Aldehyde & ketone

$R-\overset{O}{\overset{\|}{C}}-H$ $R-\overset{O}{\overset{\|}{C}}-R'$

Prep:: 1. By oxidation

$CH_3-\overset{CH_3}{\underset{H}{\underset{|}{C}}}-OH \xrightarrow{[O]} CH_3-\overset{CH_3}{\underset{}{C}}=O$ (2° alcohol)

Reagent → alkaline $KMnO_4$ (moderate), $K_2Cr_2O_7/H^+$ (strong), CrO_3/Py (moderate)

$KMnO_4/H^+$ (strong), Conc. HNO_3 (strong)

$CH_3CH_2OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3\overset{O}{\overset{\|}{C}}-OH$

2. By reduction : $CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{[H]} CH_3CHO \xrightarrow{[H]} CH_3CH_2OH$

2 Rosenmund reduction

$R-\overset{O}{\overset{\|}{C}}-OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\Delta]{+H_2/Pd,\ BaSO_4} R-\overset{O}{\overset{\|}{C}}-H$

$BaSO_4$ acts as catalyst poison

Ketone from dialkyl cadmium

$2\,CH_3-\overset{O}{\overset{\|}{C}}-Cl + Cd(CH_3)_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CdCl_2$

3. From ozonolysis

$>C=C< \ +O_3 \longrightarrow$ ozonide $\xrightarrow[H_2O]{Zn\ dust} >C=O + O=C<$

aldehyde or ketone or both

Q. On ozonolysis reⁿ: formaldehyde & acetone are obtained. What is the structure of the reactant?

$H_2C=C(CH_3)_2 + O_3 \longrightarrow H_2C=O + O=C(CH_3)_2$

4. From hydrolysis of alkyne

$H-C\equiv C-H \xrightarrow{Hg^{+2}/H_2SO_4\ (dil.)}$ addition of H_2O on symmetrical alkyne

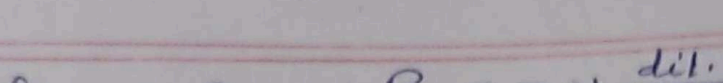
$H-C(OH)=C-H \rightleftharpoons H-CH_2-C(=O)-H$ keto enol tautomerism

$CH_3-C\equiv C-H \xrightarrow{HgSO_4/dil.\ H_2SO_4}$ Markonikoff's rule

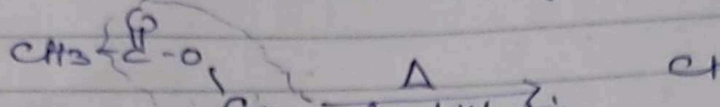
OH^- adds to the C which contain least H.

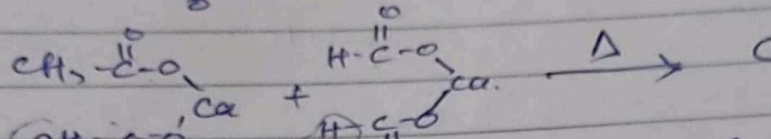
$CH_3-C(OH)=C-H \rightleftharpoons CH_3-C(=O)-CH_3$

5. Stephen rexn:



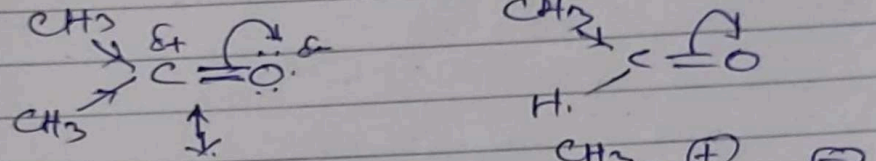
6. From Ca-salt of fatty acid





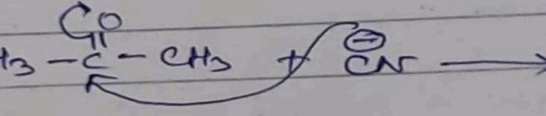
mixture of fatty acids.

Properties.

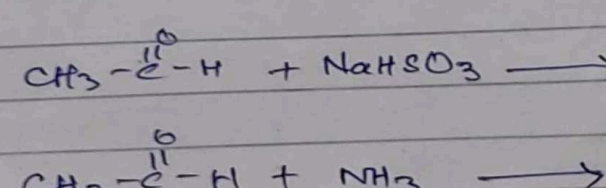


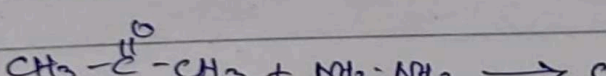
$Nu^{\ominus}$ ⇒ CN^-, NH_3, $R-NH_2$, OH^-, HSO_3^-, NH_2-NH_2 (hydrazine), $Ph-NH-NH_2$, NH_2OH

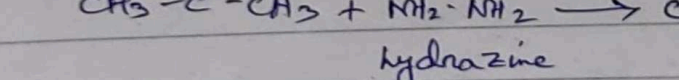
(1) Reactions:

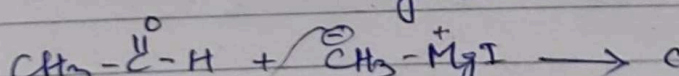


Nucleophilic addition rexn:



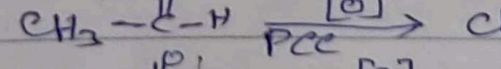


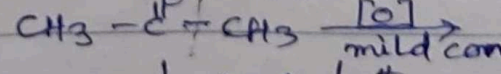




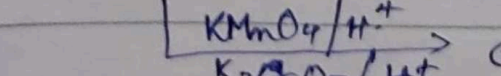
2. Oxidation

PCC / CrO_3 / PY





No rexn



oxidative degradation

** $R-CHO + \text{Ammoniacal } AgNO_3 \xrightarrow{[Ag_2O]} R-\overset{O}{\overset{\|}{C}}-OH + Ag\downarrow$ (Tollen's reagent) — Silver mirror

$R_2C=O + \text{Ammoniacal } AgNO_3 \xrightarrow{[Ag_2O]}$ No rex^n.

Distinguish bet^n aldehyde & ketone

* $R-CHO + Cu^{++}$-Fehling's reagent $\xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-OH + Cu_2O\downarrow$ red ppt.

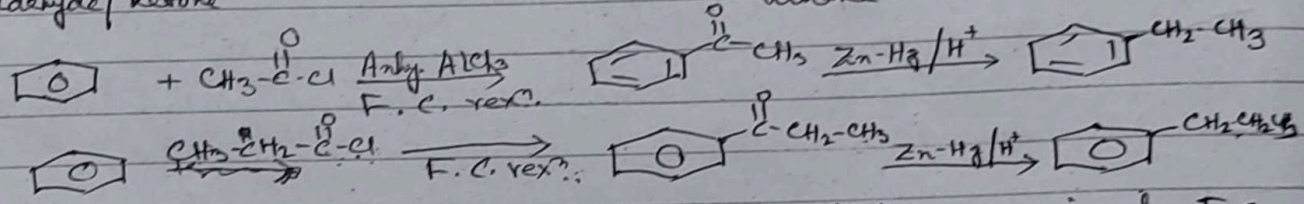
Fehling reagent $\Rightarrow$ Na,K-Tartarate + $CuSO_4 \Rightarrow$ blue Cu^{++} (colourless)

Distinguish bet^n ald. & ketone & identification of aldehyde.

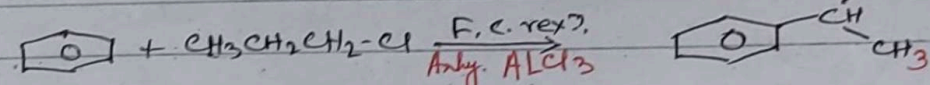
3. Reduction of aldehyde & ketone:

i) Clemmensen red^n

$>C=O$ (aldehyde/ketone) $+ Zn\text{-}Hg/HCl \longrightarrow >CH_2$ (alkane)



Utility: Long chain is difficult to introduce in benzene ring by F.C. rex^n. However, Clemmensen red^n is useful.



ii) Wolff-Kishner red^n

$>C=O + NH_2-NH_2$ (hydrazine) $\longrightarrow >C=N-NH_2$ (hydrazone H) $\xrightarrow{NaOEt.} >CH_2 + N_2\uparrow$

iii) red^n by red P/I_2.

$CH_3-\overset{O}{\overset{\|}{C}}-R \xrightarrow{\text{red P}/I_2} CH_2(I)-\overset{O}{\overset{\|}{C}}-R$

4. * Iodo form rex^n / Haloform reaction

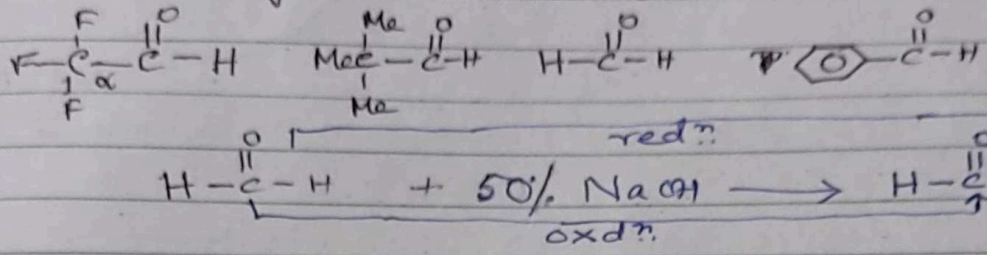
$CH_3-\overset{O}{\overset{\|}{C}}-R + I_2/NaOH \longrightarrow I-CI_2-\overset{O}{\overset{\|}{C}}-R \xrightarrow{OH^-} CHI_3\downarrow + R-\overset{O}{\overset{\|}{C}}-O^{\ominus}$ (yellow ppt)

only for $CH_3-\overset{O}{\overset{\|}{C}}-$ gr. $\Rightarrow$ Presence of CH_3CO- group

CH_3CH_2OH আয়োডোফর্ম বিক্রিয়া দেয়, কিন্তু CH_3OH দেয়না — কারণ আয়োডি NaOH দ্রবণে যোগ করলে প্রথমদিকে হাইপো আয়োডাইট NaOI তৈরী হয়। NaOI প্রবল মৃদু হওয়ায় ইহা ইথানলকে প্রথমে অ্যাসিটালডিহাইডে তৈরী করে, যা আয়োডোফর্ম বিক্রিয়া অংশগ্রহণ করে। পক্ষান্তরে, মিথানল প্রবল বিক্রিয়ার প্রথমে ফর্মালডিহাইড গঠন করে। কিন্তু CH_3CO- গ্রুপের অনুপস্থিতিতে ফর্মালডিহাইড আয়োডোফর্ম বা হ্যালোফর্ম বিক্রিয়া দেয় না।

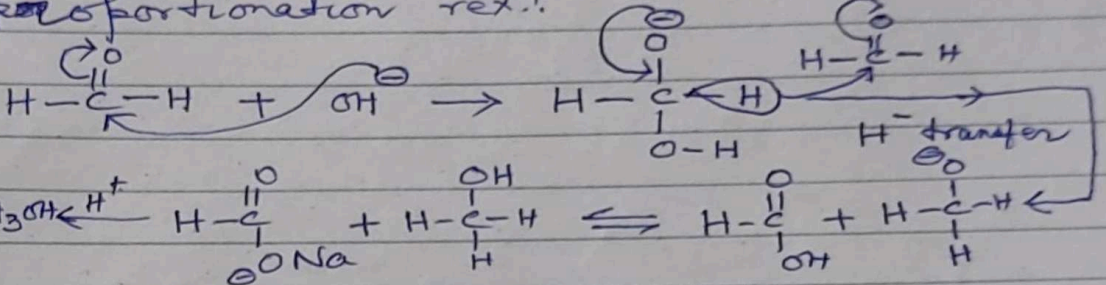
5. Cannizaro rex^n : i) given by some aldehydes only & not by ketone.

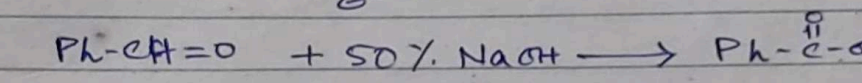
ii) aldehydes which ~~contain~~ does not contain any α H atom gives Cannizaro rex^n.



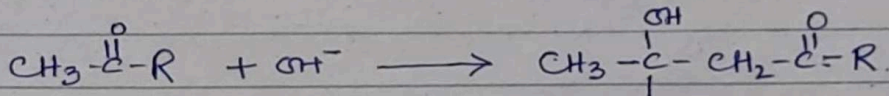
Disproportionation rex^n.

Mech.



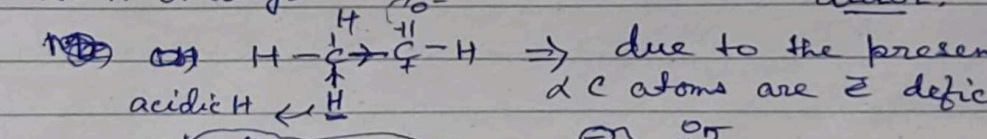


6. Aldol condensation : given by aldehyde & ketones with α H atoms.

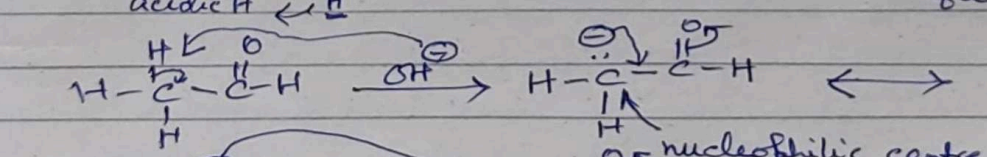


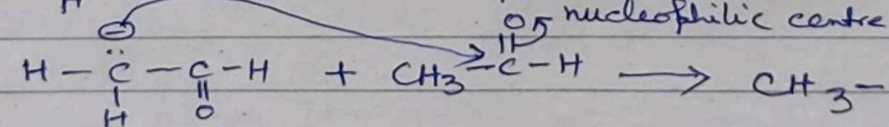
R = H or alkyl

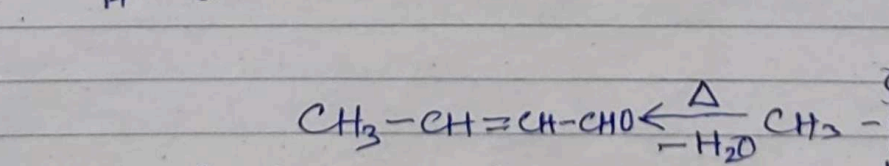
aldol.



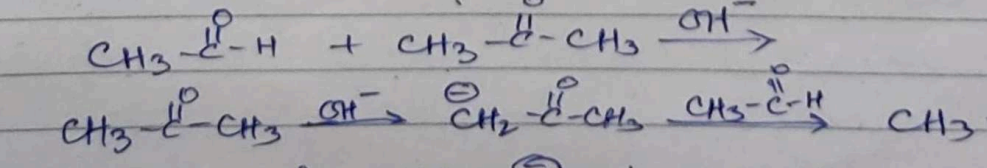
⇒ due to the presence of C=O gr. the α C atoms are ∂+ deficient







Crossed aldol condensation



Ketones form the ~~nu~~ ⊖ in greater extent,