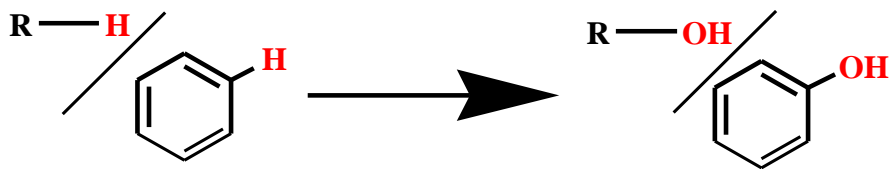


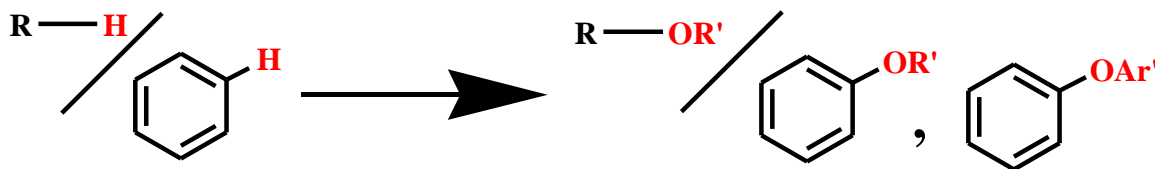
Alcohols, Phenols

Department of Chemistry
& Ethers
SNGGDCG

- **Alcohols** and **Phenols** are formed when *hydrogen atom* in aliphatic or aromatic hydrocarbon is replaced by hydroxyl group (-OH).



- An alcohol contains one or more hydroxyl group (s) (-OH) directly attached to carbon atom (s) of an aliphatic system (*e.g.* CH₃OH).
- Phenol contains hydroxyl group (s) (-OH) directly attached to carbon atom (s) of an aromatic system (*e.g.* C₆H₅OH).
- The substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group (R-O/Ar-O) yields another class of compounds known as '**Ethers**' (*e.g.* CH₃OCH₃).



- Alcohols may be classified as mono-, di-, tri-, or polyhydric compounds depending on whether they contain one or two or three or many hydroxyl group respectively
- The monohydric alcohols form a **homologous series** with the general formula $C_nH_{2n+2}O$, but their functional group is the hydroxy group, their general formula is more aptly written as $C_nH_{2n+1}OH$ or **ROH**.

e.g. when $n=1$, CH_3OH ; $n=2$, CH_3CH_2OH ,
 $n=3$, $CH_3CH_2CH_2OH$, $n=4$, $CH_3CH_2CH_2CH_2OH$.

- Monohydric alcohols are subdivided into primary, secondary and tertiary alcohols according as *the alkyl group attached to the hydroxyl group* is a primary (1°), secondary (2°) or tertiary (3°) group respectively.

Primary alcohol (1°): Ethanol (CH_3CH_2OH)

Secondary alcohol (2°): Isopropanol ($(CH_3)_2CHOH$)

Tertiary alcohol (3°): t-butanol ($(CH_3)_3COH$)

Preparation of alcohols using Grignard Reagent

What is Grignard Reagent: The alkyl magnesium halides, R-Mg-X, or Grignard reagents are extremely valuable in organic synthesis. (X= halides)

Preparation of Grignard Reagent: A Grignard reagent is generally prepared by reaction between magnesium (1 atom) and alkyl halide (1 molecule) in dry, alcohol-free ether.

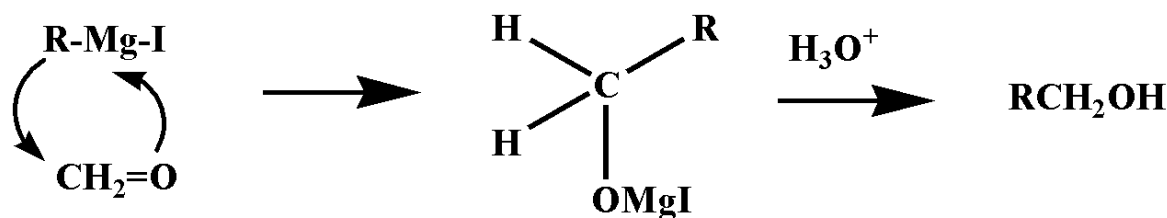
Example: CH_3MgBr , $\text{C}_2\text{H}_5\text{MgCl}$ etc

- For the given same alkyl group the ease of formation of Grignard reagent is alkyl iodide > alkyl bromide > alkyl chloride.
- Addition of the **R** group of **RMgX** takes place to a compound containing multiple bond group like **carbonyl (C=O)** or **nitrile (C≡N)** at the less electronegative (i.e. **C** centre) and that of the **MgX** Group at the more electronegative atom (i.e. **O** or **N** centre). This is evident on the basis that **R** and **MgX** are respectively the **negative** and **positive** ends of the dipole in **RMgX**

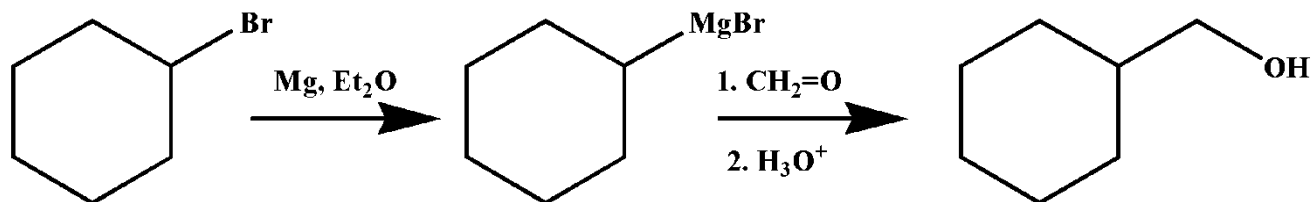
Synthesis of Primary alcohol (1°) by Grignard reagent

• Etheral solution of Grignard reagent is treated with formaldehyde (obtained by heating the polymer Formalin), followed by decomposing the magnesium complex with dilute acid to get primary alcohol containing one carbon atom more than the Grignard alkyl group.

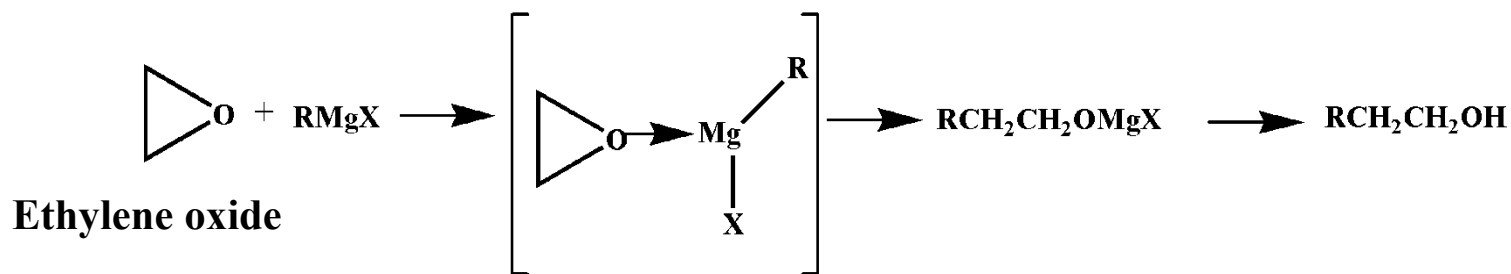
• Magnesium can coordinate to the carbonyl's oxygen atom giving the carbonyl group positive charge and therefore making it more electrophilic. The negative dipolar end i.e. alkyl (R) group of Grignard reagent eventually attached to the carbonyl carbon resulting in the -O-Mg complex.



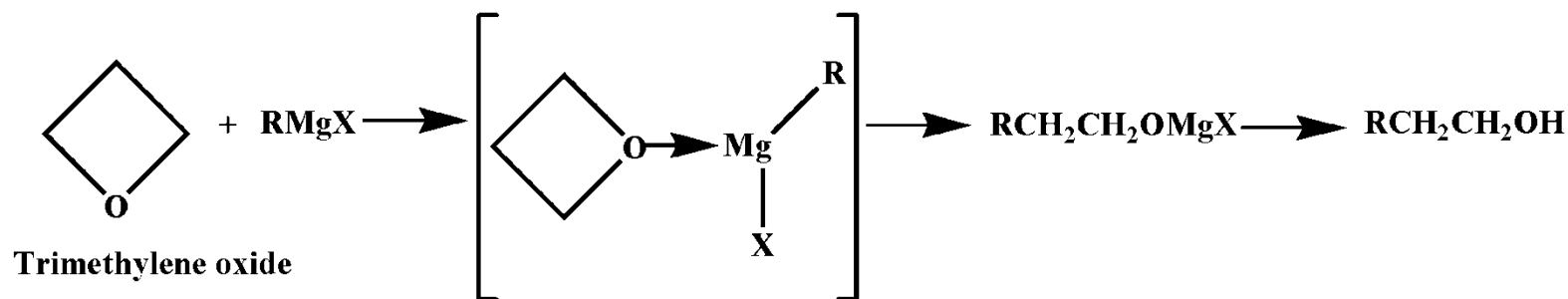
A primary alcohol from formaldehyde:



- A primary alcohol containing two carbon atom more than the Grignard alkyl group can be prepared by reacting ethylene oxide with Grignard reagent

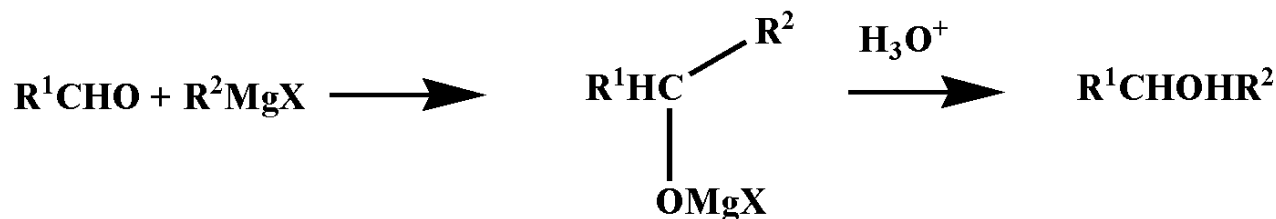


- Similarly primary alcohol containing three carbon atom more than the Grignard alkyl group can be prepared from the Grignard reagent by using trimethylene oxide.



Synthesis of Secondary alcohol (2°) by Grignard reagent

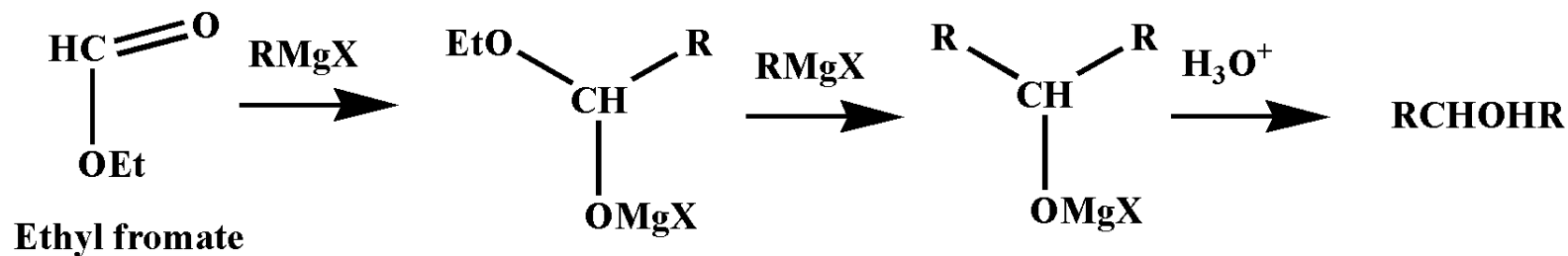
- When a Grignard reagent is treated with any aldehyde other than formaldehyde, a secondary alcohol is formed



Example:

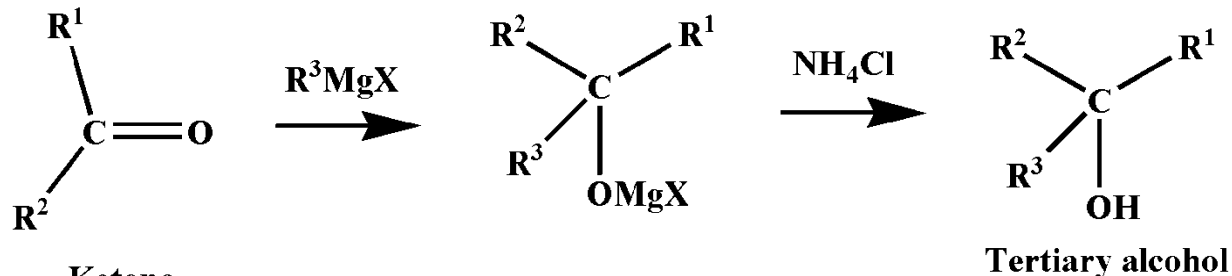


- Secondary alcohols may also be prepared by interaction of 2 molecules of Grignard reagents with 1 molecule of ethyl formate.

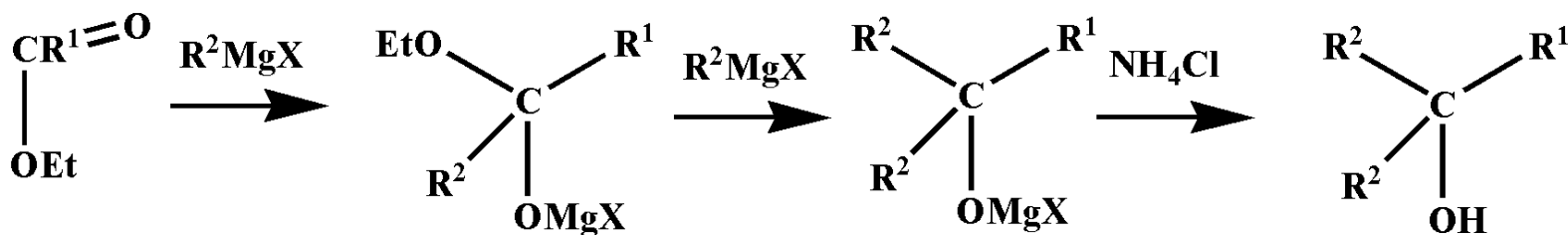


Synthesis of Tertiary alcohol (3°) by Grignard reagent

A tertiary alcohol may be prepared by the action of Grignard reagent on a ketone



- As t-alcohols are readily dehydrated to alkenes by acids, the complex is often broken up with aqueous ammonium chloride or buffered acid solution.
- Tertiary alcohols containing at least two identical alkyl groups may be prepared by the reaction between a Grignard reagent (2 molecules) and any ester other than formic ester.



- Tertiary alcohols containing three identical alkyl groups may be prepared by the reaction between 3 molecules of Grignard reagent and 1 molecule of ethyl carbonate.



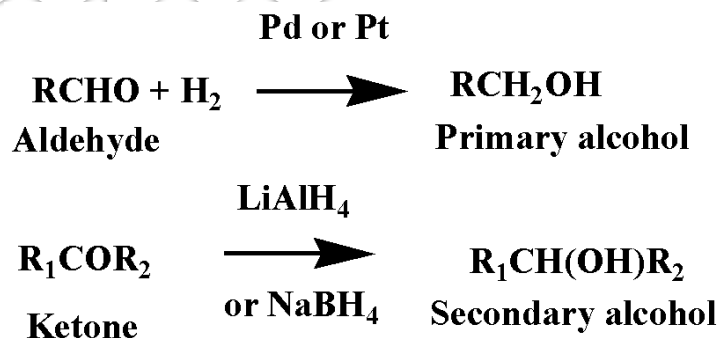
Preparation of alcohols by reduction of carbonyl compounds

(i) By reduction of aldehyde and ketone:

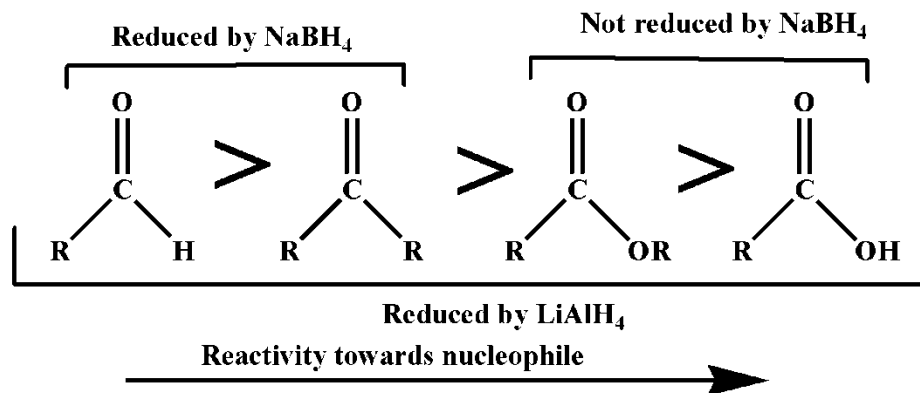
• Aldehydes and ketones are reduced to corresponding alcohol by addition of hydrogen in presence of catalyst (catalytic hydrogenation). The usual catalysts are Platinum, Palladium or Nickel.

• Lithium aluminium hydride (LiAlH_4) and Sodium borohydride (NaBH_4) are also used to reduce aldehydes and ketones .

- Aldehydes give primary alcohols
- Ketones give secondary alcohols

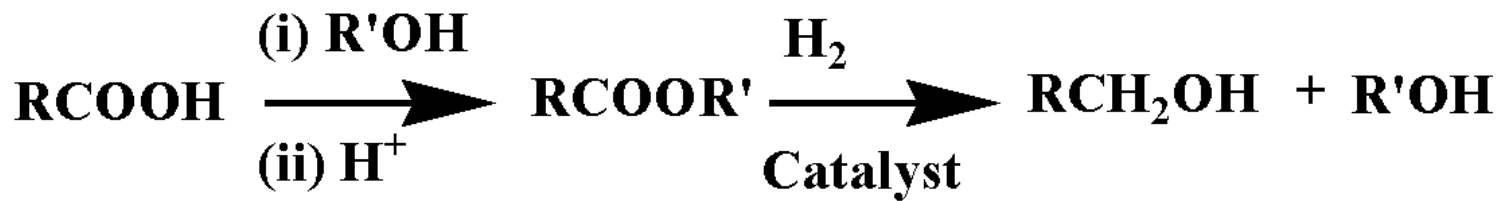
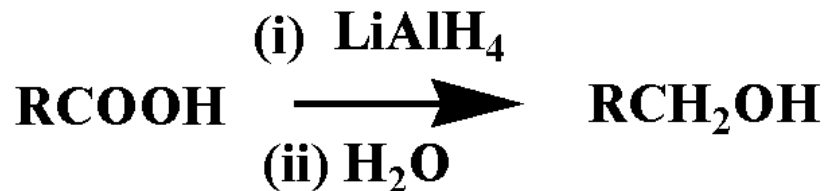


• LiAlH_4 is most versatile reducing agent which reduces most functional groups but does not normally reduce the olefinic bond. However NaBH_4 is comparatively selective and easy to handle



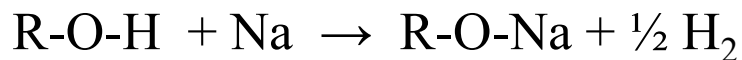
(ii) By reduction of carboxylic acid and ester:

- Carboxylic acids are reduced to primary alcohols in excellent yield by LiAlH_4
- However LiAlH_4 is expensive not difficult to handle
- Commercially carboxylic acids are reduced to alcohols by converting acids to corresponding esters followed by reduction using hydrogen in presence of metal catalyst

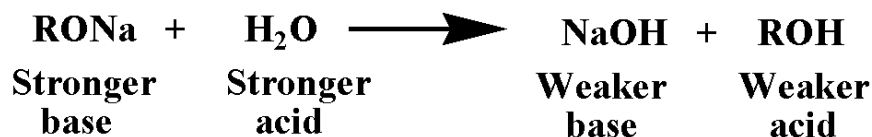


Reaction of alcohols with sodium metal:

The acidity of alcohols is shown by their reaction with sodium in which sodium alkoxide is formed and hydrogen gas liberates



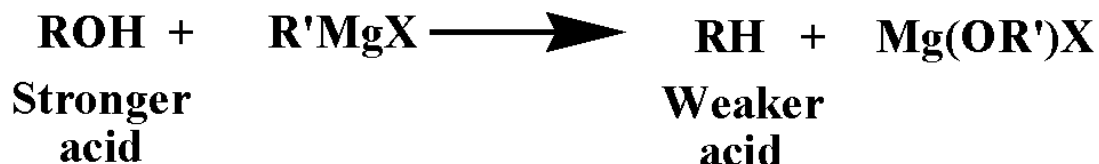
When water is added to an alkoxide, sodium hydroxide forms with the parent alcohol. The weaker acid R-OH, is displaced from its salt by the stronger acid, H-O-H.



Example:



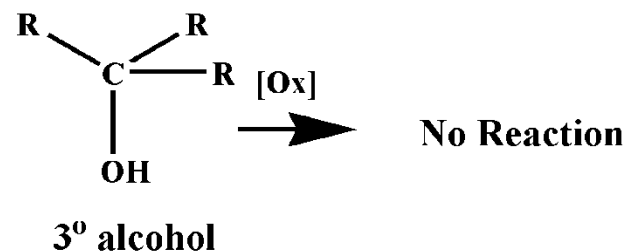
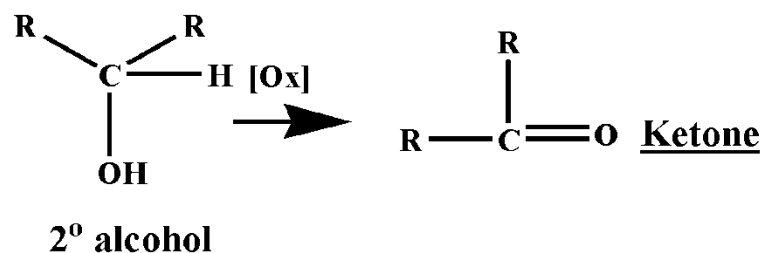
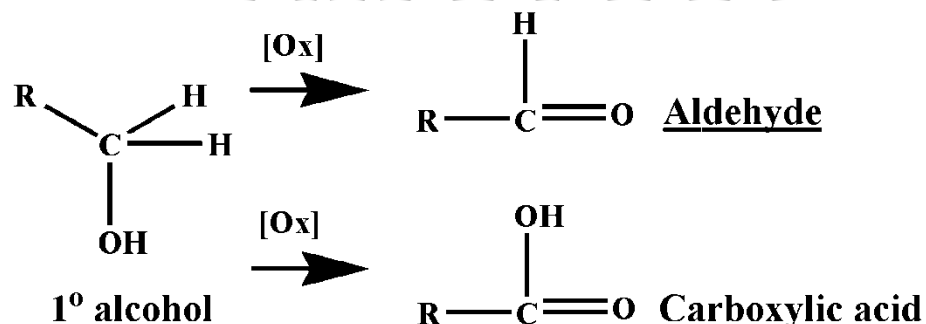
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- **Relative acidities:** $\text{H}_2\text{O} > \text{ROH} > \text{NH}_3 > \text{RH}$
 - **Relative basicities:** $\text{R}^- > \text{NH}_2^- > \text{OR}^- > \text{OH}^-$
 - Grignard reagent quench hydrogen from alcohol to give alkane following the acidic property.



Oxidation of alcohols :

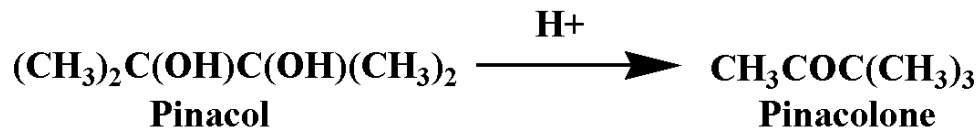
The oxidation of an alcohol involves the loss of one or more α -hydrogens from the carbon bearing $-\text{OH}$ group. The kind of product that is formed depends upon whether the alcohol is primary, secondary or tertiary.

- A **primary alcohol** contains two α - Hs and can either lose one of them to form an **aldehyde** or both of them to form a **carboxylic acid**.
- A **secondary alcohol** can lose its only α - Hs to form **ketone**
- A **tertiary alcohol** contains no α - Hs and is not oxidized



Diols: Pinacol-pinacolone rearrangement

- t-butyl methyl ketone i.e. **pinacolone** can be prepared by distilling **pinacol** with sulphuric acid



The conversion of pinacol into pinacolone is an example of the 1,2-shift and is known as pinacol-pinacolone rearrangement. Mechanistically, the first step is the addition of proton to one of the hydroxyl group of pinacol, followed by loss of water. The resulting carbocation follows 1,2 shift of methyl group which leads to the product pinacolone. The second reversible step is the rate determining one.

