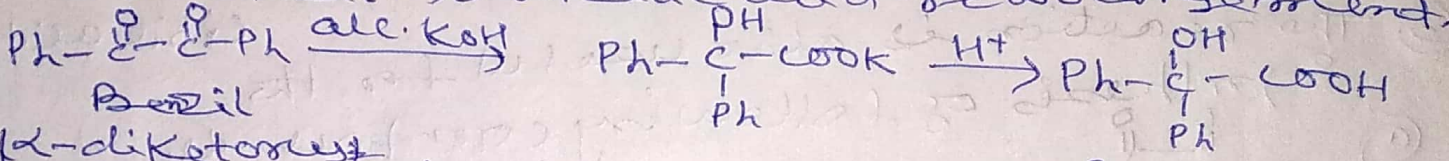
Benzil-Benzilic acid rearrangement

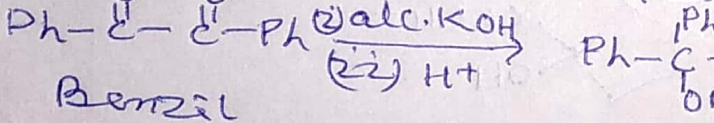
The base catalysed reaction of α-diketones (1,2-diketones) to give α-hydroxy carboxylic acid (2-hydroxy carboxylic acid) is known as benzilic rearrangement. Best result in this reaction is obtained when aryl group is present on both carbonyl carbons. The best known example is that benzil on refluxing with alcoholic potassium hydroxide gets rearranged into benzilic acid. Hence benzilic acid rearrangement is also known as benzil-benzilic acid rearrangement.



Benzil (α-diketone or 1,2-diketone.)

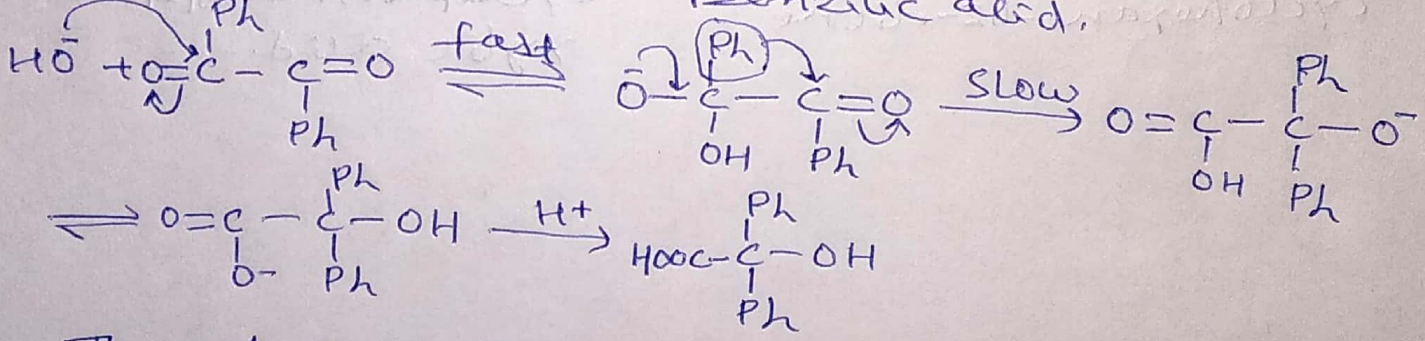
Benzilic acid (α-hydroxy acid or 2-hydroxy acid)

The rxn is not generally applicable to 1,2-diketones containing α-methylene groups because of the competing aldol condensation (but the synthesis of citric acid from ketopimelic acid is an exception).



Benzil

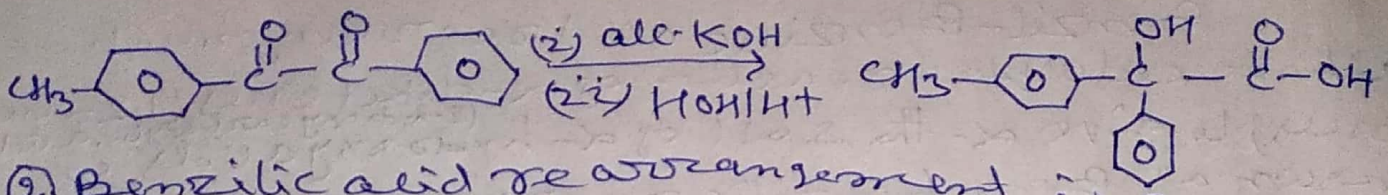
Benzilic acid.



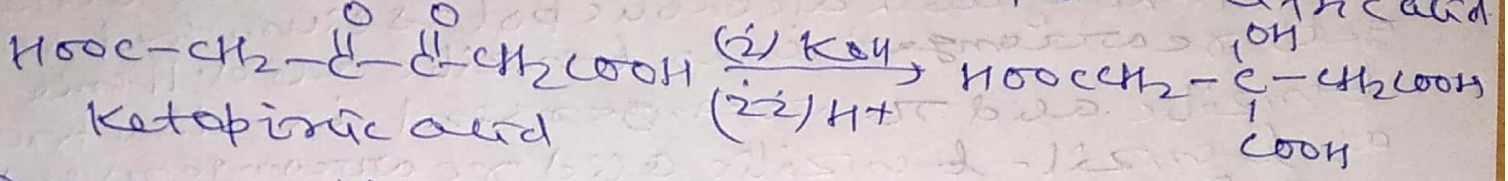
The rate of rearrangement has been found to be proportional to the concentration of benzil as well as the nucleophile i.e. Rate = K[benzil][OH]. Thus, it is a second order reaction.

Extension and application

① In this rearrangement, if the aryl group of one carbonyl carbon has +R group and the aryl group of the other carbonyl carbon has no +R group at o- or p-position, then migrating group is always the group which has no +R group.



(2) Benzilic acid rearrangement is generally applicable to aromatic ketones, however, Ketopiric acid, an aliphatic ketone, undergoes the rearrangement to form Citric acid

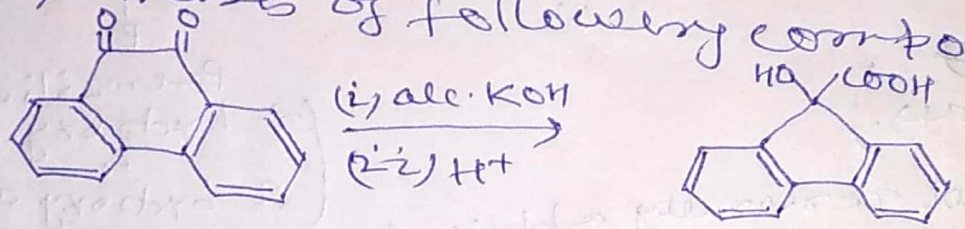


Ketopiric acid

Citric acid

(3) The reaction is also useful for the synthesis of following compounds.

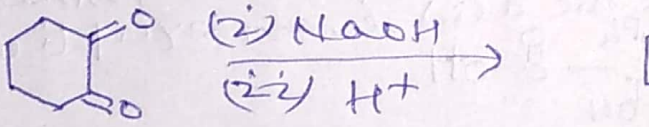
(a)



9,10-phenanthraquinone

9-hydroxyfluorene-9-carboxylic acid

(b)



Cyclohexane-1,2-dione

Cyclopentanol-1-carboxylic acid.