



## Summary

Points to include in your answers when explain deductive organic questions:

- ✓ Functional group involved in the reaction
- ✓ Type of reaction
- ✓ Identification of unknown gas or ppt formed
- ✓ Identification of functional groups formed (if any)
- ✓ Fully balanced equations if necessary

Eg: E has a alcohol functional group which undergoes elimination to form alkene F

### List of common reagents:

Reagents	Observation	Deduction
Br <sub>2</sub> in UV light	Decolourisation of reddish brown Br <sub>2</sub>	Alkane Alkyl benzene
Br <sub>2</sub> in CCl <sub>4</sub> , dark room	Decolourisation of reddish brown Br <sub>2</sub>	Alkene
Aq Br <sub>2</sub>	Decolourisation of reddish brown Br <sub>2</sub>  Decolourisation of reddish brown Br <sub>2</sub> . White ppt in xs.	Alkene  Phenol Phenylamine
Br <sub>2</sub> with anhydrous FeBr <sub>3</sub>	Decolourisation of reddish brown Br <sub>2</sub>	Benzene Substituted Benzene
Hot acidified KMnO <sub>4</sub>	Purple KMnO <sub>4</sub> decolourises  Purple KMnO <sub>4</sub> decolourises CO <sub>2</sub> evolved  Purple KMnO <sub>4</sub> decolourises White ppt on cooling  Purple KMnO <sub>4</sub> decolourises CO <sub>2</sub> evolved White ppt on cooling	Primary or Secondary alcohol Aldehyde Alkene with monosubstituted or disubstituted C=C bond  Terminal alkene C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> HCOOH  Methylbenzene  Alkylbenzene Benzene with side chain
Cold dilute KMnO <sub>4</sub>	Purple KMnO <sub>4</sub> decolourises	Alkene
Hot acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , distill	Orange solution turns green	Primary alcohol
Hot acidified K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	Orange solution turns green	Primary and secondary alcohol Aldehyde
Aq NaOH, r.t.p	-	Phenol Carboxylic Acid
Aq NaOH, heat	NH <sub>3</sub> evolved	Nitrile Primary amide



Reagents	Observation	Deduction
Aq NaOH, heat	-	Secondary or Tertiary amide
	-	Alkyl Halide
Alcoholic NaOH, heat	-	Alkyl Halide
Conc. H <sub>2</sub> SO <sub>4</sub> , r.t.p	-	Alkene
XS Conc. H <sub>2</sub> SO <sub>4</sub> 170°C	-	Alcohol
Conc. H <sub>2</sub> SO <sub>4</sub> , heat	-	If reagent present is ROH, RCOOH is present (vice versa)
Dilute H <sub>2</sub> SO <sub>4</sub>	-	Ester Amide Nitrile
Dilute H <sub>2</sub> SO <sub>4</sub>	White crystalline solid formed	Amine
Aq alkaline I <sub>2</sub>	Yellow ppt of CHI <sub>3</sub> formed	Methyl ketone Methyl alcohol
Anhydrous PCl <sub>5</sub> or SOCl <sub>2</sub>	White fumes of HCl	Alcohol Carboxylic acid
LiAlH <sub>4</sub> in dry ether	-	Aldehyde Ketone Carboxylic Acid Nitrile Esters Amide
Sn in conc HCl followed by NaOH	-	Nitrobenzene
Excess ethanolic NH <sub>3</sub> , heat in sealed tube	-	Alkyl halide
2,4-dinitrophenylhydrazine	Orange ppt is formed	Ketone Aldehyde

**The Unsaturation Rule:**

$$\text{Degree of Unsaturation} = \frac{1}{2}[(2n+2)-(H+X-N)]$$

where:

- n is the number of carbon atoms
- H is the number of hydrogen atoms
- X is the number of halogen atoms
- N is the number of nitrogen atom

Note:

- ✓ Ring count as one degree of unsaturation
- ✓ Double bonds count as one degree of unsaturation
- ✓ Triple bonds count as two degree of unsaturation.



## Organic Chemistry Café: Deductive Organic

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Q1.YJC Prelim 2007/P3/Q1(c)

A has the molecular formula  $C_9H_{10}Cl_2$ .

When compound **A** is treated with hot ethanolic sodium hydroxide, a compound **B** is formed which decolourises aqueous bromine. When compound **A** is heated with aqueous sodium hydroxide, a compound **C** is formed which rapidly loses a water molecule to form compound **D**. Compound **D** gives an orange precipitate with 2,4-dinitrophenylhydrazine. When compound **A** is treated with hot acidified potassium manganate (VII), a white precipitate **E**,  $C_9H_8Cl_2O_2$ , is observed.

Give the possible structures of compounds **A**, **B**, **D** and **E**.

[4]



**Q2. PJC Prelim 2008/P3/Q3(d)**

An organic compound **P**,  $C_{10}H_{11}O_2Br$ , does not react with aqueous sodium carbonate. **P** reacts slowly on heating with aqueous sodium hydroxide, followed by acidification to form an optically active compound **Q**, and an insoluble oil **R**,  $C_7H_8O$ . **R** gives benzoic acid on oxidation. One mole of **Q** reacts with two moles of phosphorus pentachloride to give steamy fumes.

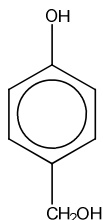
Deduce the structures of compounds **P**, **Q** and **R**. Explain the chemistry of the reactions described, writing equations where appropriate. [7]



## Organic Chemistry Café: Deductive Organic

### Q3. VJC Prelim 2008/P3/Q3(d)

When an organic halogen compound **W**,  $C_{10}H_9O_3Br$ , is boiled with aqueous sodium hydroxide followed by acidification, it gives two compounds, one of which has the following structure shown below.



When sodium hydrogencarbonate is added to the other compound **X**, effervescence of carbon dioxide is observed. In addition, **X** gives a yellow precipitate on warming with alkaline aqueous iodine. When **X** is treated with an ethanolic solution of  $NaBH_4$ , it gives **Y**. Heating **Y** in the presence of an acid catalyst gives a sweet-smelling liquid, **Z**,  $C_6H_8O_4$ .

Deduce the structures for each lettered compound, **W** to **Z**, and give an account of the chemistry involved.

[10]



## Organic Chemistry Café: Deductive Organic

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### Q4. AJC Prelim 2008/P3/Q4(b)

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 sulphuric 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 sulphuric 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.

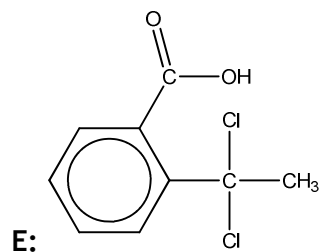
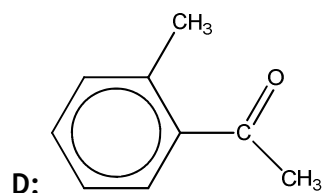
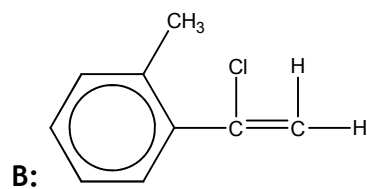
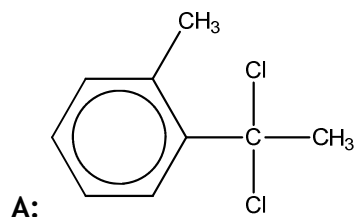
**H** can also be synthesised by treating 2-nitrobenzoic acid with tin and concentrated hydrochloric acid followed by  $NaOH(aq)$ .

Deduce the structures of compounds **D**, **E**, **F**, **G** and **H**, and explain the reactions involved. **[10]**



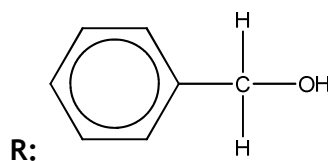
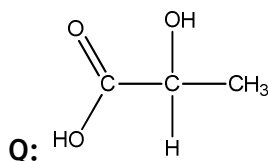
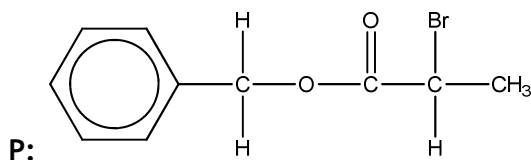
## Answers

Q1.YJC Prelim 2007/P3/Q1(c)





**Q2. PJC Prelim 2008/P3/Q3(d)**



P has an ester functional group hence it undergoes alkaline hydrolysis on heating with aqueous NaOH to give 2 products which upon acidification, it forms the alcohol functional group in R and the carboxylic acid functional group in Q.

The C-Br group on P also undergoes nucleophilic substitution on heating with aqueous NaOH to form an alcohol functional group which is found on Q.

Q is optically active as it has a chiral carbon atom attached to 4 different groups.

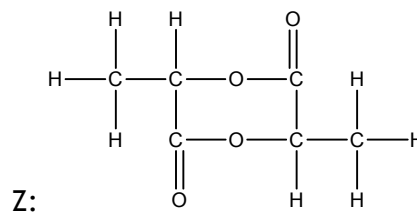
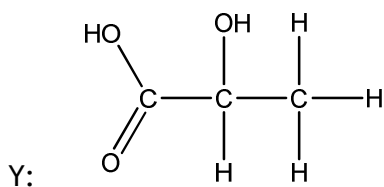
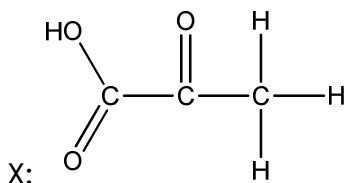
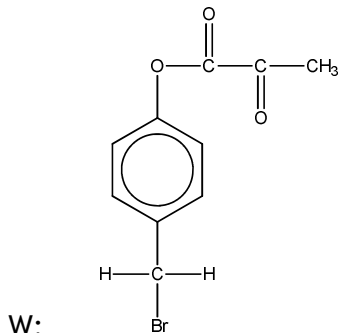
R has a -CH<sub>2</sub>OH group, attached to the benzene ring, which undergoes oxidation to form the benzoic acid

Q has an alcohol and carboxylic functional group hence it undergoes substitution with 2 moles of PCl<sub>5</sub>. The white fume released is HCl.



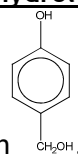


**Q3. VJC Prelim 2008/P3/Q3(d)**

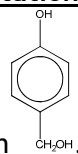


W has an ester functional group hence it undergoes alkaline hydrolysis to form the

carboxylic acid group in X and the phenol functional group in



W has a C-Br group which undergoes electrophilic substitution when boil with aqueous



NaOH to form a primary alcohol functional group seen in

X has carboxylic functional group which undergoes acid-base reaction with  $\text{NaHCO}_3$  thus  $\text{CO}_2$  is observed.

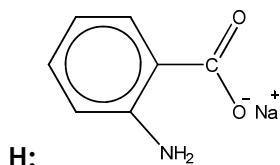
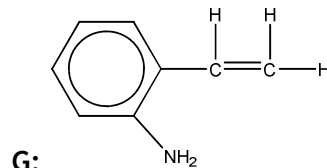
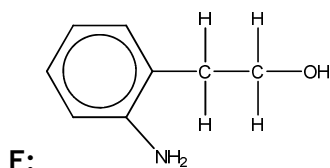
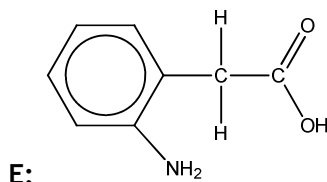
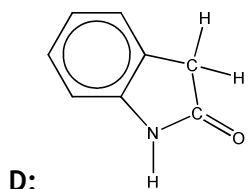
X is a methyl ketone thus undergoes oxidation in presence of alkaline aqueous iodine to give a yellow ppt of  $\text{CHI}_3$ .

X has a ketone functional group which undergoes reduction when treated with ethanolic  $\text{NaBH}_4$ , forming the alcohol functional group in Y.

When heated in presence of an acid catalyst, 2 molecules of Y undergo condensation reaction to form Z which has 2 ester functional groups.



Q4. AJC Prelim 2008/P3/Q4(b)



D is a neutral compound as it does not have a carboxylic acid, phenol, amine or phenylamine functional group.

E is soluble in dilute  $\text{H}_2\text{SO}_4$  as it has a phenylamine group thus is able to undergo acid-base reaction with dilute  $\text{H}_2\text{SO}_4$ .

E having a carboxylic functional group, is able to undergo acid-base reaction with aqueous  $\text{Na}_2\text{CO}_3$  and aqueous  $\text{NaOH}$ , thus is soluble in both reagents.

E has a carboxylic functional group which undergoes reduction in presence  $\text{LiAlH}_4$  in dry ether to form a primary alcohol group in F.

F does not react with  $\text{Na}_2\text{CO}_3$  as it does not have a carboxylic functional group.

F does not react with  $\text{NaOH}$  due to absence of carboxylic acid and phenol functional group.

F reacts with dilute  $\text{H}_2\text{SO}_4$  due to presence of phenylamine functional group.

F with the alcohol functional group, undergoes elimination when passed over hot  $\text{Al}_2\text{O}_3$  to form the alkene functional group in G.

G has a alkene functional group which undergoes oxidation in presence of alkaline  $\text{KMnO}_4$  to form the carboxylic functional group in H. Gas release is  $\text{CO}_2$  due to presence of terminal alkene.

When treated with tin and concentrated  $\text{HCl}$  followed by addition of  $\text{NaOH}$ , the nitrobenzene functional group in 2-nitrobenzene undergoes reduction to form the phenylamine functional group in H.