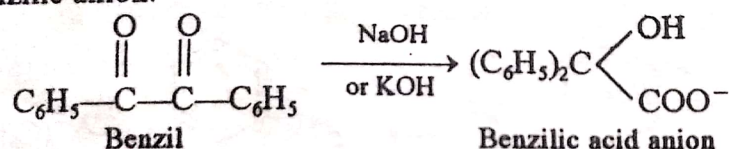


✓ **3. Benzilic acid rearrangement.** The transformation of  $\alpha$ -diketones\* to  $\alpha$ -hydroxy acids by means of hydroxide ion is known as benzilic acid rearrangement. The best known example is the conversion of benzil into benzilic anion.

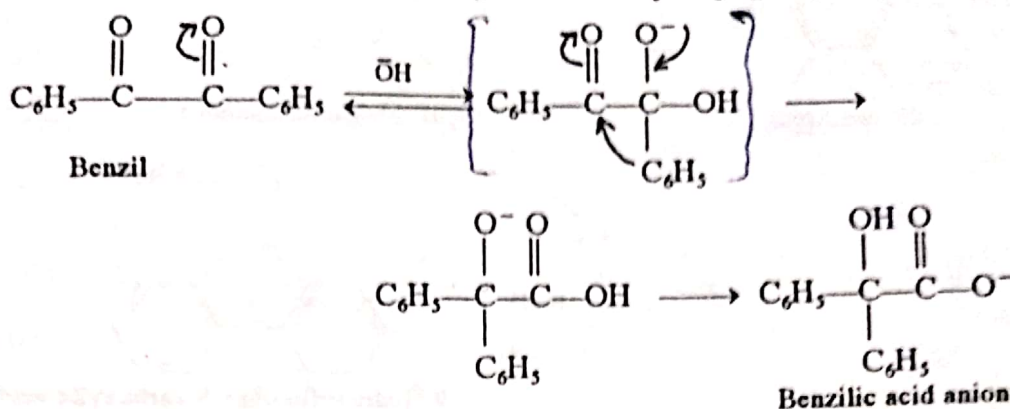


Pfeif in 1956 observed that barium and thallos hydroxides are more effective than the commonly used KOH or NaOH.

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\* Ketones which contain  $\alpha$  C—H bonds usually undergo base catalysed condensation in preference to rearrangement and hence, the reaction is mainly applicable to aromatic ketones.

**Mechanism.** The first step of the reaction is the addition of hydroxide ion to the carbonyl carbon atom. This step is found to be reversible as shown by the fact that the benzil exchanges  $O^{18}$  in basic solution faster than it rearranges. The next step being migration of the phenyl group.

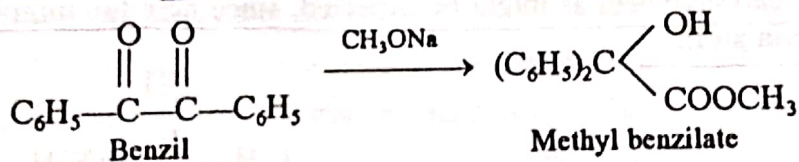


Note that the mechanism of benzilic acid rearrangement is exactly analogous to the intramolecular Cannizzaro reaction of glyoxal except that in the latter it is the hydrogen atom that migrates, while in the former phenyl group migrates.

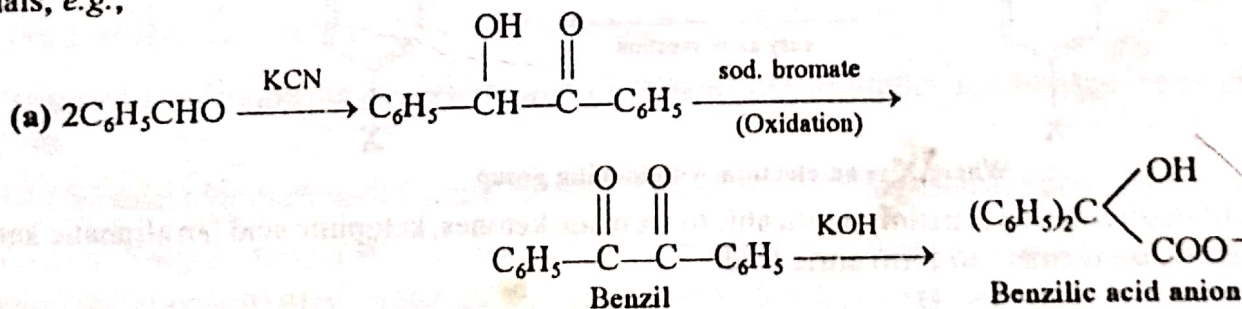
In the benzilic acid rearrangement when there is the competition between the two possible aryl groups, the less electron-releasing group will preferentially migrate because the more electron-releasing aryl group will tend to neutralise the positive charge on the carbonyl carbon atom to which it is attached by supplying the electrons and thus the hydroxide ion will attack carbon atom of the other carbonyl group. Since a phenyl group is involved, it is possible that during this 1, 2-shift a phenonium ion is formed as an intermediate.

### Extension and Applications

Doering *et al.* 1956 extended the reaction to the formation of the corresponding ester by replacing the normal alkali (*i.e.*, NaOH or KOH) by alkoxides\* (*viz.*  $\text{CH}_3\text{ONa}$ ,  $\text{Me}_3\text{COK}$ , etc.). Thus, benzil may directly be converted into alkyl benzilate by treatment with sodium alkoxide.

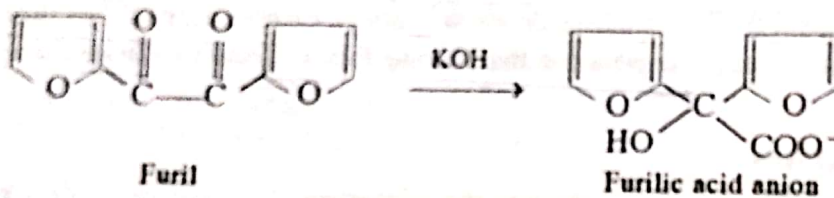
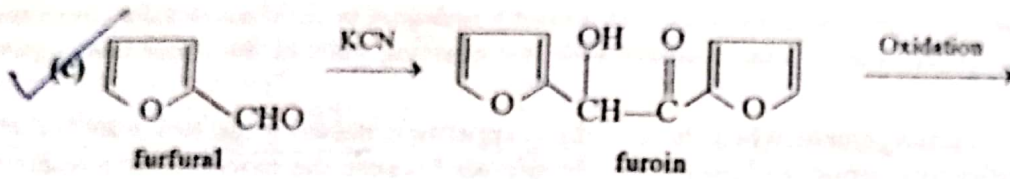
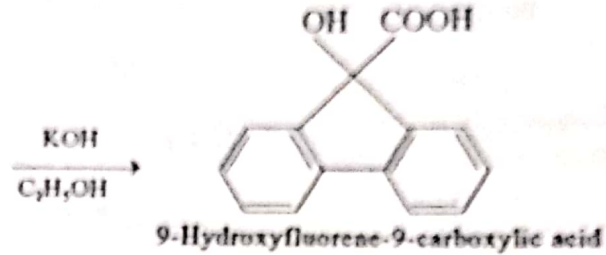
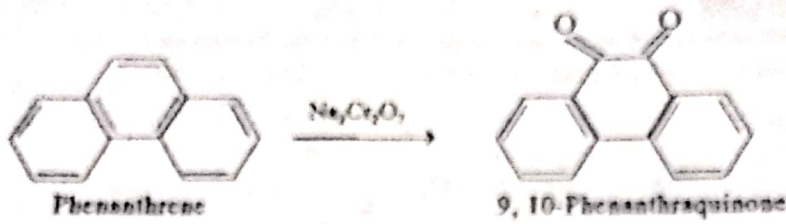


The reaction may be used for the preparation of  $\alpha$ -hydroxy acids from the easily accessible starting materials, *e.g.*,

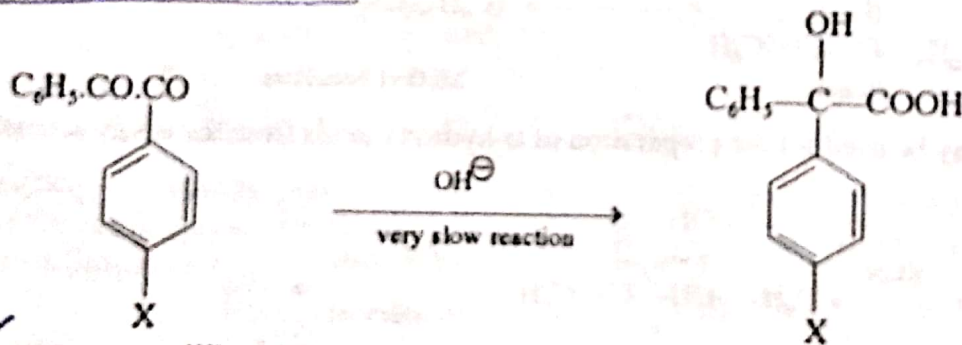


\* It is important to note that as the ethoxide and isopropoxide ions reduce benzil to benzoin, these reagents do not carry out benzilic rearrangement. Moreover, since the phenoxide ions are too weak bases to attack the carbonyl carbon atom, they are also not efficient reagents.

(b)



Diaryl diketones are the best starting materials as aliphatic diketones with enolizable hydrogen usually permit side reactions such as aldol condensation. Electron withdrawing substituents on the migrating group retard the rearrangement as might be expected, since here the migration will be to an electron-poor carbonyl carbon atom.



Where X is an electron-withdrawing group

(d) Although reaction is mainly applicable to aromatic ketones, ketopinic acid (an aliphatic ketone) undergoes the rearrangement to form citric acid.

