

NAME REACTION WITH THEIR MECHANISM

B.sc part 2

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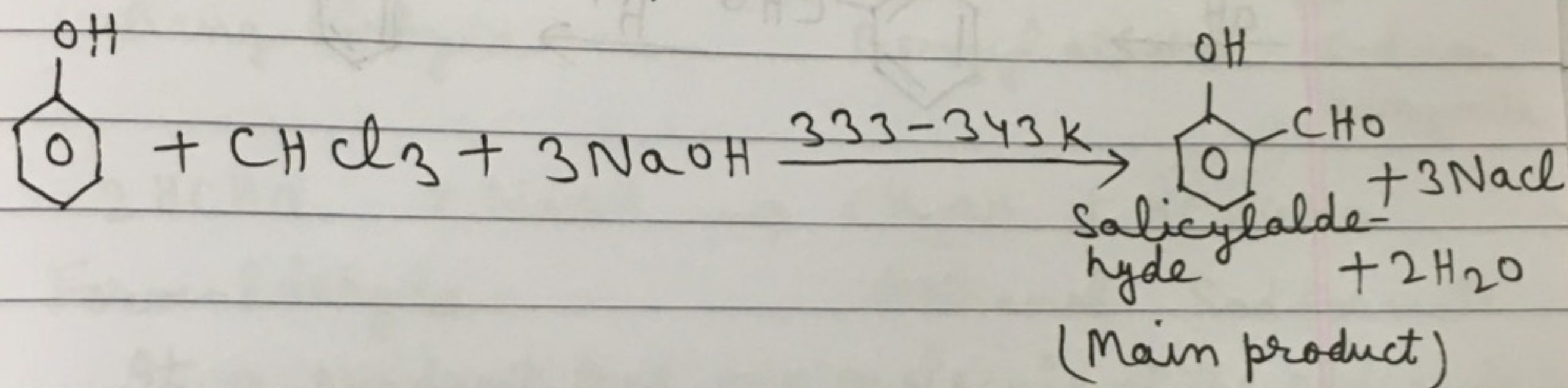
Reimer - Tiemann Reaction

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43

Date _____
Page _____

On heating with chloroform and an alkali, phenols are converted into phenolic aldehydes, an aldehyde group is introduced in the aromatic ring, generally in ortho-position to the $-OH$ group. For example, when phenol is heated with chloroform and aqueous sodium hydroxide, salicylaldehyde is obtained as the main product along with a small amount of the para isomer.



Mechanism: $\rightarrow$ The mechanism of reaction consists of the electrophilic substitution of phenoxide ion formed in solution by the action of alkali on phenol. The attacking electrophilic reagent is the electron deficient dichloromethylene, CCl_2 , a carbene generated by the action of alkali on chloroform. Dichloromethylene is electrically neutral but it acts as an electrophilic reagent as the carbon atom present in it is surrounded by only six valence electrons. The complete mechanism may be summed up as follows: -

Cannizzaro Reaction

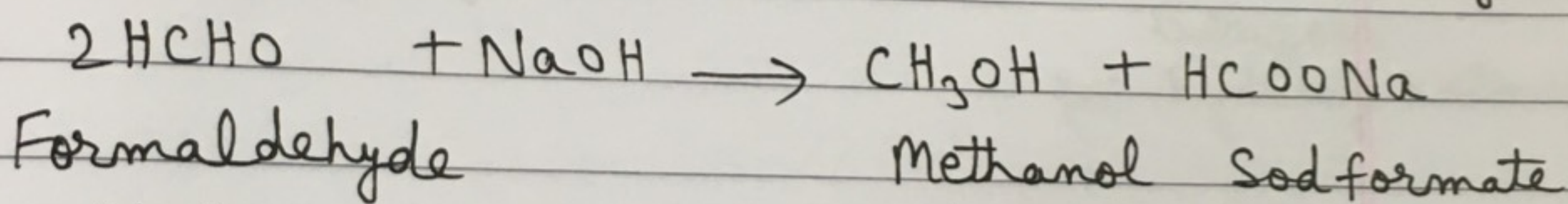
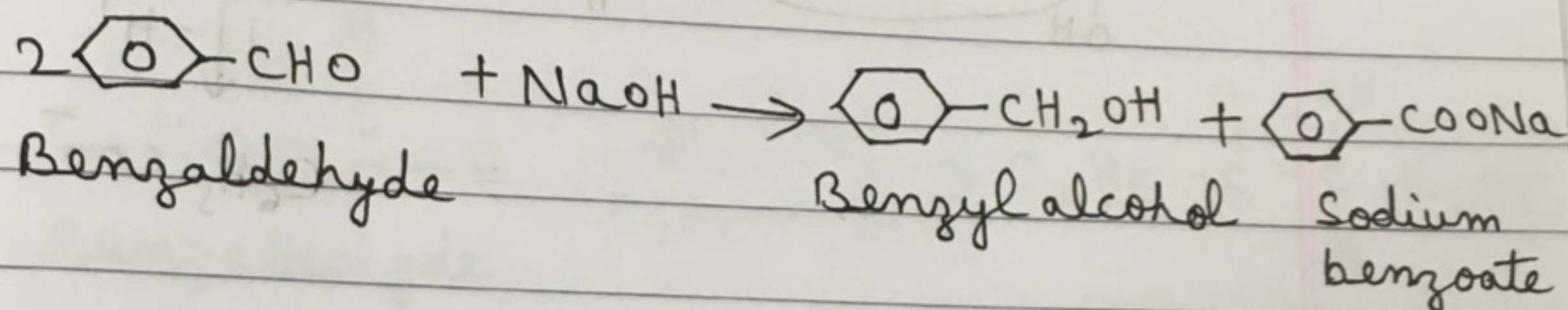
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45

Date _____

Page _____

Aldehydes having no α -hydrogen like formaldehyde and benzaldehyde undergo self oxidation and reduction. This reaction is given when an aldehyde is treated with a conc. solution of sodium or potassium hydroxide. An alcohol and a salt of carboxylic acid are produced. For example:—

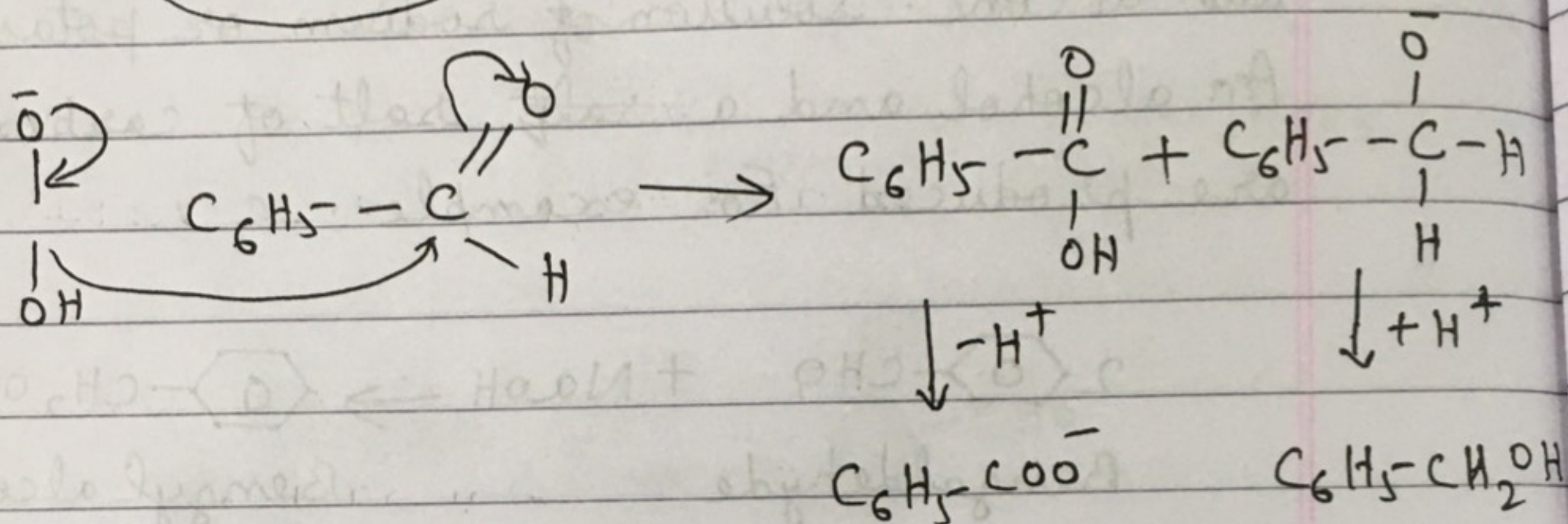
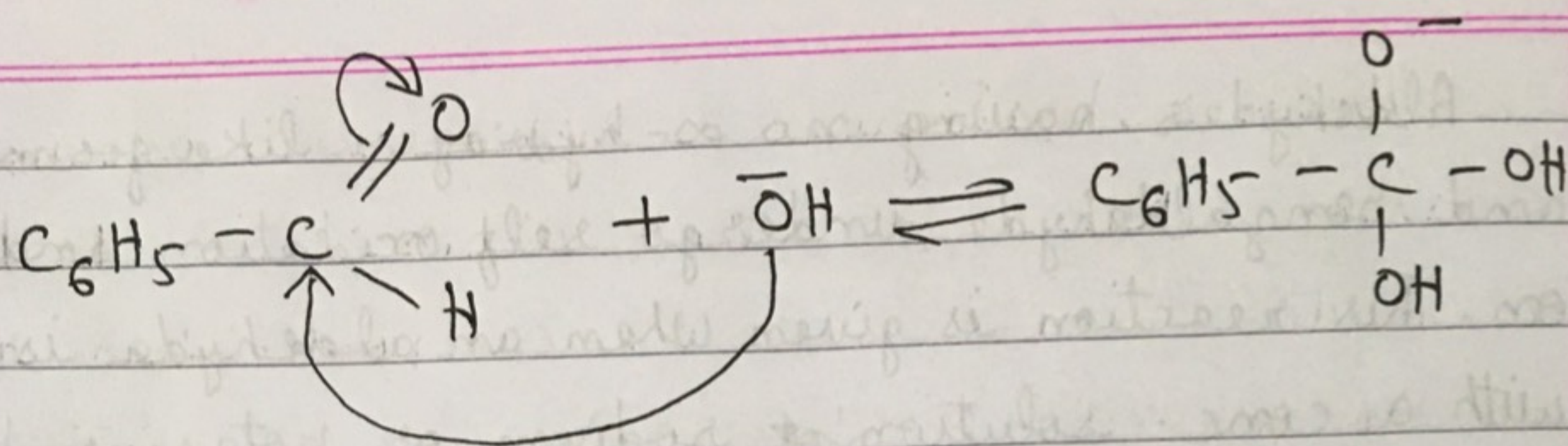


It is evident that one molecule of the aldehyde is oxidised to acid and the second molecule is reduced to alcohol.

Mechanism: → The following steps are involved:—

Step 1: → Attack by OH^- :— Hydroxide ion attacks the aldehyde molecule to form an anion.

Step 2: → Hydride ion transfer:— Oxidation-reduction takes place between the anion formed in step 1 and the second molecule of aldehyde through transfer of a hydride ion. These two steps are illustrated as:—



Benzoin Condensation

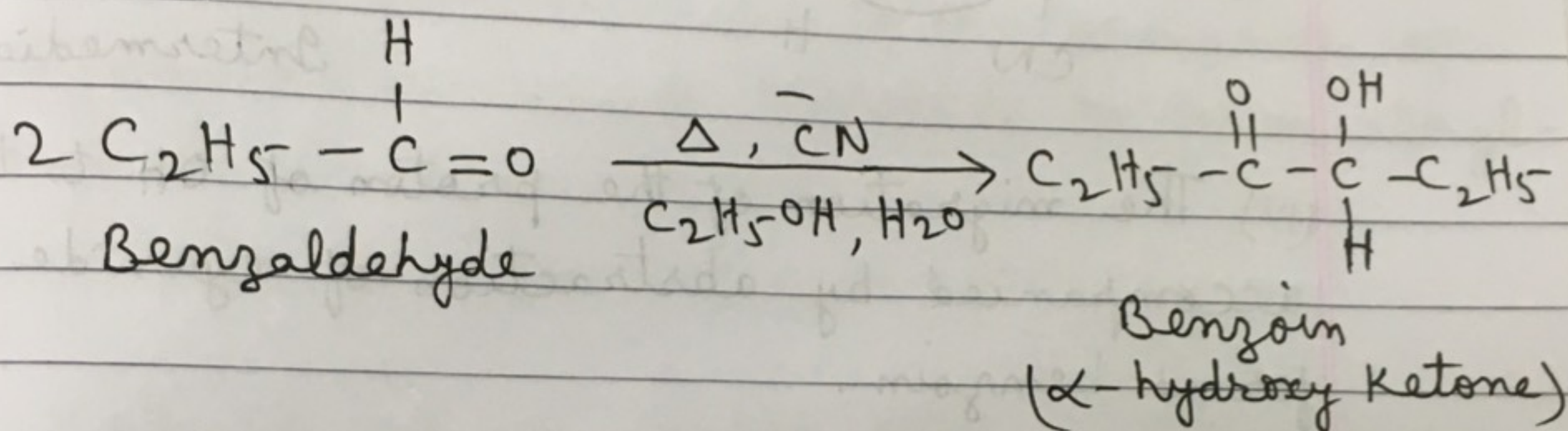
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47

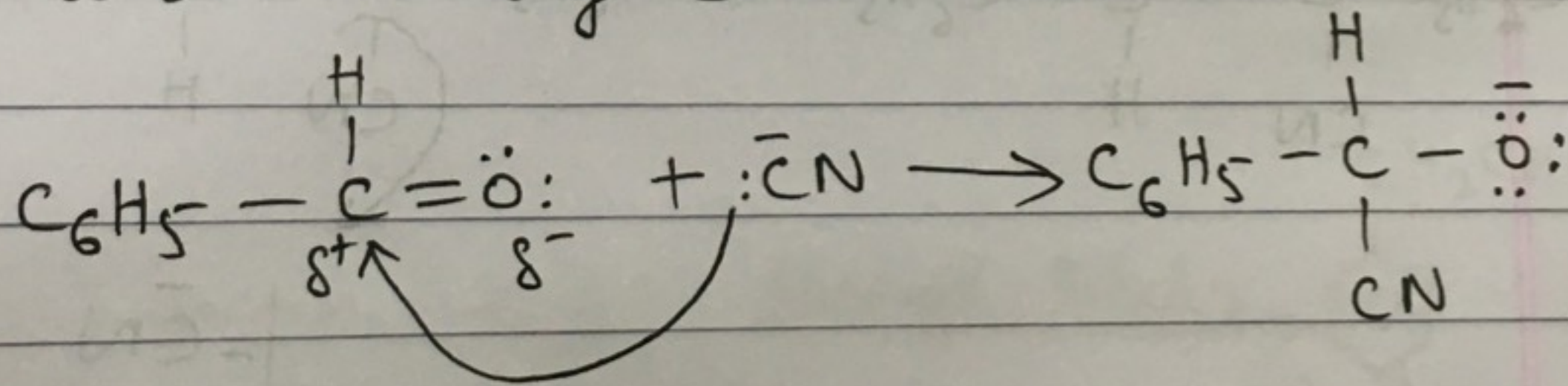
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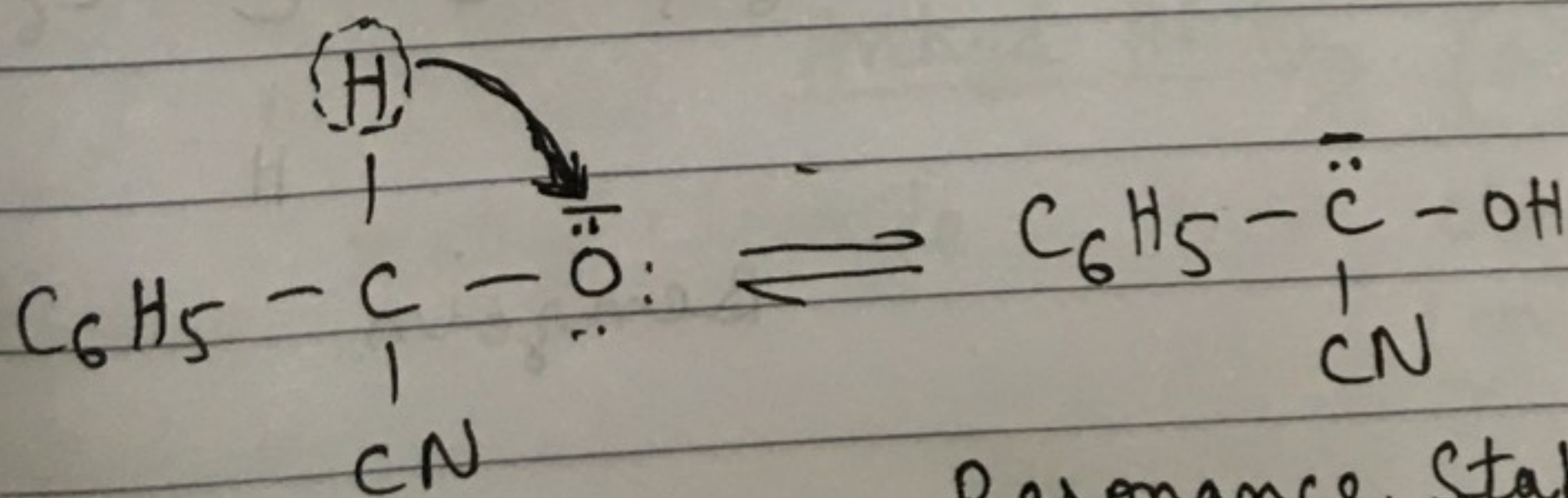
When benzaldehyde is heated with aqueous-ethanolic NaCN or KCN, it dimerizes to form an α -hydroxy ketone called benzoin. This reaction involving self-condensation of an aromatic aldehyde in the presence of CN^- anion as catalyst, is referred to as benzoin condensation.



Mechanism $\rightarrow$ (i) Nucleophilic addition of a cyanide anion to the carbonyl carbon.

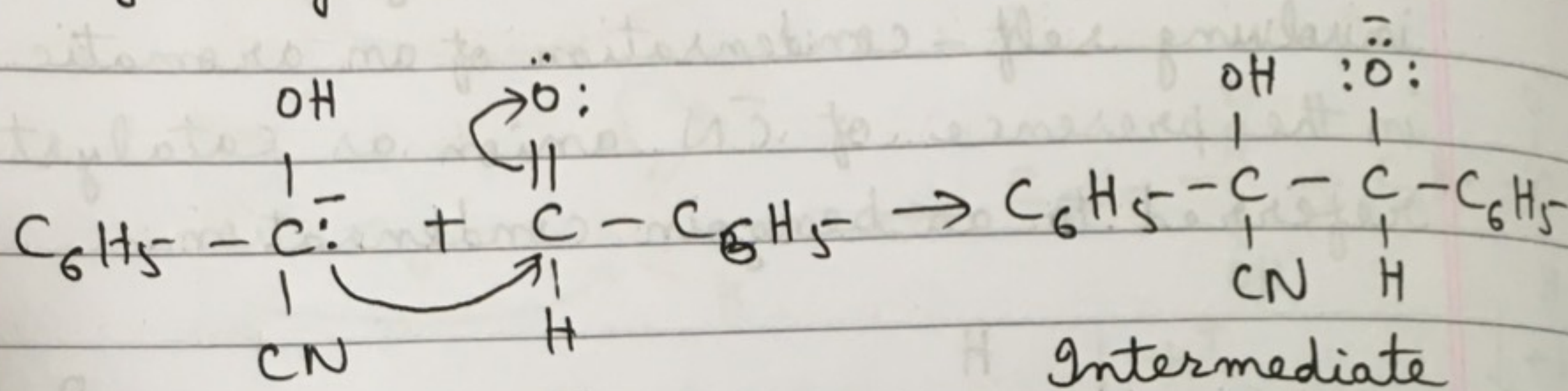


(ii) The CN group acidifies the former aldehyde H atom which migrates to the former carbonyl group.

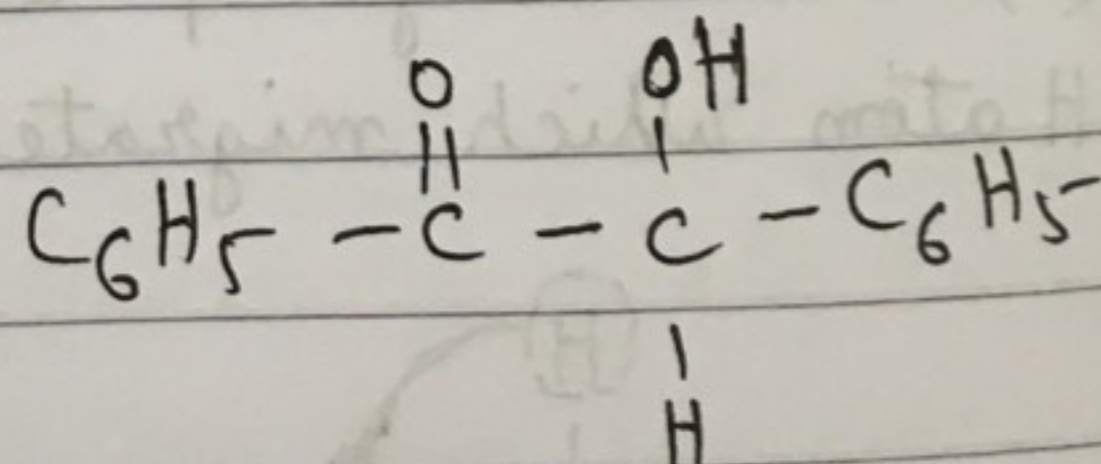
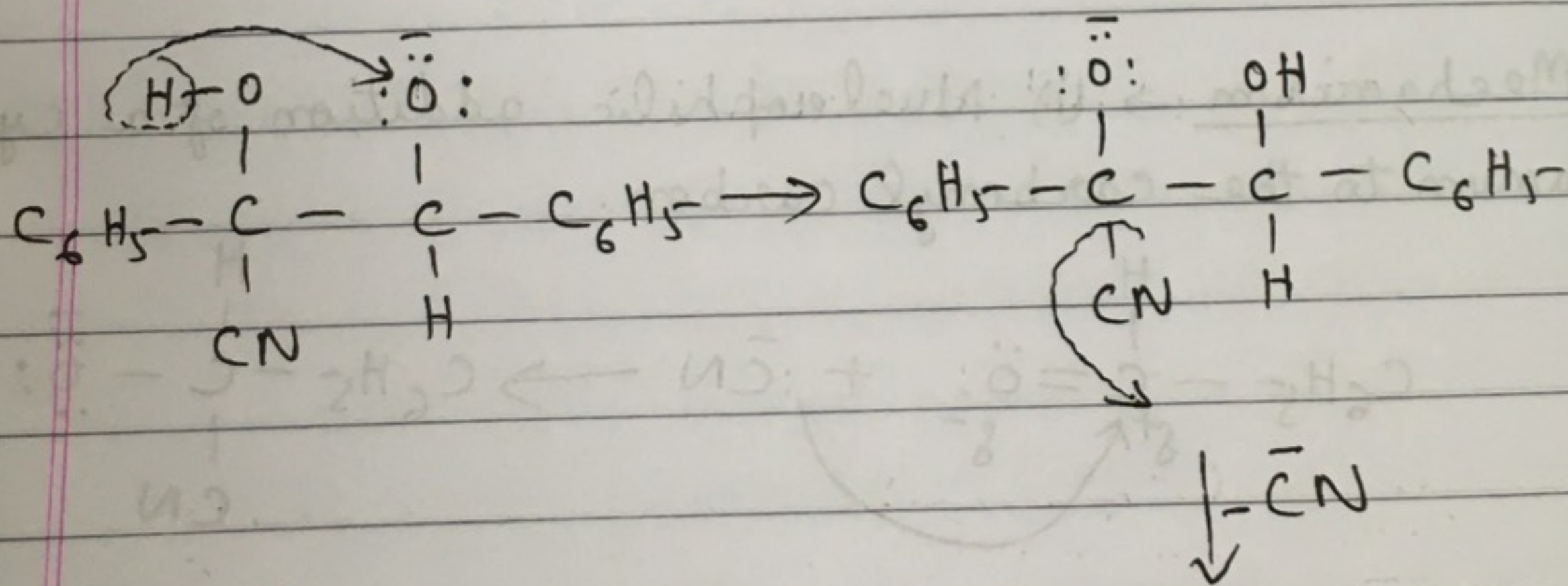


Resonance Stabilised
Carbanion

(iii) The resonance-stabilised carbanion adds to the carbonyl carbon of another molecule of benzaldehyde.



(iv) The migration of the proton of OH to the oxygen accompanied by abstraction of cyanide anion, forms benzoin.



Benzoin

Friedel - Crafts Reaction

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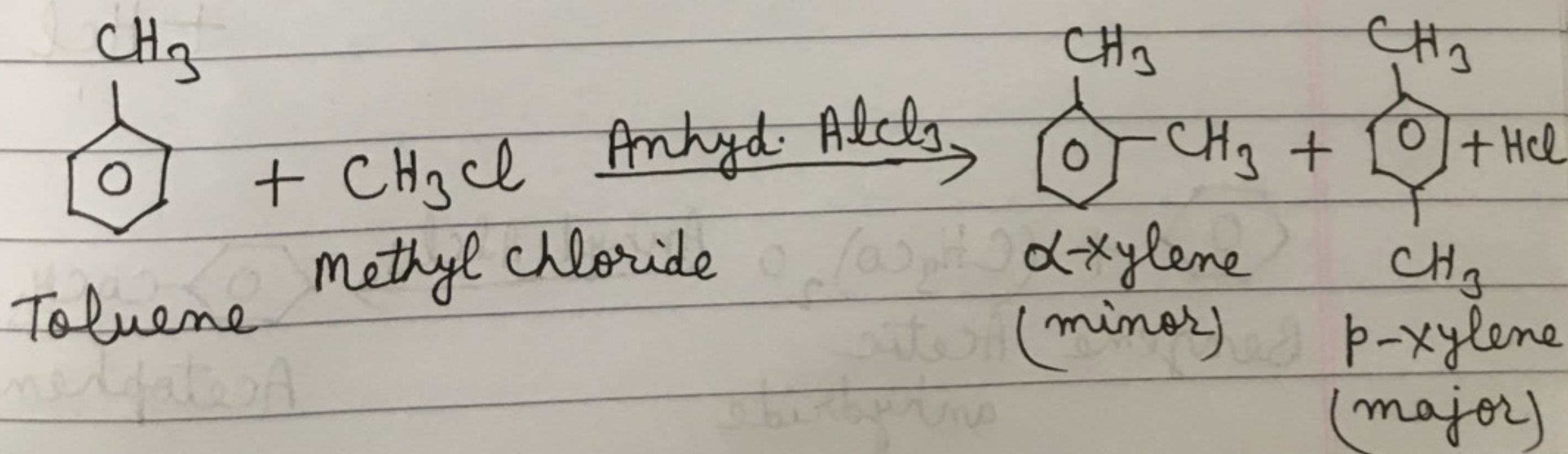
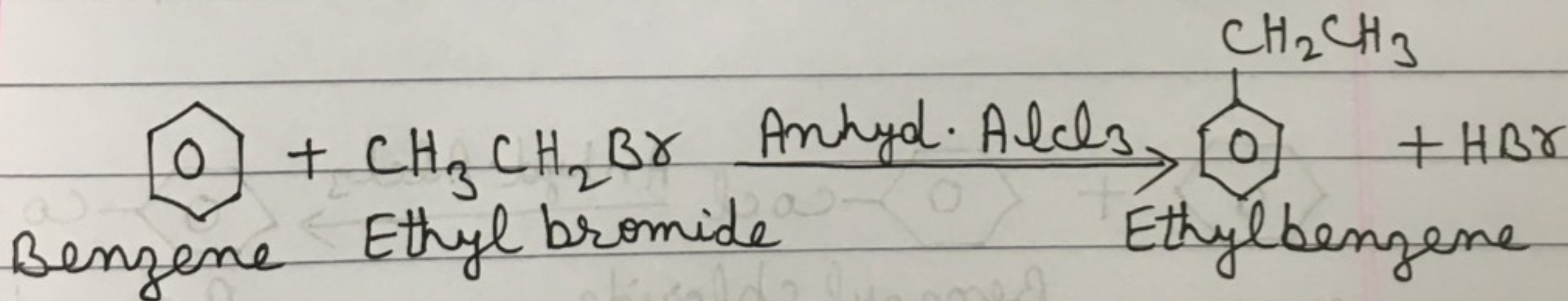
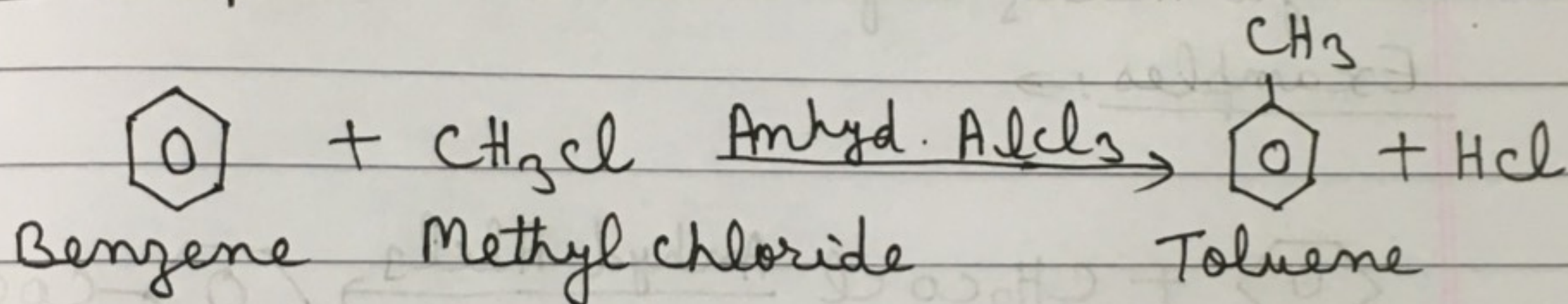
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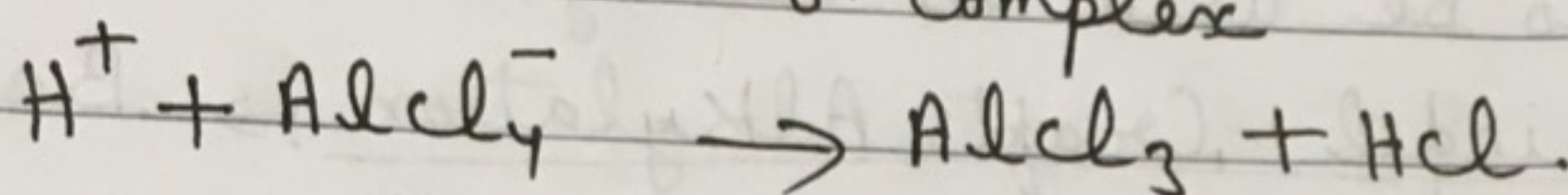
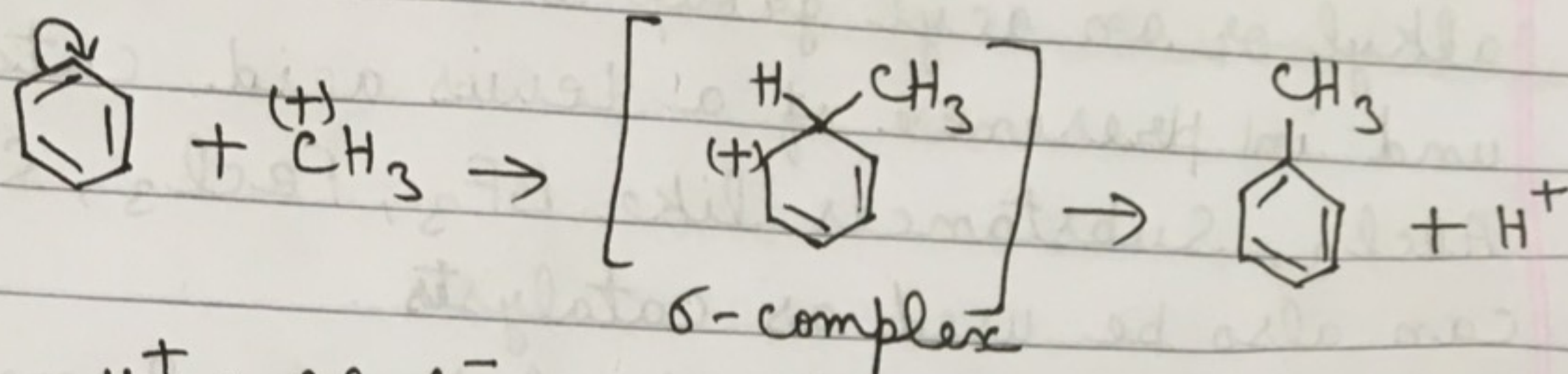
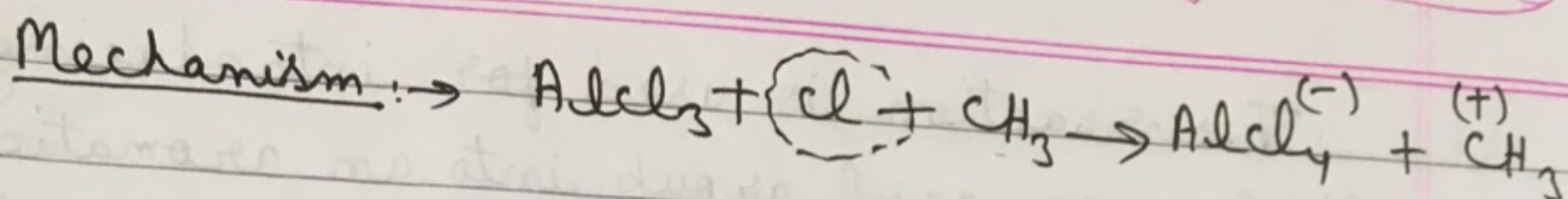
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Page _____

This reaction is used for introducing an alkyl or an acyl group into an aromatic compound in presence of a Lewis acid catalyst like $AlCl_3$. Substances like BF_3 , $FeCl_3$, $SnCl_4$ etc. can also be used as catalysts.

(a) Friedel - Crafts Alkylation $\Rightarrow$ Benzene reacts with alkyl halides in the presence of anhydrous aluminium chloride to form alkylbenzenes.

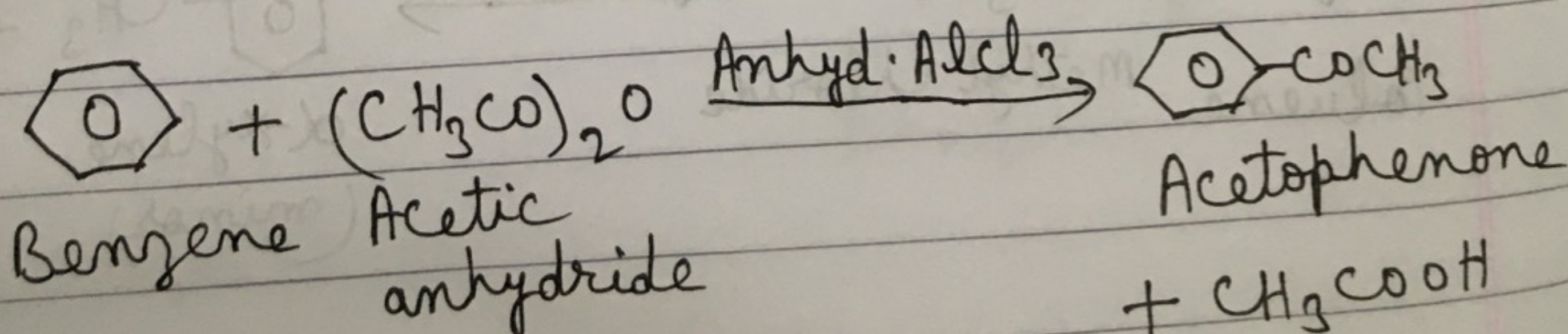
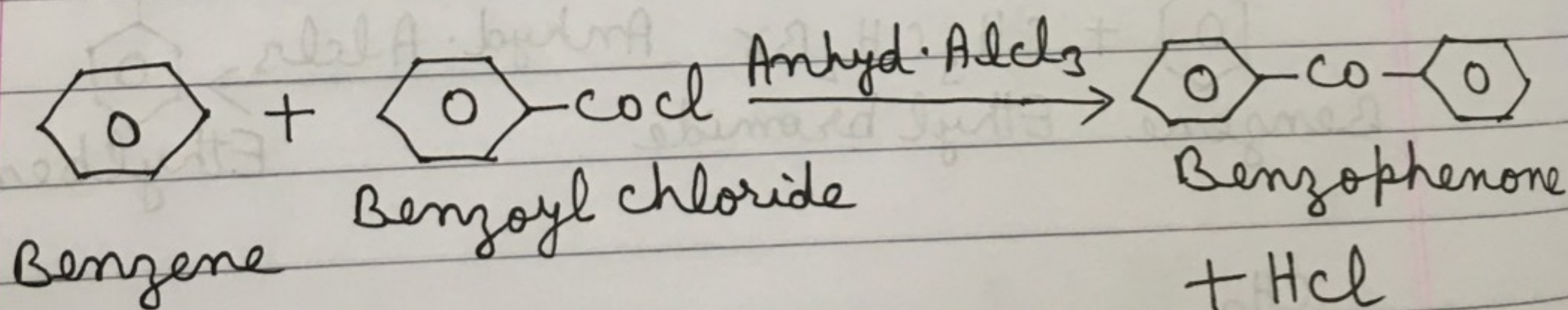
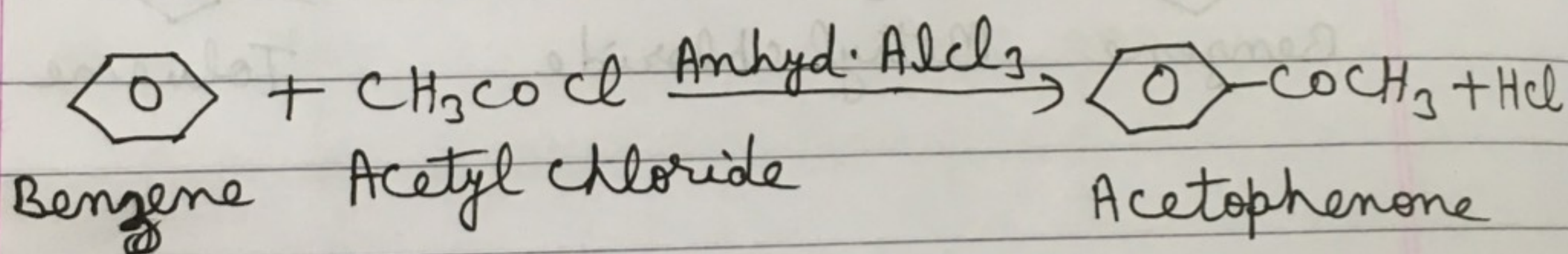
Examples $\Rightarrow$

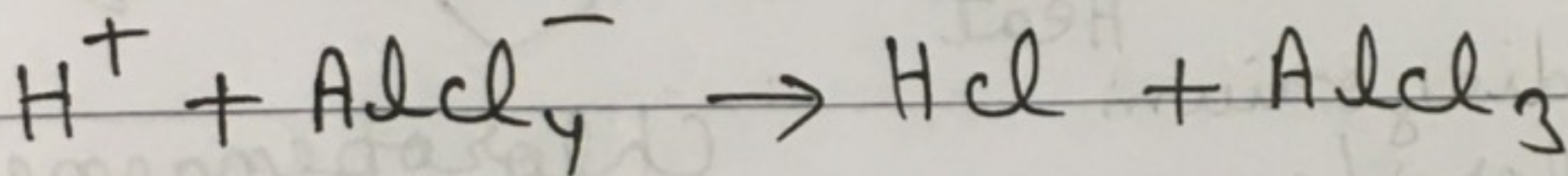
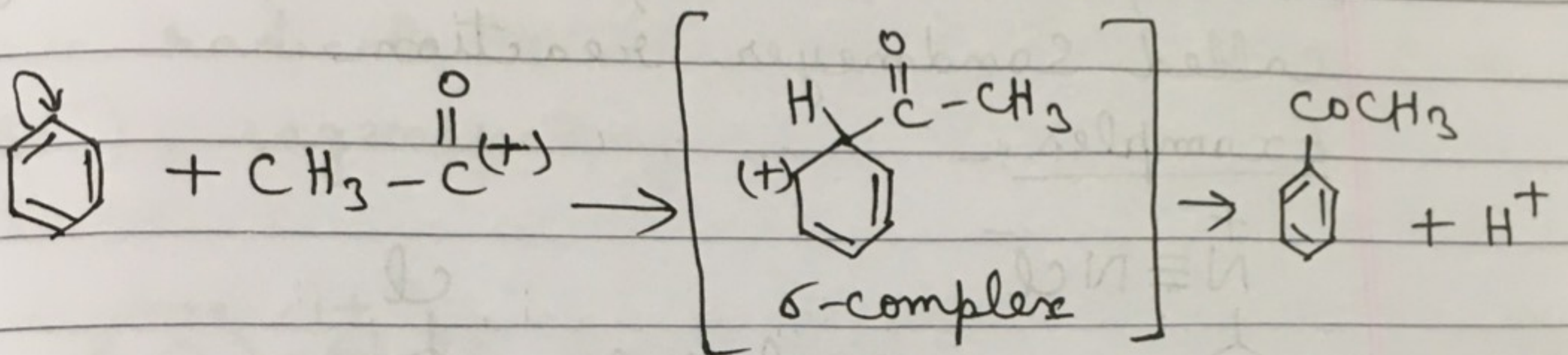
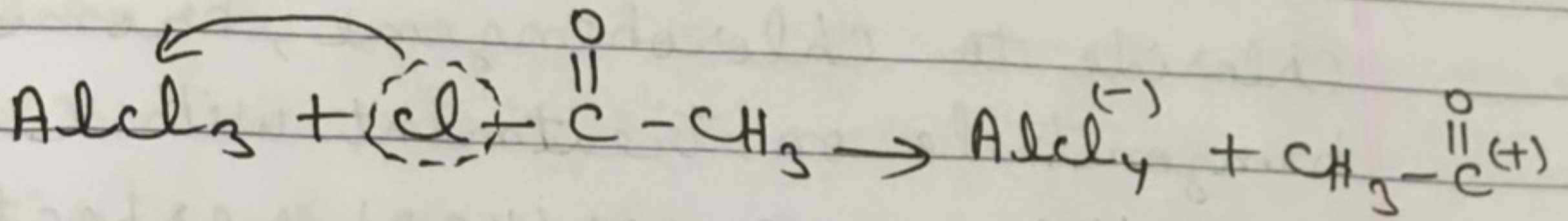




(b) Friedel-Crafts Acylation $\rightarrow$ Benzene reacts with acid chlorides or anhydrides in presence of anhyd. AlCl_3 to form Ketones.

Examples $\rightarrow$



Mechanism: →

Sandmeyer Reactions

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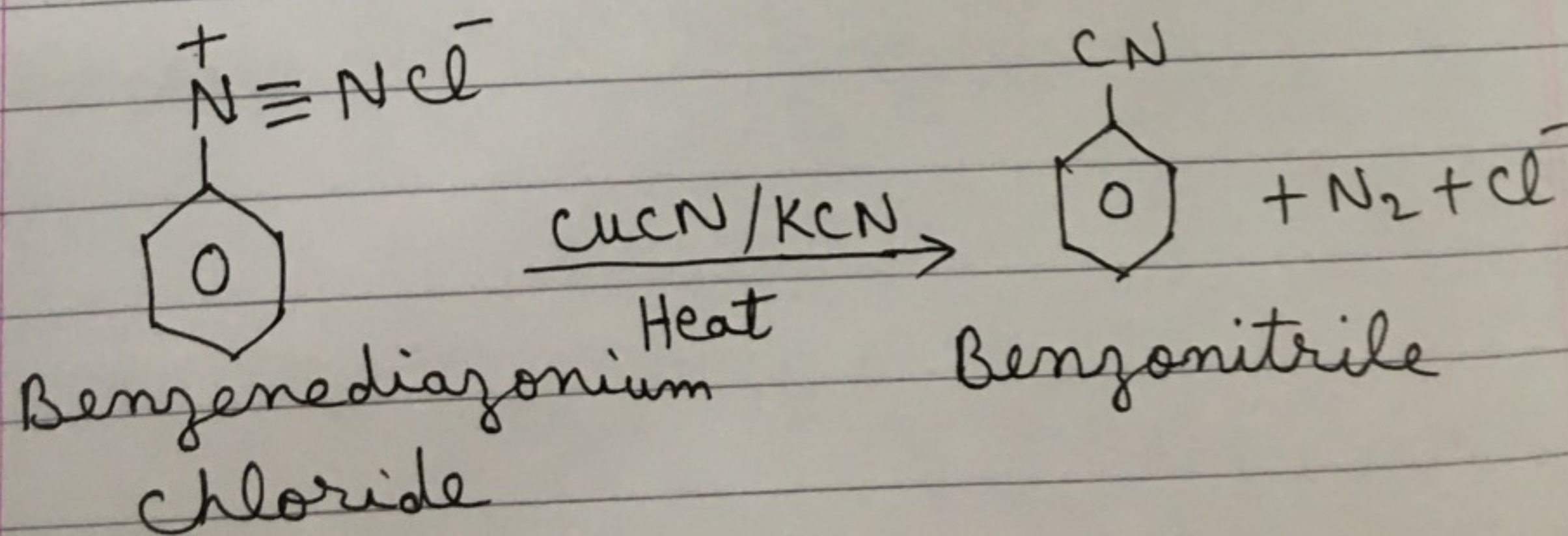
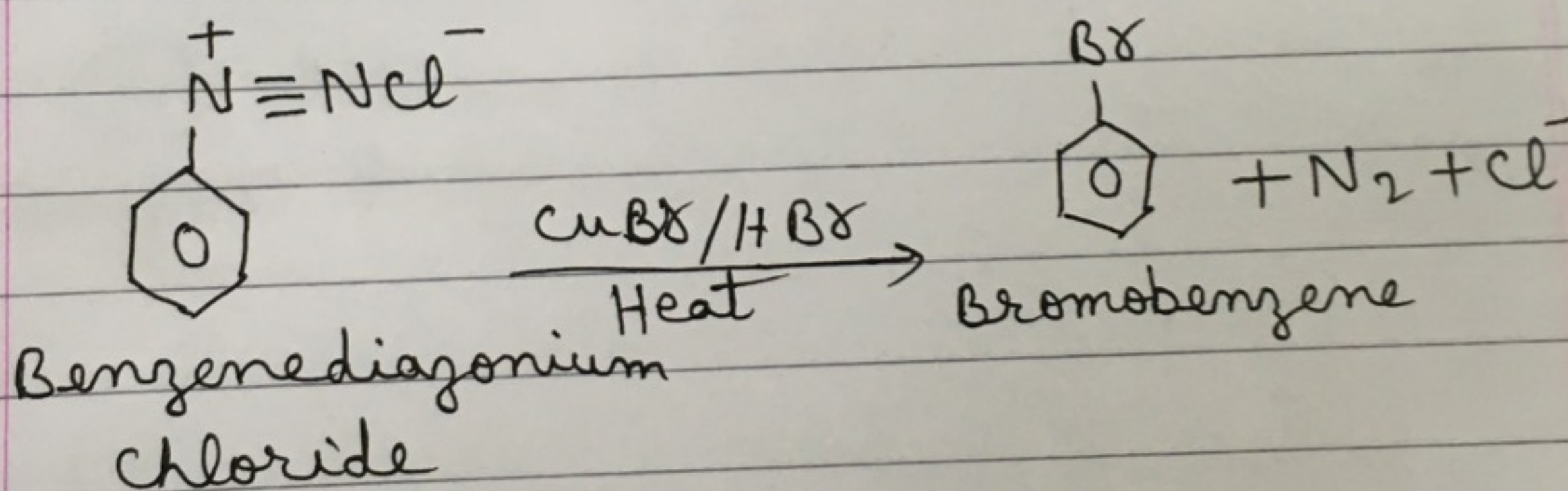
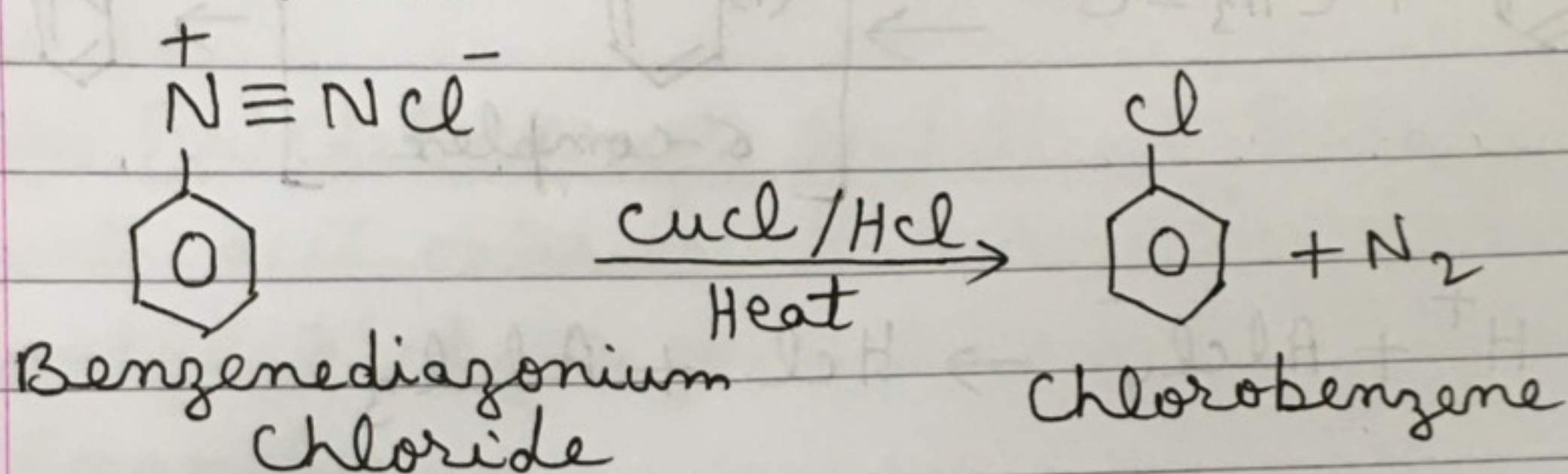
52

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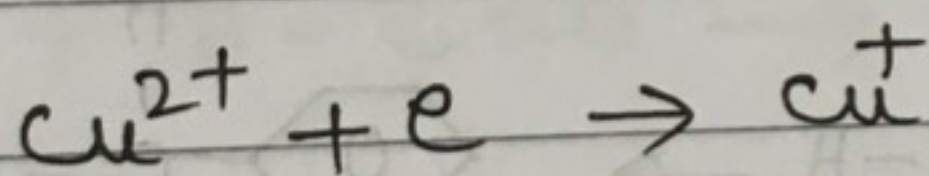
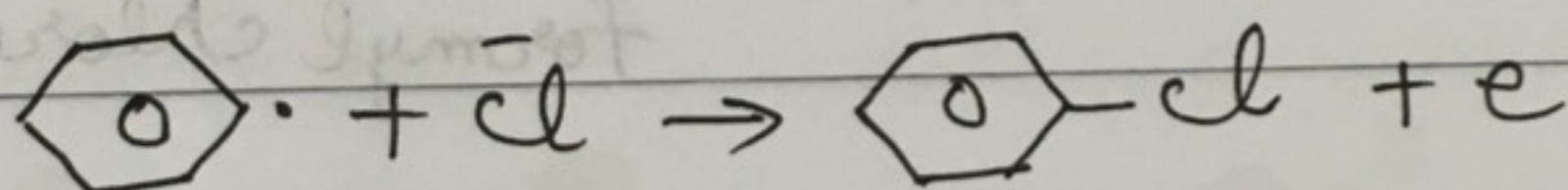
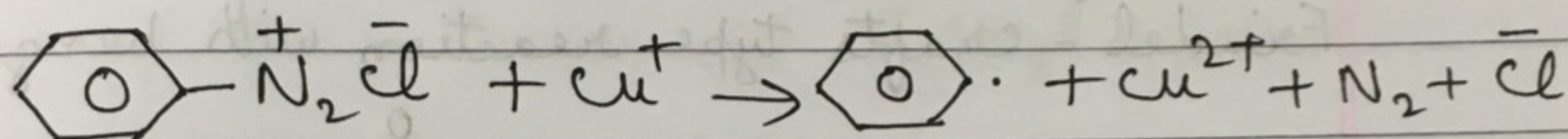
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The conversion of benzenediazonium chloride to chlorobenzene, bromobenzene and benzonitrile on treatment with CuCl/HCl , CuBr/HBr or CuCN/KCN respectively is called Sandmeyer reaction.

Examples:-



Mechanism: $\rightarrow$ Cuprous ion Cu^+ provides an electron for generation of benzene free radical, when the former is converted to cupric ion Cu^{2+} . In the subsequent step the benzene free radical combines with halide ion (Cl^- or Br^-), regenerating Cu^+ .



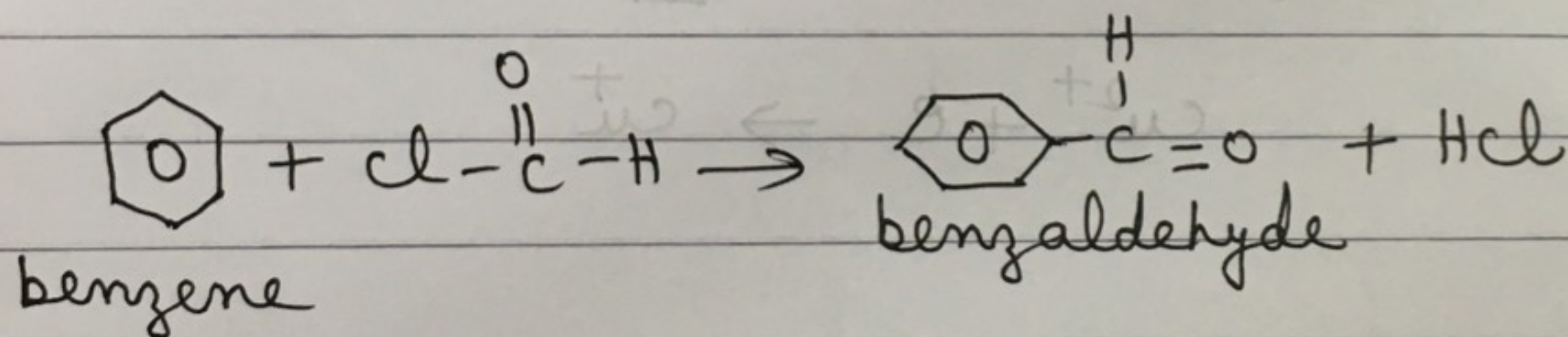
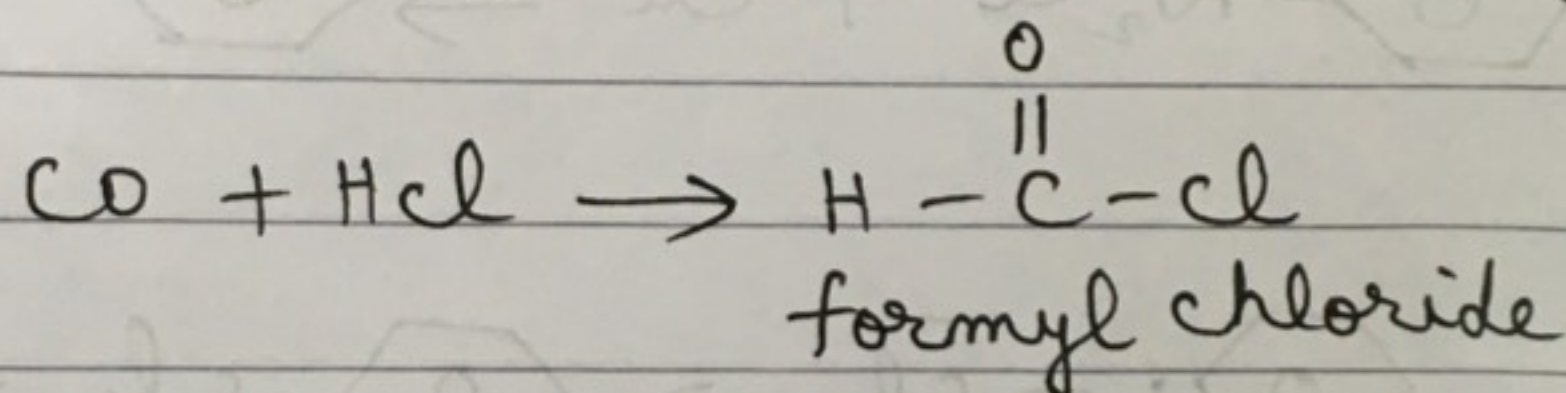
Gattermann - Koch Reaction

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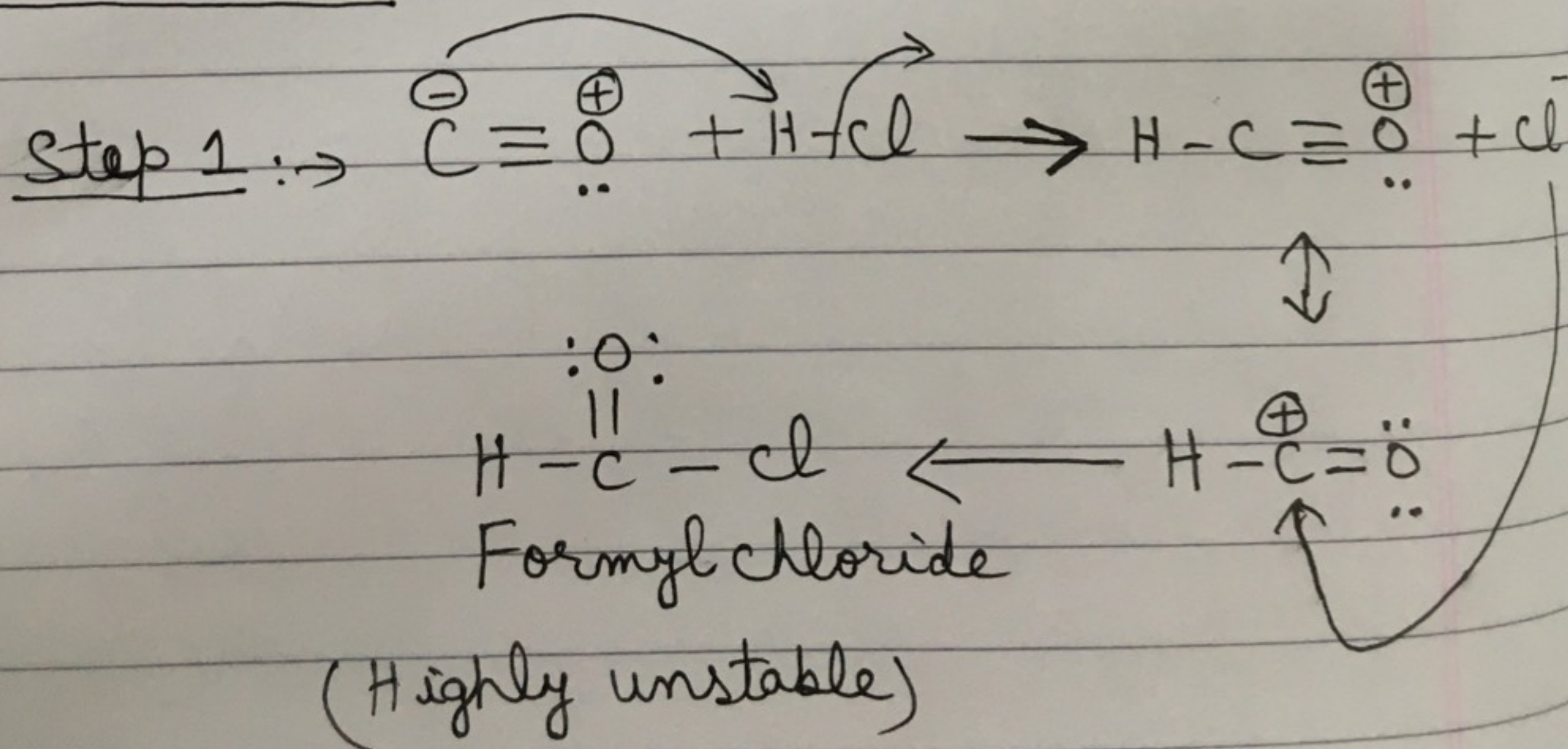
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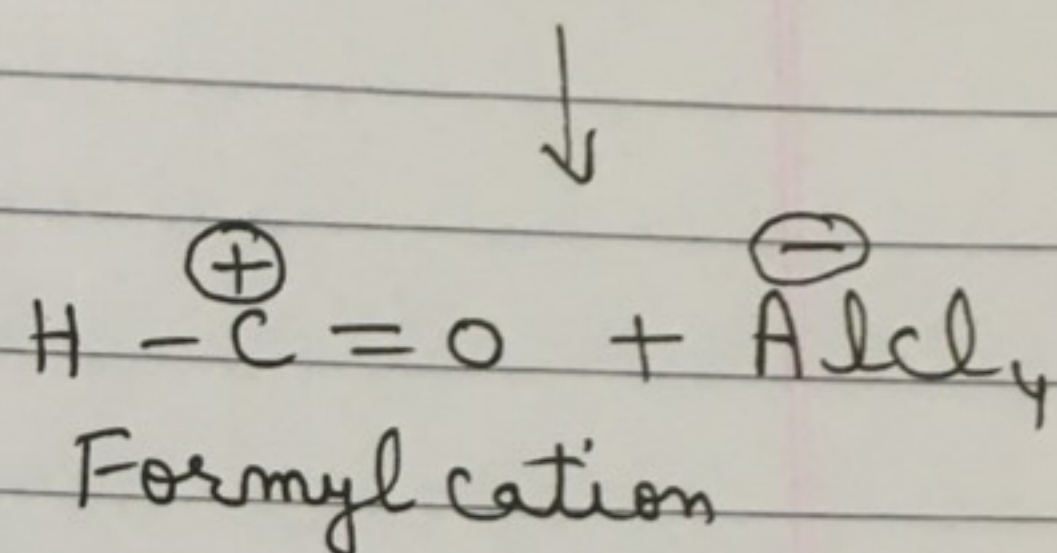
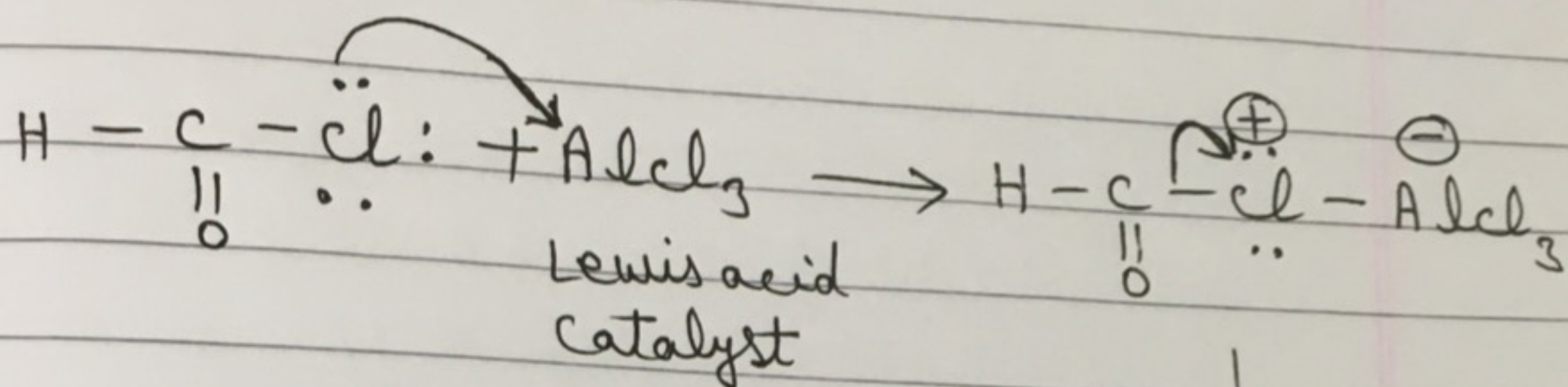
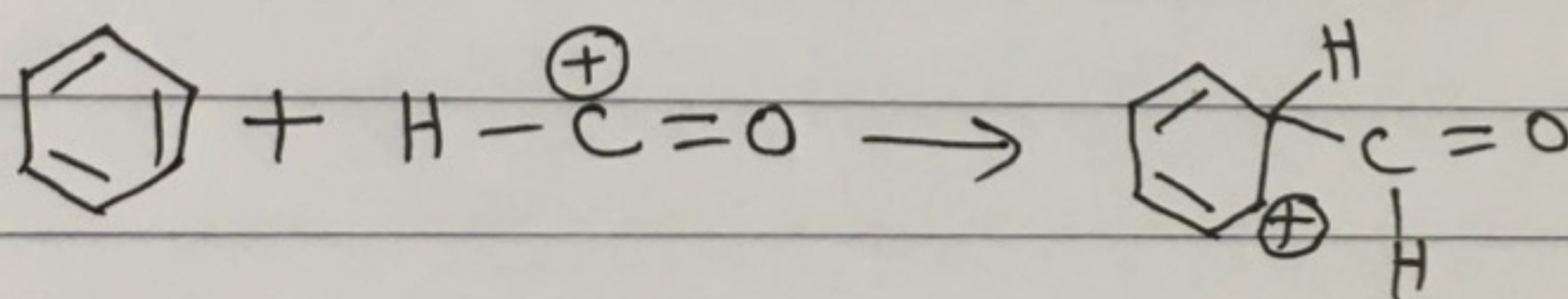
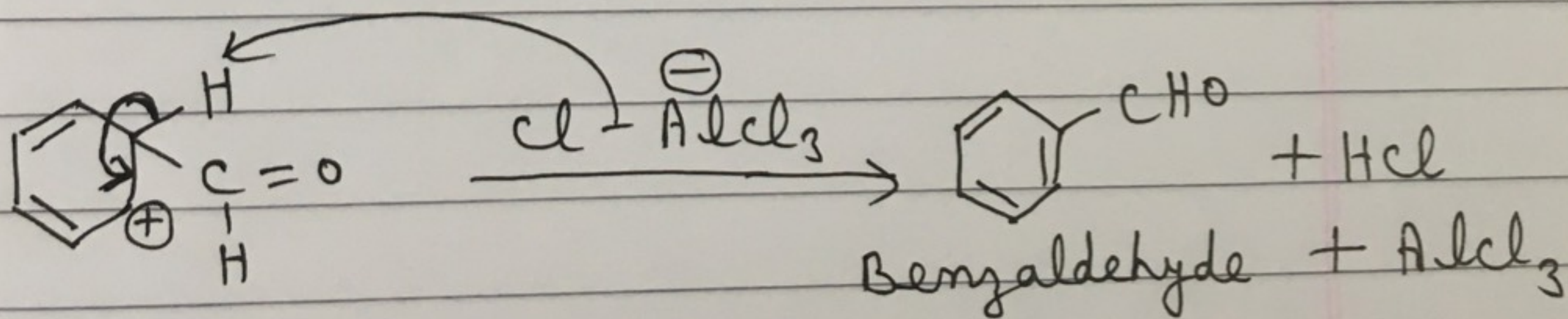
When an equimolecular mixture of carbon monoxide and hydrogen chloride is bubbled through a solution of benzene in ether containing anhydrous aluminium chloride, benzaldehyde is produced.

Carbon monoxide and hydrogen chloride behave as formyl chloride ($\text{H}-\text{CO}-\text{Cl}$), which enters into Friedel - crafts type reaction with benzene.



Mechanism $\Rightarrow$



Step 2 $\Rightarrow$ Step 3 $\Rightarrow$ Step 4 $\Rightarrow$ 

Perkin Reaction

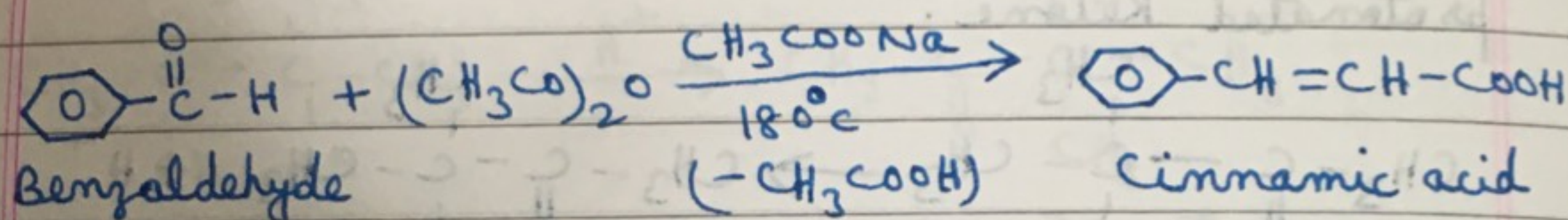
classmate 38

Date _____

Page _____

The Perkin reaction involves the treatment of an aromatic aldehyde with anhydride of an aliphatic acid and the sodium salt of that acid. Products are α, β -unsaturated acids.

For example, benzaldehyde reacts with acetic anhydride in the presence of sodium acetate at 180°C to form cinnamic acid.



Mechanism $\rightarrow$ The Perkin reaction involves the following steps:

- ① Formation of the anion of acetic anhydride (A);
- ② Addition of (A) to benzaldehyde gives (B). Notice that the anion adds to the carbonyl carbon of benzaldehyde;
- ③ Protonation of (B) gives (C). The proton is supplied by acetic acid from step (1);
- ④ Internal proton transfer in (C) followed by elimination of water molecule gives (D);
- ⑤ Hydrolysis of (D) gives cinnamic acid.

