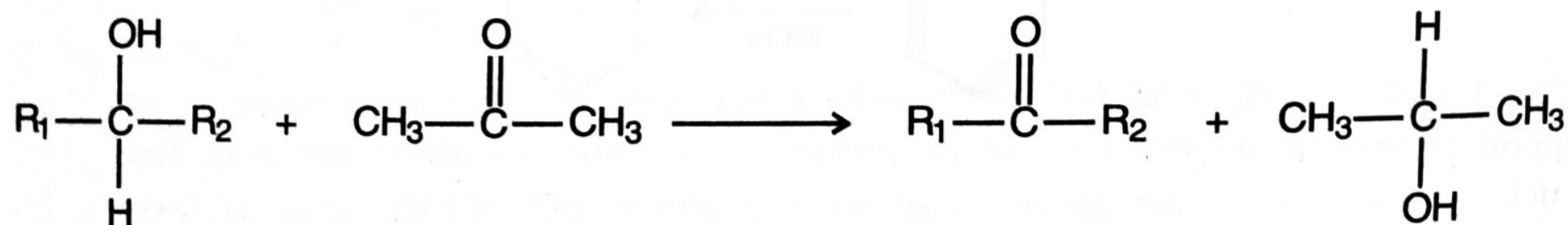


OPPENAUER OXIDATION

It is a useful method for oxidising secondary alcohols into ketones. This reaction is opposite to that of Meerwein-Ponndorf-Verly reduction.



Alcohol gets oxidised by using aluminium isopropoxide in presence of excess acetone. This oxidation is highly selective and does not occur in case of amines & sulphides. Primary alcohols do not undergo oppenauer oxidation as they show competition with aldol condensation of aldehyde products.

Mechanism

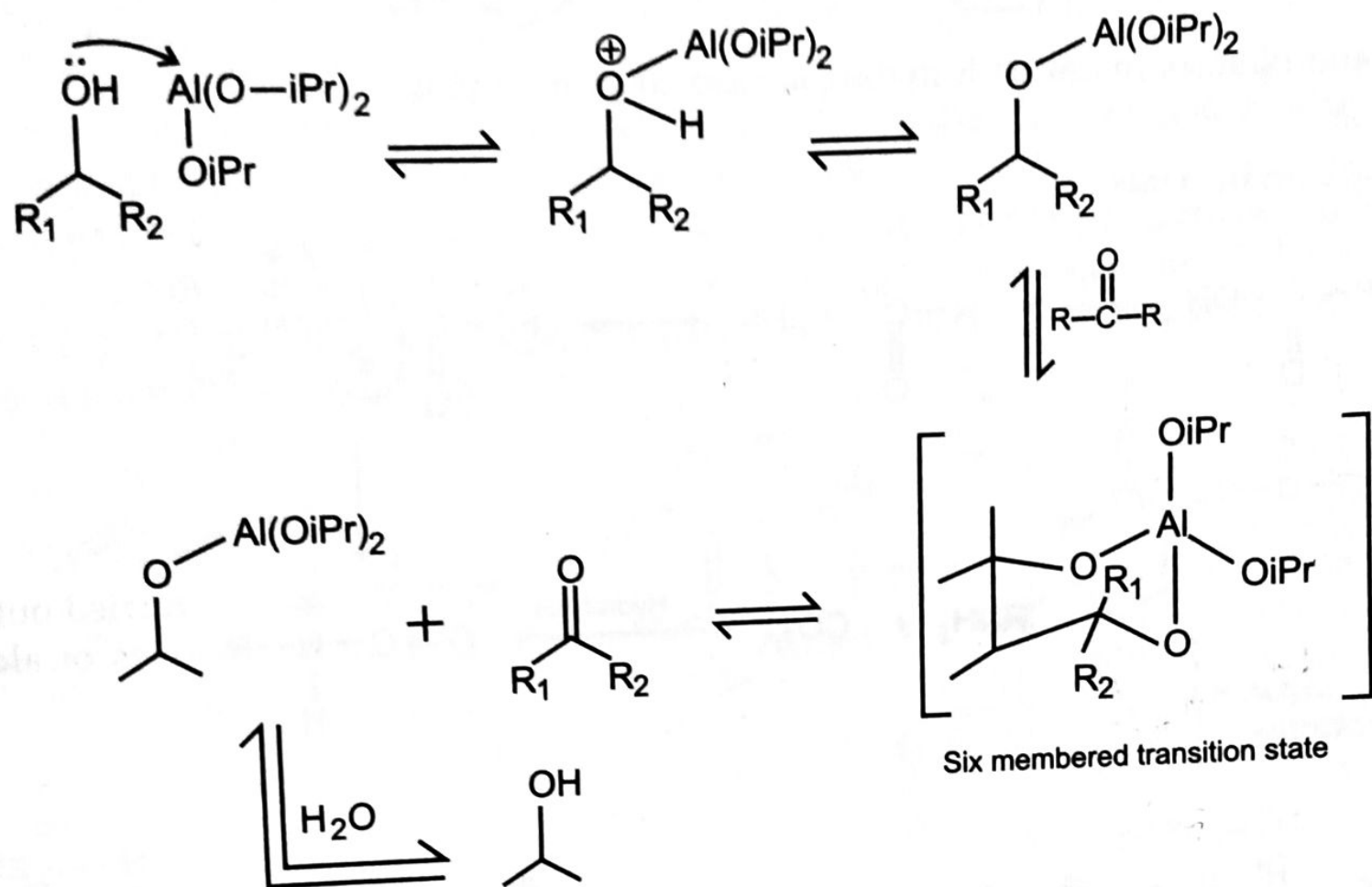
Step 1 : Alcohol forms co-ordination complex with Aluminium.

Step 2 : Complex gets deprotonated by an alkoxide ion to produce an intermediate.

Step 3 : Both the acetone and the alcohol gets bound to the aluminium.

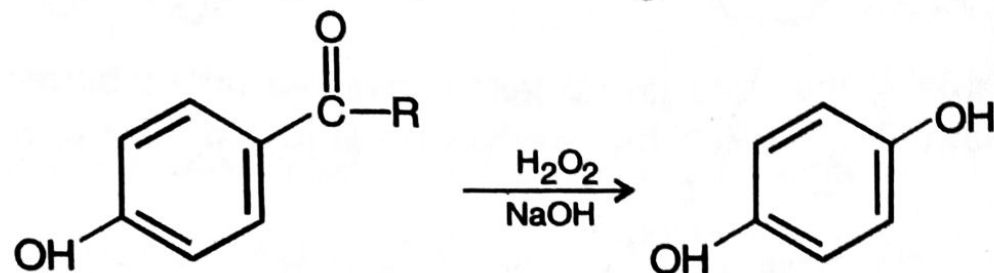
Step 4 : Aluminium catalyses hydride shift from α -carbon of alcohol to the carbonyl carbon of acetone. There occurs a formation of six-membered transition state.

Step 5 : Finally, ketone is formed after hydride transfer.



DAKIN REACTION

In Dakin reaction, phenols can be prepared from aryl aldehydes or arylketones by oxidation with hydrogen peroxide in the presence of a base. Basic requirement is that an $-OH$ or $-NH_2$ group must be present at ortho or para position. Aryl formate or alkanoate are formed as an intermediate which gets saponified to give substituted phenol product.



Overall, the carbonyl group is oxidised and the hydrogen peroxide is reduced. This reaction is closely related to Baeyer-Villiger oxidation.

Mechanism : Reaction starts with nucleophilic addition of hydroperoxide anion to the carbonyl carbon & forms a tetrahedral intermediate. Intermediate then breaks down to cause 1,2 aryl migration, hydroxide elimination & formation of phenyl ester which is then hydrolysed to form the product.

