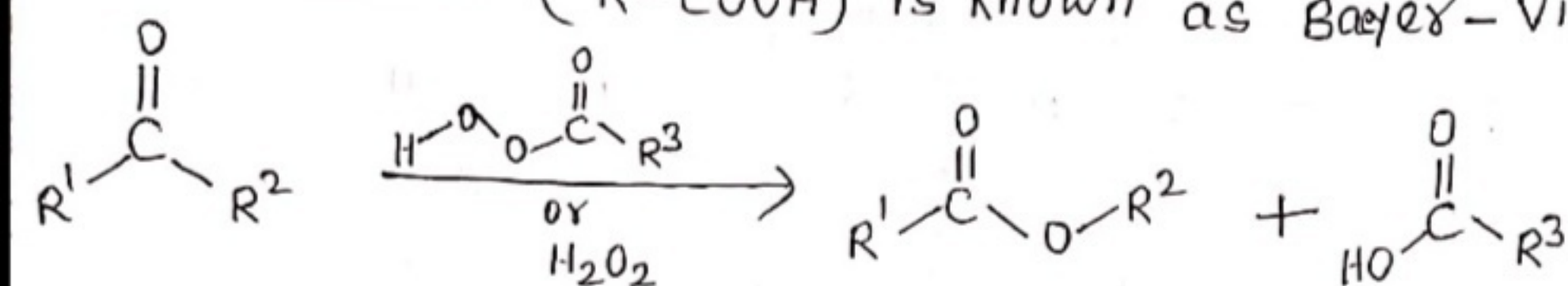


* Oxidation of ketones to esters with hydrogen peroxide or with peracids ($R-COOH$) is known as Baeyer-Villiger oxidation.



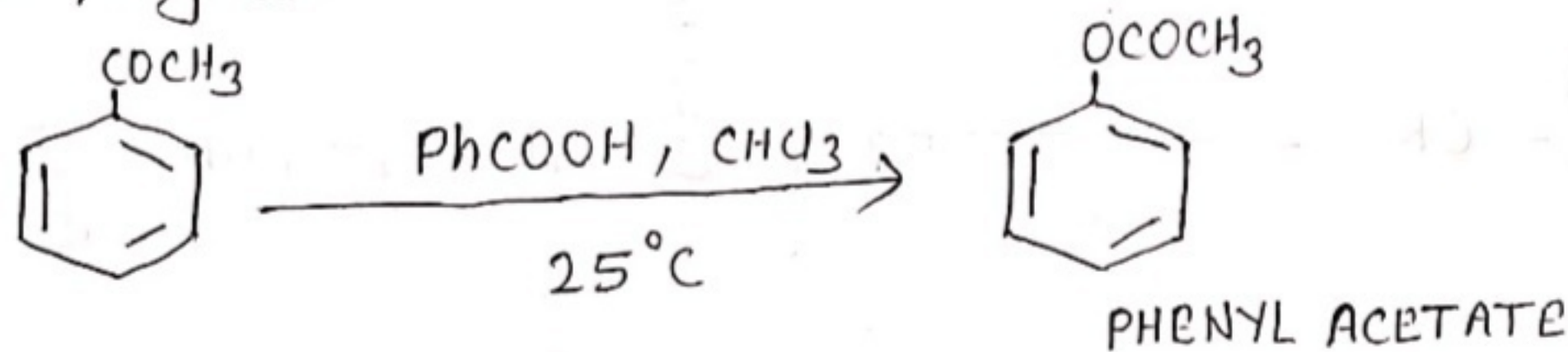
* Baeyer-Villiger used Caro's acid (peroxy sulphuric acid) in their experiments.

* The reaction can be brought about conveniently by hydrogen peroxide in weakly basic solutions.

* Typical peracids used are peracetic acid, trifluoroperacetic acid, perbenzoic acid, performic acid and *m*-chloroperbenzoic acid (*m*-CPBA).

Typical Example :-

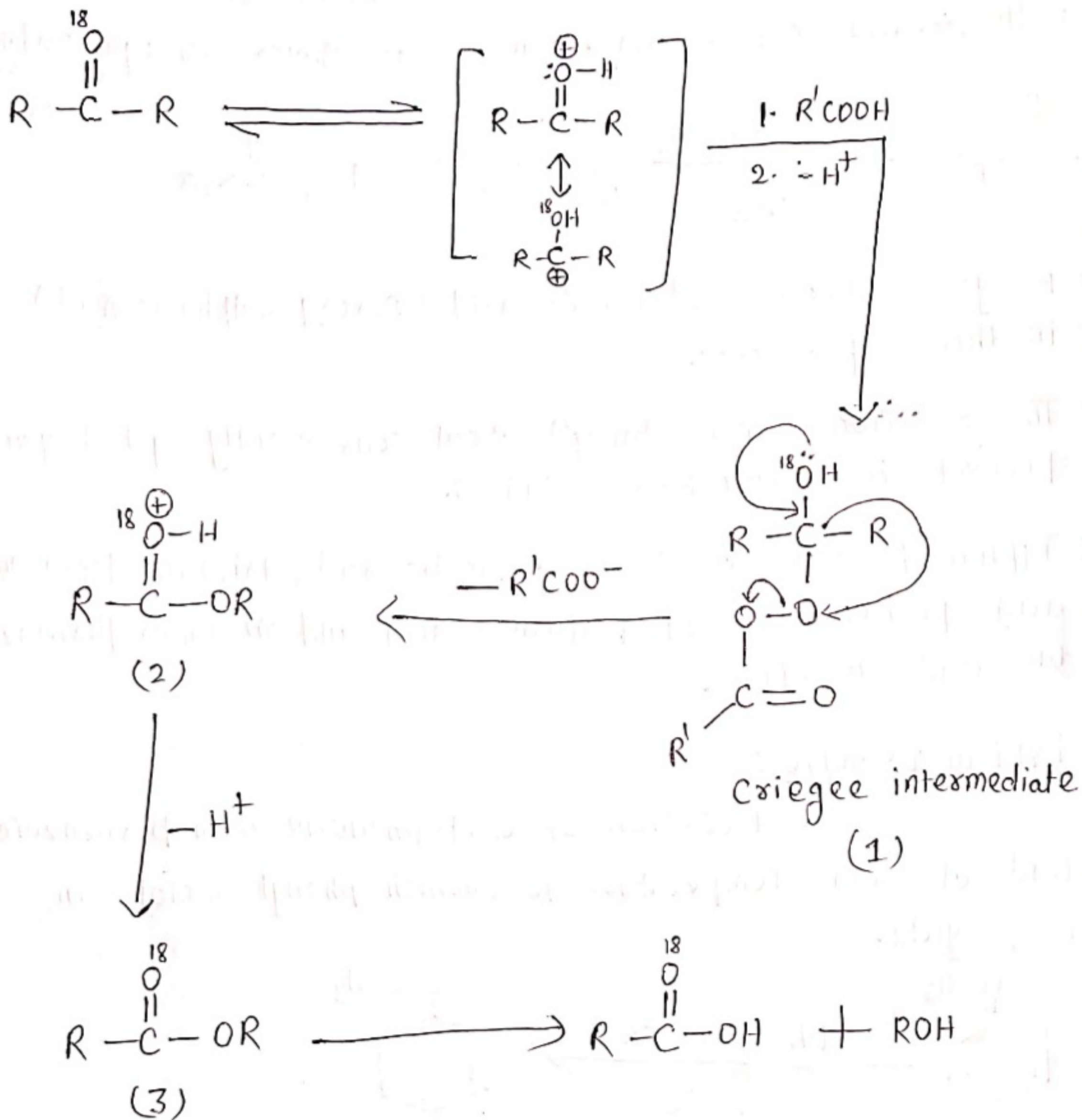
Reaction of acetophenone with perbenzoic acid at room temperature to furnish phenyl acetate in 63% yield.



* However, *m*-CPBA is the most common reagent because it is commercially available.

Mechanism

The mechanism of Baeyer-Villiger Rearrangement is not clear, however it is believed that the reaction proceeds as follows,



First step involves the protonation of carbonyl oxygen.

* The addition of peracid to the initially protonated ketones gives a tetrahedral intermediate (1).

- * Elimination of carboxylate anion and migration of 'R' to the electron deficient oxygen atom occur simultaneously.
- * The resulting protonated formed ester (2) loses a proton to yield ester (3).
- * Thus the reaction involves a migration of alkyl or aryl group from adjacent carbon to electrophilic oxygen.

Note :-

The most electron-rich alkyl group migrates first. The general migration order : - - - - -

tertiary alkyl > cyclohexyl > secondary alkyl > benzyl > phenyl > primary alkyl > methyl >> H

For substituted aryls :-

p-MeO-Ar > p-Me-Ar > p-Cl-Ar > p-Br-Ar >

p-O₂N-Ar

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Degree-II (Hons.), Paper-IV

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