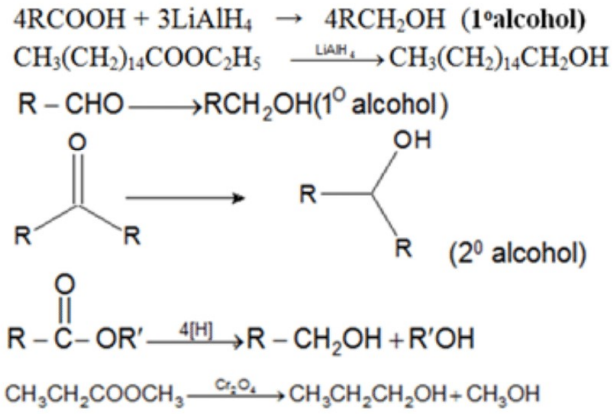
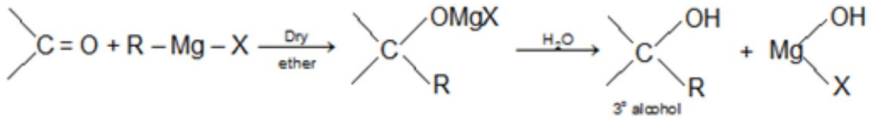
Alcohols

Preparation of Alcohols:

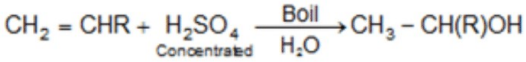
- **By hydrolysis of haloalkanes :** $R\text{-}X + aq.\ KOH \rightarrow ROH + KX$
- **By reduction of Carbonyl compounds**



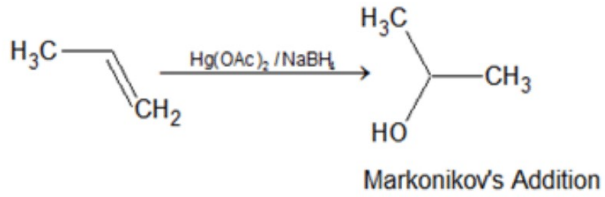
- **By the action of Grignard's Reagent on aldehydes, ketones and esters**



- **By Aliphatic Primary Amines: $RCH_2NH_2 + HNO_2 \rightarrow RCH_2OH + N_2 + H_2O$**
- **Hydration of alkenes:**

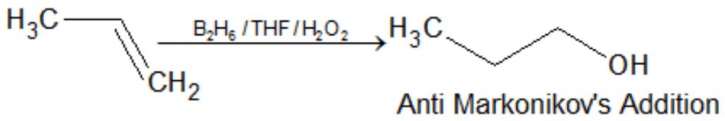


- **Oxymercuration-demercuration:**



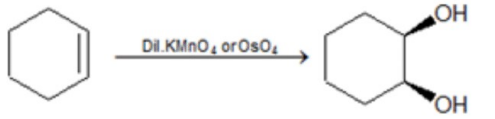
Markonikov's Addition

- **Hydroboration-oxidation:**

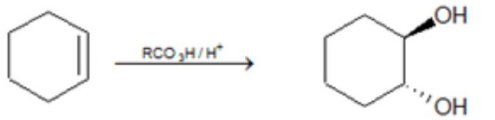


Anti Markonikov's Addition

- **Hydroxylation of alkenes:**



syn-Hydroxylation



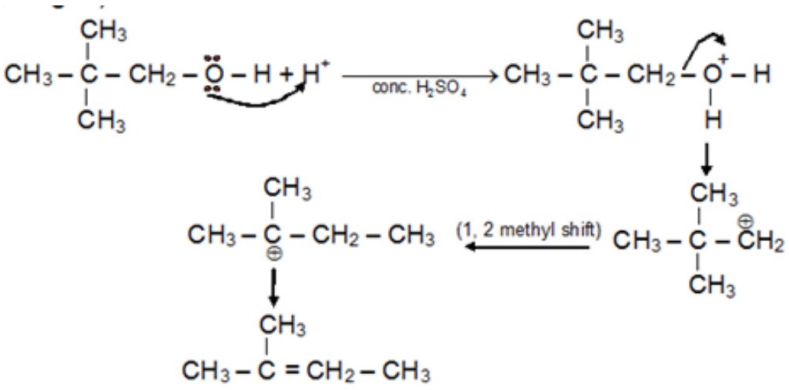
anti-Hydroxylation

Physical Properties of Alcohol:

- Lower alcohols are liquid at room temperature while higher ones are solid.
- High boiling point due to presence of intermolecular hydrogen bonding. Order of Boiling Point: primary > secondary > tertiary
- Solubility in water decreases with increase in molecular mass due to decrease in extent of intermolecular hydrogen bonding.

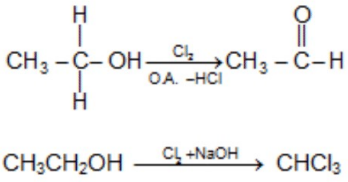
Chemical Properties of Alcohol:

- **Alcohol's reaction with metal:** $ROH + Na \rightarrow 2RO^{+}Na^{-} + H_2$
- **Formation of Halides:**
    - $3ROH + P+I2 \rightarrow 3RI + H_3PO_3$
    - $ROH + SOCl_2/PCl_3/PCl_5 \rightarrow RCl$
    - $ROH+HX \rightarrow RX$
    - $ROH+ NaBr,H_2SO_4 \rightarrow R\text{-}Br$
    - $ROH+ Zn+HCl \rightarrow R\text{-}Cl$
    - $R_2C\text{-}OH$ alcohol $+ HCl \rightarrow R_2CCl$
- **Reaction with HNO_3:** $R\text{-}OH + HO\text{-}NO_2 \rightarrow R\text{-}O\text{-}NO_2$
- **Reaction with carboxylic acid (Esterification) :** $R\text{-}OH + R'\text{-}COOH + H^{+} \leftrightarrow R'\text{-}COOR$
- **Reaction with Grignard reagent:** $R'OH + RMgX \rightarrow RH + R'OMgX$
- **Reduction of alcohol :** $ROH + 2HI + \text{Red P} \rightarrow RH + I_2 + H_2O$
- **Dehydration of Alcohol:** Dehydration of alcohols takes place in acidic medium. Intra-molecular dehydration leads to the formation of alkene while inter molecular dehydration which forms ether. Ease of dehydration: $3^{\circ} > 2^{\circ} > 1$
- **Satyzeff's Rule :** Elimination through b carbon containing minimum b hydrogen



- **Oxidation of Alcohol**:
  RCH_2-OH + [O] → RCHO → RCOOH
  RCH_2-OH + [O] +PCC → RCHO

- **Haloform Reaction:** Compound containing CH_3CO- group (or compound on oxidation gives CH_3CO – group) which is attached with a C or H, in presence of halogen and mild alkali gives haloform.CH_3-CH_2-$COCH_2$-CH_3, CH_3-CO-Cl, CH_3COOH will not respond to haloform reaction wile CH_3CH_2OH will respond to haloform Reaction.
  ?



Test for Alcohols:

1. Lucas Test:

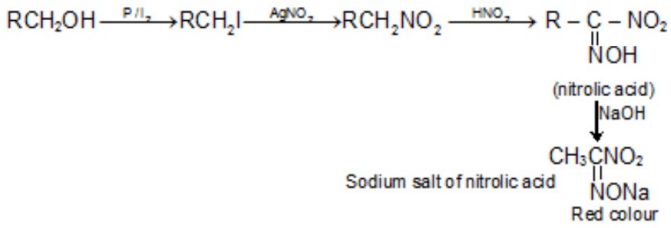
Alcohols + $ZnCl_2$ + HCl

- 1° Alcohol: RCH_2OH + $ZnCl_2$ +HCl → No reaction at room temperature

- 2^0 Alcohol: $R_2CHOH + ZnCl_2 + HCl \rightarrow R_2CHCl$ White turbidity after 5-10 min.
- 3^0 Alcohol: $R_3CHOH + ZnCl_2 + HCl \rightarrow R_3CHCl$ white turbidity instantaneously.

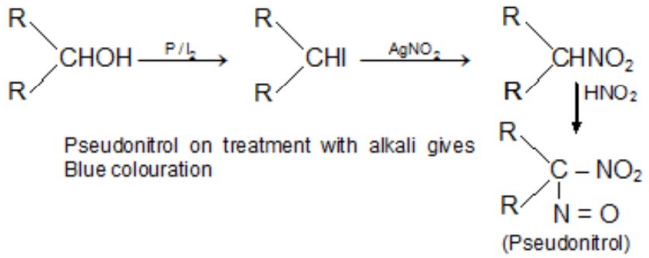
2. Victor Meyer Test

1° alcohol:



Nitrolic acid on treatment with alkali gives colouration

2° alcohol:



3° alcohol: