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Aldehydes and ketones (Lecture-10)

Degree-I (Hons. & Sub.)

Ch. No - 5
Group - 'B'
Paper - II
Organic Portion

Ch.No.- 3
Group - 'C'

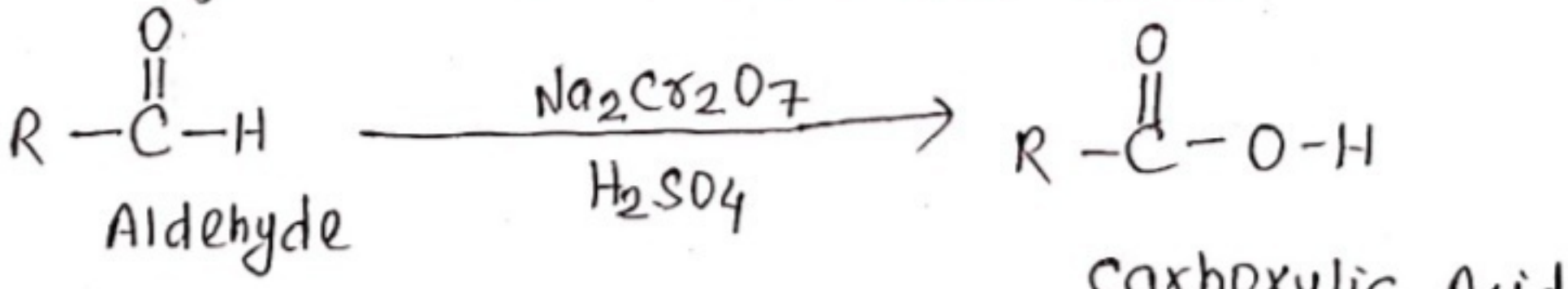
Oxidation Reaction Of Aldehydes and ketones

Although the chemical reactivity of aldehydes and ketones are very similar, their behaviour towards oxidising agent is quite different.

Aldehydes are easily oxidised but ketones are oxidised only under drastic conditions.

Oxidation of Aldehydes :-

* Aldehydes can be oxidised with sodium or potassium dichromate in acidic medium to form carboxylic acids containing the same no. of carbon atoms.



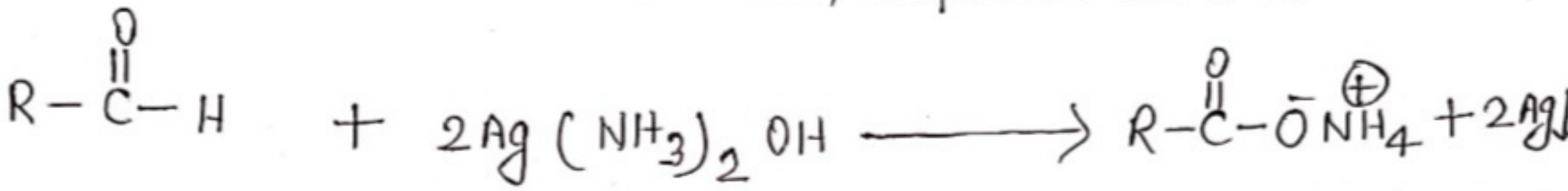
* $KMnO_4$ can be used in place of $Na_2Cr_2O_7$.

* Aldehydes can be oxidised by much milder oxidising agent such as :-

Tollens' Reagent, Fehling's solution and Benedict's solution.

Tollens'Reagent

* It is ammoniacal solution of silver oxide. It is obtained by adding ammonia to a ppt. of silver oxide present in a solution of silver nitrate and sodium hydroxide.
* When Tollens' reagent is used to oxidise an aldehyde, the silver ion is reduced to metallic form and if the reaction is carried out in a clean test tube, deposits as a mirror.

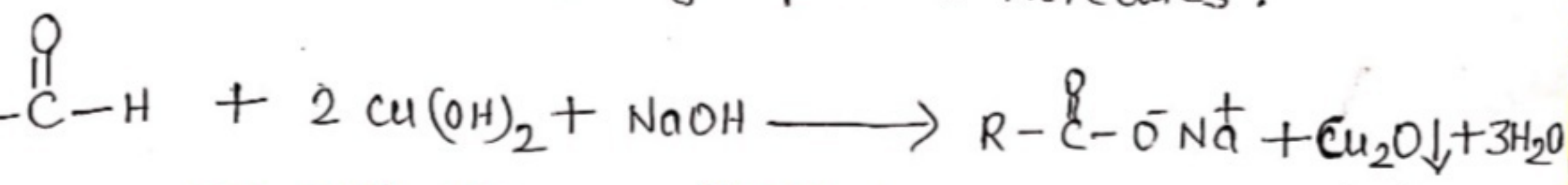


Fehling's Solution

It is an alkaline solution of cupric ion complexed with sodium potassium tartarate ions.

When Fehling's solution is used to oxidise an aldehyde, the complexed cupric ion (deep blue) is reduced to cuprous oxide (red).

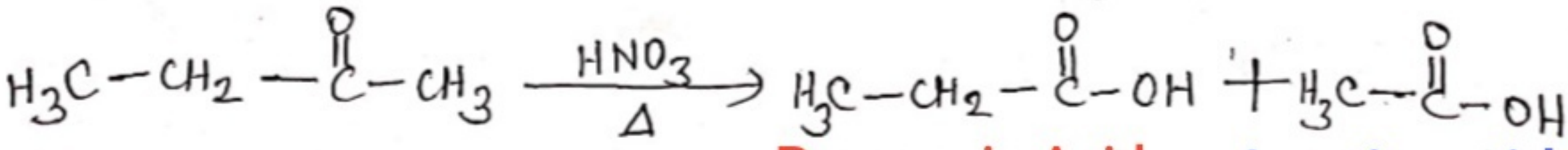
* The presence of the red ppt. of cuprous oxide serves as an indication of an aldehyde group in a molecules.



Oxidation of Ketones

Red

Ketones can be oxidised by strong oxidising agents such as alkaline $KMnO_4$ or hot conc. HNO_3 to form two carboxylic acid with fewer carbon atoms than the original ketone.



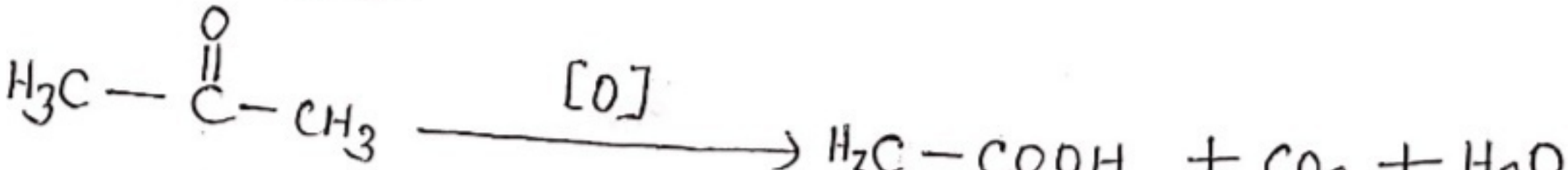
Propanoic Acid

Acetic acid

Popoff's Rule

Among the aldehydes and ketones, aldehydes easily undergo oxidation to give carboxylic acids. In the case of ketones, oxidation is difficult, though not possible.

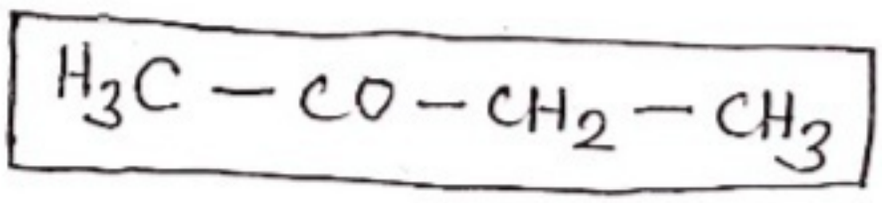
* On vigorous oxidation ketone yield acids with lesser no. of carbon atoms.



In case of unsymmetrical ketones, C=O bond remains with the smaller chain.

This rule is known as "Popoff's rule".

For example :-



In this compound the break up occurs like H_3CCO and CH_2CH_3 and not as H_3C and $COCH_2CH_3$.

Both, H_3CCO and CH_2CH_3 are oxidised to give 2 molecules of $H_3C-COOH$.

If the C=O bond remains with the larger chain then oxidation will yield HCOOH and H_3C-CH_2-COOH.

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Chapter continued.....