ALDEHYDE & KETONE (Part-III)

By

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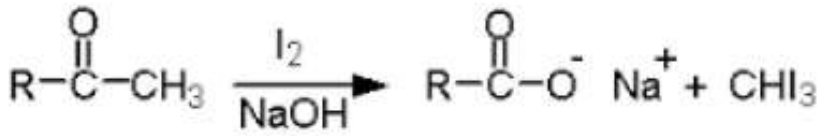
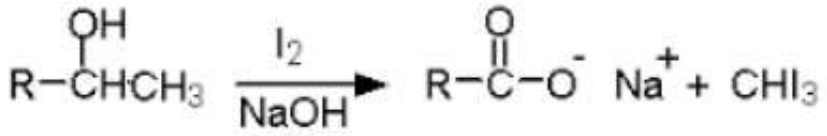
Iodoform Test

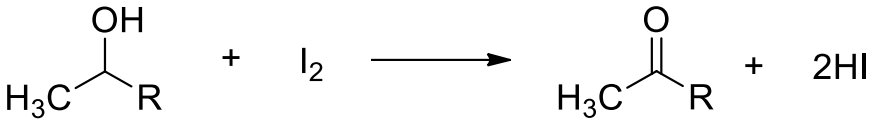
- Any compounds containing the **$CH_3C=O$** group or the **$CH_3CH(OH)$** group give a positive result with the iodoform test. When I_2 and NaOH is added to a compound containing one of these groups, a **pale yellow precipitate of iodoform** (triiodomethane) is formed.
- The iodoform test can therefore be used to identify **aldehydes** and **ketones.**
- This test can also be used to identify **alcohols.**
- If the alcohol is a tertiary then it gives no result as it cannot be be oxidised. If the alcohol is a primary alcohol then it must be ethanol (as this is oxidised to ethanal, which is the only aldehyde that gives a positive result with the iodoform test). All secondary alcohols give a positive result, as they are oxidised to ketones.



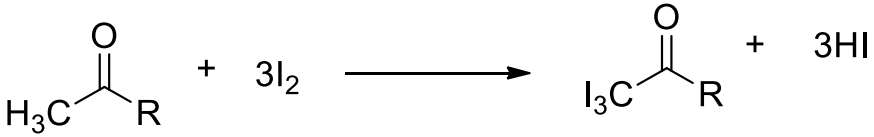


Mechanism (Iodoform of 2° alcohol)

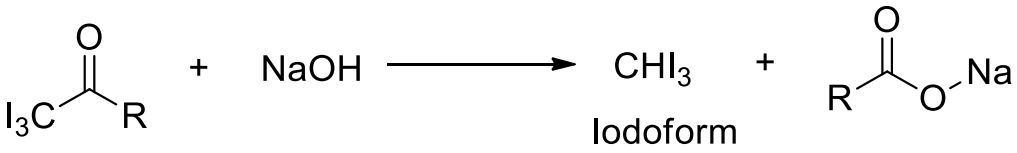
Step 1: Oxidation



Step 2: Halogenation

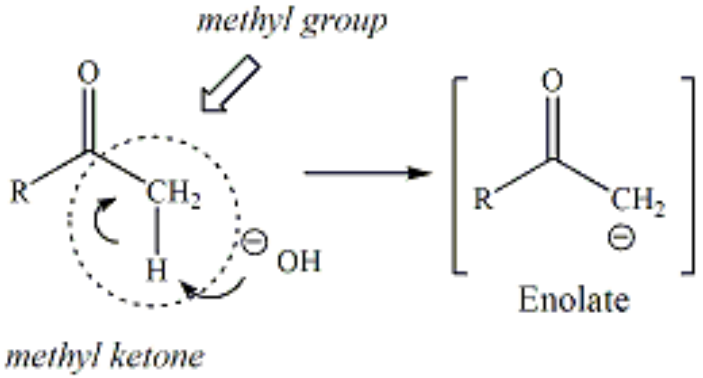


Step 3: Hydrolysis

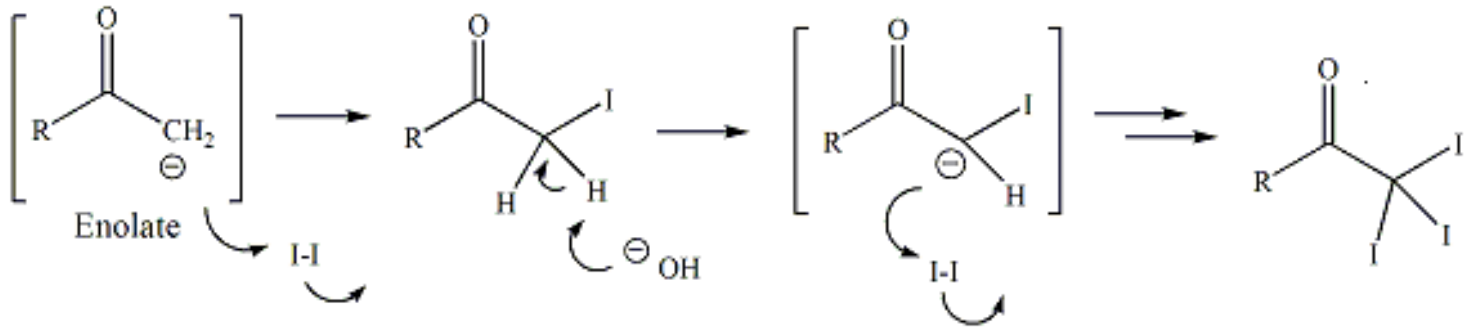


Mechanism (Iodoform of Methyl Ketones)

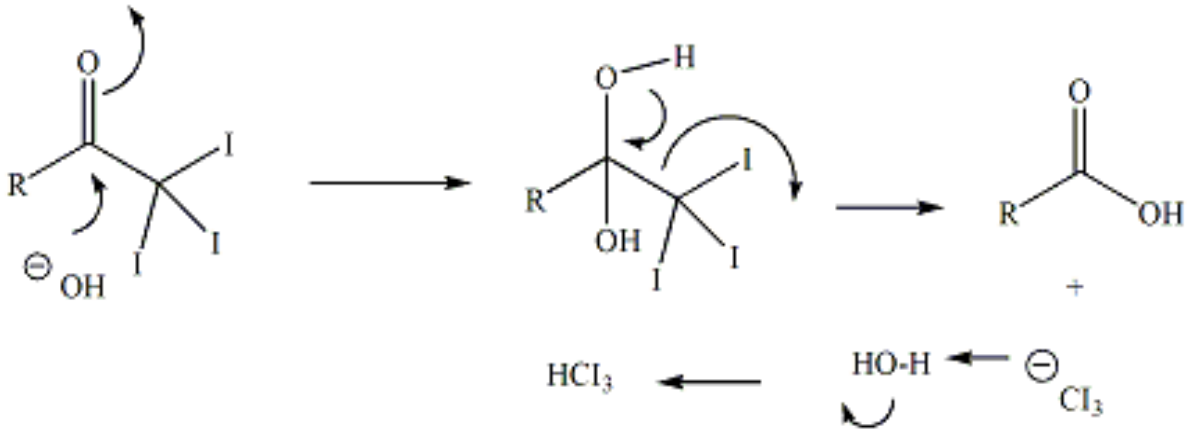
Step 1: Formation of enolate



Step 2: Halogenation



Step 3: Hydrolysis

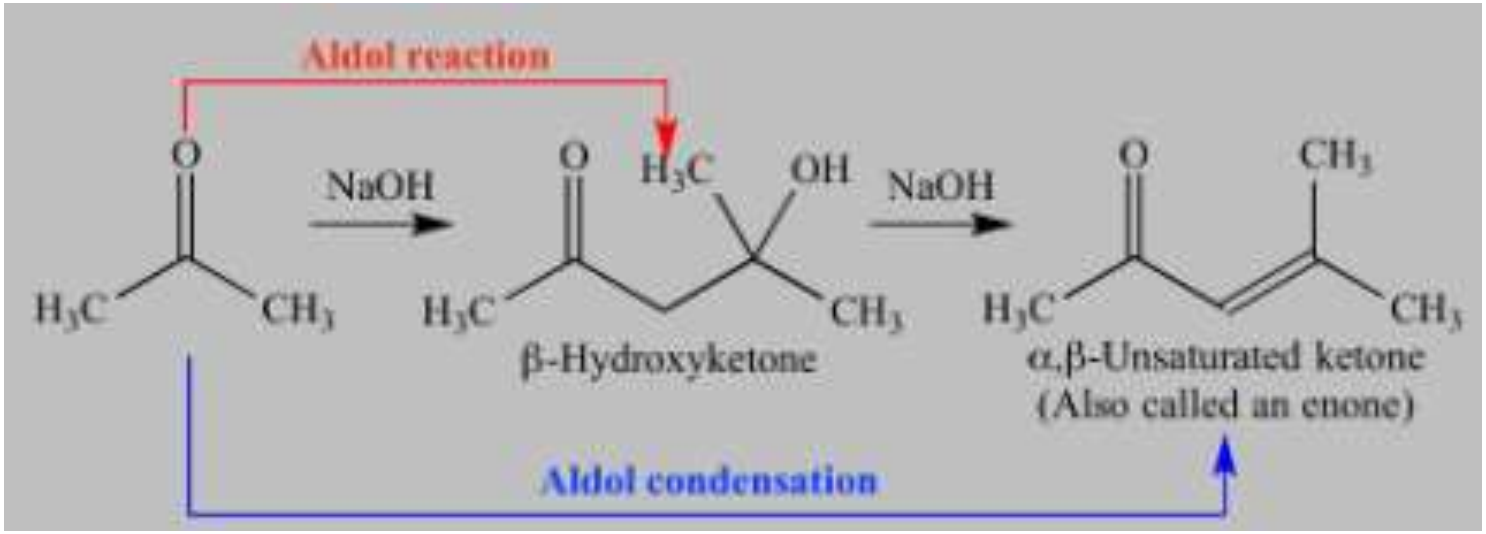


Iodoform
(precipitate)

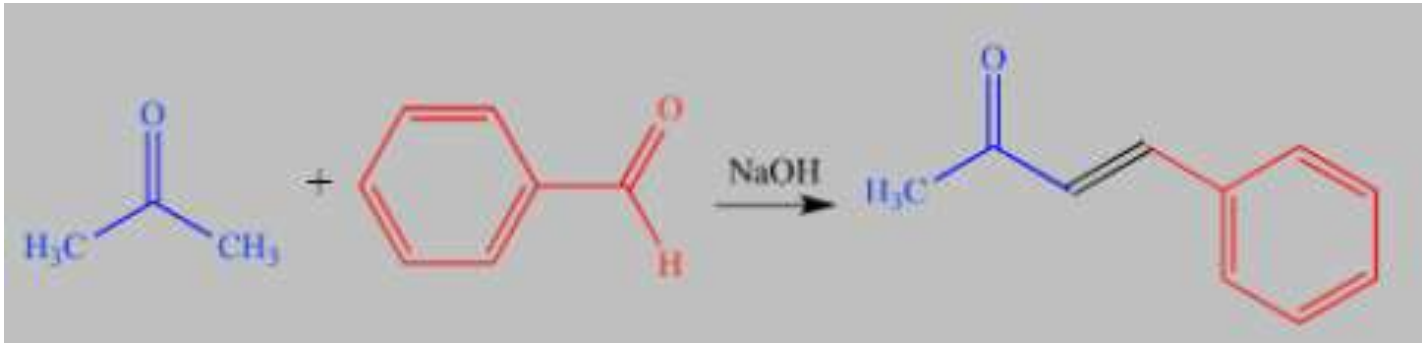
Three I-atoms replace the H atoms of $CH_3C{=}OR$, and the C-C bond breaks due to the electron withdrawing effect of the three I atoms (as I is more electronegative than C) forming CHI_3 and the salt anion of a carboxylic acid.

Aldol condensation

- Aldehydes and ketones having at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol), respectively. This is known as **Aldol reaction.** On dehydration produces an α, β unsaturated aldehyde or ketone are known as Aldol condensation.

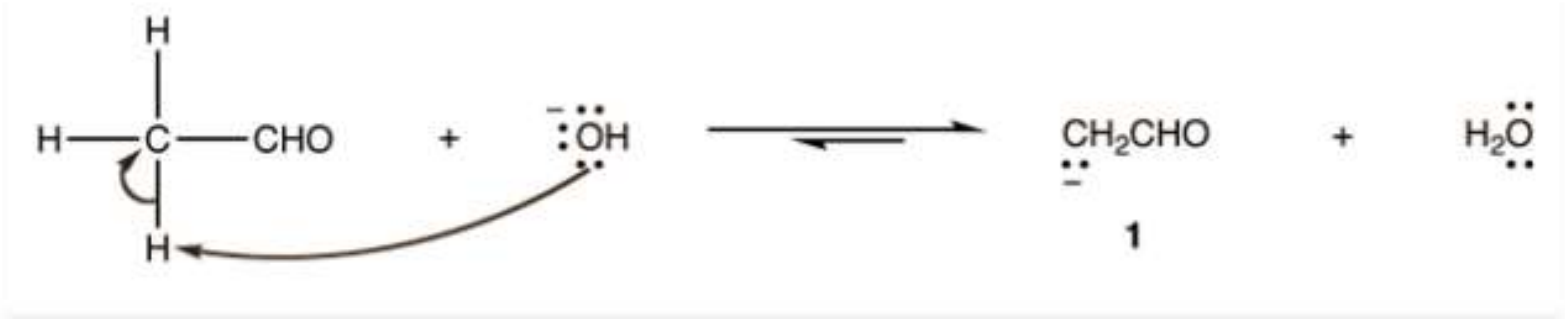


- If the condensation reaction occurs between two different carbonyl compounds it is called **crossed aldol condensation**.

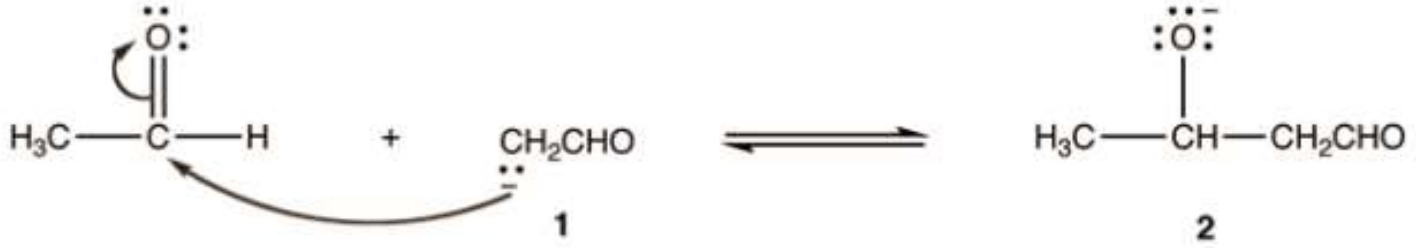


Mechanism

Step-1*:* The hydroxide ion deprotonates the aldehyde.



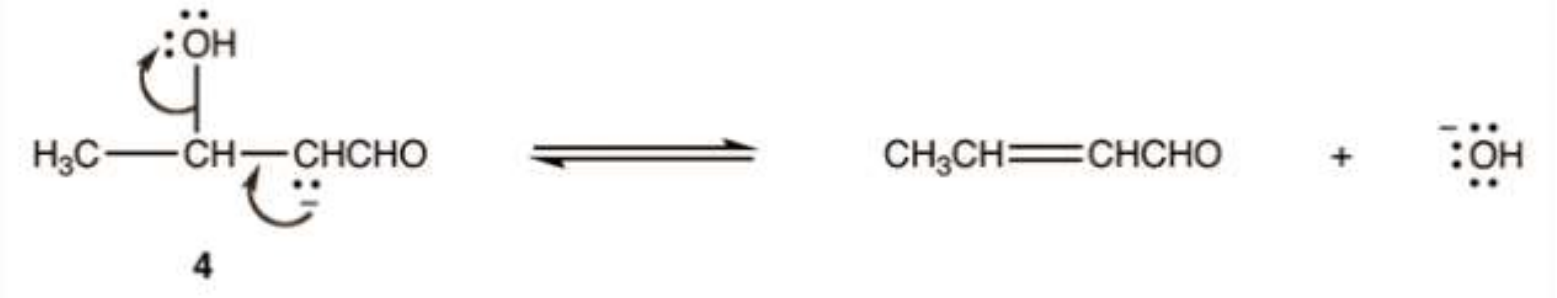
Step-2: Enolate ion 1 adds to the unreacted aldehyde.



Step-3*:* Alkoxide ion 2 is protonated by water

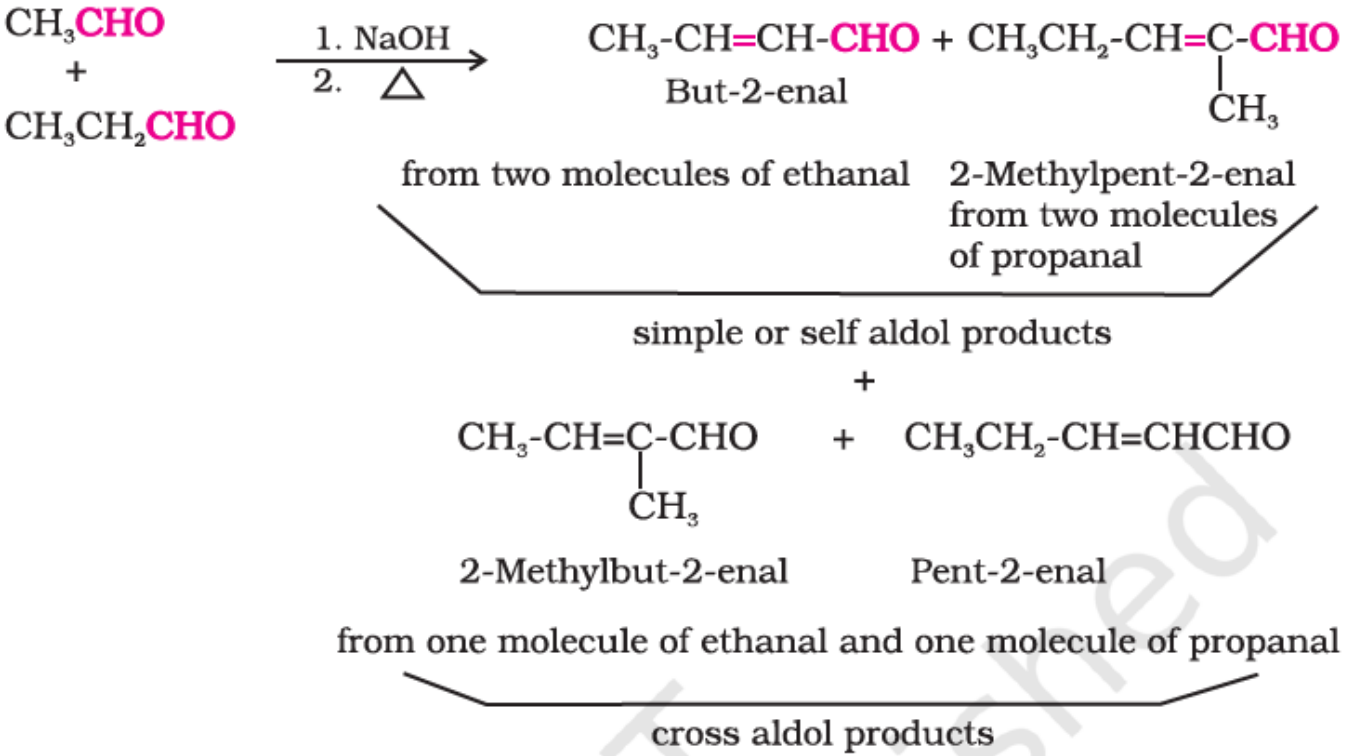
Step-4: A small amount of aldol is converted into enolate ion (4) by hydroxide ion.

Step-5: Enolate Ion(4) loses a hydroxide ion.



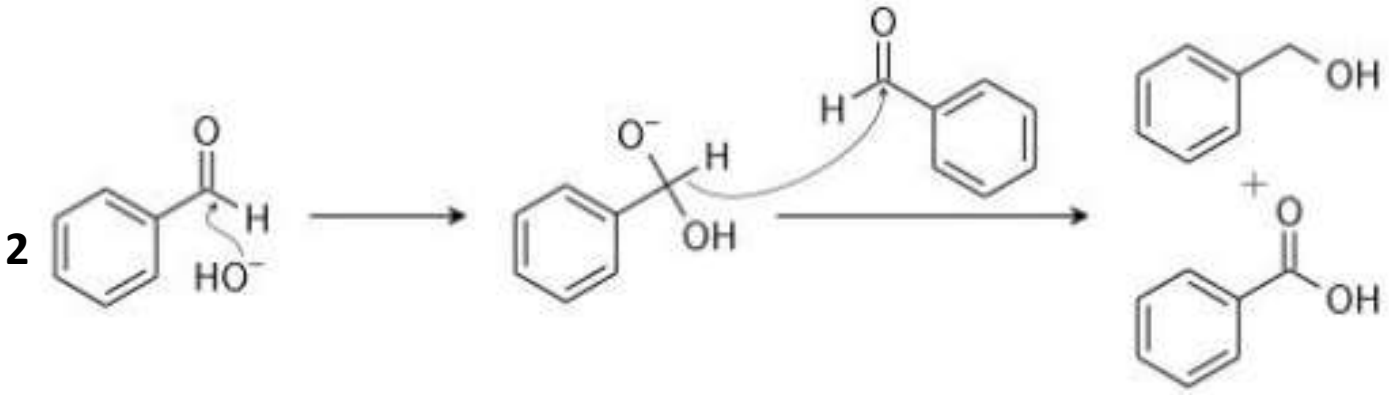
Cross Aldol condensation

- When aldol condensation is carried out between two different aldehydes and / or ketones, it is called **cross aldol condensation**. If both of them contain α-hydrogen atoms, it gives a mixture of four products. Example: **aldol reaction of a mixture of ethanal and propanal**



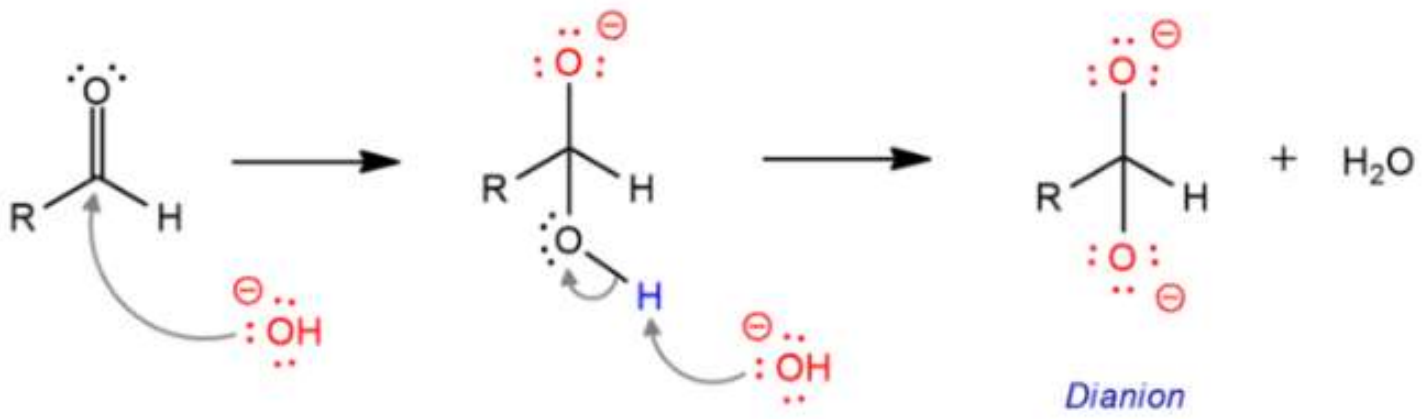
Cannizzaro Reaction

- Cannizzaro reaction is a chemical reaction named after Stanislao Cannizzaro.
- The reaction involves the base-induced disproportionation of two molecules of aldehydes which do not have an α-hydrogen atom, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt .

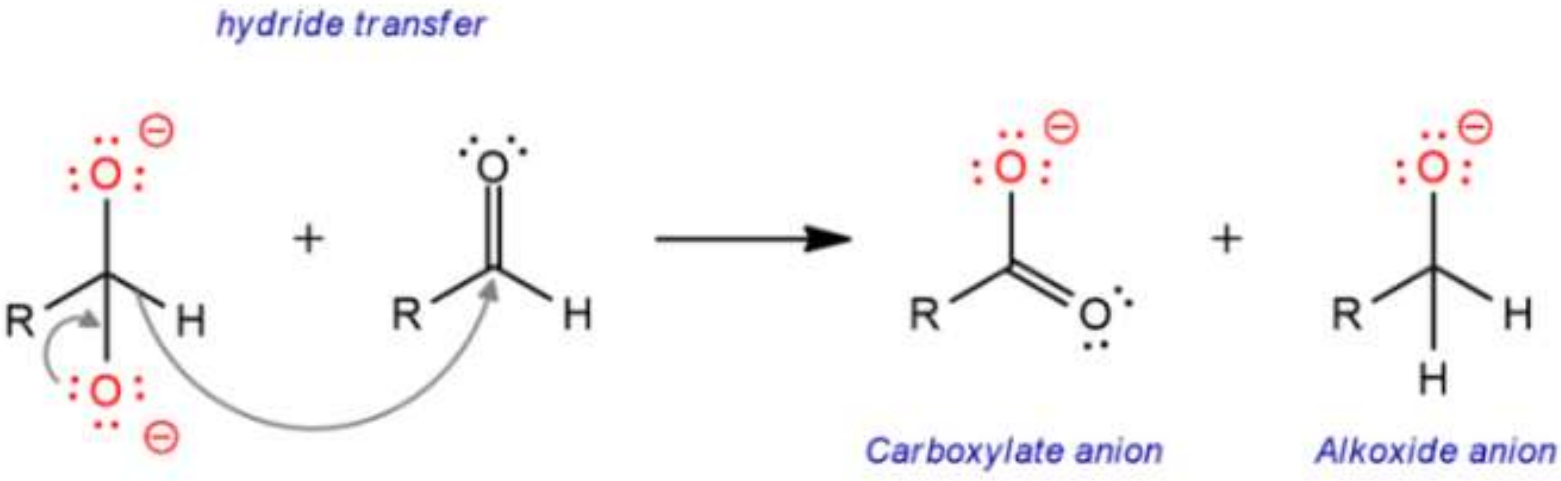


Mechanism

- **Step 1**: A nucleophile such as a hydroxide ion is used to attack the carbonyl group of the given aldehyde, causing a disproportionation reaction and giving rise to an anion carrying 2 negative charges.



- **Step 2**: This resulting intermediate can now function as a hydride reducing agent. Due to its unstable nature, the intermediate releases a hydride anion. This hydride anion proceeds to attack another aldehyde molecule. Now, the doubly charged anion is converted into a carboxylate anion and the aldehyde is converted into an alkoxide anion.



- **Step 3**: In this final step, water offers a proton to the alkoxide anion which gives rise to the final alcohol product. The reaction can proceed since the alkoxide is more basic than water. Now, the carboxylate ion gives rise to the final carboxylic acid product when acid workup is used (the acid workup is required since carboxylate is less basic than water and therefore cannot obtain a proton from water).