PROSPERITY ACADEMY

A2 CHEMISTRY 9701

Crash Course

RUHAB IQBAL

ALLIPHATIC CHEMISTRY

COMPLETE NOTES

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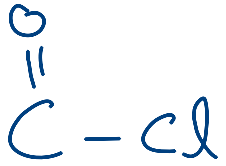
Alliphatic Chemistry:-

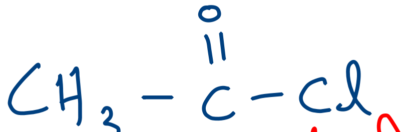
Acyl Chlorides:-

Contain

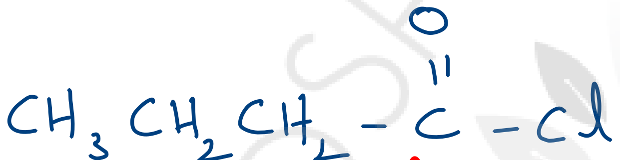

$\overset{O}{\overset{\|}{C}}-Cl$

functional group.

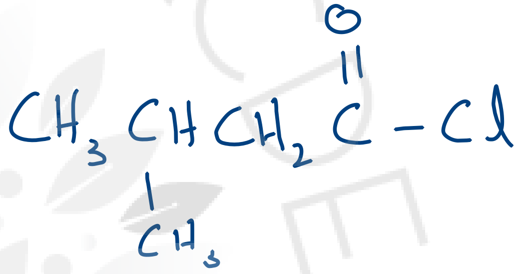
Name the following:-

1)

$CH_3-\overset{O}{\overset{\|}{C}}-Cl$

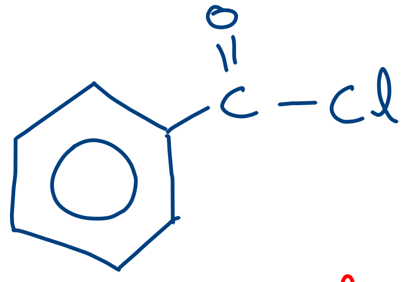
ethanoyl chloride

2)

$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-Cl$

butanyl chloride

3)

$CH_3\underset{CH_3}{\underset{|}{CH}}CH_2\overset{O}{\overset{\|}{C}}-Cl$

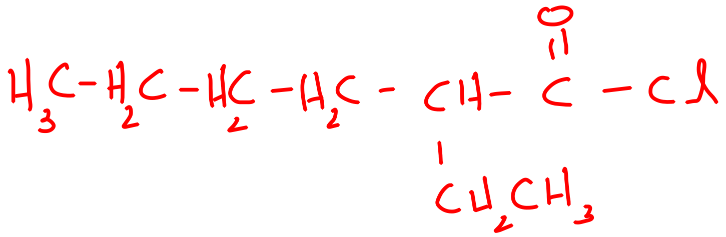
3-methylbutanoylchloride

4)


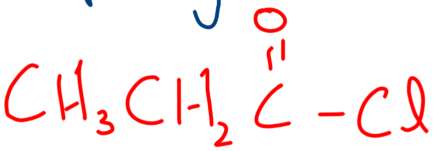
benzoyl chloride

Draw the following:-

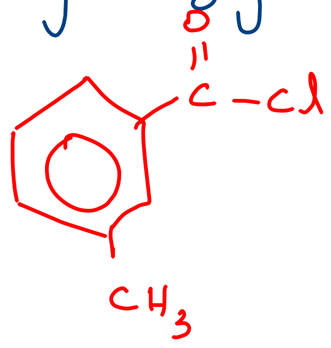
1) 2-ethyl hexanoyl chloride


$H_3C-H_2C-H_2C-H_2C-\underset{CH_2CH_3}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-Cl$

2) propanoyl chloride


$CH_3CH_2\overset{O}{\overset{\|}{C}}-Cl$

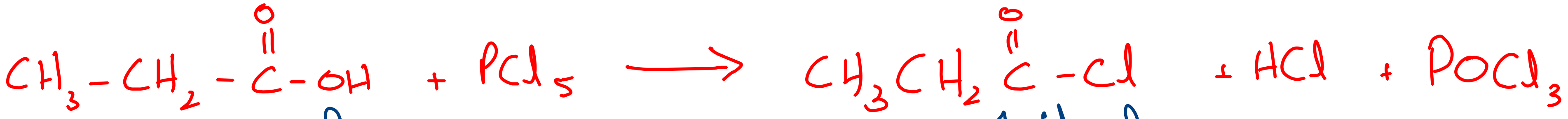
3) 3-methyl benzoyl chloride



Formation:- $SOCl_2/PCl_5$ (at room temp) or PCl_3 + heat with carboxylic acid.

$CH_3CH_2CO_2H + PCl_5 \longrightarrow CH_3CH_2COCl + HCl + POCl_3$

Observation:- Steamy fumes of HCl.

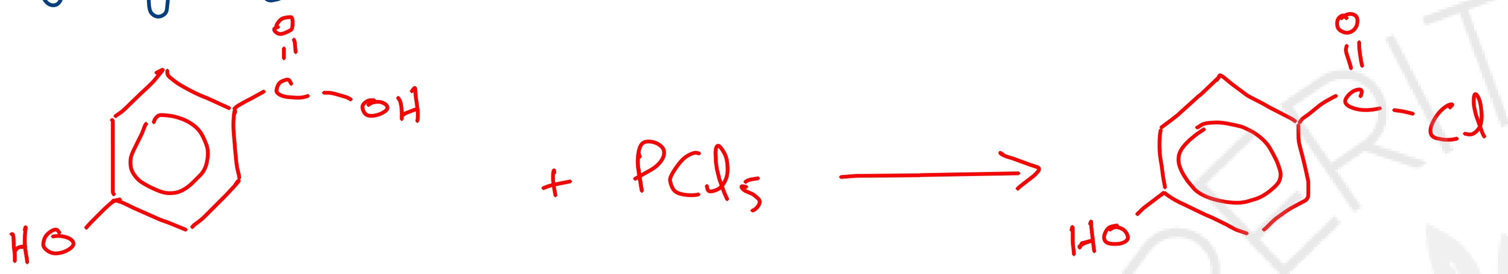

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH + PCl_5 \longrightarrow CH_3CH_2\overset{O}{\overset{\|}{C}}-Cl + HCl + POCl_3$

propanoic acid

propanoyl chloride

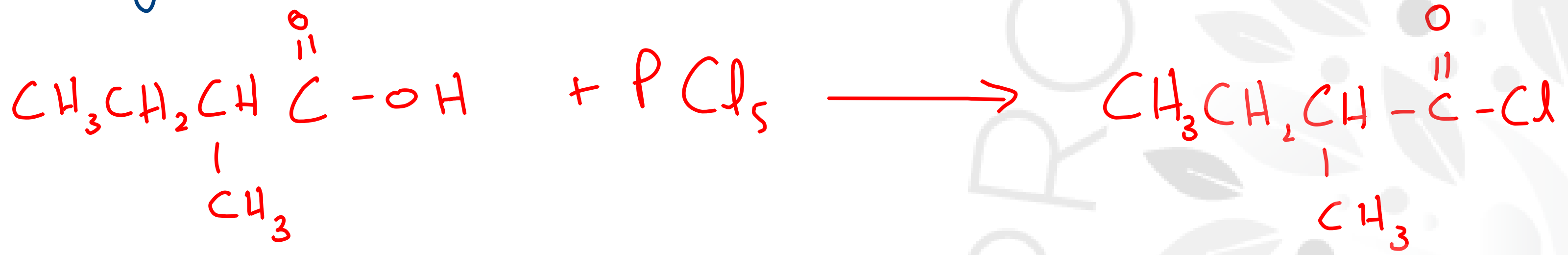
Q. Draw the structures of the carboxylic acids and the acyl chlorides formed upon reaction with PCl_5.

a) 4-hydroxy benzoic acid + PCl_5



4-hydroxy benzoyl chloride

b) 2-methyl butanoic acid + PCl_5

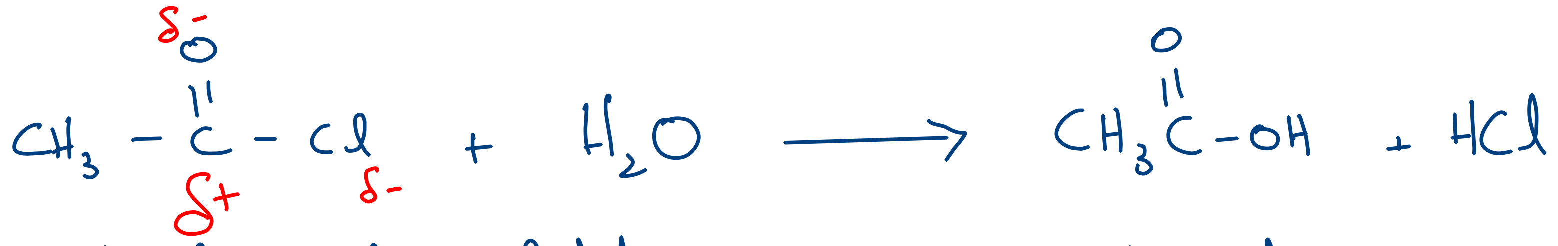


$$CH_3CH_2\underset{\substack{|\\ CH_3}}{CH}\overset{\substack{O\\ ||}}{C}-OH + PCl_5 \longrightarrow CH_3CH_2\underset{\substack{|\\ CH_3}}{CH}-\overset{\substack{O\\ ||}}{C}-Cl$$

2-methyl butanoyl chloride

Chemical Reactions of Acyl Chlorides:-

1) Hydrolysis:- Water (Carboxylic and HCl acid are formed pH: 1-2)



$$CH_3-\underset{\delta+}{\overset{\substack{\delta-\\ O\\ ||}}{C}}-\underset{\delta-}{Cl} + H_2O \longrightarrow CH_3\overset{\substack{O\\ ||}}{C}-OH + HCl$$

- Acyl chlorides react immediately and vigorously with water. No halogenoalkane shows this fast of a reaction with H_2O.
- If we add $AgNO_3(aq)$ to an acyl chloride we will get a white precipitate of AgCl immediately: test for Acyl chlorides
- Acyl chlorides are readily attacked by even weak nucleophiles as the Cl and O pull electron density from the C to a great extent leaving a significant ⊕ charge on it.

Relative order of ease of hydrolysis :- Acyl chloride > Tertiary halogenoalkane > Secondary halogenoalkane > Primary halogenoalkane > Chlorobenzene

Q. Why are tertiary halogenoalkanes easier to hydrolyse than primary halogenoalkanes?

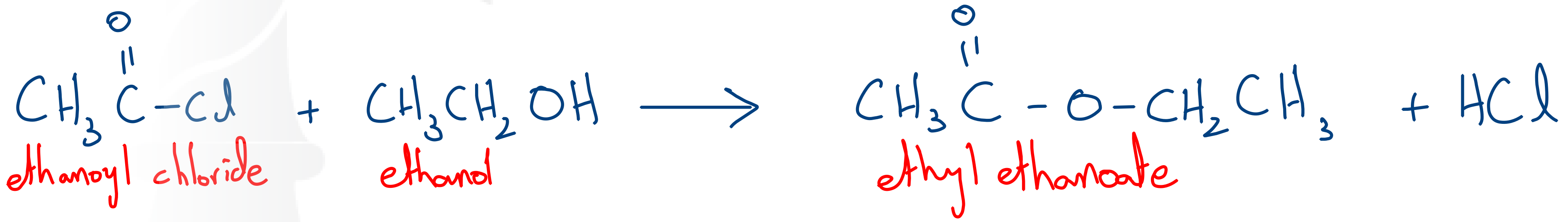
- Tertiary halogenoalkane does not need a nucleophile to attack it. Its C-Cl bond breaks spontaneously and the carbocation is stabilised by the positive inductive effect of the surrounding 3 alkyl groups.
- The C-Cl bond in a primary halogenoalkane cannot break itself due to only 1 alkyl group being present and not adequate positive inductive effect. It needs a nucleophile to attack it.

Q. Why is chlorobenzene very hard to hydrolyse?

- The lone pairs on the Cl can delocalise with the π ring resulting in more e^- density in C-Cl bond making it very hard to break.

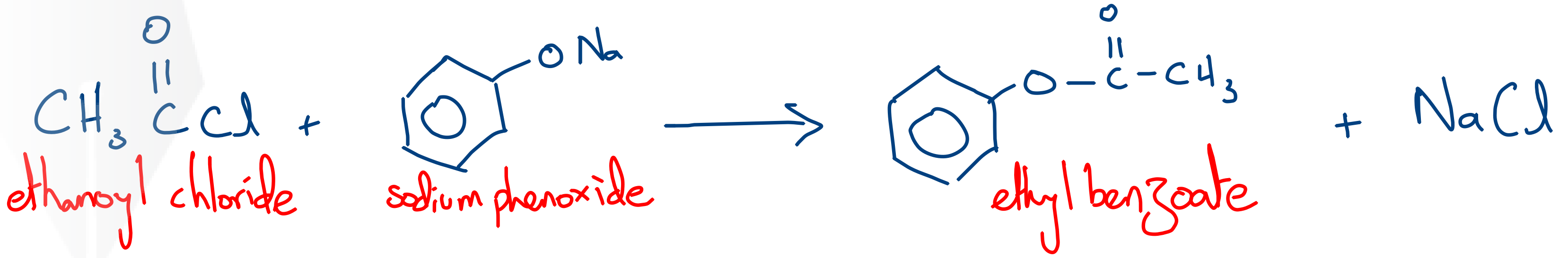
2) Esterification with Alcohols and phenols:-

1) Reaction with Alcohols (No Conditions) [Condensation]:-



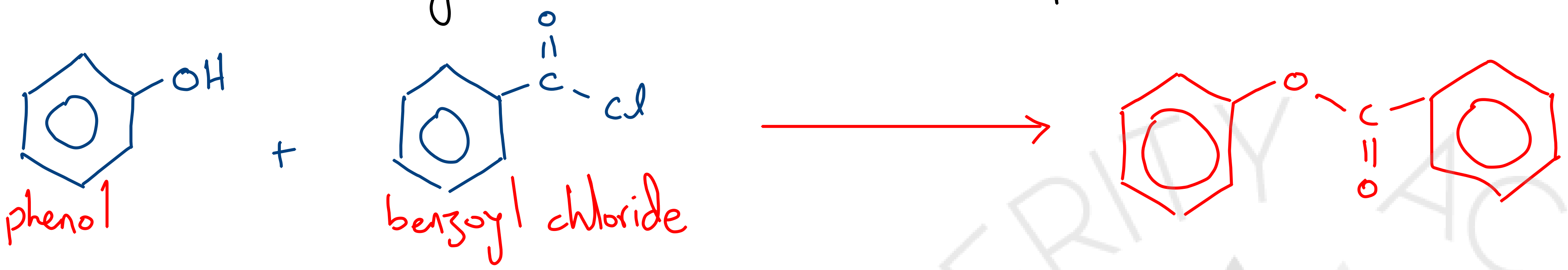
$$CH_3\overset{O}{\overset{\|}{C}}-Cl + CH_3CH_2OH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}-O-CH_2CH_3 + HCl$$

2) Reaction with Phenols (+ NaOH (to make phenoxide ion)) [Condensation]:-



Q. Predict the ester being formed and name all compounds

1)

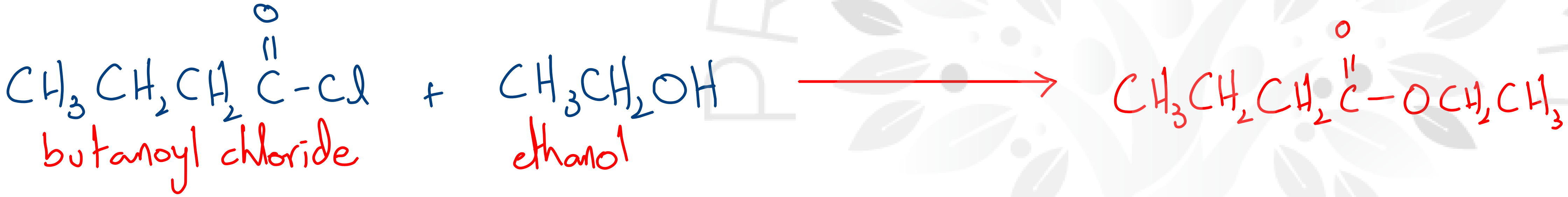


phenyl benzoate

2)

propyl benzoate

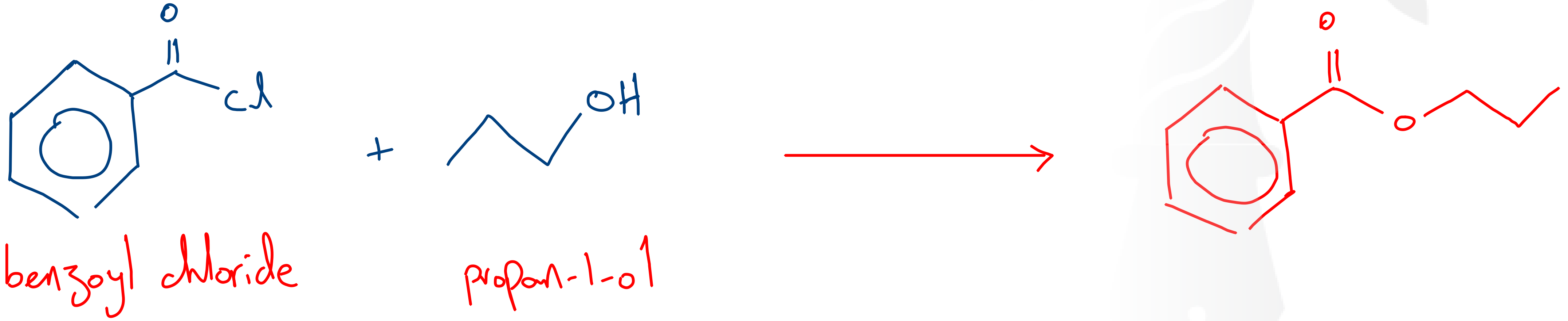
3)



$$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-Cl + CH_3CH_2OH \longrightarrow CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-OCH_2CH_3$$

ethyl butanoate

4)



propyl benzoate

3) Reaction with Ammonia:- No conditions [Condensation]

- Simple amides are produced

e.g.

$$CH_3CH_2\overset{\overset{O}{\|}}{C}-Cl + NH_3 \longrightarrow CH_3CH_2\overset{\overset{O}{\|}}{C}-NH_2 + HCl$$

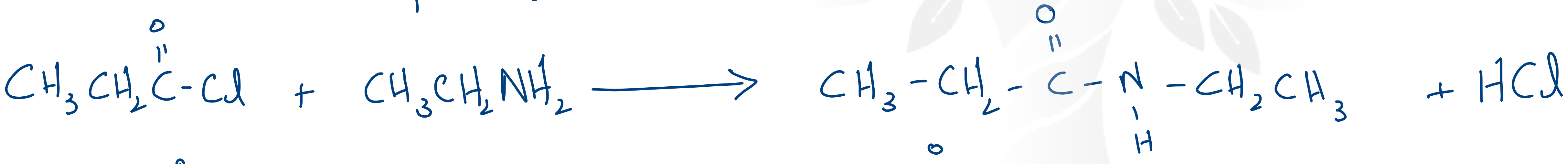
e.g.

4) Reaction with primary amines:- No conditions [Condensation]

- Substituted amides are produced.

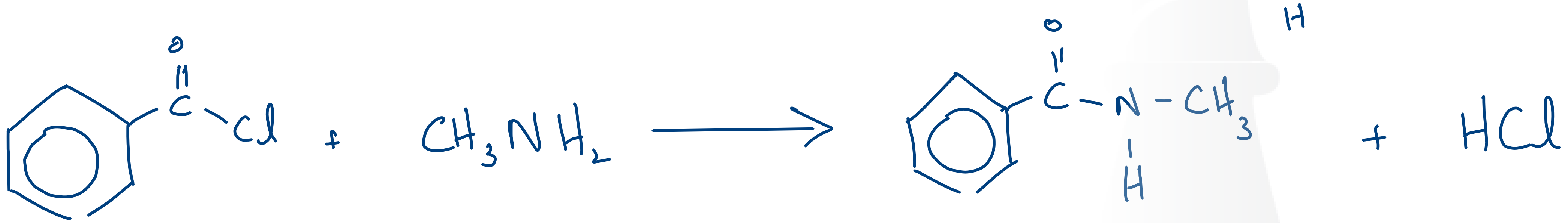
amide/peptide bond

e.g.



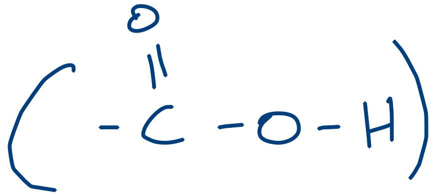
$$CH_3CH_2\overset{\overset{O}{\|}}{C}-Cl + CH_3CH_2NH_2 \longrightarrow CH_3-CH_2-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-CH_2CH_3 + HCl$$

e.g.



e.g.

Carboxylic Acids:- Contain -COOH group



$(-\overset{O}{\overset{\|}{C}}-O-H)$

- Revise AS content.

Acidity of Carboxylic Acids:-

- Carboxylic acids are weak acids i.e they partially dissociate:- $CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^{\ominus} + H_3O^{\oplus}$
- Carboxylic acids are stronger acids than phenols or alcohols as the C=O pulls electron density from the O-H bond making it weaker and easier to break. Once the acid loses the H atom, the carboxylate ion ($COO^{\ominus}$) is stabilised as the negative charge on it delocalises over the whole COO making it less negative.
- Chlorine substituted carboxylic acids are even stronger than normal carboxylic acids as chlorine helps withdraw even more e^- density from the O-H bond making it more weak and easier to dissociate and then further extends the delocalization of the negative charge making the ion more stable.

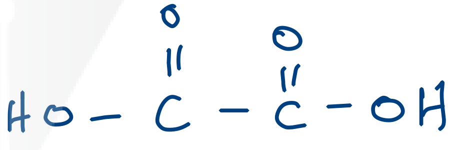
Oxidation of methanoic acid (HCOOH):-

- Use any oxidising agent e.g. Fehling's/Tollens/$KMnO_4$/$K_2Cr_2O_7$ + warm

$$HCOOH + [O] \longrightarrow CO_2 + H_2O$$

Oxidation of ethanedioic acid:-

- Use $KMnO_4$ + heat



$$HO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH + [O] \longrightarrow 2CO_2 + H_2O$$

* Only these 2 carboxylic acids can be oxidised

Amines :- Contain NH_2 group

Name the following :-

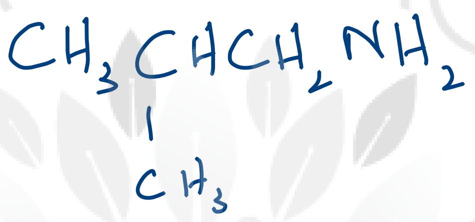
1) CH_3NH_2

methyl amine

2) $CH_3CH_2NH_2$

ethyl amine

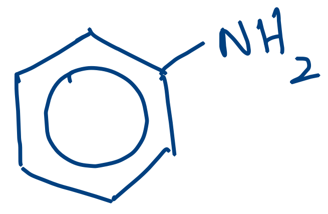
3)



$CH_3CH(CH_3)CH_2NH_2$

2-methyl propyl amine

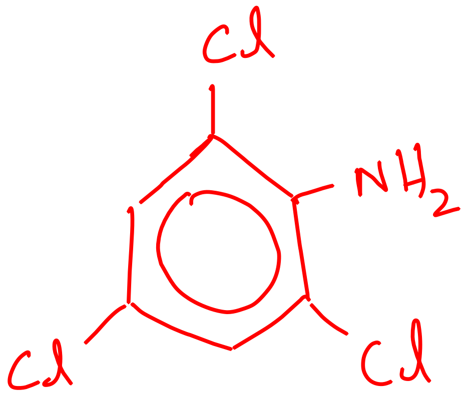
4)



phenylamine

Draw the following :-

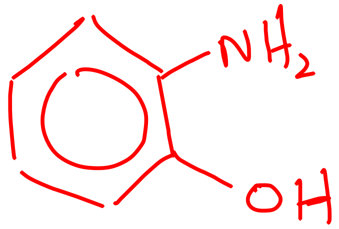
1) 2,4,6-trichloro phenyl amine



2) butyl amine

$CH_3-CH_2-CH_2-CH_2NH_2$

3) 2-hydroxy phenyl amine



Formation :-

1) Nucleophilic substitution of Ammonia :- NH_3 in ethanol + heat + sealed tube under pressure [Nucleophilic Substitution]

$$CH_3CH_2Cl + NH_3 \longrightarrow CH_3CH_2NH_2 + HCl$$

2) Reduction of Nitriles or amides:- $LiAlH_4$ in dry ether

e.g. $CH_3CH_2CN + 4[H] \longrightarrow CH_3CH_2CH_2NH_2$

propyl amine

e.g. $CH_3CH_2CONH_2 + 4[H] \longrightarrow CH_3CH_2CH_2NH_2$

propyl amine

e.g. $CH_3CH_2CONHCH_3 + [H] \longrightarrow CH_3CH_2CH_2NHCH_3$ → this is a secondary amine

3) Secondary amines can be formed by heating primary amines with halogenoalkanes:-

eg. $CH_3CH_2NH_2 + CH_3CH_2Cl \longrightarrow CH_3CH_2NHCH_2CH_3 + HCl$

Basicity:- Amines are weak bases

1) In water:-

$CH_3CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^{\oplus} + OH^{\ominus}$

2) In acid:-

$CH_3CH_2NH_2 + HCl \longrightarrow CH_3CH_2NH_3^{\oplus}Cl^{\ominus}$

3) Just like ammonia, amines can also be liberated from their salts by a strong base:-

$CH_3CH_2NH_3^{\oplus}Cl^{\ominus} + NaOH \longrightarrow CH_3CH_2NH_2 + NaCl + H_2O$

Relative order of basicities :- Ethyl amine > ammonia > Phenyl amine

- ethyl amine is more basic as the alkyl group pushes its electron density towards the N atom making the lone pair on it more available to form a dative bond to H^+.

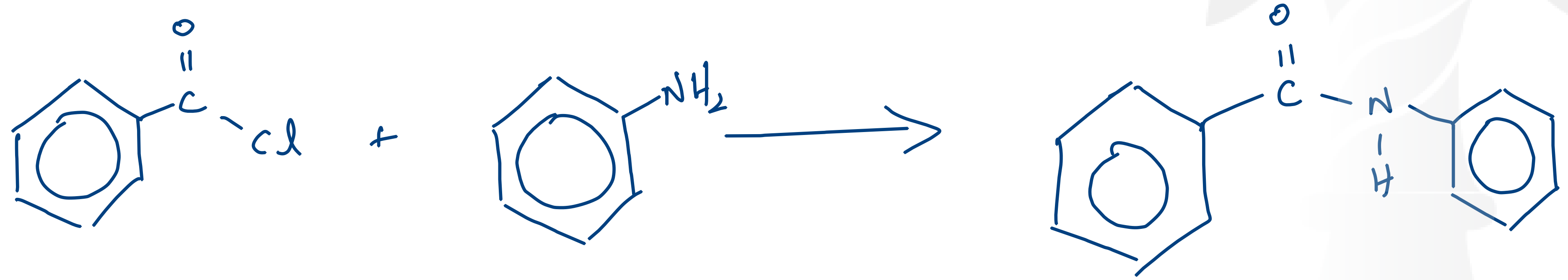
- Phenyl amine is less basic as the lone pair on the N atom delocalises with the π ring making it less available

Chemical reactions of Amines:-

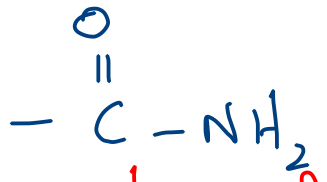
1) Reaction with Acyl chlorides:- Substituted amides are produced (No conditions) [Condensation]

e.g. $CH_3COCl + CH_3CH_2NH_2 \longrightarrow CH_3CONHCH_2CH_3$

e.g.



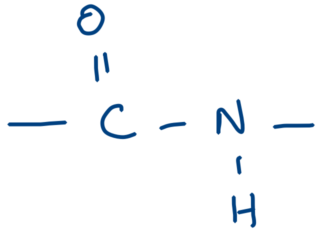
Amides :- Contain



$-\overset{O}{\overset{\|}{C}}-NH_2$

simple amide

or



$-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-$

substituted amide

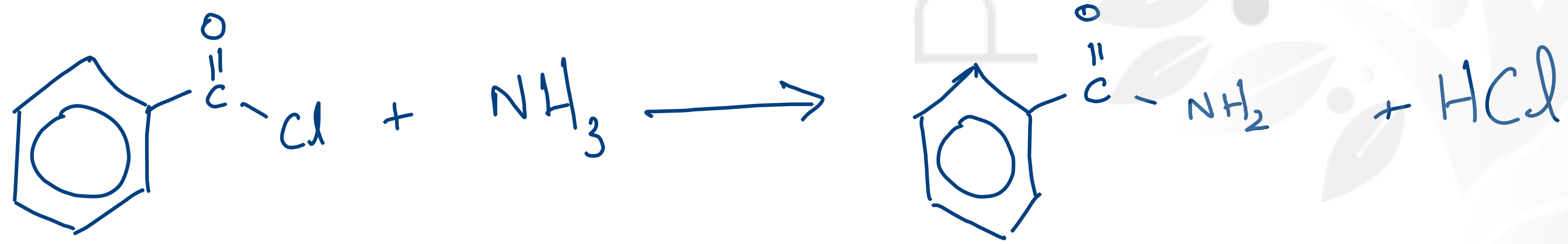
- Unlike amines, Amides are neutral. The lone pair on N atom gets delocalised with C=O making it unavailable to datively bond to H$^+$,

Formation:-

1) To produce simple amides, react NH_3 with acyl chloride :- [Condensation]

e.g. $CH_3COCl + NH_3 \longrightarrow CH_3CONH_2 + HCl$

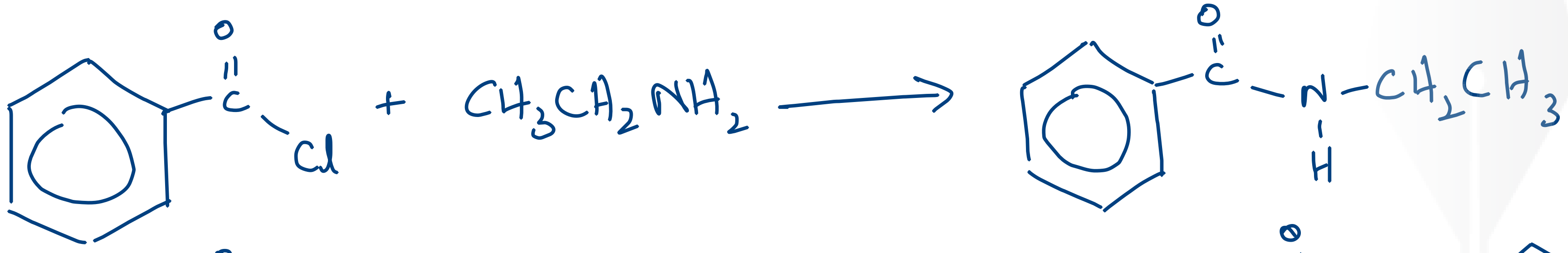
e.g.



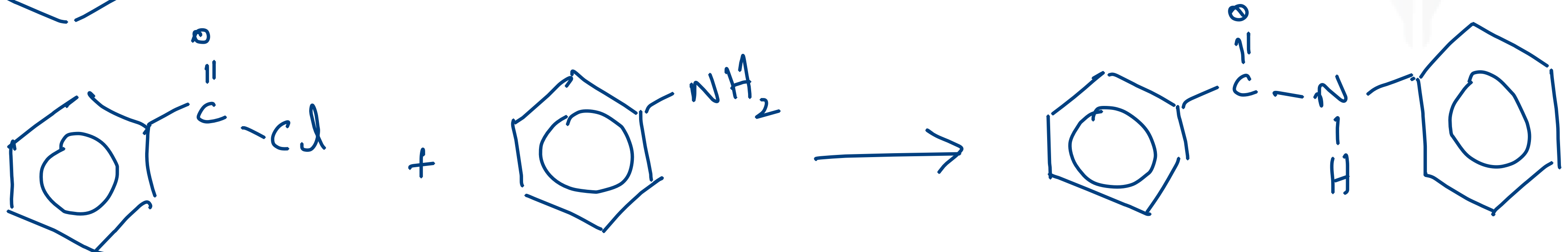
2) To produce substituted amides, react primary amine with acyl chloride:- [Condensation]

e.g. $CH_3COCl + CH_3NH_2 \longrightarrow CH_3CONHCH_3 + HCl$

e.g.



e.g.



Reactions of Amides:-

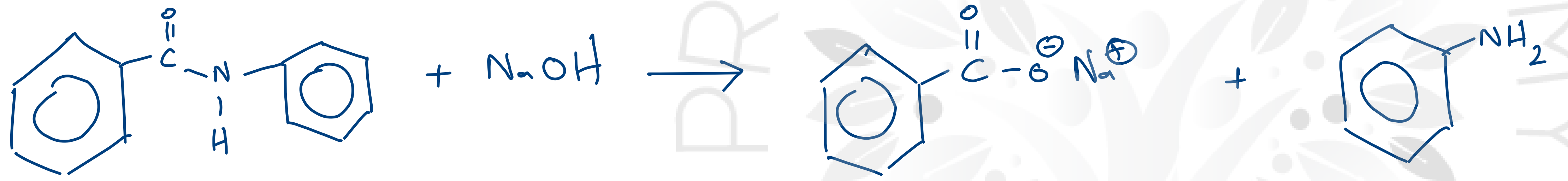
1) Hydrolysis:-

1) Alkaline hydrolysis:- dil. NaOH + heat - A carboxylate salt and amine/ammonia will be produced

e.g. $CH_3CONHCH_3 + NaOH \longrightarrow CH_3COO^{\ominus}Na^{\oplus} + CH_3NH_2$

e.g. $CH_3CONH_2 + NaOH \longrightarrow CH_3COO^{\ominus}Na^{\oplus} + NH_3$

e.g.

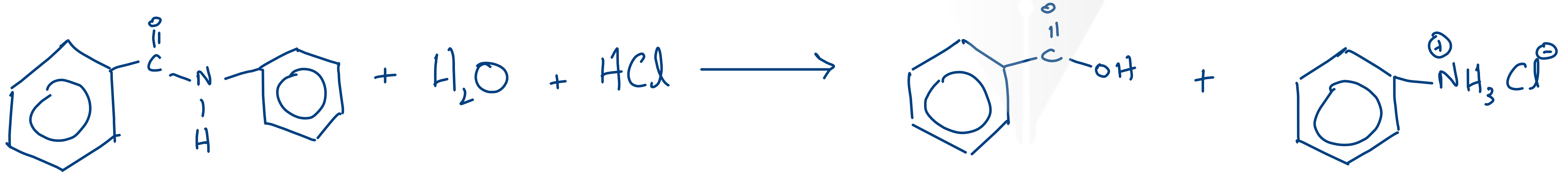


2) Acidic Hydrolysis:- dil. H_2SO_4 + heat - A carboxylic acid and simple or substituted ammonium salt is made

e.g. $CH_3CONHCH_3 + H_2O + HCl \longrightarrow CH_3COOH + CH_3\overset{\oplus}{N}H_3\,Cl^{\ominus}$

e.g. $CH_3CONH_2 + H_2O + HCl \longrightarrow CH_3COOH + N\overset{\oplus}{H}_4\,Cl^{\ominus}$

e.g.



Reduction:- $LiAlH_4$ in dry ether

- Primary amines are produced.

e.g. $CH_3CH_2CN + 4[H] \longrightarrow CH_3CH_2CH_2NH_2$

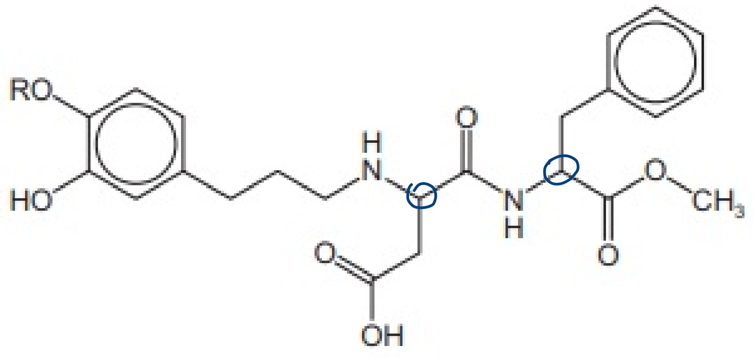
propyl amine

e.g. $CH_3CH_2CONH_2 + 4[H] \longrightarrow CH_3CH_2CH_2NH_2$

propyl amine

e.g. $CH_3CH_2CONHCH_3 + [H] \longrightarrow CH_3CH_2CH_2NHCH_3$ → this is a secondary amine

7 The compound *Advantame* is a sweetener that tastes approximately 25 000 times sweeter than sucrose.

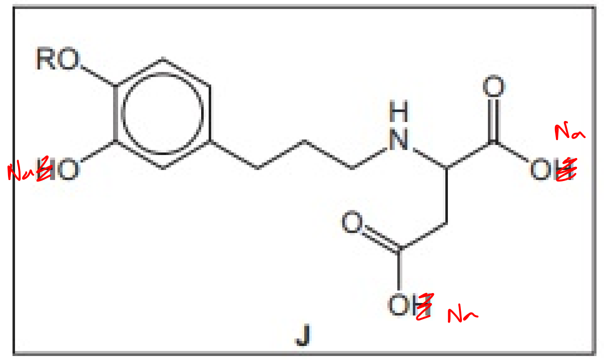


Advantame

(a) *Advantame* is optically active.

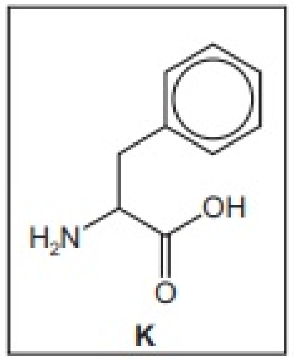
On the diagram of *Advantame*, circle all the chiral carbon atoms. [1]

(b) The decomposition of *Advantame* produces three molecules, **J**, **K** and **L**. The RO– group in *Advantame* is unreactive.



J

+



K

+

CH_3OH

L

(i) Suggest possible reagents and conditions for this decomposition.

dil. H_2SO_4 + heat [1]

(ii) Name the *type of reaction* occurring.

hydrolysis [1]

(iii) Draw the structure of **L** in the box above. [1]

(c) (i) Aqueous bromine was added dropwise to a solution of **J** until the bromine was in excess.

State what you would observe.

white Precipitate

[1]

(ii) **J** has the molecular formula $C_{14}H_{19}O_6N$.

Use this formula to write an equation for the reaction of excess aqueous sodium hydroxide with **one** mole of **J**.

$C_{14}H_{9}O_6N + 3NaOH \longrightarrow C_{14}H_6O_6NNa_3 + 3H_2O$ [2]

(d) (i) State what you would observe when an excess of aqueous bromine is added to a solution of **K**.

no reaction [1]

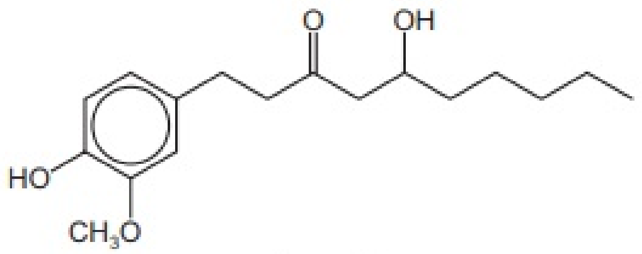
(ii) **K** can be polymerised.

Draw the structure of the polymer showing **two** repeat units. The linkage between the monomer units should be fully displayed.

[2]

8 The root of the ginger plant contains compounds with medicinal and flavouring properties. Three of the more important compounds are gingerol, shogaol and zingerone.

(a) The structure of gingerol is shown. The CH_3O– group in gingerol is unreactive.



gingerol

Gingerol reacts with acidified potassium dichromate(VI).

State the *type of reaction* and the functional group change which occurs during this reaction.

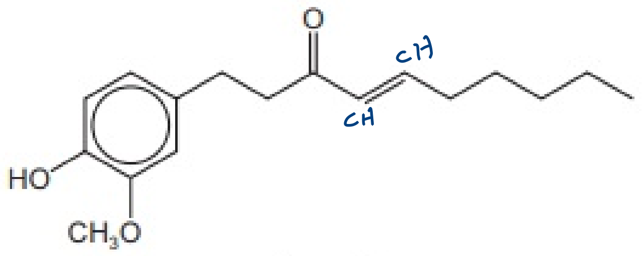
type of reaction oxidation

functional group change

from secondary (2°) Alcohol to Ketone

[1]

(b) The structure of shogaol is shown.



shogaol

(i) State the *type of reaction* needed to convert gingerol into shogaol.

dehydration [1]

(ii) State the reagents and conditions needed to convert gingerol into shogaol.

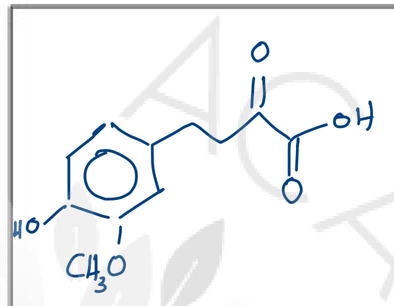
reagents conc. H_2SO_4

conditions heat

[1]

(iii) Shogaol reacts with hot, concentrated acidified manganate(VII) ions to form two organic products, **Q** and **R**.

Draw the structures of **Q** and **R**.



Q

R

[2]

(c) Zingerone is formed from gingerol.

Some reactions of zingerone are shown.

Complete the table to identify the functional groups in zingerone.

reagent and conditions	observation	functional group in zingerone indicated by the observation
benzenediazonium chloride, 5 °C, alkaline solution	red ppt.	phenol
2,4-dinitrophenylhydrazine	orange ppt.	Ketone
warm with Tollens' reagent	no change	

[2]

5 Compounds **J**, **K**, **L** and **M** are isomers of each other with the molecular formula $C_9H_{11}NO$.
All four isomers contain a benzene ring.
Two of the isomers contain a chiral centre.
The results of six tests carried out on **J**, **K**, **L** and **M** are shown in the table.

test		observations with each isomer			
		J	**K**	**L**	**M**
1	add cold HC*l*(aq)	soluble amine	soluble amine	soluble amine	insoluble
2	add 2,4-DNPH reagent	orange ppt. carbonyl	orange ppt. carbonyl	orange ppt. carbonyl	no reaction
3	add NaOH(aq) + I_2(aq)	pale yellow ppt. methyl Ketone	no reaction	pale yellow ppt. methyl Ketone	no reaction
4	warm with Fehling's solution	no reaction	red ppt. aldehyde	no reaction	no reaction
5	heat with NaOH(aq)	no reaction	no reaction	no reaction	P(C_6H_7N) and Q($C_3H_5O_2Na$) produced
6	diazotization and addition of alkaline phenol	no dye produced	orange dye produced phenyl amine	no dye produced	no dye produced

hydrolysis
peptide or ester

(a) Use the experimental results in the table above to determine the group(s), in addition to the benzene ring, present in each of the four isomers **J**, **K**, **L** and **M**.

Complete the table below, identifying the group(s) present in each isomer.

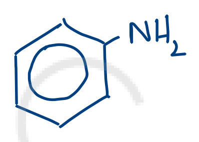
group(s) in compound			
J	**K**	**L**	**M**
amine methyl Ketone	phenyl amine aldehyde	amine methyl Ketone	amide
benzene ✓	benzene ✓	benzene ✓	benzene ✓

[5]

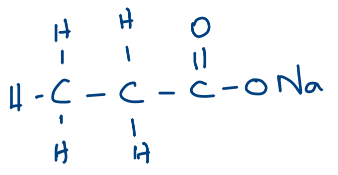
(b) (i) Name the *type of reaction* occurring in test 5 that converts **M** into **P** + **Q**.

hydrolysis [1]

(ii) Suggest structures for compounds **P** and **Q**.



P (C_6H_7N)

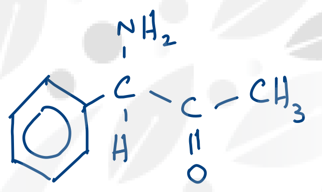


Q ($C_3H_5O_2Na$)

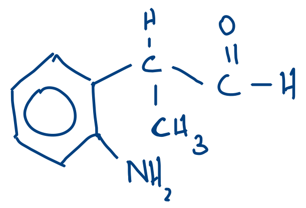
[2]

(c) Isomers **J**, **K**, **L** and **M** all have the molecular formula $C_9H_{11}NO$.

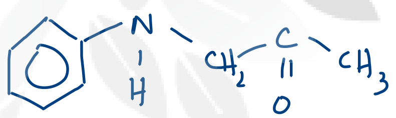
Use the information in **(a)** to suggest a structure for each of these isomers and draw these in the boxes. Draw **circles** around all chiral centres in **K** and **L**.



chiral **J**

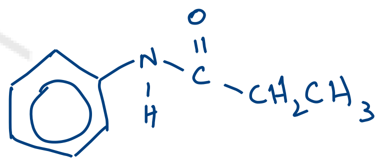


K chiral



L

not chiral

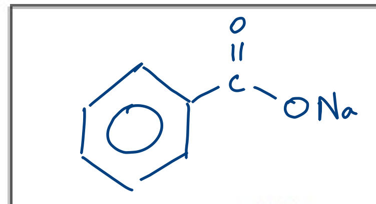


M

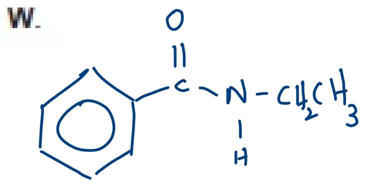
not chiral

[5]

(d) Compound **N** is another isomer which has the same molecular formula $C_9H_{11}NO$ and also contains a benzene ring.
N contains the same functional group as **M**. amide
When heated with NaOH(aq), **N** produces ethylamine and a sodium salt **W**.
$CH_3CH_2NH_2$
Suggest the structure of **W**.



W



[1]

[Total: 14]

7 Compounds **W**, **X**, **Y** and **Z** are isomers of each other with the molecular formula C_8H_7ClO.
All four isomers contain a benzene ring.
Only **one** of the isomers contains a chiral centre.
The results of six tests carried out on **W**, **X**, **Y** and **Z** are shown in the table.

chlorobenzene

	test	observations with each isomer			
		acyl chloride **W**	**X**	halogenoalkane **Y**	**Z**
1	add cold $AgNO_3$(aq)	white ppt. forms immediately	none	white ppt. forms very slowly	none
2	heat with NaOH(aq), then add dilute HNO_3 + $AgNO_3$(aq)	white ppt. acyl chloride	none 2° methyl alcohol ✗ methyl ketone	white ppt. halogenoalkane	none
3	add NaOH(aq) + I_2(aq)	none	pale yellow ppt.	none	none
4	warm with Fehling's solution	none	none	red ppt. aldehyde	none
5	add cold, dilute, acidified $KMnO_4$(aq)	no change	no change no alcohol	no change	decolourises $C=C$
6	add Br_2(aq)	no change	no change	no change	decolourises and forms white ppt. $C=C$

chlorobenzene

phenol

(a) Use the experimental results in the table above to determine the group(s), in addition to the benzene ring, present in the four isomers **W**, **X**, **Y** and **Z**.

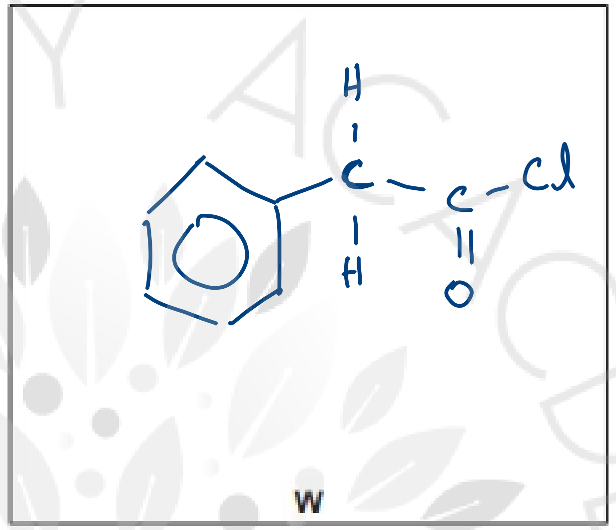
Complete the table below, identifying the group(s) present in each isomer.

group(s) in compound			
W	**X**	**Y**	**Z**
acyl chloride	methyl ketone chloro benzene	halogenoalkane aldehyde	$C=C$ phenol chlorobenzene

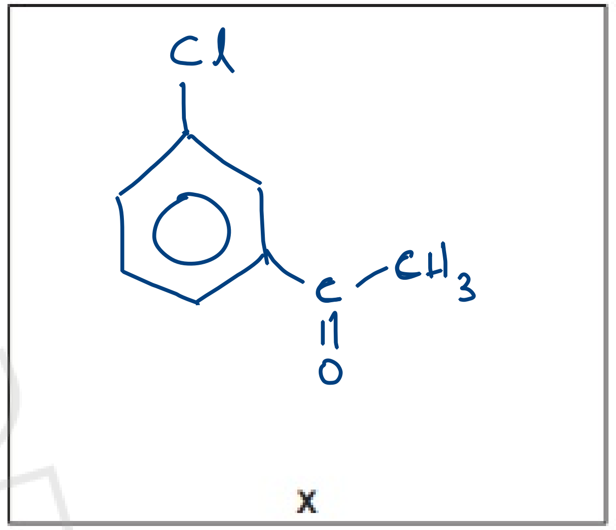
[5]

(b) Isomers **W**, **X**, **Y** and **Z** all have the molecular formula C_8H_7ClO.

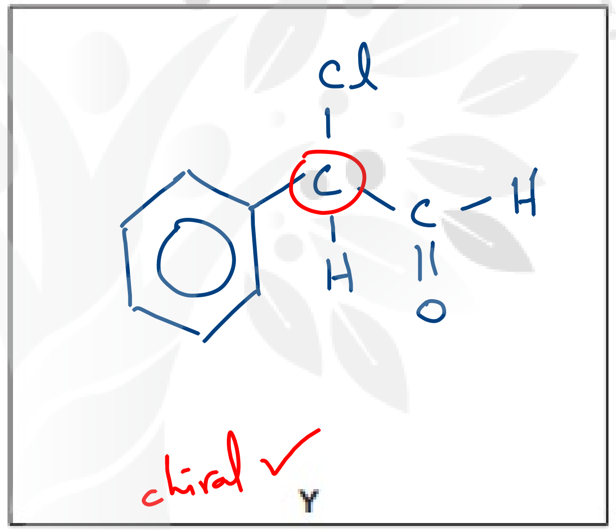
(i) Use the information in **(a)** to suggest a structure for each of these isomers and draw these in the boxes.



W

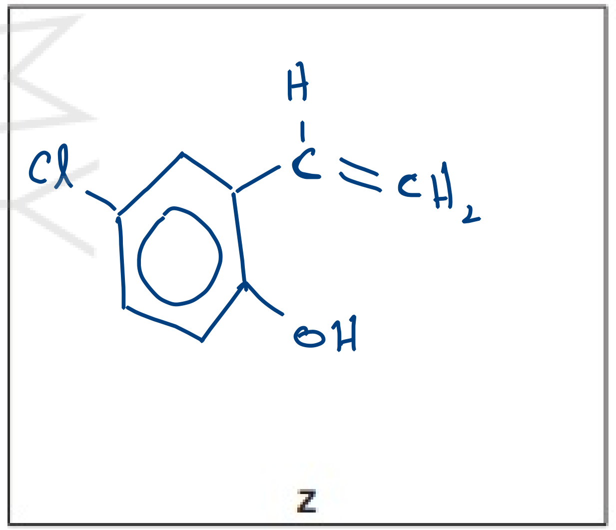


X



chiral ✓

Y



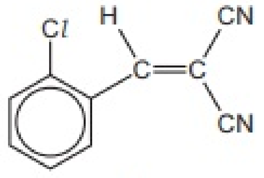
Z

[4]

(ii) Draw a **circle** around the chiral centre in **one** of the above structures. [1]

[Total: 10]

5 Compound **P** contains several functional groups.



P

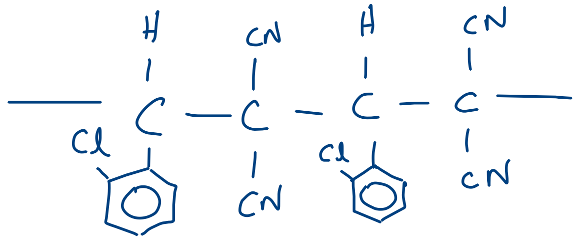
(a) Name the functional groups present in **P**.

chlorobenzene, alkene, nitrile

[2]

(b) Compound **P** can be polymerised.

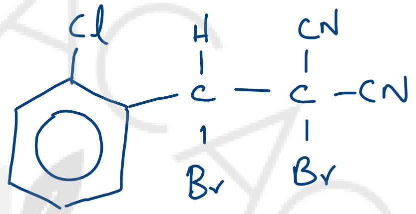
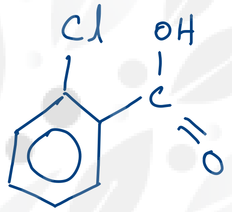
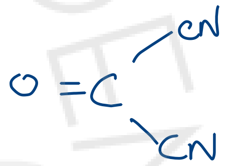
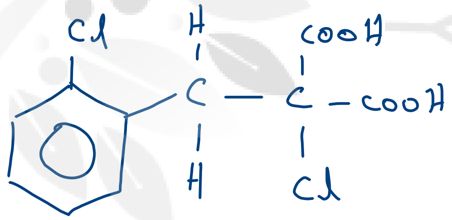
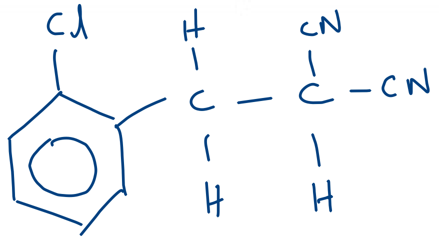
Draw a section of the polymer of **P** showing **two** repeat units.
Name the type of polymerisation.



type of polymerisation addition

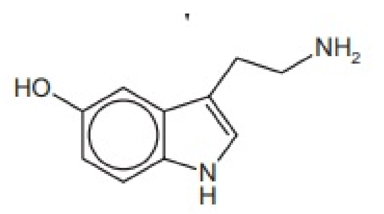
[2]

(c) Complete the following table to show the structures of the products formed and the *type of organic reaction* when **P** reacts with the four reagents.

reagent	structure(s) of product(s)	*type of organic reaction*
excess Br_2(aq)		Electrophillic addition
excess hot, concentrated, acidified MnO_4^-(aq)	 	oxidation
excess hot HCl(aq)		hydrolysis
excess H_2/Pt catalyst		hydrogenation

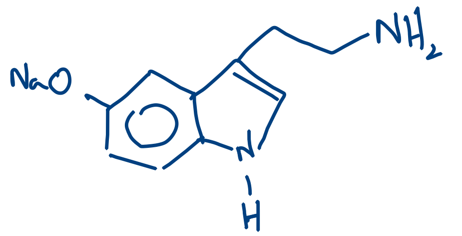
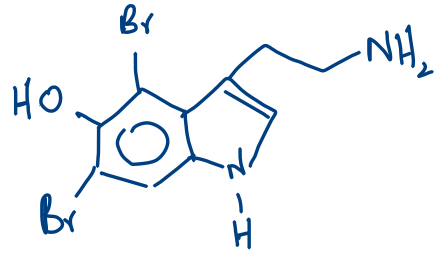
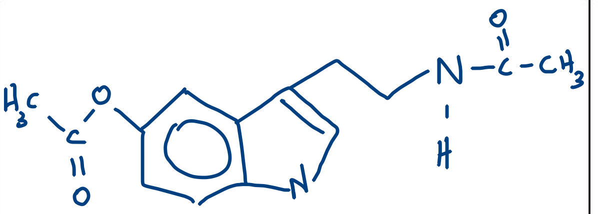
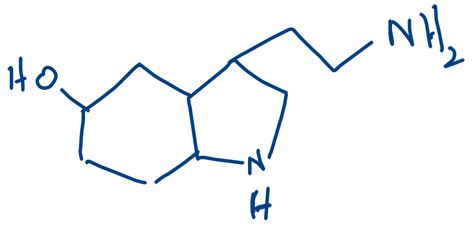
[8]

[Total: 12]



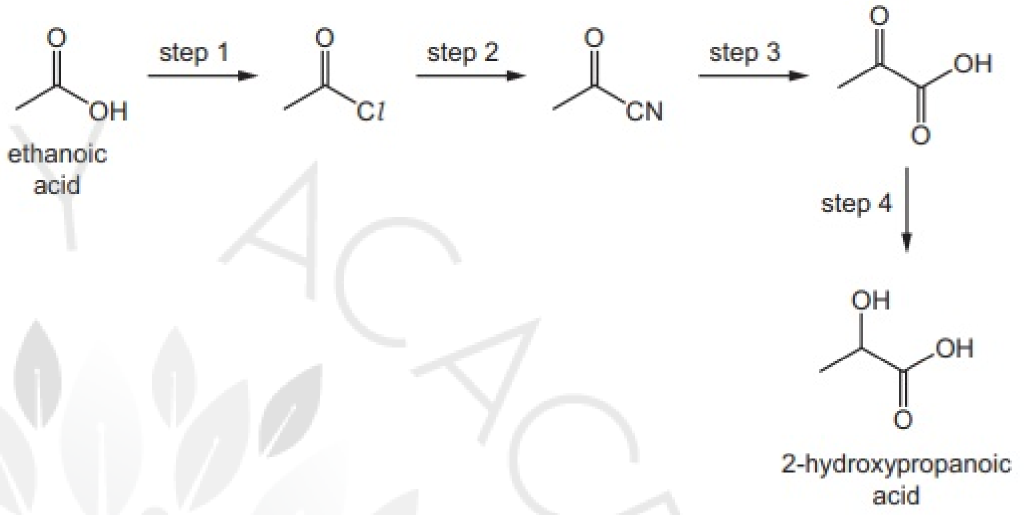
serotonin

(b) Complete the following table to show the structures of the products formed and the *type of reaction* occurring when **serotonin** reacts with the four reagents in separate reactions.

reagent	structure of product	*type of reaction*
Na		redox
excess $Br_2(aq)$		electrophilic substitution
excess CH_3COCl		Condensation
excess H_2/Pt catalyst		hydrogenation

[8]

6 2-hydroxypropanoic acid can be synthesised in four steps from ethanoic acid.



(a) (i) Suggest a reagent for step 2.

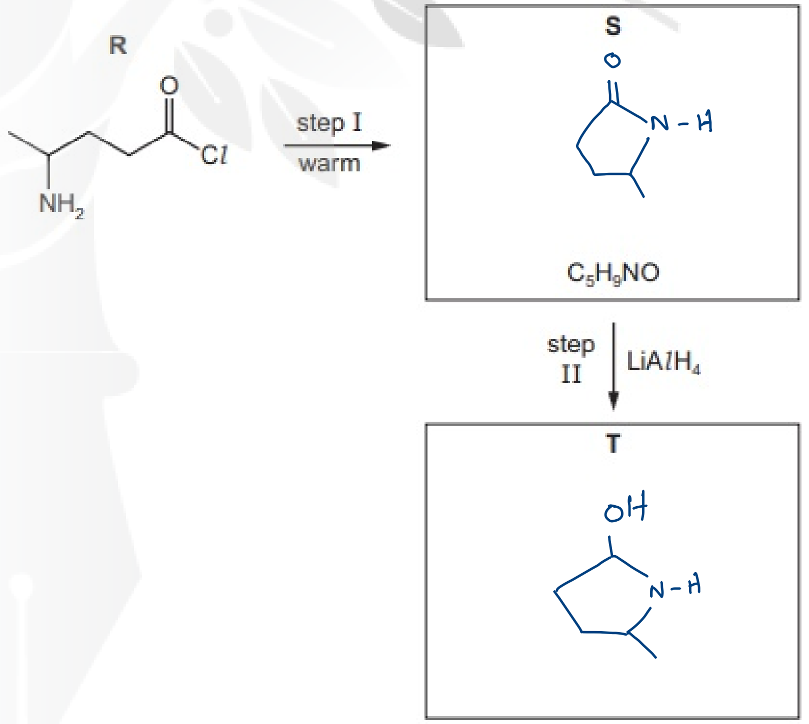
NaCN [1]

(ii) Suggest reagents and conditions for steps 1 and 4.

step 1 PCl_5

step 4 $NaBH_4$ [2]

(b) Compound **R** can be used in the synthesis of compound **T** as shown.



(i) Suggest the structures of **S** and **T** and draw them in the boxes. [2]

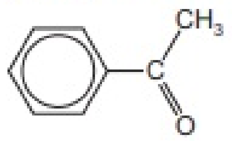
(ii) Name the *type of reaction* for step I and step II.

step I condensation

step II reduction [2]

4 Phenylethanone is an important chemical with many uses.

phenylethanone



(a) Phenylethanone can be synthesised using benzene as one of the starting materials.

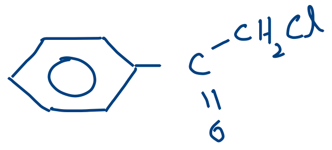
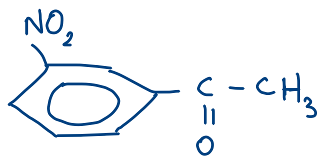
Identify the other reagents used and describe any essential reaction conditions.

CH_3COCl + $AlCl_3$ + heat

[2]

(b) Phenylethanone is treated separately with three reagents.

Complete the table, for each reagent, to give the structural formula of one organic product formed and the name of the mechanism involved. If there is no reaction you should write 'no reaction'.

reagent	organic product	name of mechanism
chlorine gas at 10 °C in the presence of ultra-violet light		Free radical substitution
a mixture of concentrated nitric and sulfuric acids at 50 °C		Electrophilic substitution
bromine water	no reaction	

[5]

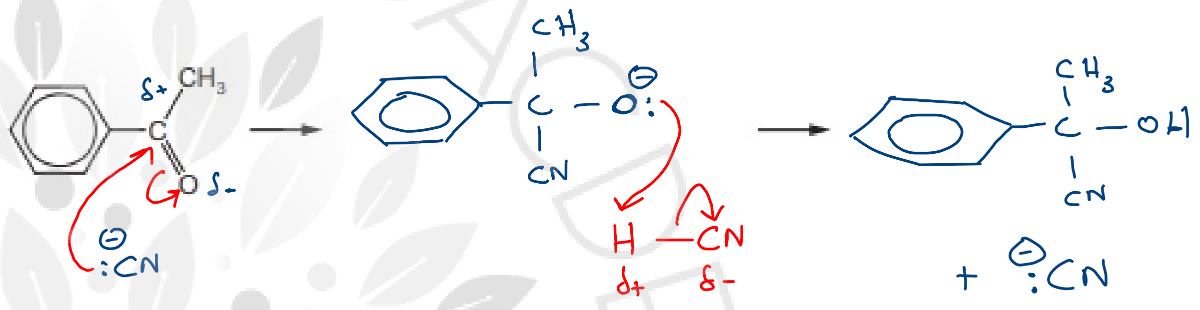
(c) Phenylethanone reacts with HCN in the presence of a small amount of NaCN.

(i) Name the mechanism of this reaction.

nucleophilic addition [1]

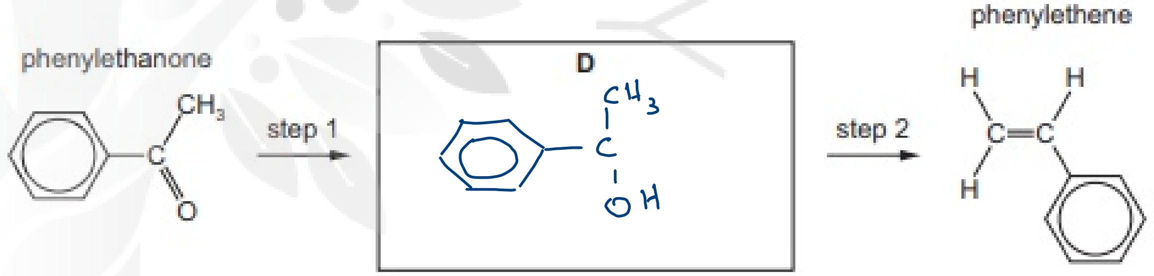
(ii) Draw the mechanism of this reaction below. Include all relevant charges, dipoles, lone pairs and curly arrows. Your mechanism should show the catalytic role of CN^- ions.

phenylethanone intermediate product



[4]

(d) Phenylethanone can be used as a starting material to make phenylethene in a two-step synthesis.



(i) Draw the structure of compound **D** in the box. [1]

(ii) Identify a suitable reagent for step 1.

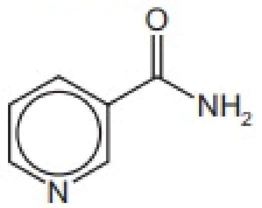
$NaBH_4$ [1]

(iii) Identify a suitable reagent for step 2.

conc. H_2SO_4 [1]

9 The structure of nicotinamide is shown.

nicotinamide



(a) The nitrogen atom in the six-membered ring has one electron in an unhybridised p-orbital. This electron becomes delocalised, becoming part of a single delocalised system of electrons. This delocalised system also includes:

- electrons from the carbon atoms in the six-membered ring
- the two electrons in the π bond of the C=O group
- the two electrons in the lone pair on the nitrogen atom of the amide group.

(i) State the number of delocalised electrons in one nicotinamide molecule.

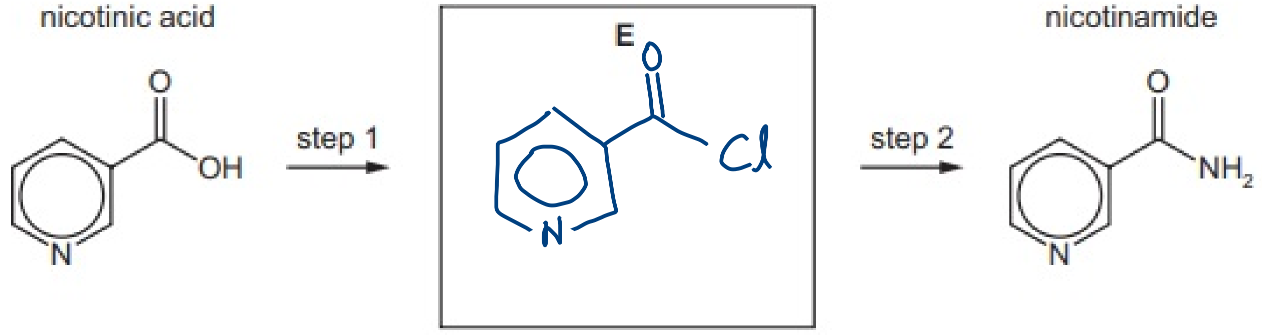
10 .... [1]

(ii) Predict the H–N–H bond angle in the NH_2 group in nicotinamide.

120° .... [1]

(b) Nicotinamide can be synthesised from nicotinic acid.

The synthesis involves two steps.



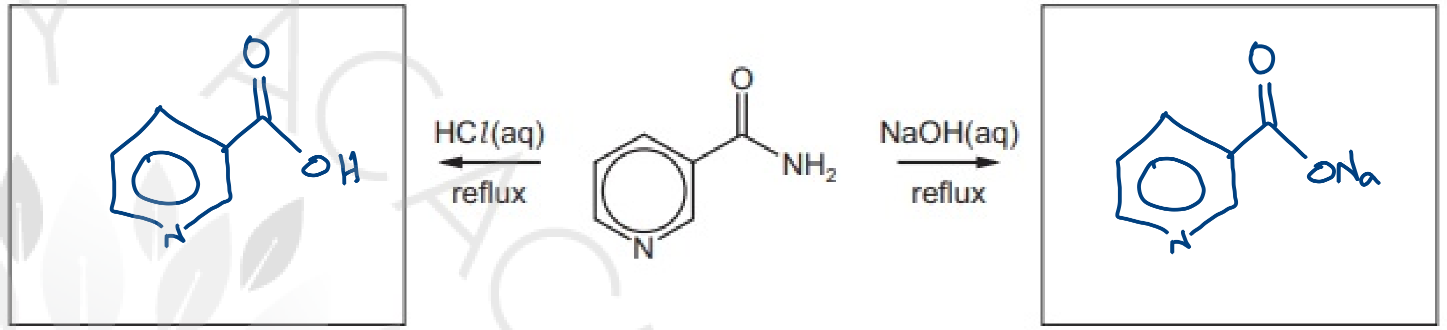
(i) Draw the structural formula of **E** in the box. [1]

(ii) Give the name or formula of a suitable reagent for step 2.

NH_3 .... [1]

(c) Nicotinamide reacts separately with aqueous acid and aqueous alkali. The six-membered ring remains unchanged in these reactions.

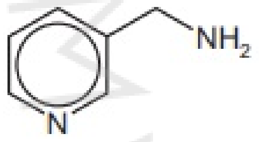
Complete the reaction scheme below to give the structural formula of the organic product of each reaction.



[2]

(d) Nicotinamide can be reduced to compound **X**.

X



(i) Identify a suitable reducing agent for this reaction.

$LiAlH_4$ .... [1]

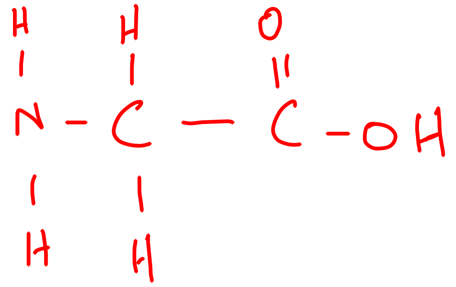
(ii) Predict and explain the relative basicities of the NH_2 groups in phenylamine, $C_6H_5NH_2$, nicotinamide and compound **X**.

X > $C_6H_5NH_2$ > nicotinamide. Nicotinamide is neutral as the lone pair on N gets delocalised over C=O. X is most basic as the alkyl group pushes electron density towards N atom making its lone pair more available while in phenylamine, the lone pair delocalises with the π ring making it less available to datively bond to H^+. [3]

Amino Acids & Polypeptides :-

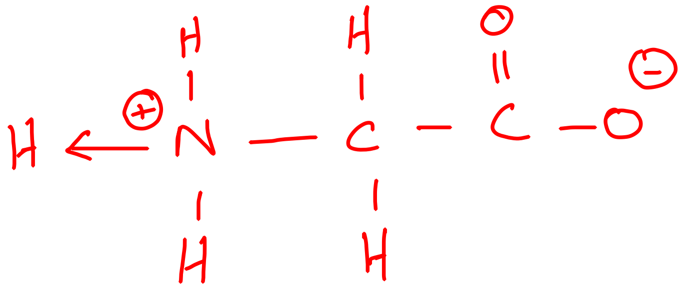
- Amino acids contain an acidic (COOH) and a basic (NH_2) group

e.g. glycine



$$H_2N-CH_2-COOH$$

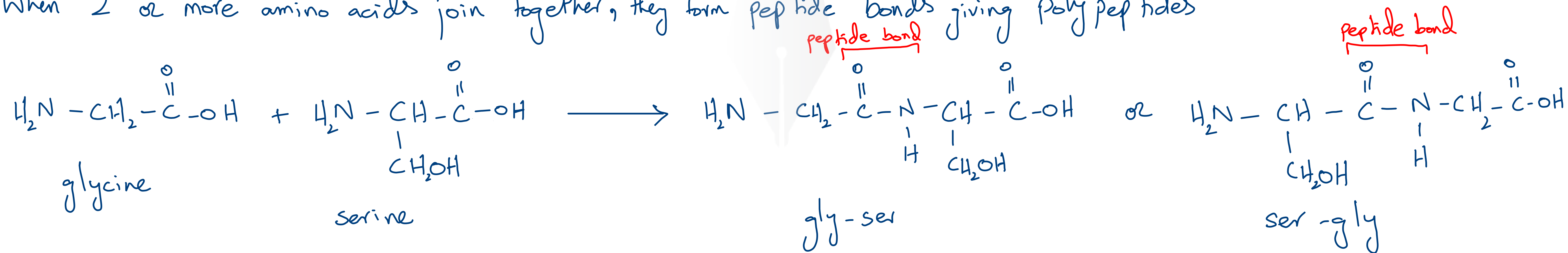
- In neutral aqueous solution, the COOH loses its hydrogen and the N in NH_2 uses its lone pair to datively bond to H^+
the amino acid becomes a zwitter ion, it carries both +ve and -ve charges.



$$H \leftarrow \overset{\oplus}{N}H_2-CH_2-C(=O)-O^{\ominus}$$

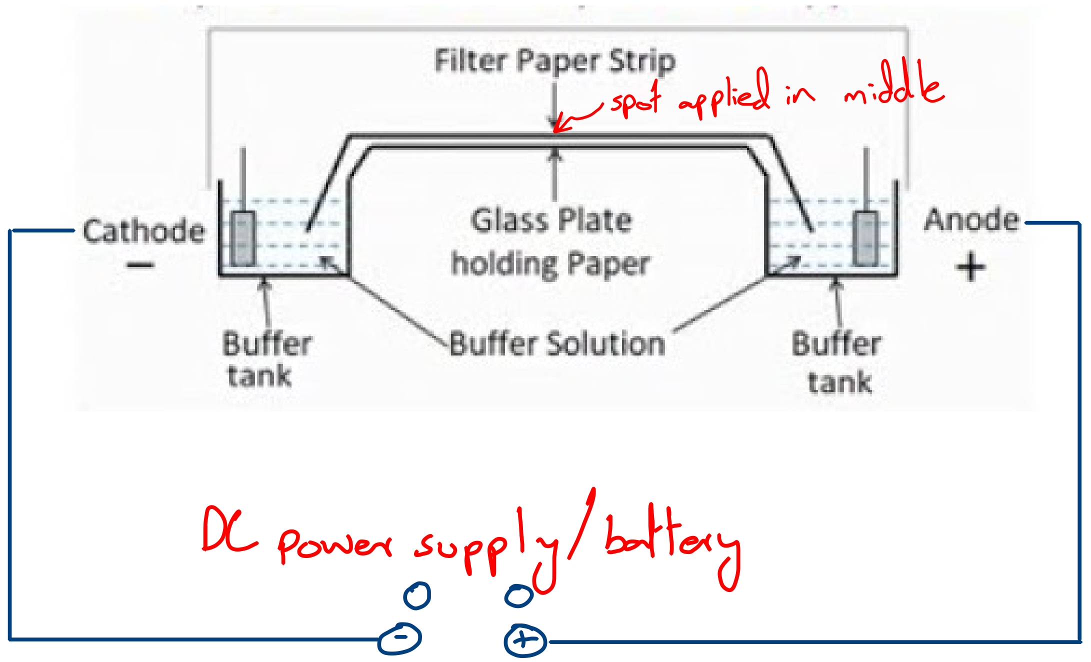
- The COOH group and NH_2 group gives their typical reactions as discussed earlier.

- When 2 or more amino acids join together, they form peptide bonds giving polypeptides



$$H_2N-CH_2-COOH + H_2N-CH(CH_2OH)-COOH \longrightarrow H_2N-CH_2-\underbrace{CO-NH}_{\text{peptide bond}}-CH(CH_2OH)-COOH \text{ or } H_2N-CH(CH_2OH)-\underbrace{CO-NH}_{\text{peptide bond}}-CH_2-COOH$$

Electrophoresis:-



- A polypeptide is broken down into its constituents by hydrolysing it with dil. NaOH or dil. H_2SO_4 + heat
- A spot containing all amino acids and the polypeptide is placed in the middle
- A constant pH is maintained by buffers as amino acids are both acidic and basic
- At a neutral pH, the following groups are affected:-

1) $R-\overset{O}{\overset{\|}{C}}-OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^{\ominus}$

2) $R-NH_2 \longrightarrow R-NH_3^{\oplus}$

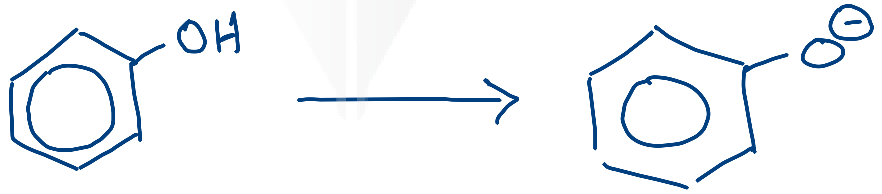
- At an acidic pH, the following groups are affected:-

1) $R-NH_2 \longrightarrow R-NH_3^{\oplus}$

- At an alkaline pH, the following groups are affected:-

1) $R-\overset{O}{\overset{\|}{C}}-OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^{\ominus}$

2)



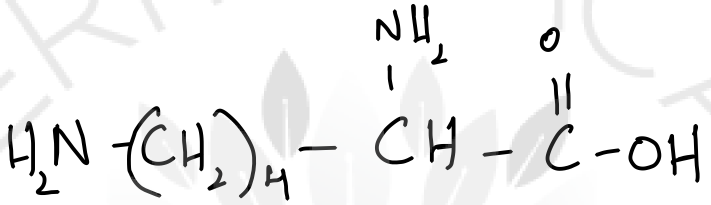
- An electric field is then applied and the amino acid and polypeptides move depending on their charge and mass.

- The pH at which an amino acid becomes electrically neutral is known as its isoelectronic point.

Q. Given are the structures of glycine, lysine and glutamic acid. Deduce what they will look like at the following pHs and the end result on their electrophoregram.

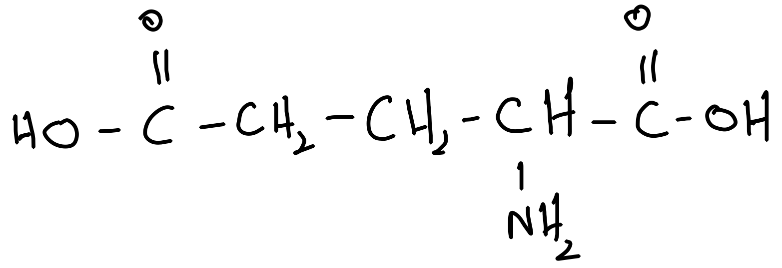
1) glycine: $H_2N-CH_2-CO_2H$

2) lysine:



$H_2N-(CH_2)_4-\overset{\overset{NH_2}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OH$

3) glutamic acid:



$HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{NH_2}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OH$

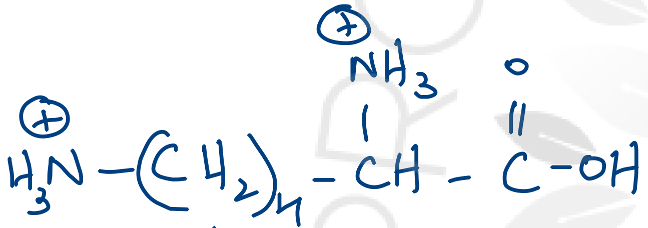
a) pH 2:-

$H_3\overset{\oplus}{N}-CH_2-CO_2H$

glycine

net charge = +1

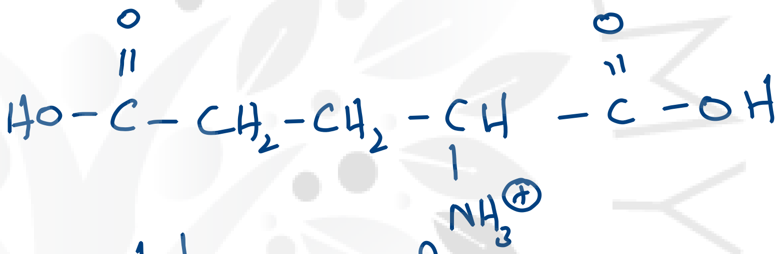
mass ↓



$H_3\overset{\oplus}{N}-(CH_2)_4-\overset{\overset{\overset{\oplus}{N}H_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OH$

lysine

net charge = +2

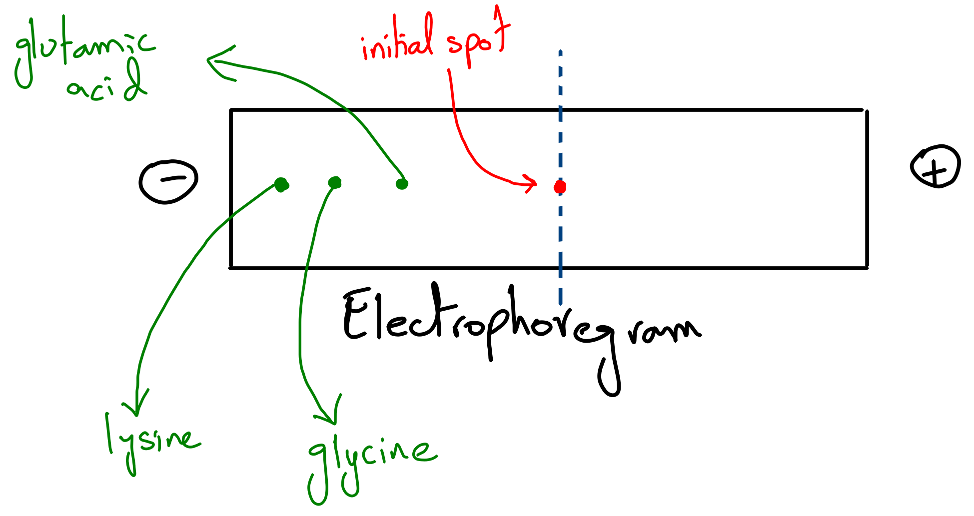


$HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{NH_3^{\oplus}}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OH$

glutamic acid

net charge = +1

mass ↑

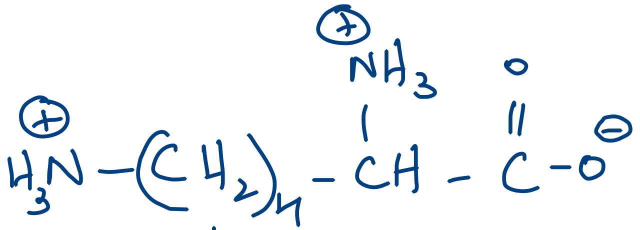


b) pH 7:-

$H_3\overset{\oplus}{N}-CH_2-CO_2^{\ominus}$

glycine

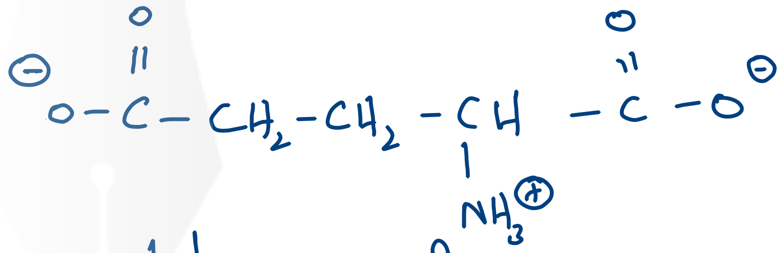
net charge = 0



$H_3\overset{\oplus}{N}-(CH_2)_4-\overset{\overset{\overset{\oplus}{N}H_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-O^{\ominus}$

lysine

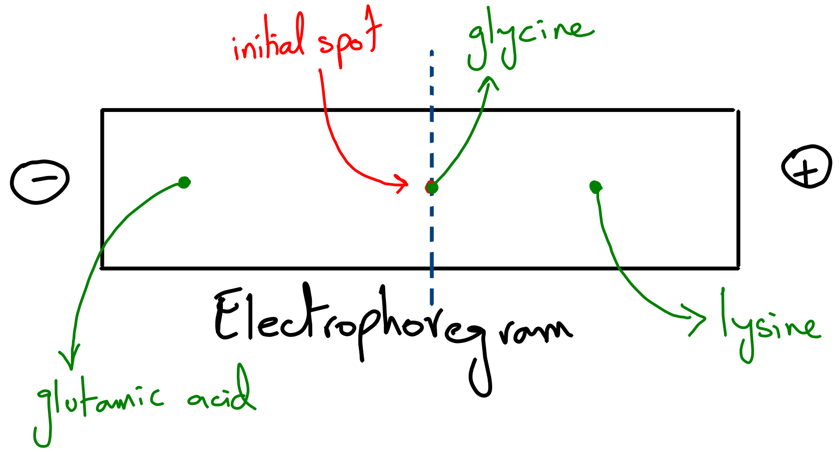
net charge = +1



$^{\ominus}O-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{NH_3^{\oplus}}{|}}{CH}-\overset{\overset{O}{\|}}{C}-O^{\ominus}$

glutamic acid

net charge = -1



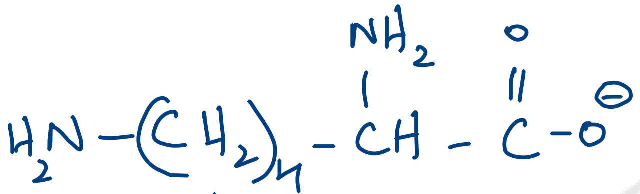
c) pH 12 :-

$H_2N-CH_2-CO_2^{\ominus}$

glycine

net charge = -1

mass ↓

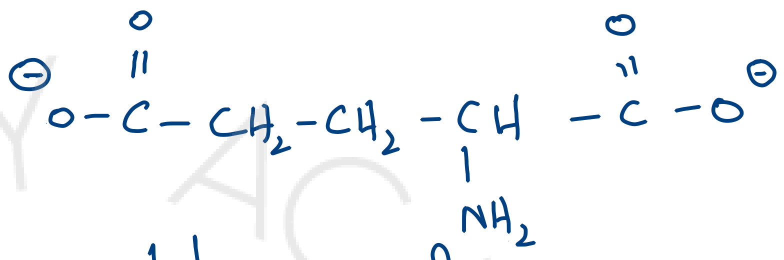


$H_2N-(CH_2)_4-\overset{NH_2}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O^{\ominus}$

lysine

net charge = -1

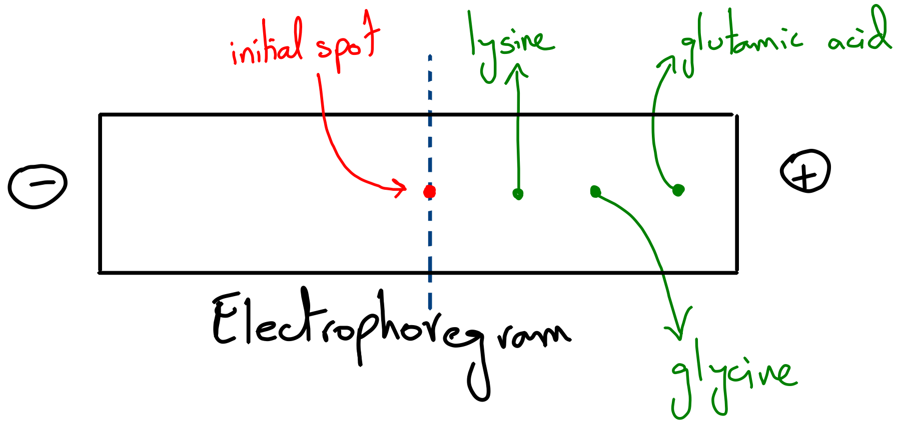
mass↑



${}^{\ominus}O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{NH_2}{\underset{|}{CH}}-\overset{O}{\overset{\|}{C}}-O^{\ominus}$

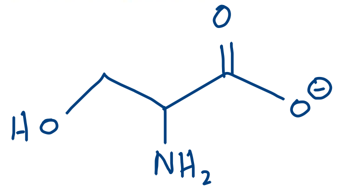
glutamic acid

net charge = -2



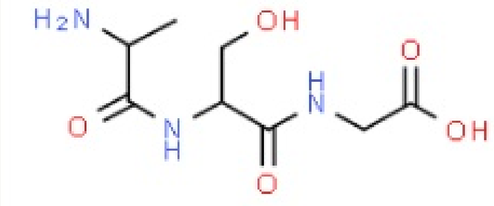
(b) Electrophoresis can be used to separate mixtures of amino acids and peptides.
A mixture of the tripeptide Ala-Ser-Gly and its three constituent amino acids was subjected to electrophoresis in a buffer at pH 11.

(i) Draw the structure of serine at pH 11.

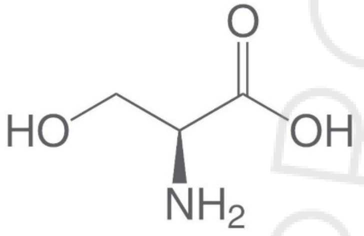


[1]

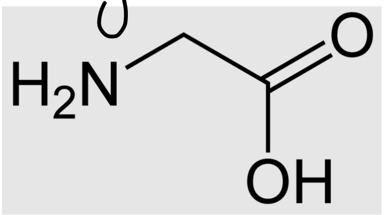
Ala-ser-gly



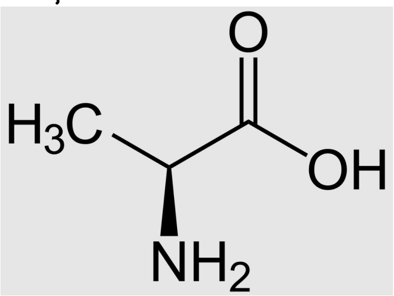
Serine



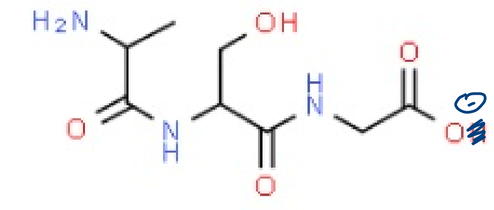
Glycine

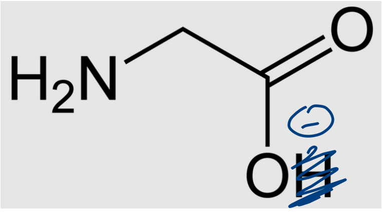


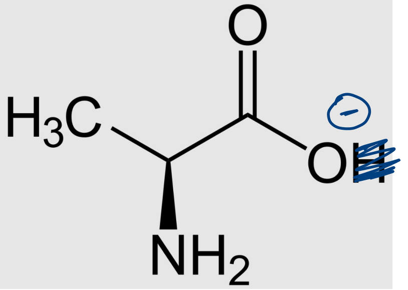
Alanine



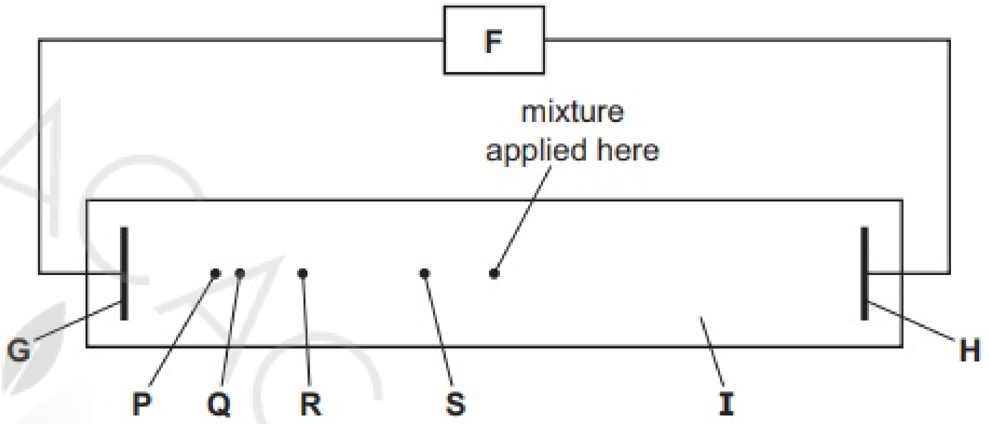
pH 11:-







At the end of the experiment the following results were seen.



(ii) Identify the components labelled **F**-**I** in the above diagram.

F DC power supply

G anode

H cathode

I filter paper soaked in buffer

[4]

(iii) Suggest the identities of the species responsible for

spot **P**, $[\text{glycine}]^{\ominus}$

spot **S**. $[\text{Ala-ser-gly}]^{\ominus}$

Explain your answers.

glycine is smallest so moves furthest while Ala-ser-gly is the largest so moves less in same amount of time [3]

(c) **(i)** State the reagents and conditions needed for converting the tripeptide into its three constituent amino acids.

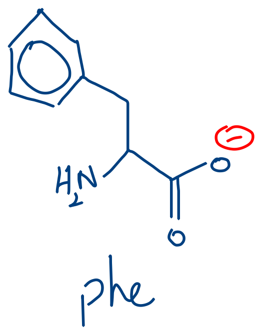
dil. H_2SO_4 + heat [1]

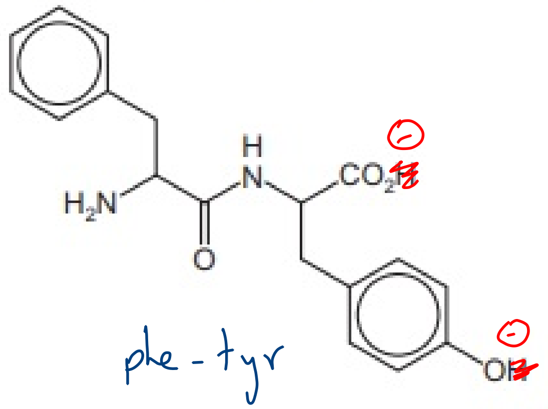
(ii) Name the *type of reaction* in **(i)**.

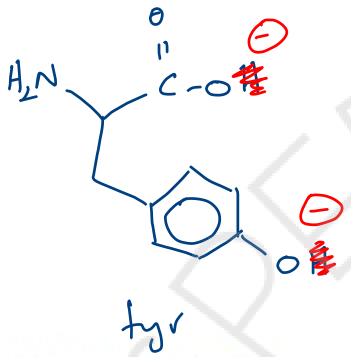
hydrolysis [1]

[Total: 13]

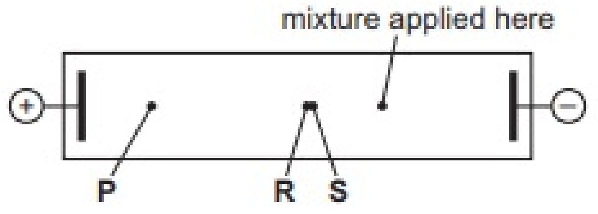
(b) The dipeptide phe-tyr has the following structure.







A mixture of this dipeptide (phe-tyr) and its two constituent amino acids (phe and tyr) was subjected to electrophoresis in a buffer at pH 12. At the end of the experiment the following results were seen. Spots **R** and **S** remained very close together.



The three spots are due to the three species phe, tyr and phe-tyr.

(i) Which species is responsible for spot **P**? Explain your answer.

tyr. It has a charge of -2 and it is also small.

[2]

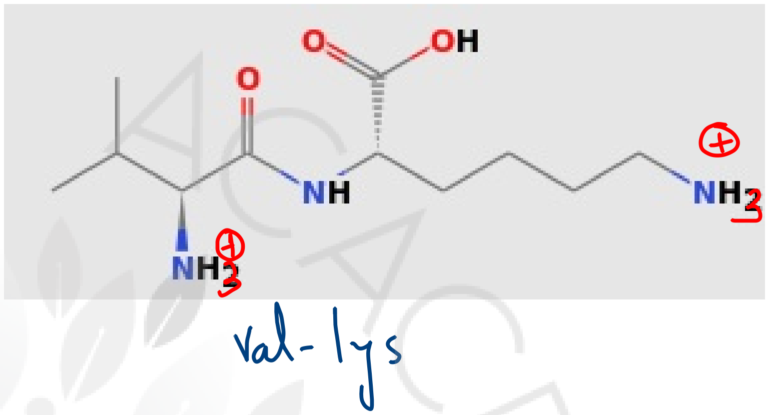
(ii) Suggest why the other two species give spots **R** and **S** that are so close together.

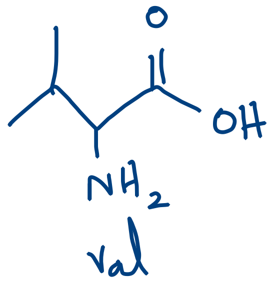
Their charge to mass ratio is the same

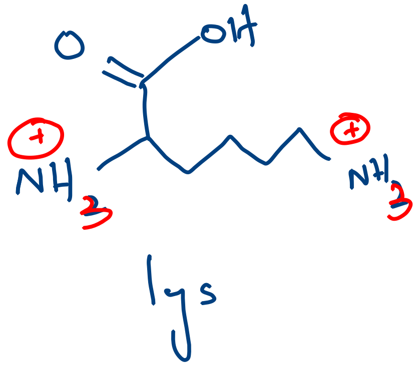
[1]

[Total: 15]

6 **(a)** Use the *Data Booklet* to draw the structure of the dipeptide val-lys. The peptide bond should be shown displayed.





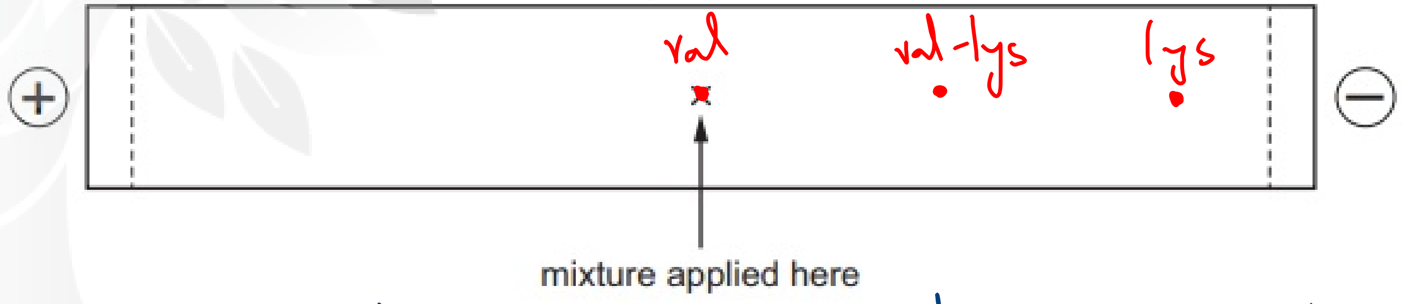


[2]

(b) The isoelectric point is the pH at which an amino acid exists as a zwitterion. The isoelectric point of valine is 6.0 and of lysine is 9.8.

A mixture of the dipeptide, val-lys, and its two constituent amino acids, valine and lysine, was analysed by electrophoresis using a buffer at pH 6.0.

Draw and label **three** spots on the diagram of the electrophoresis paper to indicate the likely position of each of these three species after electrophoresis. Explain your answer.



explanation val is isoelectronic so wont move. Both lys and val-lys have +2 charge and lys is smaller so travels further in smallest time

[5]

[Total: 7]