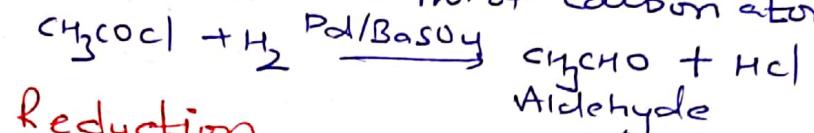


## Aldehydes and Ketones

### Method for production of only Aldehydes

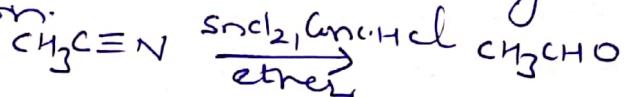
#### 1 Rosenmund Reduction -

When a stream of hydrogen gas is passed into a boiling solution of an organic acid chloride in xylene (solvent) in the presence of  $Pd$  on  $BaSO_4$ , the acid chloride is reduced to an aldehyde. Acid chloride may be converted into an aldehyde with the same no. of carbon atoms.



#### 2 Stephen Reduction -

Alkyl cyanide, dissolved in ether, is reduced by stannous chloride and conc.  $HCl$  to give aldehyde, which is recovered by steam distillation.



### Nucleophilic addition reactions of carbonyl compounds:

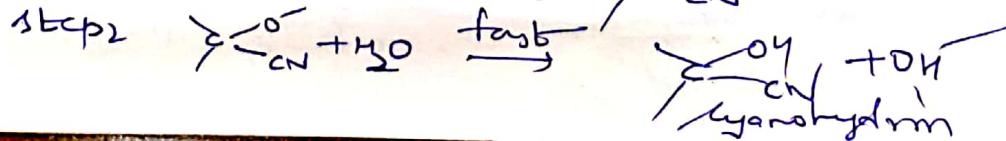
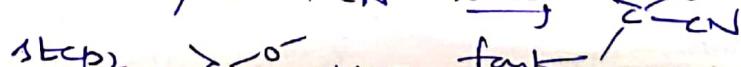
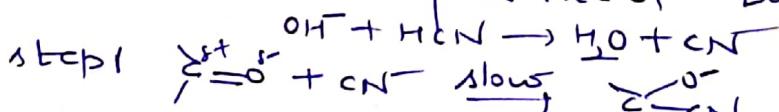


The heteroatom i.e. oxygen in the case of carbonyl compound reduces the  $\pi$ -electron density on the carbonyl carbon. Thus attack of nucleophile take place at carbonyl carbon.

#### 1 Addition of Hydrogen Cyanide -

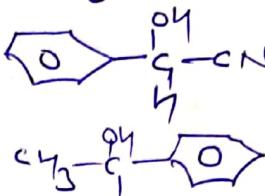
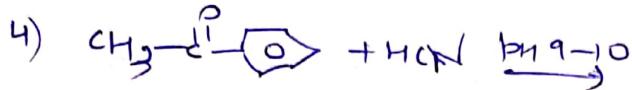
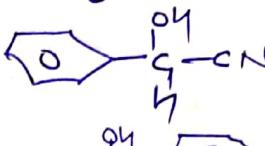
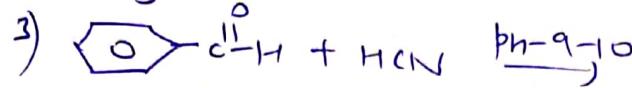
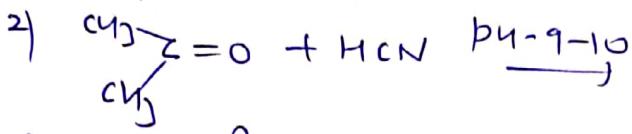
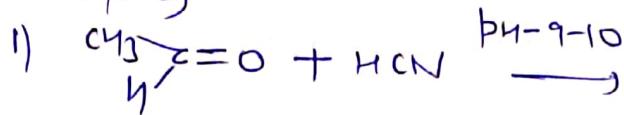
Both aldehydes & ketones add a molecule of hydrogen cyanide to form cyanohydrin. With pure  $HCN$  reaction occurs slowly, thus it is catalyzed by base. The  $CN^-$  thus generated is a strong nucleophile readily adds to carbonyl carbon.

"Reaction is reversible & the yield of cyanohydrin increases in the presence of base"



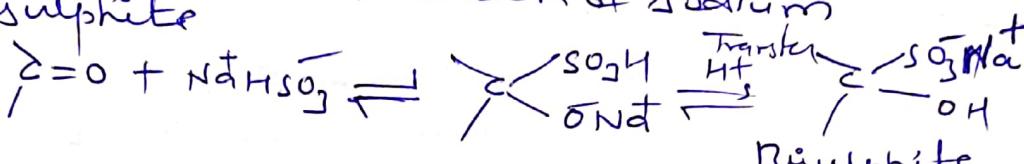
## Examples

(2)



2 Reaction with Sodium bisulphite

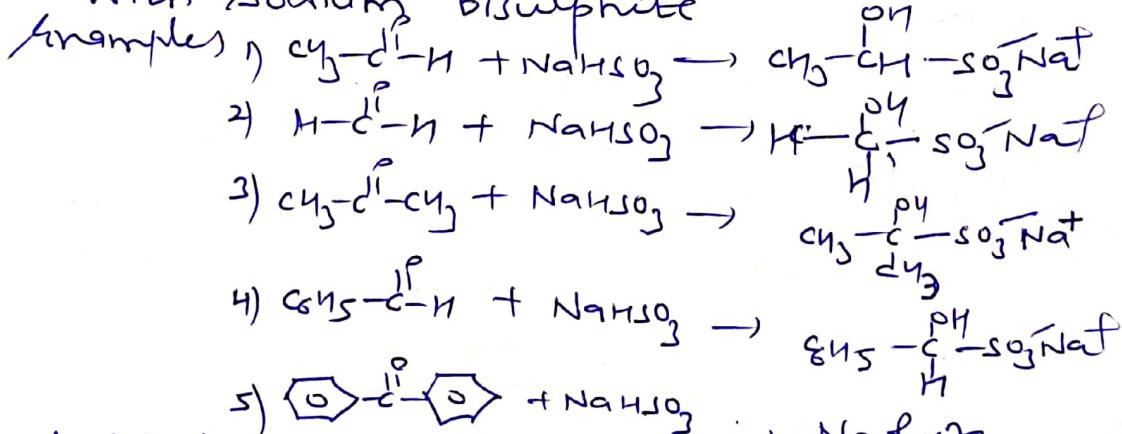
Alddehyde and lower ketone form solid crystalline addition product when shaken with saturated solution of sodium bisulphite



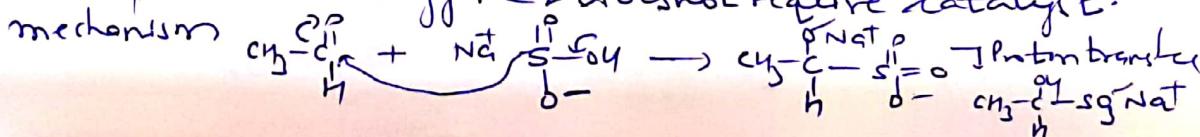
The position of equilibrium lies largely to the right hand side for most of ~~ketones~~ aldehydes & to the left for most of ketones due to steric hindrance.

The bisulphite addition product is formed by all aldehydes and only by methyl ketones

The other ketones due to decrease in the electrophilicity of the carbonyl carbon and also because of steric hindrance do not react with Sodium bisulphite

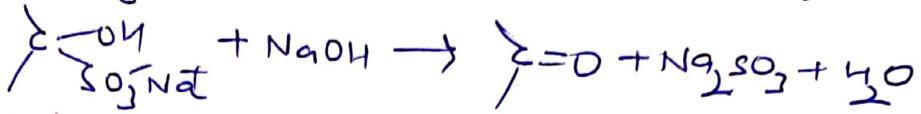
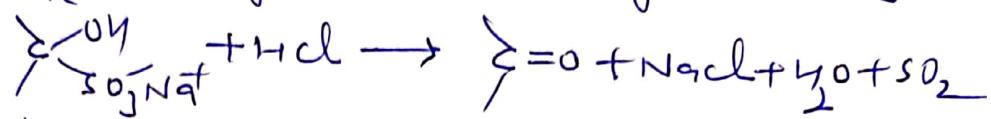


Aryl ketones do not give addition salt. The attack of Sodium bisulphite occurs through Sulphur, which is a better nucleophile than compared to oxygen & does not require catalyst.



(3)

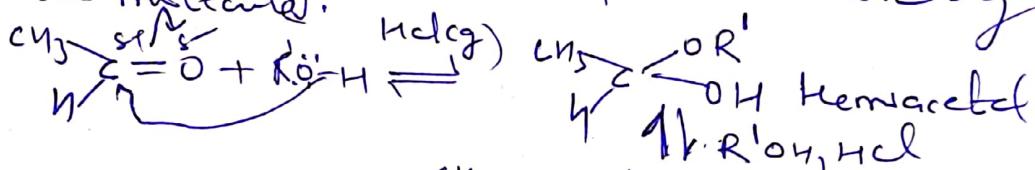
These bisulphite addition products when heated with dil mineral acid or aqueous alkali, these decompose to regenerate the original aldehyde or ketone



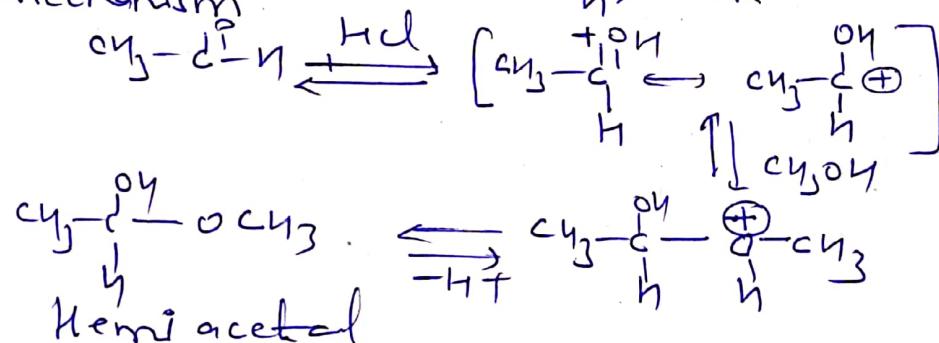
### 3 Addition of alcohols - Acetal & ketal formation

Aldehydes react with one equivalent of a monohydric alcohol in the presence of a dry HCl gas to yield first alkoxymethyl intermediate called hemiacetal. These then react with one more molecule of alcohol to give gem-dialkoxyl compound known as acetals.

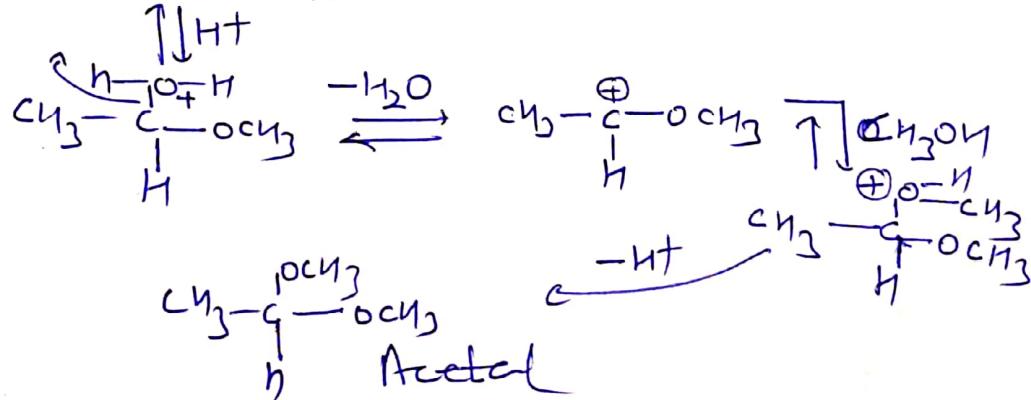
Dry HCl protonates the oxygen atom of the carbonyl group thereby increasing the electrophilicity of the carbonyl carbon and facilitating of nucleophilic attack by alcohol molecule.



mechanism

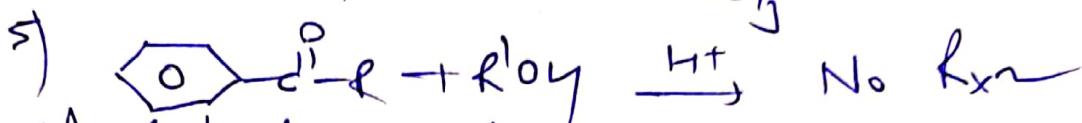
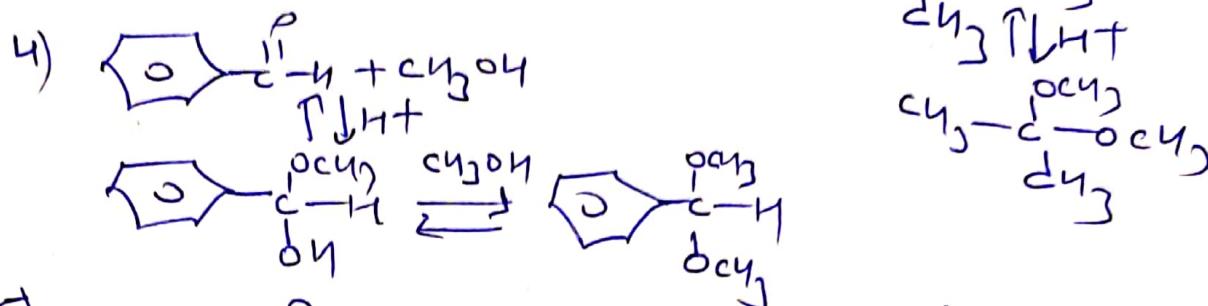
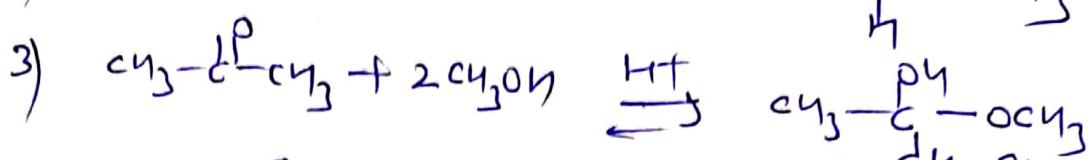
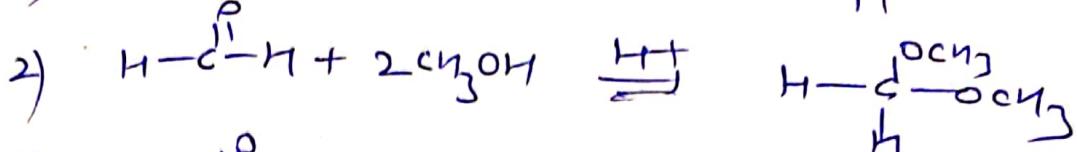
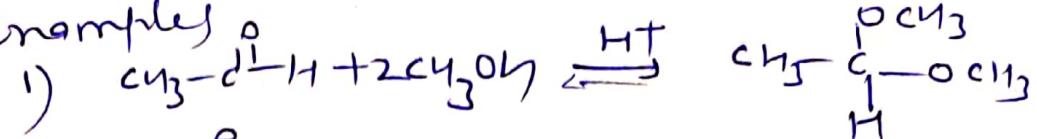


Hemiacetal



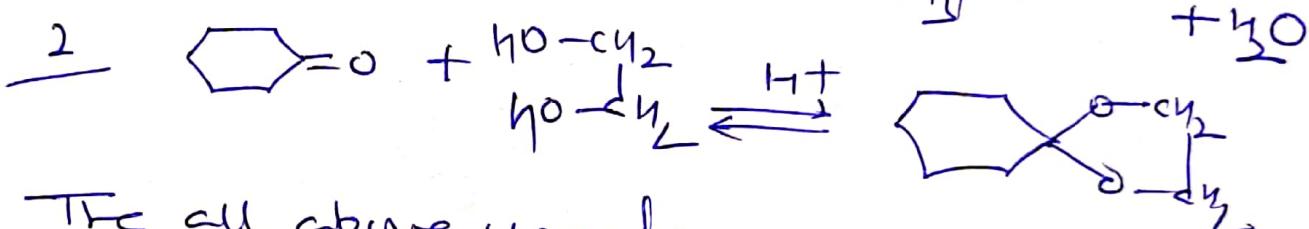
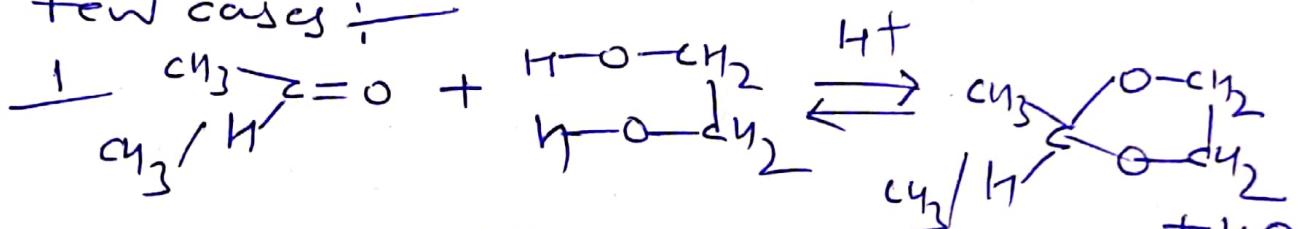
(4)

Enamples



Vinyl ketones do not undergo addition of alcohol to form hemiketal & lactal.

few cases :-



In all above reactions are reversible.  
Therefore, acetals & ketals are hydrolysed by dil acids to regenerate aldehydes + ketones.

