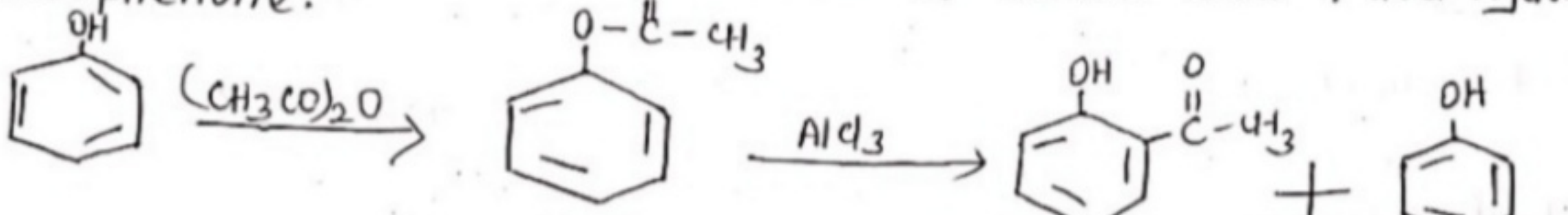
D-II (H) Fries Rearrangement 12/11/2020

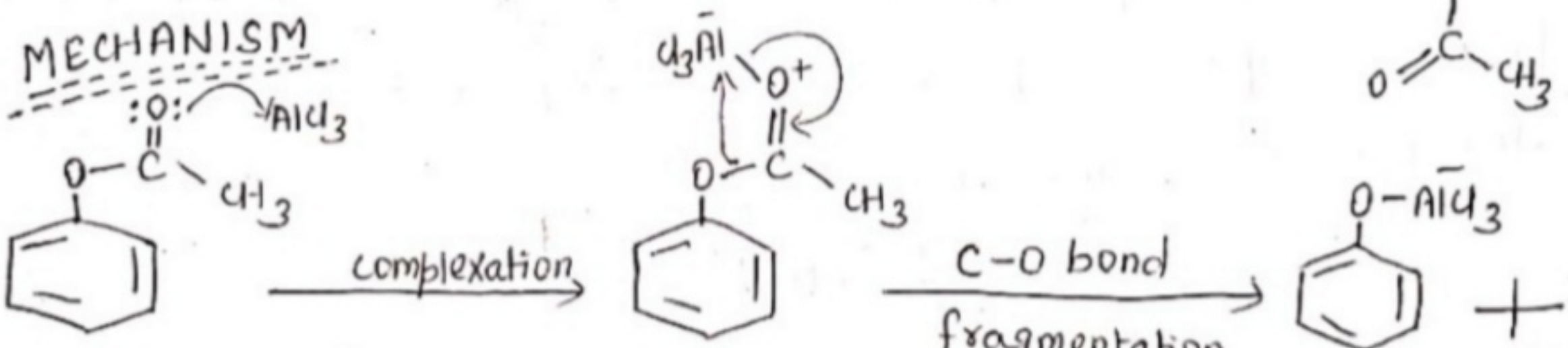
The phenol is first treated with ethanoic anhydride in the presence of aqueous sodium hydroxide to give phenyl ethanoate (Phenyl acetate)

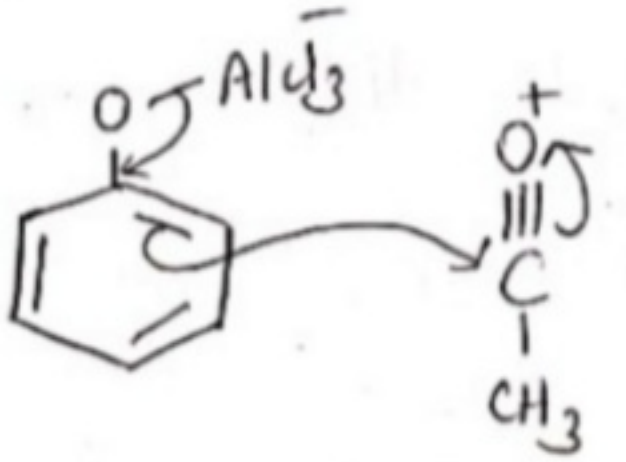
The ester is then heated with aluminium chloride catalyst when the acyl group migrates from the phenolic oxygen to an ortho or para position of the ring.

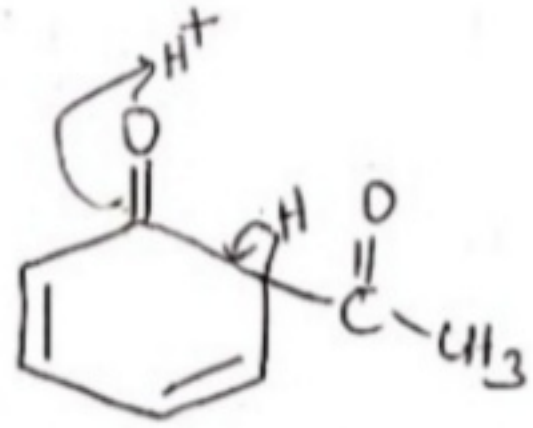
The product is a mixture of ortho and para hydroxy acetophenone.



MECHANISM

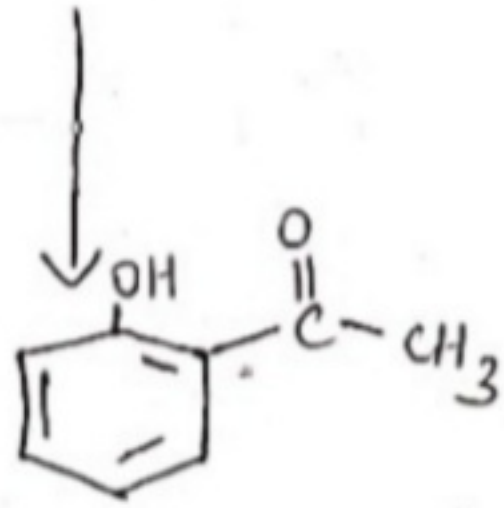


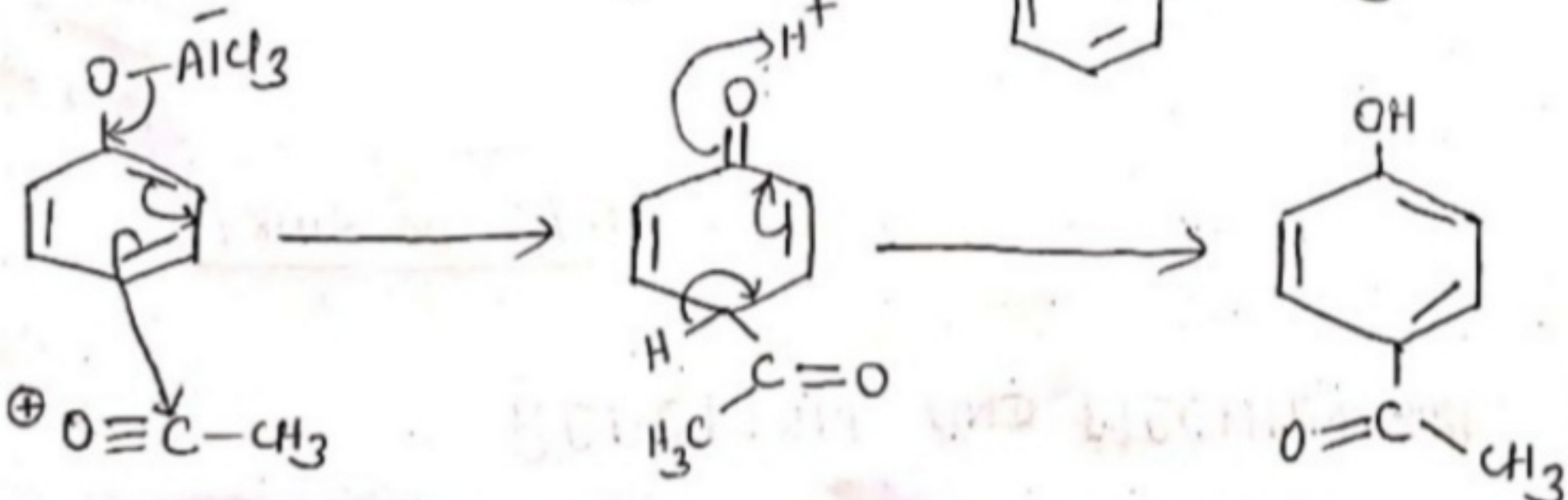




$H_3C-C\equiv O^+$

Acylium ion





Completed

D-II (H)

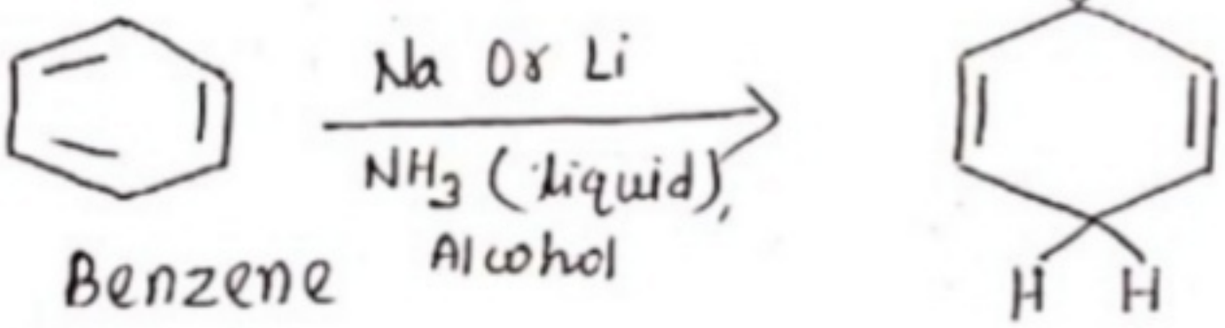
Birch Reduction

12/11/2020

* Reduction of aromatic rings by means of alkali metal (sodium or lithium) in liquid ammonia or amines with ethanol as proton donar to give mainly unconjugated dihydroderivatives is known as Birch Reduction.

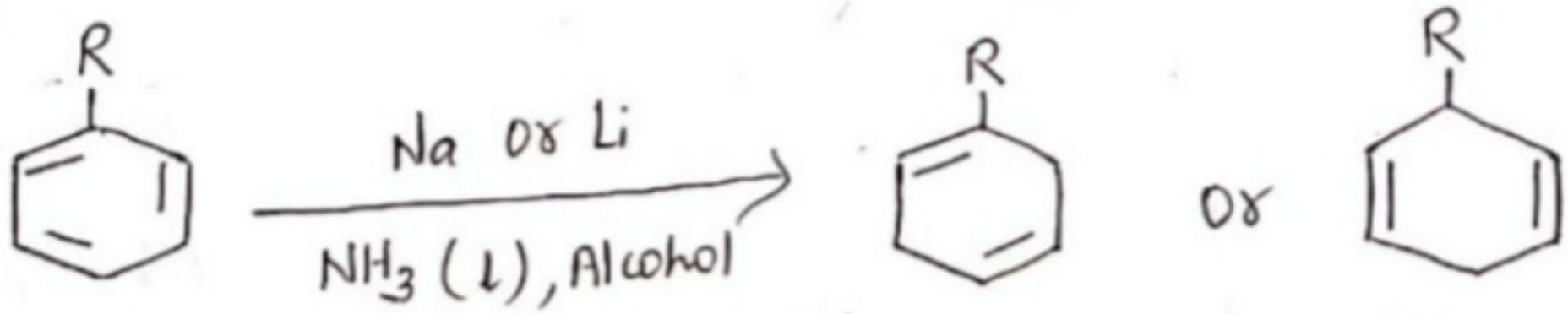
* Aromatic rings and conjugated dienes are reduced by this method, while isolated double bonds are normally not affected.
* Sometimes ether are used as a co-solvent to dissolve the aromatic compounds.
* Use of tert. butanol fulfils the dual role of proton donor and a co-solvent.

eg;



Benzene

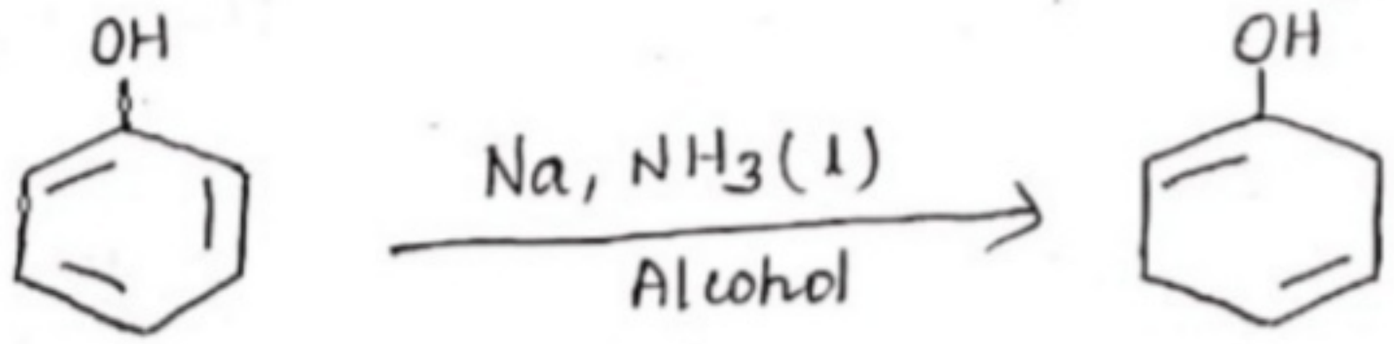
1,4-Cyclohexadiene



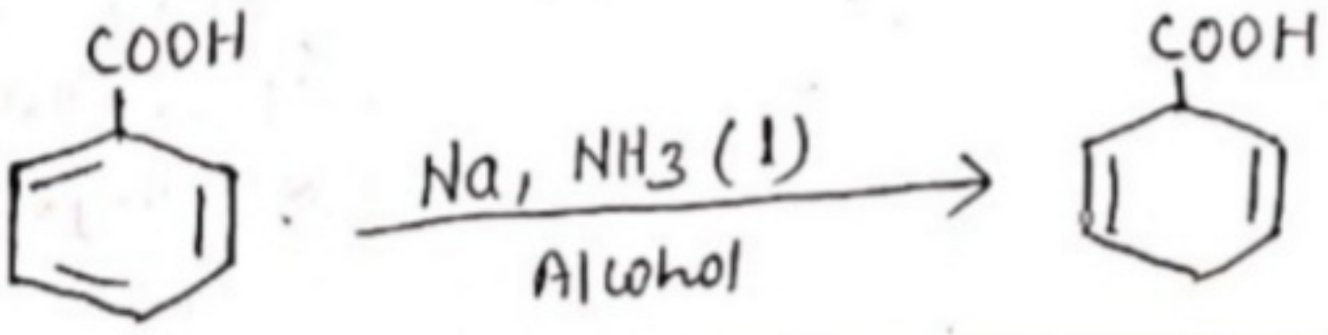
[If R = electron donating group]

[If R = Electron withdrawing group]

eg;



Note: (-OH = Electron Donating)



(-COOH = electron withdrawing)

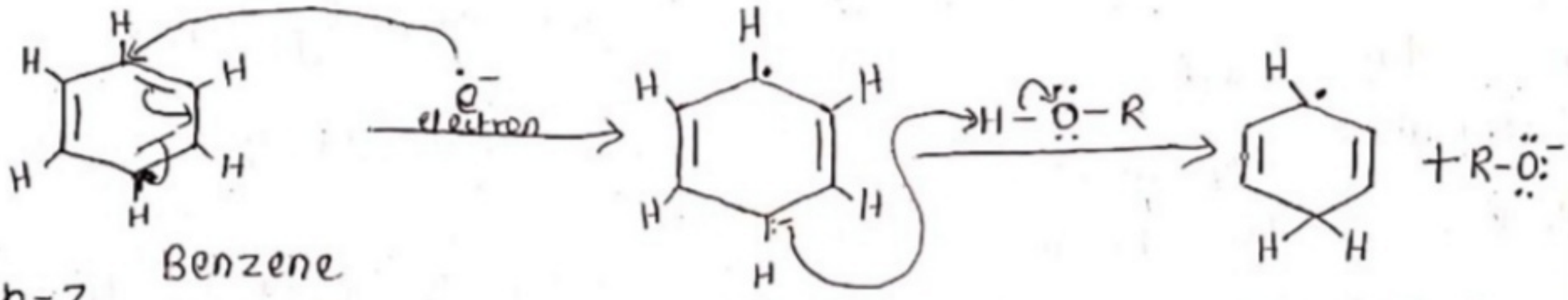
Step-1

Formation of solvated electrons in the ammonia solution.

$$NH_3 + Na \rightleftharpoons \underset{\text{solvated electron}}{NH_3 \cdot e^-} + Na^+$$

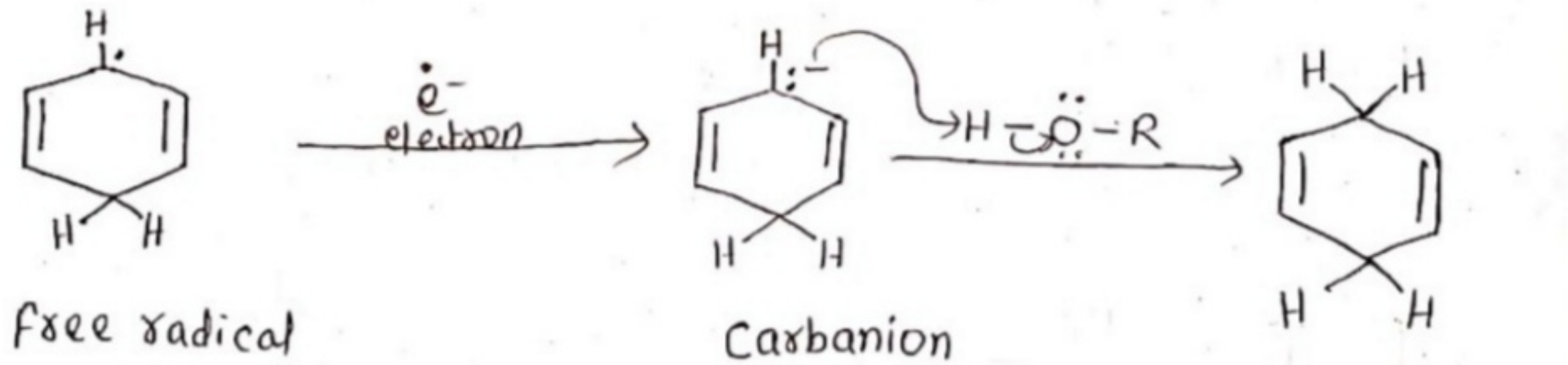
Step-2

Addition of an electron, followed by a proton, forms a free radical.



Step-3

Addition of a second electron, followed by a proton, gives the product.



Birch Reduction

Completed

Revision Notes

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