DU) - Part I, Paper II, Group B.
Chem-Col: Prep of Ald. & Ket. DR Vinay
Lec-11

Cannizzaro reaction: →

Carbonyl group Compound (Aldehyde or Ketone) having no α-hydrogen i.e formaldehyde (Methanal), benzaldehyde, trichloroethanal (trichloroacetaldehyde) or Chloral can show this reaction in presence of Conc. NaOH or Conc. KOH. During the reaction we use two mols of same no. of carbon containing aldehyde having no α-hydrogen, out of these two mole one will be oxidised & other will be reduced to give metal carboxylate & alcohol. During the reaction Oxidation and Reduction take place simultaneously thats why it is also called Redox reaction or Disproportionation reaction.

$$2H-CHO \xrightarrow{Conc.\ NaOH} H-COONa + CH_3OH.$$

$$2HCHO \xrightarrow{Conc.\ NaOD} HCOONa + CH_3OD$$

Note: Hydrogen atom present in functional group of alcohol has come from strong base like NaOH or KOH. Instead of H (Protium) if we use deuterium (D) then D will come instead of H in alcohol and O in carboxylic acid also come from Base.

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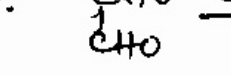
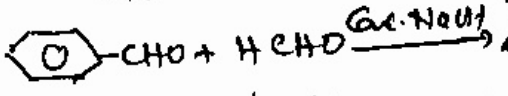
Cannizzaro reaction are of three types

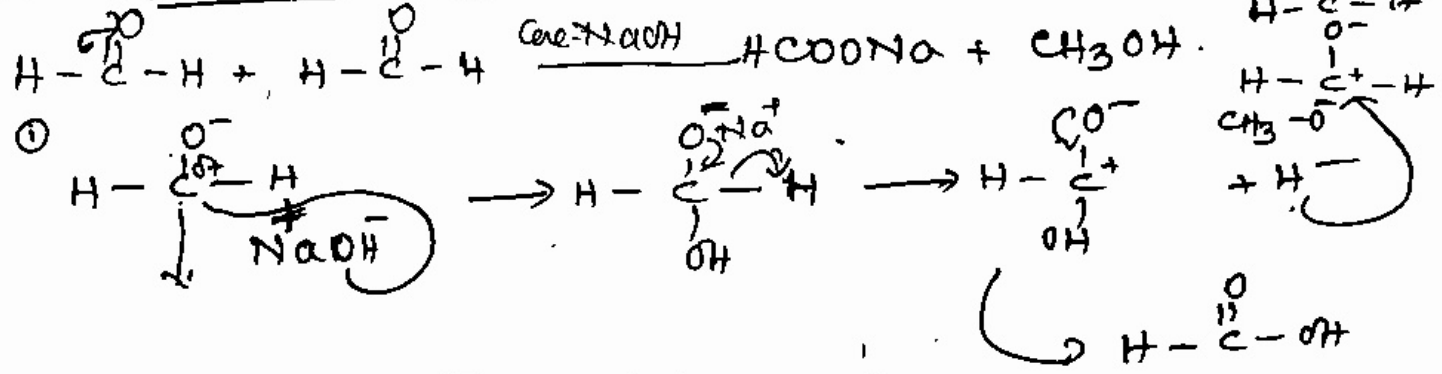
i) Intermolecular: $HCHO + HCHO \xrightarrow{Conc.NaOH} HCOONa + CH_3OH$

ii) Intramolecular: 

iii) Cross Cannizzaro 
Benzylalc. Sod. formate

In first two condition both groups are same in carbonyl compound so any one can oxidise or reduce, but in the cross cannizzaro reaction two different carbonyl compounds (one is aromatic and other is aliphatic) ~~carbonyl compound~~ take part in reaction in presence of Conc. NaOH or Conc. KOH, during Cross Cannizzaro reaction smaller carbon containing carbonyl compound will Oxidise and larger one will be reduced.

Mech of the reaction: →



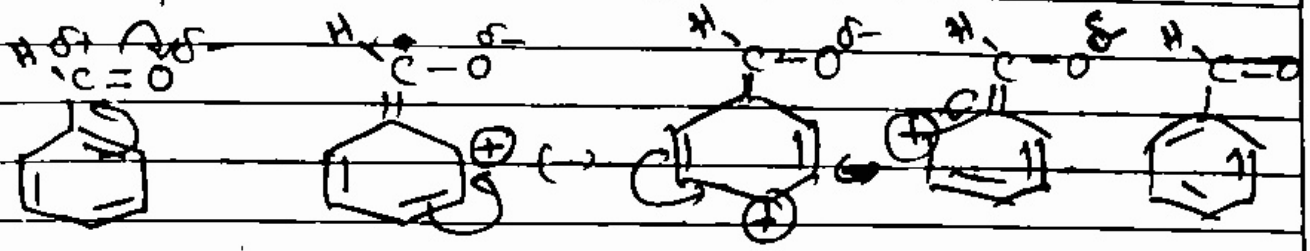
$CH_3ONa + HCOOH$	Not Stable
$CH_3OH + H-COONa$	Stable

Exception: There is a compound (Carbonyl Comp) which contain α-hydrogen ~~so~~ but it show Cannizzaro reaction i.e

$CH_3>CH.-CHO$: 2° gem Cannizzaro reaction

2-Methyl Propan-1-al.

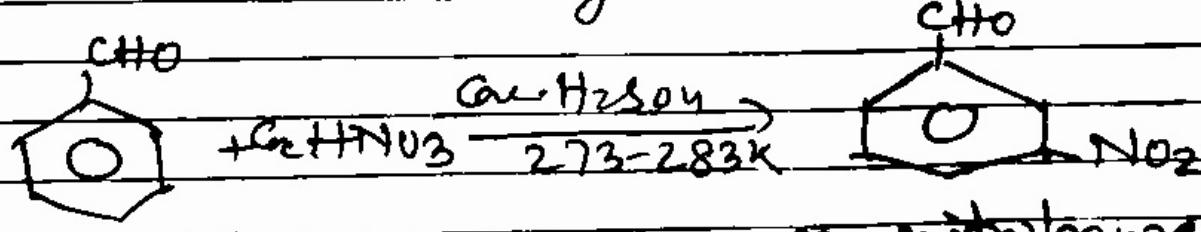
(F) Electrophilic Substitution reaction: →



In above resonance ⊕ve charge is formed on ortho and para position so meta is comparatively more negative, hence electrophilic attack will take place on meta position, So >C=O is meta directing group.

Nitration :-

Benzaldehyde react with Conc HNO3 in presence of Conc. H2SO4 at first it react with each other to form NO_2^+ which is an electrophile, during of reaction NO_2^+ will attack on meta position to form m-nitrobenzaldehyde.



Benzaldehyde m-nitrobenzaldehyde

Nitration reaction is a kind of electrophilic substitution reaction.

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(G) Haloform reaction:⟶ It is also called Iodoform test:⟶ If the $-\overset{O}{\overset{\|}{C}}-$ is on second position or OH is on second position of any compound they react with NaOH & I_2 to give CHI_3 (Iodoform) this reaction is called Iodoform test.

Except: CH_3-CH_2OH & CH_3CHO in these two Compound neither OH nor $-\overset{O}{\overset{\|}{C}}-$ is on second position still it respond for Iodoform test

i.e $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + NaOH + I_2 \longrightarrow CHI_3 + CH_3COONa + NaI + H_2O$
(Yellow ppt)

This reaction is used to identify 2-ol & 2-one with other Compound - Here, CH_3CH_2OH, CH_3CHO 2-ol, 2-one Compound give +ve iodoform test, so other Compounds except above mentioned can be identified by the help of iodoform test.

for example

Propan-1-ol & propan-2-ol.
Butan-1-ol & Butan-2-ol.
Pentan-2-one & pentan-3-one.
Ethanol & phenol
Ethanol & propan-1-ol.
Ethanal & methanal etc