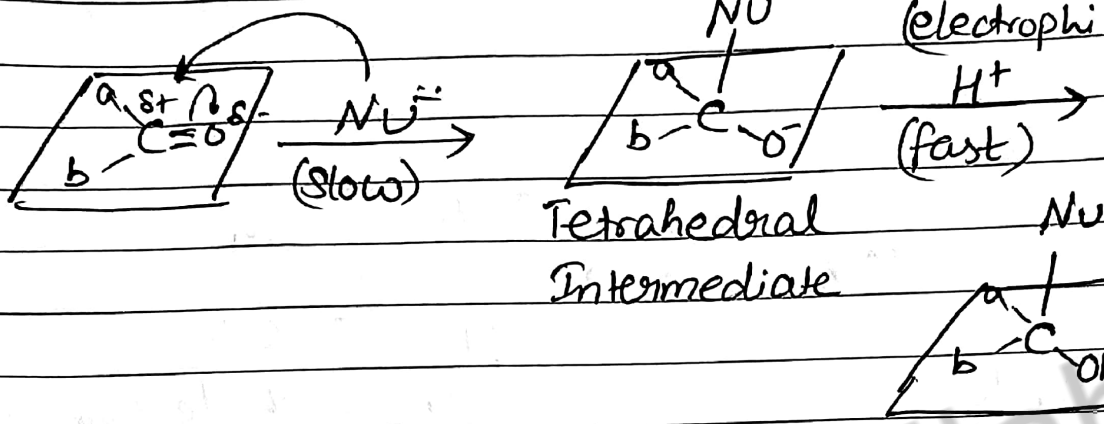
Aldehydes & Ketones – 06

Properties: Nucleophilic Addition Reaction

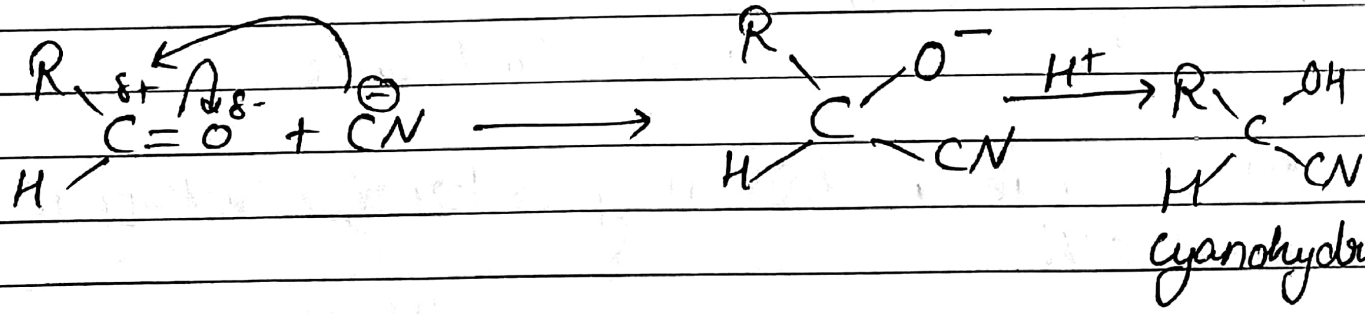
Both Aldehydes & Ketones contain $-\overset{\overset{O}{\|}}{C}-$ carbonyl group, which gives Nucleophilic Addition Product.

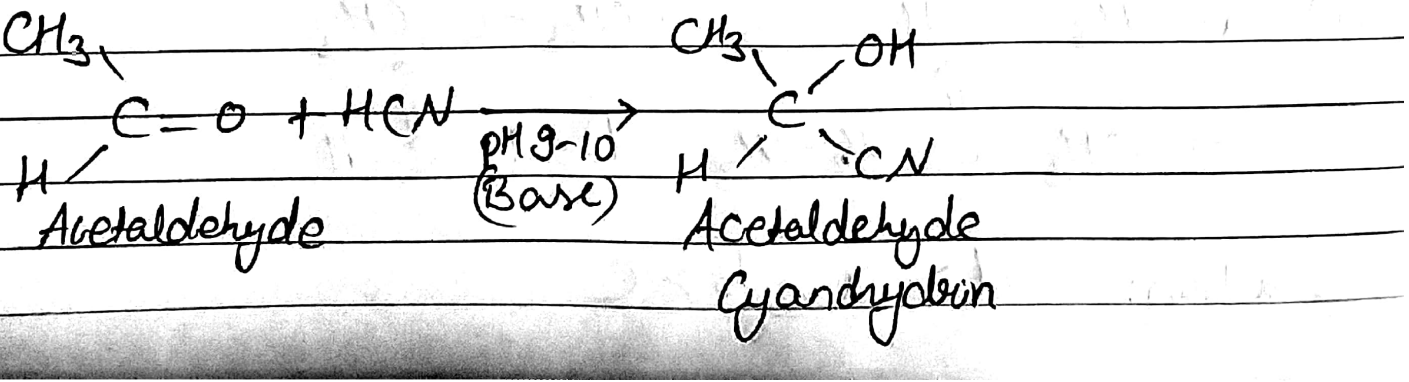


i) Addition of HCN:– with Base Catalyst

$$OH^- + H\text{-}CN \longrightarrow CN^- + H_2O$$

from base





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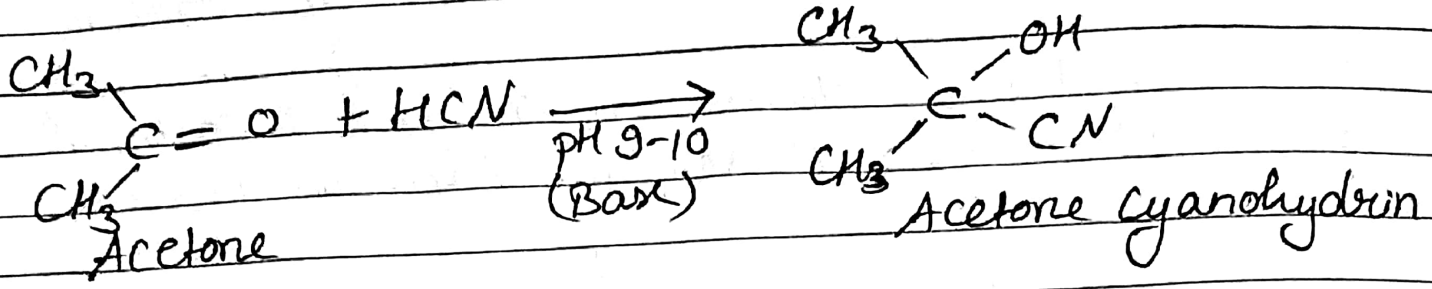

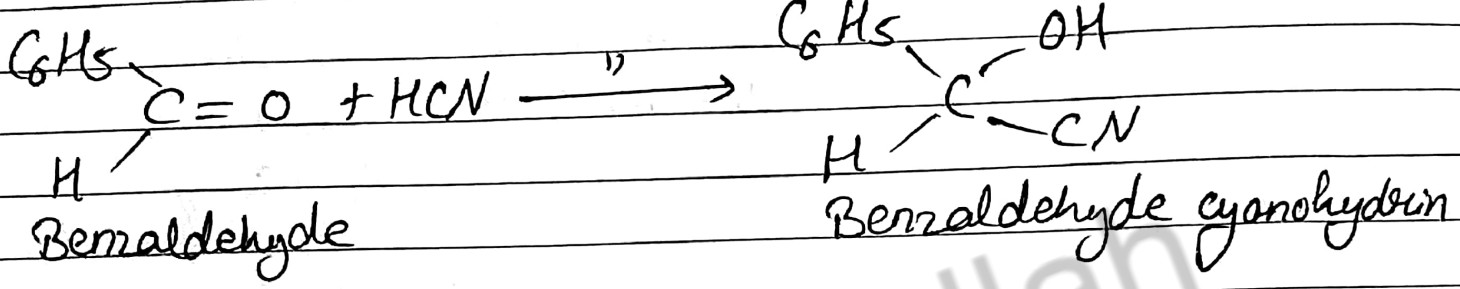

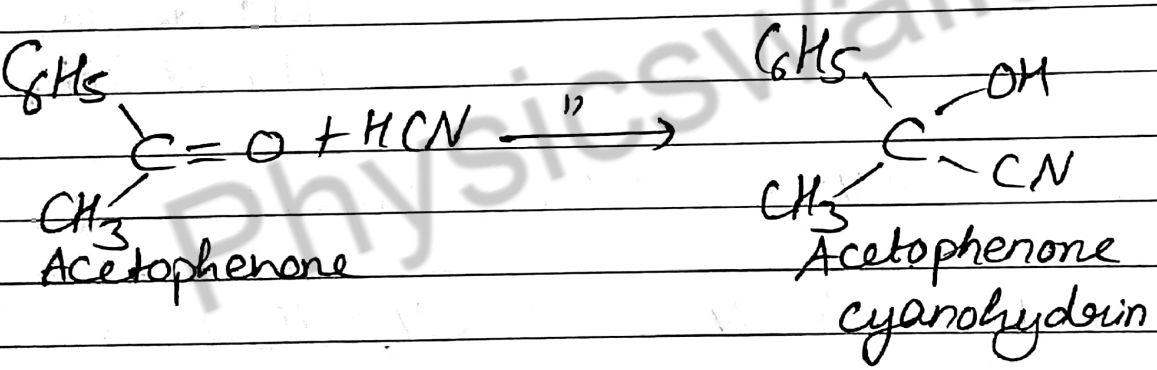

Rate of Reaction $\propto \frac{1}{\text{steric hinderance}}$

Q) Arrange in decreasing order of reactivity towards HCN.

(1) a) $CH_3-\overset{\overset{O}{\|}}{C}-H$ b) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

c) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$ d) $H-\overset{\overset{O}{\|}}{C}-H$

Solution: d > a > b > c

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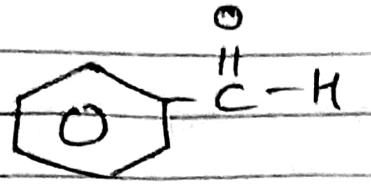
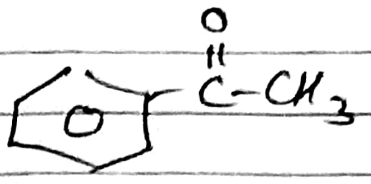
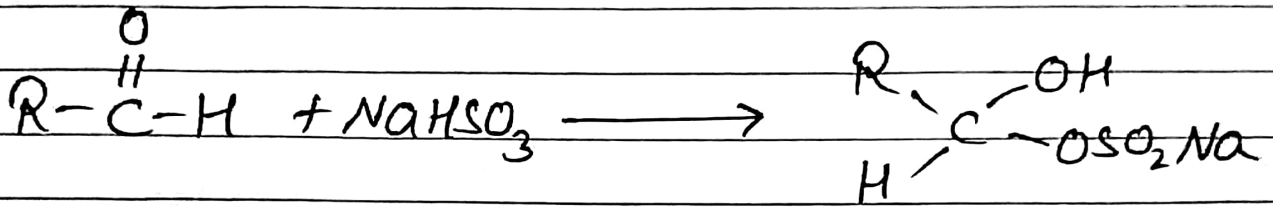
(2) a) 

b) 

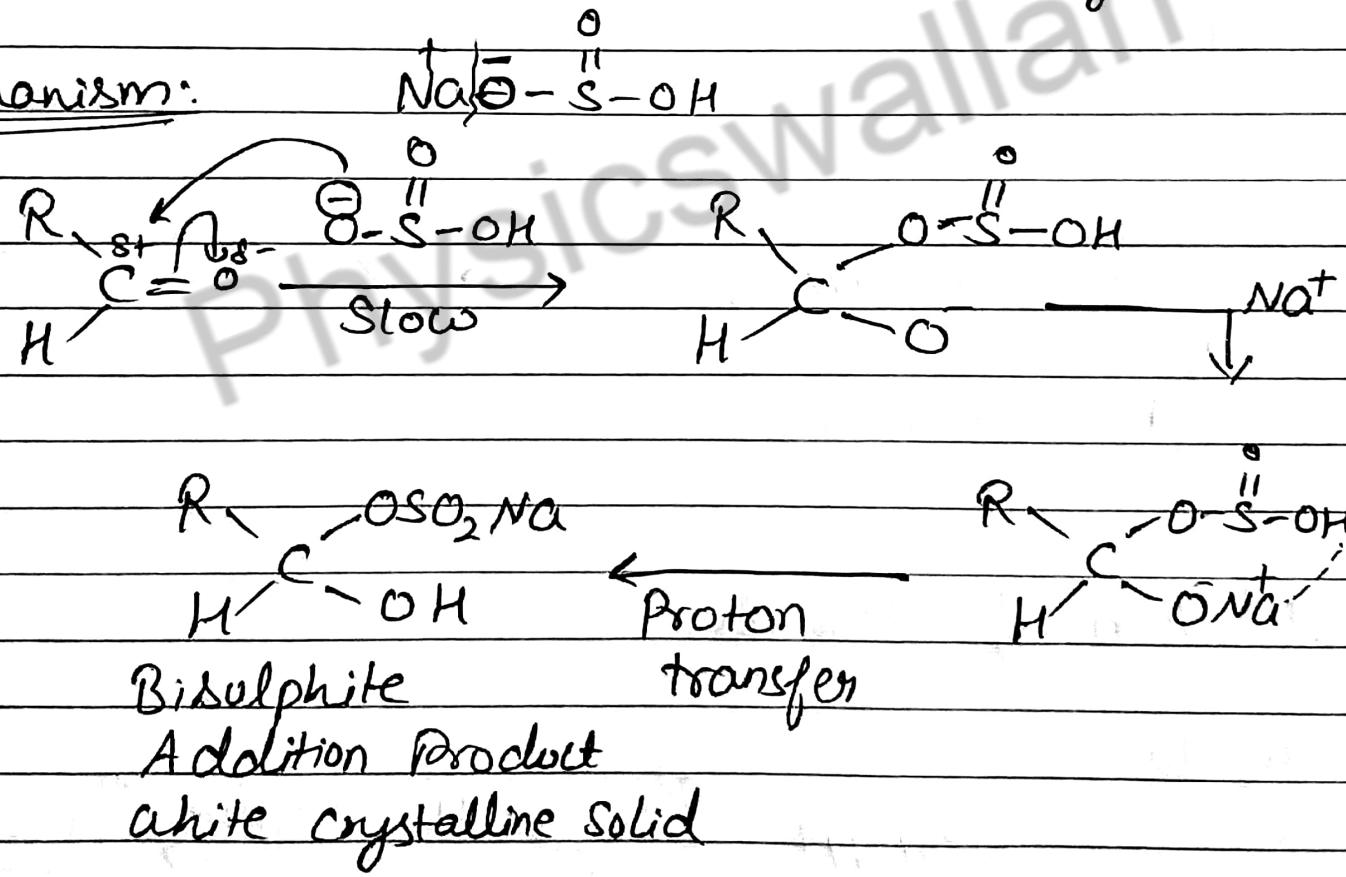
Solution: a > b

ii) Addition of $NaHSO_3$ (sodium hydrogensulphite)



white crystalline solid

Mechanism:



Bisulphite Addition Product white crystalline solid

For Ketones: lower Ketones (Methyl Ketones) gives Addition product while higher Ketones don't due to steric crowding

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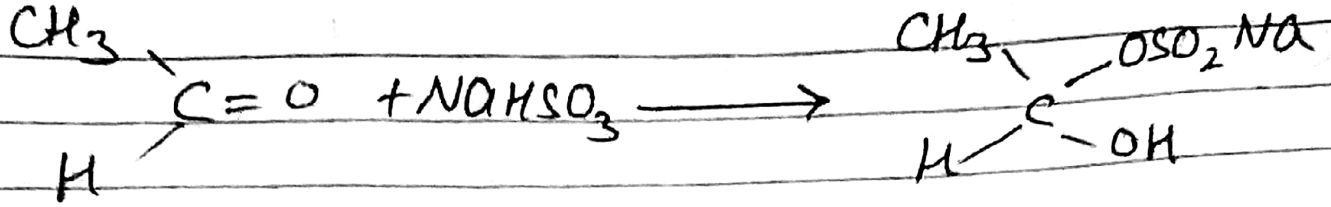
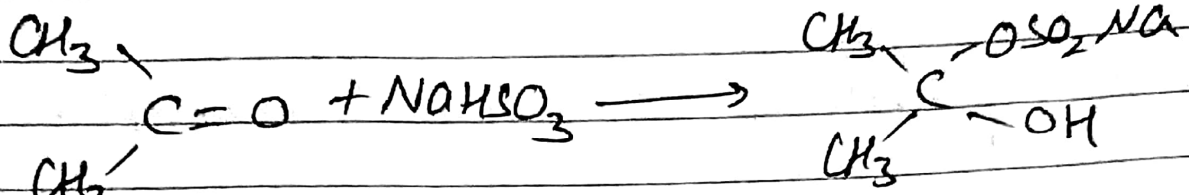
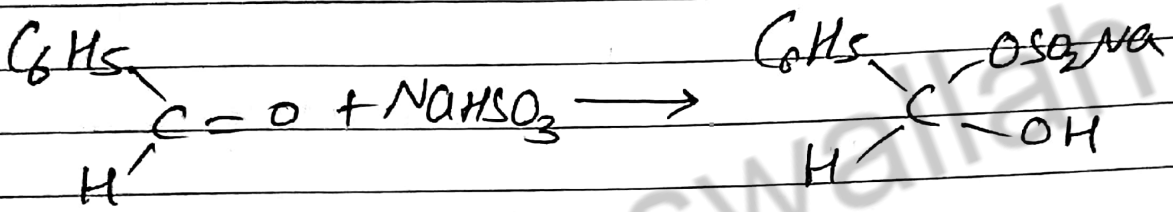
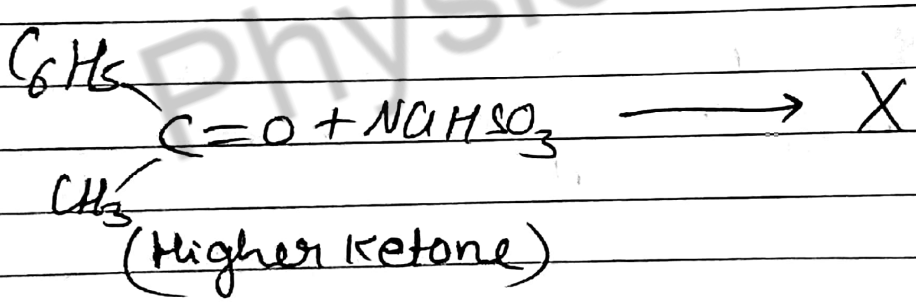


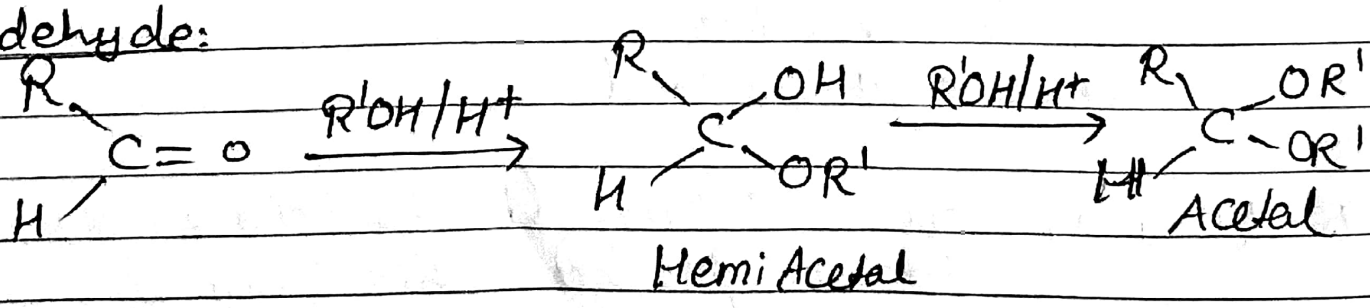






iii) Addition of alcohols:

Aldehyde:



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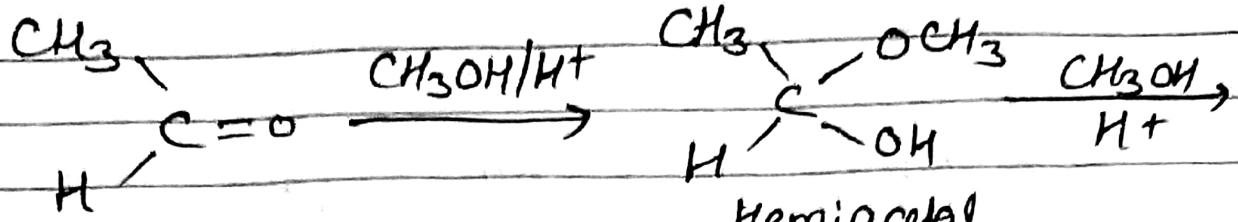
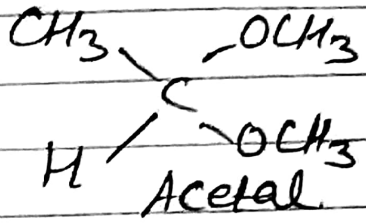
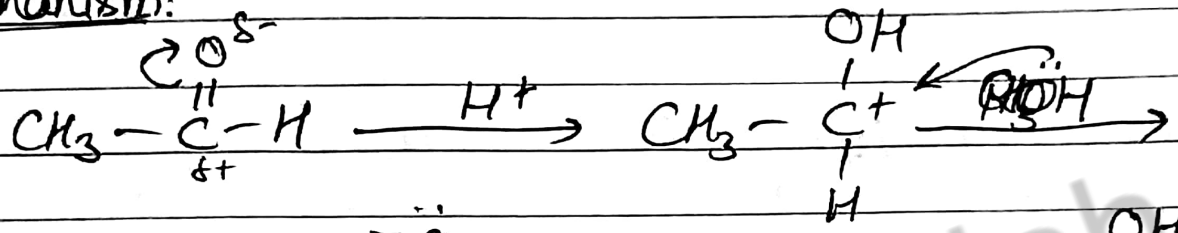
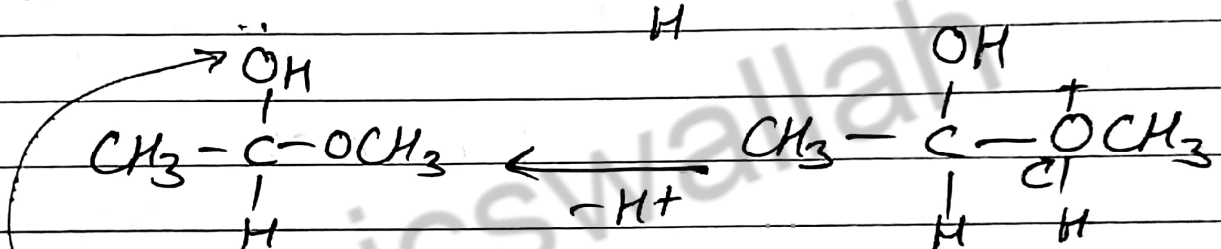
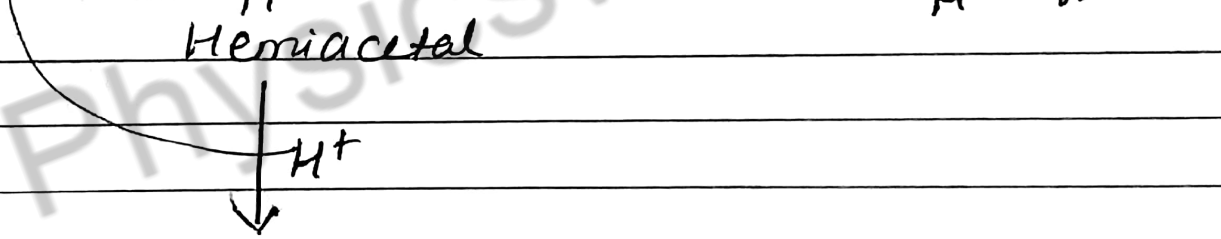


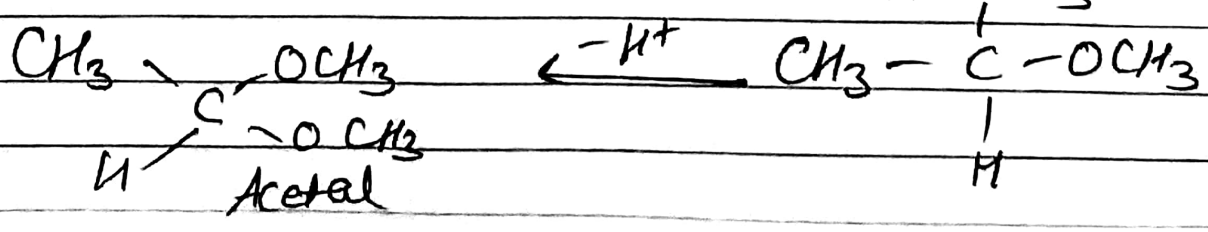


Mechanism:









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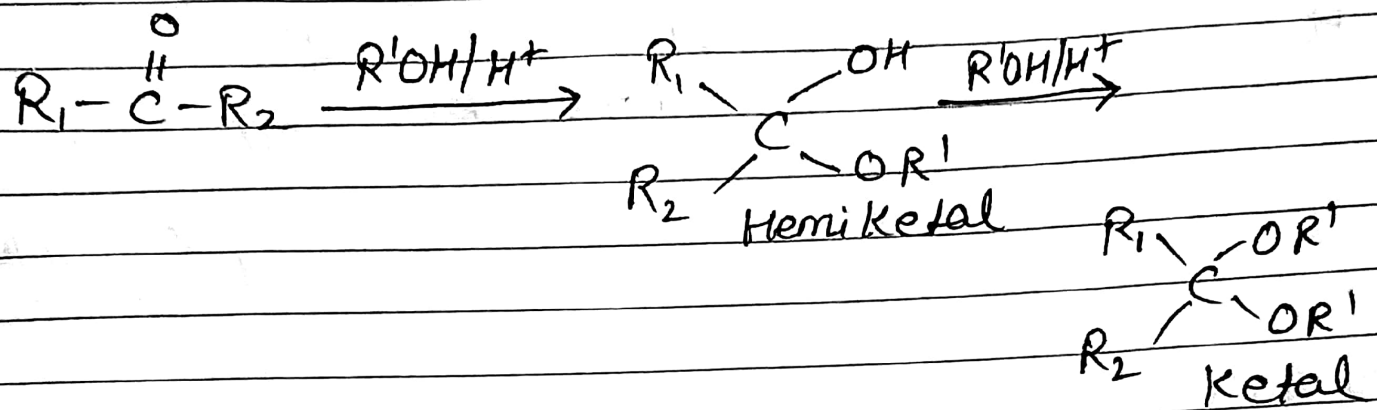
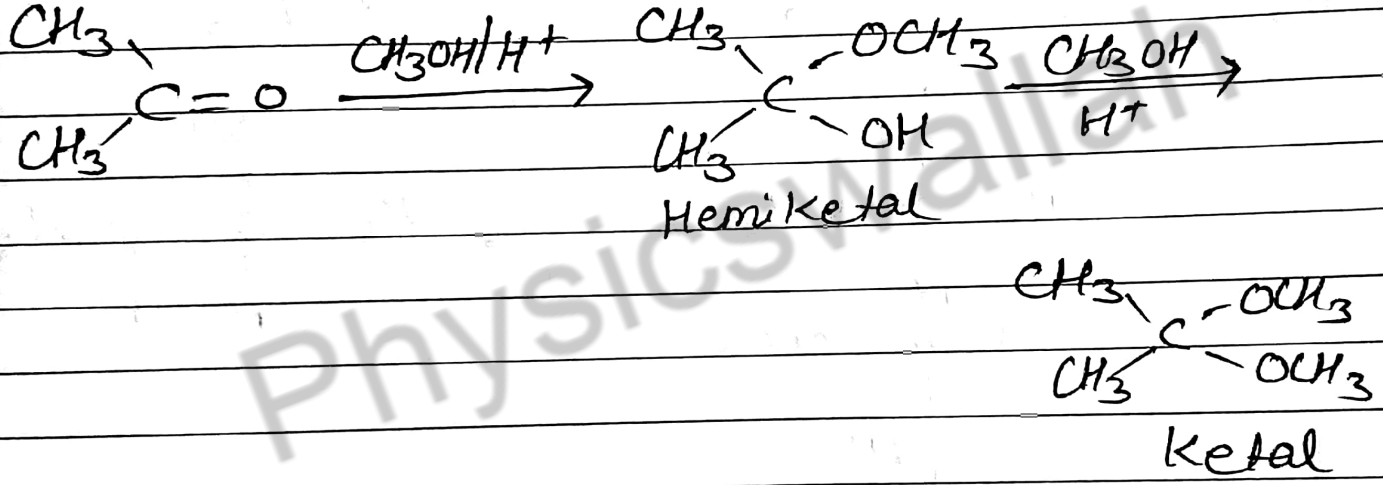
Ketones:





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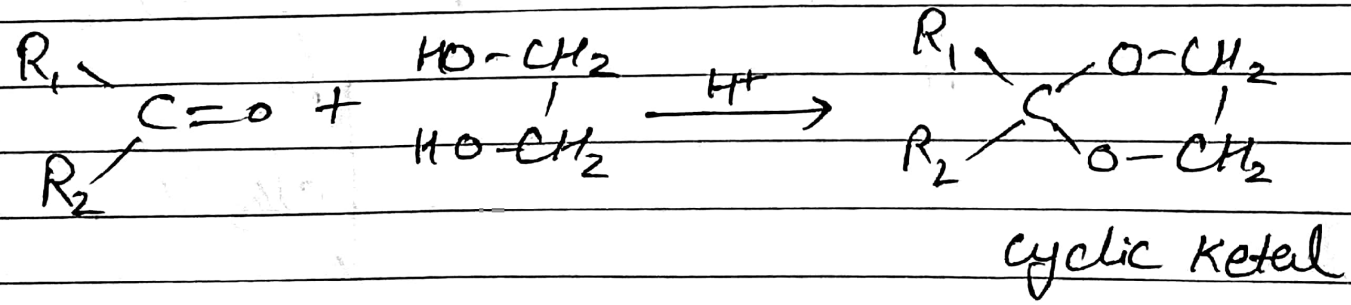
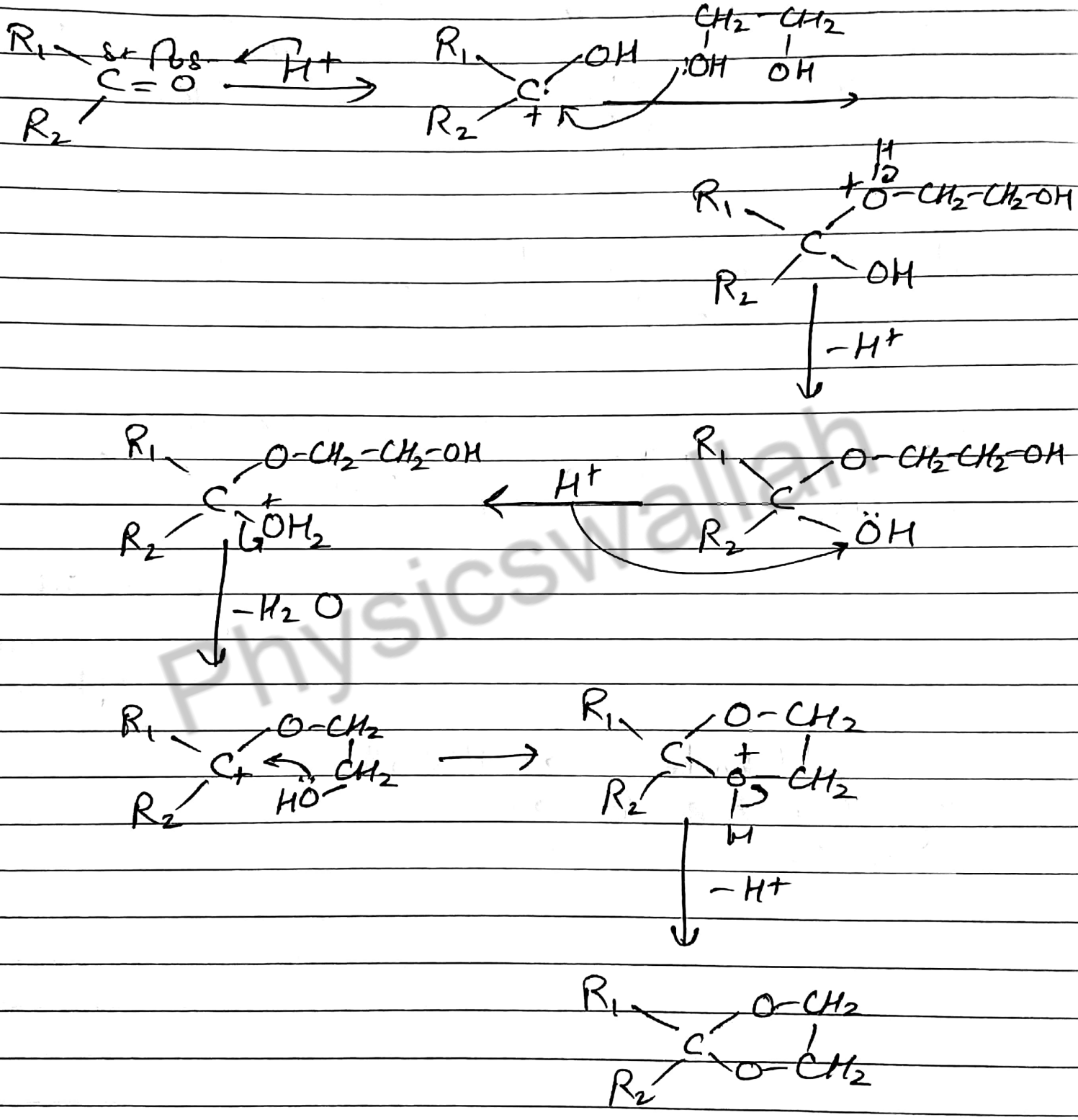
Ketones also react with glycol to give cyclic Ketal



cyclic Ketal

Mechanism:



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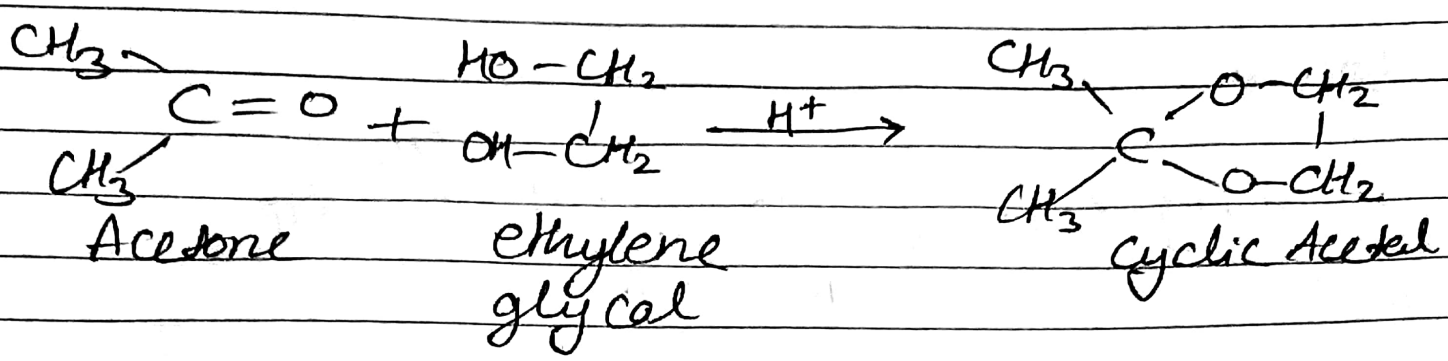
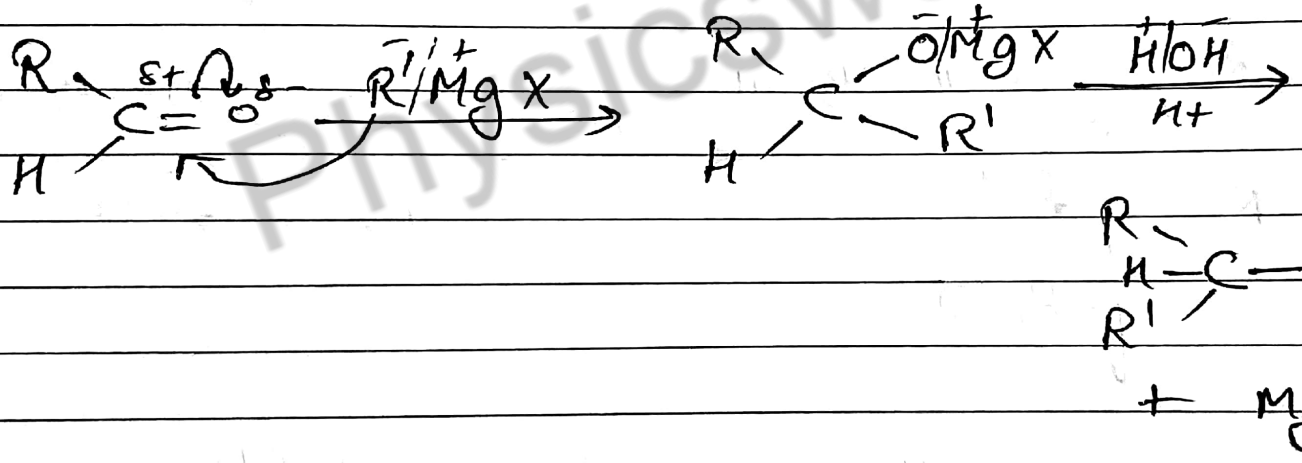


(iv) Addition of Grignard's Reagent: RMgX
— Preparation of alcohol



Formaldehyde ⟶ 1° Alcohol
Any other aldehyde ⟶ 2° "
Ketone ⟶ 3° "

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