PROSPERITY ACADEMY

A2 CHEMISTRY 9701

Crash Course

RUHAB IQBAL

AROMATIC CHEMISTRY

COMPLETE NOTES

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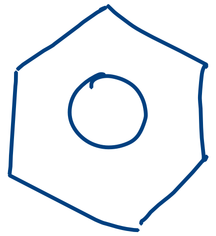
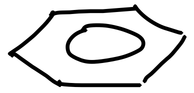
Aromatic Chemistry:-

Benzene:- C_6H_6



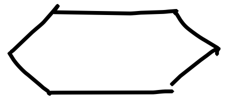
Structure of benzene



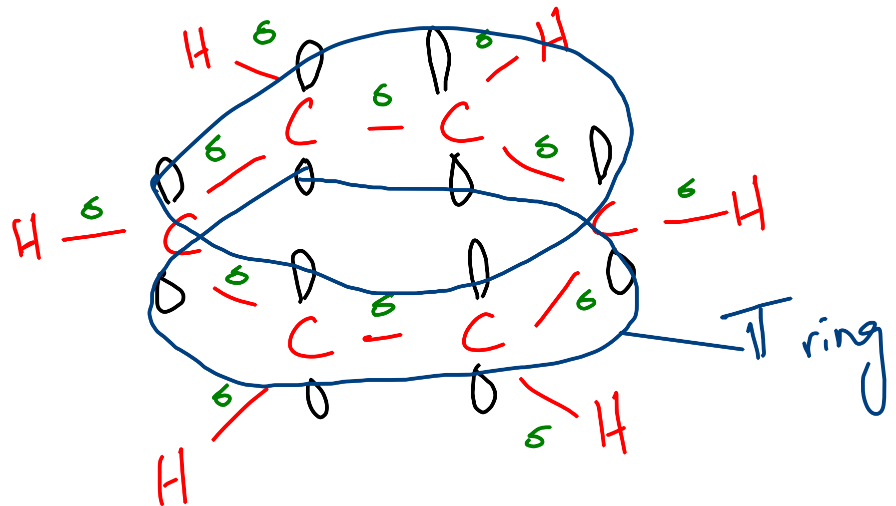
- Each carbon atom is sp^2 hybridised
- Each carbon bonds to 2 other carbon atoms and a hydrogen via σ bonds
- The unhybridised p orbital on each C atom undergoes sideways overlap
- electron density is delocalised in the ring with 6π electrons present in it
- Bond angle: 120°
- Arrangement: trigonal planar

Vs.

Structure of cyclohexane



- Each C atom is sp^3 hybridised
- Each C atom bonds to 2 C atoms and 2 H atoms via σ bonds
- electron density is localised with each carbon
- bond angle: 109.5°
- Arrangement: tetrahedral



- The π ring is very stable
- It does not go under addition reactions
- It goes under substitution reactions to preserve π ring

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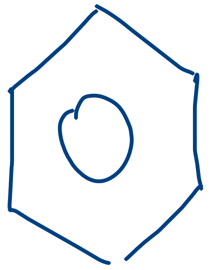
Benzene is very different from alkenes:-

1) Does not react with cold or hot $KMnO_4$
2) Does not decolourise Br_2 without catalyst
3) The bond lengths are all equal whereas C=C are shorter than C-C.

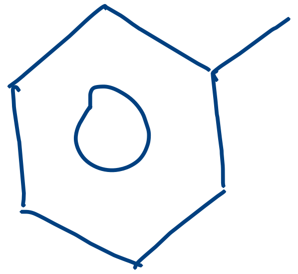
Name the following:-

1)



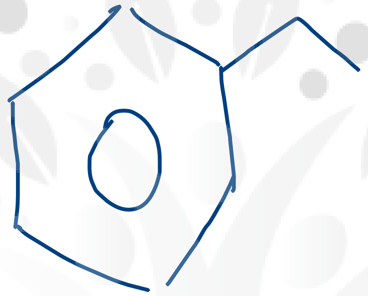
Benzene

2)



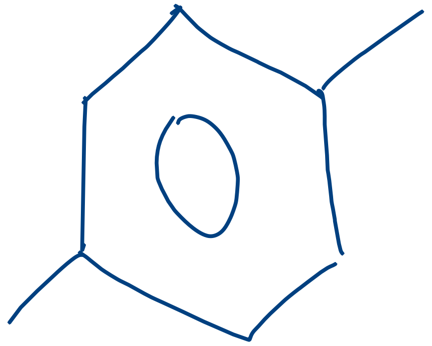
methylbenzene

3)



ethylbenzene

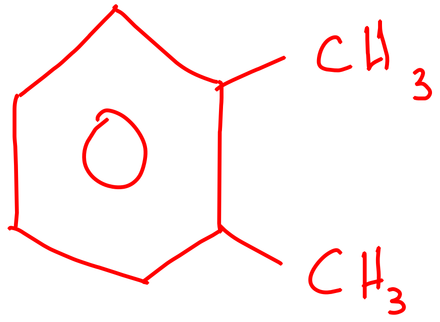
4)



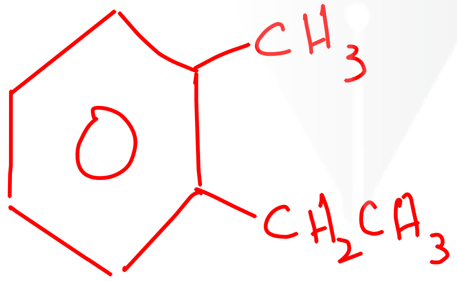
1,4- dimethylbenzene

Draw the following:-

1) 1,2-dimethyl benzene



2) 2- ethyl - methylbenzene



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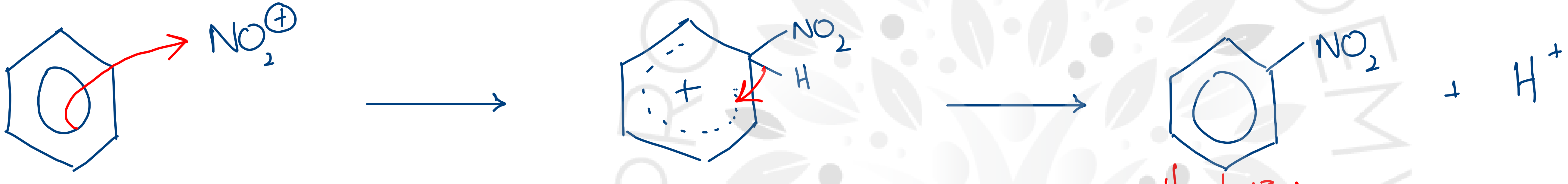
Chemical reactions of Benzene:-

i) Nitration of Benzene:- conc. HNO_3 + conc H_2SO_4 + heat (temp: 55°C) [Electrophillic substitution]

- Step 1 (Production of NO_2^+ electrophile):- $HNO_{3(aq)} + \underset{(catalyst)}{H_2SO_{4(aq)}} \longrightarrow NO^+_{2(g)} + HSO^-_{4(aq)} + H_2O_{(l)}$

- Step 2 (Electrophillic Substitution):-



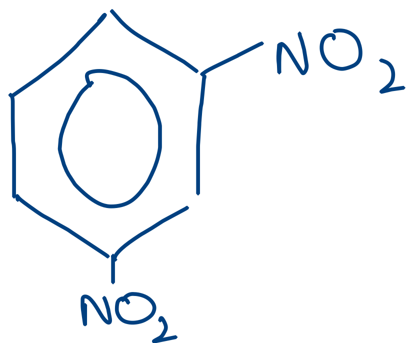
- arrow from π ring passing through carbon atom where NO_2 will attach

- disrupted π ring

Step 3 (Regeneration of Catalyst):- $H^+_{(aq)} + HSO^-_{4(aq)} \longrightarrow H_2SO_{4(aq)}$

If a higher temperature (T ≥ 60°C) is used, a further substitution takes place.

Note:- NO_2 directs to 3 position.



1,3 -dinitro benzene

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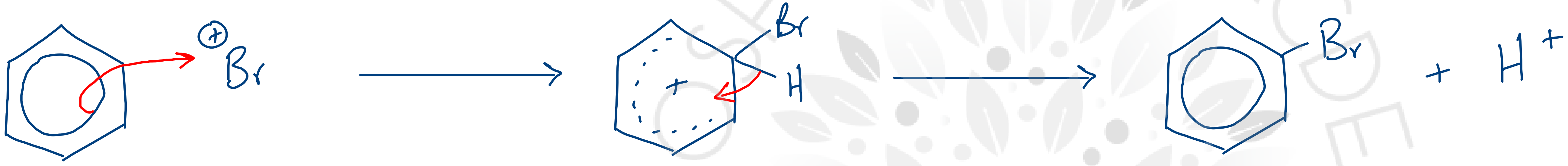
2) Bromination or Chlorination :- Br_2 / Cl_2 + $AlBr_3 / AlCl_3$ [Electrophillic Substitution]

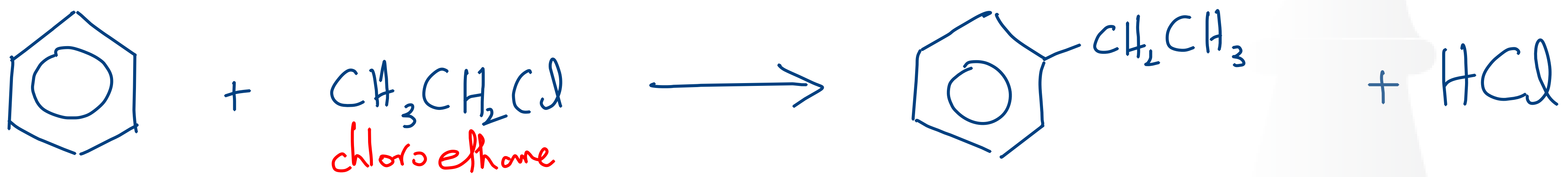
- Step 1 (Production of Br^+ electrophile) :- $Br_2 + \underset{\text{catalyst}}{AlBr_3} \longrightarrow AlBr_4^- + Br^+$
- Step 2 (Electrophillic Substitution) :-



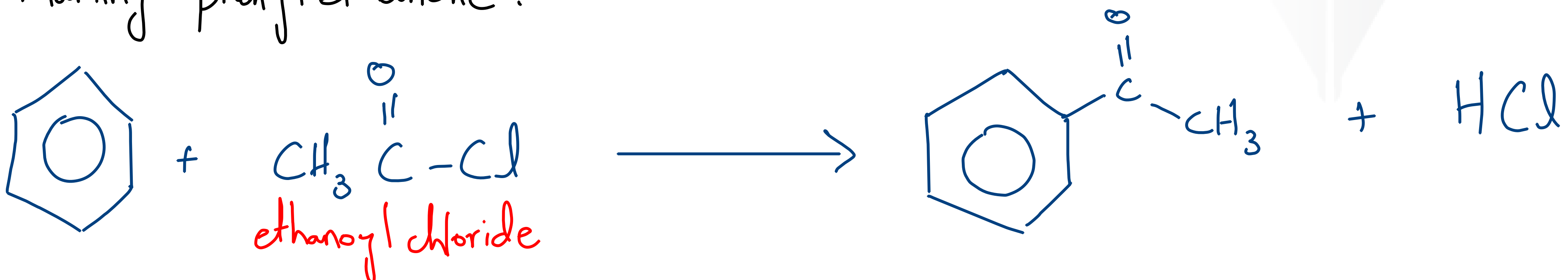
- Step 3 (Regeneration of Catalyst) :- $H^+ + AlBr_4^- \longrightarrow AlBr_3 + HBr$

3) Friedel Crafts Alkylation / Acylation :- Sidechain – Cl + $AlCl_3$ + heat [Electrophillic Substitution]

1) Making ethyl benzene :-



2) Making phenylethanone :-



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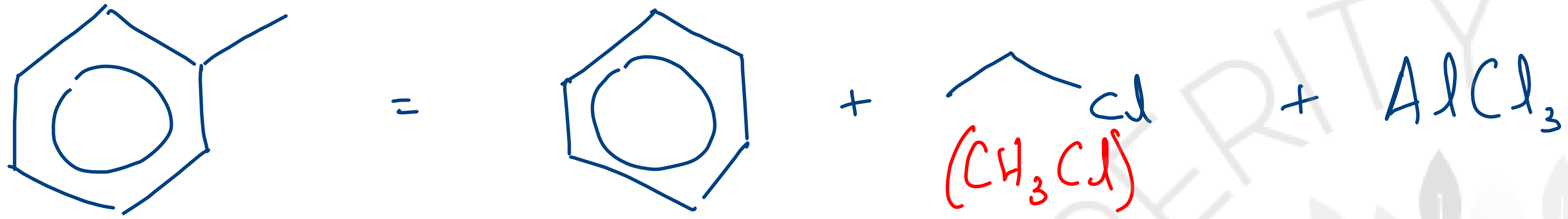
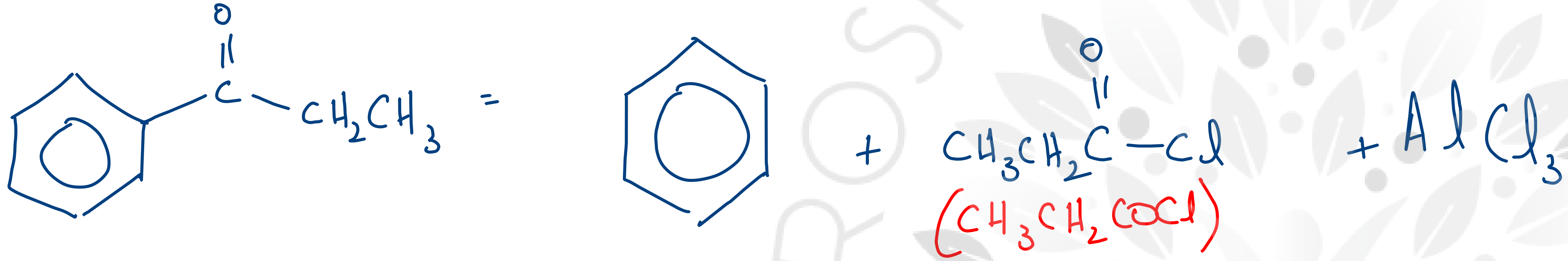
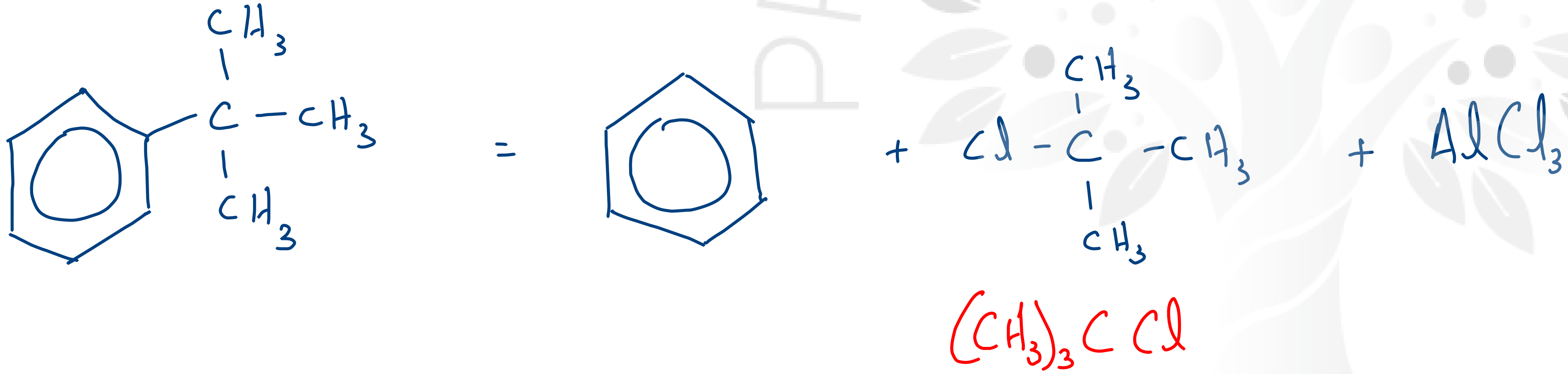
Q. Deduce reagents for making the following :-

1)


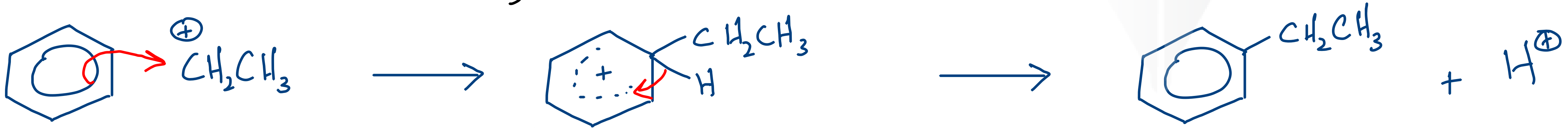
2)


3)


Mechanism for 2 :-

Step 1 (Production of electrophile) :- $CH_3CH_2COCl + AlCl_3 \longrightarrow AlCl_4^- + CH_3CH_2\overset{\oplus}{C}O$

Step 2 (Electrophilic Substitution) :-



Step 3 (Regeneration of catalyst) :- $AlCl_4^- + H^+ \longrightarrow AlCl_3 + HCl$

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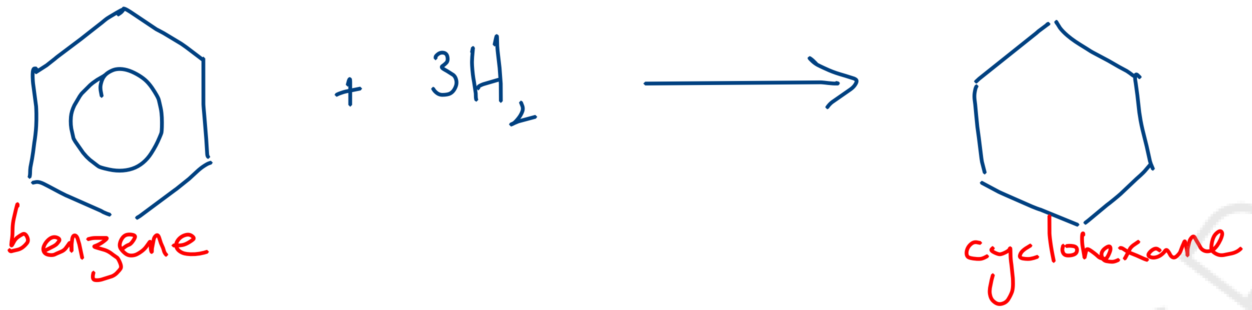
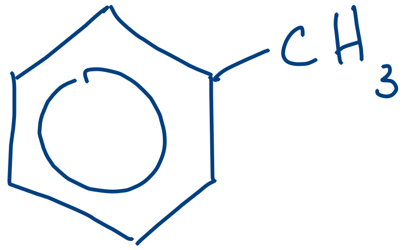
4) Hydrogenation:- $H_2(g)$ + Ni + 150°C (heat)

catalyst



Methylbenzene (or any other alkyl-benzene/arene):- $C_6H_5CH_3$

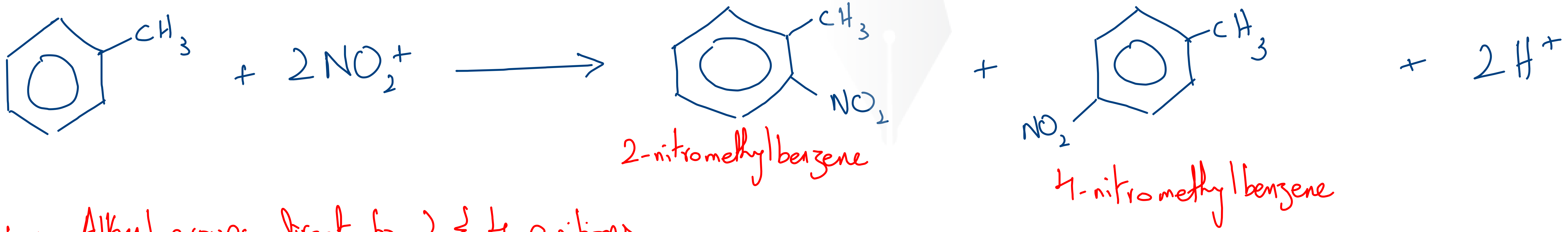


-The methyl group pushes its electron density towards the π ring making it more active!

Chemical reactions of Methylbenzene:-

1) Nitration:- conc HNO_3 + conc H_2SO_4 + heat (but only 30°C) [Electrophillic Substitution]

-This time you get 2 isomers without changing conditions:-



Note:- Alkyl groups direct to 2 & 4 positions

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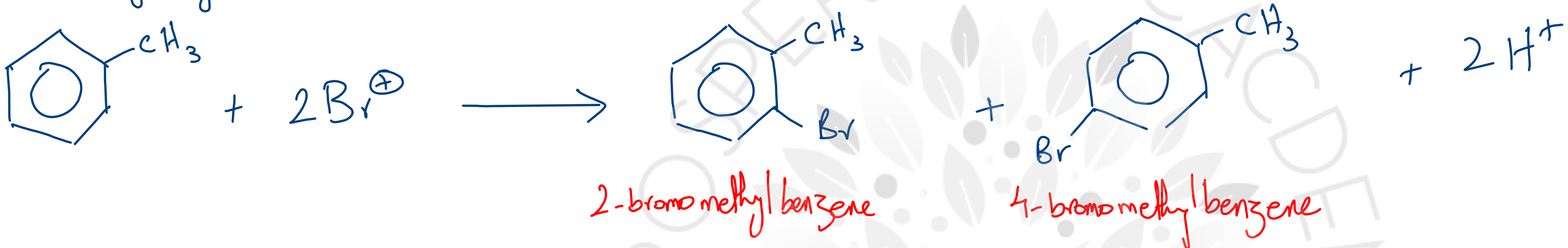
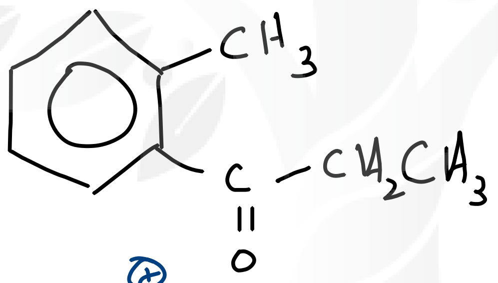
2) Bromination / Chlorination :- Br_2 / Cl_2 + $AlBr_3 / AlCl_3$ [Electrophillic Substitution]

- To make sure free radical substitution does not occur, do reaction in dark.
- This time you get 2 isomers:-

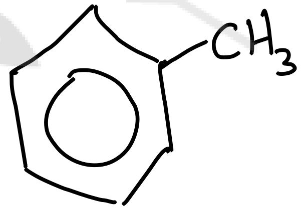


3) Friedel Crafts Alkylation/Acylation :- Sidechain -Cl + $AlCl_3$ + heat [Electrophillic Substitution]

Q. Give the complete mechanism of formation of

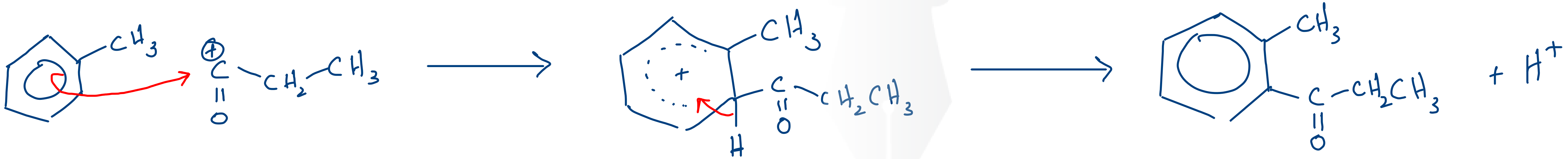


from



Step 1 :- $CH_3CH_2COCl + AlCl_3 \longrightarrow AlCl_4^- + CH_3CH_2\overset{\oplus}{C}O$

Step 2:-



Step 3:- $H^+ \; AlCl_4^- \longrightarrow AlCl_3 + HCl$

Give one observation:- Steamy fumes of HCl

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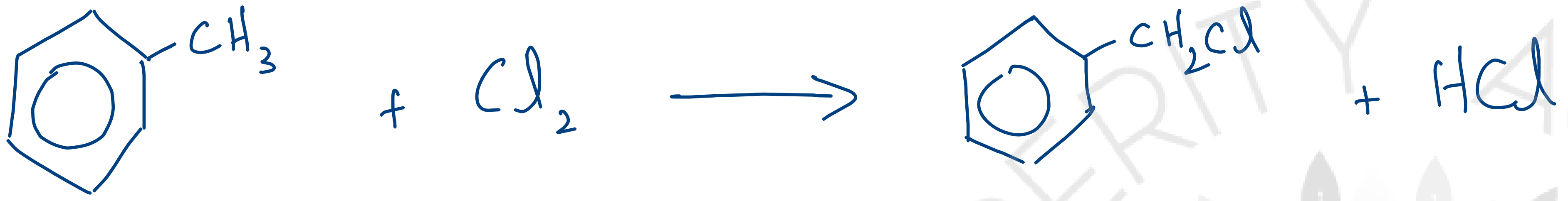
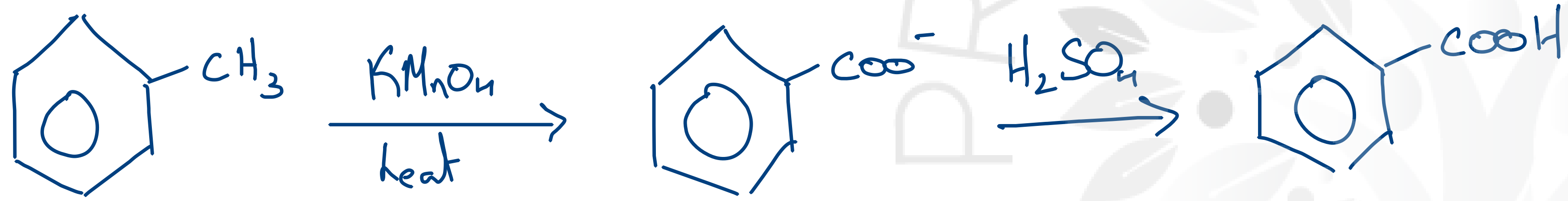
4) Free radical Substitution :- Cl_2/Br_2 + U.V light (no catalyst)



5) Oxidation to COOH :- $KMnO_4$ + heat + dil. H_2SO_4 (to protonate)

- Any carbon group attached to benzene ring will turn to COOH.

1)



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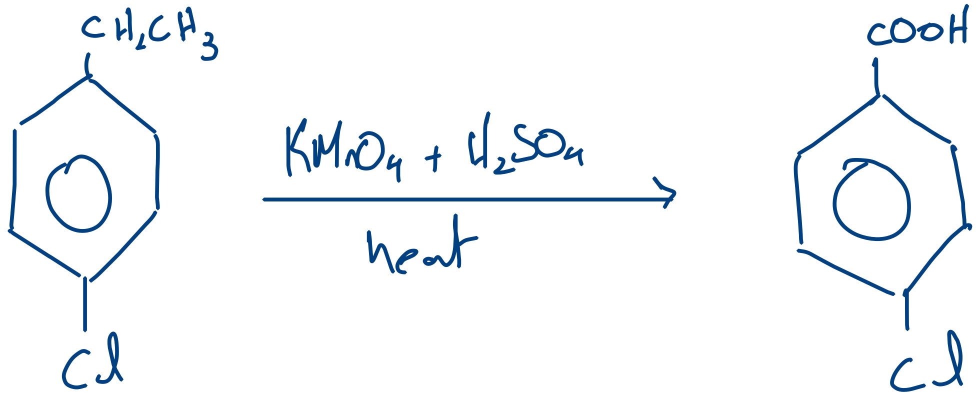

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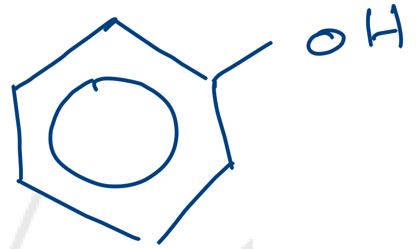
Phenols:- Benzene rings with OH group. C_6H_5OH



Name the following:-

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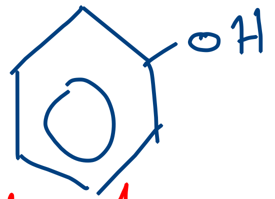
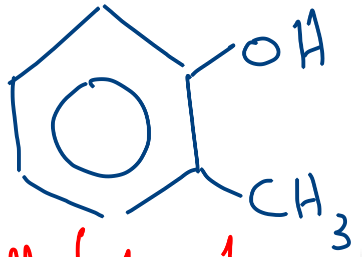


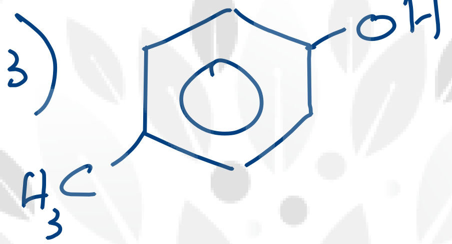
phenol

2)



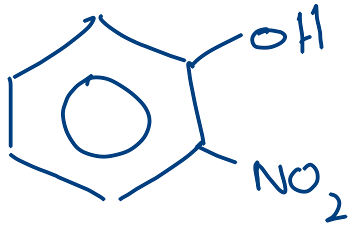
2-methylphenol

3)



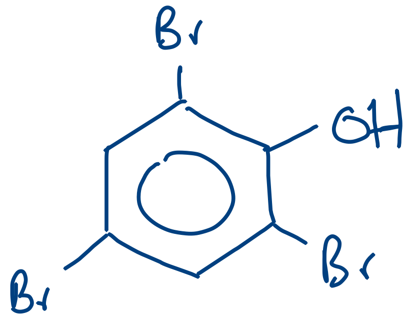
4-methylphenol

4)



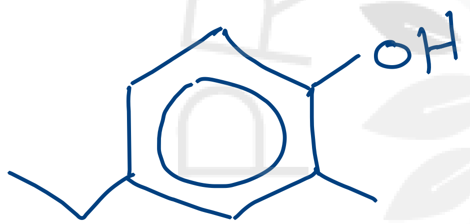
2-nitro phenol

5)



2,4,6-tribromophenol

6)



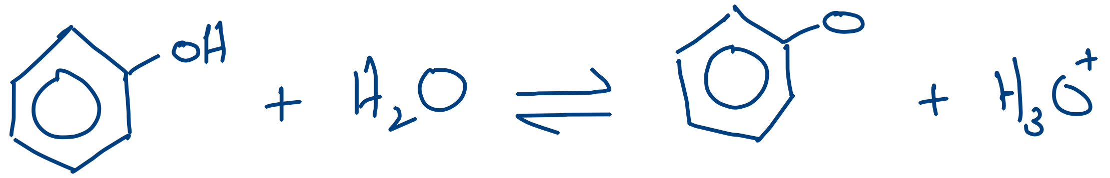
4-ethyl-2-methylphenol

Chemical reactions of phenol:-

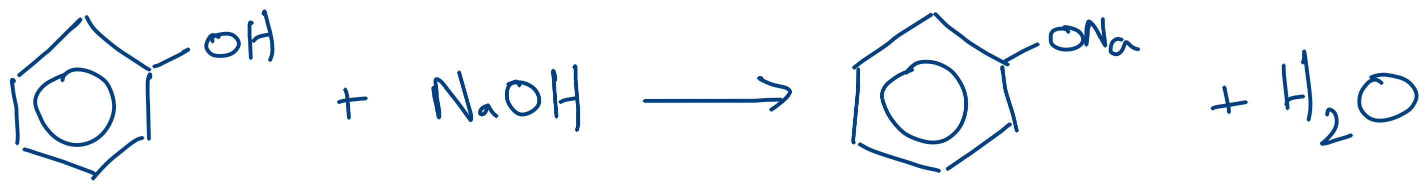
- The lone pairs on the oxygen atom delocalise in the π ring making it more active

1) Phenol is acidic:- Phenol is a weak acid.

1) In aqueous solution



2) In alkali



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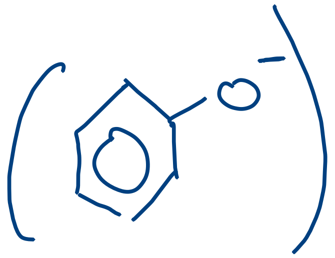
3) Phenol does not react with carbonates or hydrogencarbonates

Differentiating Alcohol, Phenol and carboxylic acids:-

Compound	Reacts with $Na_{(s)}$?	Reacts with $NaOH_{(aq)}$?	Reacts with $NaHCO_3$ or Na_2CO_3?
1) Alcohol	✓	✗	✗
2) Phenol	✓	✓	✗
3) Carboxylic	✓	✓	✓

Relative order of acidities:- ethanol $<$ H_2O $<$ phenol $<$ ethanoic acid

- When phenol acts as a Brønsted Lowry Acid and donates its H^+, the phenoxide ion formed () can be stabilised as the negative charge on the oxygen can delocalise over the π ring so that the O^- becomes less negative
- When ethanol acts as a Brønsted Lowry Acid and donates its H^+, the ethoxide ion formed ($CH_3CH_2O^-$) cannot be stabilised as the alkyl group is already pushing electron density and concentrates the negative charge on the O^-.

Q. Why is phenol not in same family as alcohols?

1) Phenol is acidic. It reacts with NaOH
2) Phenol does not get oxidised with $K_2Cr_2O_7$
3) Phenols dont undergo nucleophillic substitution with PCl_5 / PCl_3 / $SOCl_2$ / HCl. → The lone pairs on O get delocalised with the π ring and makes it very stable
4) Phenols dont react with carboxylic acids to make esters.

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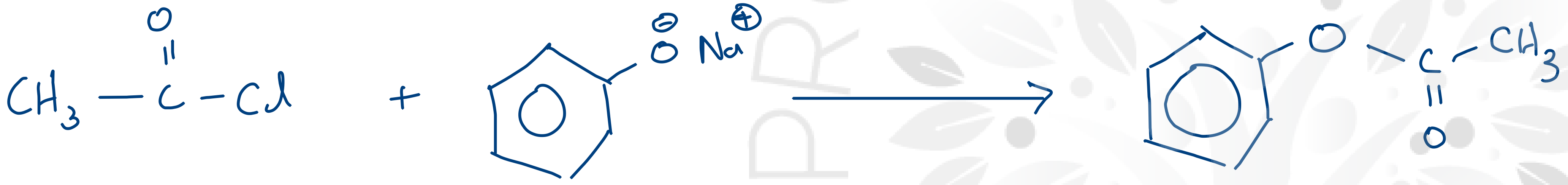
2) Reaction with Sodium :- [Redox reaction]

3) Reaction with Acyl Chlorides:- Acyl Chloride + Phenol + NaOH [Condensation reaction / Addition elimination]

- ester produced

to make phenoxide ion

1) ethanoyl chloride + phenol + NaOH



2) benzoyl chloride + phenol + NaOH

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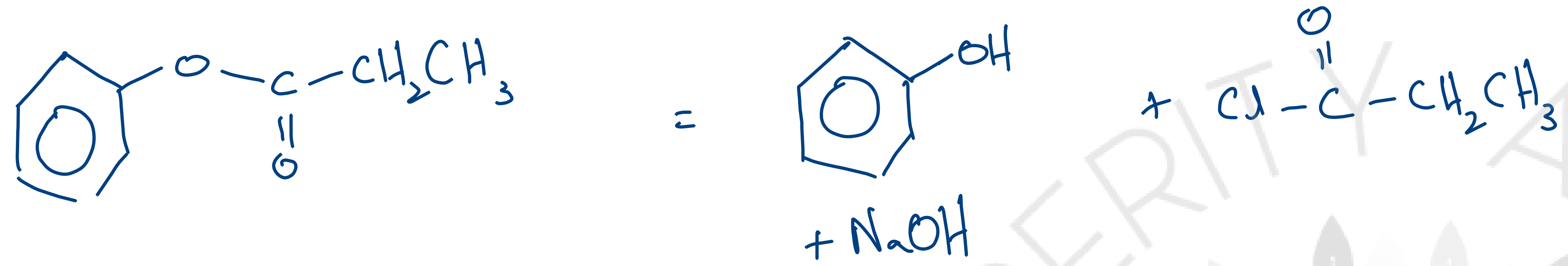
Q. Deduce the acyl chloride and phenol used to make the following:-

1)



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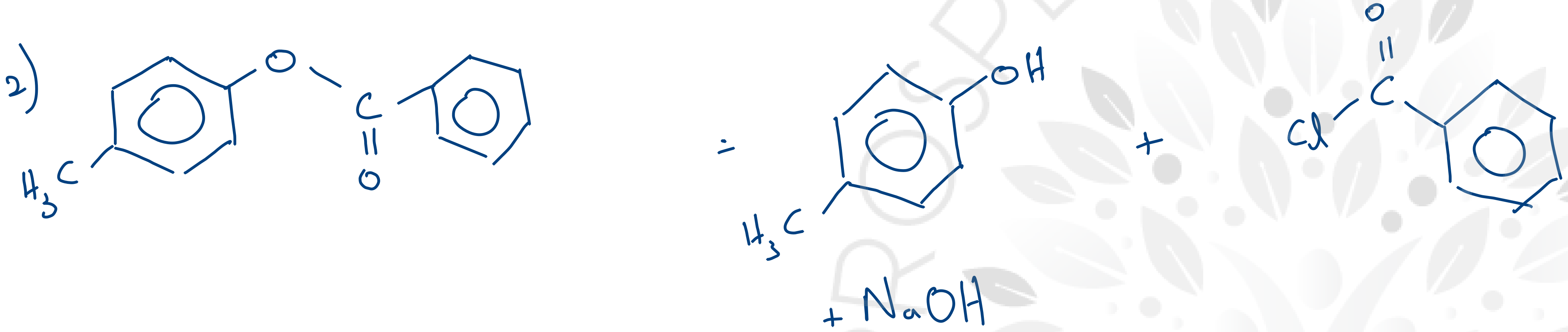
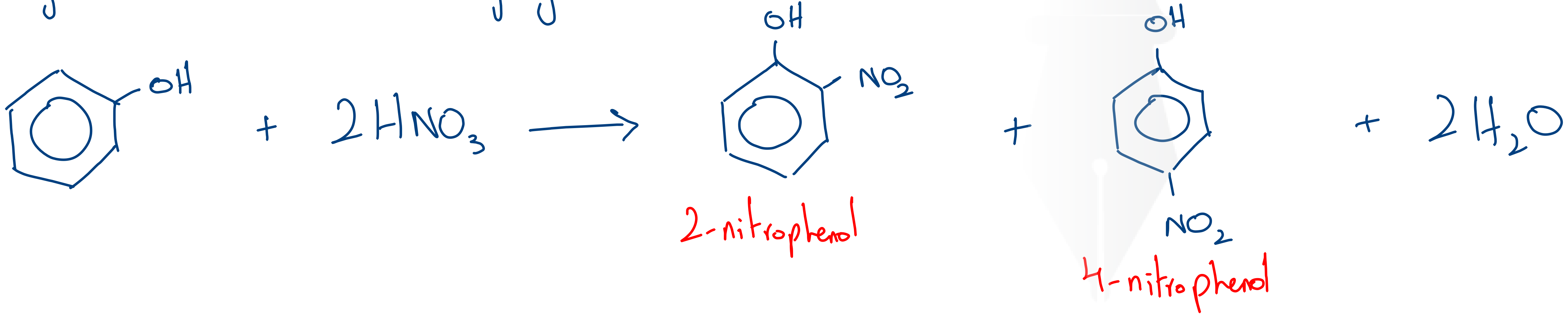


4) Nitration:- dil. HNO_3 only [Electrophillic substitution]

-milder conditions as π ring is very active due to delocalization of lone pair on Oxygen atom

- We get 2 isomers without changing conditions



Note: OH directs to 2 & 4 positions

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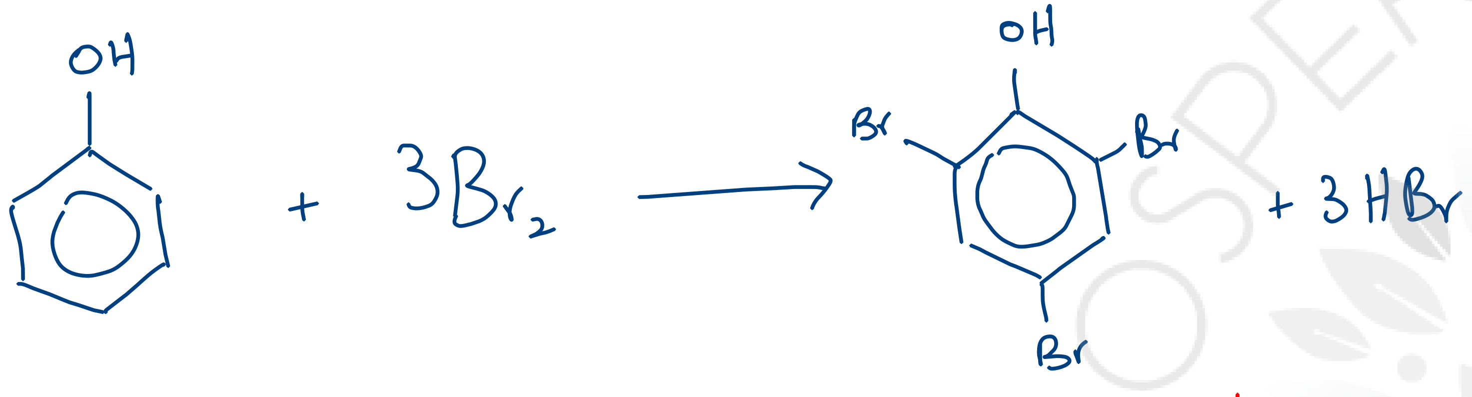
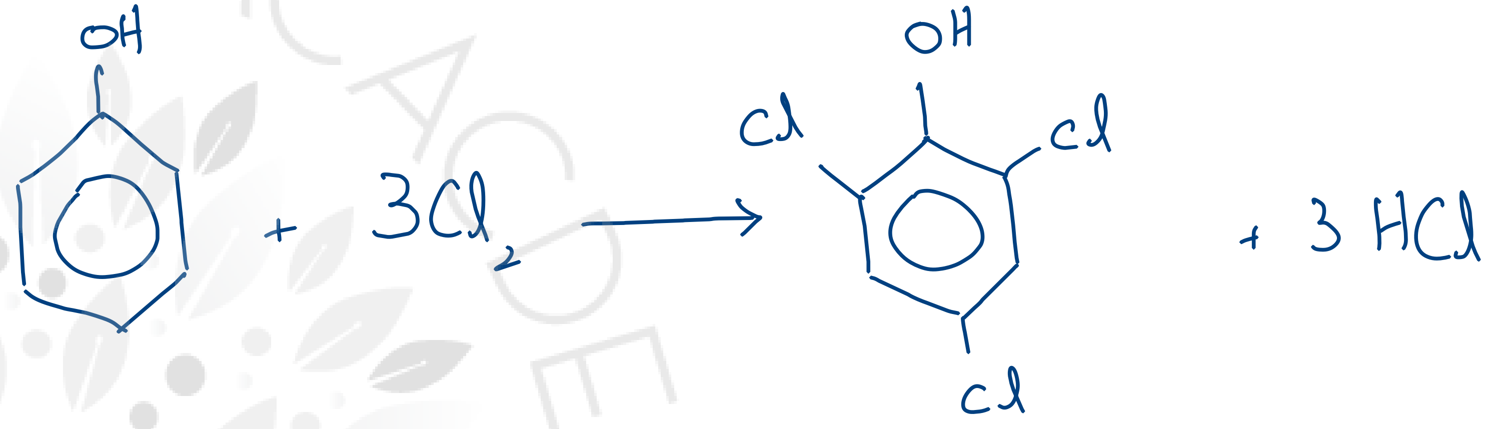
5) Bromination / Chlorination :- Br_2 / Cl_2 [Electrophillic Substitution]

- milder conditions as π ring is very active due to delocalization of lone pair on Oxygen atom
- Br/Cl gets substituted at 2,4,6 positions immediately



2,4,6-tribromophenol
(white ppt)



2,4,6-trichlorophenol
(white ppt)

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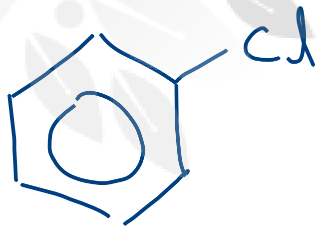
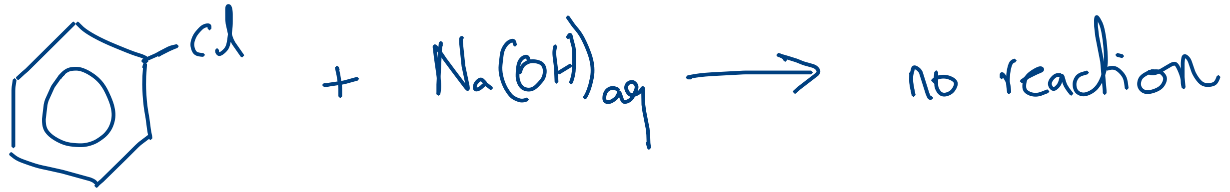
Chlorobenzene :- Cl attached to benzene ring. C_6H_5Cl



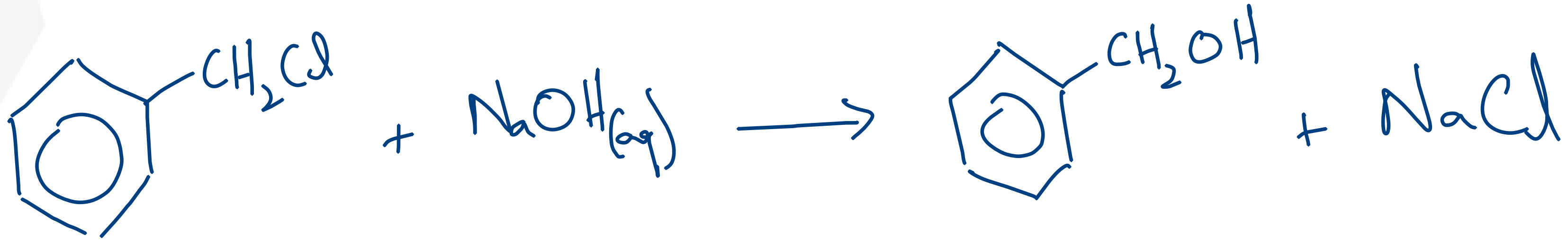
- The C-Cl bond in benzene is exceptionally strong as all of the lone pairs on chlorine delocalise over the benzene ring making it very stable
  ↳ does not give nucleophillic substitution reactions.

Q. Deduce whether or not a reaction will take place :-

i)

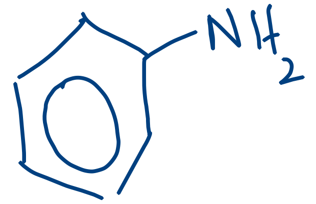


2)



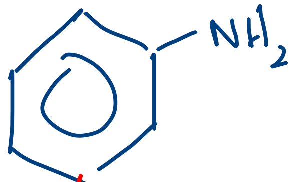
Formation of Chlorobenzene (Not very common) :- Benzene + Cl_2 + $AlCl_3$ + heat

Phenylamine:- NH_2 attached to benzene ring. $C_6H_5-NH_2$

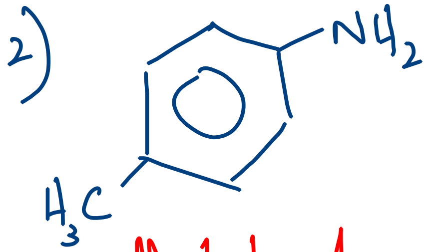


-The lone pair on nitrogen gets delocalised in the π ring making it more active.

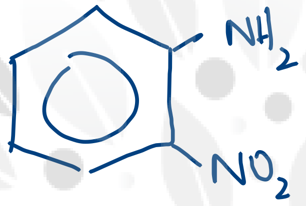
Name the following:-

1)


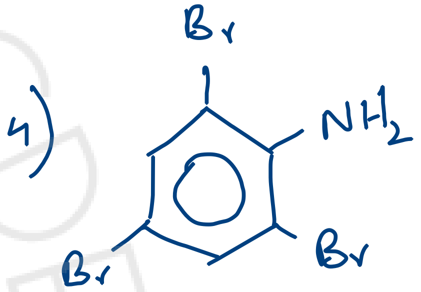
phenylamine

2)


4-methylphenylamine

3)


2-nitrophenylamine

4)


2,4,6-tribromophenylamine

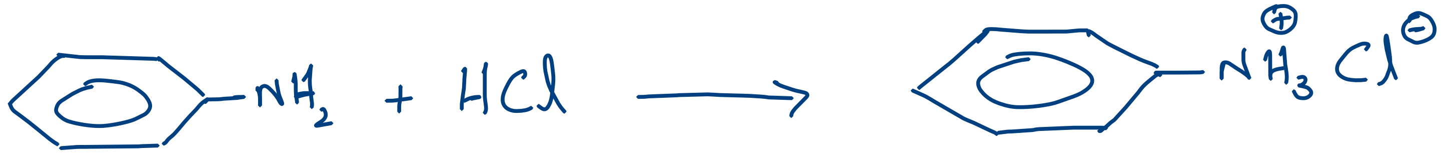
Formation:- nitrobenzene + tin metal + conc. HCl + Heat under reflux + (in the end) dil NaOH [Reduction]

Chemical reactions of phenylamine:-

1) Phenylamine is a base:- Phenylamine is a weak base

1) In aqueous solution:-

2) In acid:-



PROSPERITY ACADEMY

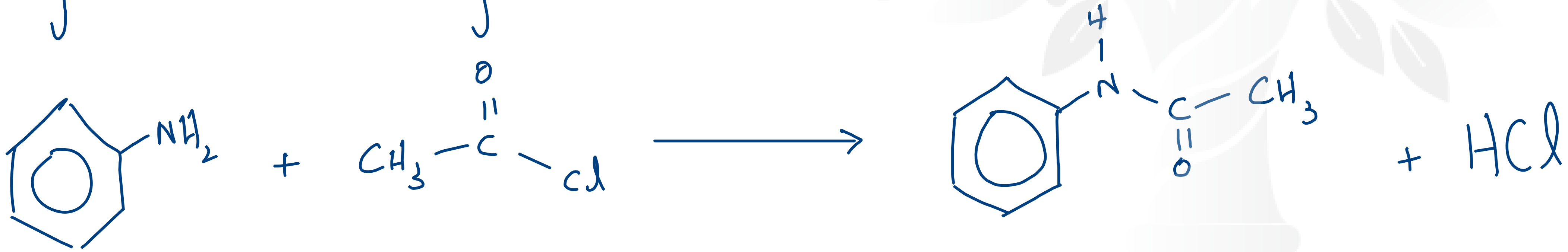
Relative order of basicities :- ethylamine ($CH_3CH_2NH_2$) > Ammonia > phenylamine

- ethylamine is a stronger base as the alkyl group pushes its electron density towards the NH_2 group making the lone pair on N more available to form a dative bond to H^+
- phenylamine is a weak base as the lone pair on the Nitrogen atom gets delocalised with the π ring making it less available to form a dative bond.

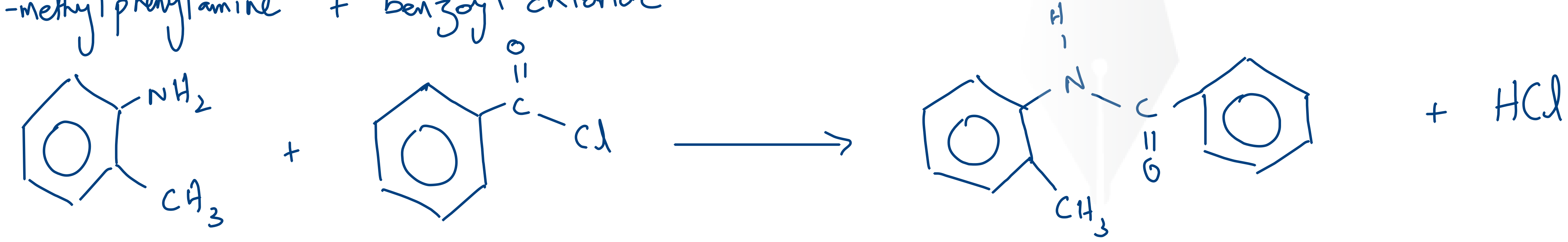
Chemical reactions of phenyl amine :-

1) Reaction with Acyl chlorides:- Acyl chloride + phenylamine [Condensation / Addition-elimination]

i) phenyl amine + ethanoyl chloride



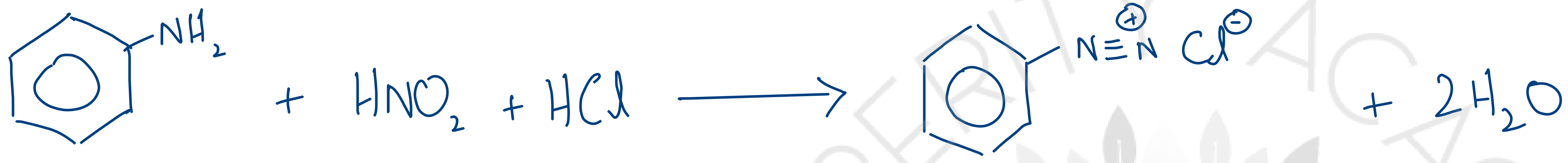
2) 2-methylphenylamine + benzoyl chloride



Steamy fumes of HCl will be observed.

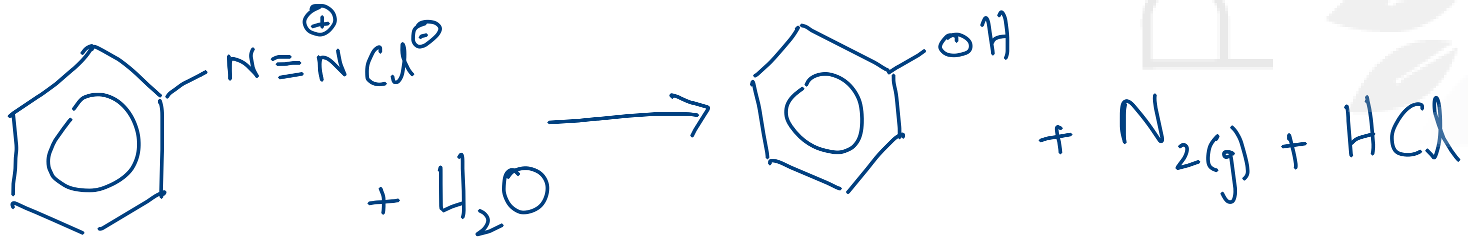
PROSPERITY ACADEMY

2) Formation of Diazonium salt:- phenylamine + HNO_2 + 5°C (ice/water bath) / phenylamine + $NaNO_2$ + HCl + 5°C (ice/water bath)



Formation of phenol:- Add water + heat [Hydrolysis]

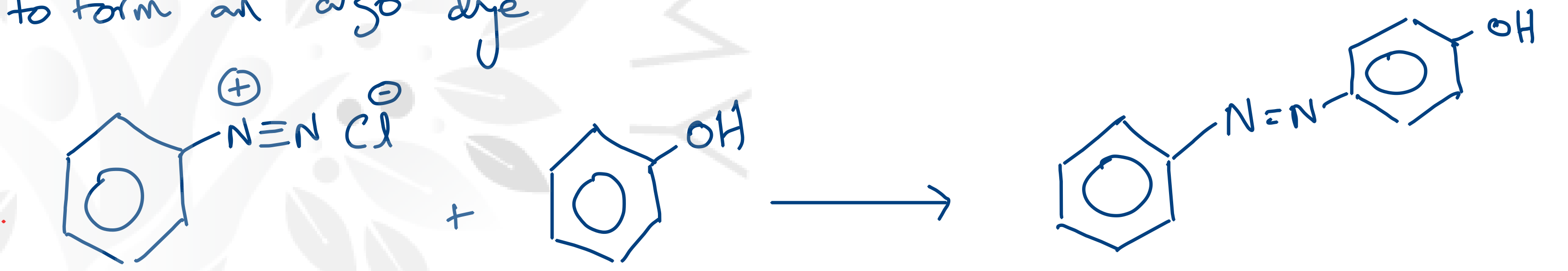
- If temperature is not kept at 5°C, the diazonium salt rapidly hydrolyses to phenol



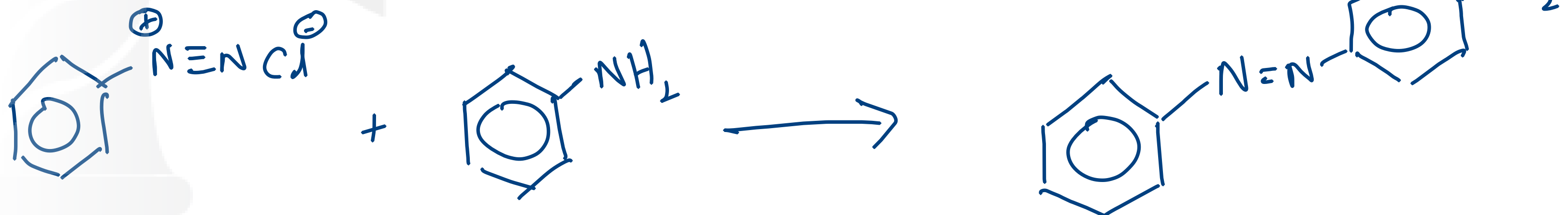
[Electrophilic Substitution] Formation of Azo Dyes:-

- the diazonium salt reacts with phenols or phenylamines (active benzene rings) to form an azo dye

e.g.



e.g.

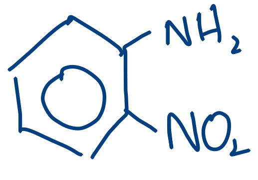


3) Nitration/Chlorination/Bromination:-

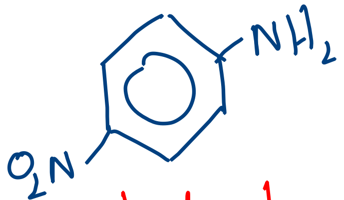
- The same conditions as phenols are used as the benzene ring is active.
- The NH_2 group also directs to 2 & 4 positions.

Draw the structure of the products formed when phenylamine is (i) nitrated (ii) chlorinated

(i)

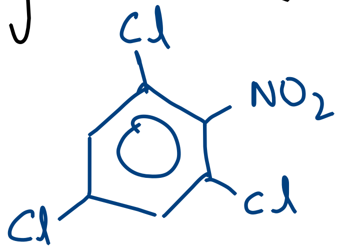


2-nitrophenylamine



4-nitrophenylamine

(ii)



2,4,6-trichlorophenylamine

Deflection by groups:-

Deflection to 2, 4, 6 position:- OH, NH_2, CH_3/ -R, Cl, Br

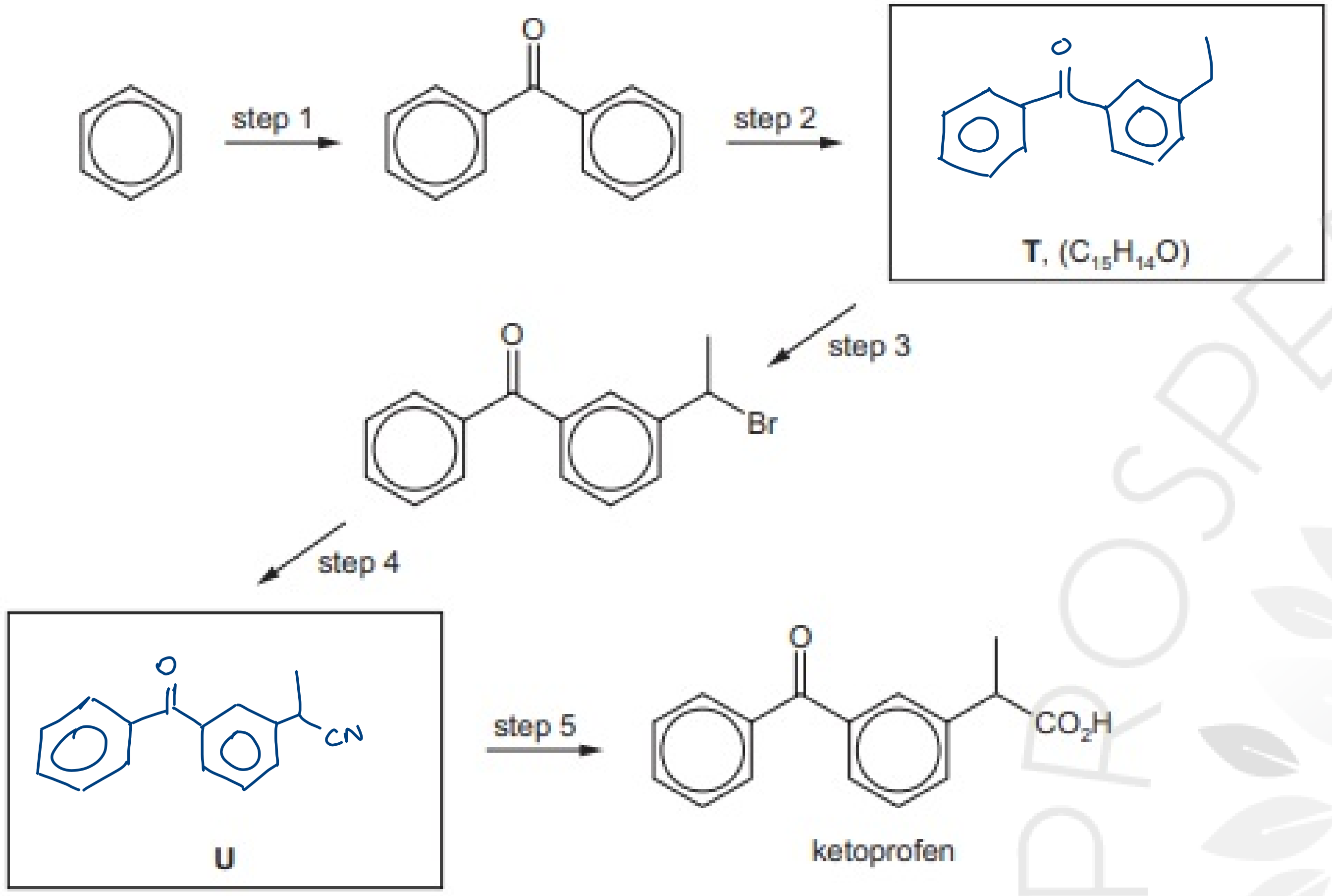
Deflection to 3 position:- NO_2, COOH, COR, COOR

carbonyl

ester

PROSPERITY ACADEMY

9 The anti-inflammatory drug ketoprofen can be synthesised from benzene via the following five steps.



(a) Suggest the structures of compounds **T** and **U** and draw them in the boxes above. [2]

(b) Suggest reagents and conditions for steps 1-5.

step 1 C_6H_5COCl + $AlCl_3$ + heat

step 2 CH_3CH_2Cl + $AlCl_3$ + heat

step 3 Br_2 + U.V light

step 4 KCN in ethanol + heat under reflux

step 5 dil. H_2SO_4 + heat

[5]

(c) What *types of reaction* are steps 1 and 5?

step 1 electrophillic substitution

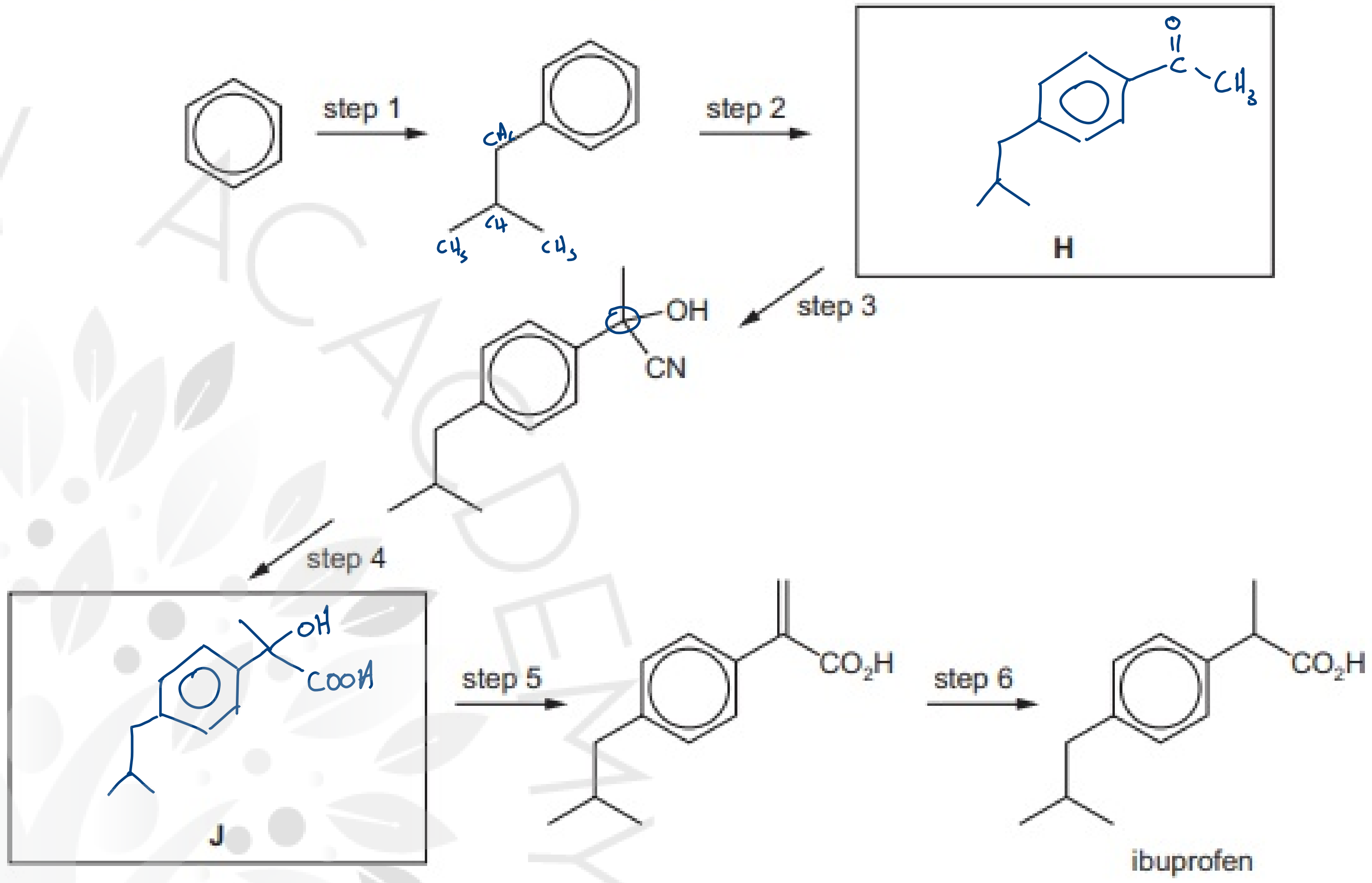
step 5 hydrolysis

[2]

[Total: 9]

---

9 The anti-inflammatory drug ibuprofen can be synthesised from benzene via the following six steps.



(a) Draw circles around any chiral carbon atoms in the above five formulae. [1]

(b) Suggest the structures of compounds **H** and **J** and draw them in the boxes above. [2]

(c) Suggest reagents and conditions for steps 1-6.

step 1 $(CH_3)_2CHCH_2Cl$ + $AlCl_3$ + heat

step 2 CH_3COCl + $AlCl_3$ + heat

step 3 HCN in NaCN

step 4 dil H_2SO_4 + heat

step 5 conc. H_2SO_4 + heat

step 6 H_2 + Ni + 150°C (heat)

[6]

(d) Name the mechanism of step 1 and state the *type of reaction* for step 6.

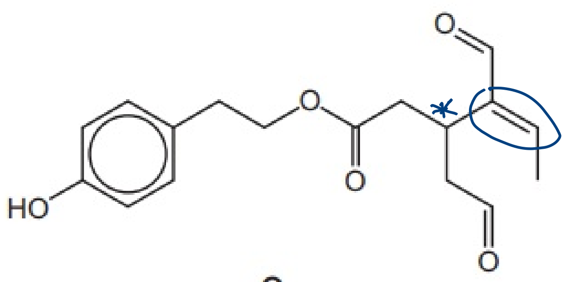
step 1 electrophillic substitution

step 6 Hydrogenation / reduction / addition

[2]

PROSPERITY ACADEMY

6 Oleocanthal, **Q**, is a natural compound found in olive oil. It has antioxidant and anti-inflammatory properties and is thought to have a protective effect against Alzheimer's disease.

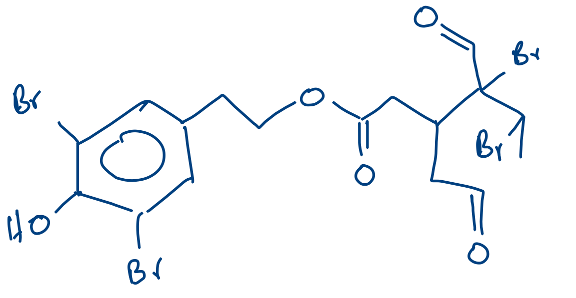
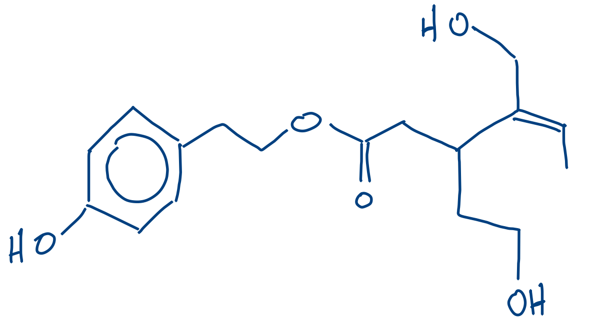
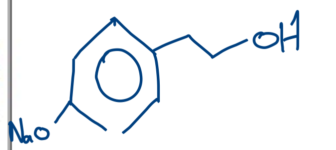
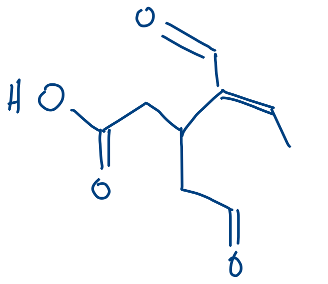


Q

(a) **Q** shows optical and cis-trans isomerism.

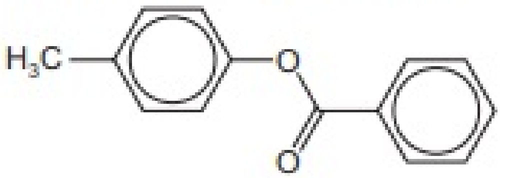
On the structure of **Q** above, **circle** the functional group that shows cis-trans isomerism and indicate with an **asterisk** (*) the chiral carbon atom. [1]

(c) Complete the following table to show the structures of the products formed when **Q** reacts with the three reagents.

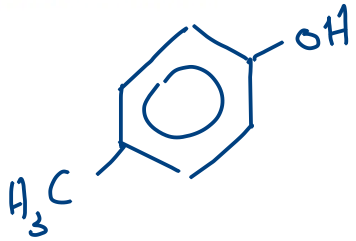
reagent	structure of product(s)		type of reaction
excess $Br_2(aq)$			electrophillic substitution and addition
$NaBH_4$			Reduction
excess hot NaOH(aq)			hydrolysis (acid-base too)

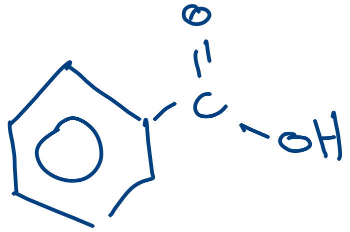
[6]

(c) The ester 4-methylphenyl benzoate is used in the manufacture of perfumes.

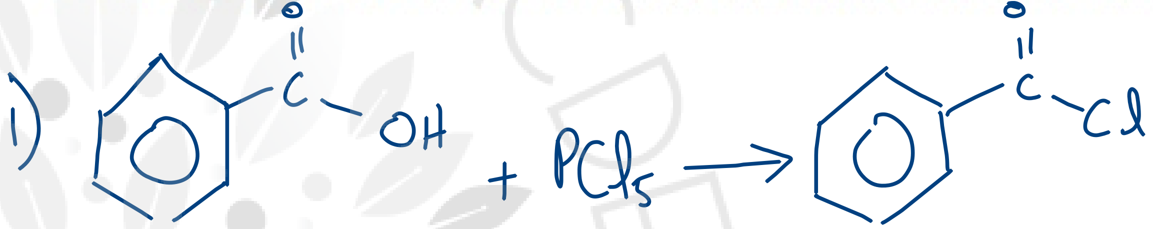


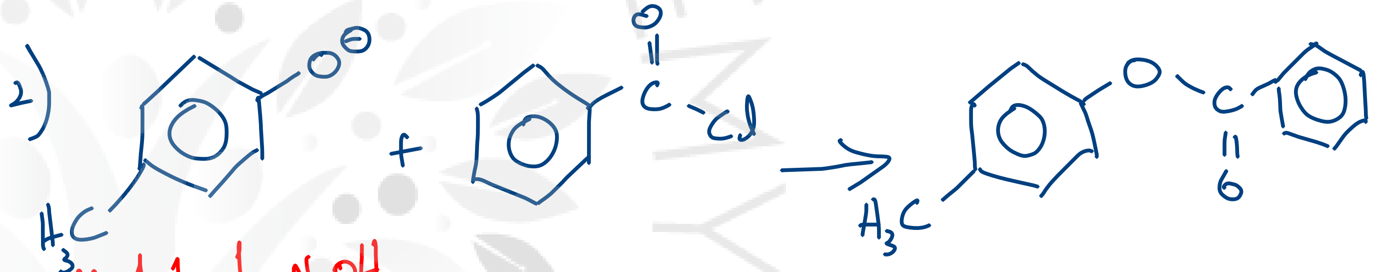
4-methylphenyl benzoate





Suggest a **two**-step route for the synthesis of 4-methylphenyl benzoate from 4-methylphenol and benzoic acid.
Include reagents and conditions for each step, and the structure of the intermediate compound.





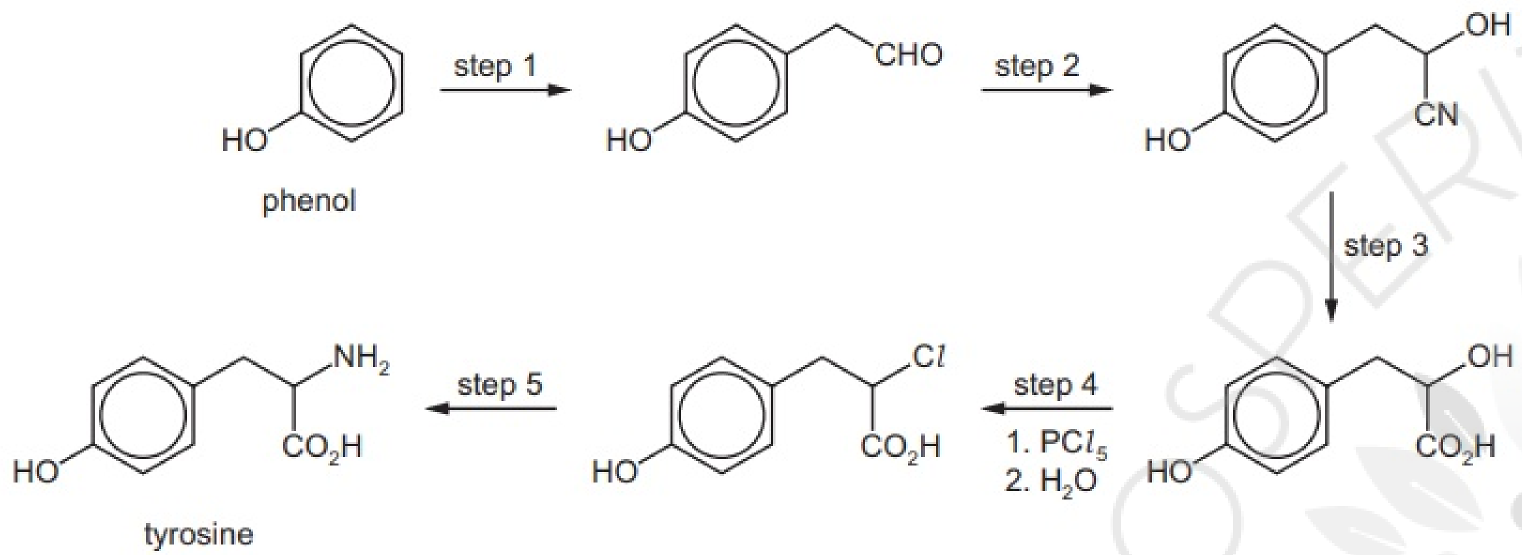
4 methyl phenol + NaOH

showing only organic products

[3]

PROSPERITY ACADEMY

8 **(a)** The amino acid tyrosine can be synthesised from phenol by the route shown.



(i) Name the mechanism occurring in the following steps.

step 1 electrophillic substitution

step 2 nucleophillic addition

[2]

(ii) What type of reaction is occurring in step 3?

hydrolysis [1]

(iii) Suggest reagents and conditions for each of the following steps.

step 1 $CHOCH_2Cl + AlCl_3$

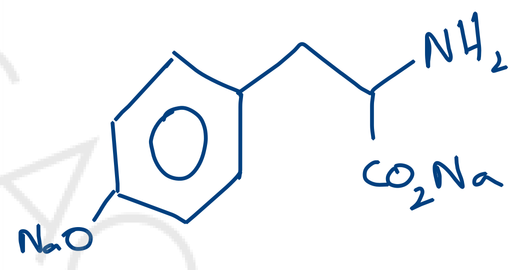
step 2 HCN in KCN/NaCN

step 3 dil. H_2SO_4 + heat

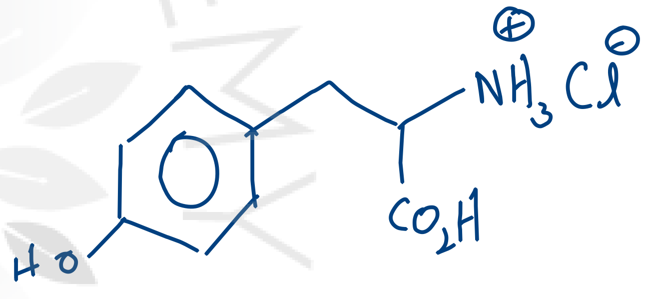
step 5 ethanolic ammonia + heat in sealed tube under pressure

[5]

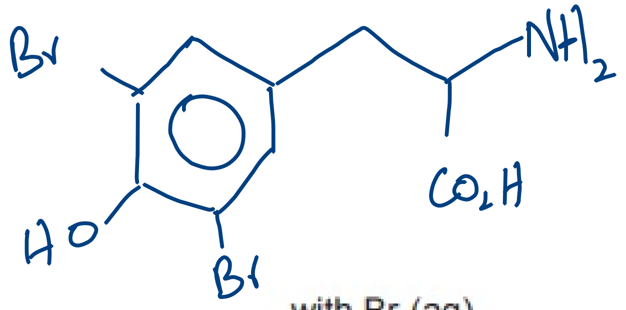
(iv) Draw the structures of the products of the reactions of tyrosine with an **excess** of each of the following reagents.



with NaOH(aq)



with HCl(aq)

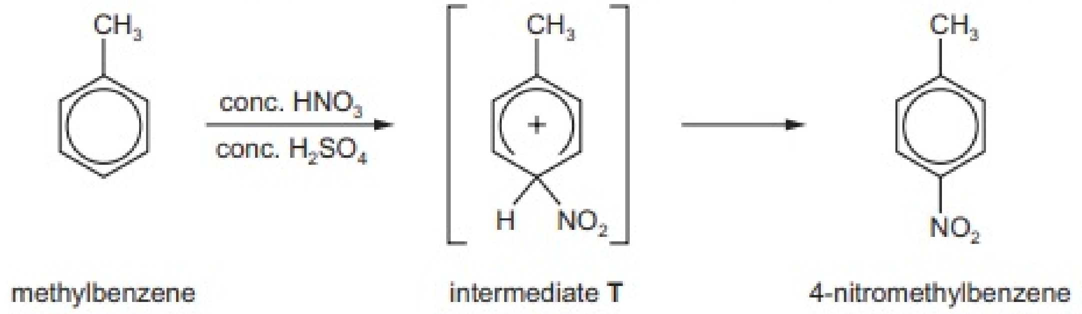


with Br$_2$(aq)

[4]

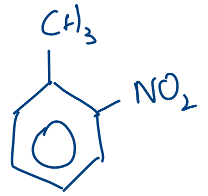
PROSPERITY ACADEMY

6 **(a)** 4-nitromethylbenzene can be prepared via an electrophilic substitution reaction as shown.



(i) This reaction also forms an isomer of 4-nitromethylbenzene as a by-product.

Draw the structure of this by-product.



[1]

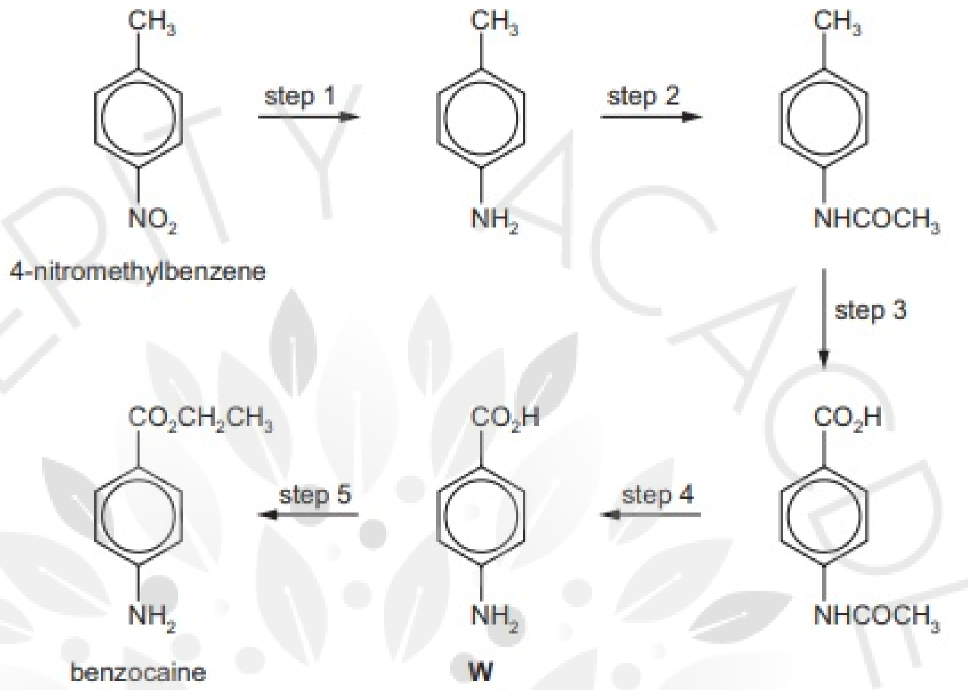
(ii) Write an equation for the reaction between HNO_3 and H_2SO_4 that forms the electrophile for this reaction.

$HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + HSO_4^- + H_2O$ [1]

(iii) Describe how the **structure and bonding** of the six-membered ring in intermediate **T** differs from that in methylbenzene.

All bond angles in the benzene ring in methylbenzene are 120° and arrangement trigonal planar while in the intermediate 1 carbon has bond angle 109.5° and arrangement tetrahedral. One of the carbon atoms in the intermediate is sp^3 hybridised while methyl benzene [3] has all sp^2 hybridised carbons in the ring. In methyl benzene the delocalised π bonding extends over 6 Carbon atoms while in the intermediate it only extends over 5 carbon atoms.

(b) Benzocaine is used as a local anaesthetic. It can be synthesised from 4-nitromethylbenzene by the route shown.



(i) Give the systematic name of compound **W**.

4-amino benzoic acid [1]

(ii) Suggest the reagents and conditions for steps 1–5.

step 1 tin metal + conc. HCl + heat under reflux followed by dil NaOH

step 2 CH_3COCl

step 3 $KMnO_4$ + heat + dil H_2SO_4

step 4 dil. H_2SO_4 + heat

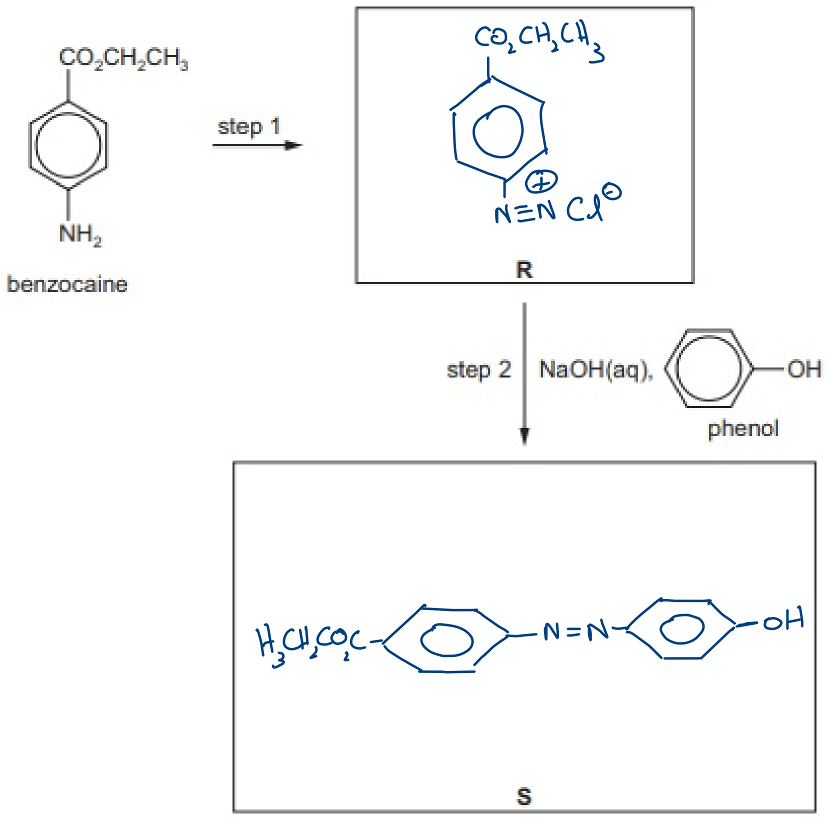
step 5 CH_3CH_2OH + dil. H_2SO_4 + heat

[6]

(c) Suggest how the basicity of benzocaine would compare to that of ethylamine. Explain your answer.

benzocaine will be less basic as the lone pair on N atom gets delocalised over the π ring making it less available to form a dative bond to H^+ while in ethylamine the lone pair on N atom is more available as the ethyl group pushes its electron density towards it. [2]

(e) Benzocaine can also be used to synthesise the dyestuff **S** by the following route.



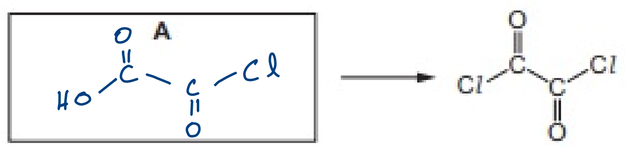
(i) Suggest the reagents used for step 1.

$NaNO_2$ + HCl + 5°C (ice/water bath) [1]

(ii) Suggest structures for compounds **R** and **S** and draw them in the boxes. [2]

PROSPERITY ACADEMY

7 Ethanedioyl dichloride, ClCOCOCl, is a useful reagent in organic synthesis. It can be made from compound **A** in one step.

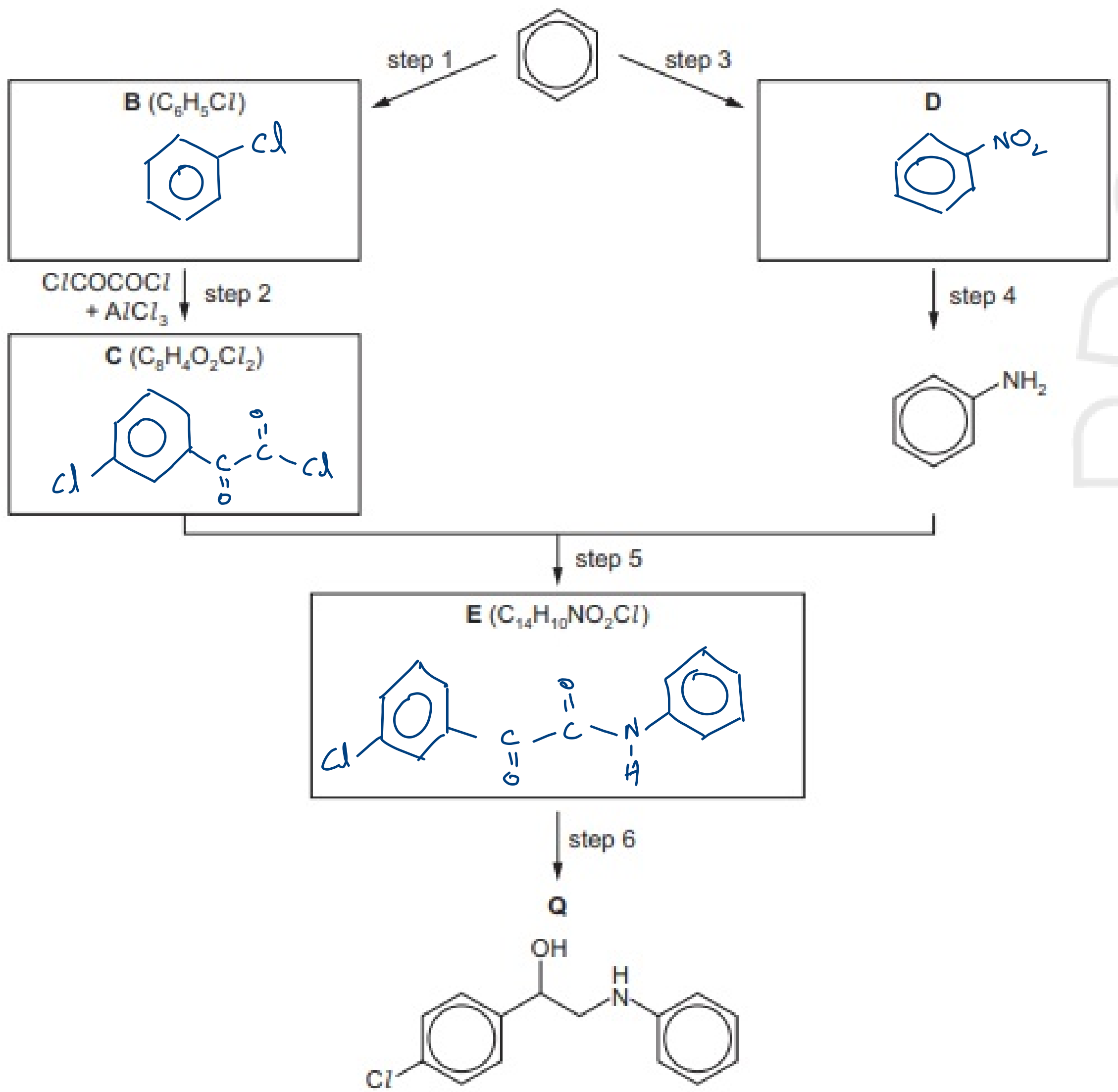


(a) (i) Suggest the identity of compound **A** by drawing its structure in the box. [1]

(ii) State the reagents and conditions needed to convert **A** into ClCOCOCl.

PCl_5 [1]

Ethanedioyl dichloride is used in the following synthesis of compound **Q**. It is used in a 1:1 stoichiometric ratio with **B** in step 2.



(b) (i) Suggest the identities of the compounds **B**–**E** by drawing their structures in the boxes. [4]

(ii) State the reagents and conditions for the following steps.

step 1 $Cl_2 + AlCl_3$ + heat

step 3 conc HNO_3 + conc H_2SO_4 + 55°C (heat)

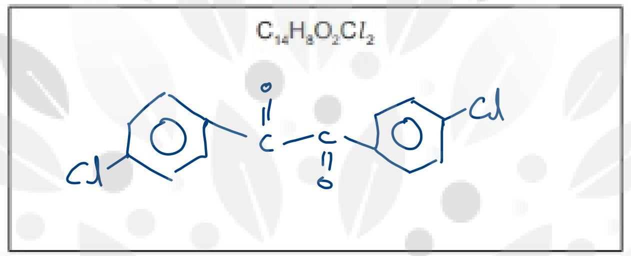
step 4 tin metal + conc. HCl + heat under reflux followed by dil NaOH

step 6 $LiAlH_4$ in dry ether

[5]

If the amount of ClCOCOCl used in step 2 is decreased, another compound is formed in step 2 with the molecular formula $C_{14}H_8O_2Cl_2$.

(iii) Suggest the structure of this compound.

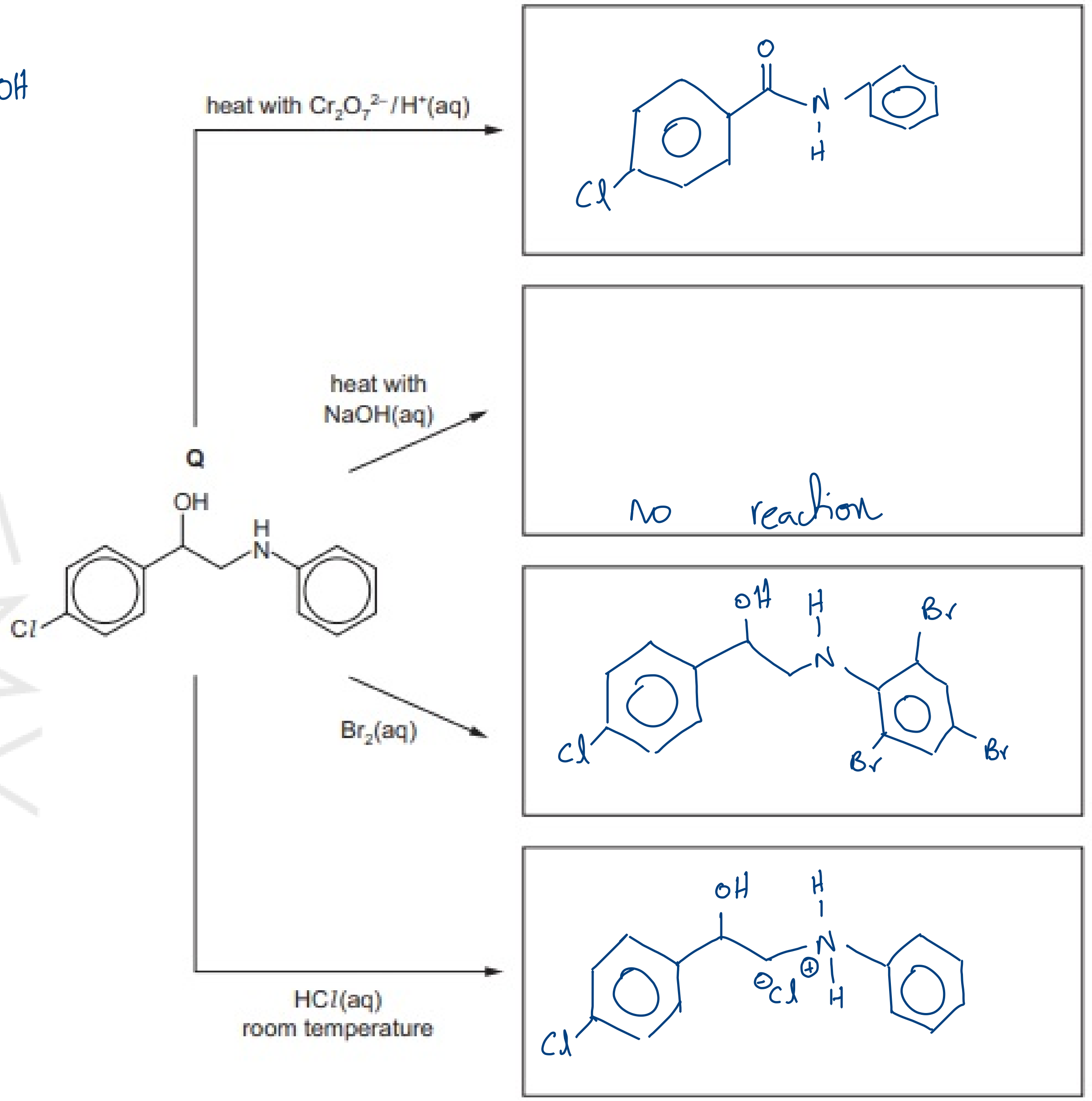


[1]

(iv) Identify **all** the steps in the synthesis of **Q** from benzene that are electrophilic substitution reactions.

1, 2, 3 [1]

(c) Draw structures of the compounds formed when **Q** is treated with the following reagents. If there is no reaction, write 'no reaction' in the box.

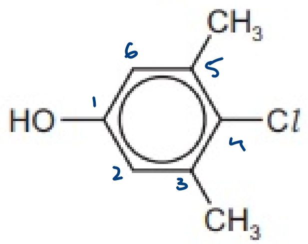


[4]

PROSPERITY ACADEMY

8 Compound **R** is shown.

R

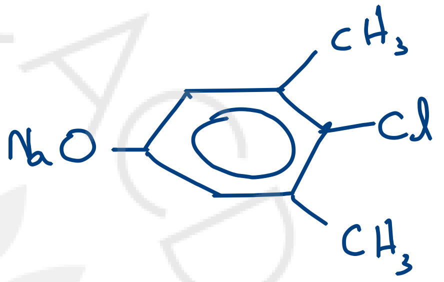
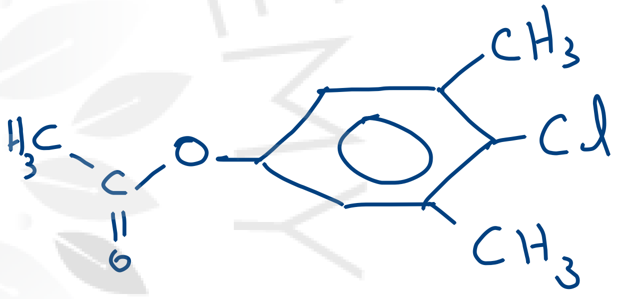
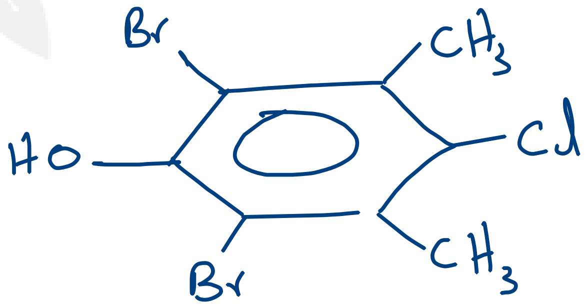
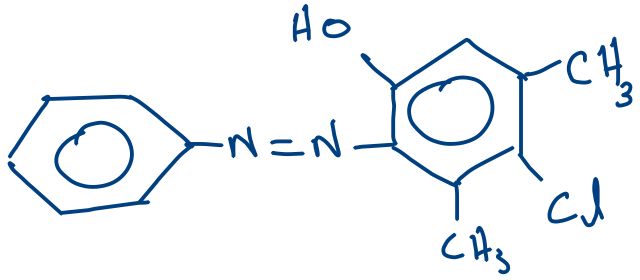


(a) State the systematic name of compound **R**.

4- chloro -3,5 - dimethyl phenol [1]

(c) Compound **R** reacts separately with the four reagents shown in the table.

Complete the table by
- drawing the structures of the organic products formed,
- stating the type of reaction.

reagent	organic product structure	type of reaction
Na		redox
CH_3COCl		condensation
$Br_2(aq)$		electrophillic substitution
		Electrophillic substitution

[6]

PROSPERITY ACADEMY