- **Cannizzaro rxn** :

molecules (aldehyde) having no α H atom.

$$H_2CO + H_2CO \xrightarrow[\Delta]{50\%\ aq.\ NaOH} H_3C-OH + HCOO^{\ominus}$$

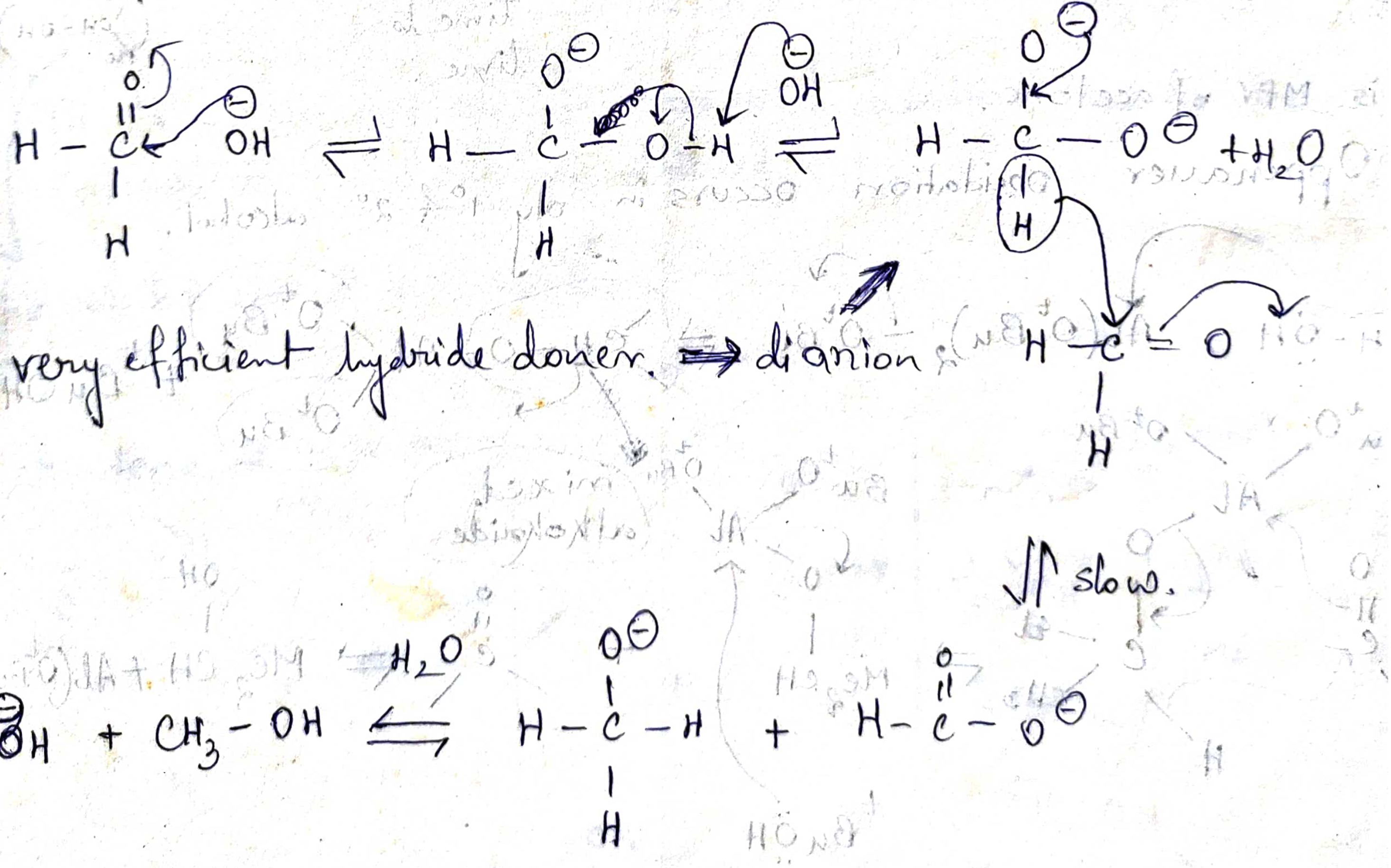
reduction

oxidation

{ Disproporsionation rxn
Self oxidation - reduction rxn
Compensatory oxidation - reduction rxn

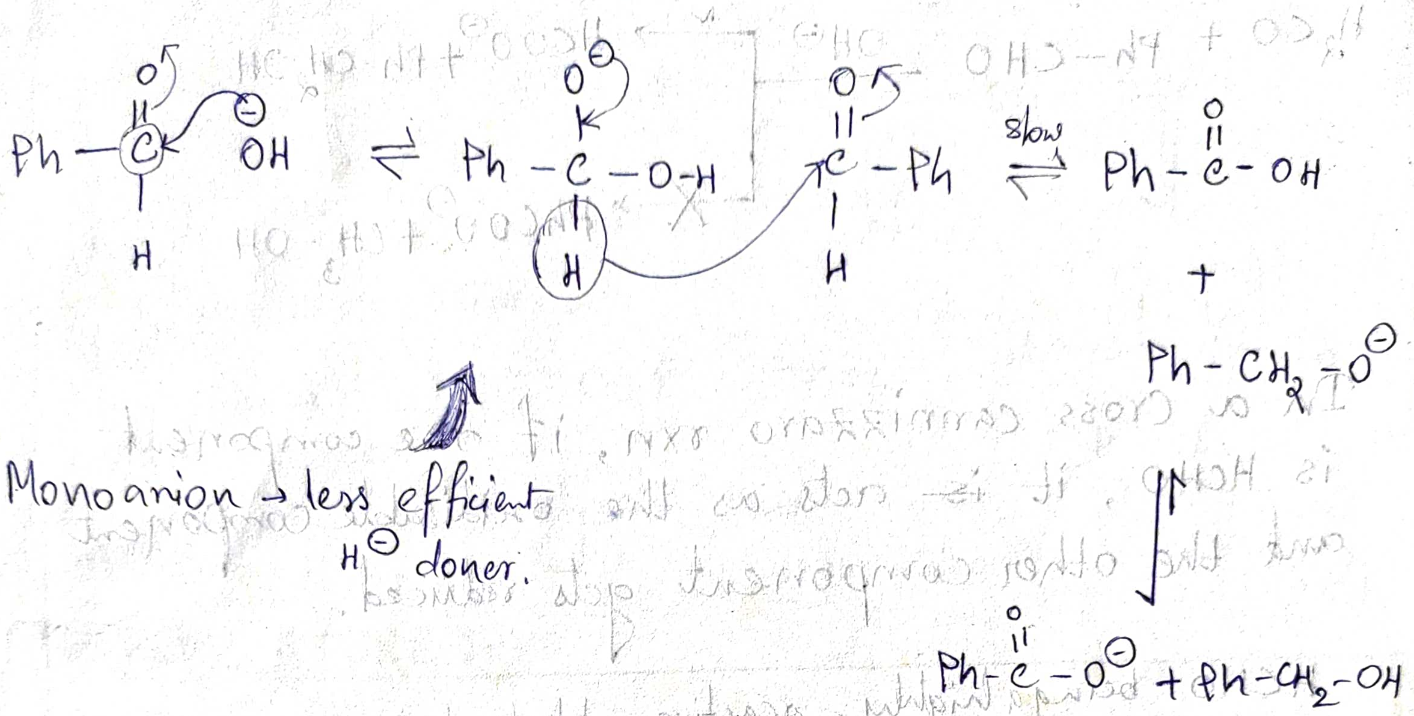
Rate $\propto [H_2CO]^2 [\overset{\ominus}{O}H]^2$

For, C_6H_5CHO ; Rate $\propto [PhCHO]^2 [\overset{\ominus}{O}H]$



very efficient hydride doner. ⇒ dianion

Mechanism with benzaldehyde :



Monoanion → less efficient $H^\ominus$ doner.

Q:) Proof of direct $H^\ominus$ transfer from one aldehyde to other:

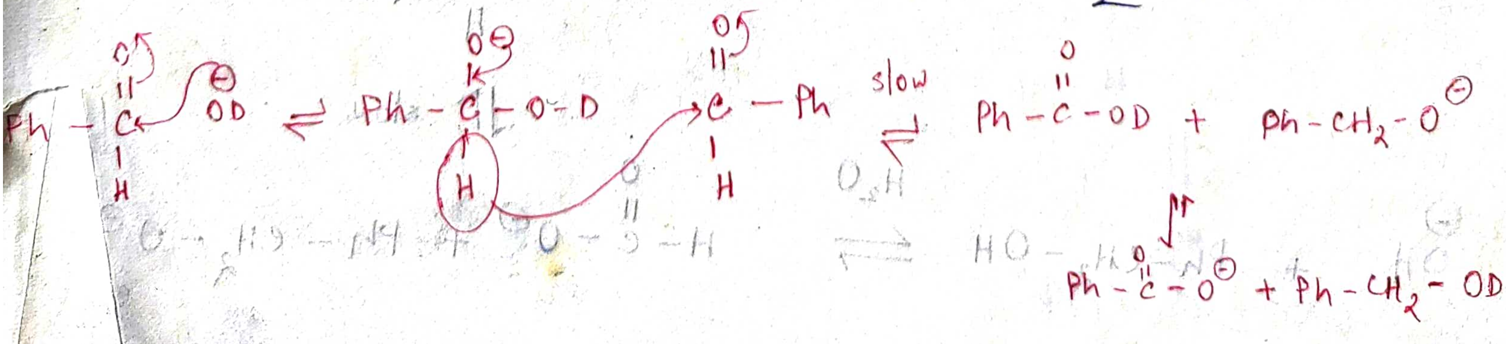
⇒ If the rxn is carried out ~~in~~ with NaOD in D_2O, no D incorporation occurs at the carbinol carbon in the alcohol.

$$Ph-CHO \xrightarrow{OD^-/D_2O} Ph-COO^\ominus + Ph-CH_2-OD$$

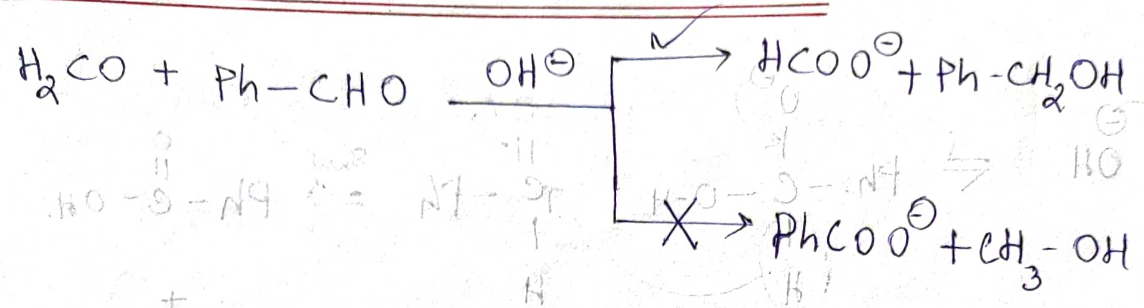
$$Ph-CDO \xrightarrow{OH^-/H_2O} Ph-COO^\ominus + Ph-CD_2-OH$$

$$Ph-CDO \xrightarrow{OD^-/D_2O} Ph-COO^\ominus + Ph-CD_2-OD$$

$$Ph-CHO \xrightarrow{OH^-/H_2O} Ph-COO^\ominus + Ph-CH_2-OH$$

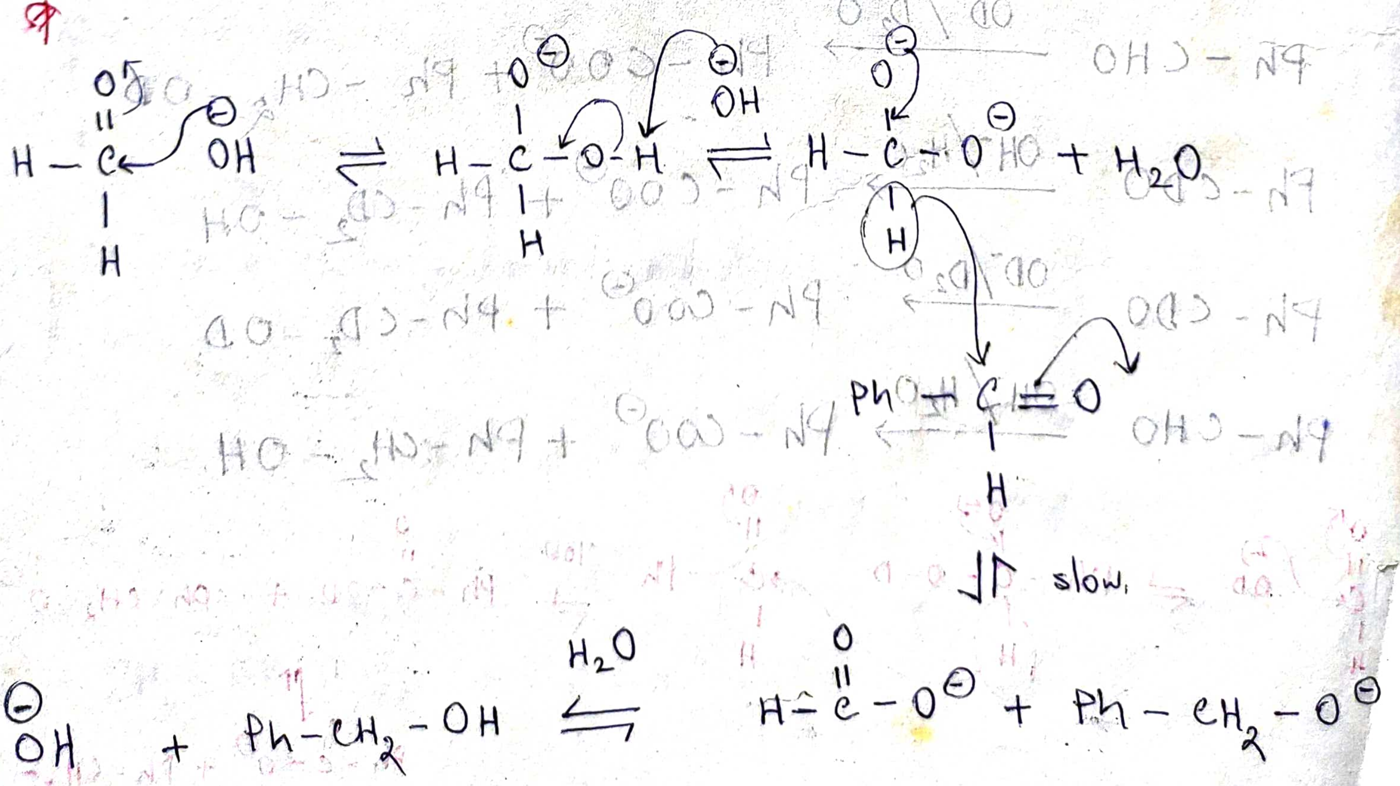


Crossed Cannizzaro rxn :

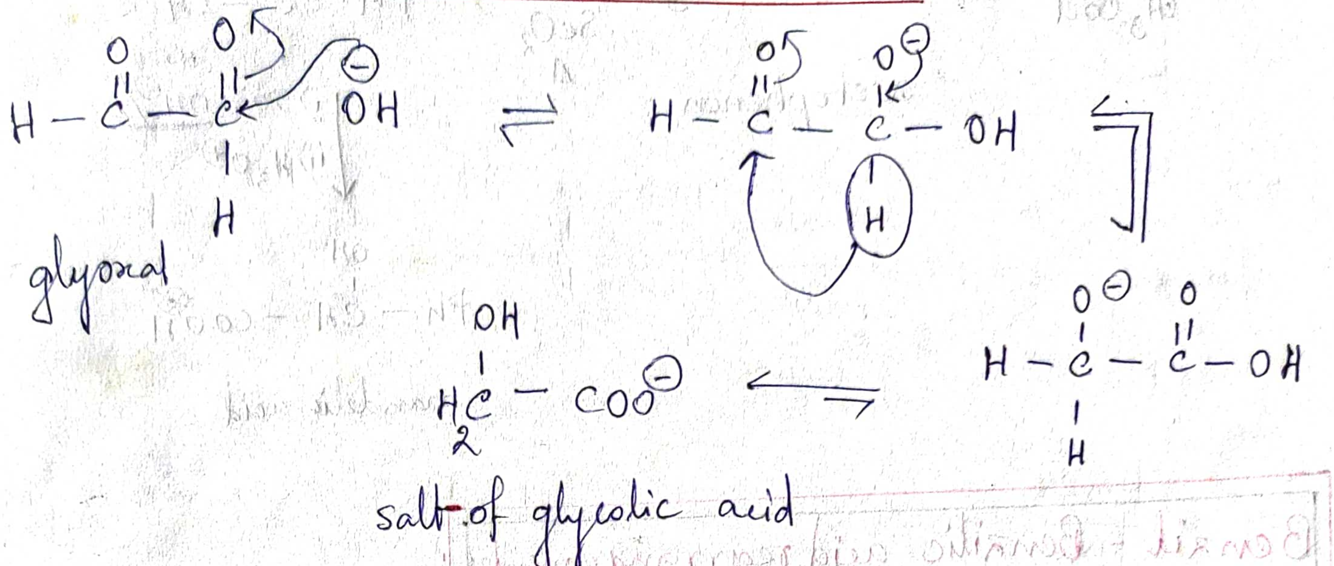


In a cross cannizzaro rxn, if one component is HCHO, it ~~is~~ acts as the oxidisable component and the other component gets reduced.

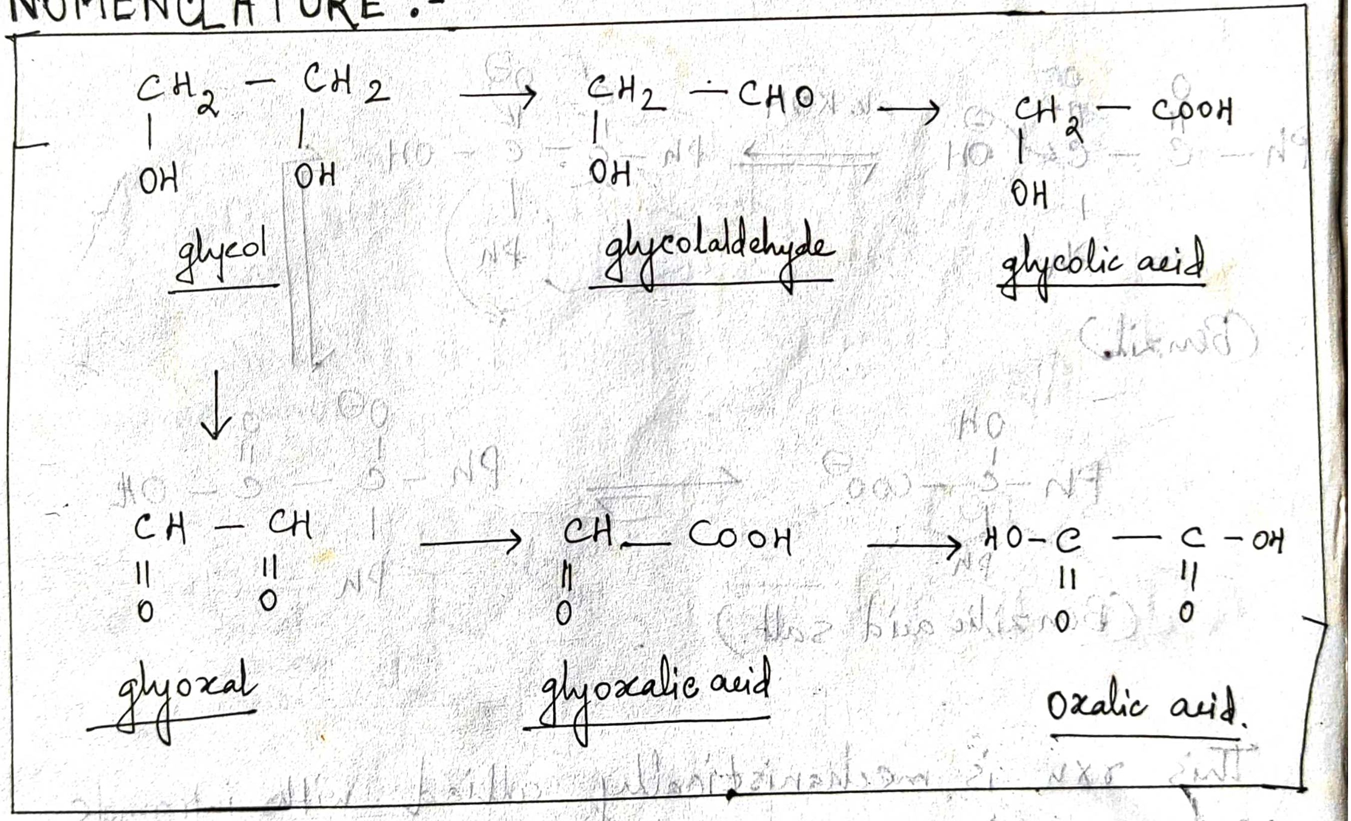
HCHO being a highly reactive aldehyde can easily form the dianion which will act as a very efficient $H^{\ominus}$ doner. So, HCHO will be oxidised & the other aldehyde will accept that $H^{\ominus}$ and will get reduced.

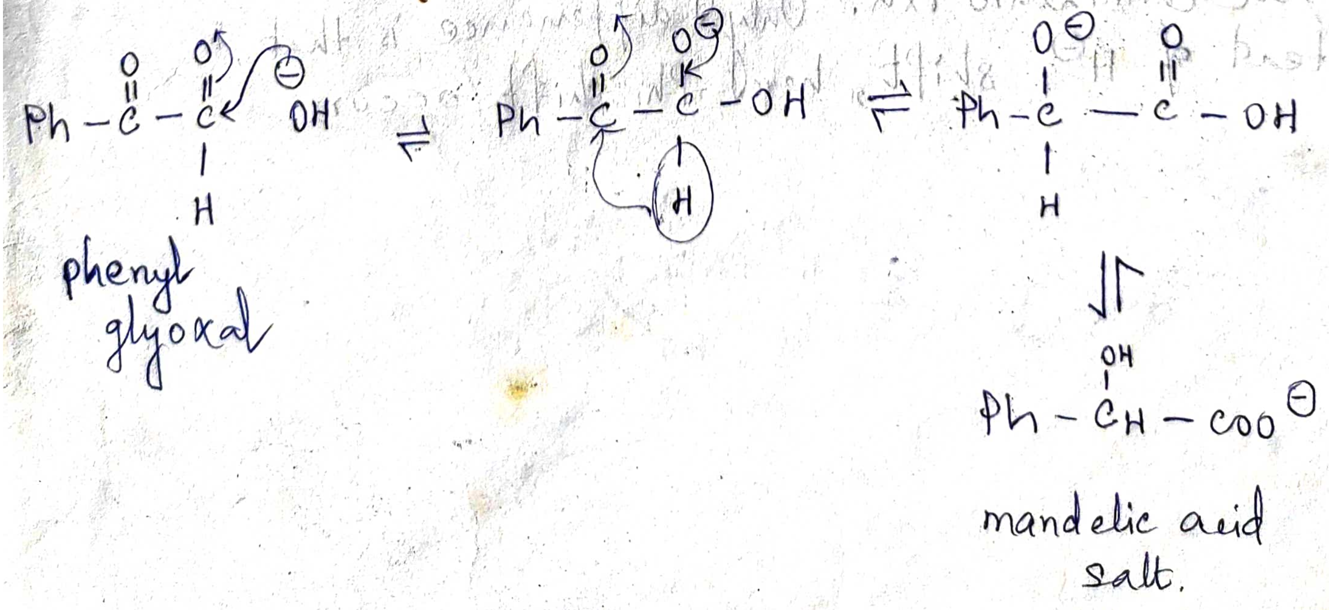


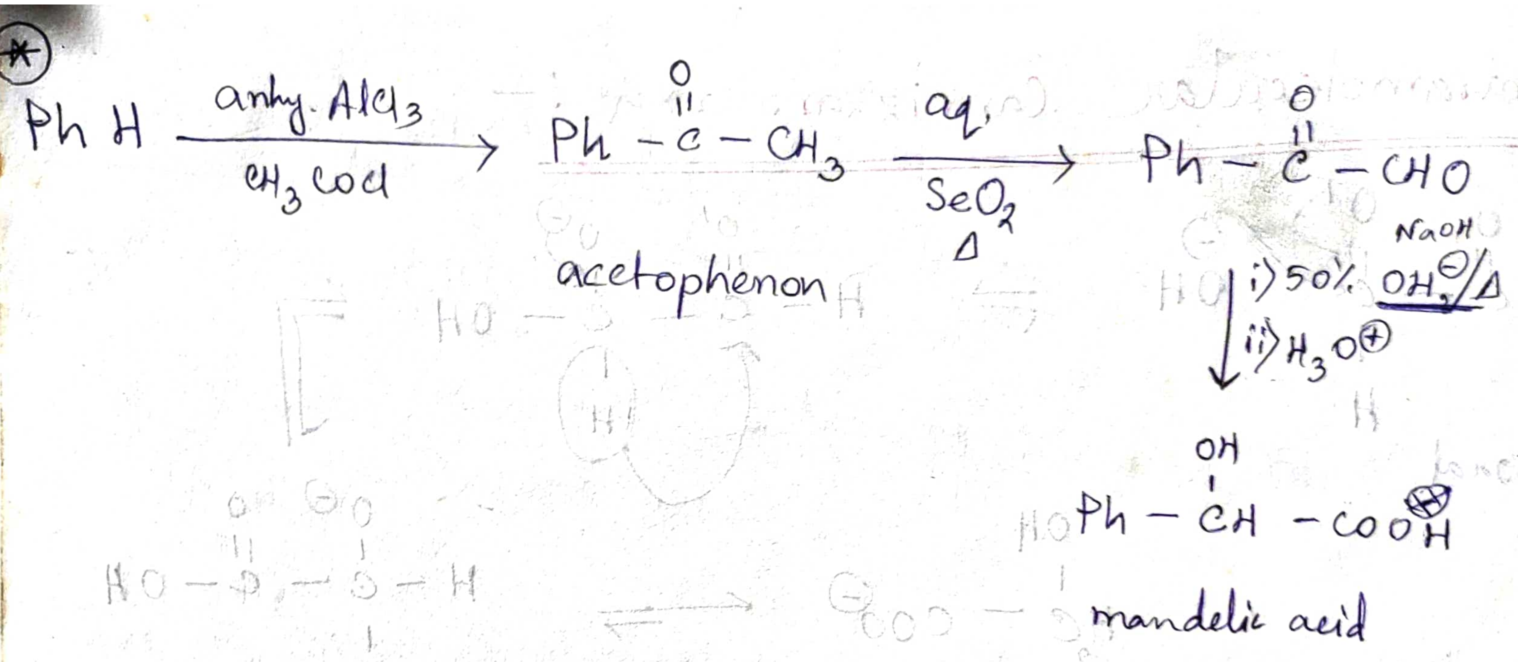
• Intramolecular Cannizzaro rxn :-



NOMENCLATURE :-

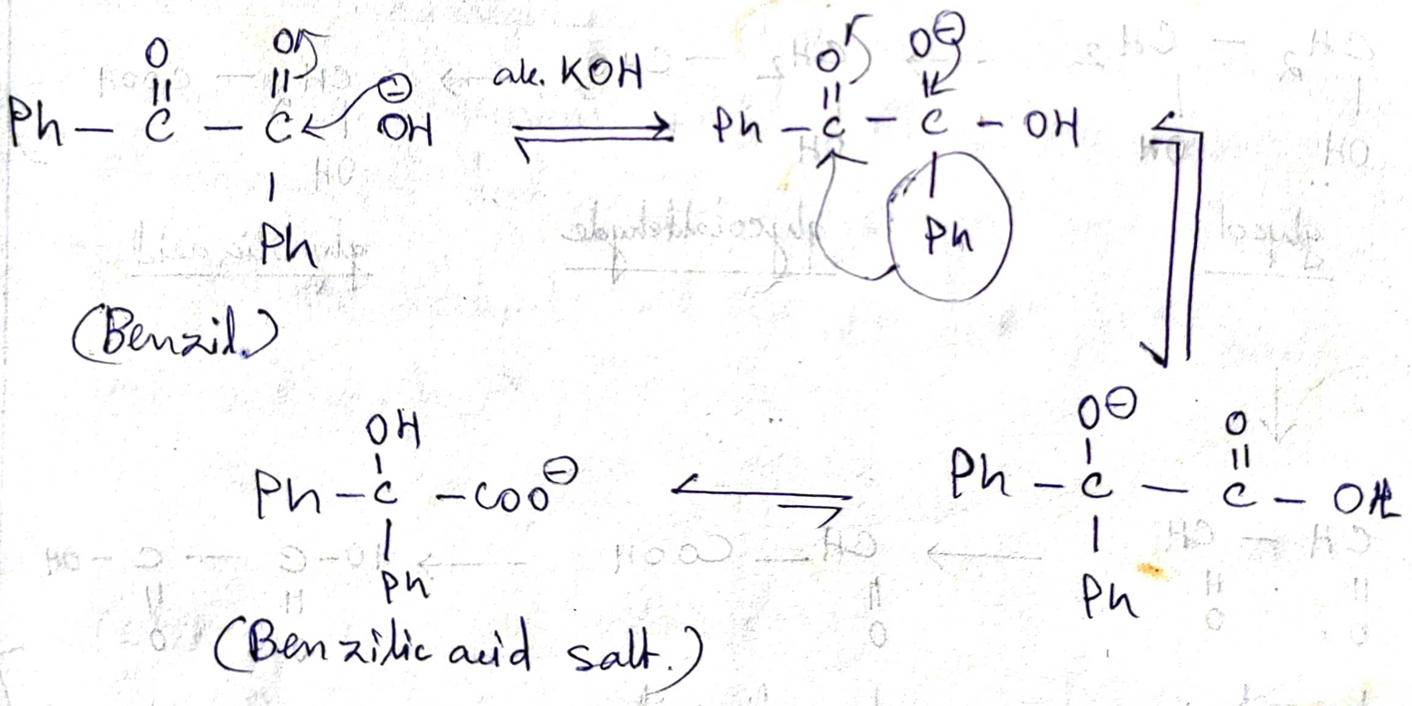




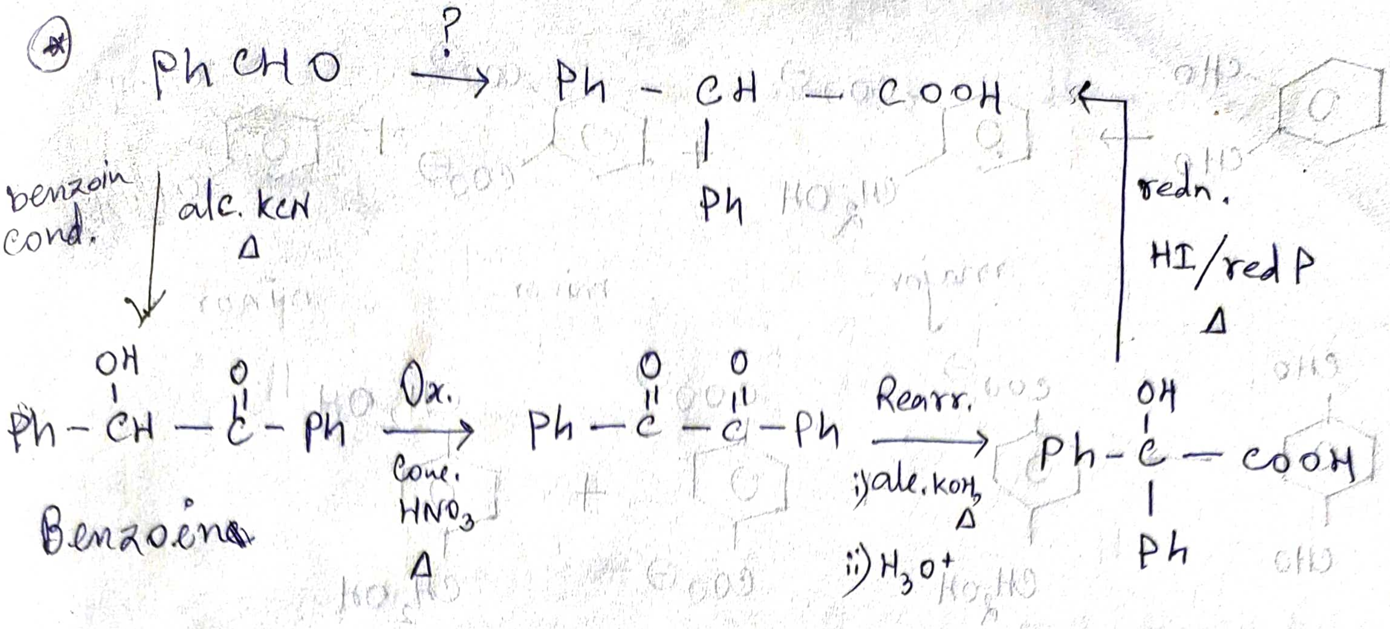


$$PhH \xrightarrow[CH_3COCl]{anhy.\ AlCl_3} Ph-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\Delta]{aq.\ SeO_2} Ph-\overset{O}{\overset{\|}{C}}-CHO \xrightarrow[ii)\ H_3O^{\oplus}]{i)\ 50\%\ OH^{\ominus}(NaOH)/\Delta} Ph-\overset{OH}{\overset{|}{C}H}-COOH$$

Benzil - Benzilic acid rearrangement :



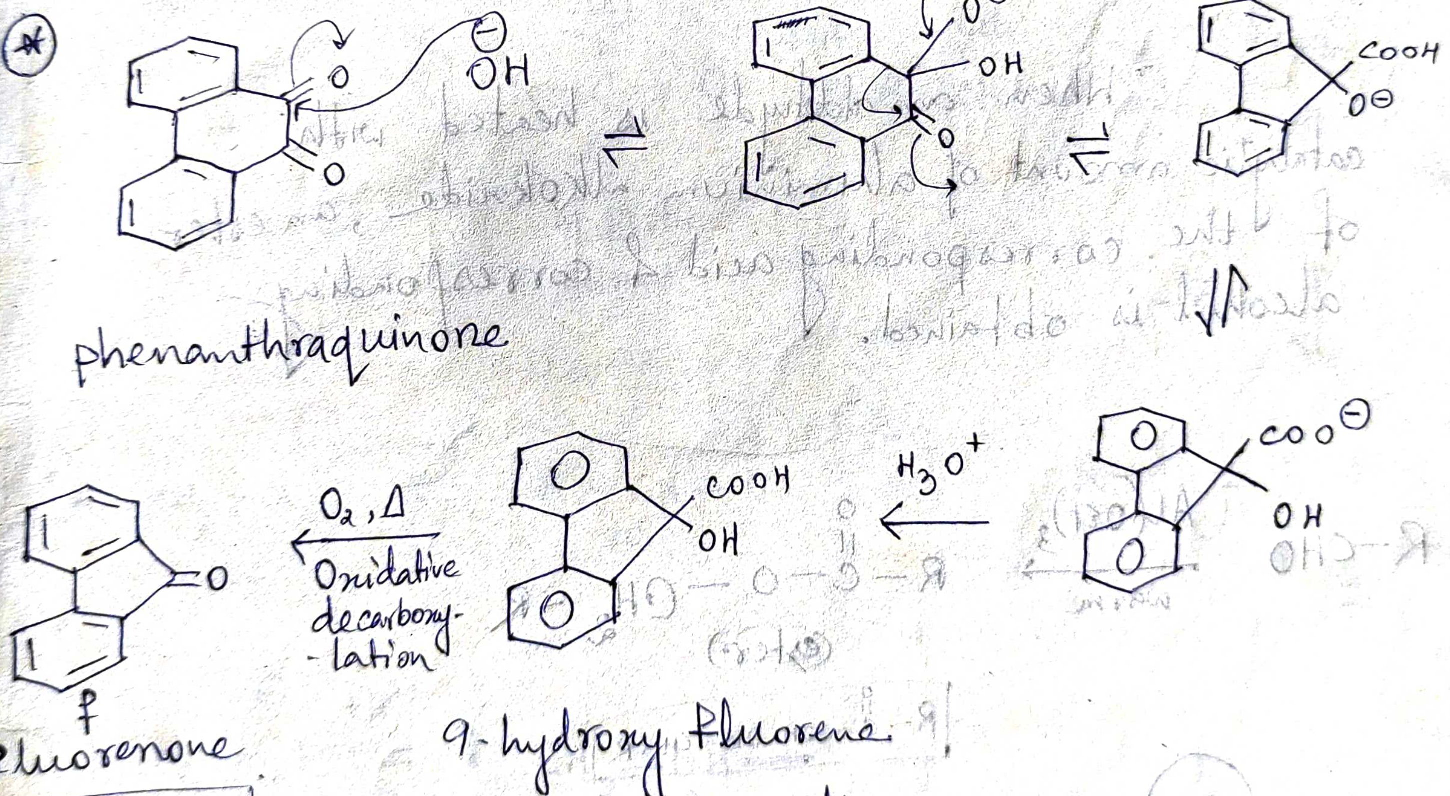
This rxn is mechanistically allied with intramolecular cannizzaro rxn. Only diffenence is that, instead of $H^{\ominus}$ shift, here -Ph shift occurs.



$$PhCHO \xrightarrow{?} \underset{\displaystyle Ph}{\underset{|}{Ph-CH}}-COOH$$

$$PhCHO \xrightarrow[\Delta]{\text{alc. KCN}} \underset{\text{Benzoin}}{Ph-\overset{\displaystyle OH}{\overset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{C}}-Ph} \xrightarrow[\text{Conc. }HNO_3,\ \Delta]{Ox.} Ph-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-Ph \xrightarrow[\text{i) alc. KOH, }\Delta\ \text{ii) }H_3O^+]{\text{Rearr.}} Ph-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle Ph}{\underset{|}{C}}}}-COOH \xrightarrow[\Delta]{\text{redn. HI/red P}} Ph-\underset{\displaystyle Ph}{\underset{|}{CH}}-COOH$$

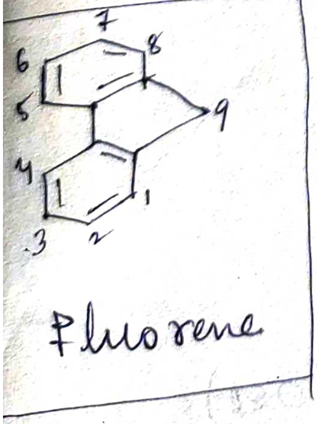
$$R-OH \xrightarrow[\Delta]{HI/red\,P} R-H$$



phenanthraquinone

fluorenone

9-hydroxy fluorene -9-carboxylic acid



Fluorene