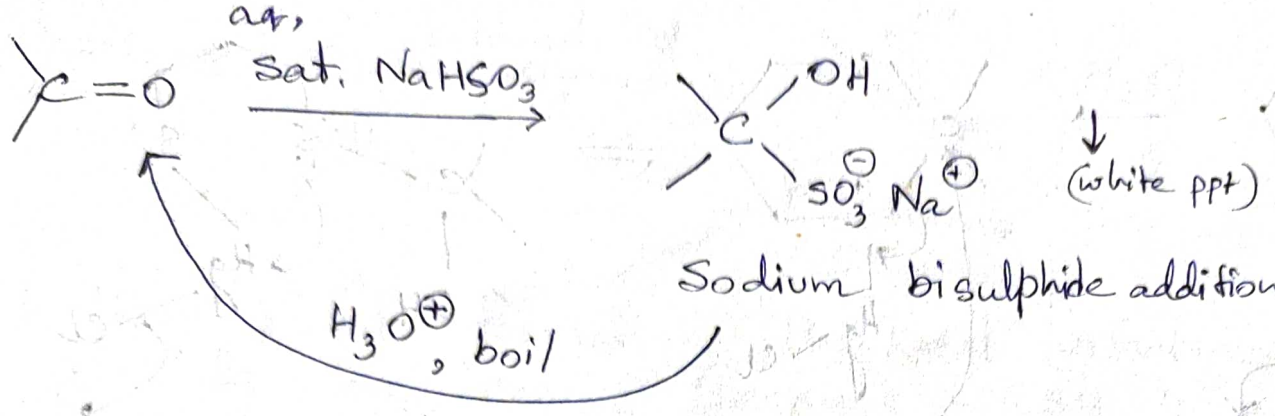
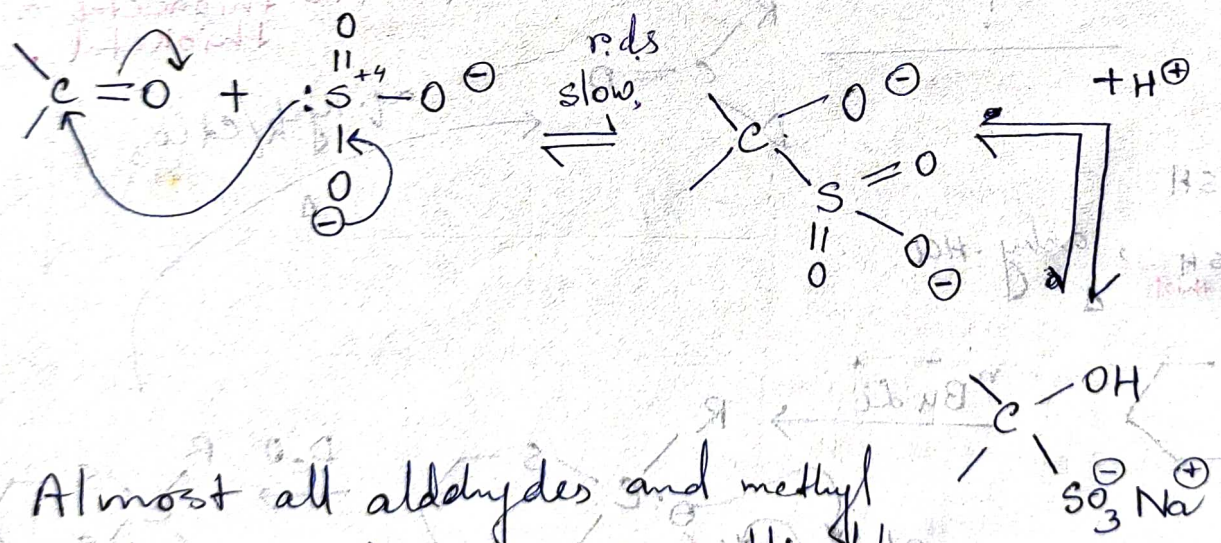
($NaHSO_3$) Sodium bisulphite addition :—



This rxn can be used for seperating and/or purifying a carbonyl compound from a mixture containing other type of compounds.

$$NaHSO_3 \rightleftharpoons Na^{\oplus} + HSO_3^{\ominus}$$

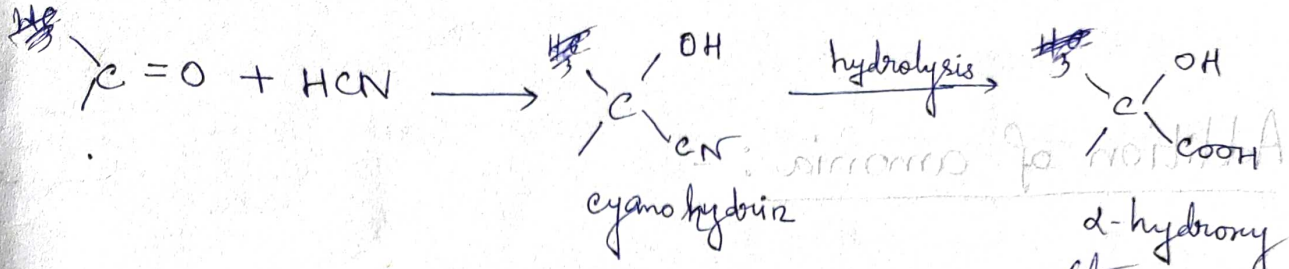
$$HSO_3^{\ominus} \rightleftharpoons \underset{\text{nu}^{\ominus}}{\underline{SO_3^{2-}}} + H^{\oplus}$$

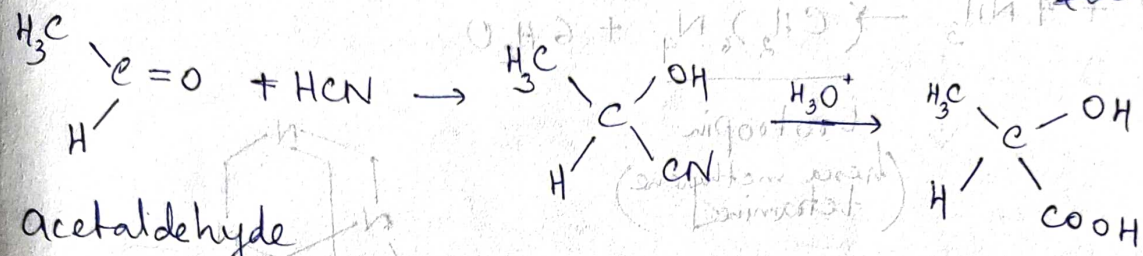


Almost all aldehydes and methyl ketones give this rxn. Highly hindered ketones can not give this rxn.

5)

Addition of HCN :-





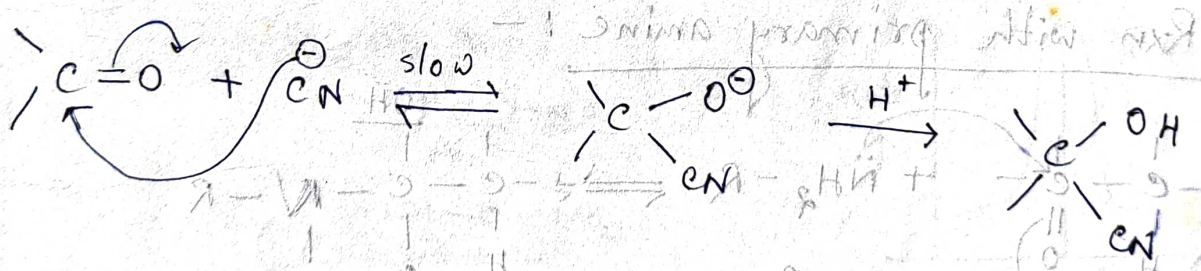
This rxn is better achieved by using little alkali catalyst.

$$HCN \rightleftharpoons H^{\oplus} + CN^{\ominus}$$

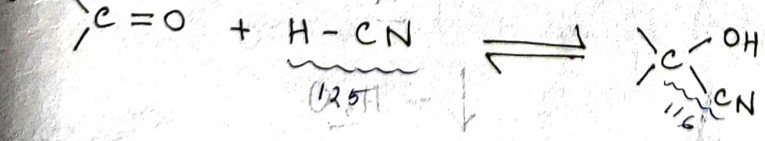
$$H-CN + OH^{\ominus} \rightleftharpoons H_2O + CN^{\ominus}$$

$(KCN + H_2SO_4) \longrightarrow$ actual reagent

নাহলে HCN + $OH^{\ominus}$ সামান্য alkali দিয়ে rxn করতে হবে, নাহলে sufficient $CN^{\ominus}$ উৎপন্ন হবে না।

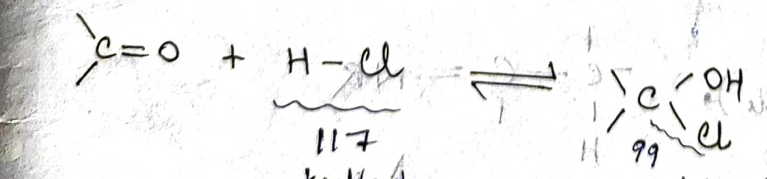


Q:)



① H-CN, C-CN

$\Delta H = +9$ kcal/mol.
(more favourable) less +ve.



② H-Cl, C-Cl

$(-99)-(-117)$

$\Delta H = 117 - 99$

$= +18$ kcal/mol.
(less favourable)

α-chlorohydrin
(highly unstable, never obtained)

Why?

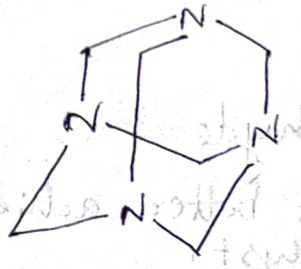
Hence, cyanohydrine formation is energetically more favourable.

more +ve, ΔG more +ve..

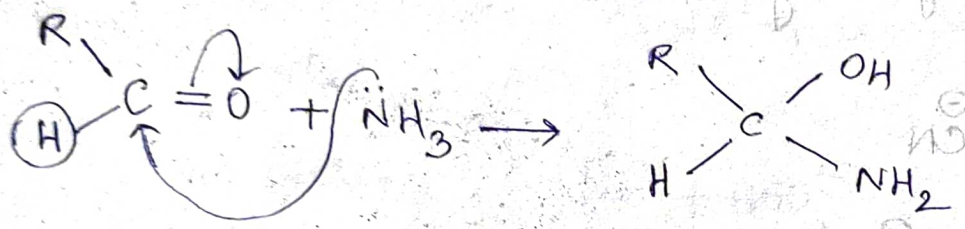
Addition of amonia :-

$$6\,CH_2{=}O + 4\,NH_3 \rightarrow (CH_2)_6N_4 + 6\,H_2O$$

Urotropin
(hexa methylene tetramine)



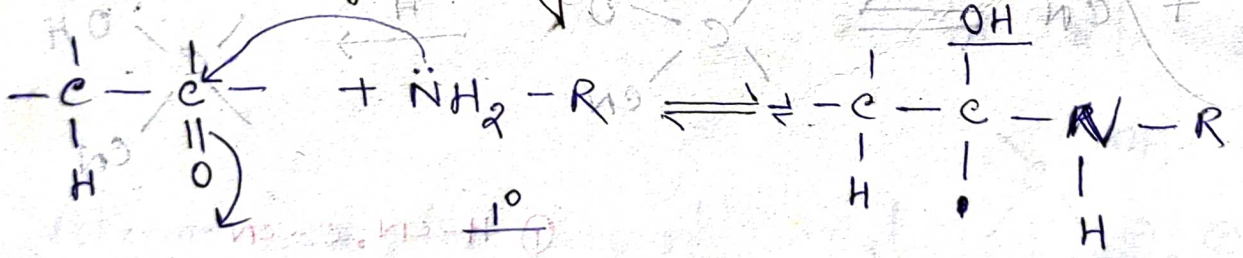
$(CH_2)_6N_4$
urotropin



(aldehyde amonia addition palt.)

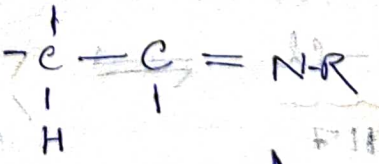
No such rxn occurs with ketone due to depressed reactivity of ketone.

Rxn with primary amine :-

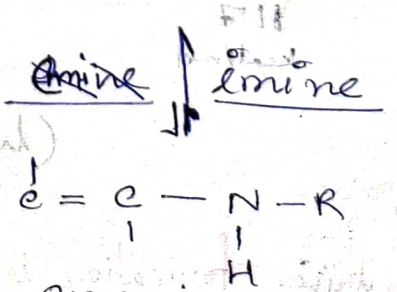


$\downarrow -H_2O$

Schiff's base (more stable)



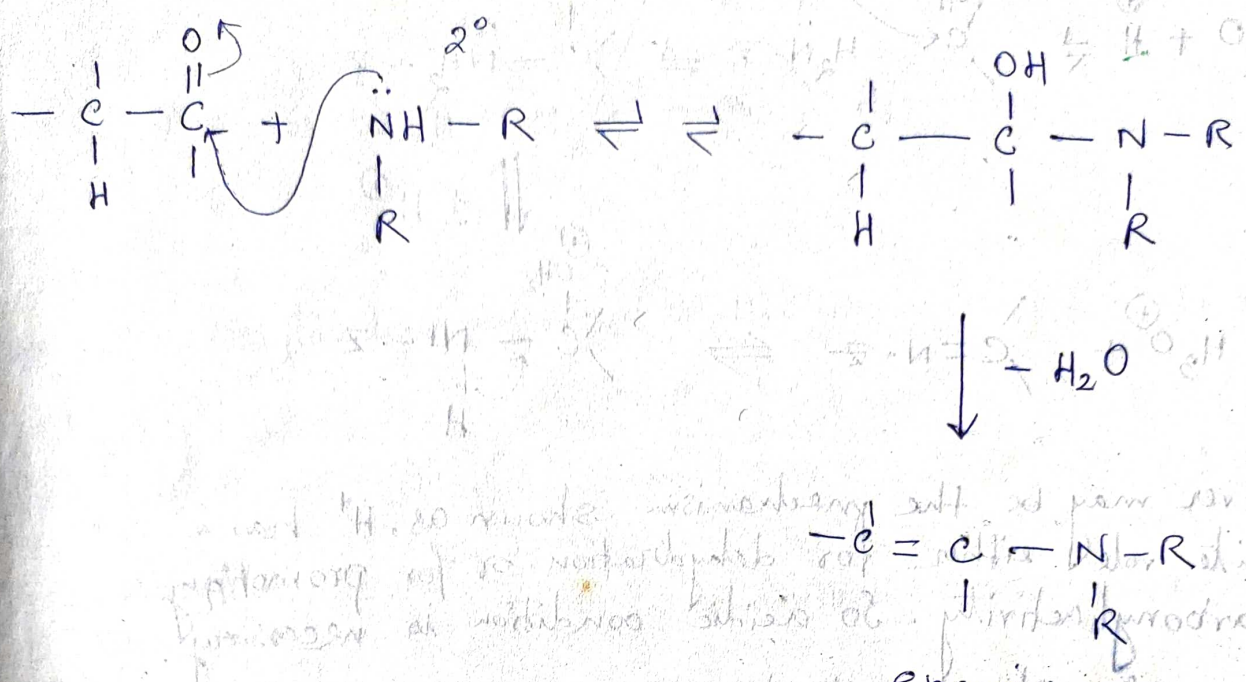
imine - enamine tautomerism



enamine

Rxn with sec. amine :

carbonyl compound must contain α H.



enamine

Such rxn not occur with 3° amine because there are no H with N. (NR_3).

- $>C=O$ + H_2N-Z $\xrightarrow{pH \approx 4.5-5.5}$ $>C=N-Z$

oxym - OH

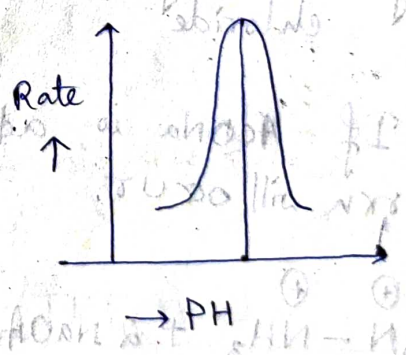
hydrazine - NH_2

phenyl hydrazine - NH - Ph

2,4 DNP - NH - (benzene ring) - NO_2, NO_2

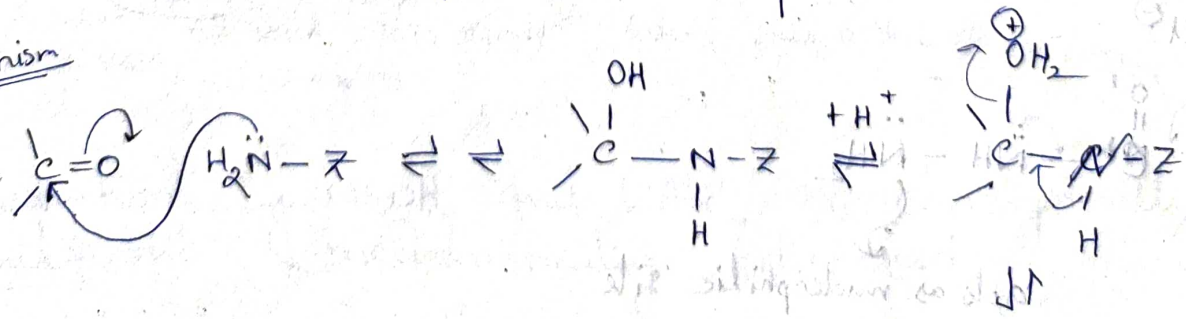
- NH - CO - NH_2

Semicarbazide

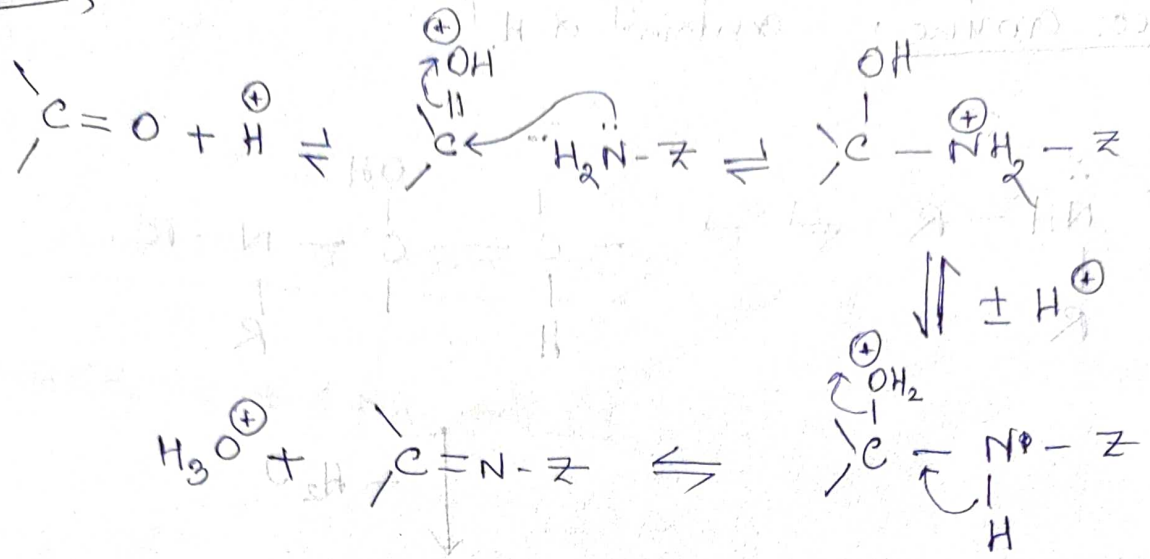


Rxn occur at optimum acidic pH.

mechanism



OR,



Whatever may be the mechanism shown as, H^+ has a definite role either for dehydration or for promoting of carbonyl activity. So acidic condition is necessary.

If acid strength increases, the nucleophile will get completely protonated & its nucleophilicity will be lost.

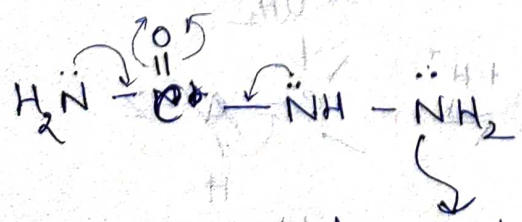
$$\ddot{N}H_2 - Z + H^{\oplus} \rightleftharpoons H_3\overset{\oplus}{N} - Z$$

- $\overset{\ominus}{Cl}\ \overset{\oplus}{N}H_3 - \overset{\oplus}{N}H_3\ \overset{\ominus}{Cl}$ $\xrightarrow[EtOH]{>C=O}$ No rxn

Hydrazine dihydro chloride

If AcONa is added to the above rxn mixture, the rxn will occur.

$$\underset{2Cl^{\ominus}}{H_3\overset{\oplus}{N} - \overset{\oplus}{N}H_3} + 2\,NaOAc \rightleftharpoons H_2N - NH_2 + 2\,NaCl + 2\,AcOH$$

- 

acts as nucleophilic site

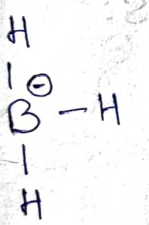
Reduction of carbonyl :-

$$>C=O \xrightarrow{*} >CH-OH \longrightarrow >CH_2$$

* • catalytic hydrogenation (cat. H_2) ✓
• $H^{\ominus}$ ✓
• electron

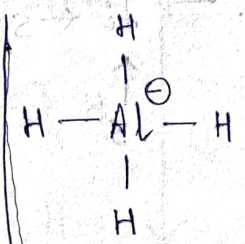
Reduction by $H^{\ominus}$:-

Simple $H^{\ominus}$ doner like - $NaBH_4$, $LiAlH_4$ etc.
$LiBH_4$, DIBALH
(di iso propyl aluminium boro hydride)



weaker $H^{\ominus}$ doner

$H^{\ominus}$ more firmly bound as size of B small.



aprotic solvent must be used, otherwise H^+ will react with $H^{\ominus}$ to give $H_2\uparrow$.

stronger $H^{\ominus}$ doner

$H^{\ominus}$ less firmly bound due to big size of Al.

No protic solvent used.

Non-protic solvent - Ether/THF used ✓

Protic solvent - MeOH ~~used~~ can be used.

As B has small size hence strong bond, loss of $H^{\ominus}$ losses the octate of B.
~~protic s~~

Reductions by $NaBH_4$ and $LiAlH_4$ are conceptually similar but mechanistically different.

↓
both are $H^{\ominus}$ reduction.

Chemoselective rxn :-

$R-CH=CH-\overset{O}{\overset{\|}{C}}-R'$

(α, β unsaturation carbonyl compound)

$\xrightarrow{NH=NH \text{ (di-imide)} \; (NH_2-NH_2 + H_2O_2)}$ $R-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-R'$

$\xrightarrow{LAH \text{ or } CatH_2}$ $R-CH_2-CH_2-\overset{OH}{\overset{|}{C}H}-R'$

$\xrightarrow{NaBH_4}$ $R-CH=CH-\overset{OH}{\overset{|}{C}H}-R'$

(generally, not always)