemoglobin and makes it ineffective as oxygen carrier in the human body → suffocation or blood poisoning	Conversion of CO to CO_2: $2CO(g) + O_2(g) \xrightarrow{Pt} 2CO_2(g)$
Colorless gas Smells like struck match **Oxides of nitrogen (NO_2, NO)** Reddish brown Colorless gas	Reaction of N_2 with O_2 at high temperatures	Catalyses formation of SO_3 (which can form acid rain) **(i) $NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g)$** **(ii) $NO_2(g) + SO_2(g) \rightarrow SO_3(g) + NO(g)$** (white solid rtp Colorless gas, pungent like sulphur Forms acid rain **$4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_3(aq)$** Forms smog	Conversion of NO to N_2: **$2NO(g) \xrightarrow{Pt} N_2(g) + O_2(g)$** **$2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$** **$25NO(g) + C_8H_{18}(l) \xrightarrow{Pt} \frac{25}{2}N_2(g) + 8CO_2(g) + 9H_2O(l)$** NO_x removed by Pt & Pd & Rh (Three way catalytic converter)
Unburnt hydrocarbon	Incomplete combustion of fuel	Forms smog ozone, NO_x, VOC	Oxidation of unburnt hydrocarbon to CO_2 and H_2O: **$2C_8H_{18}(l) + 25O_2(g) \xrightarrow{Pt} 16CO_2(g) + 18H_2O(l)$**

Ni & Mn limit HC emissions

15 oct '21, noted 16 oct '21

$\boxed{+ c\,O_2}$ ✓ now CO_2

$A\,SO_3(g) + B\,H_2O(l) \rightarrow D\,H_2SO_4(aq)$

Is it indetermined? solution if # unknowns ≥ # eq.

S: $A = D$ 3 unknowns, 3 eqs

H: $B = D$ Let ∴ $A = B = D = 1$, $c = 0$

O: $3A + B = 4D$ $\boxed{+2c}$ if $A = B = D = \frac{1}{2}$ then $c = 0$

Questions

7 Which of the following is **not** a product formed in the termination step in the reaction of ethane and Cl_2 in the presence of UV light?

A HCl

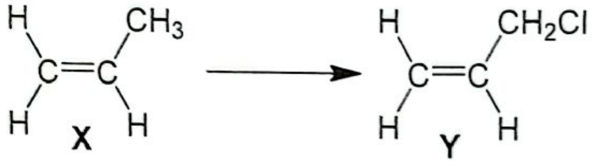
B Cl_2

C CH_3CH_2Cl

D $CH_3CH_2CH_2CH_3$

A ✓

8 In a reaction shown below, compound **X** is converted into compound **Y**.



(a) State the type of reaction occurred.

Free Radical Substitution.

(b) State the reagent and condition required for the reaction.

UV, $Cl_2(g)$ × Limited Cl_2 in the presence of UV light

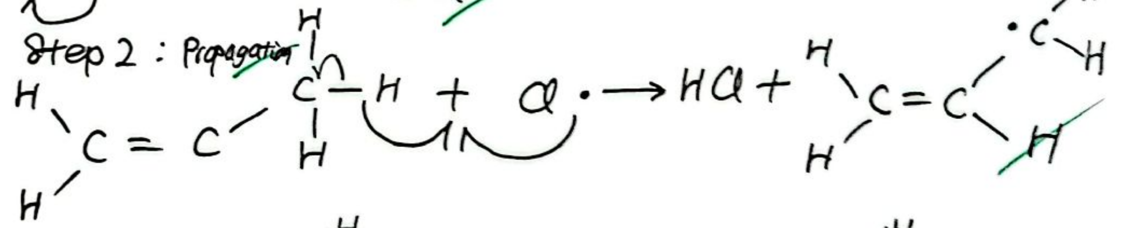
(c) Describe the mechanism for the conversion of **X** to **Y**.

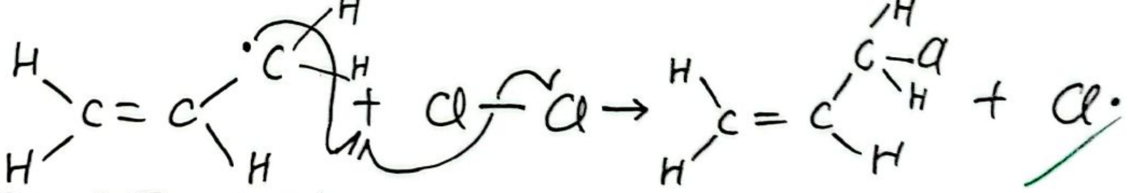
Mechanism: Free Radical Substitution

Step 1: Initiation ✓

$$Cl-Cl \xrightarrow{UV} 2Cl\cdot$$ ✓

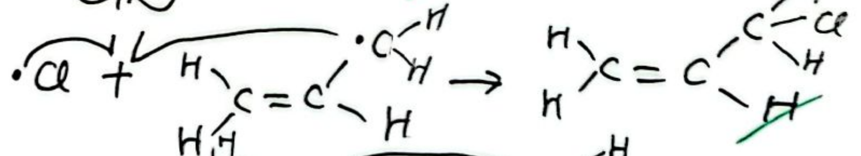
Step 2: Propagation

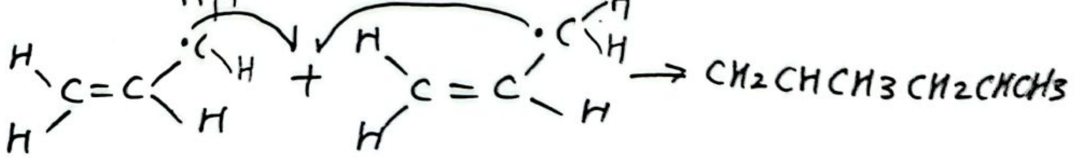




Step 3: Termination ✓

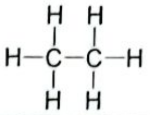
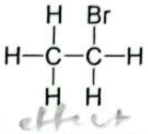
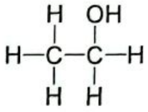
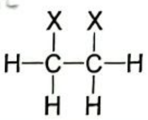
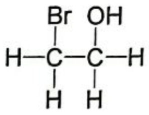
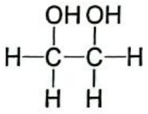
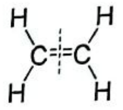
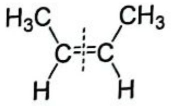
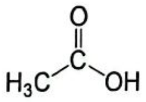
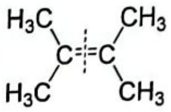
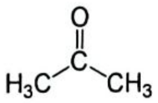
$$Cl\cdot + \cdot Cl \rightarrow Cl_2$$ ✓



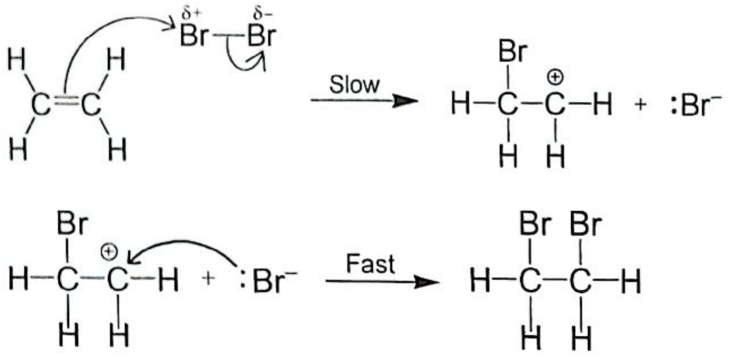


make formal charge more +ve POIL

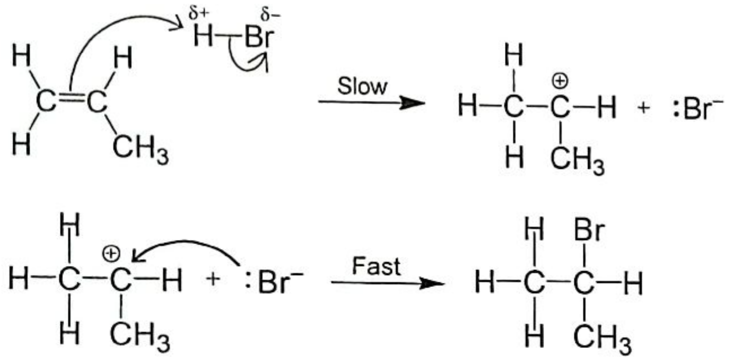
more electronegative NRIG

S/N	Reactants	Reagents and Conditions	Products	Type of Reaction / Remarks
1	$CH_2=CH_2$	$\xrightarrow[\text{heat}]{H_2\text{, Ni catalyst}}$ □? Δ Δ	 CH_3-CH_3	Reduction (Alternative condition: H_2 (g), Pt catalyst, room temp)
2	$CH_2=CH_2$	$\xrightarrow[\text{room temperature}]{HX\text{ (X = F, Cl, Br, I)}}$ reactivity: HI>HBr>HCl>HF ↑ nuclear charge outweighs screening effect	 CH_3-CH_2Br	Electrophilic Addition (Remember to apply Markovnikov's rule)
3	$CH_2=CH_2$	$\xrightarrow[300^{o}C\text{, 60 atm}]{H_2O\text{ (g), }H_3PO_4\text{ catalyst}}$	 CH_3-CH_2OH	Electrophilic Addition Alternative condition: (1). Conc. H_2SO_4 , room temp (2). H_2O (l), heat (Remember to apply Markovnikov's rule)
16 oct 21 4	$CH_2=CH_2$	colorless toxic sweet smelling liquid $\xrightarrow[\text{dark, room temperature}]{X_2\text{ (X= Cl or Br) in }CCl_4}$	 CH_2X-CH_2X	Electrophilic Addition Observations: Greenish yellow Cl_2 decolourises Reddish brown Br_2 decolourises
16 oct 21 5	$CH_2=CH_2$ ↓ chemgra:	Br^- more stable than OH^- $\xrightarrow[\text{room temperature}]{Br_2\text{ (aq)}}$ Attacks ⊕ electrophile, hence no C=C with OH OH	 CH_2Br-CH_2OH	Electrophilic Addition (Can be used a test for the presence of alkene C=C double bond) Observations: Reddish brown Br_2 decolourises
6	$CH_2=CH_2$	$\xrightarrow[\text{Cold in acidic condition}]{KMnO_4\text{(aq)}}$	 $CH_2(OH)-CH_2(OH)$	Mild Oxidation Alternative condition: $KMnO_4$(aq), cold in alkaline condition Observations Acidic condition: Purple $KMnO_4$ decolourises Alkaline condition: Purple $KMnO_4$ decolourises, brown ppt of MnO_2 formed
7		$\xrightarrow[\text{Heat in acidic condition}]{\text{Concentrated }KMnO_4}$	$2CO_2 + 2H_2O$	Oxidative cleavage Alternative condition: Concentrated $KMnO_4$, heat in alkaline condition (Can be used as a test for presence of alkene C=C double bond) Observations Acidic condition: Purple $KMnO_4$ decolourises Alkaline condition: Purple $KMnO_4$ decolourises, brown ppt of MnO_2 formed
		$\xrightarrow[\text{Heat in acidic condition}]{\text{Concentrated }KMnO_4}$	2 	
		$\xrightarrow[\text{Heat in acidic condition}]{\text{Concentrated }KMnO_4}$	2 	

Electrophilic Addition Mechanism of Ethene with Br_2



Electrophilic Addition Mechanism of Propene with HBr



(Remember to apply Markovnikov's rule)

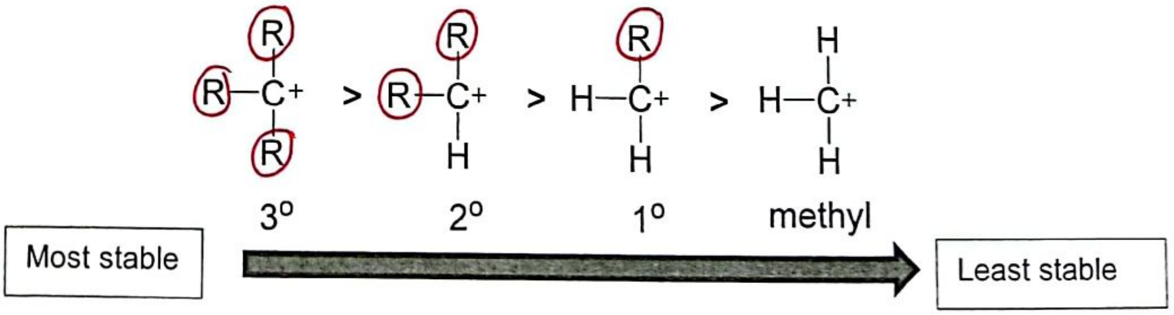
Markovnikov's rule

- When a molecule H−A adds to a C=C bond in an **unsymmetrical alkene**, the **major product** formed depends on the **stability of the carbocation intermediate (most stable carbocation intermediate favoured)**.

- Carbocations are classified as primary, secondary and tertiary according to the number of alkyl groups.

- **Relative Stability of carbocation: 3° > 2° > 1° > methyl**

R has c
C-C less electronegativity difference than C-H



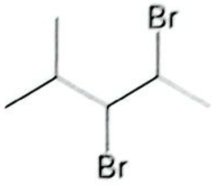
Questions

9 Which of the following is formed when compound **X** reacts with HBr?

X

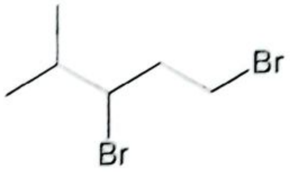
A

B



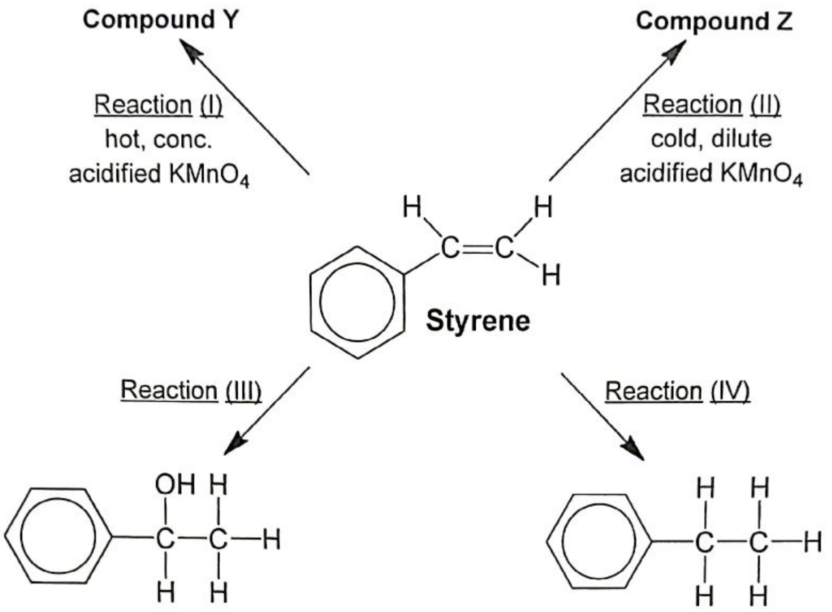
C

D



C

10 Styrene is a raw material used in the production of plastic materials like food containers. Styrene undergoes the reactions shown in the scheme below:



(a) Suggest the reagents and conditions for reactions (III) and (IV).

(b) Give the structural formulae of organic compound **Y** and **Z**.

(c) State the type of reaction that have occurred for reactions (I) to (IV).

11 But-1-ene reacts with hydrogen bromide to give the same equimolar (1:1) mixture of two isomers of the product.

(a) Draw displayed structures of the product formed and label any chiral carbon with an asterisks. Name the product formed.

(b) Draw the enantiomers of the product.

(c) Explain why the enantiomers were formed in equal amounts.

12 Propene reacts with bromine under suitable condition to give 1,2-dibromopropane.

(a) Suggest the reagent and condition for this reaction.

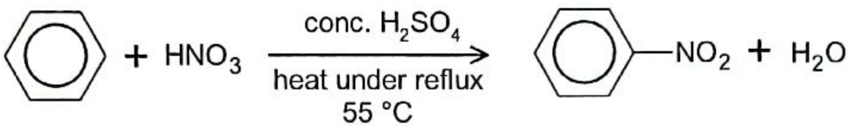
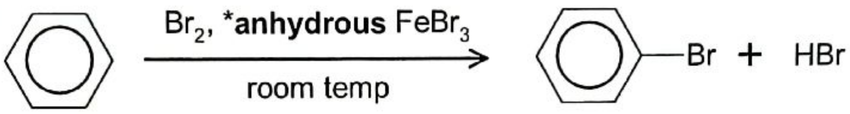
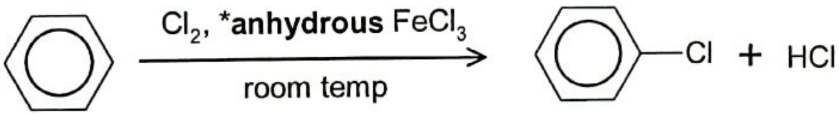
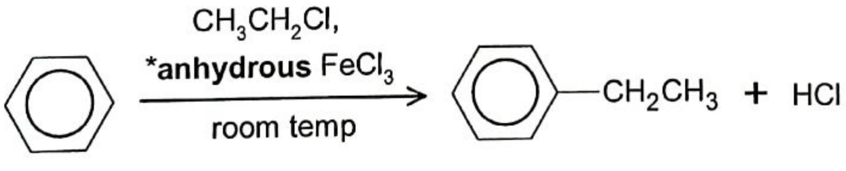
(b) State the type of reaction that have occurred.

(c) Describe the mechanism of the reaction between propene and bromine.

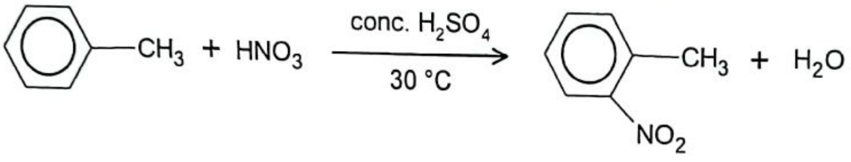
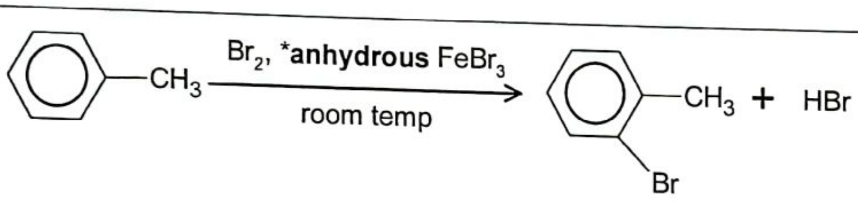
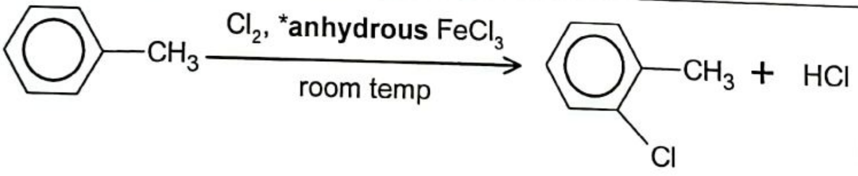
H2 Chemistry Revision Worksheet

Topic: Arenes

Reactions of benzene

S/N	Reactants	Reagent & Conditions	Products	Type of reaction/ Remarks
1				Electrophilic substitution Observations: A pale yellow liquid with the smell of almonds is produced
2	 *anhydrous AlBr3 and iron powder are also acceptable catalysts.			Electrophilic substitution Observations: Reddish brown Br_2 decolourised. White steamy fumes of HBr evolved.
3	 *anhydrous AlCl3 and iron powder are also acceptable catalysts.			Electrophilic substitution Observations: Greenish yellow Cl_2 decolourised. White steamy fumes of HCl evolved.
4	 *anhydrous AlCl3 is also an acceptable catalyst.			Electrophilic substitution Observations: White steamy fumes of HCl evolved.

Reactions of methylbenzene (involving the benzene ring ONLY)

S/N	Reactants	Reagent & Conditions	Products	Type of reaction/ Remarks
1	 A <u>mixture</u> of 2-nitromethylbenzene and 4-nitromethylbenzene are formed.			Electrophilic substitution <u>Observations:</u> A pale yellow liquid with the smell of almonds is produced. <u>Note:</u> Lower temperature of **30°C** is used for methylbenzene instead of 55°C for benzene.
2	 A <u>mixture</u> of 2-bromomethylbenzene and 4-bromomethylbenzene are formed.			Electrophilic substitution <u>Observations:</u> Reddish brown Br_2 decolourised. White steamy fumes of HBr evolved.
3	 A <u>mixture</u> of 2-chloromethylbenzene and 4-chloromethylbenzene are formed.			Electrophilic substitution <u>Observations:</u> Greenish yellow Cl_2 decolourised. White steamy fumes of HCl evolved.

Mechanism: Electrophilic substitution – Nitration of Benzene / Methylbenzene

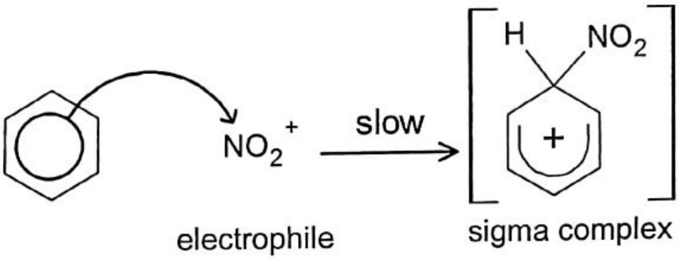
3 steps to the mechanism

(i) Formation of the electrophile

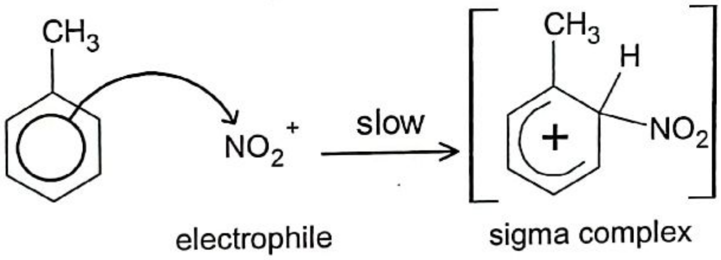
$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$

(**Note that HNO_3:H_2SO_4 is 1:2.**)

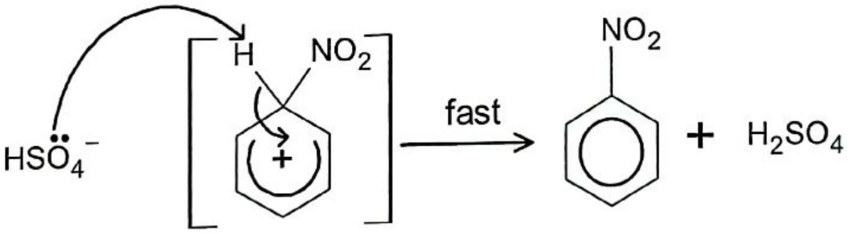
(ii) Formation of the sigma complex



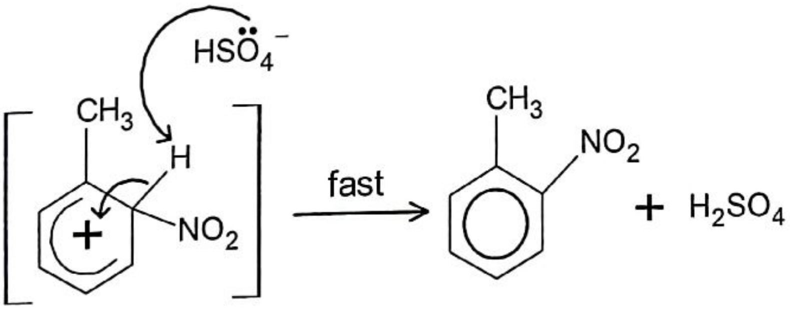
OR



(iii) Formation of the substitution product



OR



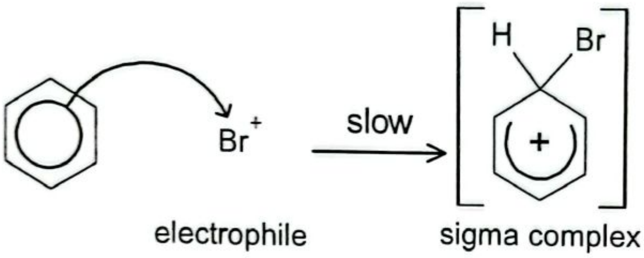
Mechanism: Electrophilic substitution – Halogenation (Bromination) of Benzene / Methylbenzene

3 steps to the mechanism

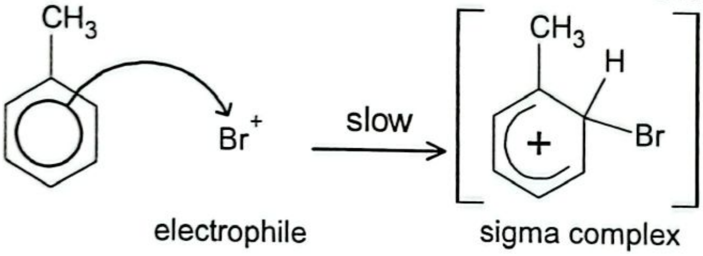
(i) Formation of the electrophile

$Br_2 + FeBr_3 \rightleftharpoons Br^+ + FeBr_4^-$

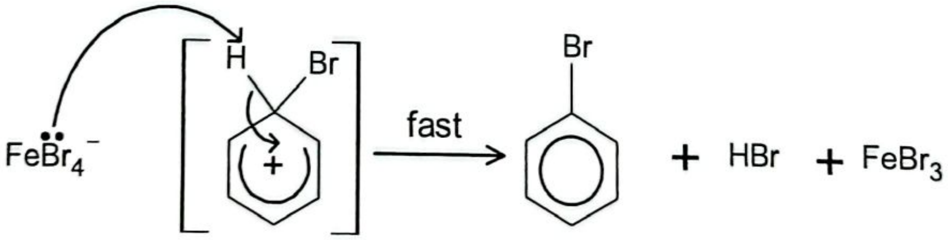
(ii) Formation of the sigma complex



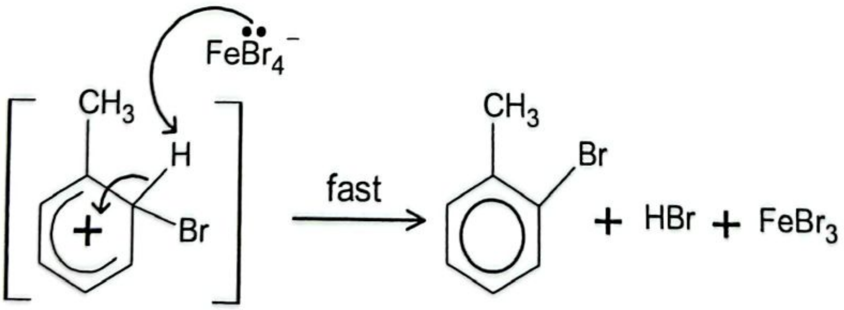
OR



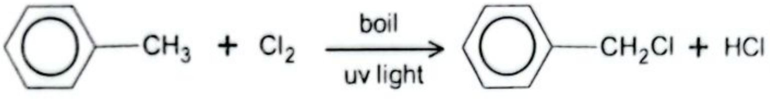
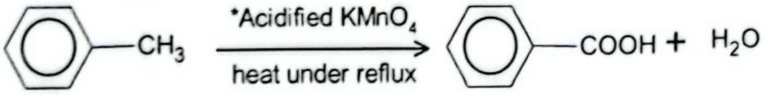
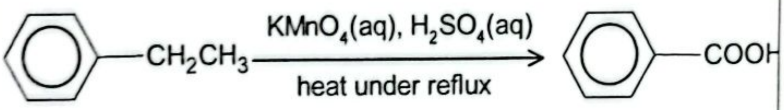
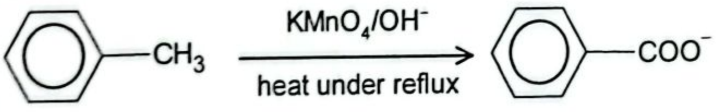
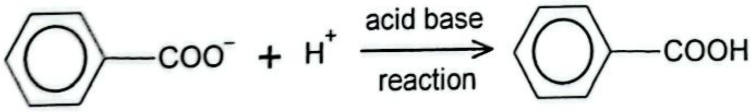
(iii) Formation of the substitution product



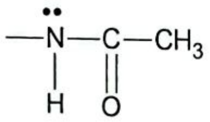
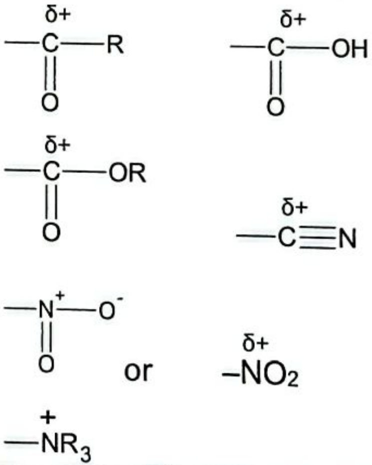
OR



Reactions of methylbenzene (involving the side chain, $-CH_3$)

S/N	Reactants	Reagent & Conditions	Products	Type of reaction/ Remarks
1				Free radical substitution Mixture of $C_6H_5CH_2Cl$, $C_6H_5CHCl_2$, $C_6H_5CCl_3$ are obtained.
2	 If there are more than 1 carbon in the alkyl side chain, 			Oxidation Observations: Purple $KMnO_4$ is decolourised and white ppt of benzoic acid is formed. Note: If the side chain contains more than one C atom, the organic product is benzoic acid and the other products will be CO_2 and water.
3	 			Oxidation Observations: Purple $KMnO_4$ is decolourised and brown ppt of MnO_2 is formed. Note: On acidifying benzoate ion, a white ppt of benzoic acid is formed.

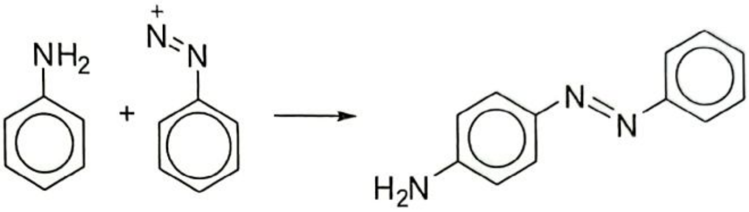
Substituent effects on electrophilic substitution

		Orientation	
		2,4–directing	3–directing
Reactivity	Activating	• Atom joined directly to ring has a lone pair of electrons $-\ddot{O}H$ $-\ddot{O}R$ $-\ddot{N}H_2$  $-\overset{\cdot\cdot}{N}(H)-C(=O)-CH_3$ • Alkyl groups $-R$	
	Deactivating	• Halogens (weakly deactivating) $-Cl$ $-Br$ $-I$	• Atom joined directly has a full or partial positive charge  $-\overset{\delta+}{C}(=O)-R$ $-\overset{\delta+}{C}(=O)-OH$ $-\overset{\delta+}{C}(=O)-OR$ $-\overset{\delta+}{C}\equiv N$ $-\overset{+}{N}(=O)-O^-$ or $-\overset{\delta+}{NO_2}$ $-\overset{+}{N}R_3$

Questions

VJC/Prelim 2008/1/21

1 A bright yellow dye, aniline yellow can be synthesised from benzene in the following synthetic route.



What is the type of reaction for the reaction shown above?

A Electrophilic substitution
B Electrophilic addition
C Nucleophilic substitution
D Nucleophilic addition

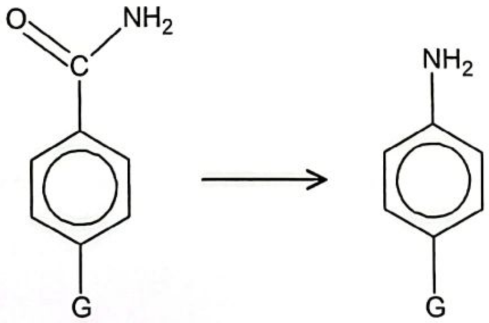
A ✓

MJC/Prelim 2007/1/26

2 The Hofmann degradation is the organic reaction where a primary amide is converted into a primary amine with one fewer carbon atom. An example is shown below:

$$R\text{-}CONH_2 \rightarrow R\text{-}NH_2$$

When the R group is an aryl group, the rate of the Hofmann degradation is dependent on the substituent in the aromatic ring.



It is found that this reaction proceeded faster when the substituent **G** is a methyl group as compared to a bromine group.

Which of the following substituents (in place of **G**) would result in the fastest rate of Hofmann degradation?

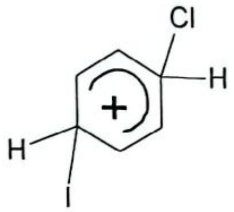
A Cl
B H
C NO_2
D OCH_2CH_3

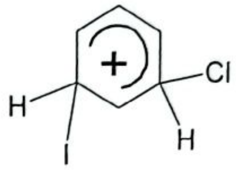
D ✓

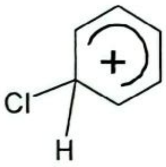
VJC/Prelim 2007/1/23

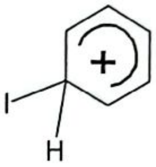
3 In the presence of a suitable catalyst, benzene undergoes a reaction with the interhalogen compound ICl.

Which one of the following species shows the correct structure of the intermediate formed?

A


B


C


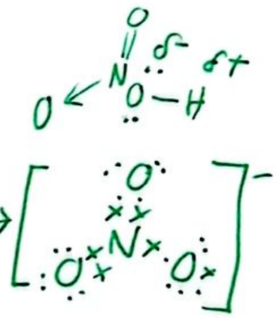
D


D ✓

NJC/Prelim 2007/1/37

4 Which of the following are both species electrophiles?

1 Br_2, NO_2^+ $\overset{\delta+}{Br}-\overset{\delta-}{Br}$ (e⁻ deficient) $O=\overset{+}{N}=O$
2 $AlCl_3$, HNO_3 Al/Be/B are e⁻ deficient
3 Na^+, $(CH_3)C^+$ ✓
not an electrophile, Na^+ can't form a covalent bond



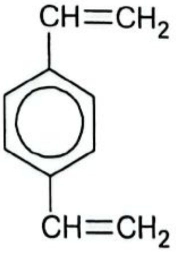
3 × 1&2

MI/Prelim 2007/1/40

5 An aromatic hydrocarbon X was made to react with an excess of hot aqueous alkaline potassium manganate(VII) and the product was treated with an excess of aqueous acid to give 1,4-benzenedicarboxylic acid. Possible structure/s of X is/are

1


2


3


1&2&3 ✓

MI/Prelim 2007/1/38

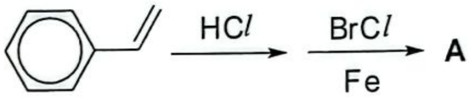
6 Which of the following methods can be used to prepare 3-nitrobenzoic acid?

1 The nitration of benzoic acid
2 The nitration of methylbenzene followed by oxidation
3 The reduction of 3-aminobenzoic acid

1&2

VJC/Prelim 2008/1/27

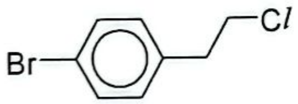
7 Styrene undergoes the following reactions to form compound **A**.



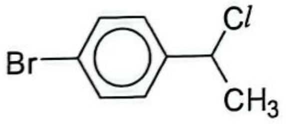
styrene

What is the structural formula of **A**?

A

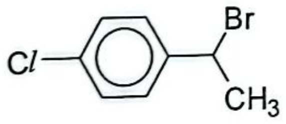


B

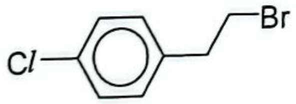


B

C

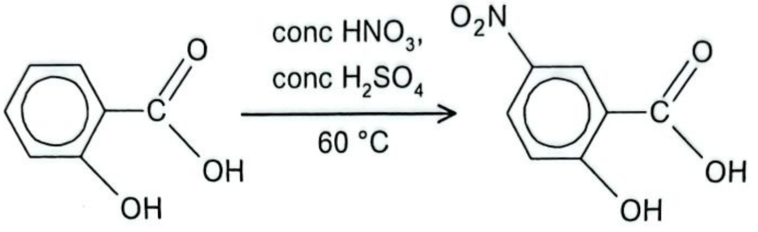


D



MJC/Prelim 2007/2/4f(iii)

8 A chemist intended to introduce a nitro group into the benzene ring of *salicyclic acid* using the reaction scheme shown below:



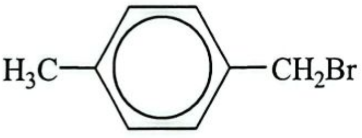
Salicyclic acid

With the help of suitable equations, outline the mechanism for the nitration of *salicyclic acid*.

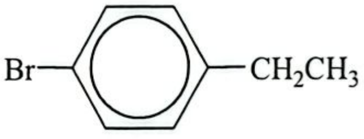
JJC/Prelim 2007/2/5b

9(a) Suggest a *simple* chemical test to distinguish between the following pairs of isomers.

(i)



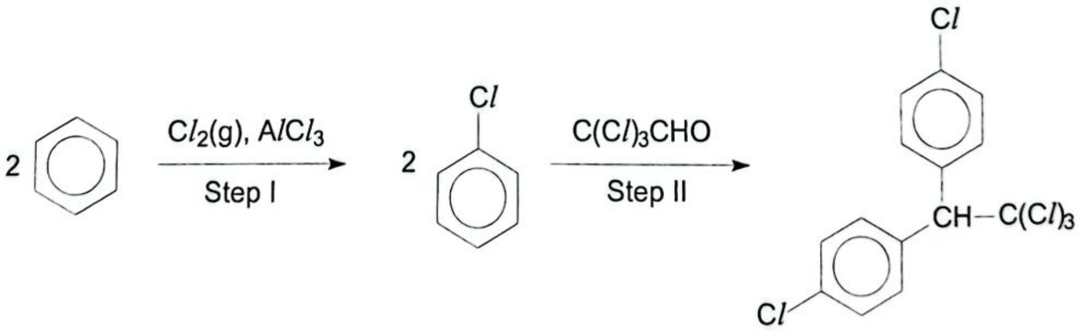
and



J **K**

SRJC/Prelim 2008/3/4

10 The reaction scheme below,
shows the synthesis of 4,4-dichlorodiphenyltrichloroethane (DDT).



4,4-dichlorodiphenyltrichloroethane
(DDT)

(a) In a school science project to study the synthesis of DDT, a student prepares some of the intermediate, chlorobenzene, by dissolving small amount of anhydrous aluminium chloride in some benzene and followed by bubbling chlorine gas into the mixture.

(i) Explain why aluminium chloride is soluble in benzene.

(ii) Will the reaction between benzene and chlorine in Step I take place if aluminium chloride is not added? Explain your answer with reference to the structure of benzene.

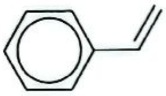
(iii) What is the role of aluminium chloride in Step I? Write a chemical equation to show how aluminium chloride takes part in the reaction.

(iv) During the preparation, the student was told to ensure that all equipment is dry before he put in the reactants. This is because the reaction will cease if water is present in the reacting mixture. With appropriate equation(s), explain how water stops the reaction.

(b) Name and outline the mechanism in step 1.

RJC/Prelim 2008/3/5d

11 Both styrene and ethylbenzene share similar reactions although the actual mechanisms usually differ.



styrene

(i) When styrene and ethylbenzene are brominated via different electrophilic mechanisms, a **total** of three constitutional isomers (C_8H_9Br) in significant quantities are formed. For each hydrocarbon, state the reagents/conditions used and give the structural formula of the product(s).

(ii) When styrene and ethylbenzene are oxidised vigorously, the same compound **K** is formed. By slightly modifying the conditions, **one** of the hydrocarbons reacts to form compound **L**. Both **K** and **L** contain two oxygen atoms. Give the structural formulae of **K** and **L** and state the reagents/conditions needed to produce **L**.

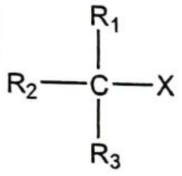
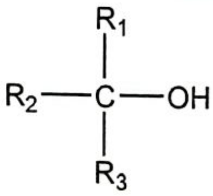
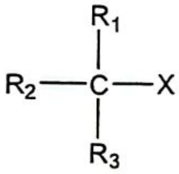
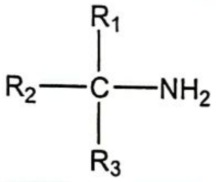
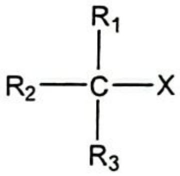
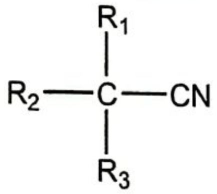
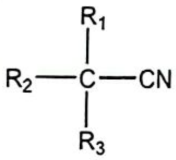
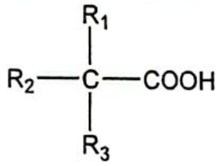
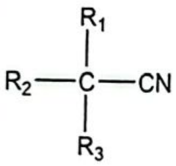
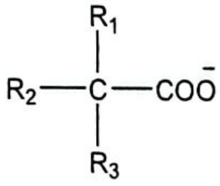
H2 Chemistry Revision Worksheet

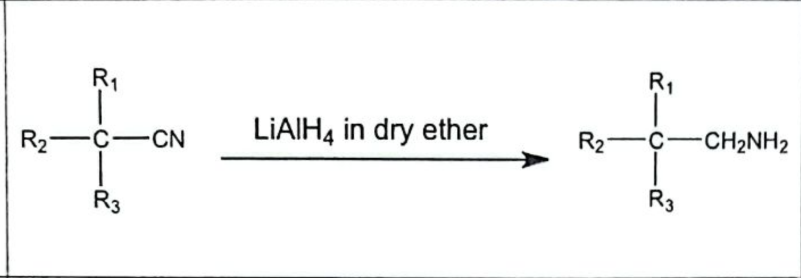
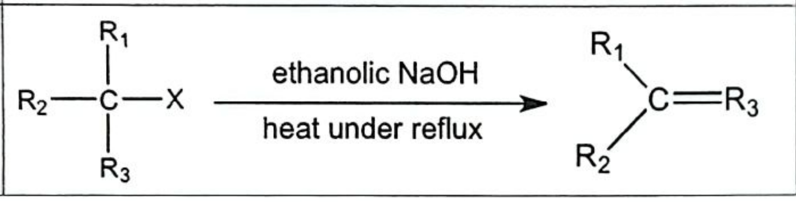
Topic: Halogen Derivatives

Preparation of Halogen Derivatives

1. From Alkanes – Free Radical Substitution (Refer to CSI: Alkanes Reaction 2)
2. From Alkenes – Electrophilic Addition (Refer to CSI: Alkenes Reaction 2 & 4)
3. From Alcohols – Nucleophilic Substitution (Refer to CSI: Alcohol Reaction 1 to 6)

Summary of Reactions of Halogen Derivatives[1,2,3,4]

S/N	Reactants	Reagents and Conditions	Products	Type of Reaction / Remarks
1	 $R_2-\overset{R_1}{\underset{R_3}{C}}-X$	NaOH(aq) heat under reflux	 $R_2-\overset{R_1}{\underset{R_3}{C}}-OH$	Nucleophilic Substitution For 1° RX: S_N2 For 3° RX: S_N1 Alternative reagents and conditions: (1) $H_2O(l)$, heat (RX can be hydrolysed **<u>very slowly</u>** by water when heated to give the alcohol.)
2	 $R_2-\overset{R_1}{\underset{R_3}{C}}-X$	excess ethanolic NH_3 heat in sealed tube	 $R_2-\overset{R_1}{\underset{R_3}{C}}-NH_2$	Nucleophilic Substitution For 1° RX: S_N2 For 3° RX: S_N1 (To convert to amines of the same carbon length.)
3	 $R_2-\overset{R_1}{\underset{R_3}{C}}-X$	ethanolic NaCN heat under reflux	 $R_2-\overset{R_1}{\underset{R_3}{C}}-CN$	Nucleophilic Substitution For 1° RX: S_N2 For 3° RX: S_N1 (To lengthen carbon chain by 1 carbon atom.)
3a	 $R_2-\overset{R_1}{\underset{R_3}{C}}-CN$	HCl(aq) heat	 $R_2-\overset{R_1}{\underset{R_3}{C}}-COOH$ + NH_4Cl	Acidic Hydrolysis (To convert nitrile to carboxylic acid.)
3b	 $R_2-\overset{R_1}{\underset{R_3}{C}}-CN$	NaOH(aq) heat	 $R_2-\overset{R_1}{\underset{R_3}{C}}-COO^-$ + NH_3	Alkaline Hydrolysis (To convert nitrile to carboxylate salt.)

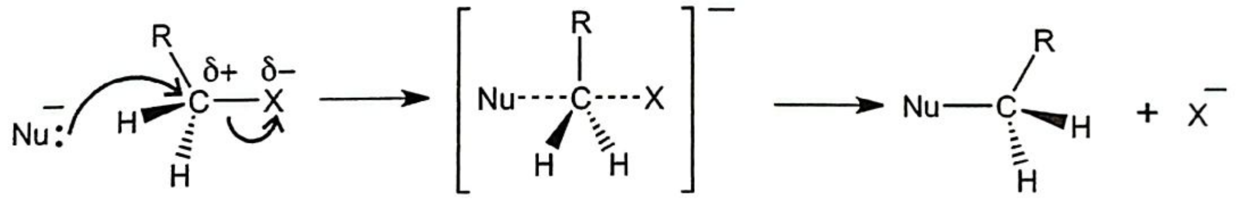
3c		Reduction Alternative reagents and conditions: (1) Na in ethanol **or** (2) H_2(g) with Pd catalyst (To convert nitrile to amine.)
4		Elimination (Apply Saytzeff's Rule.)[5]

Note:

1. X = halogen atom
2. For 1° RX, $R_1 = R_2 = H$ and R_3 = alkyl / aryl group
3. For 2° RX, R_1 / R_2 / R_3 = alkyl / aryl groups
4. Halogenoarenes do not undergo nucleophilic substitution because:
    - one of the lone pair of electrons on the halogen atom interacts with the ring of delocalised π electrons of benzene, strengthening the C–X bond.
    - the high electron density of the aromatic ring tends to repel the approaching nucleophile.
5. Saytzeff's Rule: In elimination reaction, the products with the most highly substituted double bond will predominate. This is because the more substituted alkene is more stable.

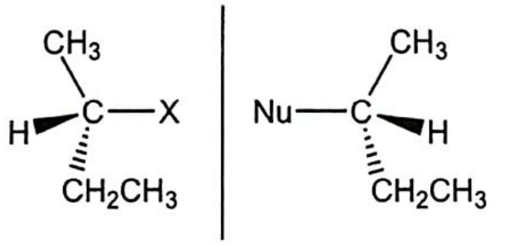
S_N2 Mechanism (For CH_3X or 1° RX)

S_N2 mechanism mainly applies to 1° RX where there is less steric hindrance.



If RX is chiral, there will be an inversion of configuration (i.e. the optical isomerism of the product will be the reverse of the chiral RX).

E.g.



chiral RX

product with inversion of configuration

Key Explanations

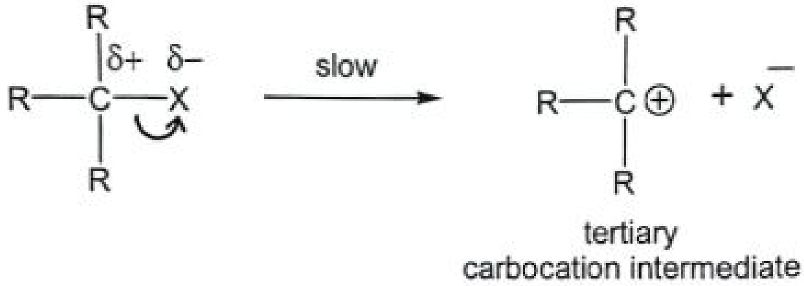
1. S_N2 mechanism mainly applies to CH_3X and 1° RX because they contain less bulky alkyl groups, therefore less steric hindrance about the electron deficient carbon centre. This makes them more susceptible to nucleophilic attack.

2. The inversion of configuration is due to the backside attack of the nucleophile on the electron deficient carbon centre.

S_N1 Mechanism (For 3° RX)

S_N1 mechanism mainly applies to 3° RX where there is more steric hindrance.

Step 1:



Step 2:

If RX is chiral, the product will be a racemic mixture (equal amount of optical isomers/enantiomers). This is because the nucleophile is attacking the carbocation (trigonal planar shape) from either side of the plane with equal probability.

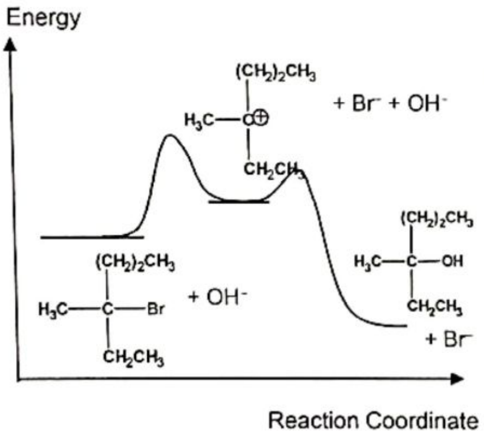
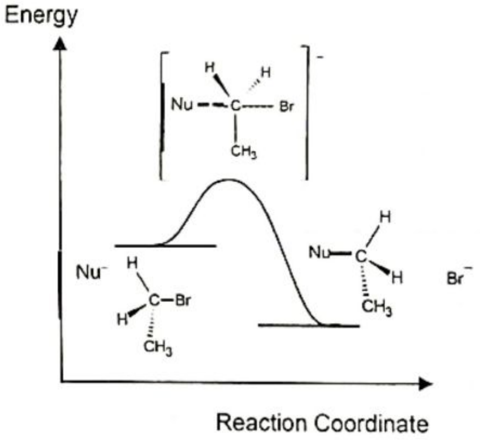
Note: Similar effect observed in Electrophilic Addition (planar carbocation intermediate) and Nucleophilic Addition (planar carbonyl carbon centre).

Key Explanations

1. S_N1 mechanism mainly applies to 3° RX because the carbocation intermediate formed is more stable due to the presence of more electron donating alkyl groups.

2. Loss of optical activity.

Note: A racemic mixture consists of the (+) and (−) optical isomers/enantiomers. The racemic mixture has no optical activity as the rotation effect of one enantiomer exactly cancels out by the opposite rotation, of the same magnitude, of the other enantiomer. However, the individual (+) or (−) enantiomer is optically active.

	Nucleophilic Substitution (S_N1)	**Nucleophilic Substitution (S_N2)**
Relative Rates	3° RX > 2° RX > 1° RX > CH_3X	CH_3X > 1° RX > 2° RX > 3° RX
Rate Equation	Rate = k [RX]	Rate = k [RX] [Nu^-]
Effect of Alkyl Groups	Electron-donating alkyl groups stabilise carbocations	Alkyl groups causes steric hindrance to carbon bearing X atom
Stereo-chemistry	Racemic mixture	Inversion of configuration
Energy Profile Diagram		

Distinguishing Tests for Halogen Derivatives

Method 1:
(1) Heat with alcoholic silver nitrate or alcoholic silver ethanoate.
Alcoholic – to increase the solubility of organic RX

Compounds	Observations	Explanations
Iodoethane	Yellow ppt, AgI, forms **immediately**	Atomic radius of I is the largest. C-I bond length is the longest & its bond strength is the weakest, so it is the easiest to break. Hence, rate of hydrolysis is the fastest.
Bromoethane	Cream ppt, AgBr formed **after a while (~3mins)**	Atomic radius of Br is smaller. C-Br bond length is shorter & its bond strength is stronger & more difficult to break. Hence, rate of hydrolysis is slower.
Chloroethane	White ppt, AgCl formed **after a long time (~12 mins)**	Atomic radius of Cl is the smallest. C-Cl bond is the shortest & its bond strength is the strongest, so it is the most difficult to break. Hence, rate of hydrolysis is the slowest.
Chlorobenzene	No ppt formed	• C—Cl bond is strengthened by the interaction with benzene ring. • No reaction occurs.

Method 2:
1) Addition of aqueous NaOH and heat
2) Acidify with dilute HNO_3
3) Addition of aqueous $AgNO_3$

Compounds	Observations	Explanations	Purpose
Iodoethane	**Immediate** yellow ppt, AgI	Step 1: $CH_3CH_2X + OH^- \rightarrow CH_3CH_2OH + X^-$ Step 2: $HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$ Step 3: $AgNO_3 + X^- \rightarrow AgX + NO_3^-$	To release the halogen as halide To remove excess NaOH, otherwise Ag_2O will be precipitated when $AgNO_3$ is added. Colour of ppt will indicate the type of halogen present.
Bromoethane	**Immediate** cream ppt, AgBr		
Chloroethane	**Immediate** white ppt, AgCl		
Chlorobenzene	No ppt formed		

Functional Groups	**1° Halogenoalkanes**	**Chlorobenzene**	**CH_2=CHCl**
Trend	• Hydrolysed	• Not hydrolysed	• Not hydrolysed
Explanation	• Rate of hydrolysis in 1° RX depends on the bond length of C–X bond C–I > C–Br > C–Cl > *C–F *(C–F bond not hydrolysed as the bond is too strong) • As the atomic radius of X increases, → C–X bond length increases, → strength of C–X bond decreases, → hence more easily broken • Rate of hydrolysis does NOT depend on the polarity of the C–X bond.	• The p orbital of Cl atom overlaps with π orbital of benzene ring resulting in the delocalisation of lone pair of electrons on the Cl atom into the benzene ring. The C–Cl bond has some double bond character/ is strengthened (therefore the bond is stronger than that in an alkyl halide). • Sterically, the rear side of the C–X bond is blocked by the bulky benzene ring. • The π electron cloud of the benzene ring will repel the lone pair of electrons of an incoming nucleophile.	• The p orbital of Cl atom overlaps with π orbital of C=C bond resulting in the delocalisation of lone pair of electrons on the Cl atom into the C=C bond. The C–Cl bond has some double bond character/ is strengthened (therefore the bond is stronger than that in an alkyl halide). • The high electron density of the C=C bond tends to repel the approaching nucleophile.

Fluorohalogenoalkanes

CFCs:

- inert and stable (C–F bond is very strong)
- non-flammable (no C–H bonds)
- non-toxic
- odourless
- good organic solvents

Harmful effects of CFCs

- Depletes ozone layer (due to the formation of Cl•) causing us to be overexposed to U.V. radiation which causes skin cancer and also widespread failure in crops cultivation.

Questions

1 **J93/IV/25**

Chloroethane is converted into carboxylic acid containing one more carbon atom through a two-stage process.

Which one of the following compounds could be the intermediate in the synthesis of the carboxylic acid?

A CH_3CH_2OH

B $CH_3CH_2CH_2CN$

C $CH_3CH_2CO_2CH_3$

D $CH_3CH_2CH_2NH_2$

E CH_3CH_2CN

E ✓

2 **J94/IV/22**

What is the product of a nucleophilic substitution reaction between 2-iodobutane and sodium ethoxide?

A $CH_3CH{=}CHCH_3$

B $CH_3CH_2CH(OCH_3)CH_2CH_3$

C $CH_3CH_2CH(CH_3)OCH_2CH_3$

D $(CH_3)_2CHCH_2OCH_2CH_3$

C ✓

3 **N94/IV/23**

Which of the following compounds could be the product of a reaction involving a nucleophilic attack by cyanide ions in aqueous ethanolic solution?

A $CH_2{=}CHCN$

B $(CH_3)_2CHCN$

C C_6H_5CN

D CH_3CONH_2

B ✓

4 **J00/III/22**

Some chlorobutanes were separately treated with hot ethanolic sodium hydroxide. Two of these gave the same hydrocarbon, C_4H_6.

From which pair of chlorobutanes was this hydrocarbon obtained?

A $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CH_2CHCl_2$

B $CH_3CHClCHClCH_3$ and $ClCH_2CH_2CH_2CH_2Cl$

C $CH_3CH_2CH_2CH_2Cl$ and $ClCH_2CH_2CH_2CH_2Cl$

D $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CHClCH_3$

D

✗ D

5 **N92/IV/23**

Dichlorodifluoromethane, CCl_2F_2, is widely used in aerosol propellants and as a refrigerant.

Which statement helps to explain why dichlorodifluoromethane is chemically inert?

A The carbon-fluorine bond energy is large.

B The carbon-fluorine bond has a low polarity.

C Fluorine is highly electronegative.

D Fluorine compounds are non-flammable.

E Dispersion forces between fluorine atoms are weak.

B

× A

6 **J91/III/8(b)**

Compound **A** undergoes the following reactions:

$$\mathbf{A} \xrightarrow{\text{bromine in trichloroethane}} CH_3CHBrCHBrCH_3 \xrightarrow{\text{II}} CH_2{=}CH{-}CH{=}CH_2$$

(i) Suggest a structural formula for **A**.

(ii) What type of reaction is step II? Suggest the conditions and reagents necessary to carry it out. [4]

7 **J92/I/8**

(a) Describe the mechanism of the hydrolysis of bromoethane by aqueous sodium hydroxide. [3]

(b) Suggest reagents, and describe the reaction conditions necessary, to convert bromoethane into

(i) $CH_3CH_2NH_2$, **(ii)** $CH_3CH_2CH_2NH_2$. [5]

(c) A by-product in the formation of $CH_3CH_2NH_2$ in **(b)** above has the formula $C_8H_{20}NBr$ and it gives an immediate precipitate with aqueous silver nitrate. Suggest a structure for this compound. [2]

8 **N96/I/8(b) (modified)**

Explain the following observations as fully as you can.
(Use of the *Data Booklet* is recommended.)

compound	observations after adding $AgNO_3$(aq) with heat
$CH_3CHICH_2CH_3$	ppt forms almost immediately
$CH_3CHBrCH_2CH_3$	ppt forms after 2 minutes
$CH_3CHClCH_2CH_3$	Ppt slowly forms after 10 minutes
C_6H_5Cl	no ppt forms

ppt = precipitate [4]

9 **N94/I/10 (modified)**

When the compound **F**, $C_6H_5CH_2Cl$, reacts with hot ethanolic KOH, two products are formed; compound **G**, C_7H_8O, and compound **H**, $C_6H_5CH_2OCH_2CH_3$.

(a)(i) The hydroxide ion and ethanol can take part in an acid-base reaction. Write an equation to represent this.

(ii) Suggest an identity for compound **G** and **H**, and state the type of reaction undergone by compound **F**, explaining how **G** and **H** are formed. [4]

(c) Draw the structures of the products and intermediates derived from compound **F** by reaction with:

(i) concentrated aqueous ammonia,

(ii) ethanolic potassium cyanide, followed by heating under reflux with dilute hydrochloric acid. [3]

10 **N97/II/4 (modified)**

An organic compound **A** has the following composition by mass: C, 35.1%; H, 6.6%; Br, 58.3%.

(a) Calculate the empirical formula of **A**.

(b) When **A** is treated with aqueous alkali, 2-methylpropan-1-ol is formed. Give the structural formula of **A**. [2]

(c)(i) When **A** is refluxed with ethanolic potassium hydroxide, an alkene **B** is formed. Give the structural formula of **B**.

(ii) When **B** reacts with hydrogen bromide, a compound **C** is formed, which is an isomer of **A**. Give the structural formula of **C**. [2]

(d) **C** reacts with aqueous alkali to form an alcohol. How can this alcohol be distinguished by a simple test from its isomer 2-methylpropan-1-ol? [2]

11 **N99/I/6(c) – (d)**

(a) Draw structural formulae of compounds **P**, **Q** and **R** in the following scheme.

$$CH_3CH_2CH_2Br \xrightarrow{NaCN} \mathbf{P} \xrightarrow{H_3O^+/\text{heat}} \mathbf{Q} \xrightarrow[\text{heat}]{C_2H_5OH/H^+} \mathbf{R}, C_6H_{12}O_2$$

[3]

(c) When hydrogen chloride is eliminated from 2-chlorobutane, three isomeric alkenes with the formula C_4H_8 are produced.

(i) Suggest reagents and conditions for this reaction.

(ii) Draw the structures of the three butenes produced. [4]

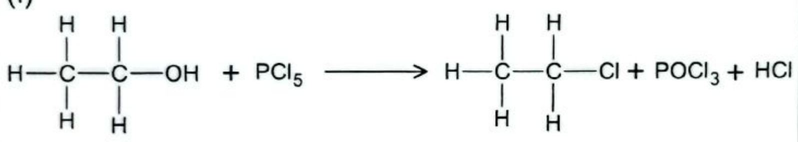
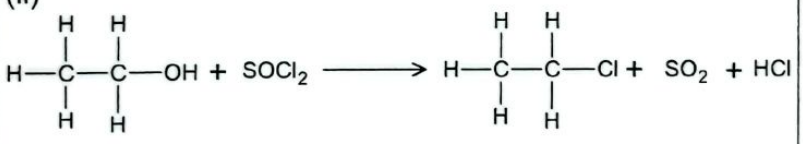
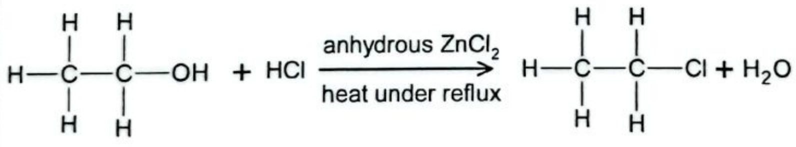
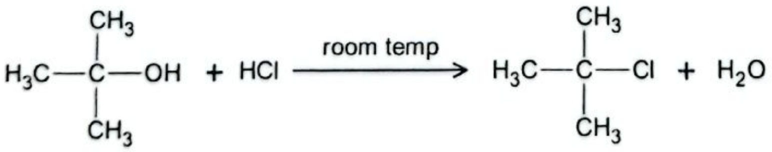
H2 Chemistry Revision Worksheet

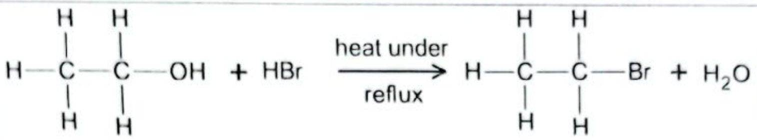
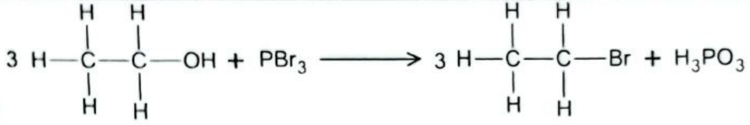
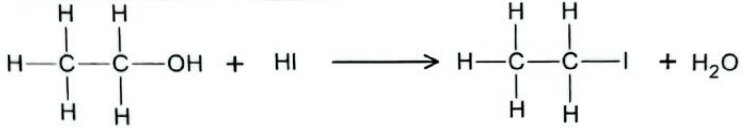
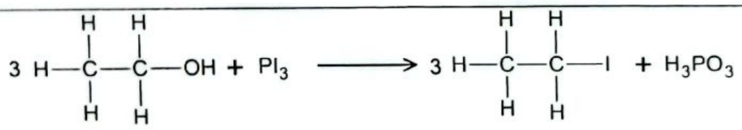
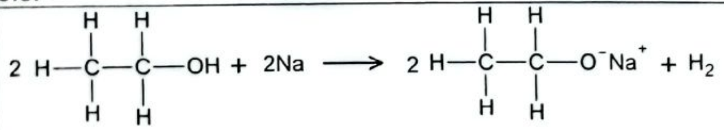
Topic: Hydroxy compounds

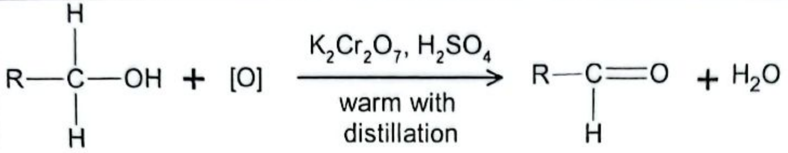
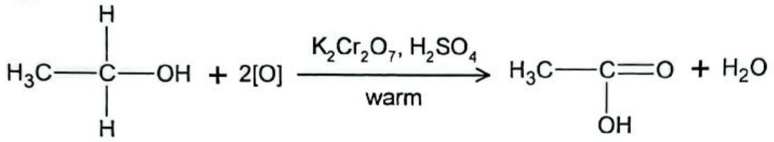
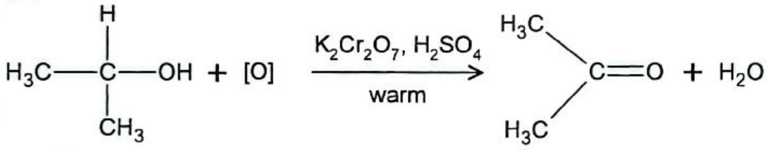
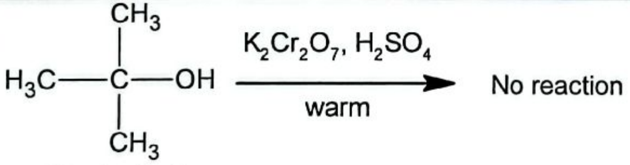
Hydroxy compounds

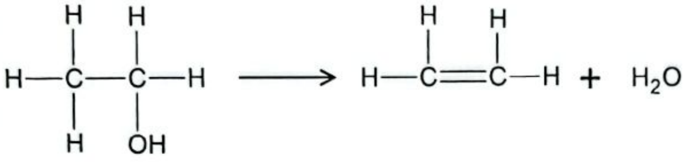
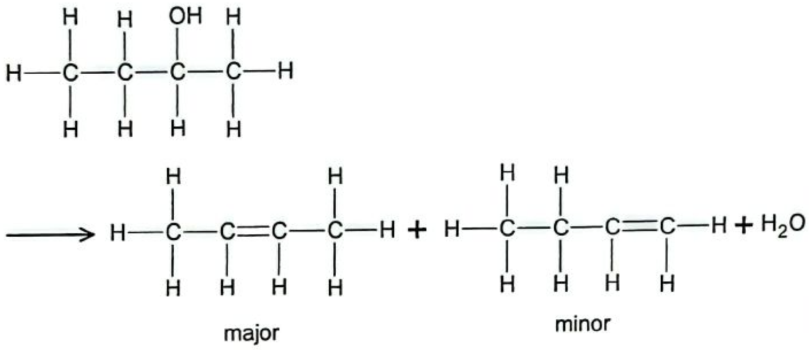
- Contain the –OH functional group.
- Can be classified as
  - aliphatic compounds called **alcohols** (i.e. –OH group bonded to alkyl group)
  - aromatic compounds, **phenols**. (i.e. –OH group directly bonded to aryl group)

A. Reactions of alcohols

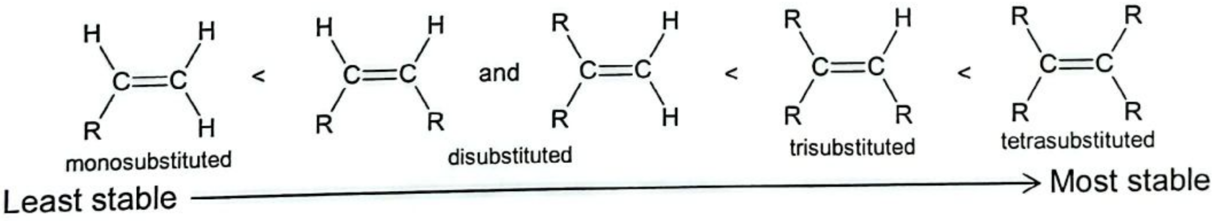
S/N	Reactants	Reagent & Conditions	Products	Type of reaction/ Remarks
To form chloroalkanes				
1	(i)  $CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + POCl_3 + HCl$ (ii)  $CH_3CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + SO_2 + HCl$			Nucleophilic Substitution Observations: White fumes of HCl seen Note: Used as a test for –OH group in alcohols and carboxylic acids.
2	For 1° and 2° alcohols:  $CH_3CH_2OH + HCl \xrightarrow[\text{heat under reflux}]{\text{anhydrous } ZnCl_2} CH_3CH_2Cl + H_2O$ For 3° alcohol:  $(CH_3)_3COH + HCl \xrightarrow{\text{room temp}} (CH_3)_3CCl + H_2O$			Nucleophilic Substitution

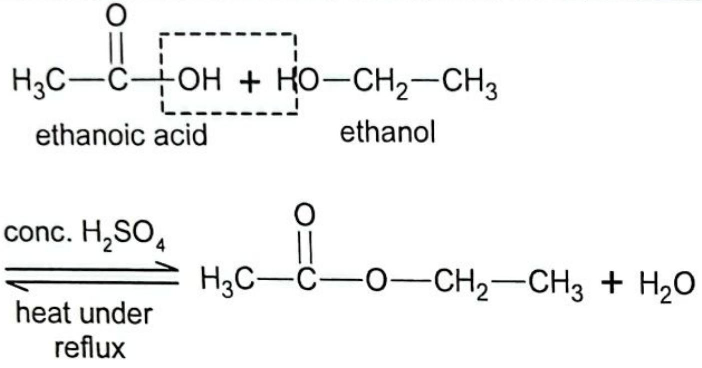
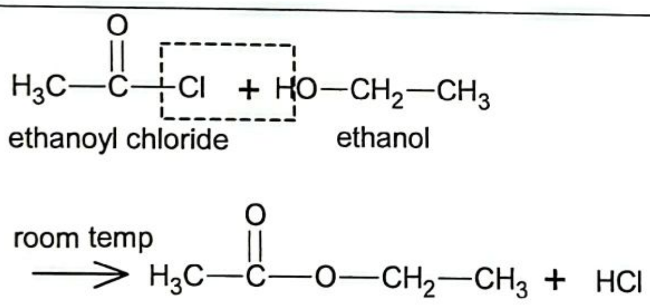
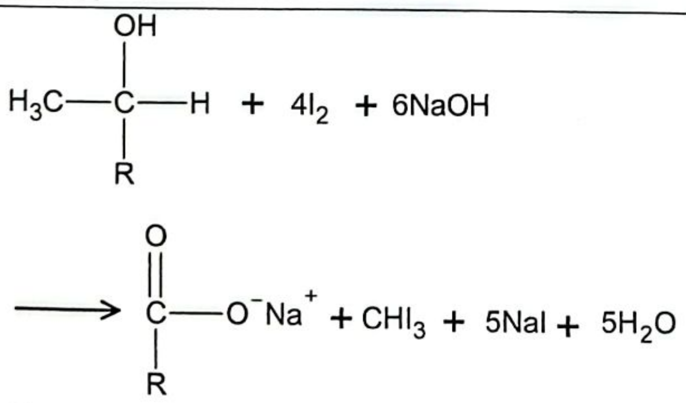
S/N	Reactants	Reagents & Conditions	Products	Type of reaction/ Remarks
To form bromoalkanes				
3	 $\mathrm{CH_3CH_2OH + HBr \xrightarrow[\text{reflux}]{\text{heat under}} CH_3CH_2Br + H_2O}$			Nucleophilic Substitution Note: HBr can be generated from **(i)** NaBr, conc. H_2SO_4, heat under reflux **(ii)** conc. hydrobromic acid, heat under reflux
4	 $\mathrm{3\,CH_3CH_2OH + PBr_3 \longrightarrow 3\,CH_3CH_2Br + H_3PO_3}$			Nucleophilic Substitution Note: PBr_3 can be generated from: 2P + $3Br_2$ → $2PBr_3$
To form iodoalkanes				
5	 $\mathrm{CH_3CH_2OH + HI \longrightarrow CH_3CH_2I + H_2O}$			Nucleophilic Substitution Note: HI cannot be prepared by heating NaI with conc. H_2SO_4 because it will be readily oxidized to I_2. HI can be generated from NaI(s) + H_3PO_4(aq) → 2HI(g) + Na_2HPO_4(s)
6	 $\mathrm{3\,CH_3CH_2OH + PI_3 \longrightarrow 3\,CH_3CH_2I + H_3PO_3}$			Substitution Note: PI_3 can be generated from 2P + $3I_2$ → $2PI_3$
Note: Reactions 1 – 6 are substitution reactions to form halogenoalkanes from alcohols.				
7	 $\mathrm{2\,CH_3CH_2OH + 2Na \longrightarrow 2\,CH_3CH_2O^-Na^+ + H_2}$			Reduction Observation: Effervescence seen. Gas evolved gives a 'pop' sound with lighted splint. Note: Use as a test for presence of –OH group in alcohols, phenols and carboxylic acids.

S/N	Reactants	Reagents & Conditions	Products	Type of reaction/ Remarks
8	 1° alcohol	$K_2Cr_2O_7$, H_2SO_4 warm with distillation	aldehyde	Oxidation Observations: Orange $K_2Cr_2O_7$ turns green. Note: If reaction involves $K_2Cr_2O_7$, $H_2SO_4(aq)$, reflux with no distillation, the 1° alcohol is oxidized to carboxylic acid directly.
9	(i)  1° alcohol	$K_2Cr_2O_7$, H_2SO_4 warm	carboxylic acid	Oxidation Observations: Orange $K_2Cr_2O_7$ turns green. OR Purple $KMnO_4$ decolourises. Note: Use as a test to distinguish 3° alcohols from 1° and 2° alcohols.
	(ii)  2° alcohol	$K_2Cr_2O_7$, H_2SO_4 warm	ketone	
10	 3° alcohol	$K_2Cr_2O_7$, H_2SO_4 warm	No reaction	Oxidation Observations: Orange $K_2Cr_2O_7$ remains. OR Purple $KMnO_4$ remains.

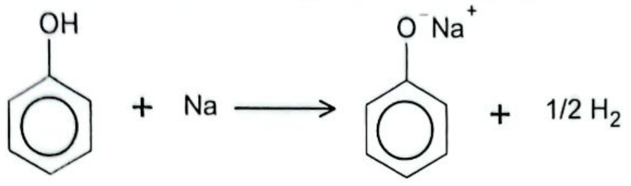
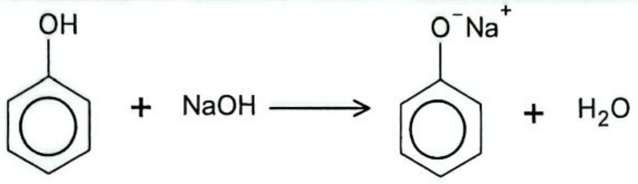
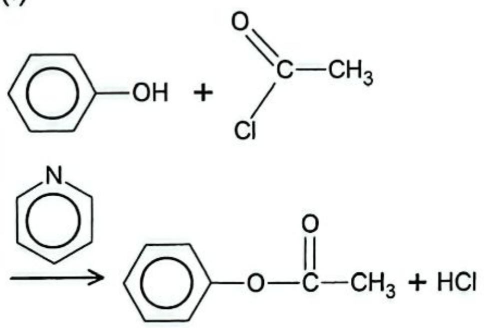
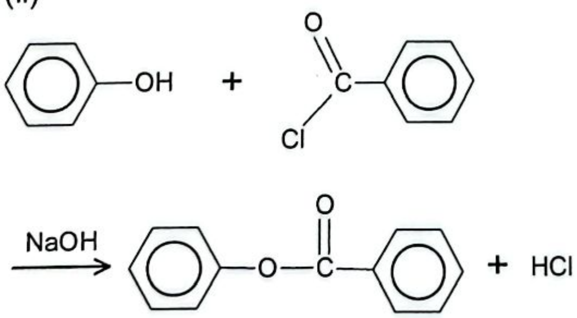
S/N	Reactants	Reagents & Conditions	Products	Type of reaction/ Remarks
11	1° alcohol  2° alcohol  Reagents & conditions: **(i)** excess conc. H_2SO_4, 170°C **(ii)** pass the alcohol vapour over Al_2O_3, 350°C			Elimination Note: • 1° alcohol gives a single product. • 2° and 3° alcohols may give a mixture of products. • Both major and minor products are both formed. • If both major and minor products possess cis-trans isomerism, each structural isomer will form its own cis-trans products, leading to a possible total of 4 isomers.

Note: In elimination reactions, the products with the highly substituted double bond will predominate. (Saytzeff's Rule)

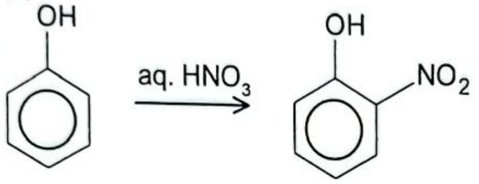
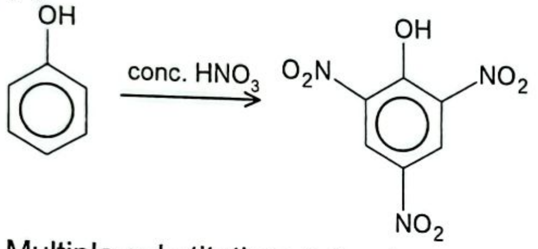
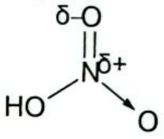
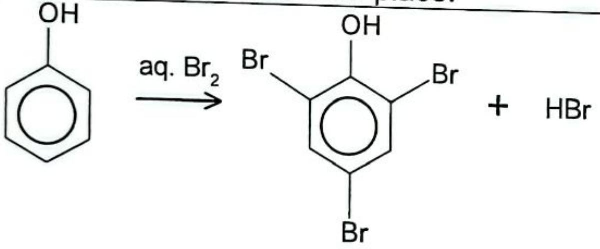


S/N	Reactants	Reagents & Conditions	Products	Type of reaction/ Remarks
12	 $H_3C-\overset{O}{\overset{\|}{C}}-OH + HO-CH_2-CH_3 \xrightleftharpoons[\text{heat under reflux}]{\text{conc. } H_2SO_4} H_3C-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3 + H_2O$			Condensation <u>Observations:</u> Sweet smell of ester detected, immiscible with water. (Cannot be used as a distinguishing test) <u>Note:</u> • Reaction is slow and reversible. • To increase yield of ester, excess of one of the reagents is added, conc. H_2SO_4 also acts as a dehydrating agent to remove water produced.
13	 $H_3C-\overset{O}{\overset{\|}{C}}-Cl + HO-CH_2-CH_3 \xrightarrow{\text{room temp}} H_3C-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3 + HCl$			Condensation <u>Observations:</u> Sweet smell of ester detected, steamy white fumes of HCl formed.
Note: Comparing reactions **12** and **13**, using acyl chloride to form the ester is the preferred method since the reaction is complete and takes place rapidly at room temperature.				
14	 $H_3C-\overset{OH}{\underset{R}{C}}-H + 4I_2 + 6NaOH \longrightarrow \underset{R}{\overset{O}{\overset{\|}{C}}}-O^-Na^+ + CHI_3 + 5NaI + 5H_2O$ Reagents & conditions: NaOH(aq) / I_2(aq), warm			Mild oxidation <u>Observations:</u> Yellow ppt of CHI_3 <u>Note:</u> Used as a test for presence of methyl alcohols and methyl ketones.

B Reactions of phenol (involving the –OH group in phenol)

S/N	Reactants	Reagent & Conditions	Products	Type of reaction/ Remarks
1				Reduction Observations: White ppt formed. Effervescence seen. Gas evolved gives a 'pop' sound with lighted splint. Note: Use as a distinguishing test for the presence of –OH in alcohol, phenols and carboxylic acids.
2				Neutralisation Observation: Phenol dissolves in aq. NaOH to form a colourless solution. Note: Phenol is acidic → dissolves in aq. NaOH but not in aq. HCl
3	(i)  (ii) 			Condensation Observation: A sweet-smelling ester layer is formed. (Cannot be used as a distinguishing test) Note: (i) Pyridine is a solvent used to neutralize the HCl formed. (ii) Benzoyl chloride does not hydrolyse; hence aq. NaOH can be used as the solvent. 2 purposes of NaOH: • To neutralize HCl formed • To generate the phenoxide ion, a stronger nucleophile than phenol for attacking the less reactive benzoyl chloride.

C Reactions of phenol (involving the benzene ring in phenol)

S/N	Reactants	Reagent & Conditions	Products	Type of reaction/ Remarks
1	(i)  A mixture of 2– and 4–nitrophenol is formed. (ii)  Multiple substitutions take place.			Electrophilic substitution Observations: Yellow ppt formed. Note: Phenol undergoes nitration much more easily than benzene. Hence conc. H_2SO_4 catalyst is not required to generate the strong electrophile NO_2^+. Weak electrophile HNO_3 is sufficient to attack the benzene ring in phenol. 
2	 2,4,6-tribromophenol Note: Monosubstitution of bromine if Br_2 in CCl_4 is used.			Electrophilic substitution Observations: Orange $Br_2(aq)$ decolourised. White ppt formed. White fumes of HBr seen. Note: • Used as a distinguishing test for presence of phenol and phenylamine. • A halogen carrier is not required to generate the strong electrophile Br^+. • Weak electrophile Br_2 is sufficient to attack the benzene ring in phenol. $\overset{\delta+}{Br}—\overset{\delta-}{Br}$

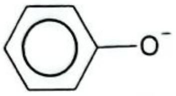
- Iron(III) chloride test for the presence of phenol
  - Reagents & conditions: Neutral $FeCl_3(aq)$
  - Observations: Purple colour seen

D Acidities

- Strength of acid depends on the stability of the conjugate base
  More stable the conjugate base, stronger the acid.

- Relative acid strength of phenol, water and ethanol
  Phenol > water > ethanol
  Most acidic **Least acidic**

- Relative stability of conjugate bases



> OH^- > $CH_3CH_2O^-$

Most stable **Least stable**

- **p orbital** of O atom **overlaps** with π **orbital** of benzene ring resulting in the delocalisation of lone pair of electrons on the O atom into the benzene ring.
- Negative charge on O atom is **dispersed** over **benzene ring** and **one oxygen atom,** hence **stabilising** the conjugate base.
- Phenol donates proton **more** readily, POE lies more to the **right**.

- Negative charge on O atom is **intensified** by **electron donating** alkyl (R) group, hence **destabilising** the conjugate base.
- ROH donates proton **less** readily, POE lies **more** to the **left**.

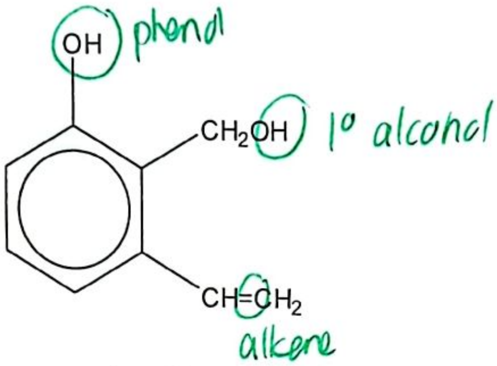
In general,

- Presence of electron donating group/electron withdrawing group
- intensifies/dispersed the negative charge on O atom, hence
- destabilising/stabilising the conjugate base.
- The alcohol donates proton less/more readily, POE lies more to the left/right.

Questions

ACJC/Prelim 2007/1/23

1 A compound has the following structure.



All of the following reagents will react with the above, except

- **A** aqueous bromine alkene, phenol
- **B** phosphorus pentachloride 1° alc
- **C** neutral iron(III) chloride phenol
- **D** potassium cyanide (reacts w carbonyl/alkyl halide) B X D

AJC/Prelim 2007/1/24

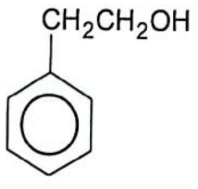
2 When an organic compound **Q** was treated with phosphorus pentachloride, fumes of hydrogen chloride were evolved. When **Q** was warmed with alkaline aqueous iodine, a yellow precipitate was formed.

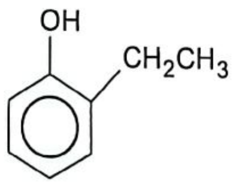
Which of the following was **Q?**

- **A** CH_3COOH
- **B** $CH_3COCH_2CH_3$
- **C** $(CH_3)_3COH$
- **D** $CH_3CH(OH)CH_2CH_3$

D ✓

3 Which of the following reagents can be used to distinguish between the following two compounds?



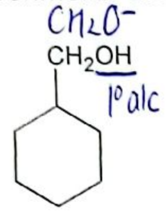


- **1** $Br_2(aq)$
- **2** $KMnO_4$
- **3** Na

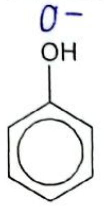
1 ✓

SRJC/Prelim 2007/1/25

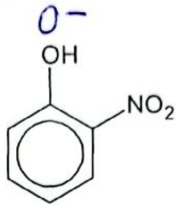
4 Experiments are carried out on three compounds **P**, **Q** and **R**.



P



Q



R

Equal volumes of 0.020 mol samples of **P**, **Q** and **R** are separately reacted with an excess of zinc powder. The volumes of hydrogen gas evolved at room temperature and pressure were recorded at 5 minutes interval. The volumes of hydrogen gas evolved at the **first 5 minutes** were 100 cm^3, 150 cm^3 and 200 cm^3. [R]

rate of rxn

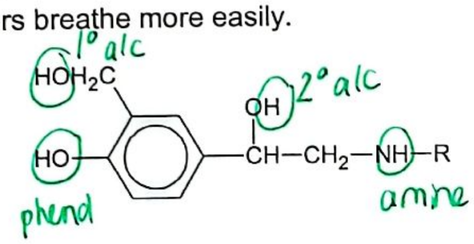
Which sequence of compounds matches these results?

	100 cm^3	150 cm^3	200 cm^3
A	**P**	**Q**	**R**
B	**P**	**R**	**Q**
C	**Q**	**R**	**P**
D	**R**	**P**	**Q**

A ✓

SRJC/Prelim 2007/1/26

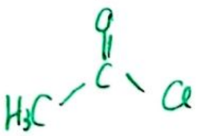
5 Salbutamol, with structure shown below, is used in *Ventolin* inhalers to help asthma sufferers breathe more easily.



R is an alkyl group, which for the purpose of this question does not affect the rest of the molecule.

How many mole(s) of ethanoyl chloride would react with one mole of Salbutamol?

- **A** 1
- **B** 2
- **C** 3
- **D** 4



c X D

VJC/Prelim 2008/1/22

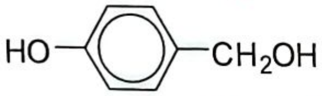
6 1 mol of an organic compound **X** reacts with 1 mol of CH_3COCl. 1 mol of **X** also reacts with PCl_5 to produce 2 mol of hydrogen chloride.

Which compound could be **X**?

$C(=O)OH + PCl_5 \rightarrow C(=O)Cl + HCl$

A 

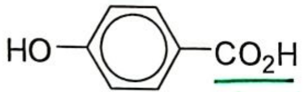
no rxn w PCl_5

B 

rxts w 2, not 1 mol of CH_3COCl

C 

B X C

D 

1 mol of HCl

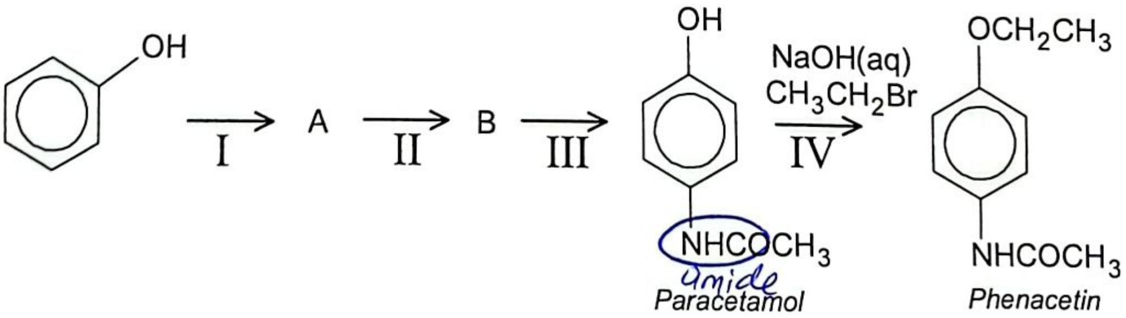
Structured Questions

VJC/Prelim 2007/2/4c,d

7(a) Benzaldehyde can be reduced to phenylmethanol, $C_6H_5CH_2OH$, which has a different acidity from that of phenol, C_6H_5OH.

Explain the difference in acidity between phenylmethanol and phenol.

(b) Phenol can be converted into the painkillers Paracetamol and Phenacetin. The synthesis pathway for this conversion is shown below:



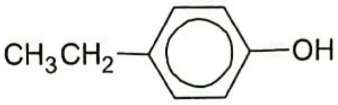
(i) With reference to the mechanism of the reaction, suggest why NaOH(aq) is added in step IV.

(ii) Draw the structures of intermediates **A** and **B**.

(iii) State the reagents and conditions for steps I, II and III.

N2000/I/8(a)

8 The compound 4-ethylphenol, **E**, and chlorinated products derived from it have useful antiseptic properties.



E

Depending on the conditions of the reaction, compound **E** can react with chlorine in two different ways, giving the two isomers **F** and **G**. In these reactions, chlorine reacts in a similar manner to bromine.

$$\underset{\textbf{F}}{C_8H_8Cl_2O} \xleftarrow[Cl_2\,(aq)]{\text{I}} \textbf{E} \xrightarrow{\text{II}} \underset{\textbf{G}}{C_8H_8Cl_2O}$$

(a) Suggest a structural formula for compound **F**.

(b) Explain whether you would expect **F** to be more or less acidic than phenol.

N2000/I/7

9 The ester formed between 3-methylbutan-1-ol and ethanoic acid contributes to the flavour of ripe pears.

(i) Draw the structural formulae of the ester.

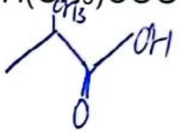
(ii) What conditions and reagents would you use in the laboratory to make the ester from the acid and the alcohol named above.

(iii) Draw the structural formulae of three primary alcohols that are isomers of 3-methylbutan-1-ol, labeling with an asterisk any chiral carbon atom they contain.

SRJC/Prelim 2007/3/1d

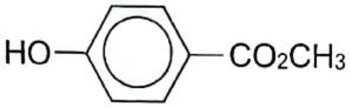
10 Suggest suitable reagents and conditions for each step in the following synthesis. Draw the structural formulae of all the intermediates formed.

(i) $CH_3CH_2CH_2OH$ → **A** → **B** → **C** → $CH_3CH(CH_3)COOH$



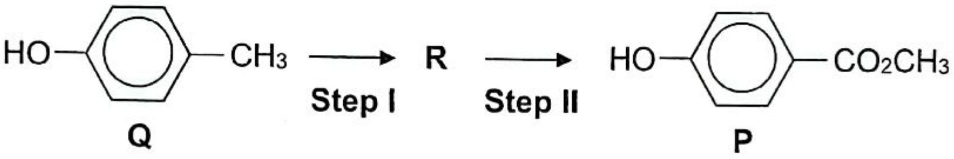
JJC/Prelim 2007/3/2(e)

11 Methanol is required for the synthesis of substance **P** that is now commonly used in antiseptic creams.



P

P can be synthesised in the laboratory from compound **Q** by a method which involves one intermediate **R**.



(i) Draw the structural formula of **R**.

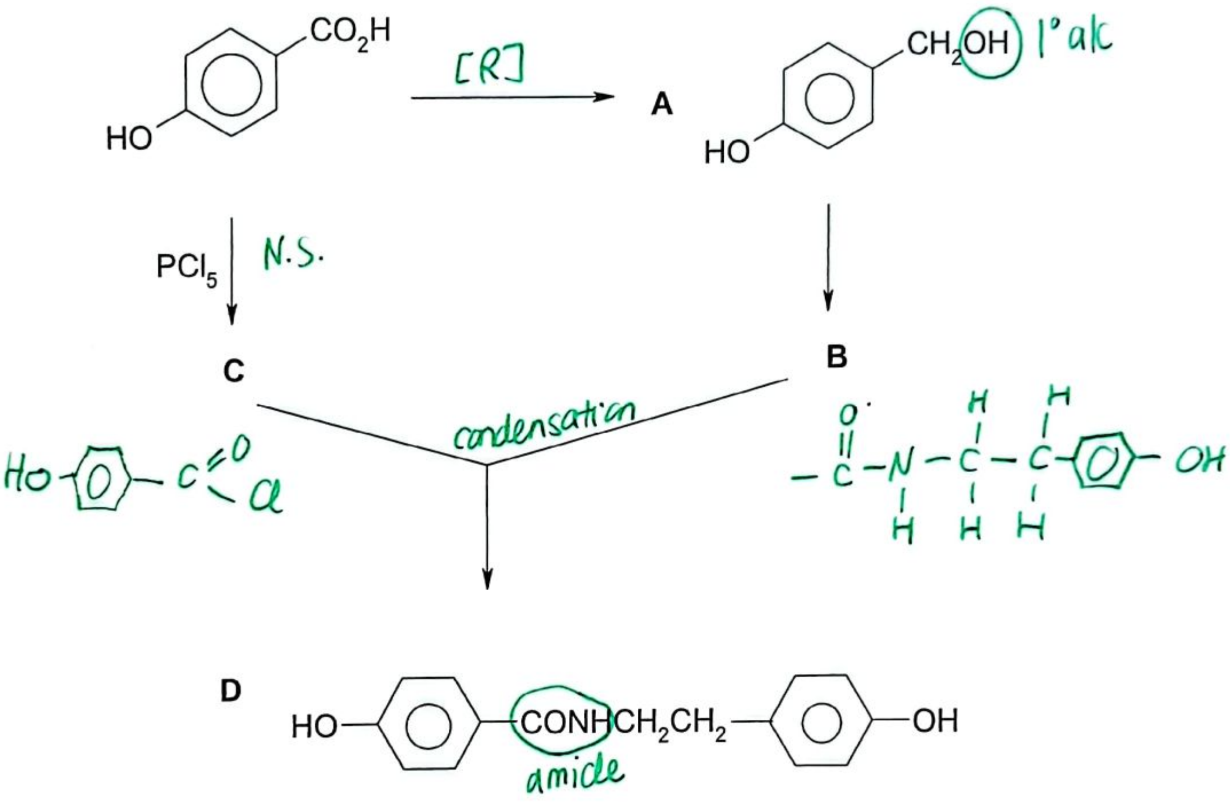
(ii) Suggest reagents and conditions for steps **I** and **II**.

(iii) Draw the structural formulae of the organic products when **P** reacts with hot dilute nitric acid.

(iv) How would you expect the acidity of **P** to compare with that of methanol? Explain your answer.

TPJC/Prelim 2007/3/4(b)

12 You are given the following scheme of reactions.

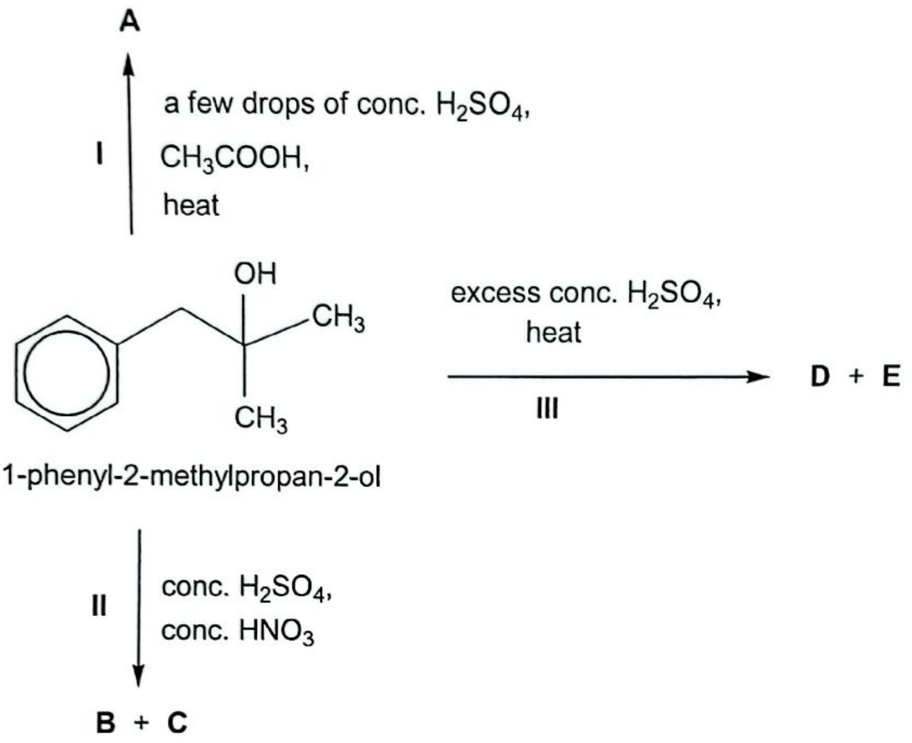


(i) Draw the displayed formula of compound **C**.

(ii) Give the synthetic route, involving *not more than three steps*, from **A** to **B**. In your answer, suggest reagents and conditions involved in each step.

JJC/Prelim 2008/3/1c

13 Concentrated sulfuric acid is also an important reagent in many organic reactions where it can perform roles such as an acid, dehydrating agent or a catalyst as illustrated in the following reaction scheme.



(i) Give the structural formulae of the compounds **A** to **E.**

(ii) When phenol undergoes the same reaction as 1-phenyl-2-methylpropan-2-ol in reaction II, concentrated H_2SO_4 is not required. Explain why this is so.

H2 Chemistry Revision Worksheet

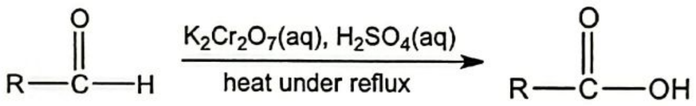
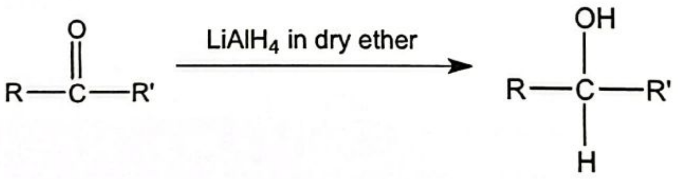
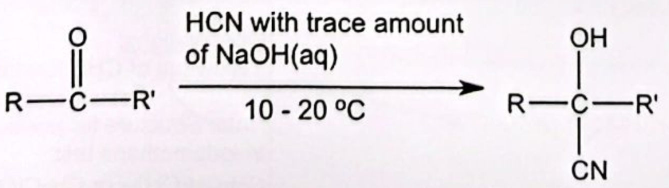
Topic: Carbonyl Compounds

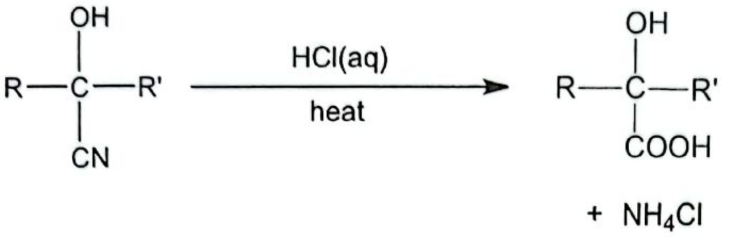
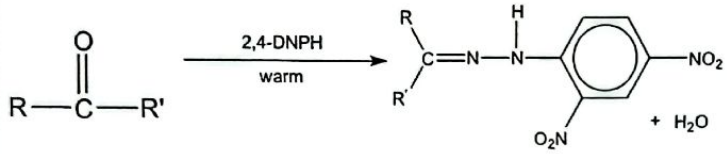
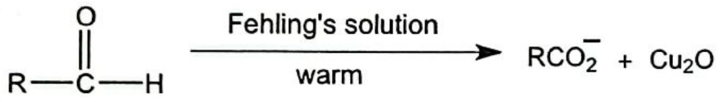
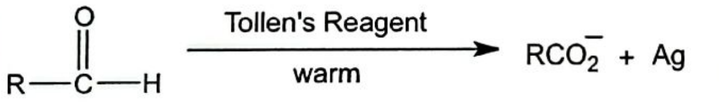
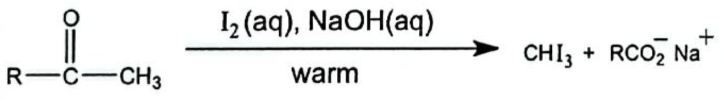
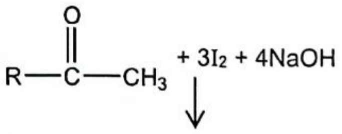
Preparation of Carbonyl Compounds

1. Aldehydes
   - From 1° Alcohols – Oxidation (Refer to CSI: Hydroxy Compounds Reaction 8)

2. Ketones
   - From Alkenes – Oxidation (Refer to CSI: Alkenes Reaction 7)
   - From 2° Alcohols – Oxidation (Refer to CSI: Hydroxy Compounds Reaction 9(ii))

Summary of Reactions of Carbonyl Derivatives[1]

S/N	Reactants	Reagents and Conditions	Products	Type of Reaction / Remarks
1	 $R-\overset{\overset{O}{\|}}{C}-H$	$K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$ heat under reflux	$R-\overset{\overset{O}{\|}}{C}-OH$	Oxidation Alternative reagents and conditions: (1) $KMnO_4(aq)$, $H_2SO_4(aq)$, heat under reflux Observations: Orange $K_2Cr_2O_7$ solution turns green. **Or** Purple $KMnO_4$ solution decolourises.
2	 $R-\overset{\overset{O}{\|}}{C}-R'$	$LiAlH_4$ in dry ether	$R-\underset{\underset{H}{\|}}{\overset{\overset{OH}{\|}}{C}}-R'$	Reduction Alternative reagents and conditions: (1) $NaBH_4(aq)$ or $NaBH_4$ in methanol **or** (2) $H_2(g)$, Ni catalyst, heat **or** $H_2(g)$, Pt/Pd catalyst at room temp (To convert aldehydes to 1° alcohols and ketones to 2° alcohols.) ($LiAlH_4$ and $NaBH_4$ will reduce C=O groups but not C=C groups. H_2 will reduce **both** C=O and C=C groups.
3	 $R-\overset{\overset{O}{\|}}{C}-R'$	HCN with trace amount of NaOH(aq) 10 - 20 °C	$R-\underset{\underset{CN}{\|}}{\overset{\overset{OH}{\|}}{C}}-R'$	Nucleophilic Addition Alternative reagents and conditions: (1) HCN with trace amount of NaCN(aq), 10 – 20 °C (Increase carbon chain by 1 carbon atom. Introduce –OH group that is directly attached to the carbonyl carbon atom to give cyanohydrin as the product.)

3a	 	Acidic Hydrolysis (To convert nitrile to carboxylic acid.)
4	 	Condensation Observations: Orange ppt formed. (A distinguishing test for carbonyl groups in a compound.)
5	 	Oxidation Overall Equation: $RCHO + 2Cu^{2+} + 5OH^- \rightarrow RCO_2^- + Cu_2O + 3H_2O$ Observations: Brick red ppt of Cu_2O formed. (A distinguishing test for **aliphatic** aldehydes only.)
6	 	Oxidation Overall Equation: $RCHO + 2Ag^+ + 3OH^- \rightarrow RCO_2^- + 2Ag + 2H_2O$ Observations: Silver mirror formed. (A distinguishing test for **aliphatic and aromatic** aldehydes.)
7	 	Oxidation Overall Equation:  $CHI_3 + RCO_2^-Na^+ + 3NaI + 3H_2O$ Observations: Yellow ppt of CHI_3 formed. Note: Structure for positive tri-iodomethane test: $CH_3CH(OH)-$ or $CH_3C(O)-$.

Note:

1. R = H / alkyl / aryl group and R' = alkyl / aryl group

Nucleophilic Addition Mechanism

E.g. Nucleophilic addition of ethanal with HCN and trace amount of NaOH(aq) or NaCN(aq) at 10 – 20 °C.

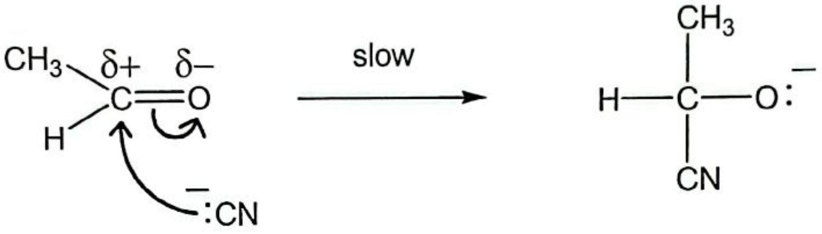
Step 1: Generation of nucleophile

$$HCN + NaOH \rightarrow Na^{+} + \overset{-}{:}CN + H_2O$$

- Alternatively, if NaCN is used, the nucleophile $\overset{-}{:}CN$ will be generated as follows:

$$NaCN \rightarrow Na^{+} + \overset{-}{:}CN$$

Step 2: Attack of the carbonyl carbon by nucleophile, $\overset{-}{:}CN$

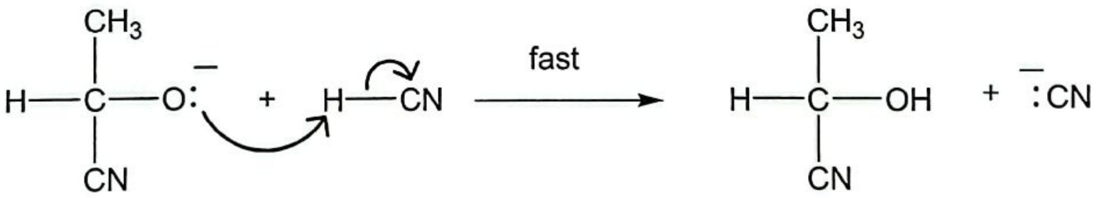


trigonal planar

tetrahedral intermediate

- $\overset{-}{:}CN$ attacks the carbonyl carbon (with the δ+ charge) and a negatively-charged intermediate is formed.
- $\overset{-}{:}CN$ can approach the planar C=O bond from above or below the plane to form a tetrahedral intermediate.

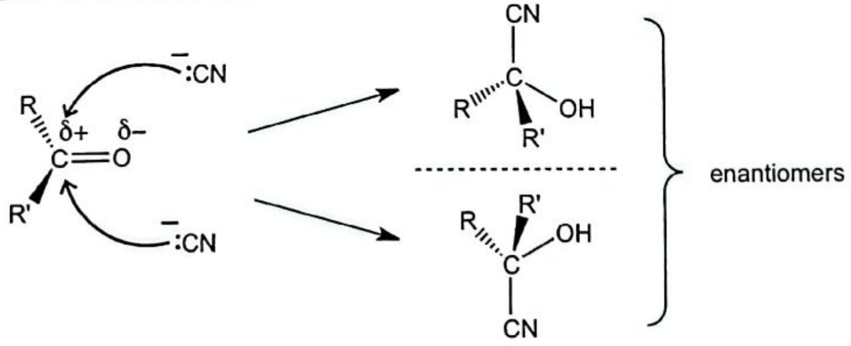
Step 3 Formation of product



tetrahedral intermediate

cyanohydrin

Optical Activity of Cyanohydrin Product



- The nucleophile has an equal chance of attacking the trigonal planar C=O group from above or below the plane. Therefore, if the resulting molecule is chiral, a **racemic mixture** is obtained. As a result, the product is **not optically active**.

Summary of Distinguishing Tests

To distinguish ...	Reagents and Conditions	Observation (Positive Test)
aldehydes and ketones from other organic compounds	2,4-dinitrophenylhydrazine	Carbonyl compounds give orange ppt.
aldehydes from ketones	1. Acidified $K_2Cr_2O_7$, heat	1. Aldehydes turn orange $K_2Cr_2O_7$ solution green.
	2. Acidified $KMnO_4$, heat	2. Aldehydes decolourises purple $KMnO_4$ solution.
	3. Fehling's solution, warm	3. Aliphatic aldehydes give brick red ppt of Cu_2O.
	4. Tollens' reagent, warm	4. Aldehydes produces Ag mirror.
methyl carbonyl compounds	I_2(aq), NaOH(aq), warm	Methyl carbonyl compounds give yellow ppt of CHI_3.

Questions

1 **N90/I/27**

Which of the following reagents will give similar results for both butanone and butanal?

~~A~~ acidified aqueous potassium dichromate(VI)

~~B~~ an alkaline solution containing complexed Cu^{2+} ions (Fehling's solution)

C an aqueous solution containing $Ag(NH_3)_2^+$ (Tollen's reagent)

~~D~~ iodine and aqueous sodium hydroxide

E 2,4-dinitrophenylhydrazine reagent

~~A~~, E ✓

2 **N92/IV/26**

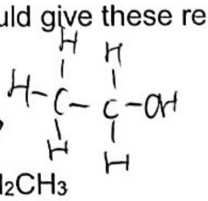
An organic compound has the following properties:

- it gives a positive tri-iodomethane (iodoform) test; methyl ketone / methyl alcohol
- it gives a yellow precipitate with 2,4-dinitrophenylhydrazine;
- it does not react with either Tollen's or Fehling's reagent. not aldehyde

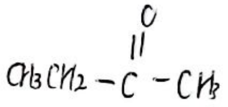
Which compound would give these results?

~~A~~ CH_3CHO

~~B~~ CH_3CH_2OH →



~~C~~ $CH_3CH_2COCH_3$ →



~~D~~ $CH_3CH_2CH_2CHO$

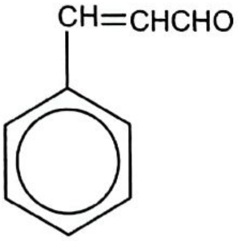
E $CH_3CH_2COCH_2CH_3$

B ✗ C

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

3 **N95/IV/40**

Cinnamaldehyde is an essential oil with distinctive odour of cinnamon.



cinnamaldehyde

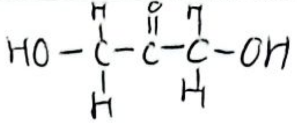
Which of the following statements about cinnamaldehyde is correct?

1 It is optically active.

2 It decolourises aqueous bromine.

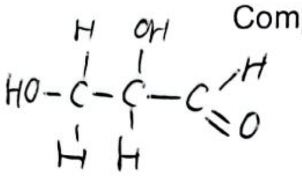
3 It reacts with 2,4-dinitrophenylhydrazine reagent.

C ✓



4 **J97/III/40**

Compounds **P** and **Q** have the following formulae:



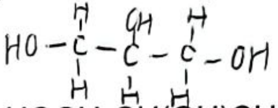
HOCH₂CH(OH)CHO → $HOCH_2CH(OH)CHO$

$HOCH_2COCH_2OH$

P **Q**

Which of the following statements apply to these compounds?

1 **P** can be directly oxidised to **Q**.



[✓ 2] **P** and **Q** can both be reduced to $HOCH_2CH(OH)CH_2OH$.

[✓ 3] Both **P** and **Q** react with ethanoyl chloride to form esters.

A X C

5 **J00/III/40**

All of the following reagents react with ethanal, CH_3CHO.

Which reagents give a product that retains the C−C= structure?

[✓ 1] 2,4-dinitrophenylhydrazine reagent

2 ethanolic hydrogen cyanide

3 lithium tetrahydridoaluminate(III), $LiAlH_4$

D

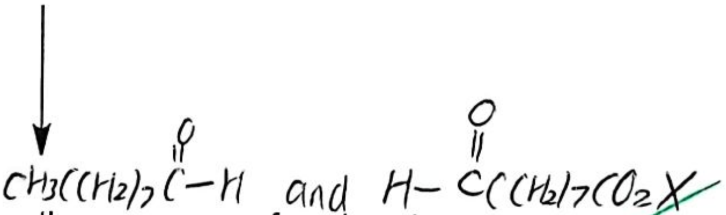
6 **J91/II/4(a), (b)**

Good cooking involves producing subtle flavours and smells from the raw materials of food. These flavours are often produced by esters and by the oxidation of unsaturated fats to aldehydes and ketones.

(a) Part of an unsaturated fat is shown below.

(i) Complete the reaction scheme below to show its partial oxidation into two aldehydes.

$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2X$ [X = rest of fat molecule]



$CH_3(CH_2)_7\overset{O}{\overset{\|}{C}}-H$ and $H-\overset{O}{\overset{\|}{C}}(CH_2)_7CO_2X$

(ii) Suggest how the presence of carbonyl compounds (aldehydes or ketones) in the cooked food could be confirmed.

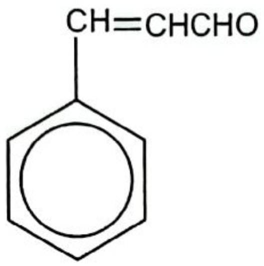
(iii) Suggest how the presence of aldehydes in the cooked food could be confirmed. [5]

(b) Only limited amounts of oxygen are allowed to reach the food during cooking or it will be oxidised to carboxylic acids that taste unpleasantly sour.

Write an equation for the oxidation of one of the aldehydes in **(a)(i)** to a carboxylic acid. [1]

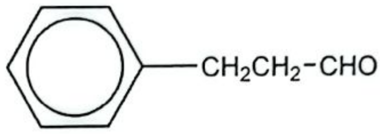
7 **J96/I/8(b)**

Suggest simple test-tube reactions (one in each case) you could use to distinguish cinnamalydehyde from compounds **A** and **B** below.

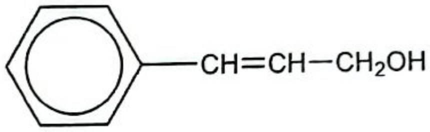


cinnamaldehyde

A



B



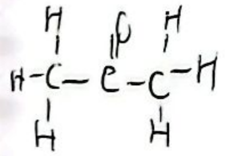
For each test, give reagents and describe what you would see. [4]

8 **J99/I/8**

(a) Describe the mechanism of the reaction between ethanal and hydrogen cyanide. Name the type of reaction undergone, state any other reagents needed, and include the structural formula of any intermediate, as well as of the product. [4]

(b) The above reaction produces two isomeric products in equal amounts. Name the type of isomerism involved, and draw displayed formulae to illustrate it. [3]

(c) As a consequence of starvation or diabetes, the blood plasma and urine of patients can contain large amounts of 'ketone bodies'. These include propanone, 3-oxobutanoic acid, and 3-hydroxybutanoic acid.



CH_3COCH_3	$CH_3COCH_2CO_2H$	$CH_3CH(OH)CH_2CO_2H$
propanone	3-oxobutanoic acid	3-hydroxybutanoic acid

Describe a separate simple chemical test in each case to distinguish 3-oxobutanoic acid from

(i) propanone,

(ii) 3-hydroxybutanoic acid.

For each test, give reagents, and conditions, and state what would be seen with each compound. [5]

9 **N93/I/11(a) – (b)(i) (modified)**

Some alcohols and ketones can be distinguished from their isomers by the tri-iodomethane test (iodoform reaction).

(a) State the reagents and conditions used for this test and the observation made for a positive result. [2]

(b) Given the molecular formula of a ketone, $C_5H_{10}O$, draw the structural formula of an isomer that gives tri-iodomethane and of an isomer that does not. Make sure you indicate which is which. [2]

10 **J97/I/7(b) (modified)**

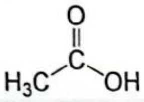
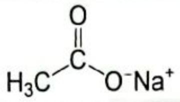
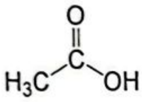
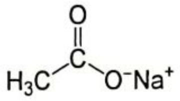
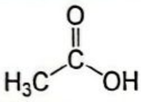
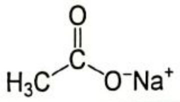
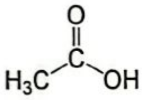
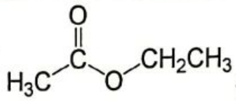
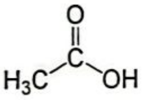
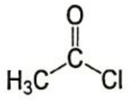
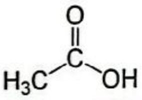
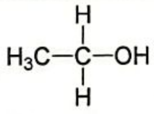
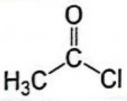
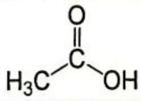
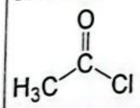
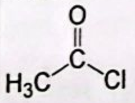
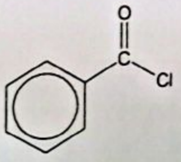
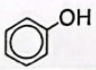
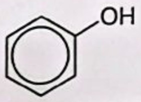
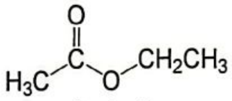
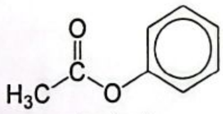
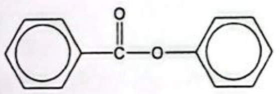
One of the compounds responsible for the flavour of butter is butane-2,3-dione. Give the structural formulae of the organic products formed when butane-2,3-dione reacts completely with

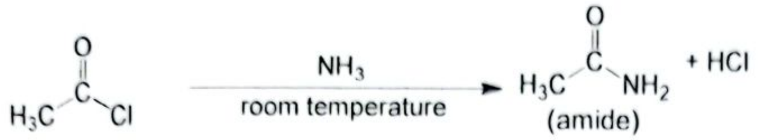
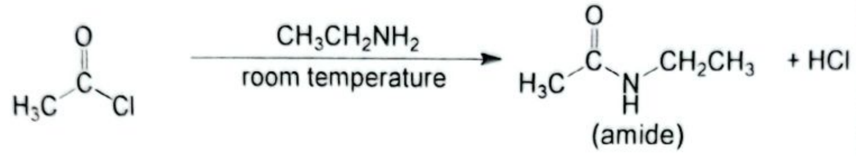
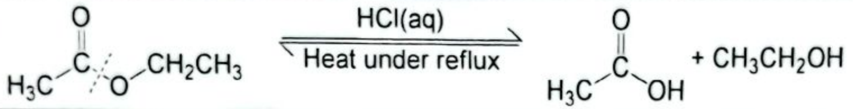
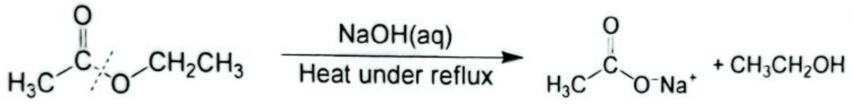
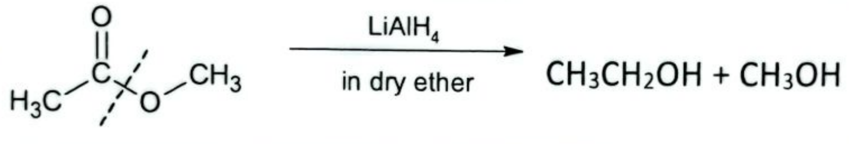
(i) H_2/Ni [R]

(ii) I_2/OH^-(aq) (triiodomethane test) [3]

H2 Chemistry Revision Worksheet

Topics: Carboxylic Acid and Derivatives

S/N	Reactants	Reagents and Conditions	Products	Type of Reaction / Remarks
1		$\xrightarrow[\text{Room Temperature}]{\text{Na}}$	 + ½ H_2	Reduction Observations: Effervescence of H_2
2		$\xrightarrow[\text{Room Temperature}]{\text{NaOH (aq)}}$	 + H_2O	Acid-base reaction
3		$\xrightarrow[\text{Room Temperature}]{Na_2CO_3}$	 $CO_2 + H_2O$	Acid-base reaction Observations: Effervescence of CO_2
4		$\underset{\text{heat under reflux}}{\overset{CH_3CH_2OH,\ \text{Conc. } H_2SO_4}{\rightleftharpoons}}$	 + H_2O	Condensation
5		$\xrightarrow[\text{room temperature}]{PCl_5}$	 + HCl + $POCl_3$	Nucleophilic Substitution Alternative: PCl_3, room temperature or $SOCl_2$, room temperature Observations: White fumes of HCl (with PCl_3/PCl_5/$SOCl_2$)
6		$\xrightarrow[\text{in dry ether}]{LiAlH_4}$	 + H_2O (1° alcohol)	Reduction **Note:** H_2, Pt catalyst, r.t. or $NaBH_4$ <u>cannot</u> be used.
7		$\xrightarrow[\text{room temperature}]{H_2O}$	 + HCl(aq)	Hydrolysis (Nucleophilic acyl substitution)
8	Aliphatic alcohol:  Phenol:  	$\xrightarrow[\text{room temperature}]{CH_3CH_2OH}$  room temperature  NaOH as solvent, room temperature	 + HCl (ester)  + HCl (ester)  + HCl	Condensation (Nucleophilic acyl substitution) Aliphatic acyl chloride: use pyridine solvent Aromatic acyl chloride: use NaOH solvent

9	 	Condensation (Nucleophilic acyl substitution) Observations: White fumes of HCl Note: Carboxylic acids cannot form amides with NH_3/amines. They will undergo neutralisation to form salt.
10		Acidic Hydrolysis Alternative: H_2SO_4(aq), heat under reflux
11		Alkaline Hydrolysis
12		Reduction **Note:** H_2, Pt catalyst, r.t. or $NaBH_4$ cannot be used.

Relative Acidity of Alcohol, Phenol, Carboxylic Acid and Benzoic Acid

Acidity: Ethanol < Phenol < Carboxylic Acid < Benzoic Acid

Alcohol

$ROH \rightleftharpoons RO^- + H^+$

- Negative charge on O atom is **intensified** by **electron donating** alkyl (R) group, hence **destabilising** the conjugate base.
- ROH donates proton **less** readily, POE lies **more** to the **left**.

Phenol

$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$

- **p orbital** of O atom **overlaps** with π **orbital** of benzene ring resulting in the delocalisation of lone pair of electrons on the O atom into the benzene ring.
- Negative charge on O atom is **dispersed** over **benzene ring** and **one oxygen atom,** hence **stabilising** the conjugate base.
- Phenol donates proton **more** readily, POE lies **more** to the **right.**

Carboxylic acid

$RCOOH \rightleftharpoons RCOO^- + H^+$

- **p orbital** of O atom **overlaps** with π **orbital** of C=O resulting in the delocalisation of lone pair of electrons on the O atom into C=O.
- Negative charge on oxygen atom is **equally dispersed** over the carbon & **two oxygen atoms**, ☆ ~~hence **stabilising** the conjugate base **even mo**~~**re**.
- RCOOH donates proton **even more** readily, POE lies **even more** to the **right**.

Benzoic Acid

$C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+$

- **p orbital** of O atom **overlaps** with π **orbitals** of C=O and benzene ring resulting in the delocalisation of lone pair of electrons on the O atom into C=O and benzene ring.
- Negative charge on O atom is equally dispersed over the C & 2 electronegative O atoms/dispersed across the carboxylate, −COO group, and is further dispersed into the benzene ring, hence stabilising the CB the most.
- C_6H_5COOH donates proton most readily, POE lies most to the right.

☆ the carboxylate, −COO group

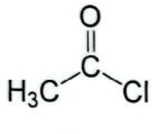
☆ the charge dispersion in the carboxylate ion is more effective than in phenoxide ion because the 2 electronegative O atoms in the carboxylate ion can better accomodate the −ve charge, hence stabilising the CB, the carboxylate ion, more than the phenoxide ion.

Factors Affecting Relative Strength of Carboxylic Acid

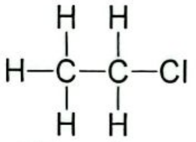
1. **Electron donating group**: Electron-donating groups intensify the negative charge on the oxygen atom, destabilising the conjugate base. Carboxylic acid donates proton **less** readily, POE lies **more** to the **left**. ➔ Acidity decrease.

2. **Electron withdrawing group**: Electron-withdrawing groups disperse the negative charge on the oxygen atom, stabilising the conjugate base. Carboxylic acid donates proton **more** readily, POE lies **more** to the **right**. ➔ Acidity increase.

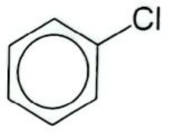
Ease of Hydrolysis of Acyl, Alkyl and Aryl Chlorides



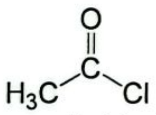
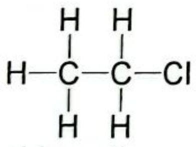
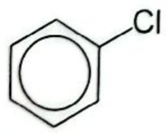
Ethanoyl chloride >



chloroethane >



chlorobenzene

Compound	**Observations** (compound warmed with ethanoic $AgNO_3$)	**Explanation**
 ethanoyl chloride (CH_3COCl)	White ppt of AgCl formed immediately	• Hydrolysis of ethanoyl chloride is the fastest • C atom in CH_3COCl is attached to 2 highly electronegative atoms, O and Cl. • It is more electron deficient (i.e. carries a larger partial positive charge δ+) than the carbon atom in CH_3CH_2Cl. Hence, it is more susceptible to nucleophilic attack. • Therefore it undergoes hydrolysis more readily.
 chloroethane (CH_3CH_2Cl)	White ppt AgCl appears after ≈12 minutes	• C atom in CH_3CH_2Cl is attached to only 1 electronegative atom, Cl. • It is less electron deficient (i.e. carries a smaller partial positive charge δ+) than the carbon atom in CH_3COCl. Hence, it is less susceptible to nucleophilic attack. • Therefore, it undergoes hydrolysis less readily.
 chlorobenzene (C_6H_5Cl)	No ppt observed	• Chlorobenzene is resistant to hydrolysis. • The p orbital of Cl overlaps with the π orbital of benzene ring, resulting in the delocalisation of lone pair of electrons on the Cl into the benzene ring. The C–Cl bond has some double bond character (therefore the bond is stronger than that in an alkyl halide). • Sterically, the rear side of the C–Cl bond is blocked by the bulky benzene ring. • The π electron cloud of the benzene ring will repel the lone pair of electrons of an incoming nucleophile. • Hence, no nucleophilic substitution can take place.

Questions

1 The same carboxylic acid is obtained either by the hydrolysis of a nitrile **P** or by the oxidation of an alcohol **Q**.

Which of the following pairs could be **P** and **Q**?

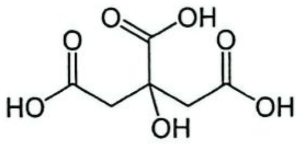
	P	**Q**
A	CH_3CH_2CN	CH_3CH_2OH
B	$(CH_3)_2CHCN$	$(CH_3)_2CHOH$
C	$C_6H_5CH(CH_3)CN$	$C_6H_5C(CH_3)_2OH$
D	$C_6H_5CH_2CN$	$C_6H_5CH_2CH_2OH$

A ✗ D

2 Write equation in the boxes where chemical reactions take place between the organic compounds and metal/bases. If there is no chemical reaction, write "no reaction".

	Na(s)	NaOH(aq)	Na_2CO_3(aq)
CH_3CH_2OH	$Na + CH_3CH_2OH \rightarrow CH_3CH_2ONa + \frac{1}{2}H_2$ ✓	No rxn ✓	No rxn ✓
C_6H_5OH	$Na + C_6H_5OH \rightarrow C_6H_5ONa + \frac{1}{2}H_2$ ✓	$NaOH + C_6H_5OH \rightarrow C_6H_5ONa + H_2O$ ✓	No rxn ✓
CH_3COOH	$Na + CH_3COOH \rightarrow CH_3COONa + \frac{1}{2}H_2$ ✓	$NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O$ ✓	$Na_2CO_3 + 2CH_3COOH \rightarrow H_2O + 2CH_3COONa + CO_2$ ✓

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



Which of the following react completely with **one mole** of citric acid?

A 1 mole of CH_3COCl

B 2 moles of Na_2CO_3

C 3 moles of sodium metal

D 4 moles of NaOH

C ✗ A

4 Which of the following gives the lowest pH when 1 mole of the compound dissolves in water?

A CH_3CH_2OH
B C_6H_5OH
C CH_3COOH
D CH_3COCl

D ✓

5 Which of the following compound react with $SOCl_2$ to produce an organic compound that reacts vigorously with water at room temperature?

A $C_6H_5CH_2OH$
B C_6H_5OH
C C_6H_5COOH
D $C_6H_5COOCH_3$

C

6 Which of the following compound will be reduced by $LiAlH_4$ but **not** $NaBH_4$?

A CH_3CHO
B $(CH_3)_2CO$
C C_6H_5COOH
D $CH_2{=}CHCH_3$

C

7 One of the products from the vigorous hydrolysis of oil of bitter almonds is mandelic acid, **H**. It can be synthesized from benzaldehyde in two steps:

$$C_6H_5CHO \xrightarrow{\textbf{Step I}} \textbf{J} \xrightarrow{\textbf{Step II}} \underset{\textbf{H}}{C_6H_5CH(OH)CO_2H}$$

(a) Suggest reagents and conditions for step **I** and **II**, and draw the structural formula of the intermediate **J**.

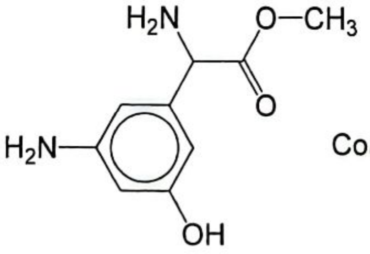
(b) Suggest structural formulae for the products of the reaction of mandelic acid with the following reagents.

(i) CH_3COCl
(ii) PCl_5
(iii) C_2H_5OH in the presence of conc. H_2SO_4, heat under reflux
(iv) Na metal
(v) NaOH(aq)
(vi) Na_2CO_3(aq)

8 Compound **Y**, $C_5H_8O_2$, can be obtained through a three step synthesis. Suggest reagents and conditions for step **I**, **II** and **III**, and draw the structural formula of the **Y**.

$$HO(CH_2)_3CH_2Br \xrightarrow{\textbf{Step I}} HO(CH_2)_3CH_2CN \xrightarrow{\textbf{Step II}} HO(CH_2)_4COOH \xrightarrow{\textbf{Step III}} \underset{\textbf{Y}}{C_5H_8O_2}$$

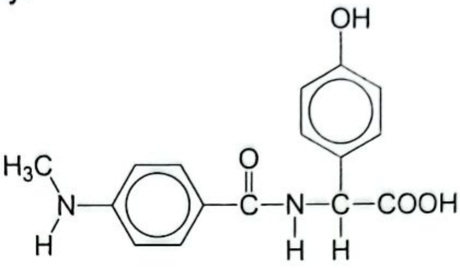
9 Suggest structural formulae for the organic products of the reaction of compound **Z** with the following reagents.



Compound **Z**

(i) CH_3COCl
(ii) HCl(aq), heat under reflux
(iii) NaOH(aq), heat under reflux
(iv) Na metal

10 Compound **X** has two functional groups that may exhibit acidic properties. State and explain which of these two groups has a higher acid strength. Give an equation for the reaction of the functional group with a common reagent to illustrate its stronger acidic property.

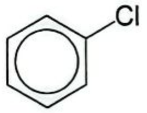


Compound **X**

11 Arrange the following compounds in increasing trend of pK_a value:

(a) CH_3COOH, CCl_3COOH, $CH_2ClCOOH$
(b) CBr_3COOH, CCl_3COOH, CF_3COOH
(c) $CH_2FCH_2CH_2COOH$, $CH_3CH_2CHFCOOH$, CH_3CHFCH_2COOH

12 Arrange the following compounds in increasing ease of hydrolysis. Explain your answer.



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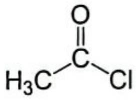

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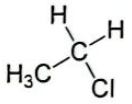


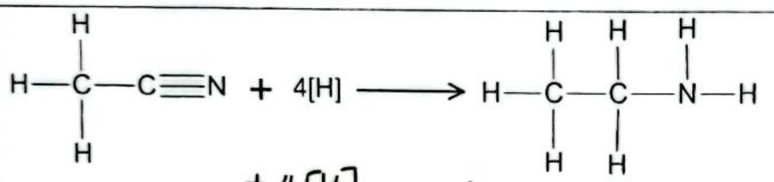
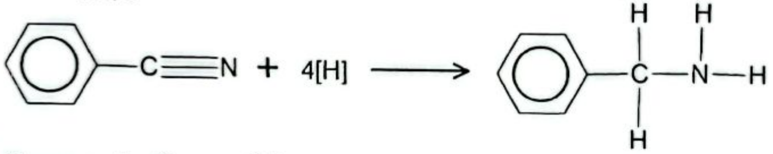
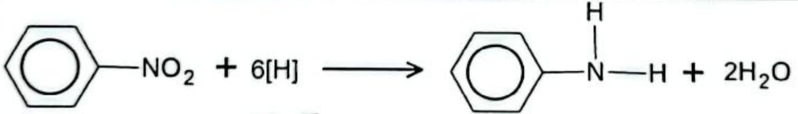
(refer to pg 4 notes)

H2 Chemistry Revision Worksheet

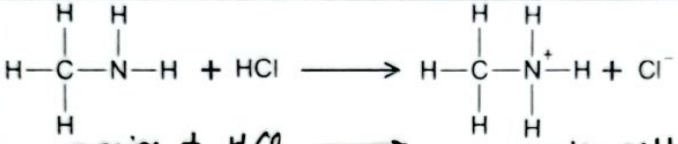
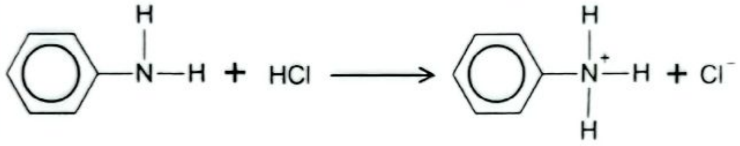
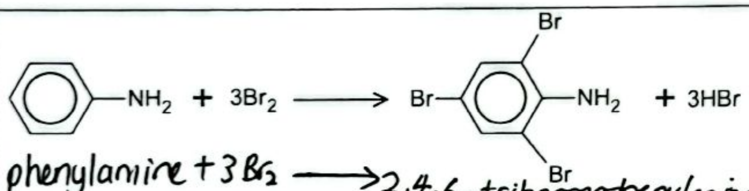
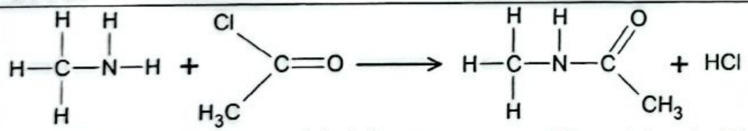
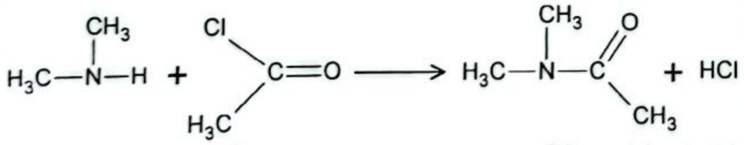
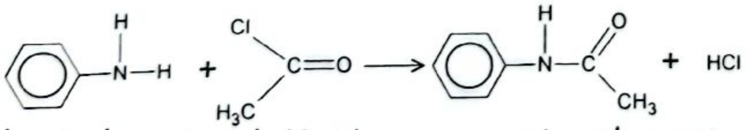
Topic: Organic Nitrogen Compounds & Proteins

Organic Nitrogen Compounds

(I) Formation of amines

S/N	Reactants Products	Type of reaction/ Remarks
1	 nitrile +4[H] ⟶ amine  Reagents & conditions: **(i)** $LiAlH_4$ in dry ether, room temp **or** **(ii)** $H_2(g)$ with Pd/Pt catalyst **or** **(iii)** $H_2(g)$ with Ni catalyst, heat **or** **(iv)** Na in ethanol	Reduction Note: This method is used to obtain 1° amines.
2	 nitrobenzene + 6[H] ⟶ phenylamine + $2H_2O$ Reagents & conditions: **(i)** Sn in conc. HCl, heat under reflux, followed by addition of NaOH(aq) **or** **(ii)** $H_2(g)$ with Ni catalyst, heat	Reduction Note: - This is the only method used to obtain aromatic amines (from nitrobenzene). - NaOH is used to liberate phenylamine. $C_6H_5NH_3^+ + OH^- \rightarrow C_6H_5NH_2 + H_2O$

Reactions of amines

S/N	Reactants	Products	Type of reaction/ Remarks
1	 amine + HCl ⟶ amine salt 		Acid-base Observations: Amine salts are usually white crystalline solids formed on evaporation. Note: - The amine can be regenerated from the salt by reacting with an alkali. - This can be used as a test to identify amines. - Either HCl or H_2SO_4 can be used to react with amine.
2	 phenylamine + $3Br_2$ ⟶ 2,4,6-tribromophenylamine + 3HBr Reagents & conditions: Br_2(aq) Note: Monosubstitution of bromine if Br_2 in CCl_4 is used.		Electrophilic substitution Observations: Orange Br_2(aq) decolourises. White ppt of 2,4,6-tribromophenylamine formed. White fumes of HBr seen. Note: Cannot be used to distinguish between phenylamine and phenol. (Similar observations for both)
3	 1° amine + acyl chloride ⟶ 2° amide + HCl  2° amine + acylchloride ⟶ 3° amide + HCl  phenylamine + acyl chloride ⟶ N-phenylalkylamide + HCl Reagents & conditions: acyl chloride		Condensation (Nucleophilic acyl substitution) Observations: White fumes of HCl seen Note: • 2° amines react faster than 1° amines. 3° amines do not undergo acylation. Reaction is used to prepare 2° and 3° amides. • There is no condensation reaction between carboxylic acids and amines to form amides in normal laboratory preparation. Only neutralisation occurs. **CH_3NH_2 + CH_3CO_2H → $CH_3NH_3^+$ $CH_3CO_2^-$**

Relative basicity of ammonia, ethylamine and phenylamine in aqueous solution

- Basic strength of amines and phenylamines depends on the availability of the lone pair of electrons on N atom to form dative bond with a proton, H^+.

Ethylamine	>	ammonia	>	phenylamine
Relatively strong		NH_3		**very weak**

- Ethylamine is a stronger Bronsted-Lowry base than NH_3
  - Electron–donating $-CH_2CH_3$ group increases electron density on the N atom
  - Lone pair of electrons on N atom much more available for dative bonding with H^+
- Phenylamine is a weaker Bronsted-Lowry base than NH_3 (no effect on litmus)
  - In phenylamine, the p orbital of N atom overlaps with π orbital of benzene ring.
  - Lone pair of electrons on N atom is delocalised into the benzene ring, hence less available to accept a proton.

Relative Basicity of Primary, Secondary and Tertiary Aqueous Amine

2° amine	>	1° amine	>	3° amine
Strongest				**Weakest**

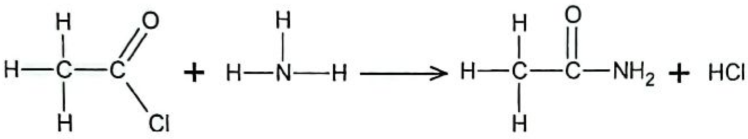
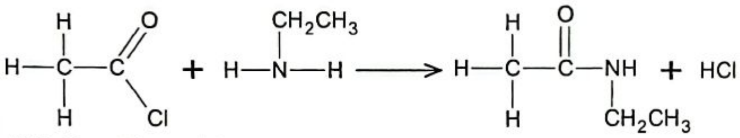
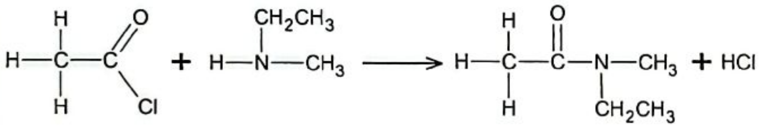
- 2° amine is a stronger Bronsted-Lowry base than 1° amine
  - More electron donating alkyl groups increases electron density on N atom on 2° amine.
  - Lone pair of electrons on N atom much more available for dative bonding with H^+.
- 3° amine is a weaker Bronsted-Lowry base than 1° or 2° amine
  - Presence of bulky substituents sterically hinders the approach of the H^+ to form dative bond with lone pair of electrons on N atom.

Relative Basicity of Primary, Secondary and Tertiary Gaseous Amines

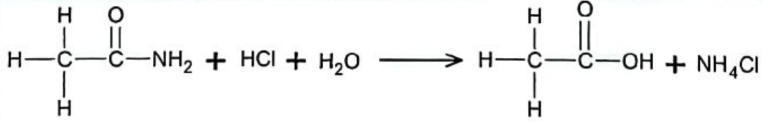
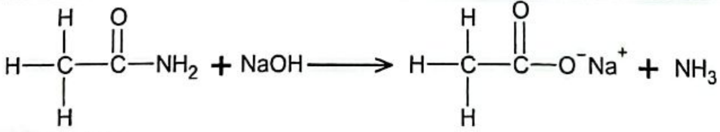
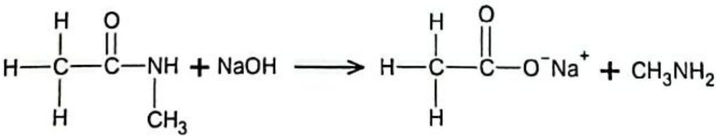
3° amine	>	2° amine	>	1° amine
Strongest				**Weakest**

- 3° amine is a stronger Lewis base than 2° amine and 2° amine is a stronger Lewis base than 1° amine
  - More electron donating alkyl groups increases electron density on N atom on 3° amine compared to 2° amine and 2° amine compared to 1° amine.
  - Lone pair of electrons on N atom much more available for donation to an empty orbital.

(II) Formation of amides

S/N	Reactants	Products	Type of reaction/ Remarks
1	**(i)** For 1° amide: Reagents & conditions: acyl chloride and ammonia  **(ii)** For 2° amide: Reagents & conditions: acyl chloride and 1° amine  **(iii)** For 3° amide: Reagents & conditions: acyl chloride and 2° amine 		Condensation (Nucleophilic acyl substitution)

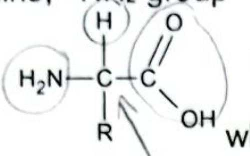
Reactions of amides

S/N	Reactants	Products	Type of reaction/ Remarks
1	 Reagents & conditions: Heat under reflux with HCl(aq) or H_2SO_4(aq)		Acidic Hydrolysis
2	 1° amide  2° amide Reagents & conditions: Heat under reflux with NaOH(aq)		Alkaline Hydrolysis Observations: 1° amide reacts to produce pungent, colourless NH_3 gas which turns moist red litmus blue Note: Used to test for 1° amides

3	$CH_3CONH_2 + 4[H] \rightarrow CH_3CH_2NH_2 + H_2O$ 1° amide 1° amine $CH_3CONHCH_3 + 4[H] \rightarrow CH_3CH_2NHCH_3 + H_2O$ 2° amide 2° amine $CH_3CON(CH_3)_2 + 4[H] \rightarrow CH_3CH_2N(CH_3)_2 + H_2O$ 3° amide 3° amine Reagents & conditions: $LiAlH_4$ in dry ether, room temperature	Reduction **Note:** H_2, Pt catalyst, r.t. or $NaBH_4$ cannot be used.

(III) Amino Acids

- They are compounds which have an acidic carboxyl, $-CO_2H$ group and a basic amino, $-NH_2$ group



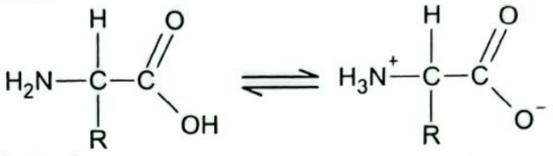
where R may be H, alkyl, aryl or any other groups

Physical Properties

A zwitterion has equal no. of +ve & -ve charges present. It has no net charge & is electrically neutral.

(a) Zwitterion formation

Zwitterions are formed when the proton from the -COOH group adjacent to the α-carbon migrates to the $-NH_2$ group adjacent to the α-carbon.



zwitterion

(b) High melting point

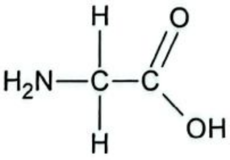
- Amino acids exist as zwitterions in solid state.
- It has giant ionic lattice structures with strong electrostatic forces of attraction between the oppositely charged ~~ions.~~ groups.
- Large amount of energy is required to overcome these strong forces of attraction.

(c) Solubility

- Soluble in water
    - due to strong ion-dipole interactions between zwitterions and water molecules
    - hydrogen bonding between amino acid molecules and water molecules

(d) Optical Activity

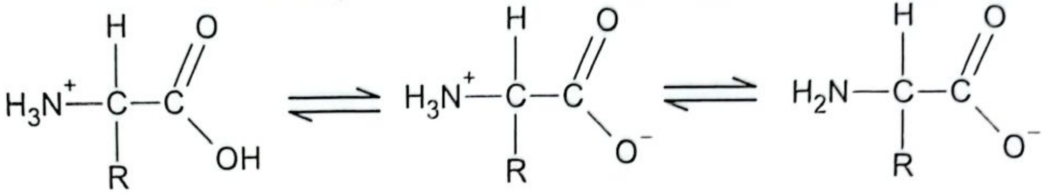
- Except for glycine, the α carbons (2nd carbon) of amino acids are chiral centers.



glycine

Acid-base properties

- Amino acids are amphoteric and can exist in three forms depending on pH:



low pH (protonated) isoelectric pH (electrically neutral) high pH (deprotonated)

In an electric field, amino acid migrates towards

- the cathode (–) at low pH,
- the anode (+) at high pH

Isoelectric point (pI)

- pH at which amino acid has no net charge **or**
- pH at which the amount of positive charge on an amino acid exactly balances the amount of negative charge

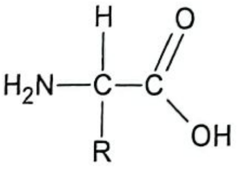
Separation of Amino acid: Electrophoresis

$\text{distance migrated} \propto \frac{\text{charge}}{\text{mass}}$

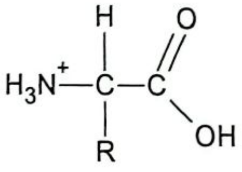
pI of amino acid vs pH of buffer solution	Overall charge on the amino acid	Migration to cathode or anode
pI = pH	No net charge	No migration
pI > pH	Positive charge	Cathode
pI < pH	Negative charge	Anode

Titration curve of amino acid

- Titration of protonated amino using NaOH(aq)



molecular form

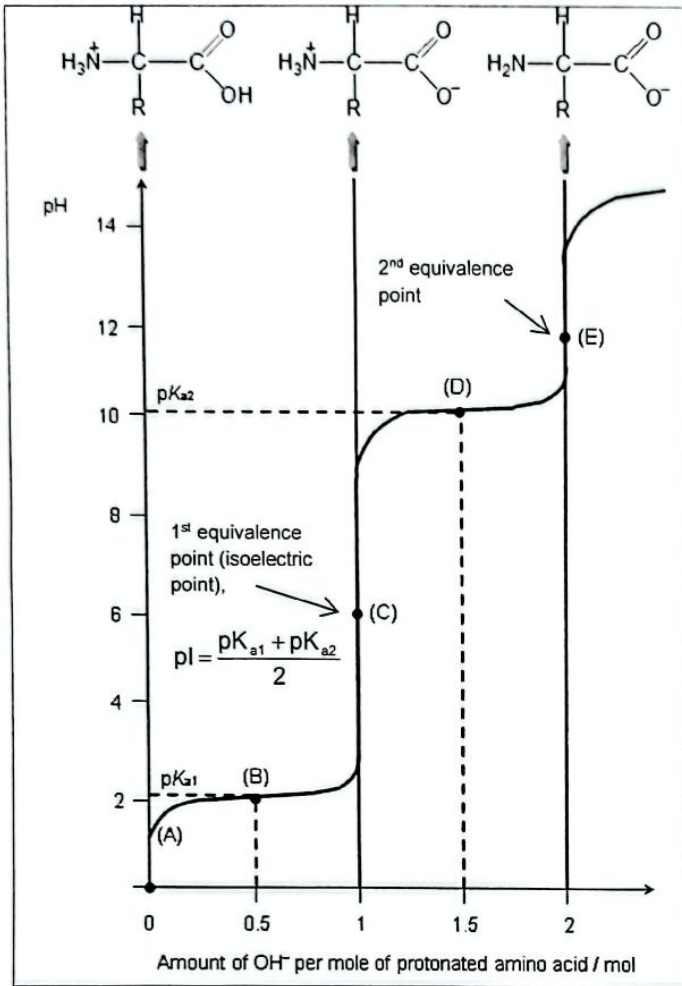


protonated form

$H_3N^+CHRCO_2H + H_2O \rightleftharpoons H_3N^+CHRCO_2^- + H_3O^+$ pK_{a1}

$H_3N^+CH_2CO_2^- + H_2O \rightleftharpoons H_2NCHRCO_2^- + H_3O^+$ pK_{a2}

Note: Assuming the R group is non–polar.

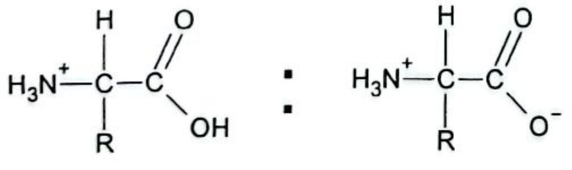


(A) Start of titration

At pH ≈ 1, the amino acid is entirely protonated.

(B) First halfway point

When 0.5 mol of OH⁻ per mole of the protonated amino acid is added, it reacts with exactly one half of the strongest acid (–COOH has the smaller pKa). At this point, concentrations of the first conjugate acid/base pair are the same.



acid : conjugate base

50 : 50

Therefore, pH = pK_{a1}

(C) First equivalence point

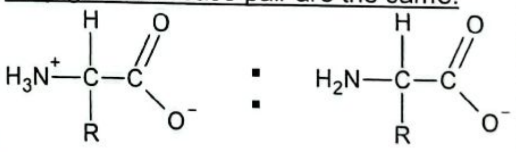
When 1.0 mol of OH⁻ per mole of the protonated amino acid is added, the slope of the curve is at a maximum. The H^+ has completely dissociated from –COOH group. The amino acid exists as a zwitterion.

$$\boxed{pH = \frac{pKa_1 + pKa_2}{2} = pI}$$

→ isoelectric point: where total charge on the amino acid is zero.

(D) Second halfway point

When 1.5 mol of OH⁻ per mole of the protonated amino acid is added, it reacts with exactly half of the next strongest acid, NH_3^+.
At this point, concentrations of the second conjugate acid/base pair are the same:



acid : conjugate base

50 : 50

Therefore, pH = pK_{a2}

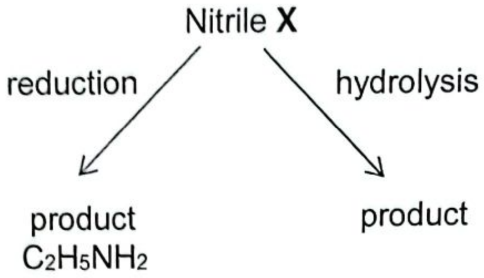
(E) Second equivalence point

When 2.0 mol of OH⁻ per mole of the protonated amino acid is added, the second H^+ has completely dissociated from $-NH_3^+$.

Questions

AJC/Prelim 2007/1/28

1 A nitrile **X** undergoes the following two reactions:



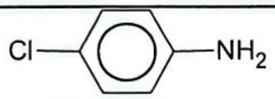
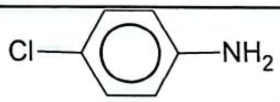
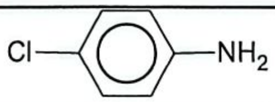
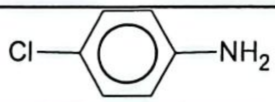
What would be produced when the products from the two reactions are mixed together?

A $[CH_3CH_2NH_3^+]\ [^-O_2CCH_3]$
B $[CH_3CH_2NH_3^+]\ [^-O_2CCH_2CH_3]$
C $CH_3CONHCH_2CH_3$
D $CH_3CH_2CONHCH_2CH_3$

A ✓

AJC/Prelim 2007/1/29

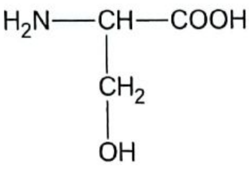
2 Which sequence shows the nitrogen compounds in increasing order of basic strength?

	Least basic	→	*most basic*
A	CH_3CONH_2		CH_3NHCH_3
B	CH_3CONH_2	CH_3NHCH_3	
C	CH_3NHCH_3		CH_3CONH_2
D		CH_3CONH_2	CH_3NHCH_3

A
D
X

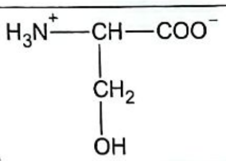
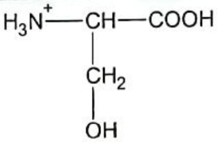
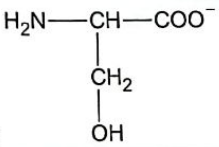
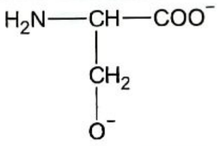
AJC/Prelim 2007/1/30

3 A sample of *serine* is dissolved in a buffer solution of pH 12.


$H_2N-CH(CH_2OH)-COOH$

Serine

Which form will be predominant at this pH?

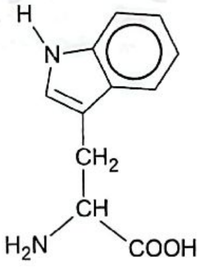
A  $H_3\overset{+}{N}-CH(CH_2OH)-COO^-$	**B**  $H_3\overset{+}{N}-CH(CH_2OH)-COOH$
C  $H_2N-CH(CH_2OH)-COO^-$	**D**  $H_2N-CH(CH_2O^-)-COO^-$

D ✗ C

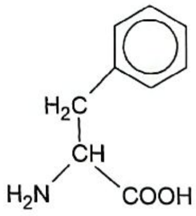
SAJC/Prelim 2007/1/29

4 Electrophoresis is a technique of separating and studying amino acids. A solution of amino acids is absorbed into paper that is moistened with a buffer solution and stretched between two electrodes. Positively charged species move towards the cathode, negatively charged species towards the anode. With a buffer at pH 3, which of the following amino acids will move most readily towards the cathode?

A

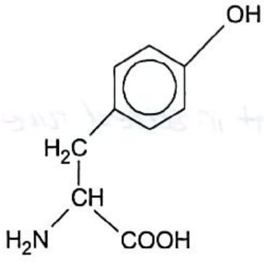


B

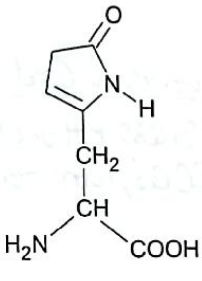


D ✗ A

C



D



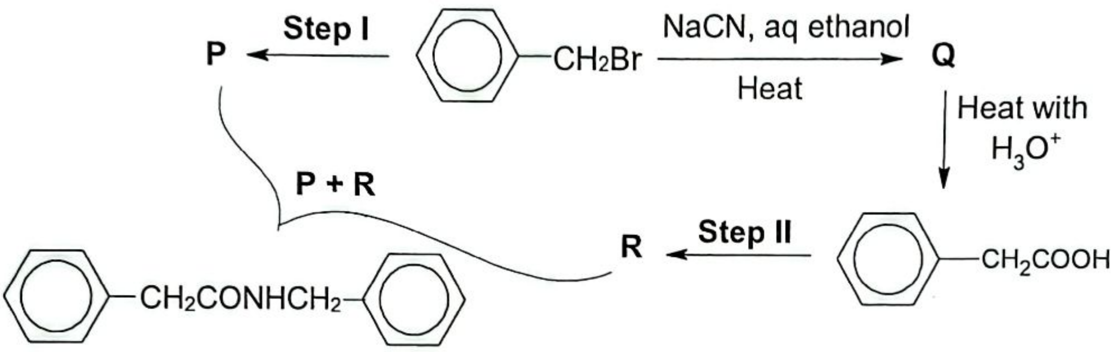
JJC/Prelim 2007/2/6a

5 **(a)** Amino acids exist as crystalline solids with high melting points. Explain why this is so.

(b) Draw the structural formula of a portion of a protein containing the three amino acid residues thr-met-asp, showing the form in which it would exist at pH 12.
Label clearly a peptide bond on your structure. (Refer to your lecture notes for the structure of thr, met and asp.)

JJC/Prelim 2007/3/4c

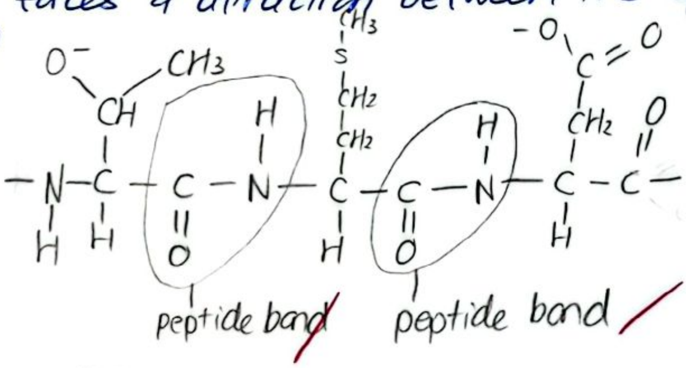
6 (Bromomethyl)benzene is used as the starting material in the following synthesis.



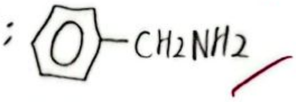
Suggest the structures of **P**, **Q** and **R** and hence suggest suitable reagents and conditions for steps **I** and **II**.

5a) In solid state, AAs exist as zwitterions. Hence, AAs are crystalline solids with high m.p.s as they have giant ionic structures with strong electrostatic forces of attraction between the oppositely charged ~~ions~~ groups of the zwitterions, hence large amt of energy needed to overcome the strong IBs.

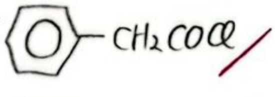
5b)



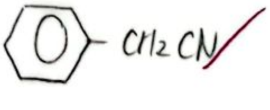
6. P:



R:



Q:



Reagents & Conditions

I: excess ethanolic NH_3, heat in sealed tube

II: $SOCl_2$, PCl_5 room temperature

H2 Chemistry Revision Worksheet

Topics: Synthesis, Distinguishing Test and Elucidation

Synthesis

1 C_4H_9Br undergoes the following reactions:

$$C_4H_9Br \xrightarrow[\text{heat under reflux}]{\text{NaOH(aq),}} C_4H_{10}O \xrightarrow[\text{heat under reflux}]{K_2Cr_2O_7,\ H_2SO_4(aq)} C_4H_8O$$

What could C_4H_9Br be?

A 1-bromobutane Br - C-C-C-C

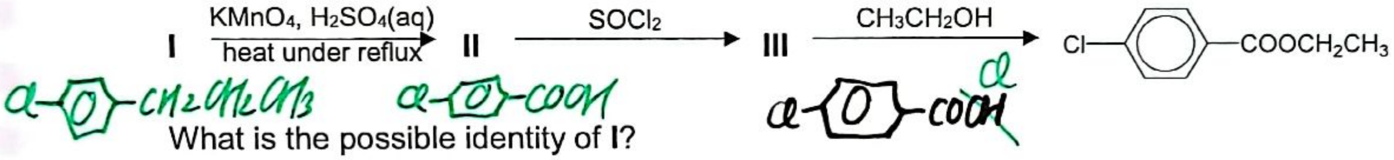
B 2-bromobutane

C 1-bromo-2-methylpropane

D 2-bromo-2-methylpropane

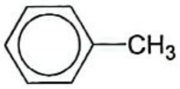
B ✓

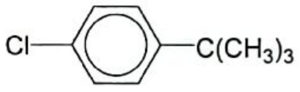
2 Consider the reaction scheme below:

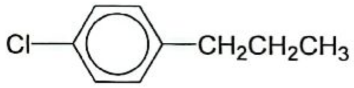


What is the possible identity of **I**?

A 

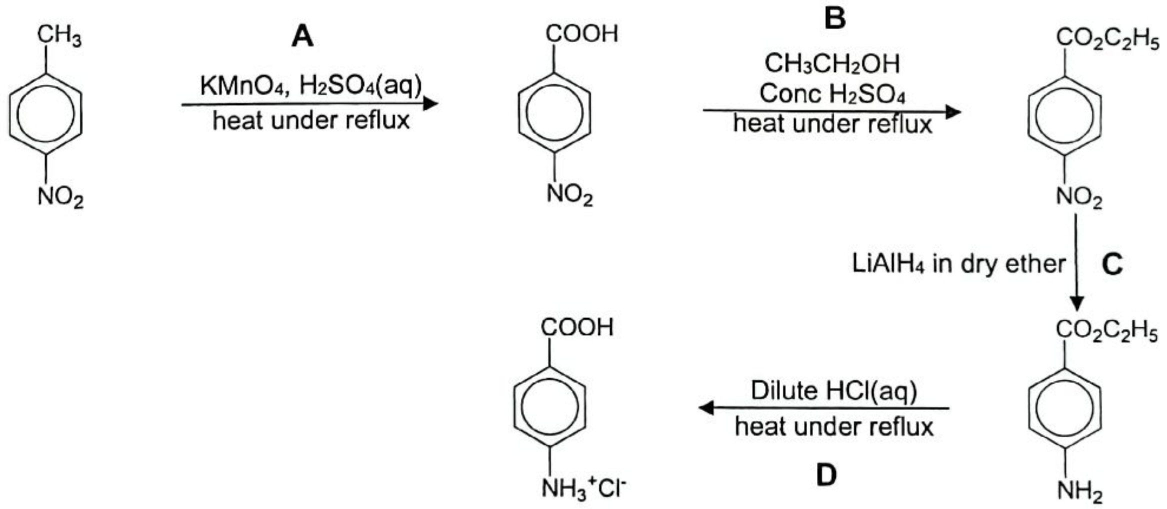
B 

C 

D 

B 0

3 Which step in the following reaction scheme is incorrect?



C ✓

4 Suggest the reagent and conditions required to carry out the transformation from ethane to 1-chloropropane. Draw the displayed formula of compounds **A** and **B**.

$$\begin{tikzcd}
CH_3CH_3 \arrow[r, "\text{Step I}"] & \textbf{A} \arrow[r, "\text{Step II}"] & CH_3CH_2CN \arrow[r, "\text{Step III}"] & CH_3CH_2COOH \arrow[r, "\text{Step IV}"] & \textbf{B} \arrow[dl, "\text{Step V}"] \\
 & & & CH_3CH_2CH_2Cl &
\end{tikzcd}$$

5 Suggest a synthetic route to convert benzene to 4-bromophenylamine.

6 **(a)** Give the reagents and conditions for the conversion for each of the following.

(i) Benzene to nitrobenzene

(ii) Phenol to 4-nitrophenol

(b) Explain the difference in the reagents and conditions used for the two conversions.

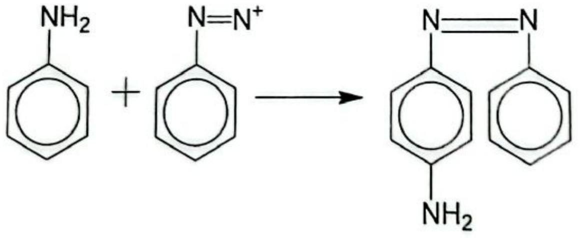
7 2-bromobutane undergoes nucleophilic substitution when heat under refluxed with NaOH(aq) via two possible mechanism, S_N1 or S_N2.

(i) Write down the rate equation if 2-bromobutane undergoes S_N1 mechanism.

(ii) Write down the rate equation if 2-bromobutane undergoes S_N2 mechanism.

(iii) Describe the two possible mechanisms between 2-bromobutane and NaOH.

8 A bright yellow dye, aniline yellow can be synthesised from benzene in the following synthetic route.

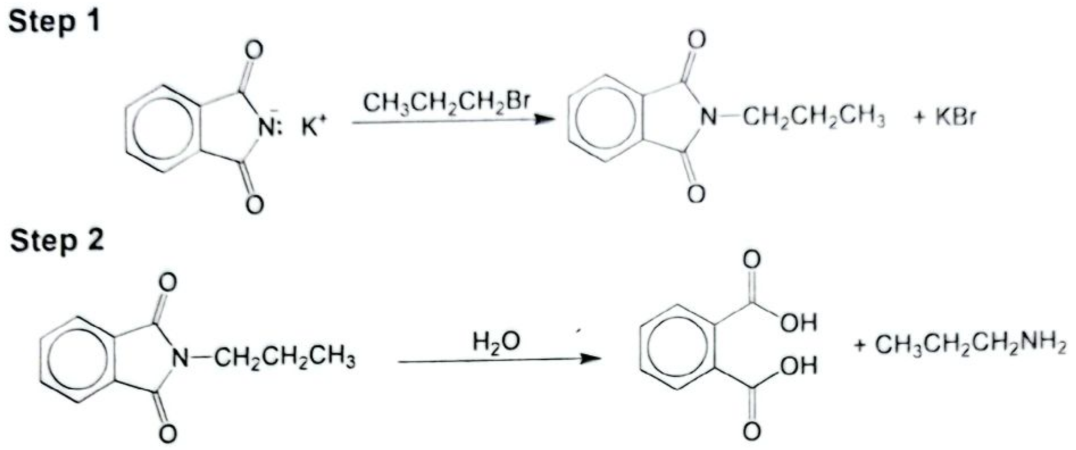


Which one of the following shows the correct type of reaction for the above reaction?

A Electrophilic substitution
B Electrophilic addition
C Nucleophilic substitution
D Nucleophilic addition

B A

9 The Gabriel synthesis shown below gives a high yield of primary amines.



What is the type of reaction occurring at each step?

	Step 1	**Step 2**
~~A~~	Electrophilic substitution	Oxidation
B	Nucleophilic substitution	Hydrolysis
~~C~~	Electrophilic addition	Oxidation
D	Nucleophilic addition	Hydrolysis

B ✓

Distinguishing Test

10 Certain chemical tests were performed on the anti-arthritic agent *Fenoprofen*. The results of these test are given in the table below.

Test	**Result**
Tollen's reagent	No silver mirror
Br_2(aq)	Remained orange
$K_2Cr_2O_7$, dilute H_2SO_4, heat under reflux	Remained orange
Na_2CO_3(aq)	Effervescence of CO_2 evolved

Which one of the following functional groups do these results suggest that *Fenoprofen* contains?

~~A~~ Aldehyde

~~B~~ Alkene

C Carboxylic acid

D Primary alcohol

C ✓

11 The table shows the results of simple tests on a compound **X**.

Test	**Result**
2,4-dinitrophenylhydrazine	Positive
Tollen's reagent	Positive
Alkaline aqueous iodine	Positive
Na metal	Negative

From the results of the tests, what could **X** be?

A CH_3CHO

B CH_3COCH_3

~~C~~ CH_3CH_2CHO

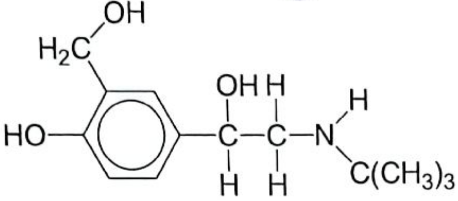
~~D~~ $CH_3CH(OH)CH_3$

A ✓

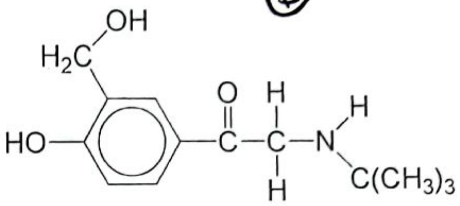
12 Describe a simple chemical test that can distinguish between each pair of compound.

(i)

Ⓐ

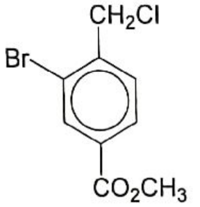


Ⓑ

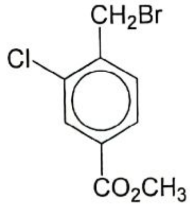


(ii)

Ⓒ

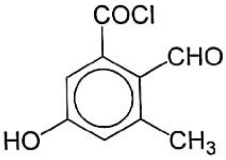


Ⓓ



(iii)

Ⓔ



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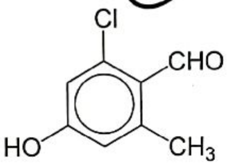

i) NaOH (aq), heat under reflux. B reacts to produce pungent, colarless $NH_3(g)$ which turns moist red litmus blue.

ii) Heat with alcoholic $AgNO_3$. Ⓒ produces a cream ppt, AgBr after a while. Ⓓ produces a white ppt, AgCl, after a long time.

iii) Add $AgNO_3$ (aq) at room temperature. Ⓔ forms white ppt. No white ppt formed with Ⓕ ✓

Elucidation

13 This question is about **L**, C_9H_8O.

- Compound **L** is insoluble in water and aqueous sodium hydroxide.
- With liquid bromine, **L** gives **M**, $C_9H_8OBr_2$.
- **L** does **not** react with Fehling's solution but reacts with Tollens' reagent to give a silver mirror.
- On heating with acidified potassium manganate(VII), **L** gives **N**, $C_8H_6O_4$.

Compound **N** is soluble in aqueous sodium hydroxide. Treatment of **N** with thionyl chloride followed by ethylamine gives **O**.

Deduce the structures of compounds **L**, **M**, **N** and **O**. Explain the chemistry of the reactions described.

14 PCl_5 is used for substitution reactions in organic chemistry.

An optically active compound **A**, with molecular formula $C_3H_7O_2N$, reacts with PCl_5 to give white fumes.

When a solution containing **A** is warmed with aqueous sodium hydroxide, a pungent gas is evolved. Upon acidification of the resulting mixture, compound **B**, $C_3H_6O_3$, can be isolated. When **B** is warmed with concentrated sulphuric acid, a cyclic compound **C**, $C_6H_8O_4$, is formed.

Compound **D** is a structural isomer of **B** and is not optically active. When **D** is warmed with concentrated sulphuric acid, a non-cyclic compound **E**, $C_3H_4O_2$, is produced.

Deduce the structures of compounds **A**, **B**, **C**, **D** and **E**. Explain the chemistry of the reactions described.

15 Neutral organic compound **P** contains 49.3% carbon, 6.85% hydrogen and 43.85% oxygen by mass. When heated with aqueous sodium hydroxide, **P** gives a compound **Q**, $C_2H_6O_2$ and sodium ethanoate.

When 1 mole of **Q** reacts with 1 mole of hydrogen chloride with some anhydrous zinc chloride, **R,** C_2H_5OCl is formed. **R** gives **S**, C_3H_5ON on heating with ethanolic potassium cyanide.

When **S** is heated with dilute hydrochloric acid, an optically inactive liquid **T**, $C_3H_6O_3$ is obtained. On heating **T** alone, a liquid **U**, $C_3H_4O_2$ which rapidly decolourises aqueous bromine, is formed. Oxidation of **T** gives a solid **V**, $C_3H_4O_4$ which is soluble in water.

Deduce the structural formulae of compounds **P** to **V**, giving your reasoning. Chemical equations are not required.

16 This question is about the neutral compound **D**, C_8H_7ON.

On heating **D** with dilute hydrochloric acid, only compound **E** ($C_8H_9O_2N$) is obtained.

E is soluble in dilute sulfuric acid, aqueous sodium carbonate and aqueous sodium hydroxide. **E** also reacts with lithium aluminium hydride to give **F** ($C_8H_{11}ON$). **F** is no longer soluble in sodium carbonate and aqueous sodium hydroxide but is still soluble in dilute sulfuric acid.

On passing **F** over hot Al_2O_3, **G** (C_8H_9N) is produced. Heating **G** with alkaline potassium manganate(VII) gives **H** ($C_7H_6NO_2Na$) together with the evolution of a gas.

H can also be synthesised by treating 2-nitrobenzoic acid with tin and concentrated hydrochloric acid followed by NaOH(aq).

Deduce the structures of compounds **D**, **E**, **F**, **G** and **H**, and explain the reactions involved.