



STUDY MATERIAL

VIVEKANANDA COLLEGE

THAKURPUKUR

NAAC ACCREDITED GRADE—'A'

Subject: Chemistry

Topic

Dakin Reaction

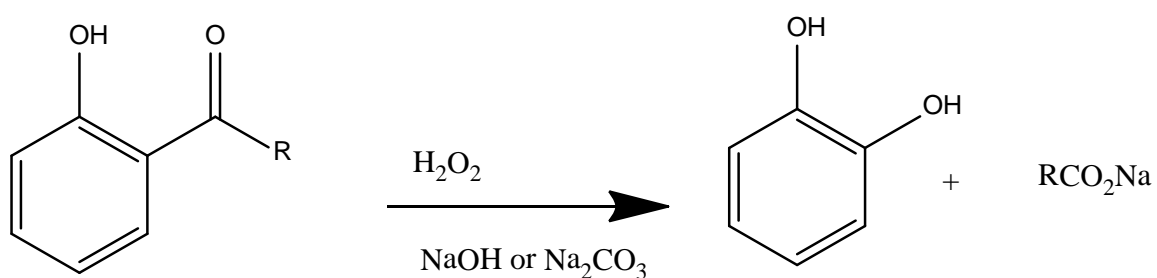
Name of the Teacher

Sirsendu Gayen

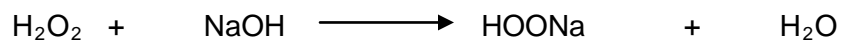
Department of Chemistry

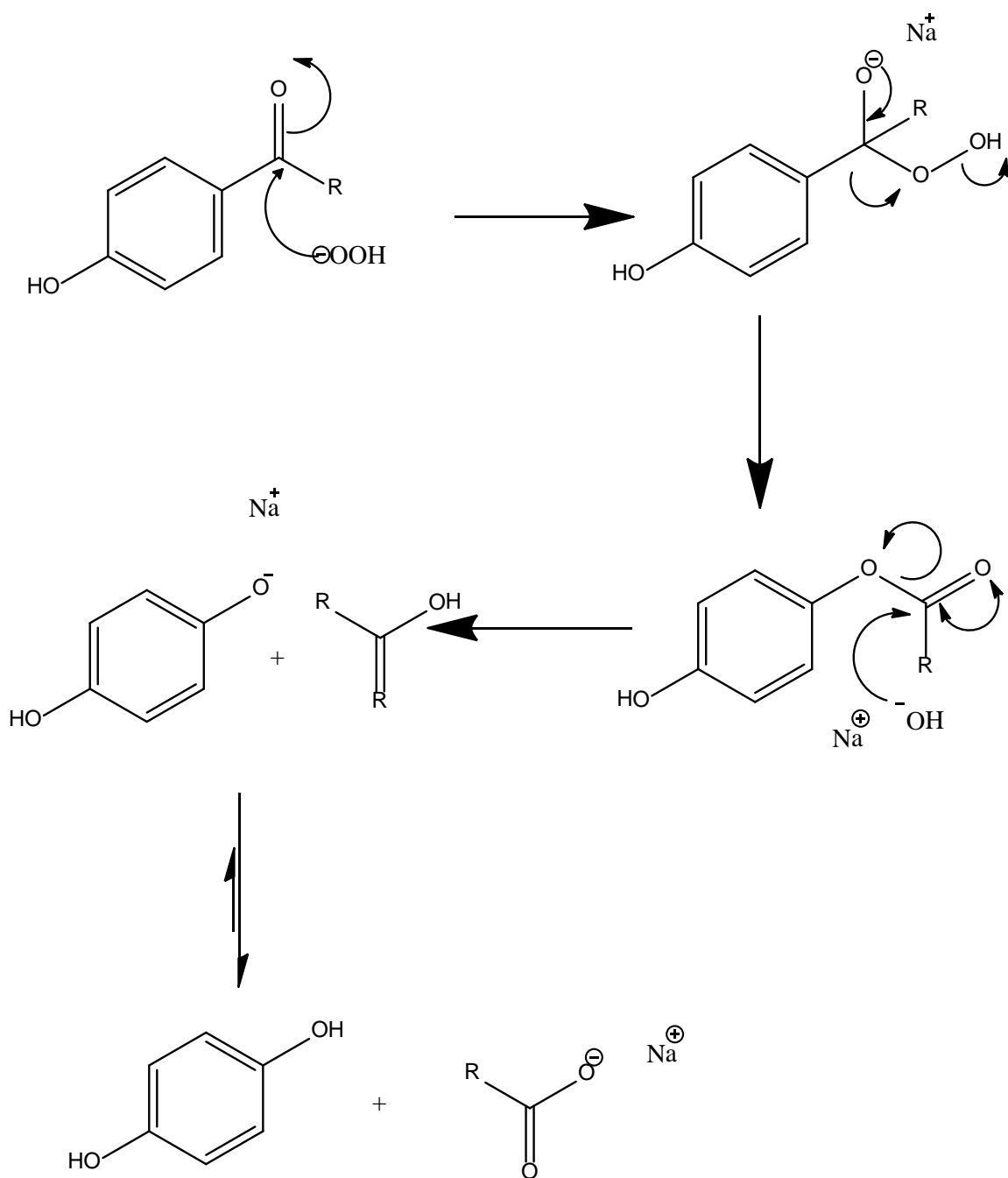
DAKIN REACTION:

An aromatic aldehyde or ketone is converted to a phenol ArOH on treatment with alkaline H_2O_2 but there must be an -OH or -NH₂ group in the ortho or para position. The reaction has also been performed on aromatic aldehyde with an alkoxy group in the ring. In this case acidic H_2O_2 (aq solution in CH_3OH) was used.



MECHANISM:

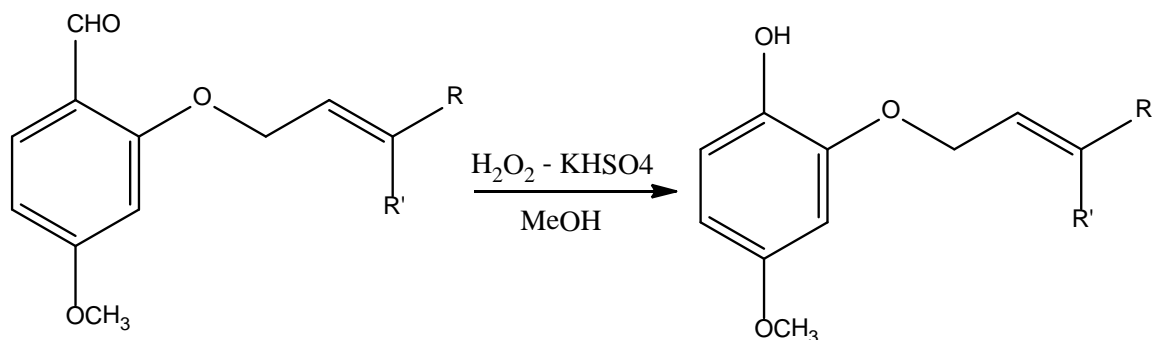




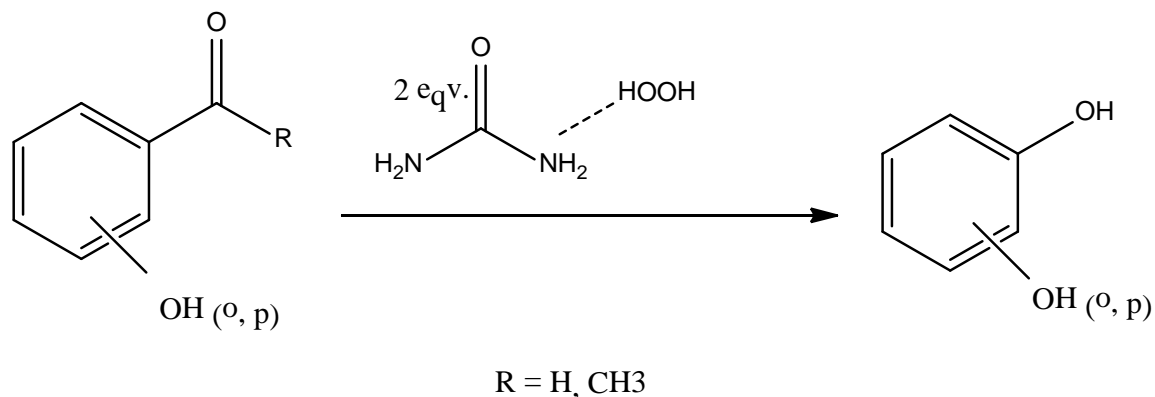
o- and p- hydroxy benzaldehyde undergo Dakin reaction whereas m- hydroxybenzaldehyde does not. This is due to the absence of electronic presence in case of m-hydroxybenzaldehyde.

Example:

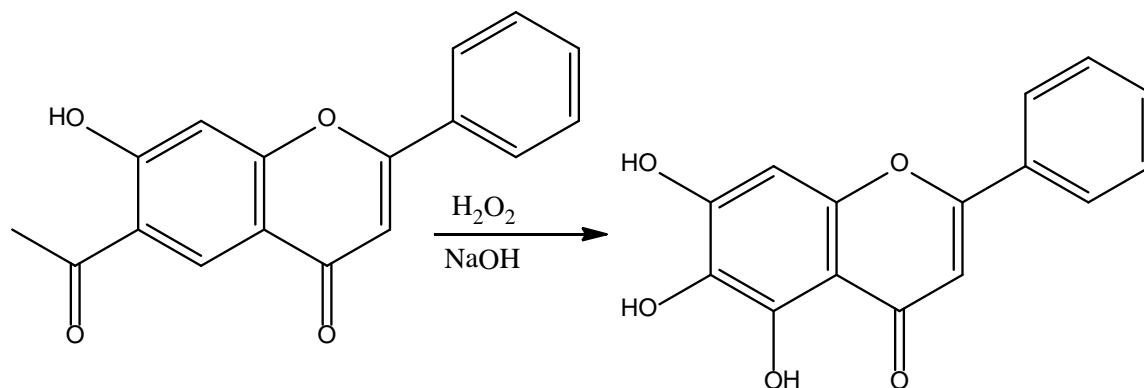
i).



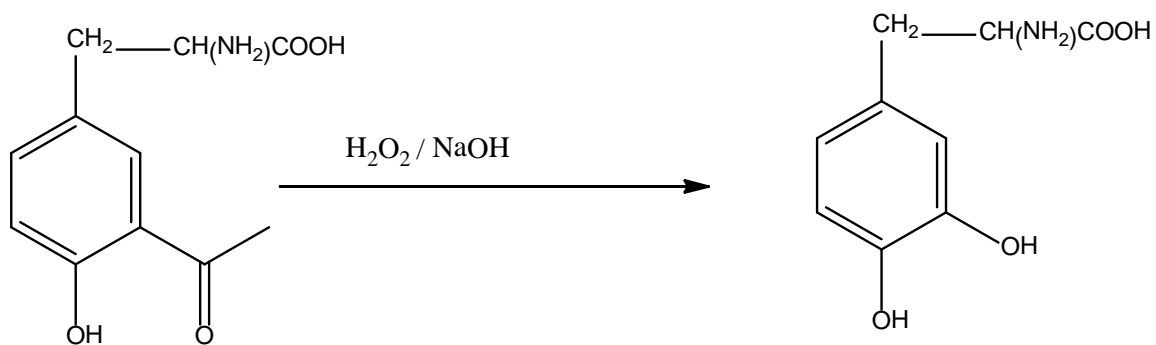
ii) Urea - hydrogen peroxide adduct is stable, inexpensive and an easily handled reagent. Varma and Naicker have used this reagent in an efficient solid-state oxidation of hydroxylated aldehydes and ketones to the corresponding phenol derivatives.



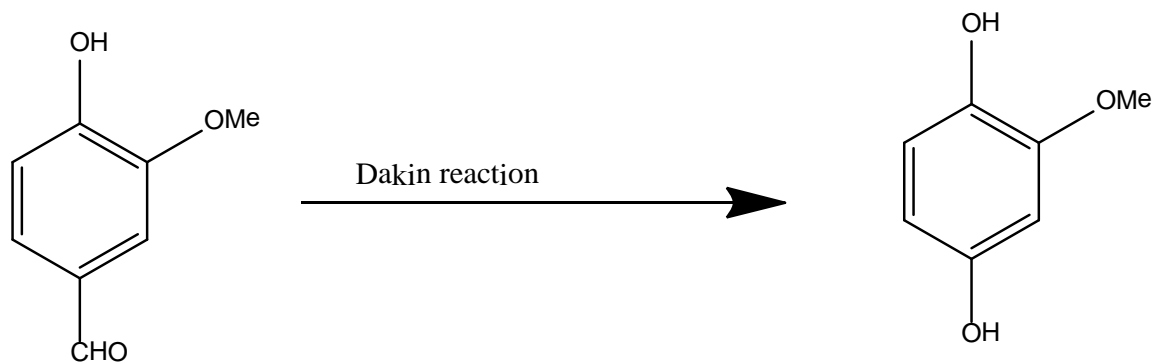
iii)



iv)



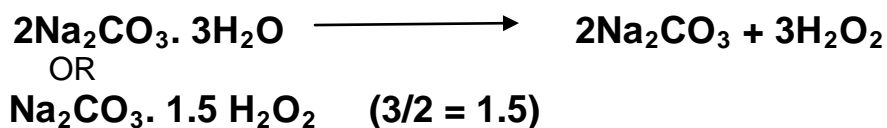
v)



Sodium percarbonate is a white crystalline water soluble chemical compound of sodium carbonate and hydrogen peroxide. It is an oxidizing agent and ingredient in a number of home and laundry cleaning products. Despite the name, it in fact a carbonate perhydrate.

Perhydrate, a hydrate in which the water molecule has been replaced by molecules of hydrogen peroxide.

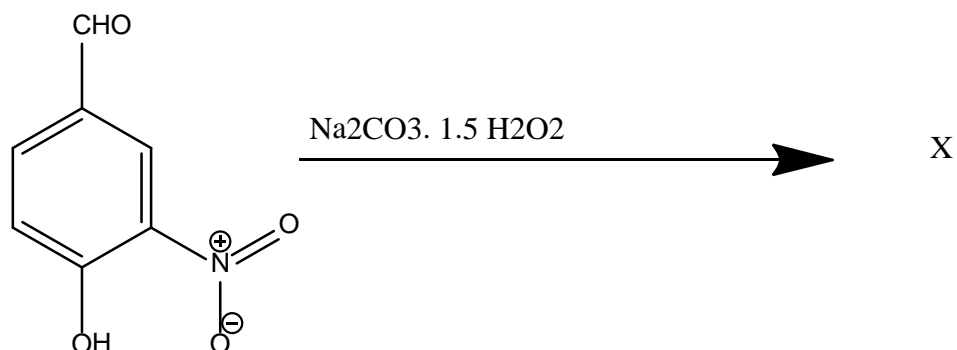
Dissolved in water it releases H_2O_2 and soda ash (sodium carbonate).



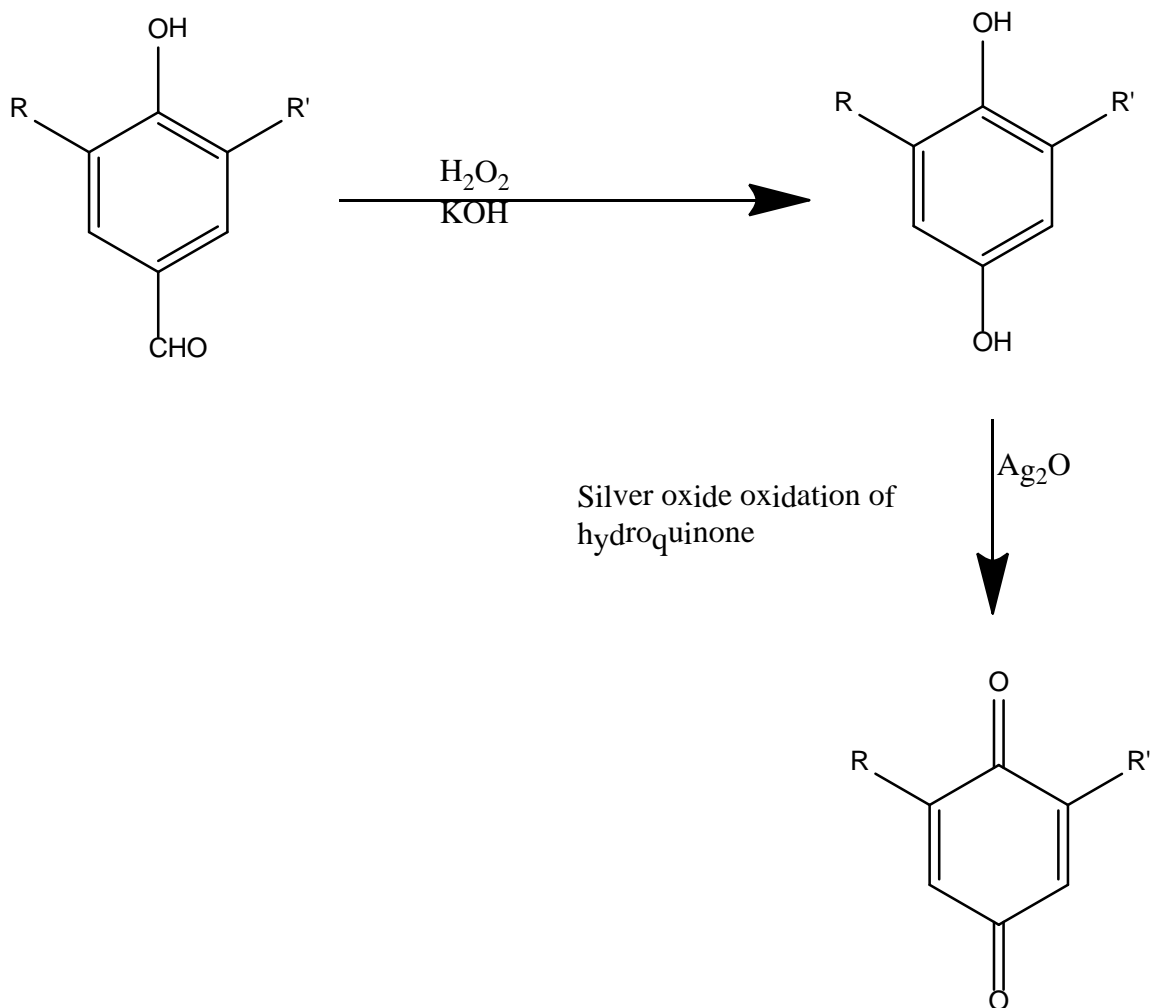
Sodium percarbonate is a very inexpensive large scale industrial chemical which is extensively used in the detergent industry as a bleaching agent.

Sodium percarbonate oxidizes hydroxylated benzaldehyde and acetophenone to hydroxy phenols in good yields.

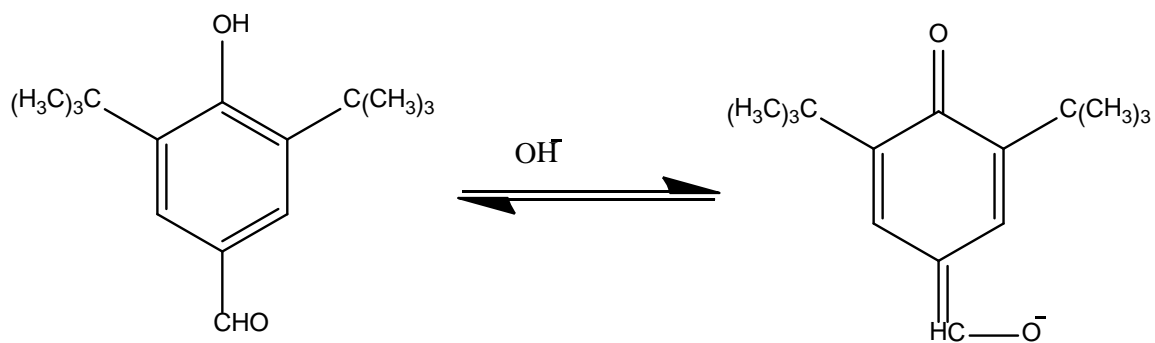
4-hydroxy-3-nitrobenzaldehyde also failed to react with $\text{Na}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}_2$ which may be due to intramolecular hydrogen bonding.



2,6-dialkylbenzoquinones which are extremely difficult compounds to prepare can be synthesized by using Dakin reaction on 4-hydroxy-3,5-dialkylbenzaldehydes.



In case of p-hydroxybenzaldehydes having the maximum steric hindrance around the phenolic hydroxyl group [for examples $R = C(CH_3)_3$]. The amount of aldehyde form is decreased sharply in alkaline medium (condition for the Dakin reaction) owing to the existence of a reversible equilibrium between free aldehyde and its diene-enolate salt form.



The slower reaction rate for hydroxyaldehydes having the more sterically hindered phenolic hydroxyl group is apparently connected with the fact that most of the starting aldehyde as already mentioned, is in the diene-enolate form under the reaction conditions.