

# BAEYER-VILLIGER REACTION: NEW DEVELOPMENTS TOWARD GREENER PROCEDURES

Dr. A. K. YADAV

Assistant Professor-Chemistry

Maharana Pratap Govt. P.G. College, Hardoi

Baeyer- Villiger rearrangement is the migration of group from carbon to electron deficient oxygen

Adolf Baeyer and Victor Villiger for the first time reported oxidation of Menthone to lactone with sodium persulfate and con. sulfuric acid. Persulfuric acid was subsequently replaced by organic peracid since then Baeyer-Villiger reaction became the most important and widely used in organic reaction.

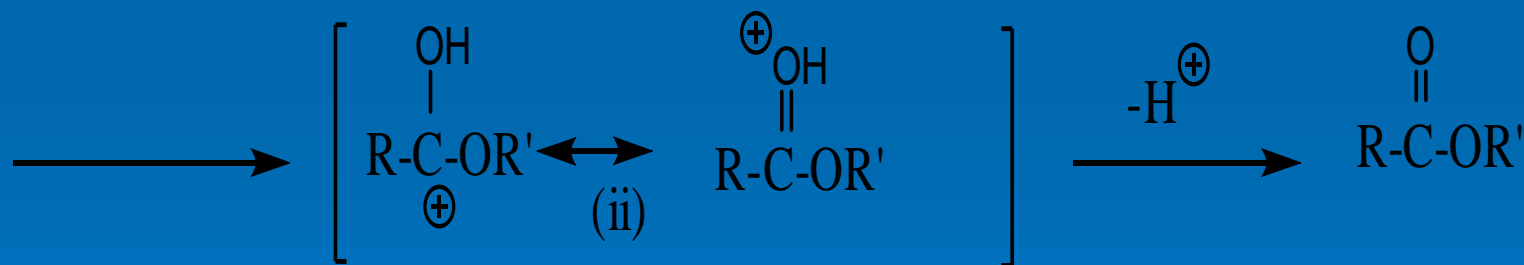
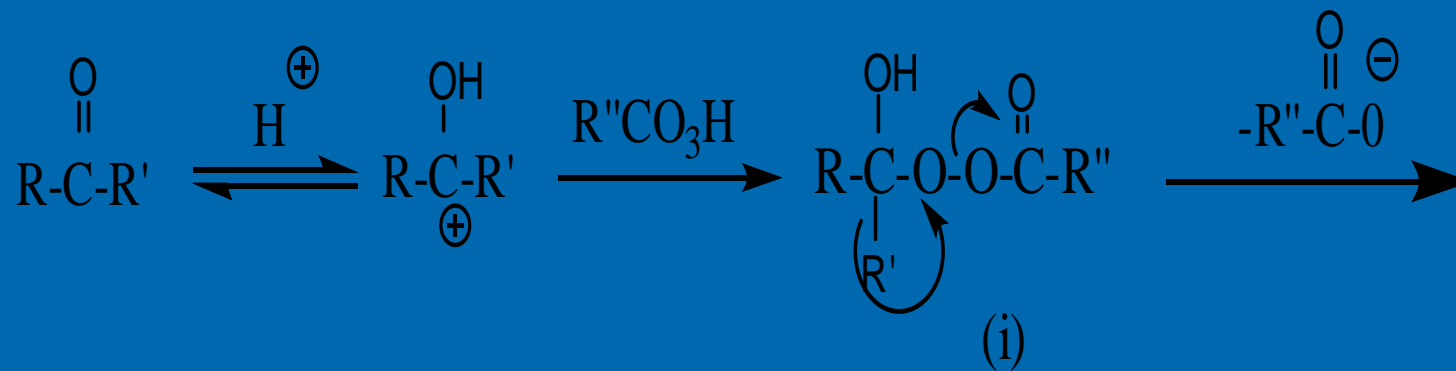
Aliphatic ketones are oxidised to esters in presence of peracid such as peracetic acid, perbenzoic acid, pertrifluoroaceticacid, permonosulfuric acid, etc,



Cyclic ketone converted into lactones with ring expansion.



## Mechanism:



## Success of the reaction is due to its versatility:

- (i) A variety of carbonyl compounds can be oxidized; that is, ketones are converted into esters, cyclic ketones into lactones, benzaldehydes into phenols, or carboxylic acids and  $\alpha$ -diketones into anhydrides.
- (ii) A large number of functional groups are tolerated.
- (iii) The regiochemistry is highly predictable with the migratory aptitude being tertiary alkyl > cyclohexyl > secondary alkyl > benzyl > phenyl > primary alkyl > cyclopropyl > CH<sub>3</sub>.
- (iv) The reaction is generally stereoselective; that is, the migrating group retains its configuration.
- (v) A wide range of oxidants may be used with their activity decreasing in the order: CF<sub>3</sub>CO<sub>3</sub>H > monopermaleic acid > monopерphthalic acid > 3,5-dinitroperbenzoic acid > *p*-nitroperbenzoic acid > *m*-CPBA > HCO<sub>3</sub>H > C<sub>6</sub>H<sub>5</sub>CO<sub>3</sub>H > CH<sub>3</sub>CO<sub>3</sub>H . H<sub>2</sub>O<sub>2</sub> > *t*-BuOOH.

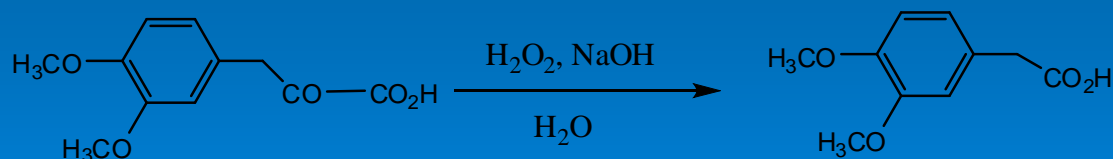
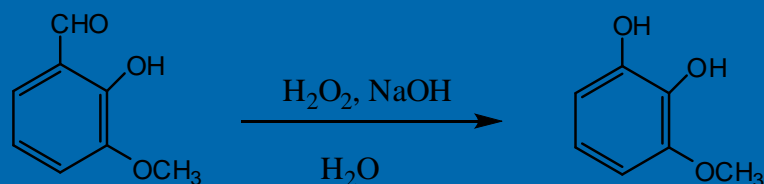
- Baeyer- Villiger oxidation suffers from several disadvantages. The use of an organic peracid results in the formation of one equivalent of the corresponding carboxylic acid salt as waste.
- Organic peracids are expensive and/or hazardous which limits their commercial application.
- In place of organic peracid aqueous hydrogen peroxides as the stoichiometric oxidant is used in an environmentally friendly solvent or solvent free condition.
- In organic synthesis, this method exhibits high degrees of chemo-, regio-, and enantioselectivity and broad substrate specificity.

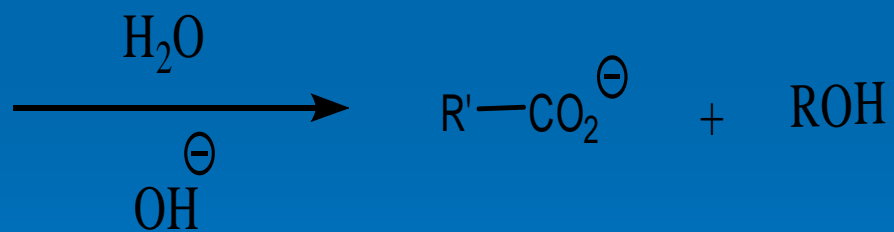
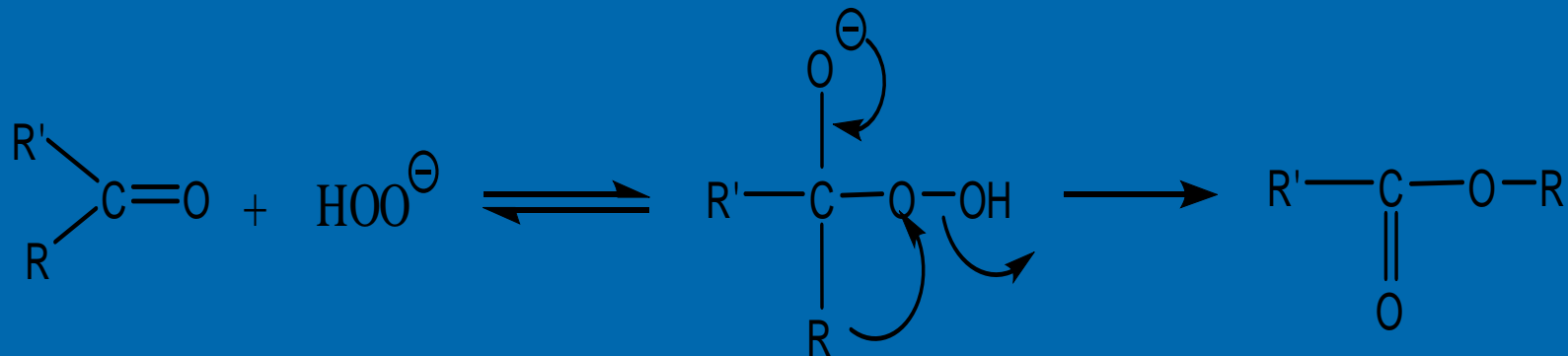
## **Hydrogen peroxide has many advantages:**

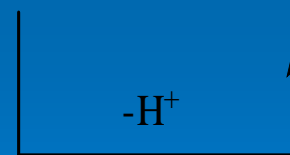
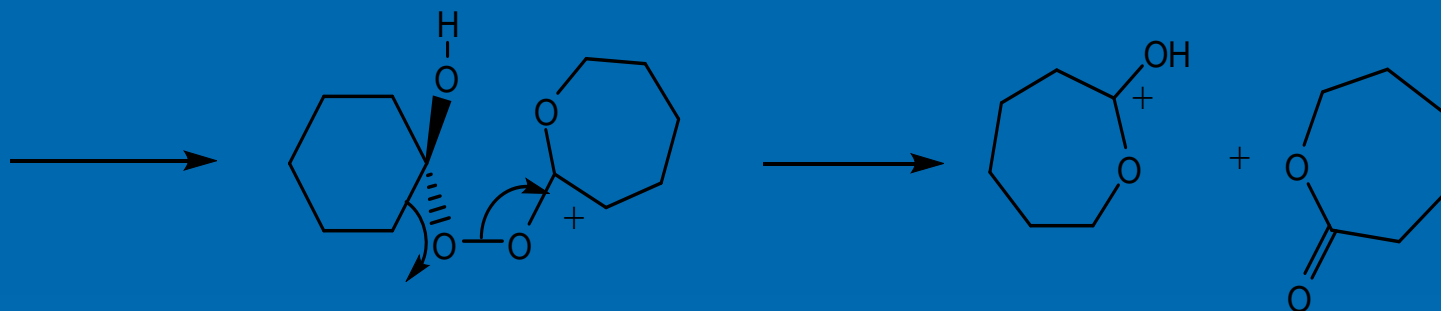
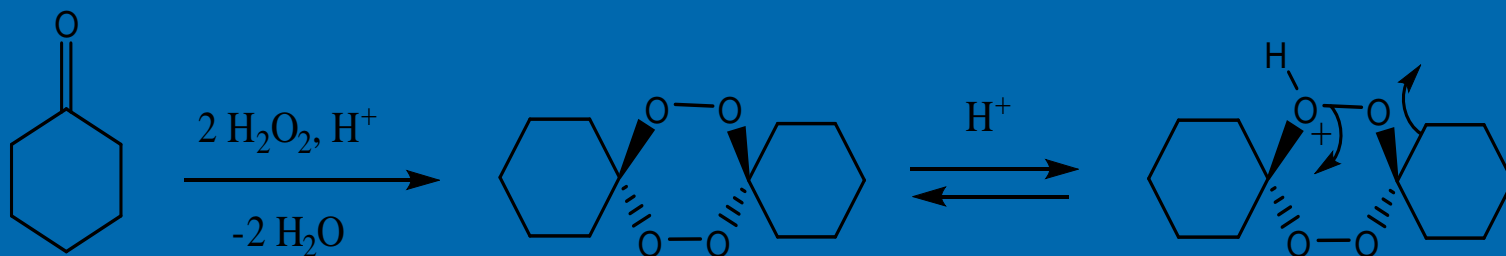
- \* It is safe and cheap
- \* Active hydrogen content is high
- \* It does not require a buffer,
- \* It is clean, since the byproduct formed is water.
- \* These points make the use of hydrogen peroxide extremely interesting from an industrial point of view

## Hydrogen peroxide has disadvantages also:

- \* Since water is present in solution, hydrolysis of the product esters may occur, and not all substrates are therefore compatible with water.
- \* Hydrogen peroxide is one of the weakest oxidants of a wide range of available peroxides and peracids and a catalyst is required to activate it
- \* Some catalysts show a low selectivity on hydrogen peroxide.



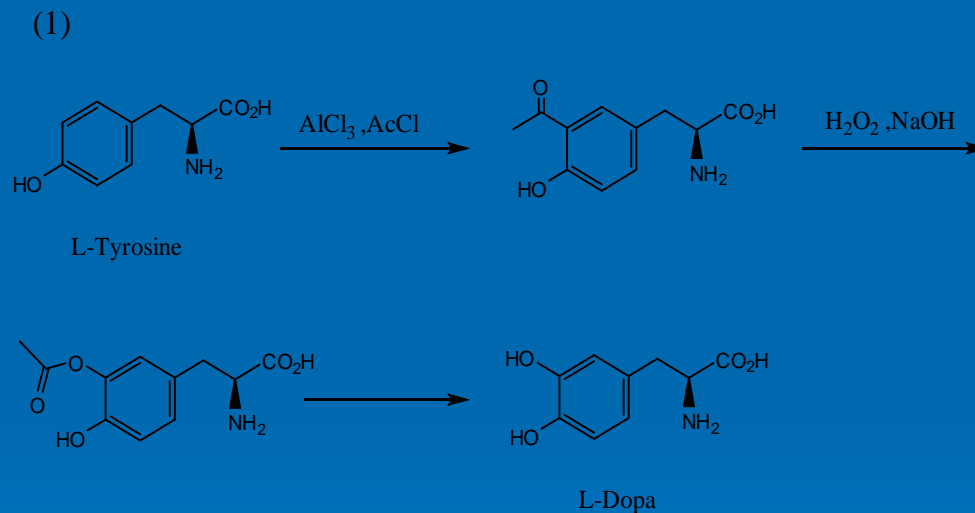


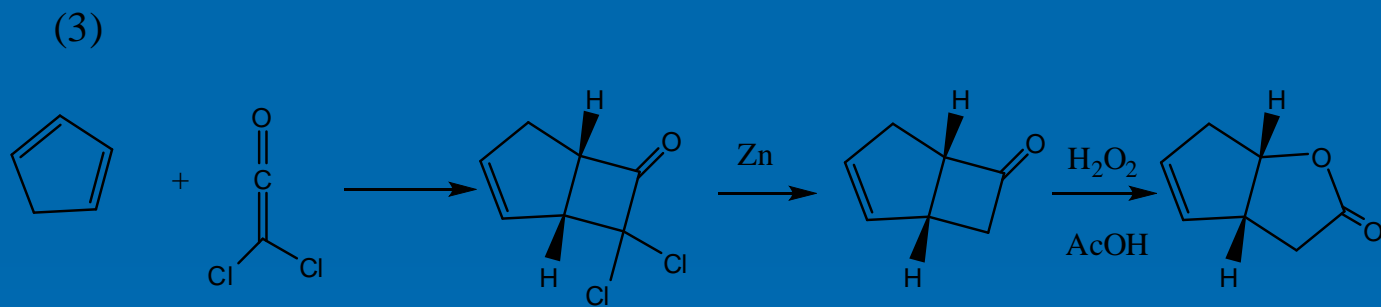
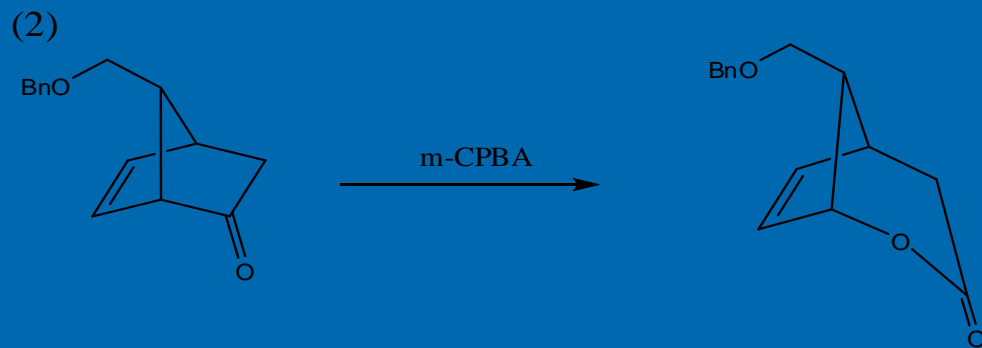




## Applications of Baeyer-Villiger oxidation:

1. Synthesis of Parkinson's disease drug (L-Dopa)
2. Synthesis of key intermediate of Corey's prostaglandin synthesis
3. Synthesis of an intermediate of perfumery compound *cis-jasmone*





## Conclusion:

- Esters and anhydrides which are difficult to synthesize can be easily prepared by this method.
- Large ring size ketones are used to prepare long chain hydroxyesters by this method.
- Some condensed cyclic ketones give two lactones in varying proportions like camphor, it is due to steric factor



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*THANK YOU*

