VICTORIA JUNIOR COLLEGE
CHEMISTRY DEPARTMENT

JC2 H2 CHEMISTRY
ORGANIC CHEMISTRY REVISION

LECTURE OUTLINE

1. REACTION MECHANISMS

(a) Mechanism: **Free radical substitution**

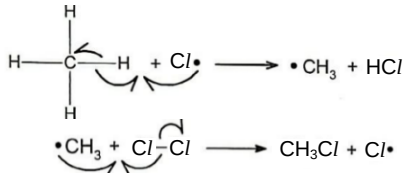
Stoichiometric equation:

$CH_4 + Cl_2 \xrightarrow{uv} CH_3Cl + HCl$

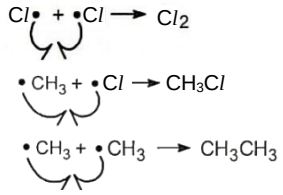
Mechanism:

Initiation: Generation of free radicals.

Propagation: Free radicals generate other free radicals.



Termination: Free radicals combine to form molecules.

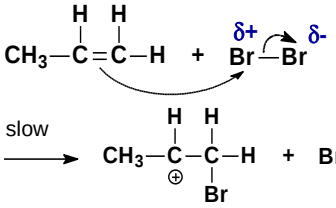


(b) Mechanism: **Electrophilic addition**

Stoichiometric equation:

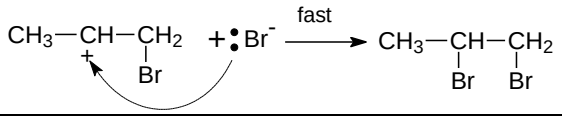
$CH_3CH{=}CH_2 + Br_2 \rightarrow CH_3CHBrCH_2Br$

Mechanism:



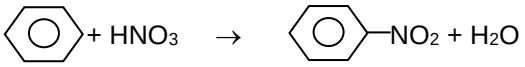
N.B.: The most stable carbocation intermediate will be formed (Markovnikov's rule). In the case, Br is attached to C with more hydrogen atoms to form the **more stable** carbocation.

Relative stability of carbocations:
tertiary > secondary > primary, because alkyl groups exert **electron – donating inductive effect** which **disperse the positive charge** on the carbocation, **stabilising the carbocation**.



(c) Mechanism: **Electrophilic substitution**

Stoichiometric equation:

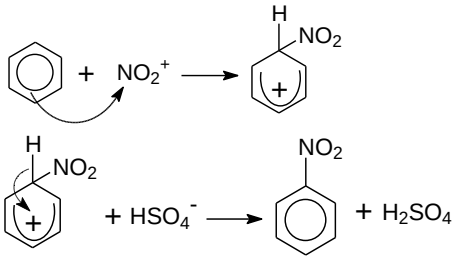


Mechanism:

Generation of strong electrophile:

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

nitronium ion

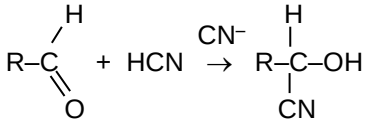


Brønsted- Lowry acid catalyst H_2SO_4 regenerated.

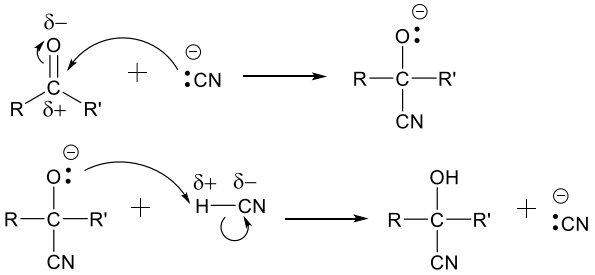
For chlorination, bromination and Friedel – Crafts alkylation, **Lewis acid catalysts** (e.g anhydrous $AlCl_3$ or $FeBr_3$) are used to form strong electrophiles.

(d) Mechanism: **Nucleophilic addition**

Stoichiometric equation:



Mechanism:

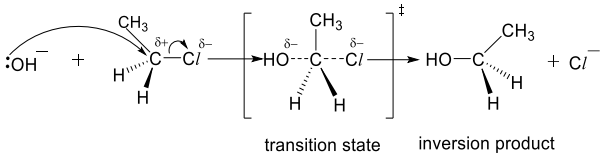


Catalyst CN^- regenerated.

(e)(i) Mechanism: **Bimolecular nucleophilic substitution, S_N2 (for primary RX)**

Stoichiometric equation:
CH_3CH_2**Cl** + NaOH(aq) → CH_3CH_2**OH** +NaCl

Mechanism:



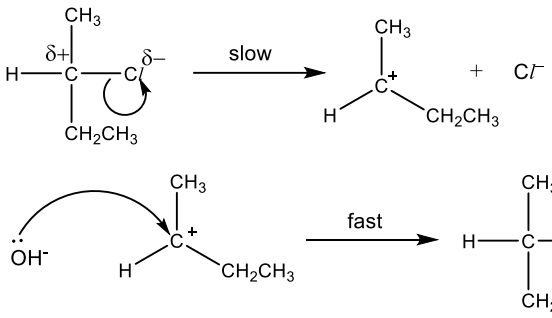
Factors favouring the mechanism
Low steric hindrance [due to less alkyl groups attached to electron deficient carbon atom] – usually favoured **by primary halogenoalkanes**

Stereochemistry (applicable if the molecule is chiral)
Nucleophile attacks **electron deficient** carbon atom from the side **opposite** to the halogen atom, resulting in **inversion of the spatial arrangement** of the organic molecule.

(ii) Mechanism: **Unimolecular nucleophilic substitution, S_N1 (for tertiary RX)**

Stoichiometric equation:
$CH_3CH(CH_2CH_3)$**Cl** + NaOH(aq)
→ $CH_3CH(CH_2CH_3)$**OH** +NaCl

Mechanism:

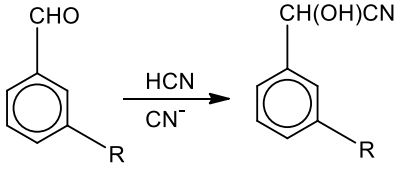


Factors favouring the mechanism
High carbocation stability
[tertiary > secondary > primary], also benzylic ($C_6H_5CH_2^+$)

Stereochemistry
Nucleophile attacks **trigonal planar carbocation from top and bottom with equal chance**, resulting in **equal proportions of both enantiomers (racemic mixture)**.

Examples

1 Describe the mechanism for the following conversion.

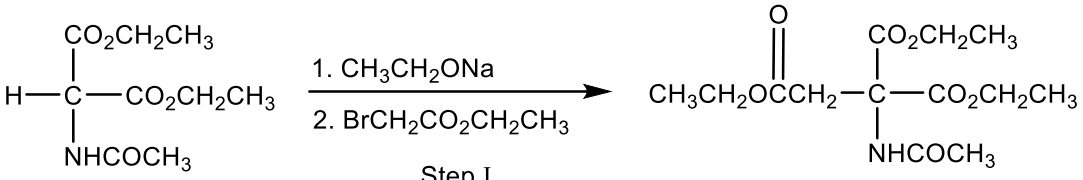


, where R is an alkyl group,

Solution

2 CJC Prelim 11/III/5 (modified)

A general method for the preparation of α-amino acids is the amidomalonate synthesis. The reaction below forms part of the synthesis of aspartic acid using this method:



A **B**

In Step **I**, the reaction begins with a treatment of compound **A** with CH_3CH_2ONa which acts as the base, followed by the reaction with $BrCH_2CO_2CH_2CH_3$ to form **B**.

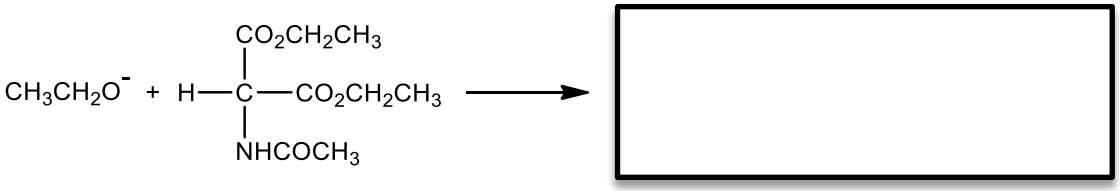
(a) Suggest the type of reaction undergone in Step I to form **B**.

(b) Hence, construct a balanced equation for the acid-base reaction between **A** and CH_3CH_2ONa.

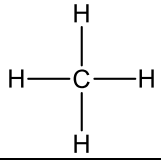
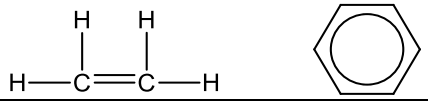
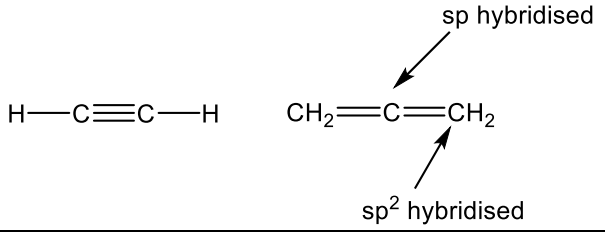
Solution

(a)

(b)



2. HYBRIDISATION

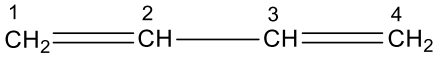
Type of hybridization	Bonds formed by carbon	Shape and bond angle	Example
sp^3	4 sigma bonds	Tetrahedral, 109.5°	
sp^2	3 sigma and 1 pi bonds	Trigonal planar, 120°	
sp	2 sigma and 2 pi bonds	Linear, 180°	

Example

3 N2008/I/19

The bond lengths in buta-1,3-diene differ from those which might be expected.

The carbon-carbon bond length in ethane is 0.154 nm and in ethene 0.134 nm. The central single bond in buta-1,3,-diene (C2–C3), however, is shorter than the single bond in ethane: it is 0.147 nm.



What helps to explain this C2–C3 bond length?

A It is an sp^2–sp^2 overlap.
B It is an sp^2–sp^3 overlap.
C The electrons in the filled p orbitals on C2 and C3 repel each other.
D The sp^3–sp^3 bonding is pulled shorter by a p–p (π-bond) overlap.

Solution

C1 to C4 are _____ hybridised. Hence the sigma bond between C2 and C3 must be formed from the overlap of sp^2 hybrid orbitals (options **B** and **D** incorrect).

Both C atoms in ethane are _____ hybridised. Hence, the C–C bond in ethane is formed from the overlap of sp^3 hybrid orbitals.

s-orbitals are closer to the nucleus. sp^2 orbital has _____ degree of s character, hence resulting in more effective overlap and a shorter and stronger bond.

Answer:

3. ISOMERISM

ISOMERISM
(compounds with the *same* molecular formula)

Structural (Constitutional) isomerism
(*same* molecular formula, *different* structural formula)

Stereoisomerism
(*same* molecular formula, *same* structural formula, *different* arrangement in space)

Enantiomerism
- presence of chiral centre
- ability to rotate plane-polarised light
- no plane of symmetry in the molecule

Cis–trans isomerism
- arises due to *restricted rotation,* for example, *about C=C*, whereby 2 different groups attached to each alkene C

N.B.

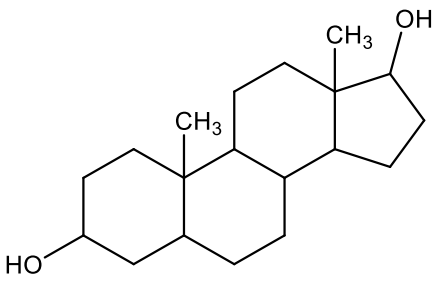
(a) To determine <u>all</u> the isomers:
(1) If molecular formula is given, <u>determine all the structural isomers first</u> followed by stereoisomers.
(2) If structural formula is given, determine only the stereoisomers.

(b) Maximum no. of stereoisomers = 2^n, where n = chiral centres + C=C that demonstrate cis-trans isomerism

Examples

4 HCI Prelim 10/I/19

A *pheromone* is a secreted or excreted chemical factor that triggers a social response in members of the same species. Compound **A** below is an example of *pheromones*.



Compound **A**

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

A 2^6 **B** 2^7 **C** 2^8 **D** 2^9

Solution

Consider <u>structural isomers first</u>:

<u>For each structure, identify chiral centre and C=C that show cis-trans isomerism:</u>

Answer:

5 The complete hydrolysis of 1.76 g of an ester with molecular formula $C_nH_{2n}O_2$ required 2.0×10^{-2} mol of sodium hydroxide.

(a) Deduce the value of n. Hence, state the molecular formula of the ester.

(b) Hence, give the structural formulae of all the esters with this molecular formula.

Solution

(a)

(b)

4. ACIDITY AND BASICITY OF ORGANIC COMPOUNDS

In general, organic compounds can be classified as:

(a) Acidic: Carboxylic acid, phenol, acyl chloride, RNH_3^+, amino acids with acidic R groups
(b) Basic: Amines, carboxylates (RCO_2^-), amino acids with basic R groups
(c) Neutral: Hydrocarbon, alcohol, aldehyde, ketone, ester, halogenoalkane, amide or amino acids with neutral R groups

N.B: Pure acyl chlorides are neutral as no water is present for hydrolysis to take place.

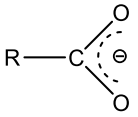
Acidity
Relative acidity is explained in terms of the relative **stability of the anions** formed after dissociation.

- ***Dissociation equations***:

Alcohol or phenol $ROH \rightleftharpoons RO^- + H^+$ where R = alkyl or phenyl group.

Carboxylic acid $RCO_2H \rightleftharpoons RCO_2^- + H^+$

(I) Comparing <u>different classes</u> of compounds,

Alcohols	Phenols	Carboxylic Acids
Neutral	Acidic	
⟶ Acid strength / K_a **increases** ⟶		
⟶ **pK_a decreases** ⟶		
• Alkyl group exerts ***electron-donating inductive*** effect. • Hence charge on alkoxide ion RO^- is ***intensified***. • Anion is ***destabilised***. • Low **extent of dissociation**.	• ***p orbital*** of O ***overlaps*** with ***π orbital*** in benzene ring. • Hence, ***lone pair*** of electrons on O is ***delocalised*** into benzene ring. • Charge on phenoxide ion $C_6H_5O^-$ is ***dispersed***. • Anion ***stabilised***. • **Extent of dissociation** is greater than aliphatic alcohols.	• ***p orbitals*** of the $–COO^-$ group ***overlap*** with one another, resulting in delocalisation of electrons and resonance stabilisation:  • Hence, charge on carboxylate ion is ***dispersed***. • Anion ***stabilised***. • Greatest **extent of dissociation** amongst the 3 substances.

- Dissociation equilibria for phenol and carboxylic acid lie more to the ***right*** compared to alcohol. This explains why phenol and carboxylic acid are ***stronger acids*** than alcohol.

(II) Comparing the <u>same class</u> of compounds (e.g. alcohols compared to other alcohols),

- Groups with **<u>electron-withdrawing</u>** inductive effect disperses the negative charge, stabilise anion and hence **<u>increase acidity.</u>**
- Strength of inductive effect **<u>increases</u>** with **<u>greater number</u>** of groups and **<u>shorter distance</u>** from the negative charge.

Basicity of nitrogen compounds

<u>Gaseous phase basicity</u>

Gaseous phase basicity can be explained in terms of the **<u>availability of the lone pair of electrons</u>** on the nitrogen atom **<u>for donation</u>** to an acid.

(I) Comparing different classes of nitrogen compounds

Amides	Phenylamine	NH_3	RNH_2
Neutral	Basic		
⟵ Basic strength / K_b **increases** ⟶			
⟵ **pK_b decreases** ⟶			
p orbital of N overlaps with those of the adjacent C=O group **Lone pair of electrons is delocalised onto the C=O group** Lone pair is thus ***<u>not</u> available*** for donation to an acid.	• ***p orbital*** of N ***overlaps*** with **π orbitals** of benzene ring. • ***Lone pair*** of electrons on N atom is ***delocalised*** into the benzene ring. • Lone pair is thus ***less available*** for donation to an acid.		• Alkyl group exerts ***electron-donating inductive effect***. • Lone pair of electrons on N atom is thus ***more available*** for donation to an acid.

(II) Comparing the same class of nitrogen compounds (e.g. amines with other amines)

- Any other group with **electron-donating** inductive effect increases availability of the lone pair and hence **increase basicity** e.g. 2-methylphenylamine is more basic than phenylamine due to the additional electron-donating inductive effect of the methyl group.

Aqueous phase basicity

$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$

With respect to the above equilibrium, the more stable the alkylammonium ion (RNH_3^+), the further the position of equilibrium lies to the ***right***, the greater the extent of dissociation, and the ***stronger*** the base is. The stability of the alkylammonium ion is affected by:

1. The electron-donating inductive effect of the alkyl groups

   The electron-donating inductive effect of alkyl groups will stabilise the alkylammonium ion as it will disperse the positive charge. More alkyl groups will lead to stronger electron-donating inductive effect and thus greater stabilisation.

2. Extent of solvation of the alkylammonium ion

   The alkylammonium ions are also stabilised by forming hydrogen bonds with water molecules. More N-H bonds will lead to more hydrogen bonds formed, and so greater stabilisation (solvation can also be explained in terms of ion-dipole interactions – the smaller the cationic size, the stronger the ion-dipole interactions formed with water.)

3. Steric hindrance of alkyl groups

   The alkyl groups cause steric hindrance by blocking the formation of H-bonds between N-H and water molecules. More alkyl groups will lead to greater steric hindrance, leading to lower stabilisation of the alkylammonium ions.

Examples

6 VJC 2004 Prelim (modified)

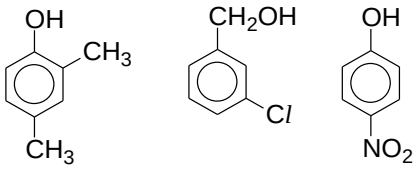
Ammonium, NH_4^+, and ammonia, NH_3, form a conjugate acid-base pair. The following are the conjugate acids of some common organic nitrogen compounds.
$C_2H_5NH_3^+$, $(CH_3)_2NH_2^+$, $C_6H_5NH_3^+$

By considering the gaseous phase basicity of the amines, which sequence shows the ions in increasing order of acid strength?

A $(CH_3)_2NH_2^+$, $C_2H_5NH_3^+$, $C_6H_5NH_3^+$
B $C_6H_5NH_3^+$, NH_4^+, $C_2H_5NH_3^+$
C $C_2H_5NH_3^+$, $(CH_3)_2NH_2^+$, NH_4^+
D $(CH_3)_2NH_2^+$, $C_6H_5NH_3^+$, NH_4^+

Solution

7 Arrange the following compounds, **A** to **C**, in order of increasing pK_a value. Explain your reasoning.



A **B** **C**

Solution

Recognise the general classes of compound

$ROH + H_2O \rightleftharpoons RO^- + H_3O^+$

A and **C** are _____ whereas B is an _____. The _____ of O in the phenoxide ion with the π orbitals of the benzene ring. _____ of electrons on O is thus _____ into the ring, resulting in the _____ of the negative charge on O. This increases the _____ of the phenoxide ion relative to the alkoxide ion. Hence, dissociation equilibrium lies more to the _____ for **A** and **C**, which are hence _____ acidic than **B**.

Decide within the same class of compound by looking at inductive effects of substituents.

C contains a _____ which exerts an _____ effect. This _____the negative charge on the phenoxide ion of **C**. Furthermore, **A** contains 2 $-CH_3$ groups, which exert _____effect. This will _____ the negative charge on the phenoxide ion of **A**, rendering it _____. Hence, dissociation equilibrium lies more to the _____ for **C** and **C** is _____.

Hence, the order of the compounds in increasing pK_a are

8 **VJC 2003 Prelim**

When organic compounds **P**, **Q**, **R** and **S** are added separately to water, solutions of increasing pH values are obtained. The possible identities of the compounds **P** to **S** (not necessarily in that order) are given.

$CH_3CH_2CO_2H$ CH_3CH_2COCl $(CH_3)_2CHNH_2$ $H_2NCH_2CH_2CO_2H$

Which is the correct set of identities of compounds **P** to **S**?

	P	**Q**	**R**	**S**
A	CH_3CH_2COCl	$CH_3CH_2CO_2H$	$H_2NCH_2CH_2CO_2H$	$(CH_3)_2CHNH_2$
B	CH_3CH_2COCl	$CH_3CH_2CO_2H$	$(CH_3)_2CHNH_2$	$H_2NCH_2CH_2CO_2H$
C	$CH_3CH_2CO_2H$	CH_3CH_2COCl	$H_2NCH_2CH_2CO_2H$	$(CH_3)_2CHNH_2$
D	$CH_3CH_2CO_2H$	CH_3CH_2COCl	$(CH_3)_2CHNH_2$	$H_2NCH_2CH_2CO_2H$

Solution

5. HYDROLYSIS REACTIONS

Relative rate of hydrolysis:

<table>
<tr><td>*C_6H_5X</td><td>CH_2= CHX</td><td>CH_3F</td><td colspan="3">CH_3Cl | CH_3Br | CH_3I</td><td>CH_3COCl</td></tr>
<tr><td>Halogenoarene</td><td>vinyl halide</td><td>fluoroalkane</td><td colspan="3">halogenoalkane</td><td>acyl chloride</td></tr>
<tr><td colspan="3">Unreactive towards nucleophiles under normal laboratory conditions</td><td colspan="4">——— Reacts with <u>increasing ease</u> ⟶</td></tr>
<tr><td colspan="2">p-orbital of X overlaps with π orbitals of benzene ring or C=C group (for vinyl halide). This enables the lone pair of electrons on X to be delocalised.

C-X bond hence acquires partial double bond character.

C-X bond is stronger and requires more energy to break.

*Benzene ring also poses steric hindrance to rear attack of nucleophile.</td><td colspan="3">Atomic radius increases from F to I.

Extent of orbital overlap decreases from F to I.

Bond strength decreases from C–F to C–I and requires less energy to break.</td><td>C atom is attached to an additional electronegative atom, O.

C atom is more electron-deficient and hence more susceptible to nucleophilic attack.

sp^2 hybridised C atom (trigonal planar) also experiences less steric hindrance than the sp^3 hybridised α-carbon of CH_3X (tetrahedral).</td></tr>
</table>

6. ENVIRONMENTAL CONCERNS OF ORGANIC COMPOUNDS

(a) Pollutants from car exhausts emissions

Car exhausts emissions contain the following pollutants.

(i) **<u>Unburnt hydrocarbons</u>** due to **<u>incomplete combustion of fuel</u>**. In strong sunlight it becomes **<u>smog</u>** and can cause **<u>lung damage</u>**.

(ii) **<u>Carbon monoxide, CO</u>** due to **<u>incomplete combustion of fuel</u>**. CO **<u>combines with haemoglobin in blood</u>** and reduces the oxygen–carrying ability of the haemoglobin. This can lead to **<u>oxygen starvation</u>** and eventual death.

(iii) **<u>Nitrogen oxides, NO and NO_2</u>**, formed from the **<u>reaction of nitrogen and oxygen</u>** in the car's engine. These oxides cause '**<u>acid rain'</u>**.

To remove the above pollutants, a **<u>platinum catalytic converter</u>** is fitted onto the motor car exhausts. It catalyses a redox reaction where CO and unburnt hydrocarbons are **<u>oxidised</u>** to CO_2 and H_2O, and oxides of nitrogen, NO and NO_2 are **<u>reduced</u>** to N_2.

E.g. hydrocarbons + oxides of nitrogen → carbon dioxide + water + nitrogen
$2CO + 2NO \rightarrow 2CO_2 + N_2$

(b) Enhanced greenhouse effect

"Enhanced" greenhouse effect is the **<u>result of human activities</u>**.
Processes such as the **<u>burning of fossil fuels</u>** release greenhouse gases like **carbon dioxide, methane and oxides of nitrogen** into the atmosphere.

<u>Chlorofluorocarbons</u>, or CFCs, are also potent greenhouse gases [as an added danger, they also destroy the ozone layer – see **(c)** below].

More **infrared radiation is trapped** and held, which gradually **increases the temperature** of the Earth's surface and the air in the lower atmosphere.

(c) Effect of CFCs on ozone layer

Uses of CFCs
RFX and RF are useful due to their **inertness** arising from **strong C–F bond**. They are used as aerosols, refrigerants and fire extinguishers (for those without H atoms).

Effect on ozone layer
In the atmosphere, the **C–C*l* bond is broken** in the presence of **uv light**, forming highly reactive ***Cl* radicals**, which **catalyse** the destruction of O_3 and are **regenerated** in the process.

Note that C–F bond, a stronger bond, is **not** broken by uv light.

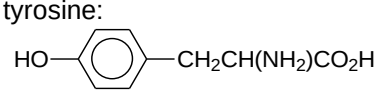
7. AMINO ACIDS

Physical properties of amino acids
(1) High m.p. due to strong ionic bonding between the zwitterions
(2) High solubility in water due to strong ion-dipole interactions between zwitterions and water molecules

Examples

9 VJC 2003 Prelim
Isoelectric point is the pH at which amino acid exist as zwitterions. Which of the following amino acids have a lower isoelectric point than glycine (2-aminoethanoic acid)?

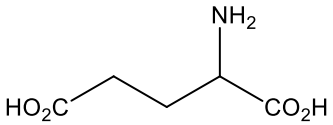
1 lysine: $H_2NCH_2CH_2CH_2CH_2CH(NH_2)CO_2H$
2 glutamic acid: $HO_2CCH_2CH_2CH(NH_2)CO_2H$
3 tyrosine:



Solution:

10 N2010/III/2(a)

Soy sauce is produced by the fermentation of soybeans by the mould *Aspergillus oryzae*. The distinctive salty taste of the sauce is due to salts of glutamic acid formed during fermentation.



glutamic acid

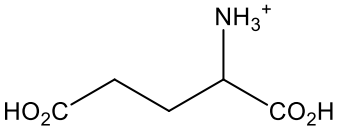
There are three pK_a values associated with glutamic acid: 2.1, 4.1 and 9.5.

Make use of these pK_a values to suggest the major species present in solutions of glutamic acid with the following pH values:

- pH 1
- pH 3
- pH 7
- pH 11

Solution

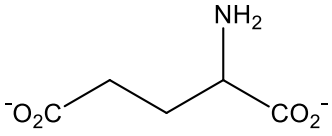
pH 1 (all three acidic groups are protonated)



pH 3

pH 7

pH 11 (all three acidic groups deprotonated)

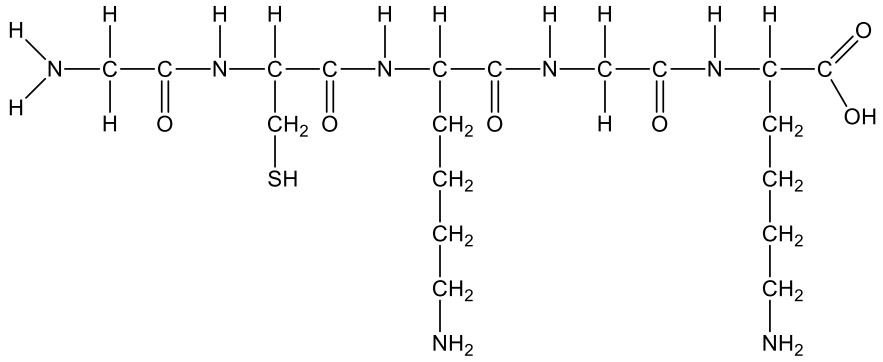


11 N2016/I/40

The enzyme trypsin will only hydrolyse a polypeptide chain at a peptide bond where the carboxyl group has been donated by either lysine or arginine.

The polypeptide shown is made from the following amino acids.

glycine $H_2NCH_2CO_2H$
cysteine $H_2NCH(CH_2SH)CO_2H$
lysine $H_2NCH((CH_2)_4NH_2)CO_2H$



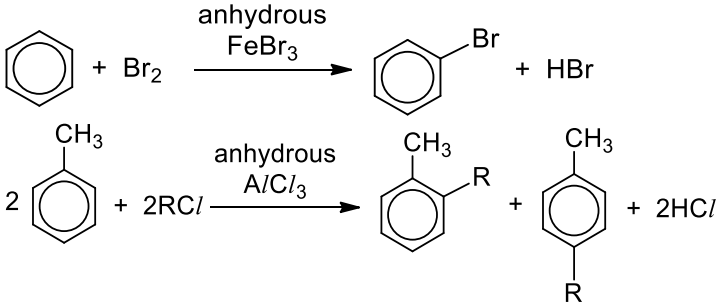
Which fragments could be made when trypsin acts on this polypeptide chain?

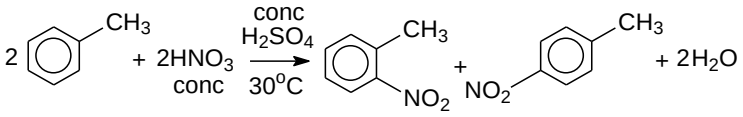
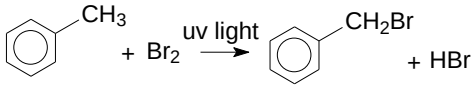
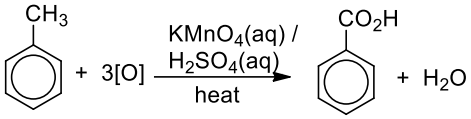
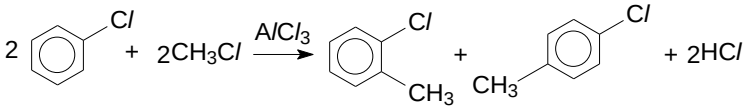
1 glycine **–** cysteine
2 glycine – lysine
3 glycine – cysteine – lysine

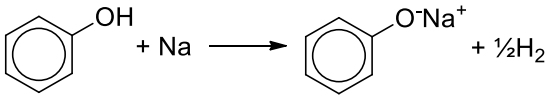
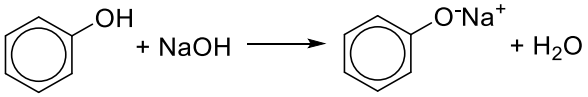
A **1**, **2** and **3**
B **1** and **2** only
C **2** and **3** only
D **1** only

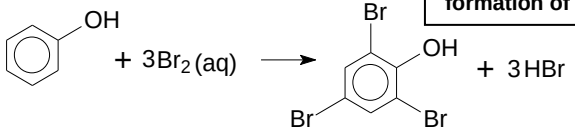
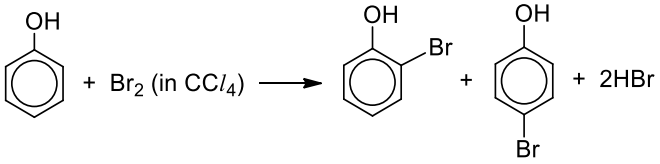
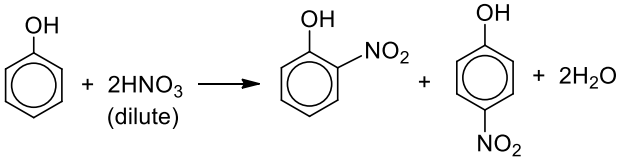
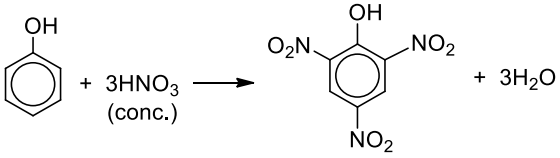
Solution

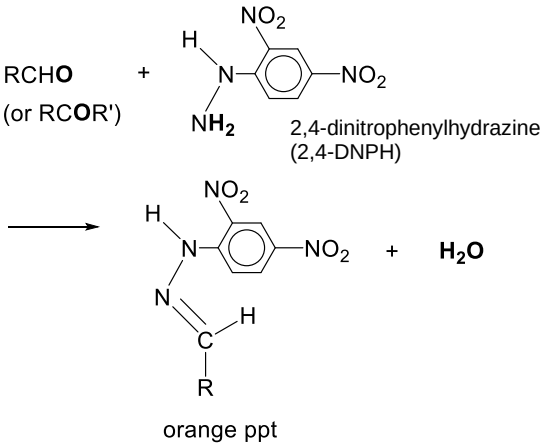
8. REACTIONS OF ORGANIC COMPOUNDS BY HOMOLOGOUS SERIES

Class of Compound	Chemical nature	Reaction type and example
Alkane (C_nH_{2n+2}) and cycloalkane (C_nH_{2n})	Non-polar saturated compound, i.e. lack of electron–poor and electron–rich regions $\Rightarrow$ no reaction with polar reagents.	**Free radical substitution** *excess* uv $RH + Br_2 \rightarrow RBr + HBr$ Combustion, e.g. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
Alkene (C_nH_{2n})	Pi bond in the C=C group is weaker than the sigma bond. Hence, pi electrons are more readily used for reactions, making the electron rich C=C readily attacked by electrophiles $\Rightarrow$ **<u>not</u>** attacked by nucleophilic reagents like HCN, $LiAlH_4$ or $NaBH_4$.	**Electrophilic addition**, e.g. $CH_3CH=CH_2 + Br_2(l) \rightarrow CH_3CHBrCH_2Br$ $CH_3CH=CH_2 + Br_2 + H_2O \rightarrow CH_3CH(OH)CH_2Br^* + HBr$ $CH_3CH=CH_2 + HBr \rightarrow CH_3CHBrCH_3^*$ *cold conc. H_2SO_4 then heat with H_2O* $CH_3CH=CH_2 + H_2O \rightarrow CH_3CH(OH)CH_3^*$ Other reagent: steam, H_3PO_4 catalyst *: Apply Markovnikov's rule for unsymmetrical alkenes.
	---	**Reduction** Pt or Pd catalyst (or Ni catalyst, heat) $CH_3CH=CH_2 + H_2 \rightarrow CH_3CH_2CH_3$
	---	**Oxidative cleavage** $KMnO_4(aq)$, $H_2SO_4(aq)$, heat $CH_3CH=CH_2 + 5[O] \rightarrow CH_3CO_2H + CO_2 + H_2O$ $C(CH_3)_2=CH_2 + 4[O] \rightarrow CH_3COCH_3 + CO_2 + H_2O$ *Note*: If **hot alkaline** MnO_4^- is used, RCO_2^- and CO_3^{2-} are formed instead of RCO_2H and CO_2. **Mild oxidation** $KMnO_4(aq)$, $NaOH(aq)$, cold $CH_3CH=CH_2 + [O] + H_2O \rightarrow CH_3CH(OH)CH_2OH$
Benzene (C_6H_6) and methylbenzene	Electron rich but resonance-stabilised ring with delocalised pi electrons. Hence ring is ***less nucleophilic***, compared to alkenes. $\Rightarrow$ benzene can only be attacked by	**Electrophilic substitution** e.g.  Excess benzene / methylbenzene for monosubstitution.

Benzene (C_6H_6) and methylbenzene	**strong** electrophiles. $\Rightarrow$ undergoes ***substitution*** instead of addition to ***preserve its resonance structure***	 *Note:* (1) 55 ^oC for nitration of benzene. (2) The methyl group on methylbenzene is activating and 2, 4–directing.
Methylbenzene/ Alkylbenzene	Presence of an alkyl side-chain	**Free radical substitution**  *Excess*
	Presence of benzylic H	**Oxidation**  *Note***:** All alkylbenzenes are oxidised to the <u>same</u> product, <u>benzoic acid</u>. Any additional carbon atoms on the side chain are oxidised to carbon dioxide and water.
Halogenoalkane, RX ($C_nH_{2n+1}X$)	Saturated, polar $C^{\delta+}–X^{\delta-}$ bond	**Nucleophilic substitution**, e.g. heat (i) RC*l* + KCN(alc) $\rightarrow$ RCN + KC*l* *Note***:** This is a step-up reaction. heat in a sealed tube (ii) RC*l* + NH_3(alc) $\rightarrow$ RNH_2 + HC*l* excess If RC*l* is in excess, other amines / ammonium salts are also formed: R_2NH, R_3N and $R_4N^+Cl^-$ heat (iii) RC*l* + NaOH***(aq)*** $\rightarrow$ ROH + NaC*l*
	X atoms and H atoms bonded to adjacent C atoms	**Elimination** heat major product $CH_3CHClCH_2CH_3$ + NaOH***(alc)*** $\rightarrow$ $CH_3CH=CHCH_3$ + NaC*l* + H_2O *Note:* $CH_2=CHCH_2CH_3$ is also formed as a minor product (less substituted alkene).
Halogenoarene / chlorobenzene	(i) Presence of benzene ring	**Electrophilic substitution**  **Note:** The chloro group on chlorobenzene is deactivating and 2,4–directing.

	(ii) Polar $C^{\delta+}–X^{\delta–}$ with partial double bond character	Does not undergo nucleophilic substitution under ordinary laboratory conditions.
Alcohol ($C_nH_{2n+2}O$) and Phenol	Phenol is a stronger acid than alcohol.	**Redox** $ROH + Na \rightarrow RO^-Na^+ + ½H_2$ 
		Neutralisation  **Note:** Alcohols do **not** react with NaOH(aq).
	To form esters with phenol, an **acyl chloride** must be used.	**Condensation**, e.g. $CH_3CH_2OH + CH_3CO_2H \overset{\text{conc. } H_2SO_4 \text{ catalyst, heat}}{\rightleftharpoons} CH_3CO_2CH_2CH_3 + H_2O$ $CH_3CH_2OH + CH_3COCl \rightarrow CH_3CO_2CH_2CH_3 + HCl$  **Note:** • NaOH can be added to form phenoxide, which is a better nucleophile. • Phenol does **not** react with RCO_2H to form esters.
	Phenol is less reactive towards nucleophiles due to partial double bond character of C–O.	**Nucleophilic substitution** $ROH \rightarrow RX$ Reagents and conditions: (i) PX_3 (X = C*l*, Br), heat (ii) PCl_5, (iii) $SOCl_2$, heat (iv) HX (X = C*l*, Br, I) (conditions vary with identity of X) Observation for PCl_5 and $SOCl_2$: White fumes of HC*l*(g). **Note:** Phenol does **not** react with above reagents.
Alcohols only	–H and –OH bonded to adjacent C atoms	**Elimination** $CH_3CH(OH)CH_2CH_3 \overset{\text{excess conc. } H_2SO_4, \text{ heat}}{\rightarrow} CH_3CH{=}CHCH_3 + H_2O$ major product *Note:* $CH_2{=}CHCH_2CH_3$ is also formed as a minor product (less substituted alkene).
	primary and secondary alcohols with H atom(s) bonded to C with -OH group	**Oxidation** With $K_2Cr_2O_7$ (aq), H_2SO_4(aq), heat with immediate distillation primary alcohol $CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$ *aldehyde* With $KMnO_4$(aq) or $K_2Cr_2O_7$(aq), H_2SO_4(aq), heat under reflux

Alcohols only		<u>primary alcohol</u> $CH_3CH_2OH + 2[O] \rightarrow CH_3CO_2H + H_2O$ *carboxylic acid* With $KMnO_4(aq)$ or $K_2Cr_2O_7(aq)$, $H_2SO_4(aq)$, heat <u>secondary alcohol</u> $CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$ **Note:** tertiary alcohols **<u>cannot</u>** be oxidised due to absence of H atom at α-carbon (carbon with the OH group).
Alcohols only	–$CH(CH_3)OH$ group present	**Oxidative cleavage** (iodoform test) warm **$RCH(OH)CH_3$** + 6NaOH + $4I_2$ → CHI_3 + **$RCO_2^-Na^+$** + 5NaI + $5H_2O$ **Note:** CHI_3 is a yellow ppt.
Phenol only	Lone pair on O is delocalised into the ring, making the ring more electron–rich and hence more readily attacked by electrophiles.	**Electrophilic substitution** observation: **$Br_2(aq)$ decolourised with formation of white ppt.** (i) With Br_2  *White ppt*  (ii) With HNO_3   **Note:** –OH is **strongly** activating and 2, 4–directing.
	---	Test for phenol with neutral $FeCl_3$ solution. Observation: Violet colouration seen.
Carbonyl ($C_nH_{2n}O$): Ketone RCOR' and Aldehyde RCHO	Unsaturated, presence of polar $C^{\delta+}=O^{\delta-}$ bond	**Nucleophilic addition** $CH_3CHO + HCN \xrightarrow{CN^- \text{ catalyst}} CH_3CH(OH)CN$ **N.B:** This is a step-up reaction.
		Reduction $LiAlH_4$ in dry ether $RCHO + 2[H] \rightarrow RCH_2OH$ (primary alc) aldehyde

		RCOR' + 2[H] → RCH(OH)R' (secondary alc) ketone Other possible reducing agents: (1) H_2 with Pt or Pd catalyst [or Ni catalyst, heat] (2) $NaBH_4$ in ethanol or methanol
Carbonyl ($C_nH_{2n}O$): Ketone RCOR' and Aldehyde RCHO	Unsaturated, presence of polar $C^{\delta+}=O^{\delta-}$ bond	**Condensation** (test for carbonyl compounds)  orange ppt
	-$COCH_3$ group present, i.e. ethanal and methyl ketones	**Oxidative cleavage** (iodoform test), e.g. warm $RCOCH_3 + 4NaOH + 3I_2 \rightarrow CHI_3 + RCO_2^-Na^+ + 3NaI + 3H_2O$
For aldehydes only	Easily oxidised	**Oxidation**, e.g. (i) $K_2Cr_2O_7$(aq) or $KMnO_4$(aq), H_2SO_4(aq), heat $RCHO + [O] \rightarrow RCO_2H$ (ii) Tollens' reagent $[Ag(NH_3)_2^+]$, warm (test for **<u>all</u>** aldehydes) Observation: Ag mirror $2Ag(NH_3)_2^+ + RCHO + 3OH^- \longrightarrow 2Ag + RCOO^- + 4NH_3 + 2H_2O$ (iii) Fehling's reagent [alkaline Cu^{2+}], warm (test for **<u>aliphatic</u>** aldehydes only) Observation: Brick–red ppt. (Cu_2O) $2Cu^{2+} + RCHO + 5OH^- \rightarrow RCOO^- + Cu_2O + 3H_2O$ **N.B.** Ketones cannot be oxidised.
Carboxylic acid, RCO_2H	Proton donor	**Neutralisation**, e.g. $RCO_2H + NaOH \rightarrow RCO_2^-Na^+ + H_2O$ $2RCO_2H + Na_2CO_3 \rightarrow 2RCO_2^-Na^+ + H_2O + CO_2$ $RCO_2H + NaHCO_3 \rightarrow RCO_2^-Na^+ + H_2O + CO_2$ $RCO_2H + R'NH_2 \rightarrow (RCO_2^-)(R'NH_3^+)$ **N.B.** A salt, not amide, is formed from reaction between carboxylic acid and amine.
	---	**Redox** $RCO_2H + Na \rightarrow RCO_2^-Na^+ + ½H_2$

<table>
<tr><td>Carboxylic acid, RCO_2H</td><td>Polar molecule, with electron-deficient C</td><td>Condensation
conc. H_2SO_4 catalyst, heat
$CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$</td></tr>
<tr><td></td><td></td><td>Nucleophilic substitution
$RCO_2H \rightarrow RCOCl$

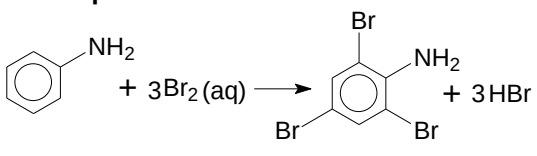
Reagents / conditions:
(i) PCl_3, heat
(ii) PCl_5
(iii) $SOCl_2$, heat

Observation for PCl_5 and $SOCl_2$: White fumes of HCl(g).</td></tr>
<tr><td></td><td>---</td><td>Reduction
$LiAlH_4$ in dry ether
$RCO_2H + 4[H] \rightarrow RCH_2OH$ (primary alc) $+ H_2O$</td></tr>
<tr><td>Acid derivatives:
(1) Acid chloride, RCOCl</td><td>$R–C^{\delta+}(=O^{\delta-})–Cl^{\delta-}$</td><td>Hydrolysis
$RCOCl + H_2O \rightarrow RCO_2H + HCl$
$RCOCl + 2NaOH(aq) \rightarrow RCO_2^-Na^+ + NaCl + H_2O$</td></tr>
<tr><td></td><td></td><td>Condensation
(1) With R’OH to form ester e.g.
$CH_3COCl + CH_3CH_2OH \rightarrow CH_3CO_2CH_2CH_3 + HCl$

(2) With NH_3 / NH_2R / NHRR’ to form amide e.g.
$CH_3COCl + CH_3CH_2NH_2 \rightarrow CH_3CONHCH_2CH_3 + HCl$</td></tr>
<tr><td>(2) Esters $RCO_2R’$</td><td>---</td><td>Hydrolysis with acid or base as catalysts, e.g.

<u>Acid hydrolysis</u>
$CH_3CO_2CH_3 + H_2O \overset{H_2SO_4(aq),\ heat}{\rightleftharpoons} CH_3CO_2H + CH_3OH$

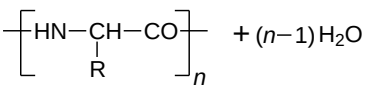
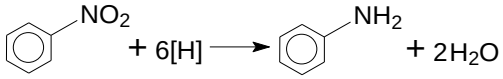
<u>Base hydrolysis</u>
$CH_3CO_2CH_3 + NaOH(aq) \overset{heat}{\rightarrow} CH_3CO_2^-Na^+ + CH_3OH$</td></tr>
<tr><td>Organic nitrogen compounds
(1) Amines (RNH_2, RR’NH, RR’R”N) and phenylamine</td><td>Lone pair donor (Lewis base)</td><td>Neutralisation, e.g.

$CH_3CH_2NH_2 + HCl \rightarrow CH_3CH_2NH_3^+Cl^-$
$(CH_3CH_2)_2NH + HCl \rightarrow (CH_3CH_2)_2NH_2^+Cl^-$</td></tr>
<tr><td>Phenylamine only</td><td>Lone pair on N is delocalized into the ring, making the ring more electron–rich and hence more readily attacked by electrophiles.</td><td>Electrophilic substitution
 

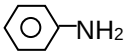
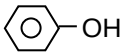
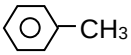
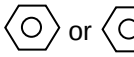
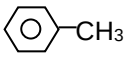
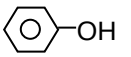
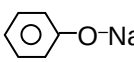
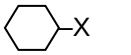
White solid

N.B.: –NH_2 is strongly activating and 2, 4–directing.

observation: Br_2(aq) decolourised with formation of white ppt.</td></tr>
</table>

(2) Amides *-RCONH$_2$,* *-RCONHR',* *-RCONR'R''*	---	**Hydrolysis** with acid or base as catalysts, e.g. <u>Acid hydrolysis</u> heat $CH_3CONH_2 + H_2O + H^+ \rightarrow CH_3CO_2H + NH_4^+$ heat $CH_3CONHR + H_2O + H^+ \rightarrow CH_3CO_2H + NH_3R^+$ <u>Base hydrolysis</u> heat $CH_3CONH_2 + NaOH(aq) \rightarrow CH_3CO_2^-Na^+ + NH_3$ *(able to test for primary amides due to NH_3 formed)* heat $CH_3CONHR + NaOH(aq) \rightarrow CH_3CO_2^-Na^+ + NH_2R$ **Reduction** $LiAlH_4$ in dry ether $RCONH_2 + 4[H] \rightarrow RCH_2NH_2 + H_2O$
(3) Amino acid, $H_2NCHRCO_2H$	(i) Exists as zwitterion / dipolar ion, $^+H_3NCHRCO_2^-$	**Neutralisation**, e.g. $^+H_3NCHRCO_2^- + H^+ \rightarrow {}^+H_3NCHRCO_2H$ $^+H_3NCHRCO_2^- + OH^- \rightarrow H_2NCHRCO_2^- + H_2O$
	(ii) Amphoteric	
	(iii) Protein formation	*α-amino acids* condense to form polypeptides or proteins. 
Proteins	Contains peptide linkage	**Hydrolysis** Proteins $\rightarrow$ shorter polypeptide chains or amino acids Reagents: $H^+(aq)$ or $OH^-(aq)$, heat or enzymes
(4) Nitrile, RCN	---	**Reduction** $LiAlH_4$ in dry ether $RCN + 4[H] \rightarrow RCH_2NH_2$ (primary amine) Other reagents: 1. H_2 with Ni catalyst, heat 2. H_2 with Pt or Pd catalyst **Hydrolysis** with acid or base as catalysts heat $RCN + H^+ + 2H_2O \rightarrow RCO_2H + NH_4^+$ heat $RCN + OH^- + H_2O \rightarrow RCO_2^- + NH_3$
(5) Nitrobenzene	---	**Reduction** Sn, conc. HC*l*, heat followed by NaOH(aq) 

9. REACTIONS OF ORGANIC COMPOUNDS BY REAGENTS AND CONDITIONS

Reagents and Conditions	*Homologous series*	*Compound(s) formed and Observation(s) (if any)*
(I) HALOGENS		
(a) Br_2 in CCl_4 (inert solvent)	$RCH{=}CH_2$	Rapid decolourisation of orange-red bromine. $RCHBrCH_2Br$ formed.
(b) Br_2(aq)	$RCH{=}CH_2$	Rapid decolourisation of orange bromine. $RCH(OH)CH_2Br$ formed.
	 or 	Rapid decolourisation of orange bromine and formation of white precipitate which is 2,4,6-tribromophenylamine or 2,4,6-tribromophenol.
(c) Br_2 with uv or heat	CH_4 or 	Rapid decolourisation of reddish-brown bromine. CH_3Br or (bromomethyl)benzene formed. (more substituted products are possible).
(d) Br_2, Fe or Br_2, anhydrous $FeBr_3$	 or 	Rapid decolourisation of reddish-brown bromine. Formation of bromobenzene or 2-bromomethylbenzene and 4-bromomethylbezene.
(II) BASES		
(a)(i) NaOH(aq)	(1) 	 formed.
	(2) RCO_2H	$RCO_2^-Na^+$ formed.
	(3) $RCOCl$	$RCO_2^-Na^+$ formed.
	(4) $RCH(NH_3^+)CO_2^-$	$RCH(NH_2)CO_2^-$ formed.
(a)(ii) NaOH(aq), heat	(1) RX	ROH formed.
	(2) RCO_2R'	$RCO_2^-Na^+$ and R'OH formed.
	(3) $RCO_2C_6H_5$	$RCO_2^-Na^+$ and $C_6H_5O^-Na^+$ formed.
	(4) $RCONH_2$; RCONHR; RCONRR'	$RCO_2^-Na^+$ and NH_3(g)/ NH_2R / NHRR' formed.
	(5) RCN	$RCO_2^-Na^+$ and alkaline NH_3(g) evolved.
(b) NaOH(alc), heat	C_2H_5X or 	C_2H_4 or  formed.
(c) NaOH(aq), I_2, warm	CH_3COR or $CH_3CH(OH)R$ (R = H or alkyl group)	$RCO_2^-Na^+$ and yellow precipitate of CHI_3 formed.
(d) NH_3(alc), heat in a sealed tube	(1) RCl (excess)	R_2NH, R_3N, $R_4N^+Cl^-$ formed.
	(2) RCl (NH_3 in excess)	RNH_2 preferentially formed (since NH_3 in excess).
(e) Na_2CO_3(aq) or $NaHCO_3$(aq)	(1) RCO_2H	$RCO_2^-Na^+$ and CO_2(g) formed.
	(2) Amino acids with acidic R groups (side chain)	
(III) STRONG ACIDS		
(a)(i) Aqueous acids, e.g. HCl(aq) or H_2SO_4(aq)	(1) RNH_2	RNH_3^+ formed.
	(2) $RCH(NH_3^+)CO_2^-$	$RCH(NH_3^+)CO_2H$ formed.
	(1) RCO_2R'	RCO_2H and R'OH formed.

(a)(ii) Aqueous acids, heat	(2) $RCONH_2$; RCONHR; RCONRR'	RCO_2H and NH_4^+; NH_3R^+; $NH_2RR'^+$ formed.
	(3) RCN	RCO_2H and NH_4^+ formed.
(b) conc. H_2SO_4 functioning as a catalyst, regenerated in the reaction	(1)  , conc. H_2SO_4, conc. HNO_3 at 55 °C	Nitrobenzene formed.
	(2)  , conc. H_2SO_4, conc. HNO_3 at 30 °C	2-nitromethylbenzene and 4-nitromethylbenzene formed.
	(3) ROH + $R'CO_2H$, conc. H_2SO_4, heat	$R'CO_2R$ formed.
(IV) OXIDISING AGENTS		
(a) $KMnO_4$(aq), H_2SO_4(aq), heat	(1) $RCH=CH_2$	Decolourisation of purple $KMnO_4$, RCO_2H and CO_2(g) formed.
	(2) RCH_2OH, RCHO	Decolourisation of purple $KMnO_4$, RCO_2H formed.
	(3) RCH(OH)R'	Decolourisation of purple $KMnO_4$, RCOR' formed.
	(4) 	Decolourisation of purple $KMnO_4$, white precipitate of benzoic acid, $C_6H_5CO_2H$ formed.
(b) $KMnO_4$(aq), NaOH(aq)		
(i) heat	(1) $RCH=CH_2$	Decolourisation of purple $KMnO_4$ with brown MnO_2 ppt, RCO_2^- (and CO_3^{2-}) formed.
	(2) 	Decolourisation of purple $KMnO_4$ with brown MnO_2 ppt. $C_6H_5CO_2^-$ formed.
	(3) RCH_2OH, RCHO	Decolourisation of purple $KMnO_4$ with brown MnO_2 ppt, RCO_2^- formed.
	(4) RCH(OH)R'	Decolourisation of purple $KMnO_4$ with brown MnO_2 ppt, RCOR' formed.
(ii) cold	(1) $RCH=CH_2$	Decolourisation of purple $KMnO_4$ with brown MnO_2 ppt. $RCH(OH)CH_2OH$ (diol) formed.
(c) $K_2Cr_2O_7$(aq), H_2SO_4(aq)		
(i) heat (*heat under reflux for primary ROH*)	(1) RCH_2OH (1°) (2) RCH(OH)R' (2°) (3) RCHO	Colour change from orange to green, RCO_2H formed. Colour change from orange to green, RCOR' formed. Colour change from orange to green, RCO_2H formed.
(ii) heat with immediate distillation	RCH_2OH (1°)	Colour change from orange to green, RCHO formed.

(V) REDUCING AGENTS		
(a) Na(s)	(1) ROH	RO^-Na^+ and H_2(g) formed.
	(2) 	 and H_2(g) formed.
	(3) RCO_2H	$RCO_2^-Na^+$ and H_2(g) formed.
(b) $LiAlH_4$ in dry ether	(1) RCHO (2) RCOR' (3) RCO_2H (4) RCN (5) $RCONH_2$, RCONHR or $RCONR_2$	RCH_2OH (primary alc) formed. RCH(OH)R' (secondary alc) formed. RCH_2OH (primary alc) formed. RCH_2NH_2 (primary amine) formed. RCH_2NH_2 (primary amine), RCH_2NHR (secondary amine) or RCH_2NR_2 (tertiary amine) formed.
(c) $NaBH_4$ in ethanol or methanol	RCHO, RCOR'	RCH_2OH (primary alc) and RCH(OH)R' (secondary alc) formed respectively.
(d) H_2 with Ni catalyst, heat (or H_2, Pt catalyst)	(1) $RCH=CH_2$	RCH_2CH_3 formed.
	(2) aldehydes, ketones and nitriles	Reduced to primary alcohol, secondary alcohol and primary amine respectively.
(e) Sn in conc. HCl, heat, followed by NaOH(aq)		 formed as the intermediate.  liberated upon neutralisation with NaOH.
(VI) Cyanide (-CN) CONTAINING COMPOUNDS		
(a) KCN(alc), heat	RX	RCN formed (step-up reaction).
(b) HCN, NaCN		 (cyanohydrin) formed (step-up reaction).
(VII) CHLORINE CONTAINING COMPOUNDS		
(a) CH_3COCl	(1) ROH (2) RNH_2 (3) H_2O	CH_3CO_2R and HCl formed. CH_3CONHR and HCl formed. CH_3CO_2H and HCl formed.
(b) PCl_5 or PCl_3, heat or $SOCl_2$, heat	(1) ROH (2) RCO_2H	White HCl fumes. RCl formed. White HCl fumes. RCOCl formed.

Examples

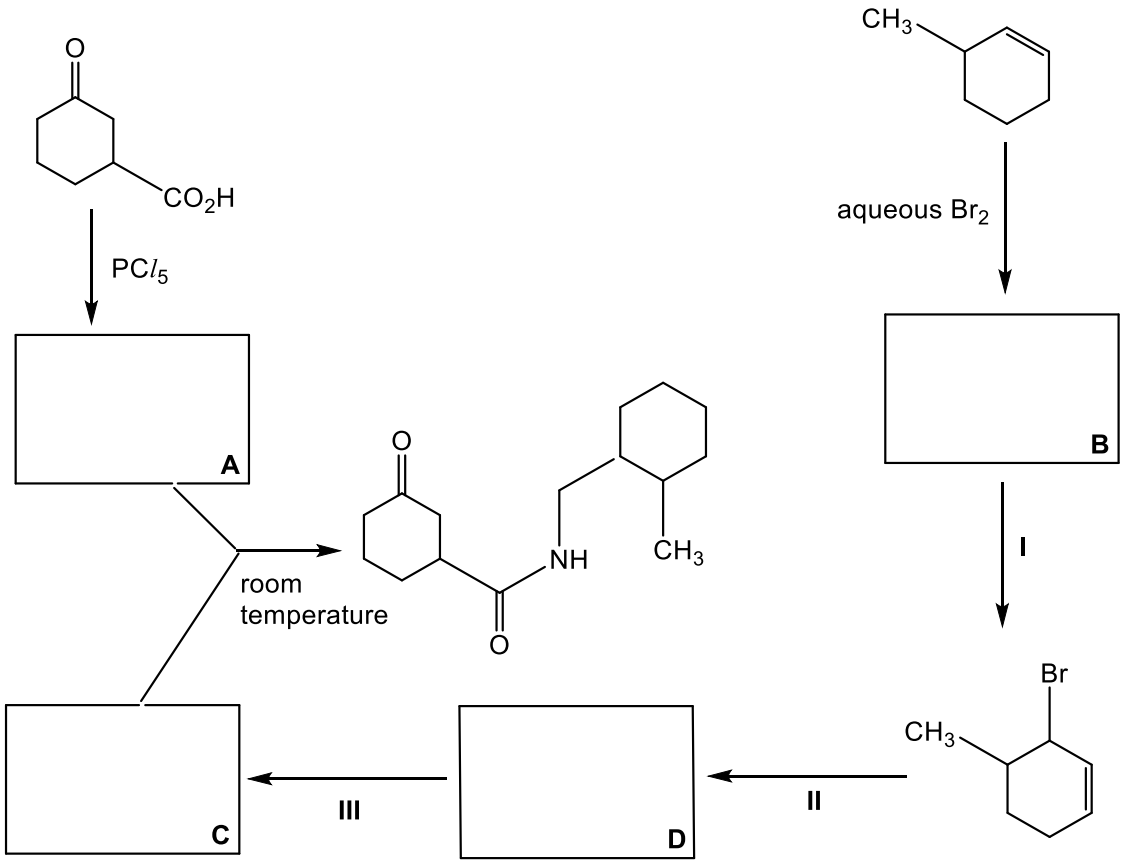
12 J89/I/6(a) (Distinguishing test)

Draw the structural formulae for **two** isomers of molecular formula C_7H_7Cl which can be distinguished by a simple chemical test. State clearly how **each** compound would behave in the test.

Solution

13 ACJC Prelim 11/II/2 (modified)

Complete the reaction scheme below by writing the structural formula of the organic products (**A** – **D**) and the reagents and conditions for steps **I** – **III** in the spaces below.

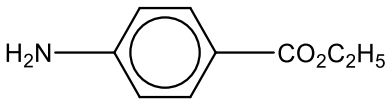


Solution

A	
B	
C	
D	

Step	Reagents and conditions
I	
II	
III	

14 The structure of *benzocaine*, an active ingredient found in sunburn ointments, is shown below:



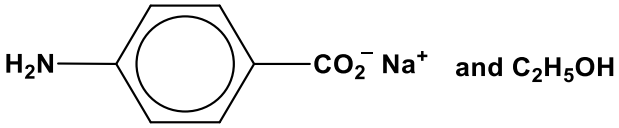
Give the structural formulae of the organic products of the reaction of *benzocaine* with the following reagents: [3]

a) aqueous hydrochloric acid
b) aqueous sodium hydroxide, heat
c) aqueous bromine.

Solution

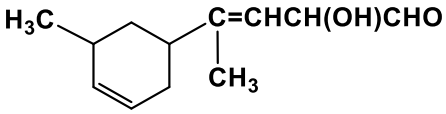
(a)

(b)



(c)

15 Compound **Y** has the following structural formula.



(a) Identify the functional groups present in **Y**. [2]

(b) How would you expect **Y** to react when it is

(i) shaken with aqueous bromine;

(ii) boiled under heat with acidified aqueous potassium dichromate(VI);

In each case, describe the type of reaction and draw structural formula of the organic products formed. [3+2]

Solution

(a)

(b)

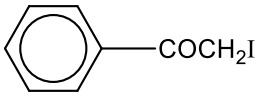
	Type of reaction	Structure of product
(i)		

(ii)		

16 **N10/I/25**

Which compound will **not** give tri-iodomethane on warming with alkaline aqueous iodine?

A $CH_3COCHClCOCH_3$

B 

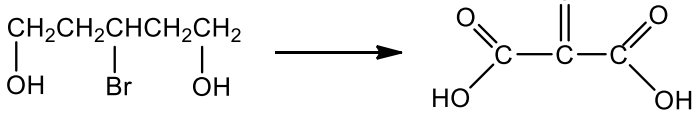
C $I_2CHCH(OH)CO_2H$

D $CI_3CO_2CH_3$

Solution

17 **HCl Prelim 09/II/4(b) (modified)** (Organic synthesis)

Suggest a three–step synthesis pathway for the following conversion of compound **P** into mesoxalic acid:

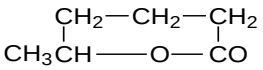


compound **P** mesoxalic acid

Solution - ***give reagents, conditions and intermediate***

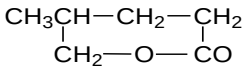
18 **N04/III/7** [Distinguishing test]

Suggest a method by which the following compounds could be distinguished from each other by chemical tests.



A

and



B

[3]

Solution

10. STRUCTURAL ELUCIDATION

1 Molecular formula

Some information on the structure and functional group of the compound can be obtained from the molecular formula.

Molecular formula	***Deduction***
6 carbon atoms or more, high C:H ratio (e.g. C_7H_8, C_8H_{10})	compound may contain a benzene ring
C_nH_{2n+2}	alkane present
C_nH_{2n}	alkene or cycloalkane present
(i) rapidly decolourises aqueous bromine (ii) does not decolourise aqueous bromine	alkene present cycloalkane present
$C_nH_{2n+2}O$	Alcohol present
$C_nH_{2n}O$	Aldehyde or ketone present
$C_nH_{2n}O_2$	carboxylic acid or ester present
(i) acidic (ii) neutral	carboxylic acid present ester present

2 Physical Data

(i) Exhibits cis-trans isomerism $\Rightarrow$ presence of C=C bond

(ii) Exhibits enantiomerism $\Rightarrow$ presence of chiral centre

(iii) Acidity or basicity of compound:

(a) Acidic: carboxylic acid, phenol, RNH_3^+

(b) Basic: amine, RCO_2^-, phenoxide, alkoxide

3 Chemical Data

Certain functional groups can be identified from the chemical tests shown in the table below.

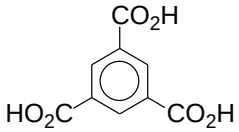
Test	*Observation*	*Deduction*
Shake compound with aqueous bromine.	(a) Rapid decolourisation of orange bromine. (b) Rapid decolourisation of orange bromine with **formation of white precipitate.**	C=C (alkene) present phenol or phenylamine present
Add solid phosphorus pentachloride to compound.	Fumes of HC*l* gas formed.	alcohol present if compound is neutral OR carboxylic acid present if compound is acidic.
Add sodium metal to compound.	Effervescence of hydrogen gas which pops a lighted splint.	alcohol, phenol or carboxylic acid present
Add aqueous sodium hydrogencarbonate or sodium carbonate to compound.	Effervescence of carbon dioxide gas which gave a white precipitate with limewater.	carboxylic acid present
Heat compound with acidified potassium dichromate(VI) solution.	Colour of solution changed from orange to green.	primary alcohol, secondary alcohol or aldehyde present
Add 2,4-dinitrophenylhydrazine (2,4-DNPH) to compound.	Orange precipitate formed.	aldehyde or ketone present
Warm compound with Tollen's reagent or $Ag(NH_3)_2^+(aq)$.	Silver mirror formed.	aldehyde present
Warm compound with Fehling's reagent or alkaline $Cu^{2+}(aq)$.	Brick-red precipitate formed.	aliphatic aldehyde present
Heat compound with I_2 and NaOH(aq).	Yellow precipitate, CHI_3, formed.	compound with $CH_3CH(OH)–$ or $CH_3CO–$ group present
Boil compound with aqueous sodium hydroxide.	Alkaline gas, NH_3, evolved which turned red litmus paper blue.	amide or –CN (nitrile) present
Heat compound with acidic $KMnO_4$ (or alkaline $KMnO_4$ and acidify products).	White precipitate formed.	benzene with side-chain containing benzylic H present
Add aqueous silver nitrate to compound.	White precipitate formed immediately in strongly acidic solution.	acyl chloride present
Heat compound with NaOH(aq); acidify products with HNO_3, then add aqueous $AgNO_3$.	(a) White precipitate formed. (b) Pale cream precipitate formed. (c) Yellow precipitate formed.	chloroalkane present bromoalkane present iodoalkane present

Example 19 N03/III/7 (modified) [Structural elucidation]

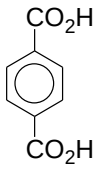
The aromatic compounds **H**, **J**, **K** and **L** are isomers with the molecular formula $C_9H_{12}O$ (M_r = 136.0). All four react with sodium metal but only compound **K** reacts with aqueous sodium hydroxide. **K** also reacts with aqueous bromine to form a white solid which has M_r = 214.9. On warming with acidified $K_2Cr_2O_7$, the reagent does not change colour with isomers **K** and **L**, but turns green with **H** and **J** producing compounds **M**($C_9H_{10}O_2$) and **N**($C_9H_{10}O$) respectively.

Only isomer **J** reacts with alkaline aqueous iodine.

When heated with acidic $KMnO_4$, isomers **H** and **J** give the acids **P** and **Q** respectively.



P



Q

Suggest a structure for each lettered compound, and explain the reactions involved.

***Solution** - give functional group and reaction type to explain*