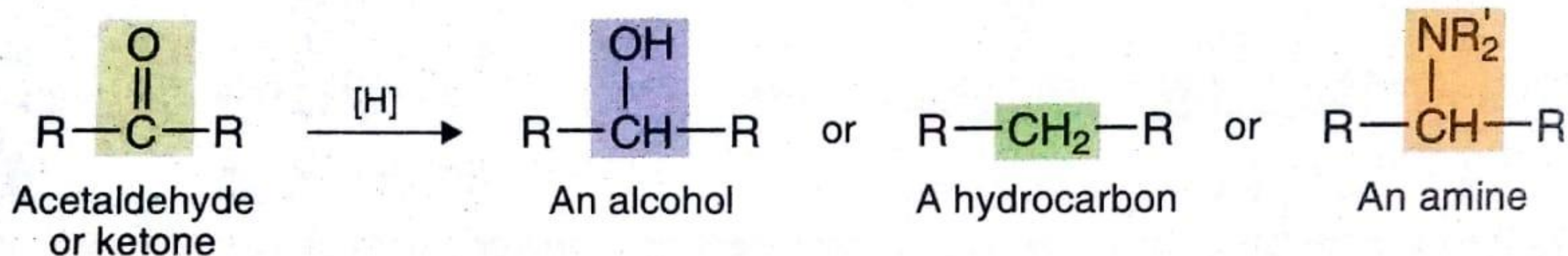


Metal Hydride Reduction

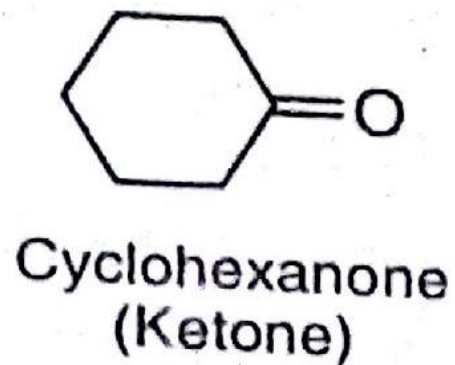
Reduction of Aldehydes And Ketones

An aldehyde or a ketone can be reduced to an **alcohol**, a **hydrocarbon**, or an **amine**. The product of the reaction depends on the reducing agent and on the structure of the carbonyl compound.

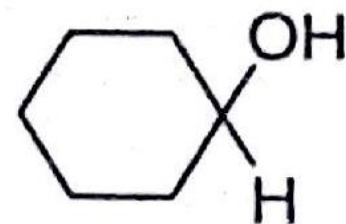
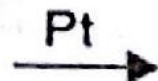


Catalytic Hydrogenation

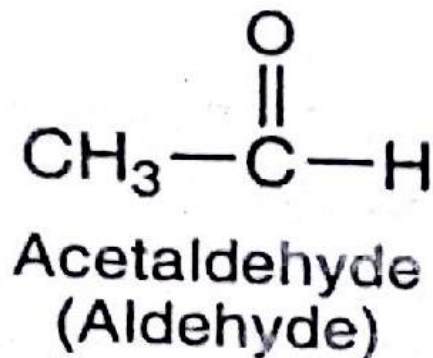
The pi-bond of carbonyl group can undergo hydrogenation, just as the pi-bond of an alkene. For example, ketones such as cyclohexanone, can be hydrogenated under room temperature and 4 atmospheres of pressure with a platinum catalyst.



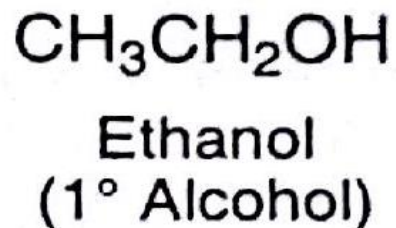
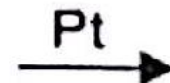
+



Cyclohexanol
(2° Alcohol)

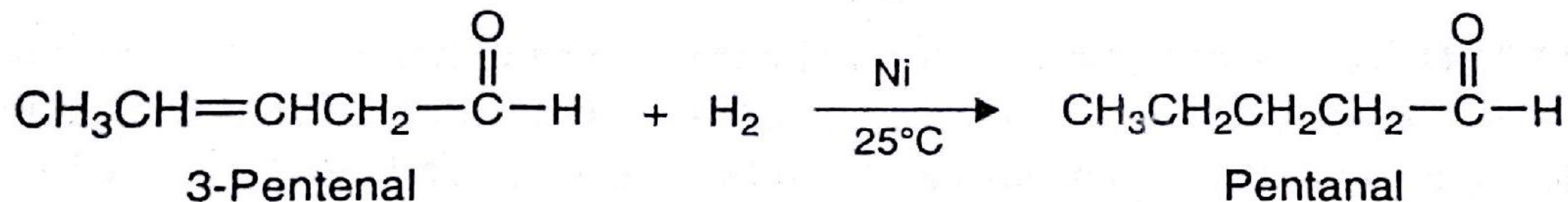


+

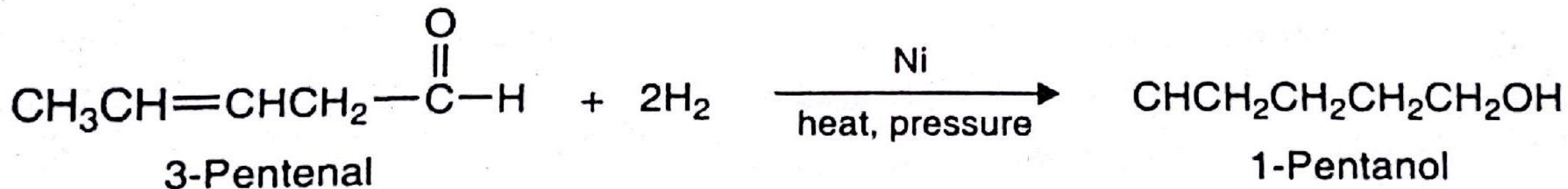


But if both a double bond and carbonyl group is present in a structure, the double bond may be hydrogenated, leaving the carbonyl intact or both may be hydrogenated.

C=C reduced (but not C=O) :



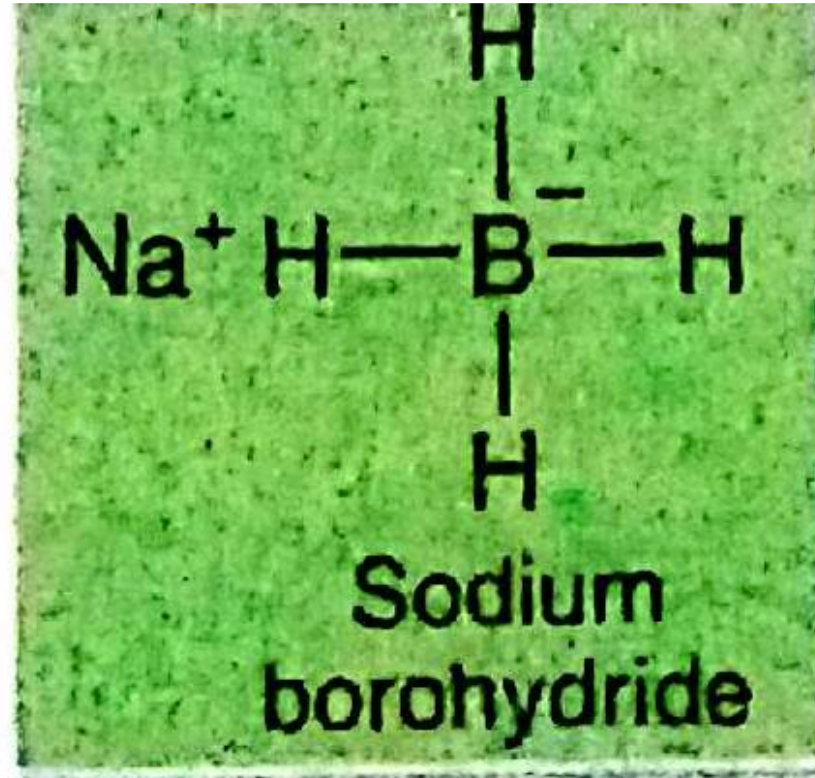
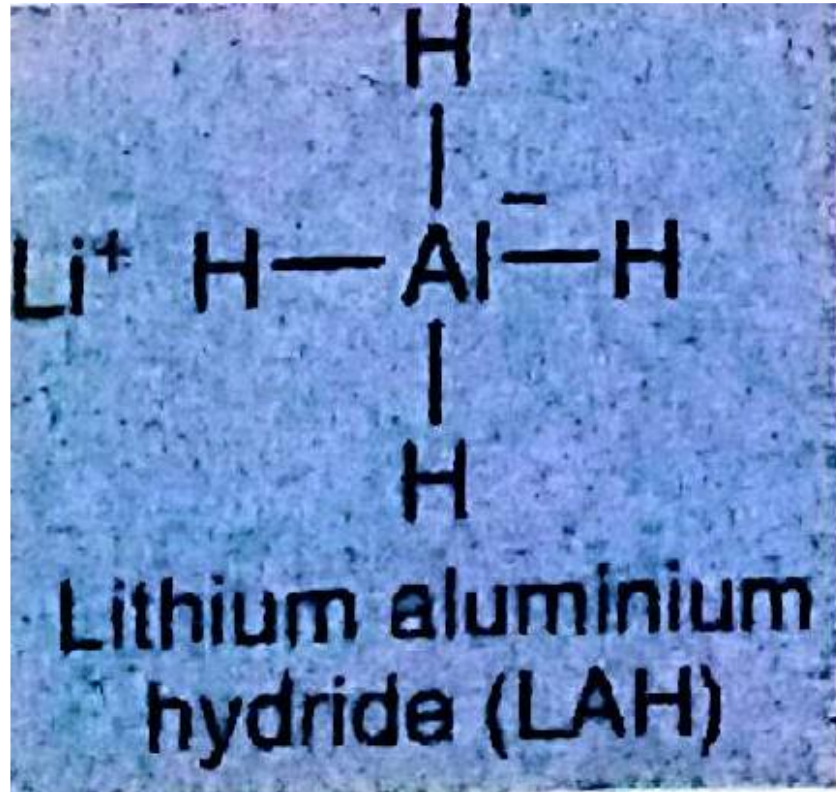
C=C and C=O reduced :

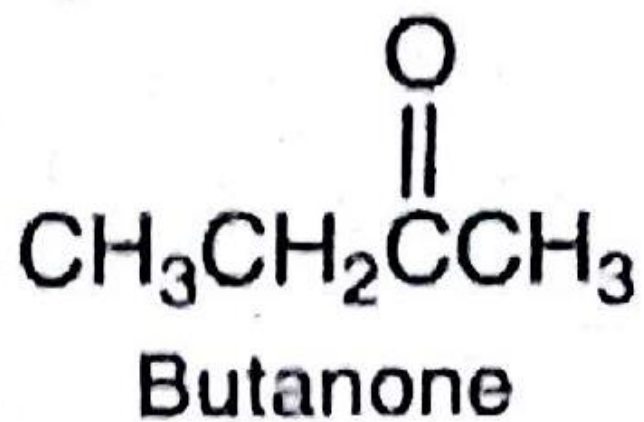


However, the carbonyl group cannot be catalytically hydrogenated independently of the carbon-carbon double bond. Now to reduce a carbonyl group and leaving a carbon-carbon double bond intact, a **Metal Hydride Reduction** is the preferred method of choice.

Hydrogen gas is inexpensive, however a hydrogenation reaction is rather inconvenient because the apparatus usually consist of **gas tanks** and a **metal pressure vessel**. Therefore, the use of metal hydrides are the preferred alternative reducing agents.

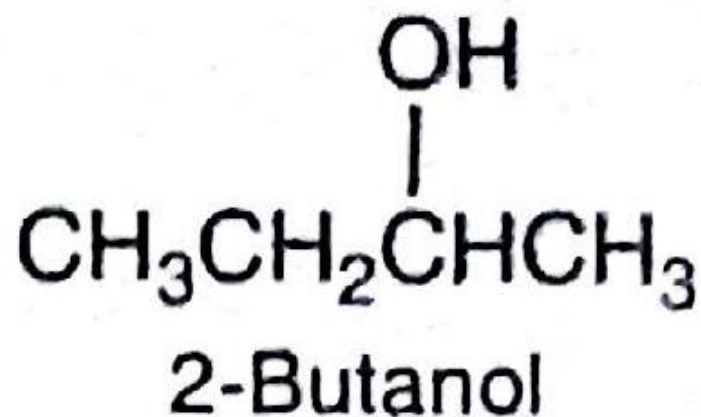
Two valuable reducing agents commonly used are lithium aluminum hydride (LAH) and sodium borohydride (NBH). Both reduce aldehydes and ketones to alcohols.





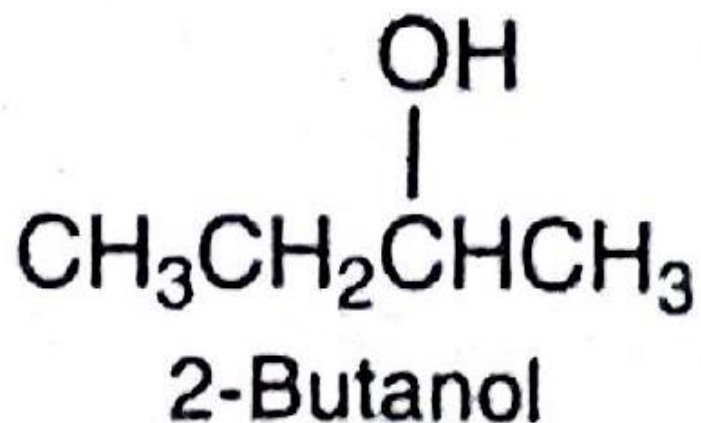
(1) LiAlH_4

(2) $\text{H}_2\text{O}, \text{H}^+$



(1) NaBH_4

(2) $\text{H}_2\text{O}, \text{H}^+$



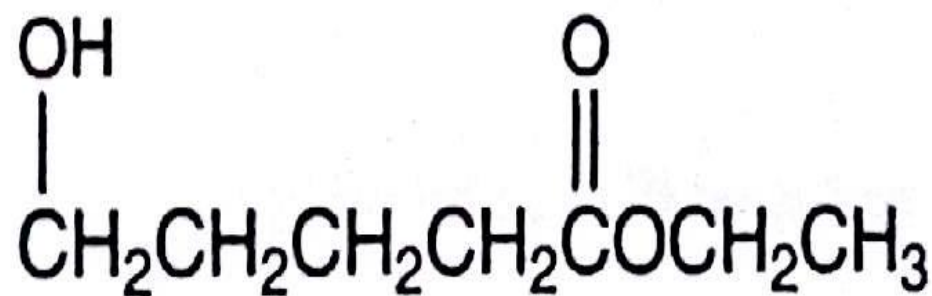
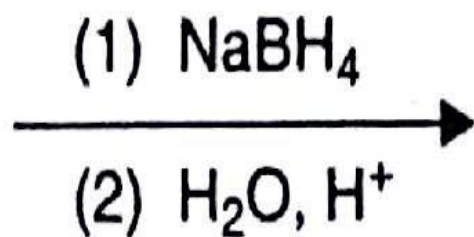
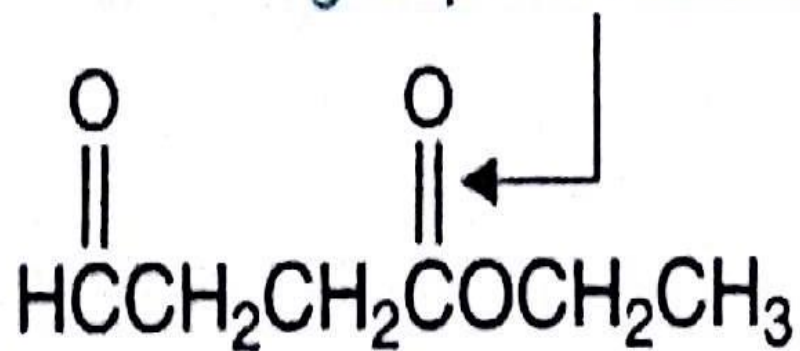
These two metal hydrides are quite different in their reactivities. LiAlH_4 is a powerful reducing agent that reduces not only aldehydes and ketones, but also carboxylic acids, esters, amides, and nitriles.

LiAlH_4 undergoes violent reaction with water, therefore reductions are usually carried out in a solvent such as anhydrous ether.

NaBH₄ is a milder reducing agent than LAH. Its reactions can be carried out in water or aqueous alcohol as a solvent. For the reduction of aldehyde or ketone, NaBH₄ is the preferred reagent; it is certainly more convenient to use because of its lower reactivity towards water.

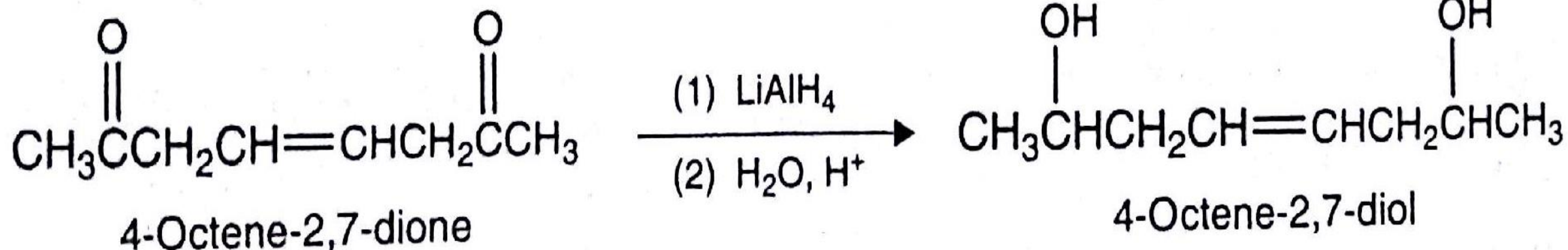
NaBH₄ reduces aldehydes and ketones rapidly while it reduces esters slowly. Therefore, an aldehyde or ketone carbonyl group can be reduced without the simultaneous reduction of an ester group in the same molecule. **This selectivity is not possible with LAH.**

Ester carbonyl
group not reduced



Neither NBH nor LAH reduces isolated carbon-carbon double bonds, although C=C in conjugation with a carbonyl group is sometimes attacked. Consequently, a structure that contains both a double bond and a carbonyl group can often be reduced selectively at the carbonyl position. In this respect, metal hydrides are complementary to the hydrogen gas as reducing agents.

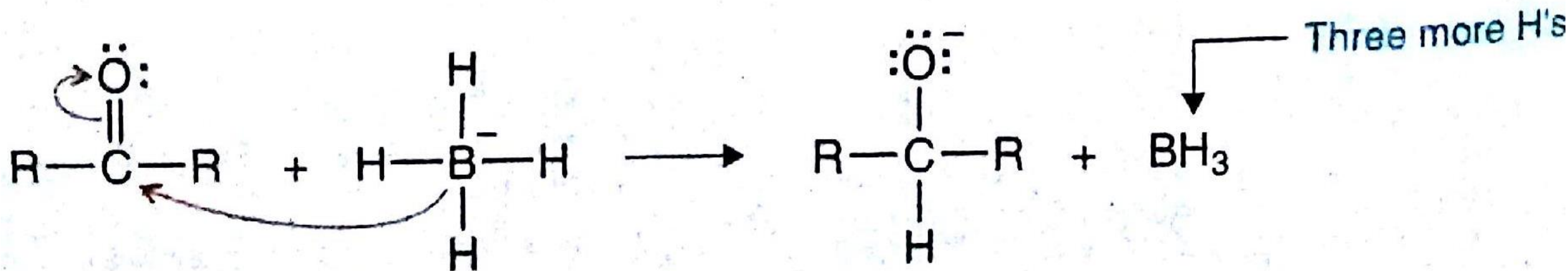
C=O reduced (but not C=C) :



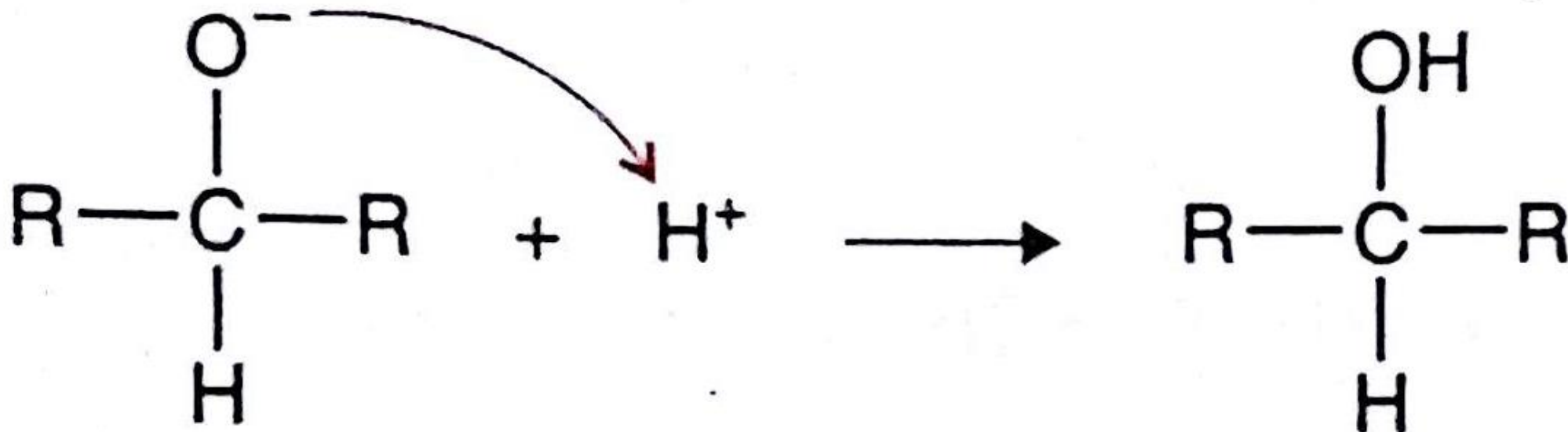
Diisobutylaluminium hydride (DIBAL-H) is a newer but popular metal hydride reducing agent that is similar to LAH. Besides reducing aldehydes and ketones to alcohols, DIBAL-H reduces carboxylic acids and esters to aldehydes or alcohols.

Mechanism

Step-1: Metal hydrides react by transferring a negative hydride ion to the positive carbon of a carbonyl group.

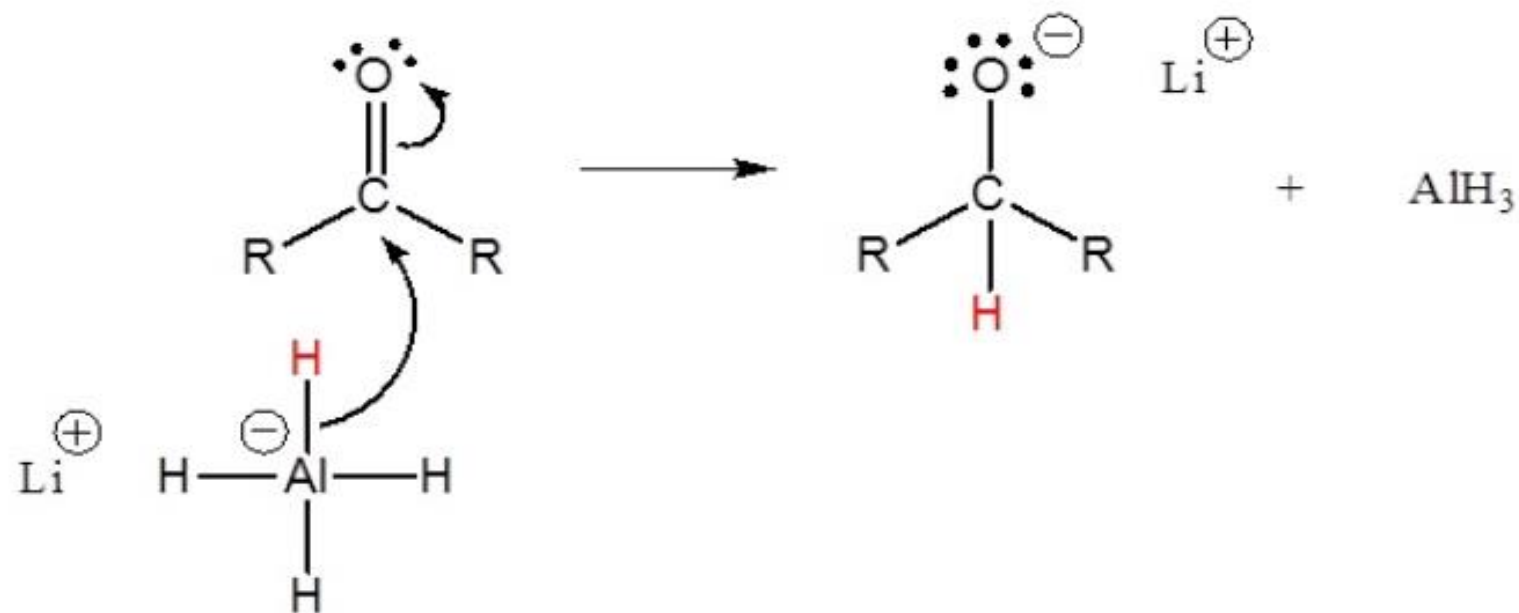


Step-2: Protonation of alkoxide

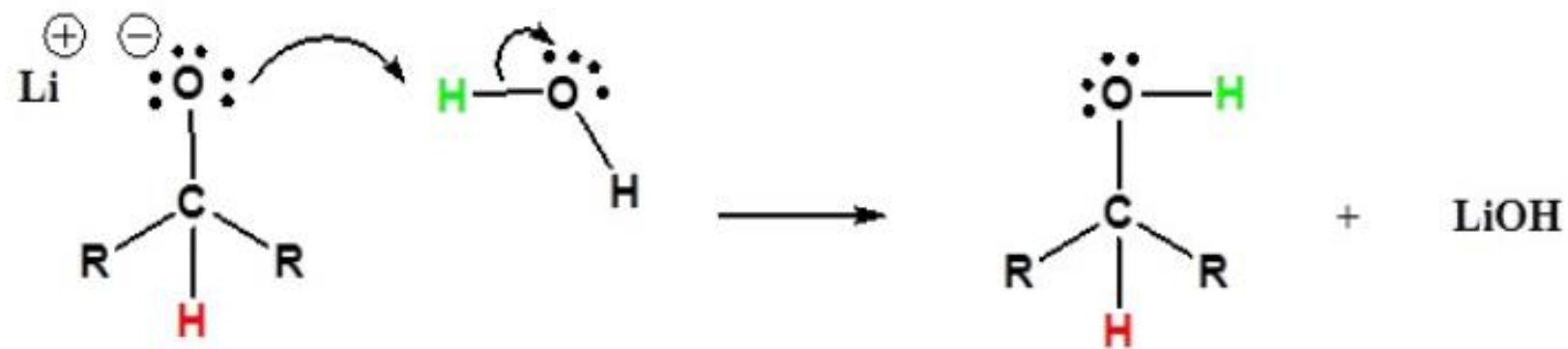


Each hydride ion can reduce one carbonyl group. Therefore, one mole of NaBH_4 can reduce four moles of aldehydes or ketones.

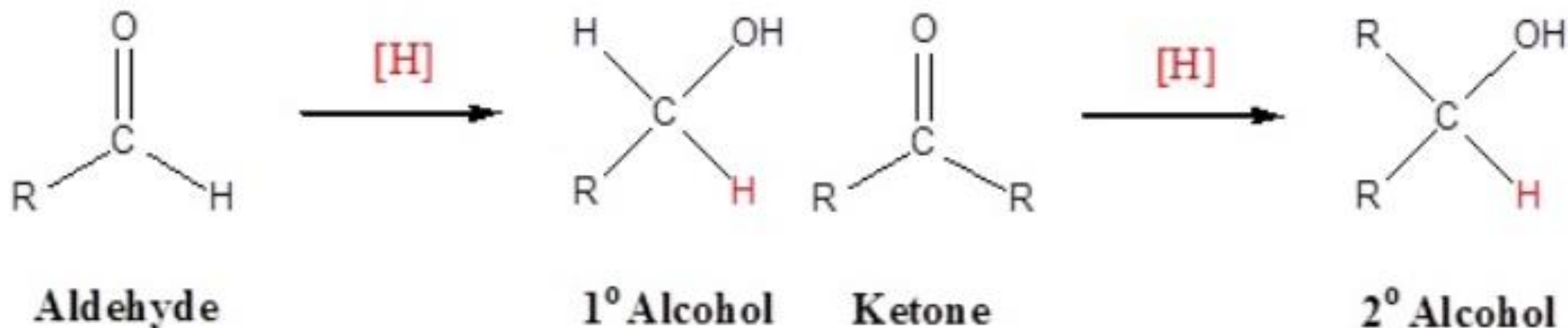
1) Nucleophilic attack by the hydride anion



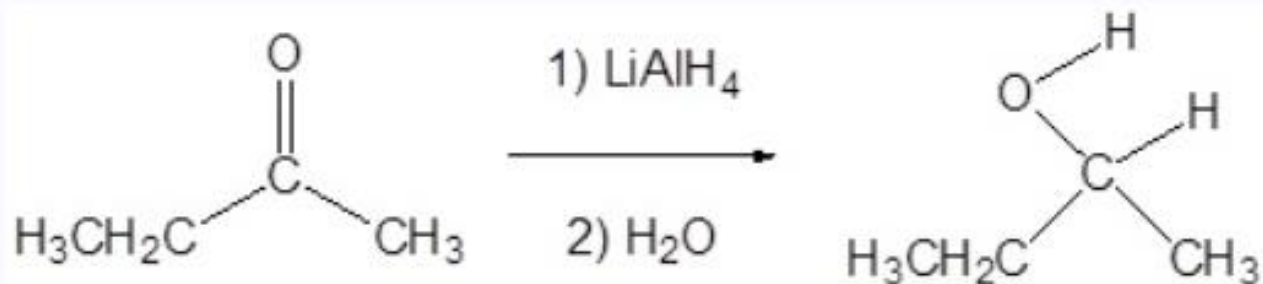
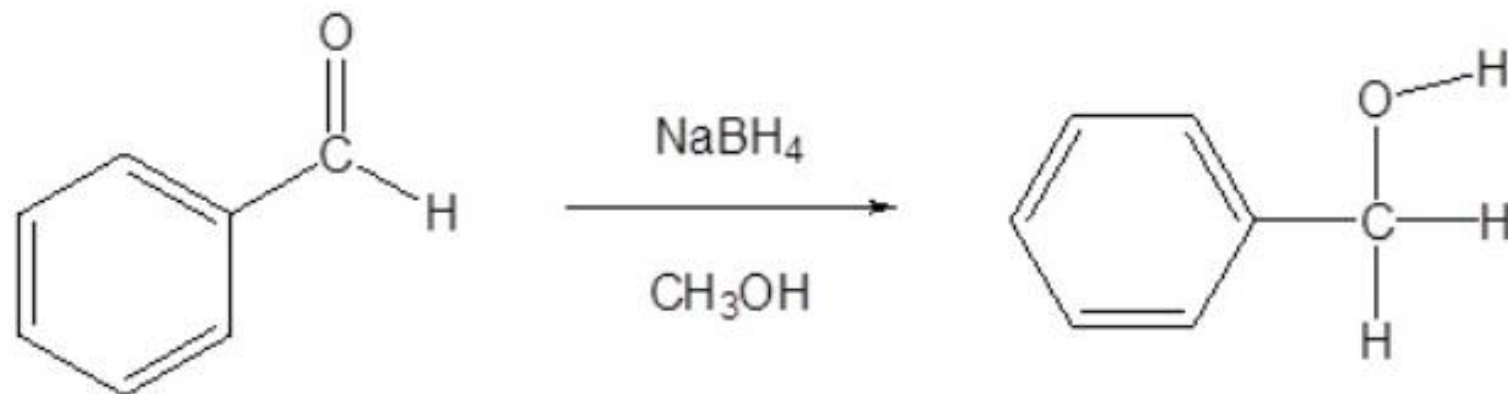
2) The alkoxide is protonated



Addition of a hydride anion (H^-) to an aldehyde or ketone gives an alkoxide anion, which on protonation yields the corresponding alcohol. Aldehydes produce 1° -alcohols and ketones produce 2° -alcohols.



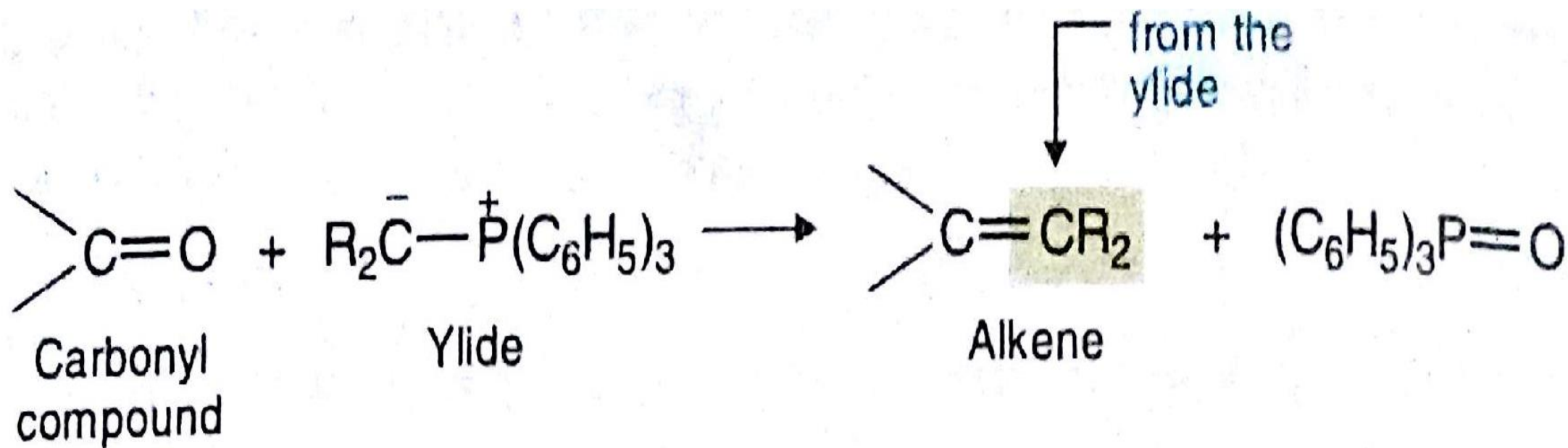
In metal hydrides reductions, the resulting alkoxide salts are insoluble and need to be hydrolyzed (with care) before the alcohol product can be isolated. In the sodium borohydride reduction the methanol solvent system achieves this hydrolysis automatically. In the lithium aluminum hydride reduction water is usually added in a second step.



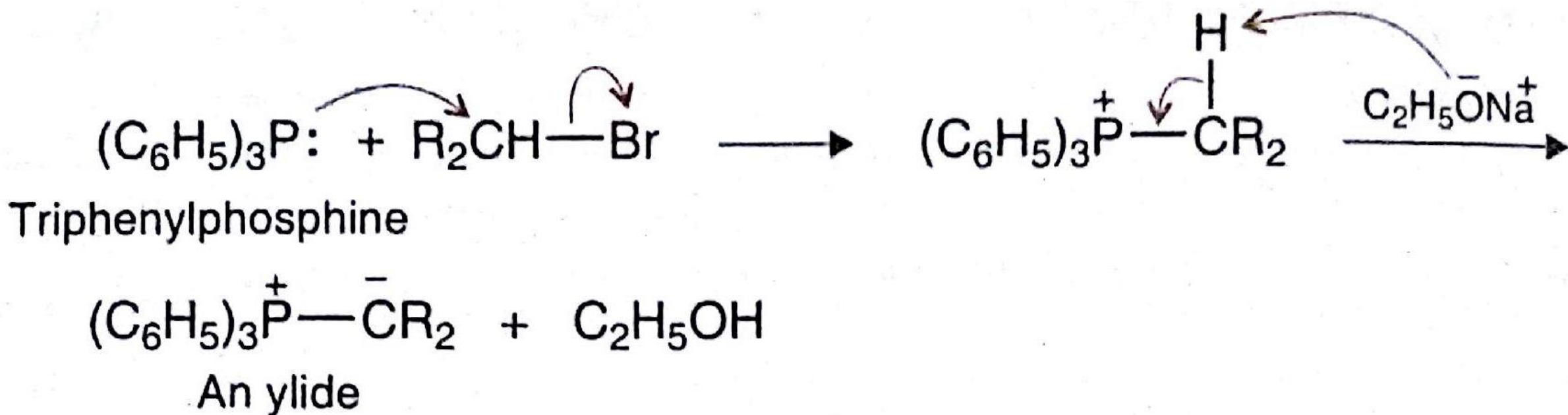
Wittig Reaction

Wittig Reaction

This reaction involves the treatment of aldehydes and ketones with phosphorous ylides to form alkenes. This reaction is an excellent method of making alkenes from aldehydes and ketones.

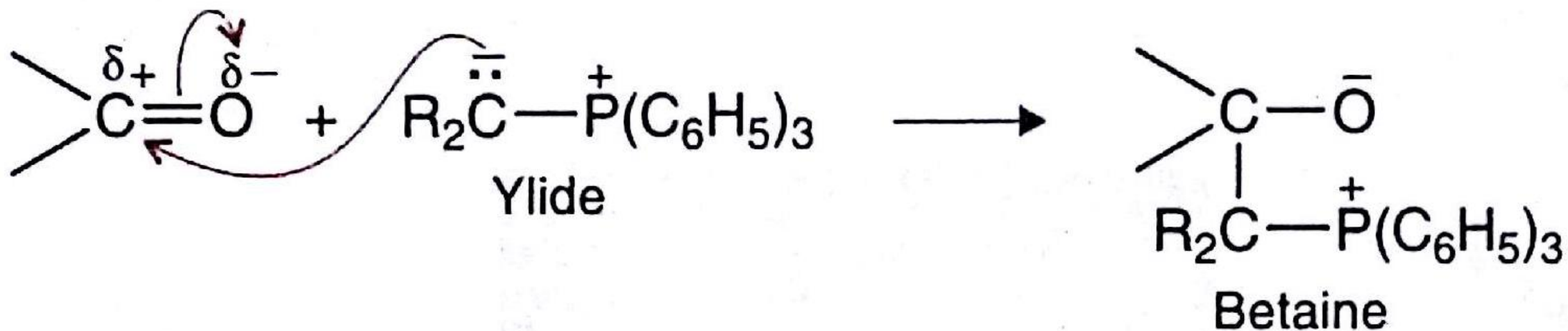


Ylide is a molecule with adjacent opposite charges. Phosphorus ylides are prepared from alkyl halides and triphenylphosphine.

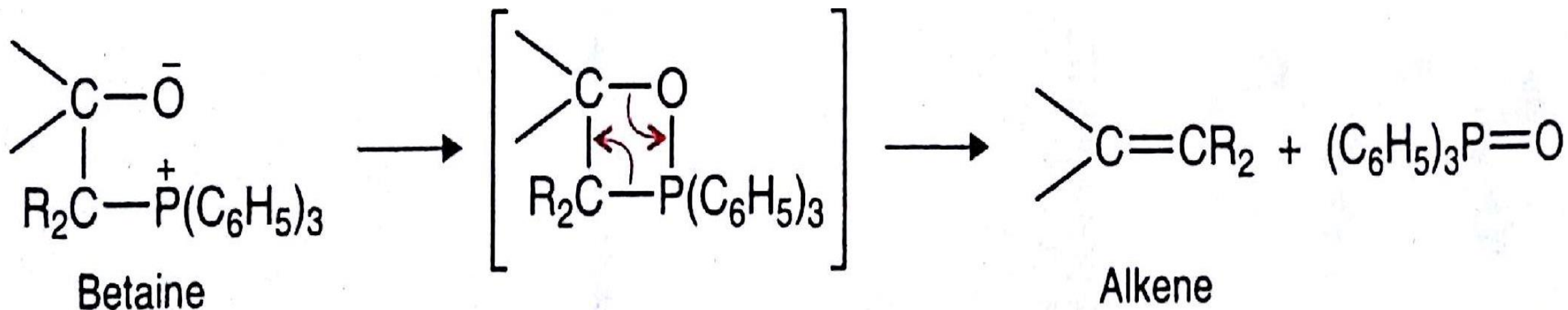


Mechanism

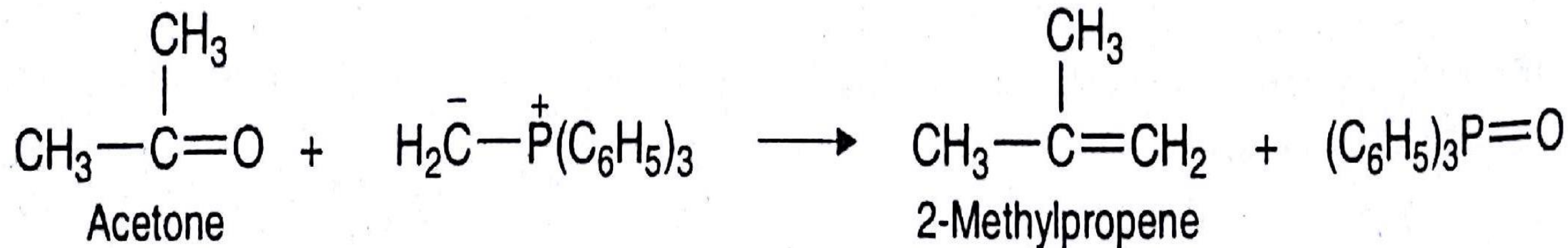
Step-1: The negative carbon of the ylide attacks the carbonyl carbon to form a betaine. A **betaine** is a molecule having non-adjacent opposite charges.



Step-2: The betaine undergoes elimination of triphenylphosphine oxide to give the alkene.



Write its mechanism???

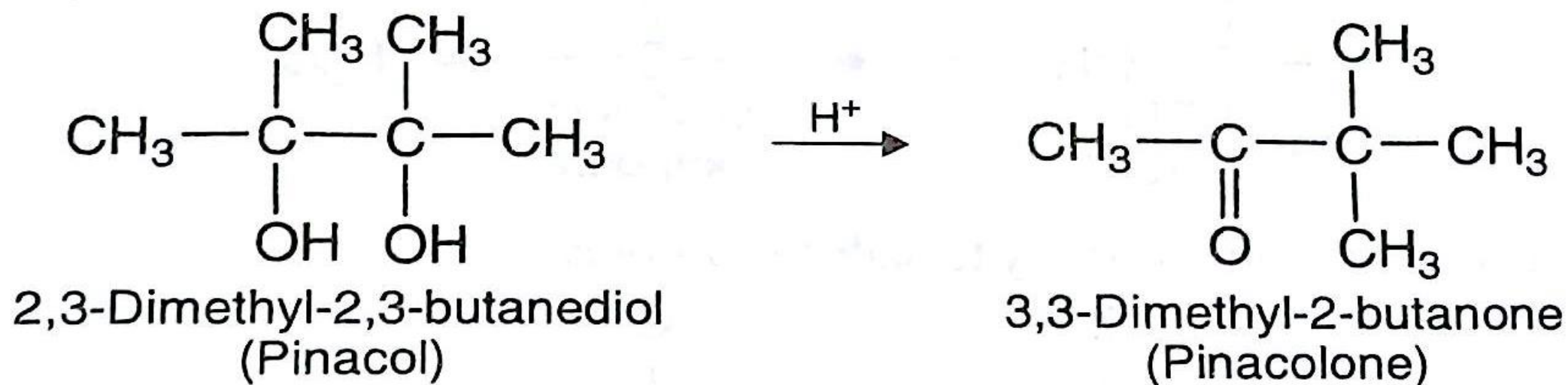


Pinacol-Pinacolone Rearrangement

Pinacol-Pinacolone Rearrangement

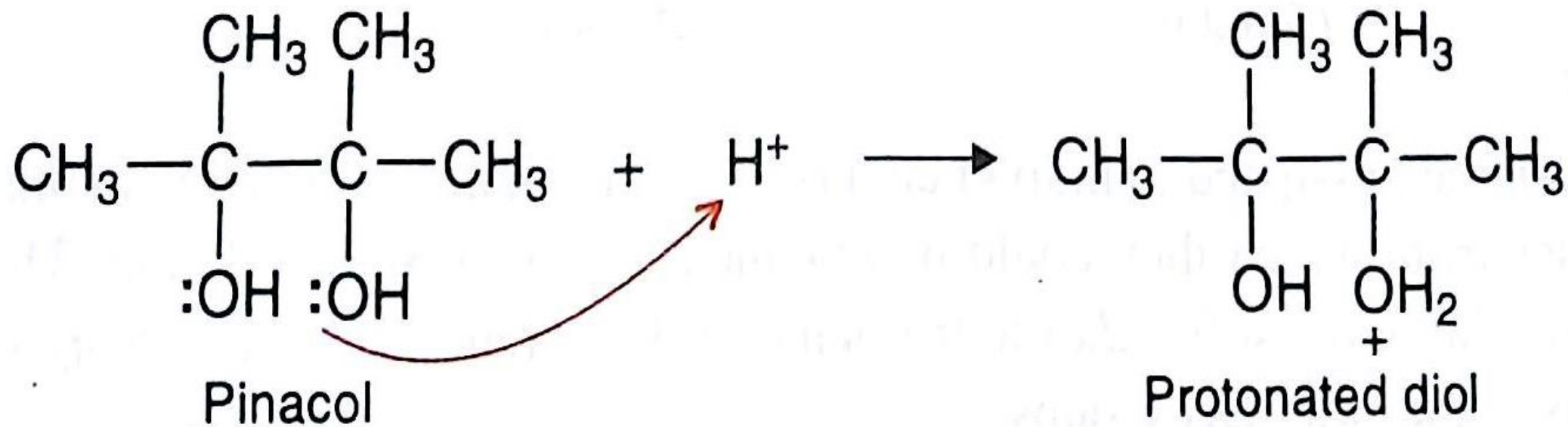
Completely substituted 1,2-diols such as 2,3-dimethyl-2,3-butanediol, are known as pinacols. In the presence of an acid, pinacol undergoes skeletal rearrangement to form highly branched ketones called **pinacolones**. This type of rearrangement is known as *Pinacol-pinacolone rearrangement*.

Chemical Reaction



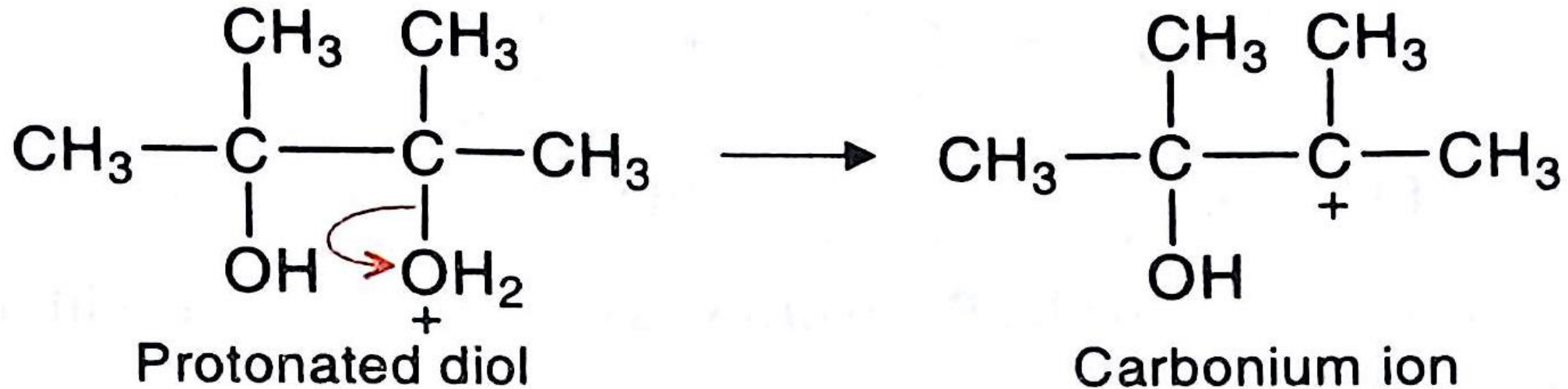
Mechanism: Four steps are involved

Step-1: Protonation of 1,2-diol



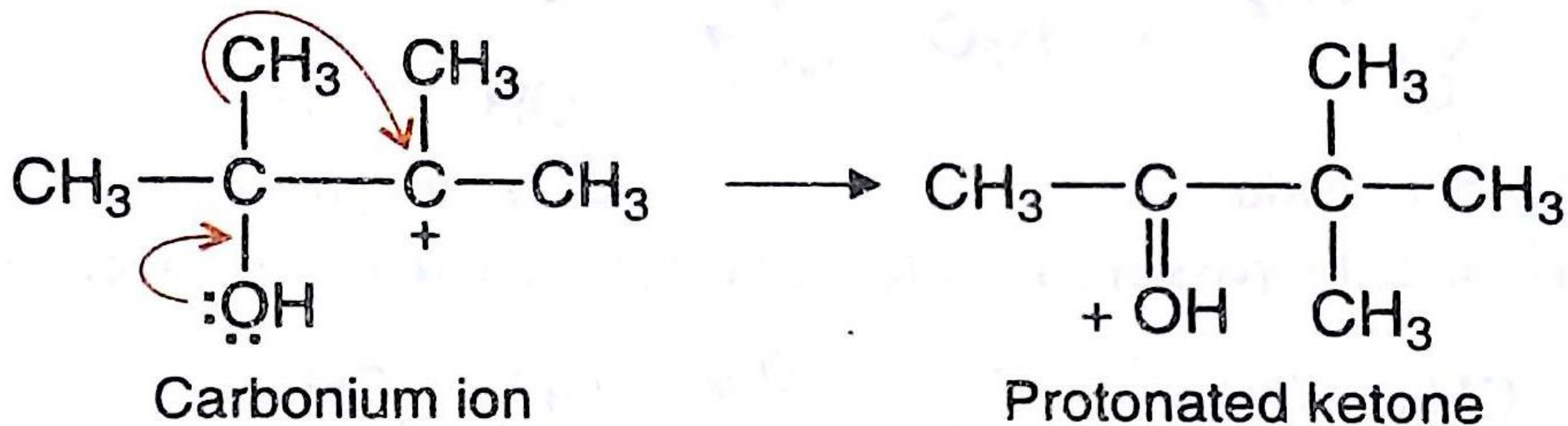
Mechanism:

Step-2: Formation of carbonium ion by loss of water from protonated diol



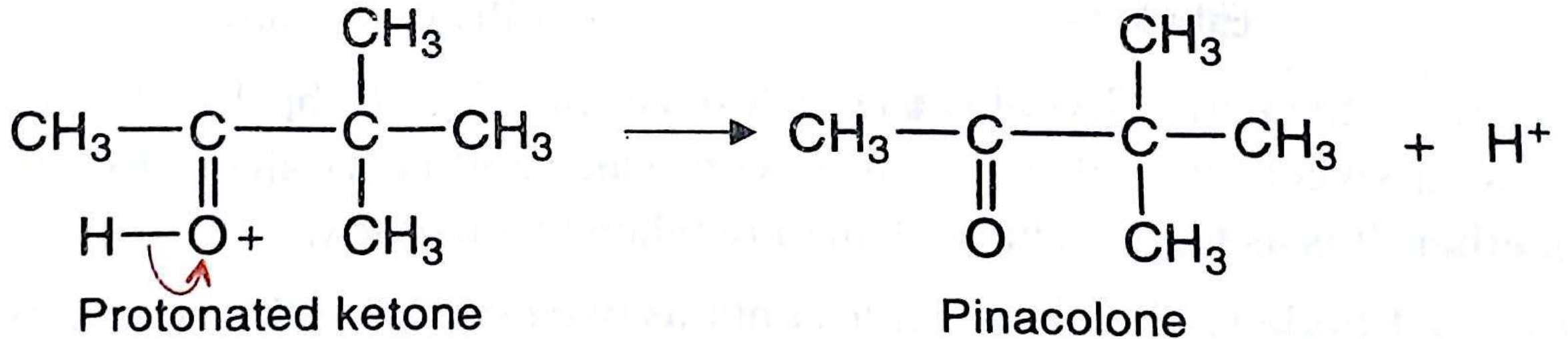
Mechanism:

Step-3: Rearrangement of carbonium ion by 1,2-shift to give protonated ketone



Mechanism:

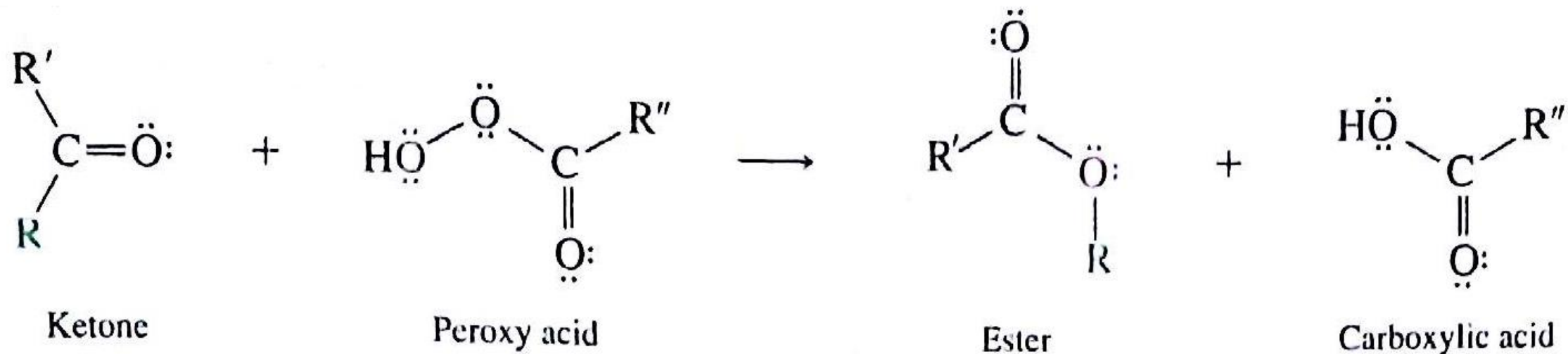
Step-4: Formation of ketone by loss of proton from the protonated ketone



Baeyer-Villiger Oxidation

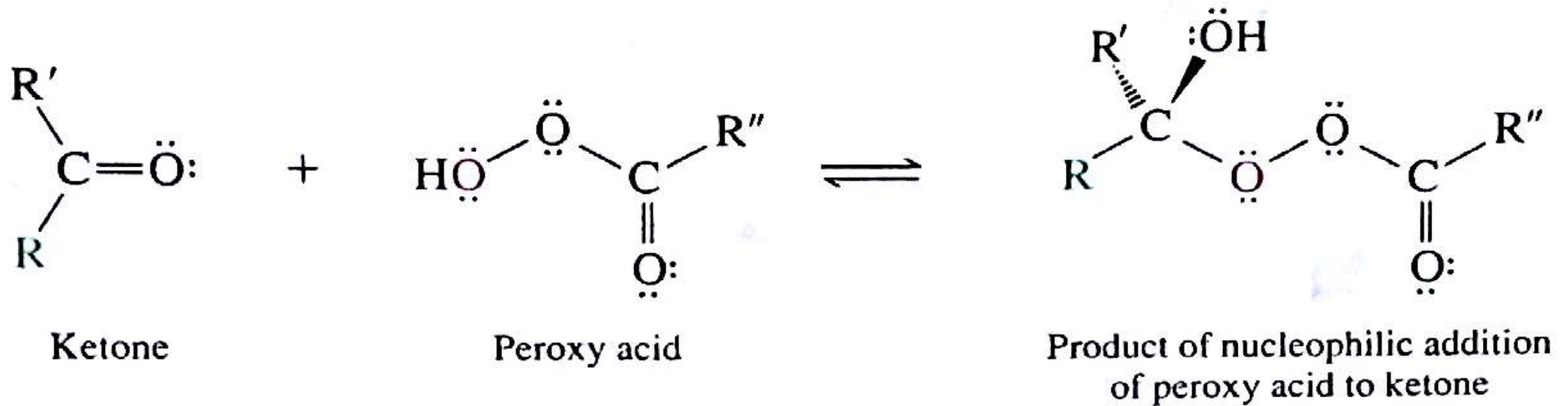
Baeyer-Villiger Oxidation

In this reaction ketones are transformed into esters and aldehydes can be transformed into carboxylic acids by using peracids (peroxyacids). This reaction is first described by **Adolf von Baeyer and Victor Villiger in 1899**.

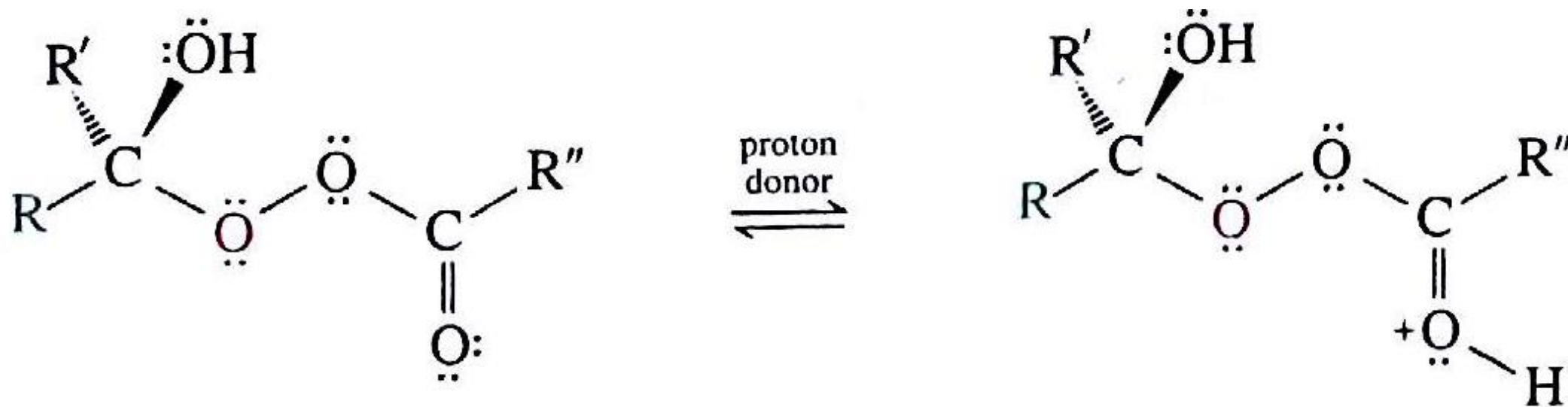


Mechanism

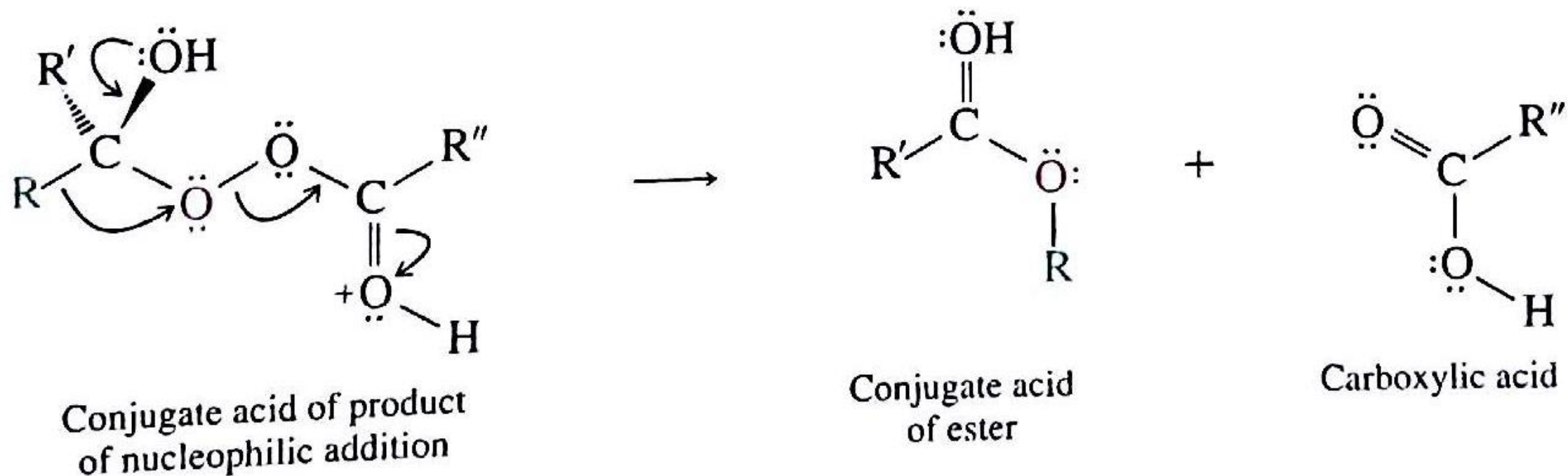
Step-1: Addition of peroxy acid to the carbonyl group of ketone. This step is nucleophilic addition.



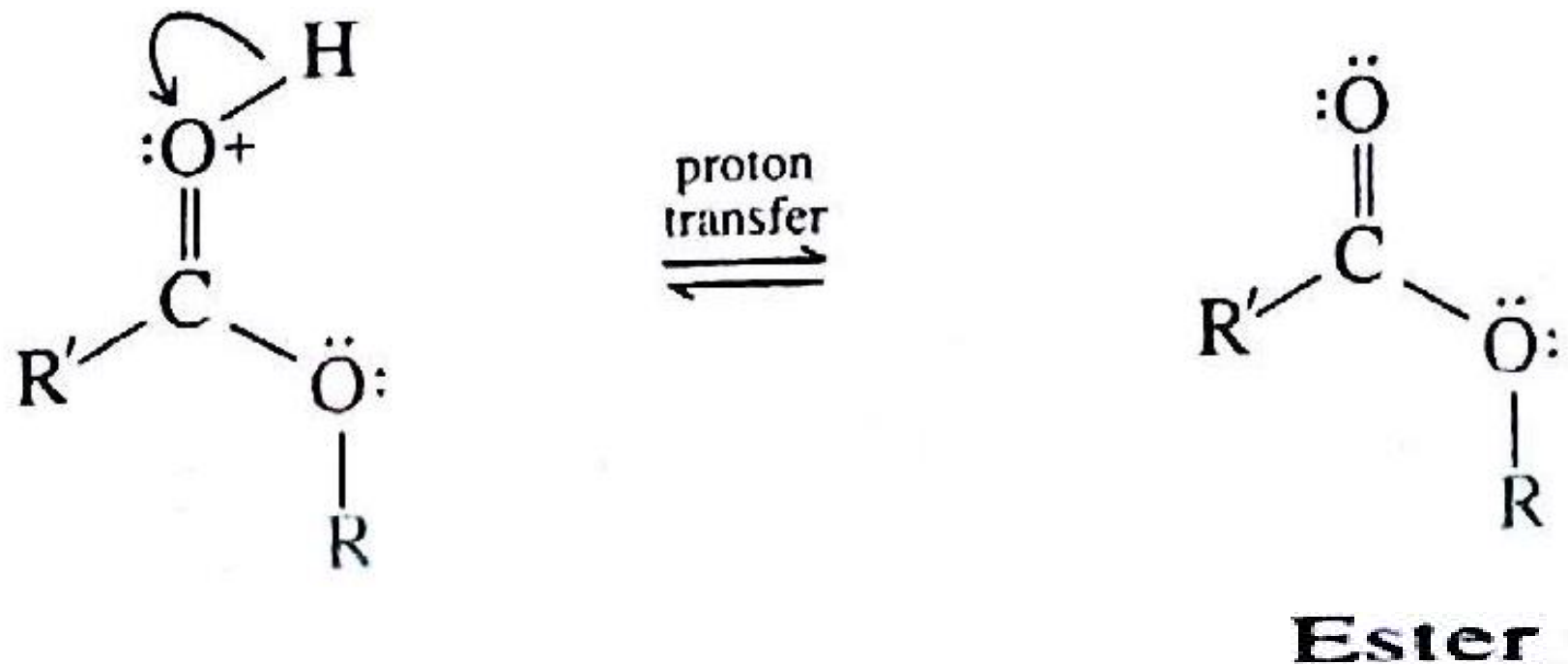
Step-2: The solution in which Baeyer-Villiger reaction occur are acidic owing to the presence of peroxy acid reactant and the carboxylic acid product. Therefore, **the product of step-1 is in equilibrium with its conjugate acid.**



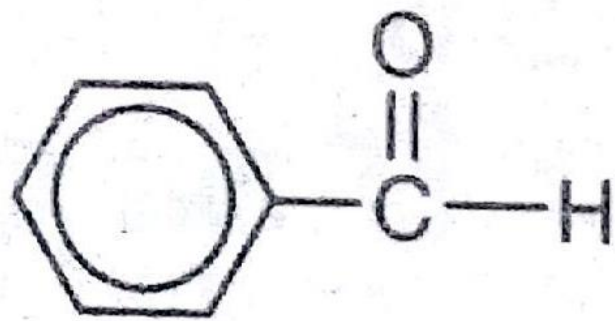
Step-3: In this step cleavage of the weak **O–O** bond takes place, followed by migration of one of the alkyl groups from carbon to oxygen. The group R migrates with its pair of electrons in much the same way as alkyl groups migrate in carbocation rearrangements.



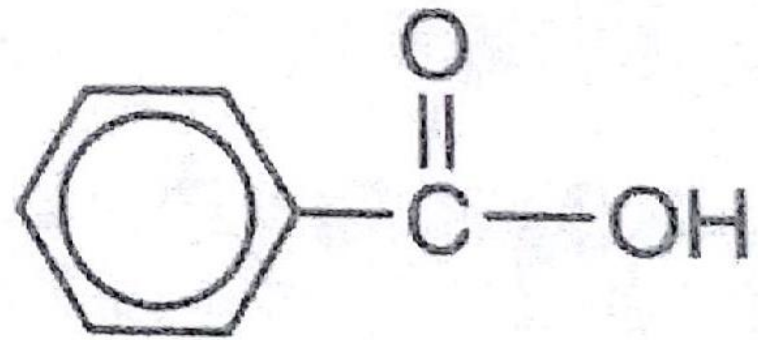
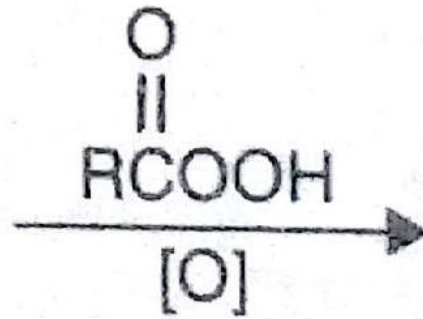
Step-4: Transfer of proton



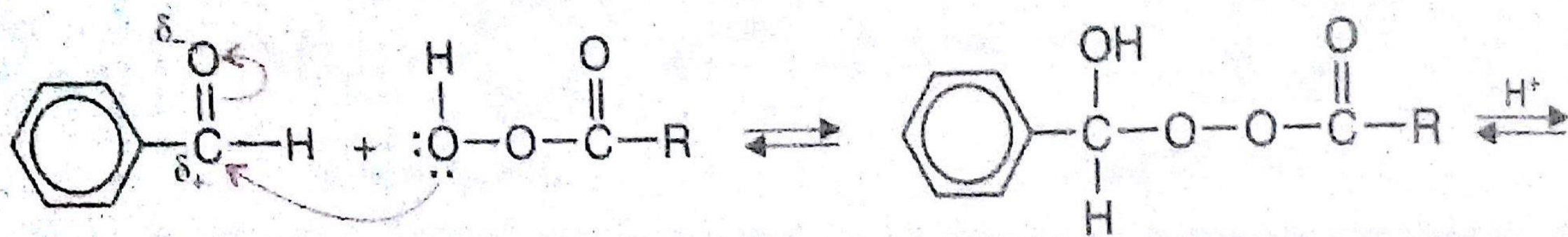
Write its mechanism???



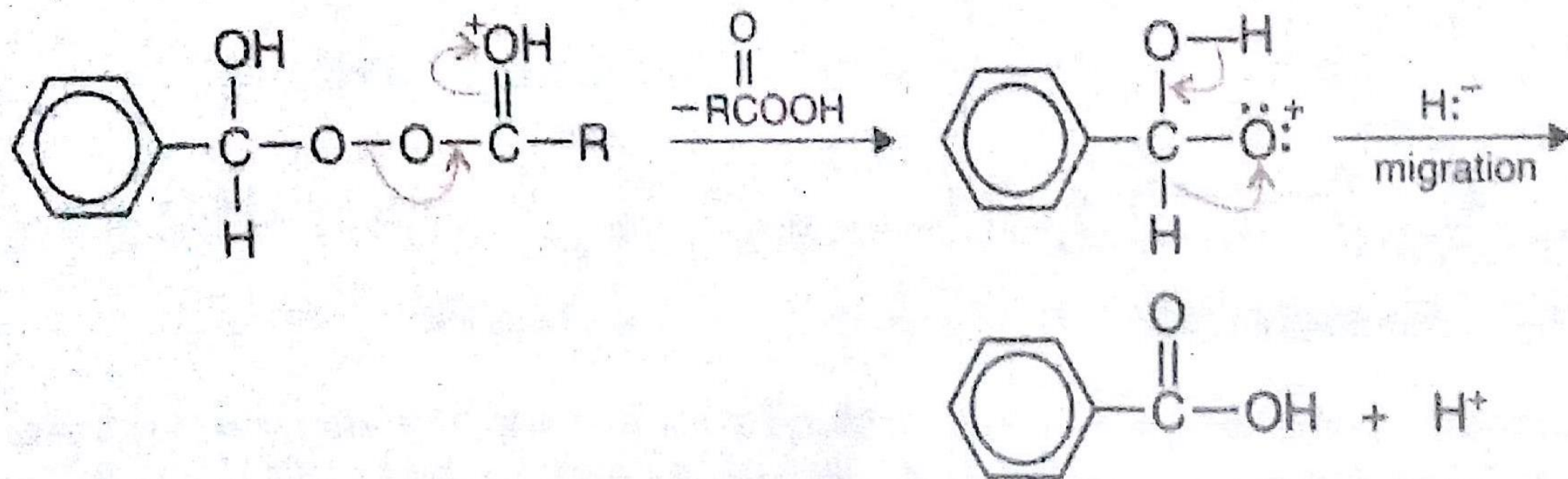
Benzaldehyde



Benzoic acid



Benzaldehyde

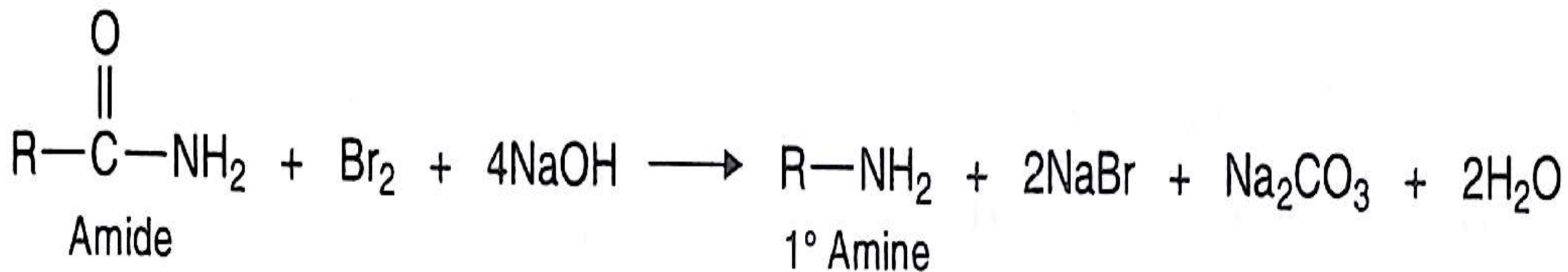


Benzoic acid

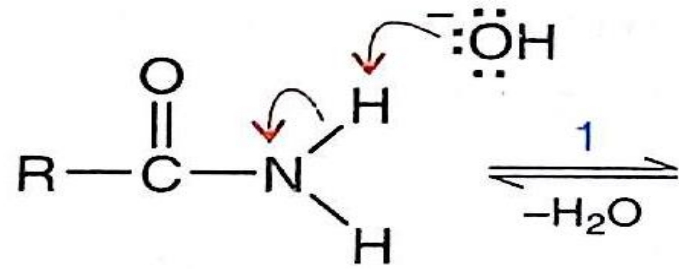
Hoffmann Rearrangement

Hoffman Rearrangement

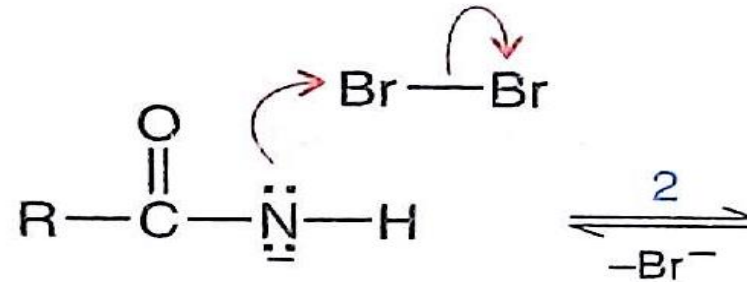
The Hofmann rearrangement is an organic reaction used to convert a primary amide to a primary amine using a halogen, base, water, and heat. In this reaction there is an overall removal of carbonyl group from amide. This reaction is also called Hoffmann Degradation because the product contain one carbon less than the reactant.



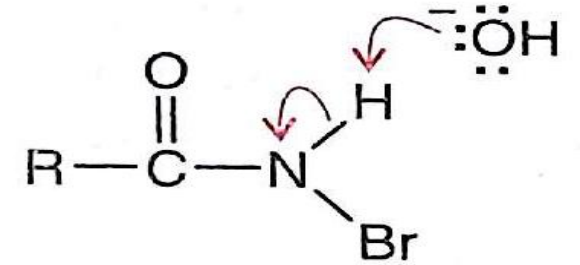
Mechanism



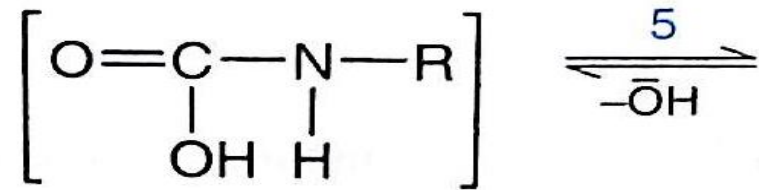
1° Amide



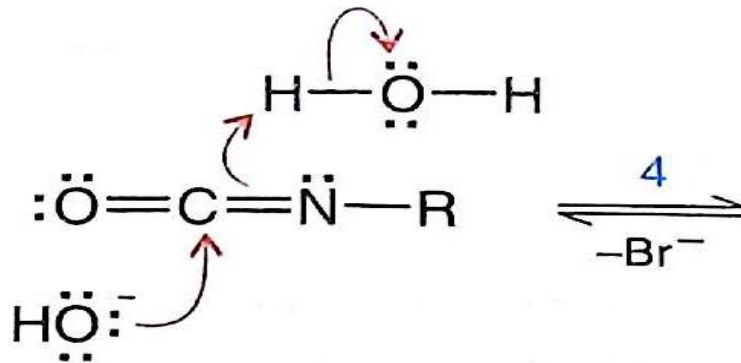
Amide anion



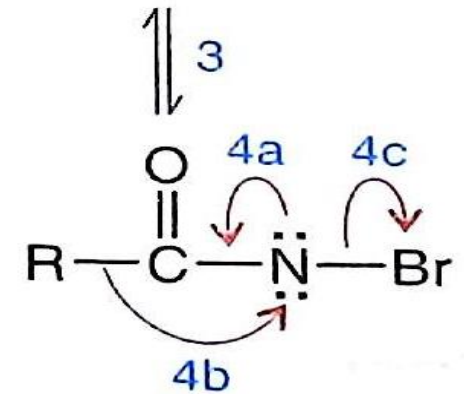
N-Bromoamide



N-Alkyl carbamic acid



Alkyl isocyanate



N-Bromoamide anion



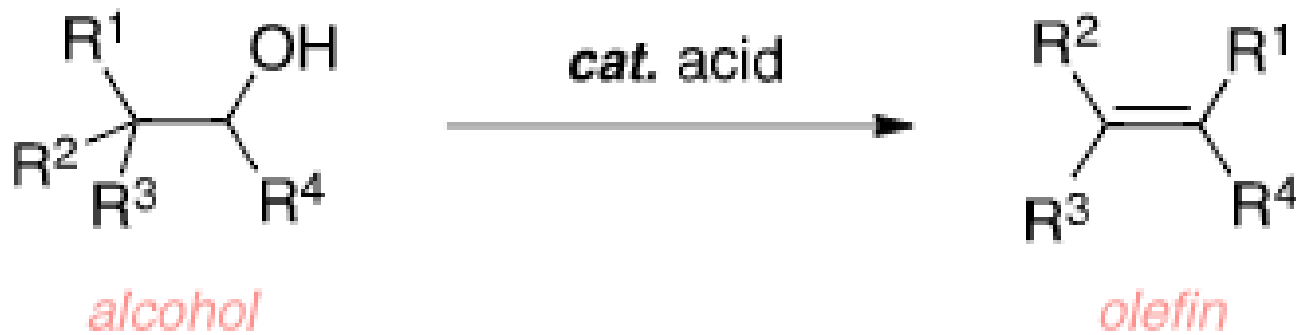
1° Amine

Wagner-Meerwein Rearrangement

Wagner-Meerwein Rearrangement

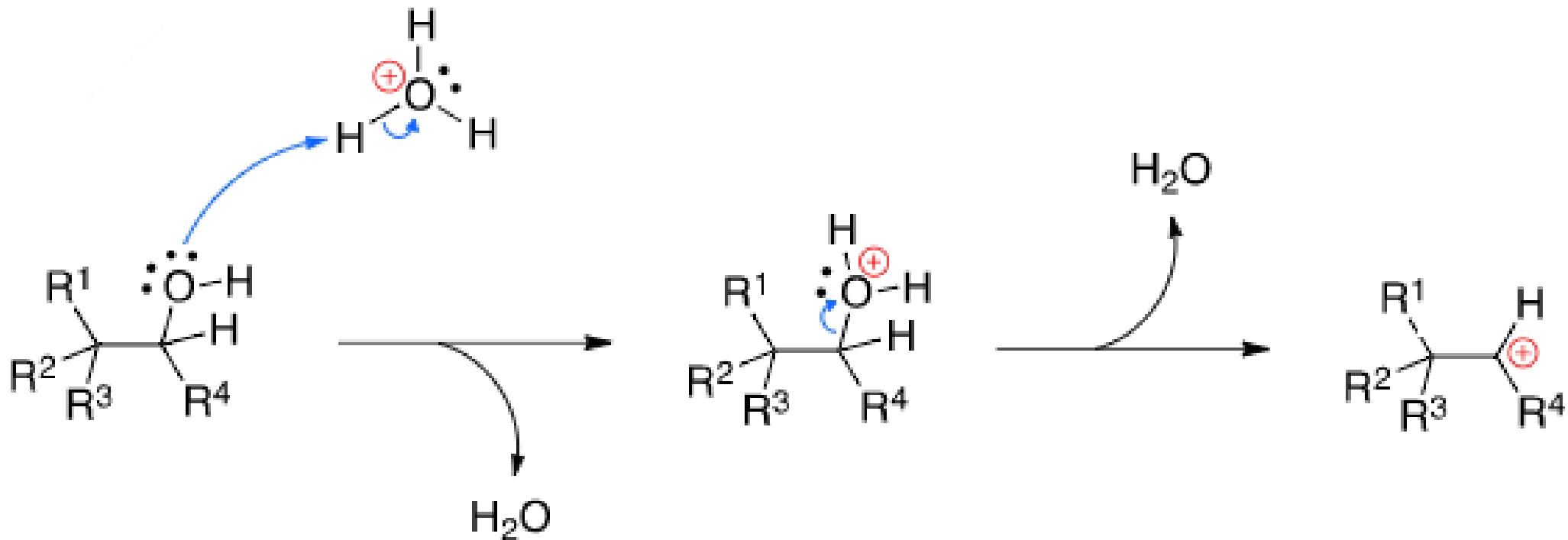
The Wagner-Meerwein rearrangement is an organic reaction used to convert an alcohol to an olefin using an acid catalyst.

Olefin, also called alkene, compound made up of hydrogen and carbon that contains one or more pairs of carbon atoms linked by a double bond. **The words alkene and olefin are often used interchangeably.**

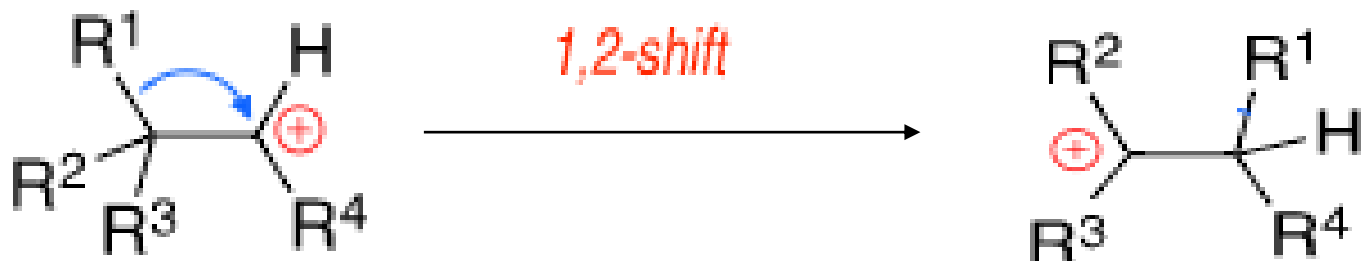


Mechanism

Step-1: The mechanism begins with protonation of the alcohol by the acid which is then released as water to form a carbocation.



Step-2: A 1,2-shift then occurs to form a more substituted and stabilized carbo-cation.



Step-3: A final deprotonation with water produces the final olefin (Alkene) product and regenerates the acid catalyst.

