

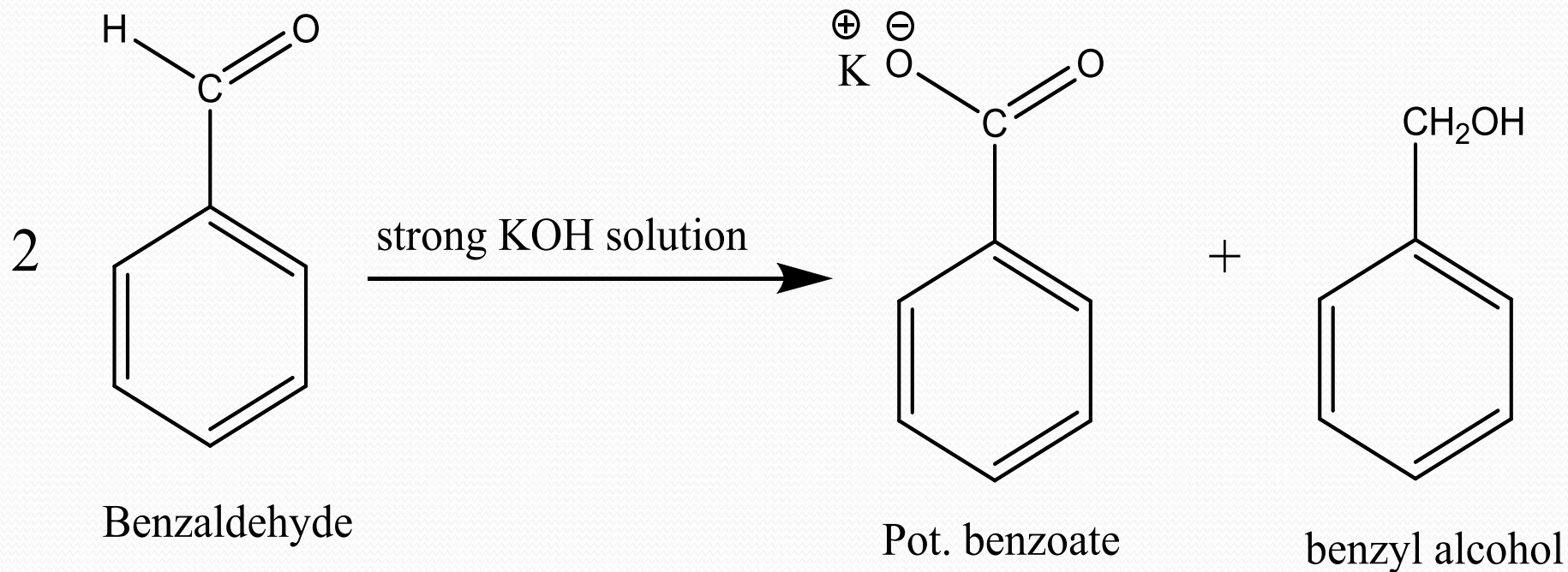
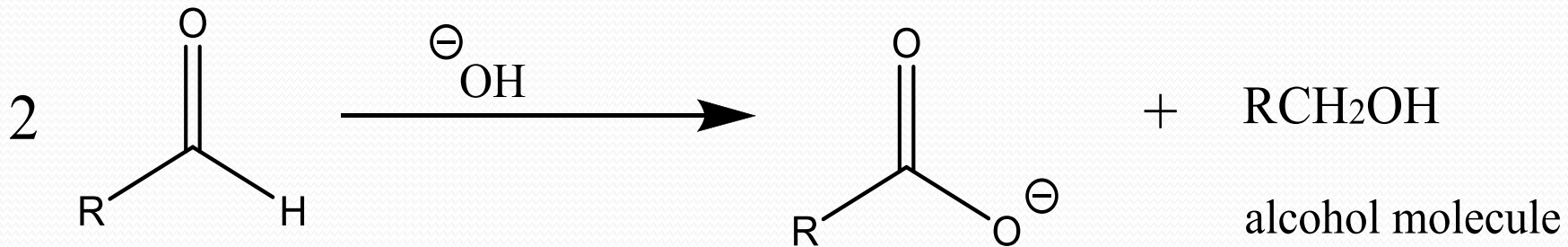
Cannizaro reaction

Cannizaro reaction

- In the presence of conc. alkali (strong aqueous alkali) ,aldehydes containing no α -hydrogen undergoes self-oxidation-reduction to yield a mixture of an alcohol and a salt of a carboxylic acid.
- Or we can said: It is a reaction of two aldehydes molecules in strongly basic solution to give a carboxylate anion and a molecule of carbinol (alcohol).

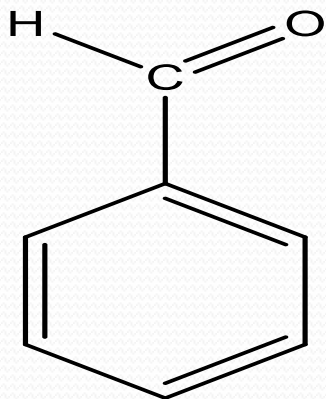
Cannizzaro reaction

- Overall reaction:

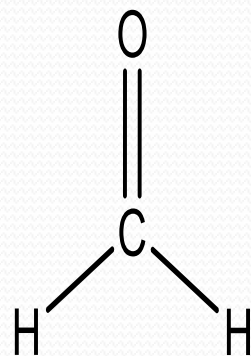


Cannizaro reaction

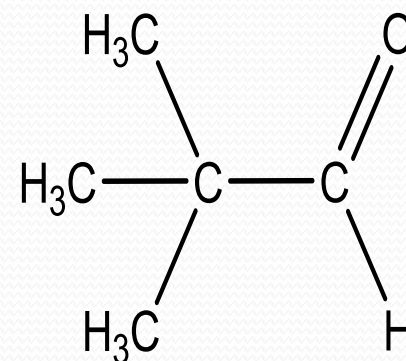
- Examples:



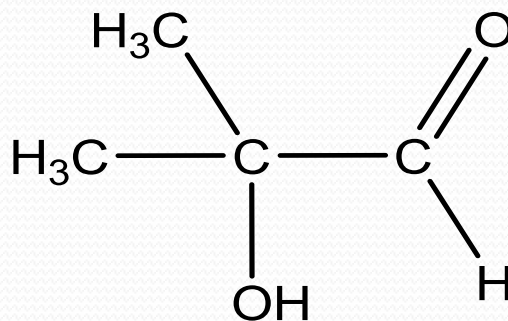
Benzaldehyde



Formaldehyde



2,2,-dimethyl propanal

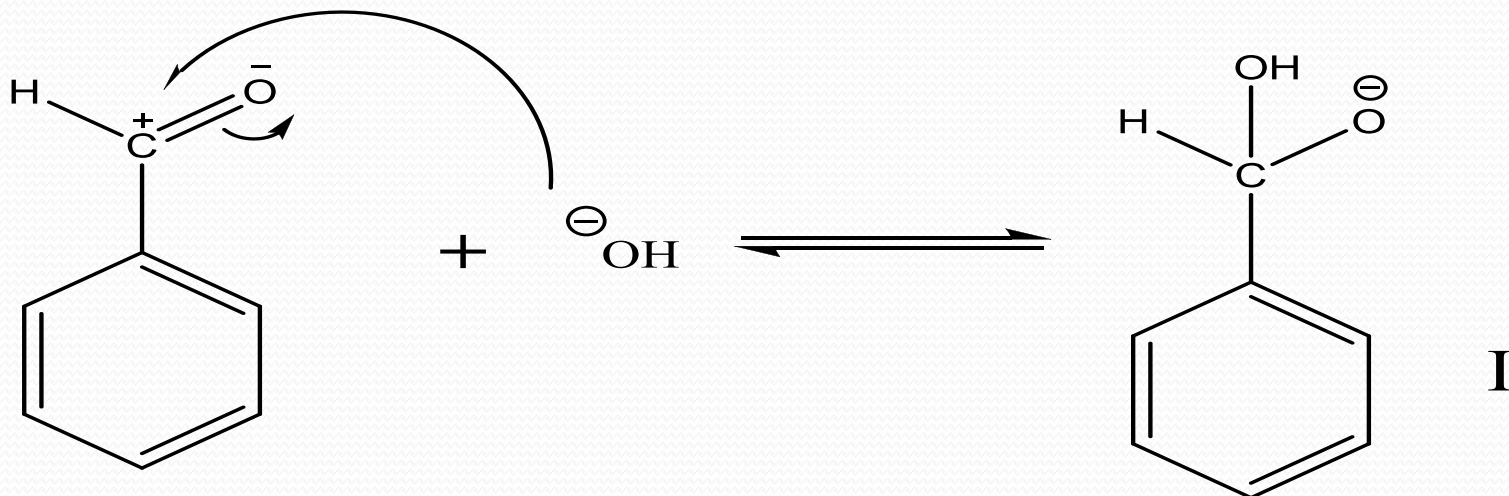


2-methyl-2-hydroxy-propanal

Cannizaro reaction

- **First Mechanism:** Nucleophilic addition, two successive additions are involved.

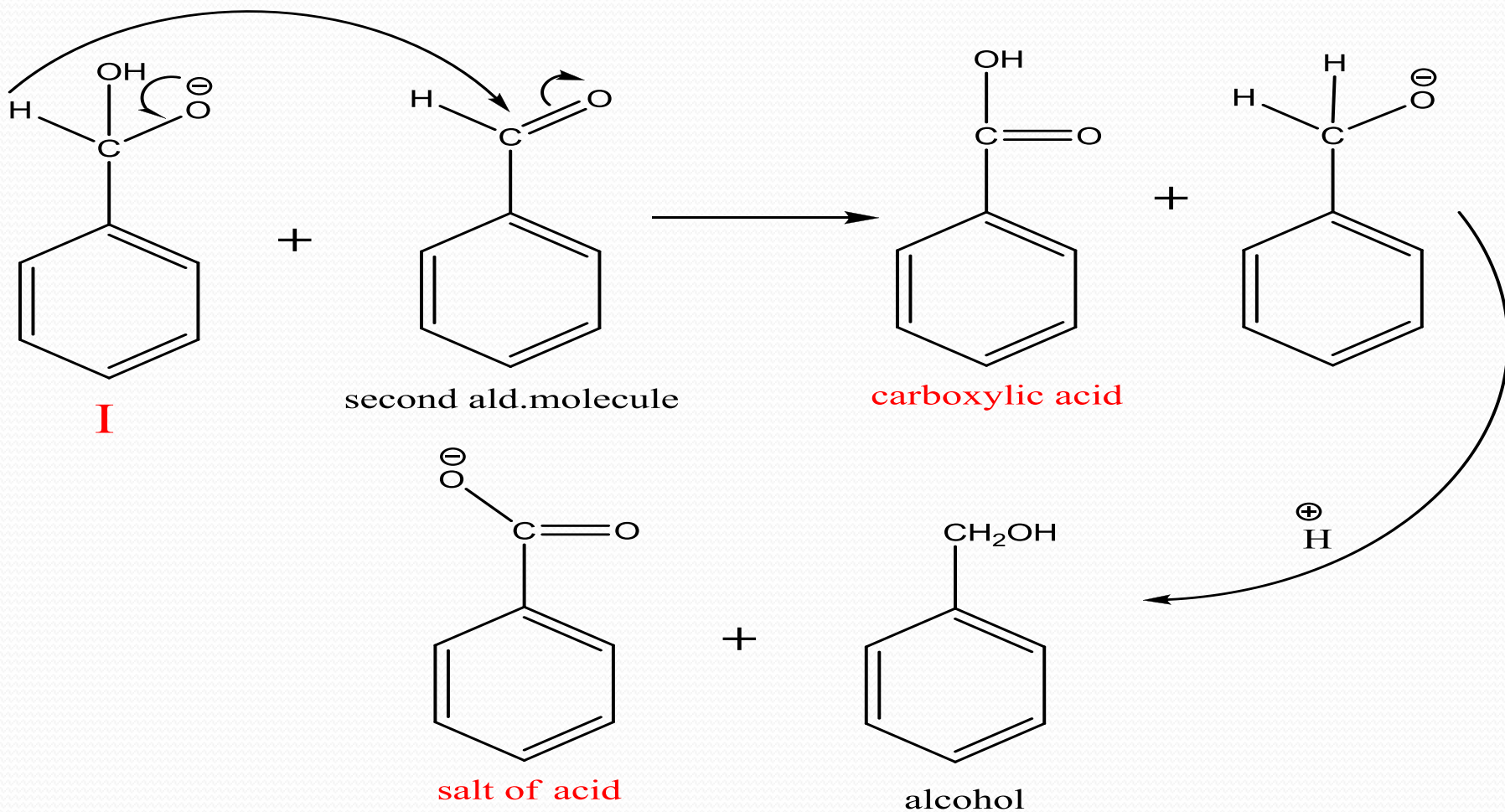
- **(step 1)** Addition of OH^- to give the intermediate I, **(oxidation)**



first ald. molecule

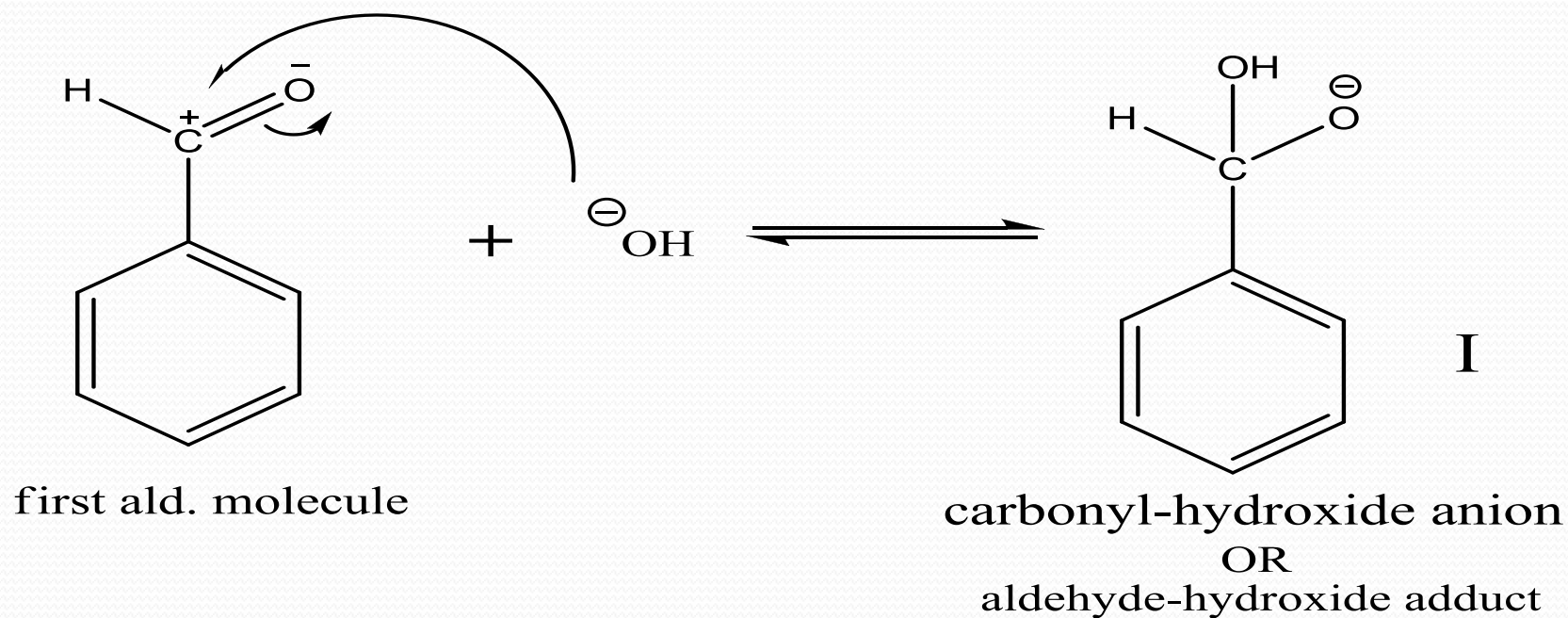
carbonyl-hydroxide anion
OR
aldehyde-hydroxide adduct

- (step 2) Hydride- transfer (shift) reaction, which includes the addition of a hydride ion from (step 1) to a second molecule of aldehyde (the presence negative charge on intermediate I aide in the loss of hydrogen ion) (Reduction).

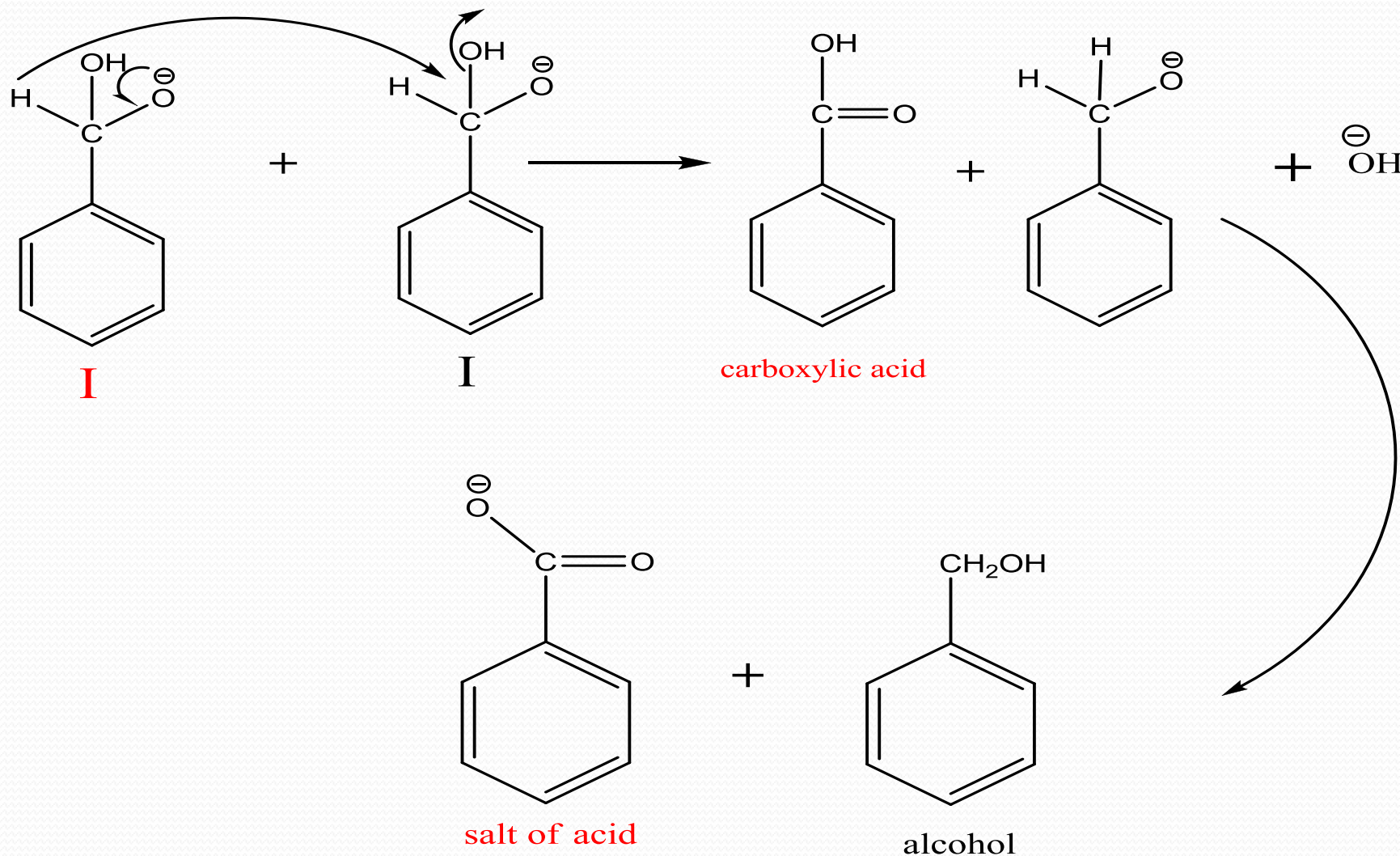


Cannizaro reaction

- **Second Mechanism:**
- **(step 1)** Also nucleophilic addition to give aldehyde-hydroxide adduct as in the first mechanism .

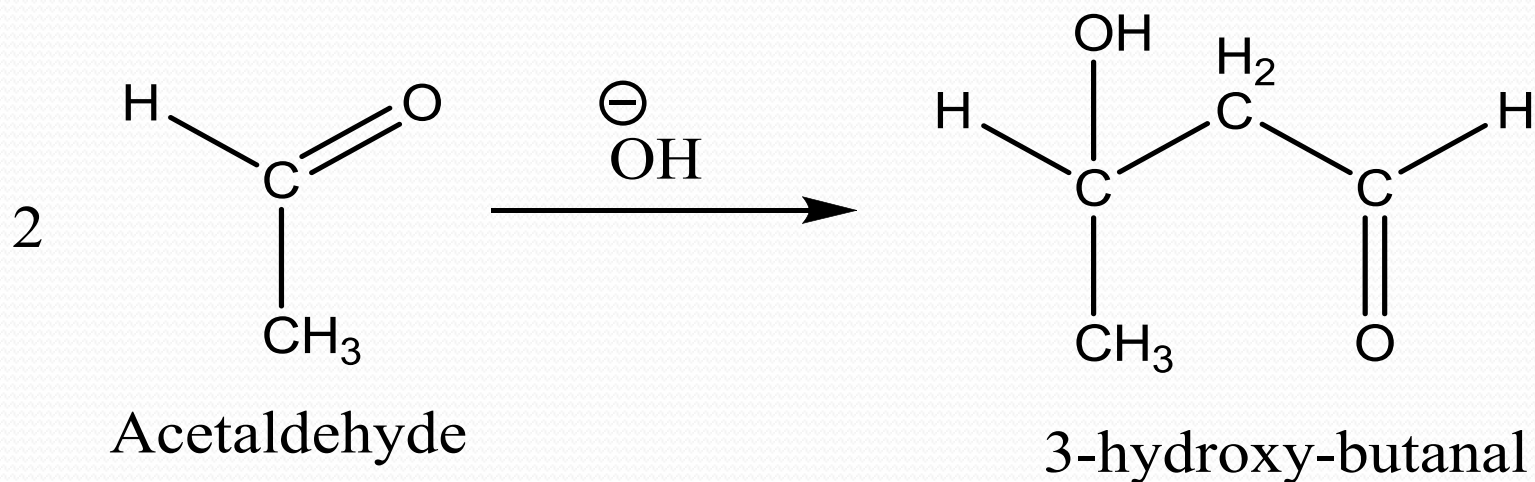


- **(step 2)** Hydride is transferred from one carbonyl-hydroxide anion to another one.



Cannizzaro reaction

- **Third Mechanism: (H.W)**
- Aldehyde with an α -hydrogen would undergo aldol condensation faster, under the influence of dilute base or acid, two molecules of aldehyde, ketone may combine to form a β -hydroxy aldehyde or β -hydroxy ketone, respectively. The product of addition will be in such a way that the α -carbon of the first becomes attached to the carbonyl carbon of the second one.



Cannizaro reaction

- (H.W) propanal , acetone
- ***Properties of benzyl alcohol:-***

Oily liquid

Colorless

Immiscible with water

Miscible with organic solvents like ether

B.P. 204-207

Cannizaro reaction

- ***Properties of benzoic acid:-***

Crystalline plates or needles, white

M.P. = 121-123

Sparingly soluble in water

Soluble in hot or boiled water

Volatile with steam

Reacts with sodium bicarbonate to give CO_2 gas.

Cannizaro reaction

- ***Part I***
- 1-dissolve 3.6 gm KOH in 5 ml D.W in a reagent bottle.
- 2-cool
- 3-add 3.6 ml benzaldehyde & shake vigorously in one direction for 30 min. until thick emulsion is formed and leave it over night to complete the reaction.

Cannizaro reaction

- ***Part II***
- Add 30 ml of H₂O to ensure complete dissolve of Pot. Benzoate ((transfer to separatory funnel))
- Add 20 ml ether to the reagent bottle and shake ((transfer to separatory funnel))
- Shake 2 min. and stand.

Lower layer(H₂O)

Beaker

20 ml conc. HCl
10 ml H₂O

ppt. (benzoic acid)

cool

Filter(collect ppt.)

Benzoic acid on filter papper.

Upper layer(Ether)

5 ml sod. bisulfite
NaHSO₃ (why)

lower aq.
reject

upper (ether)

5 ml sod. carbonate

lower aq.
reject

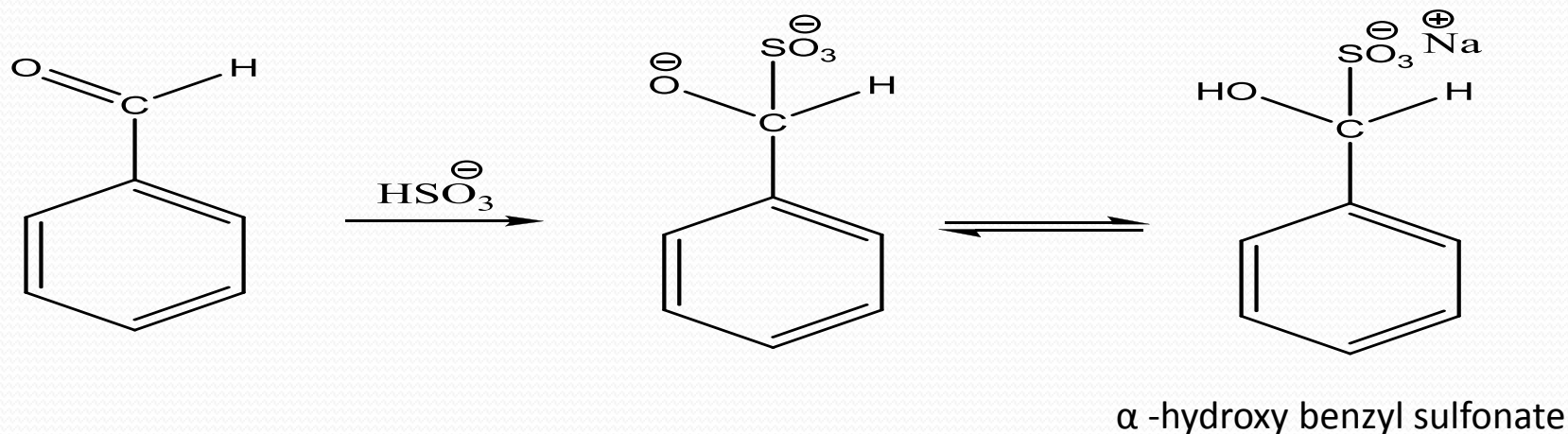
upper (ether)

collect in beaker
add drying agent

allow ether to
evaporate

measure benzyl alc.

- Why we use Sod. bisulfite NaHSO_3 solution in the purification of benzyl alcohol to the ethereal layer?
- To get rid of excess unreacted of benzaldehyde



- Why we add sodium carbonate to ethereal layer after that?
- To get rid any excess unreacted of sodium bisulfite

