

Alcohols

- ✦ Nomenclature
- ✦ Properties
- ✦ Preparation
- ✦ Reactions
- ✦ Spectroscopy

Alcohol

Nomenclature

IUPAC

Common

Carbinol

PREPARATION REACTIONS

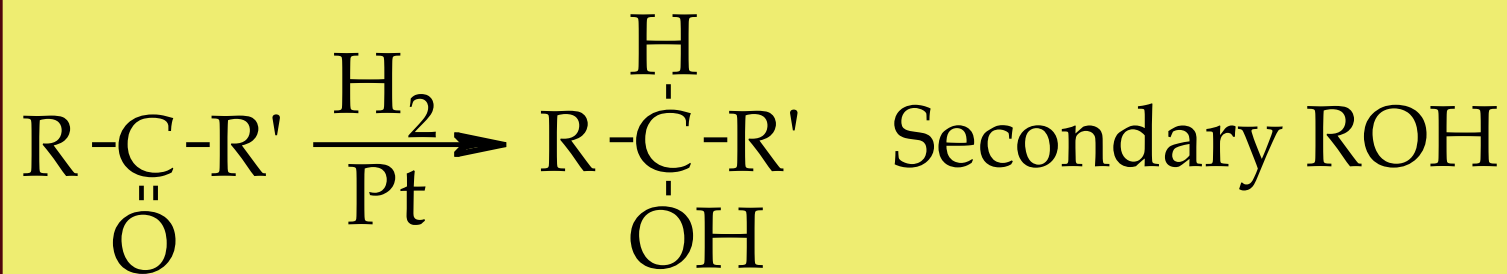
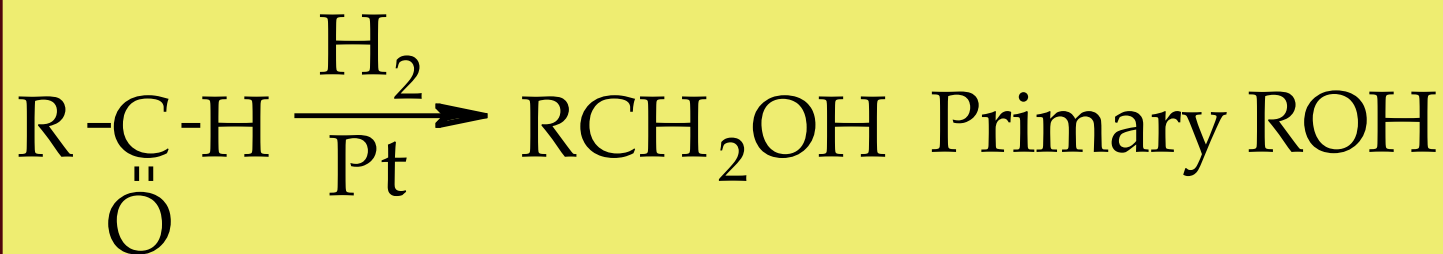
- ✧ Reduction of carbonyl compounds
- ✧ Hydration of Alkenes
- ✧ Grignard reactions

Reduction of Carbonyl Compounds

- Reduction of Aldehydes/ketones
- Reduction of Carboxylic acids/Esters

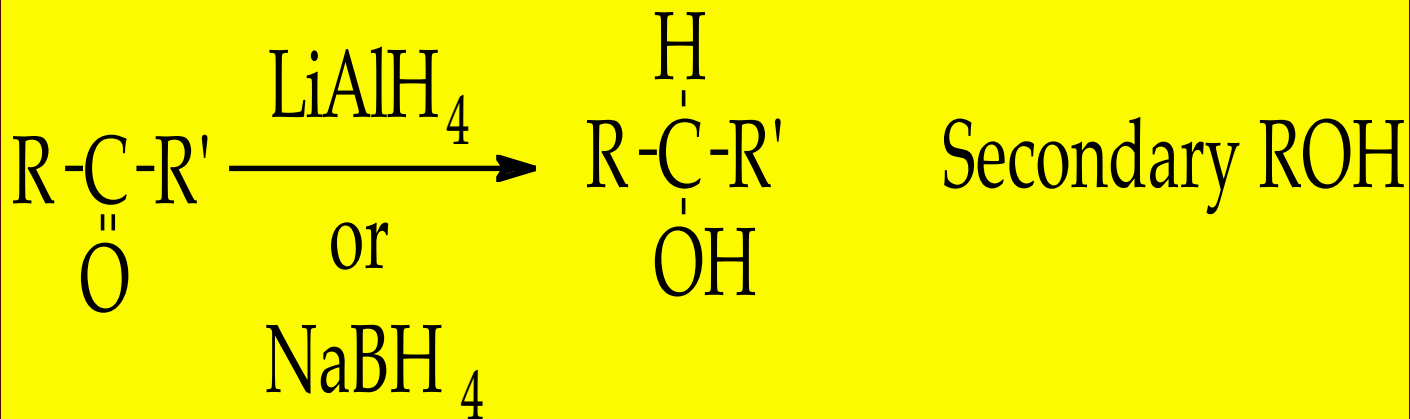
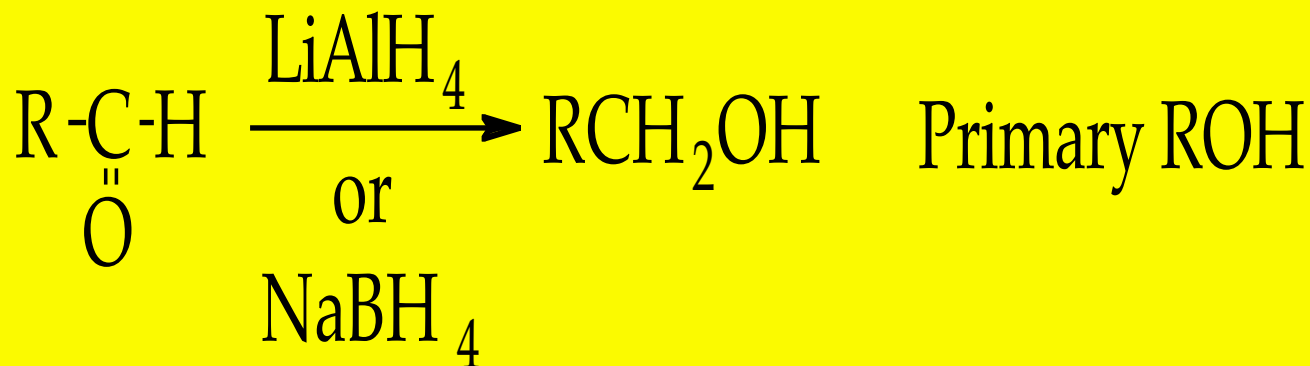
Reduction of Aldehydes/Ketones

Hydrogenation



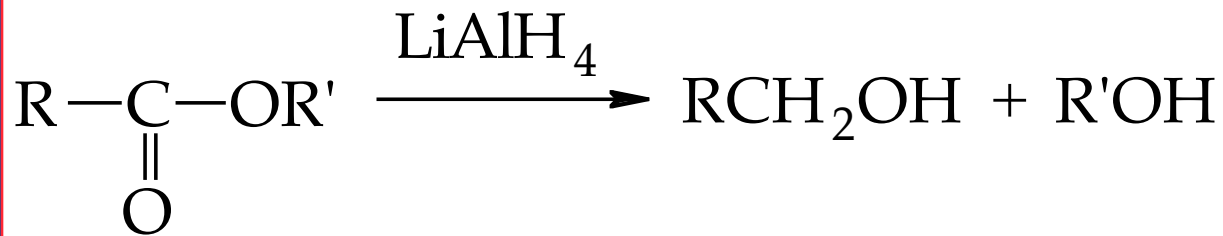
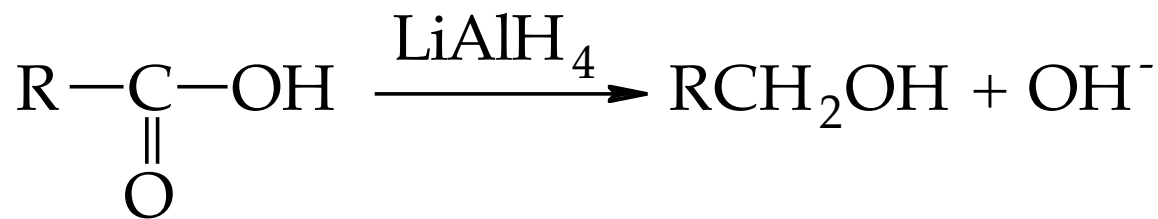
Reduction of Aldehydes/Ketones

Hydride Reductions



Reduction of Carboxylic Acids and Esters

Lithium Aluminum Hydride Reduction

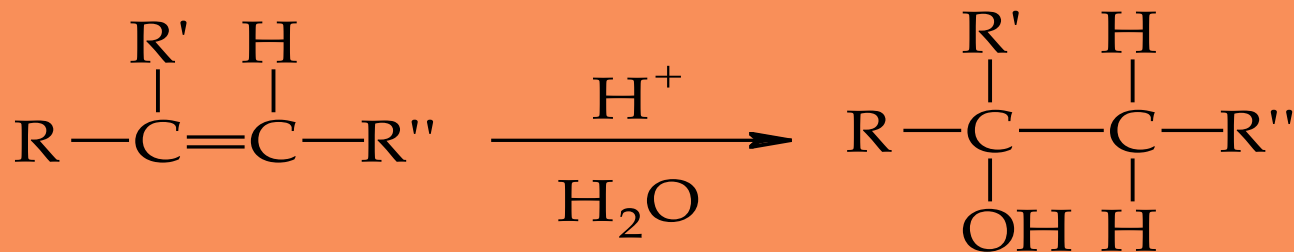
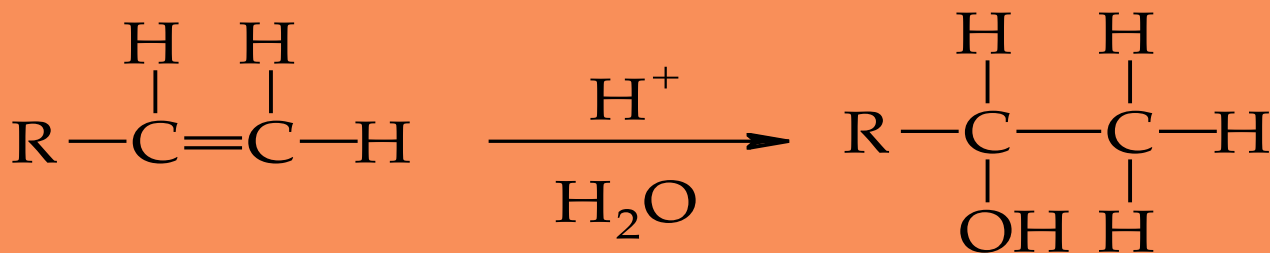


Hydration of Alkenes

- ❖ Acid catalyzed Hydration
- ❖ Oxymercuration-Demercuration
- ❖ Hydroboration-Oxidation

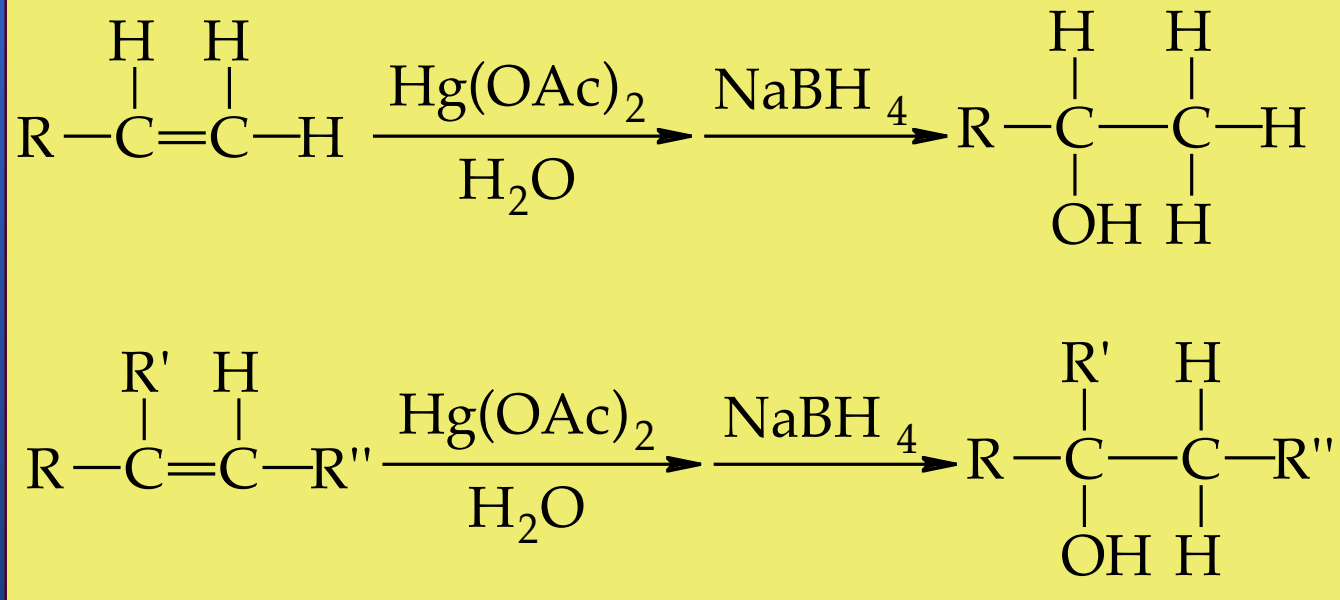
Acid-Catalyzed Hydration of Alkenes

- ✦ Markovnikov addition
- ✦ Formation of most stable carbocation
- ✦ Shifts/rearrangements possible



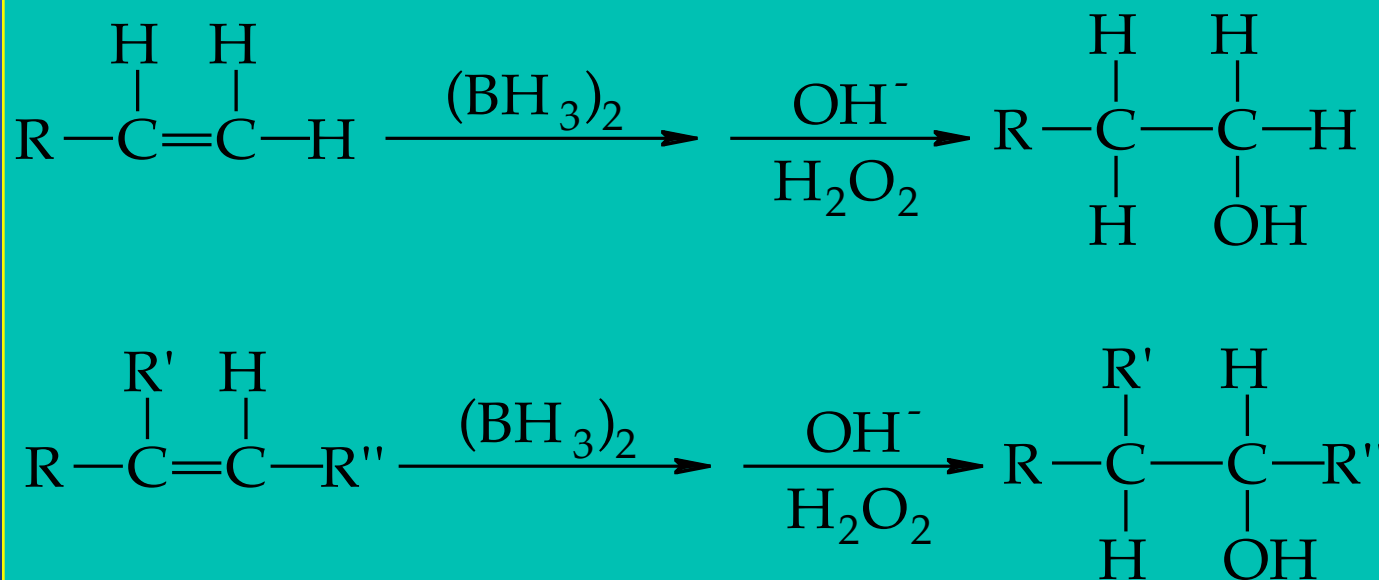
Hydration of Alkenes via Oxymercuration/Demercuration

- * Markovnikov addition
- * Typically no shifts/rearrangements
- * Mercurinium ion involvement



Hydroboration-Oxidation of Alkenes

- ◆ Anti-Markovnikov addition
- ◆ No shifts/rearrangements
- ◆ Syn addition

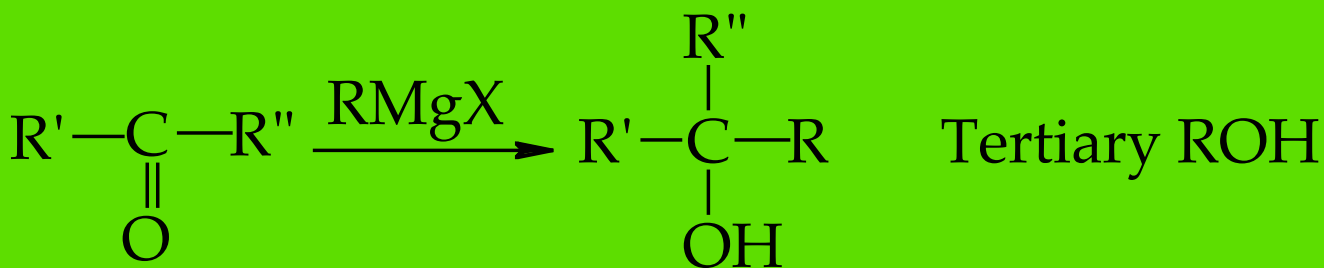
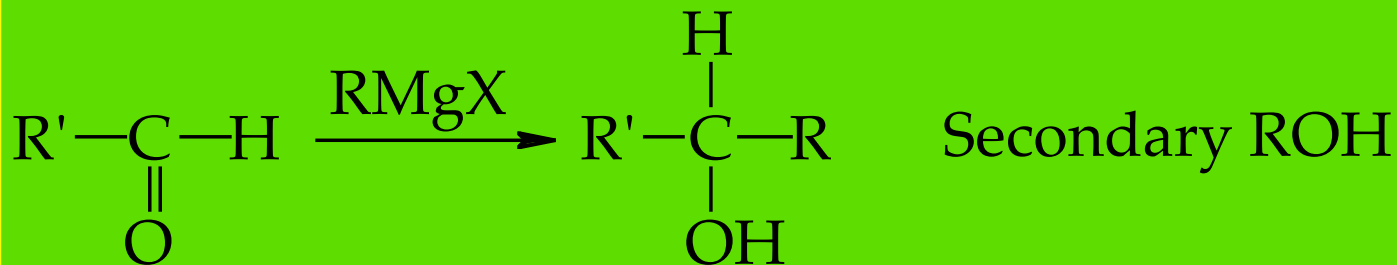


Grignard Addition Reactions

- Addition to Aldehydes/Ketones
- Addition to Esters
- Addition to Epoxides

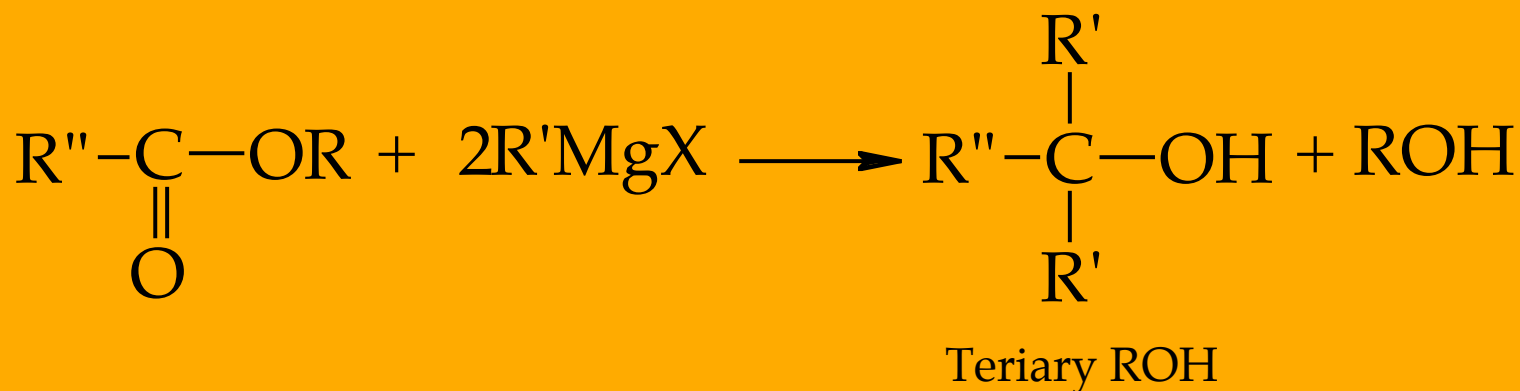
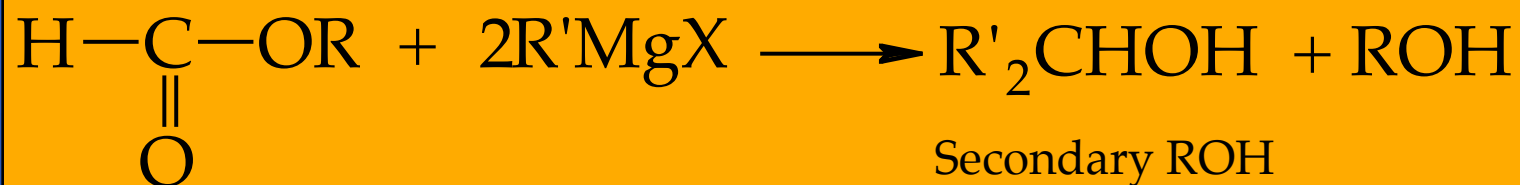
Grignard Additions to Aldehydes/ Ketones

Formation of primary, secondary, and
tertiary alcohols

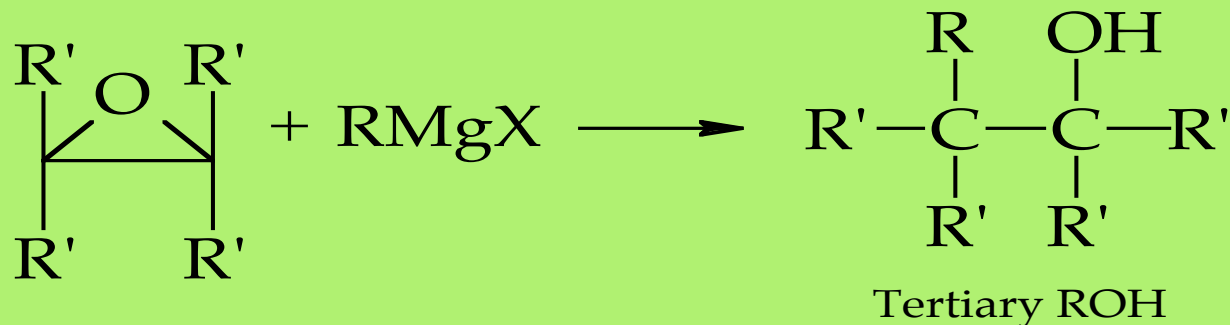
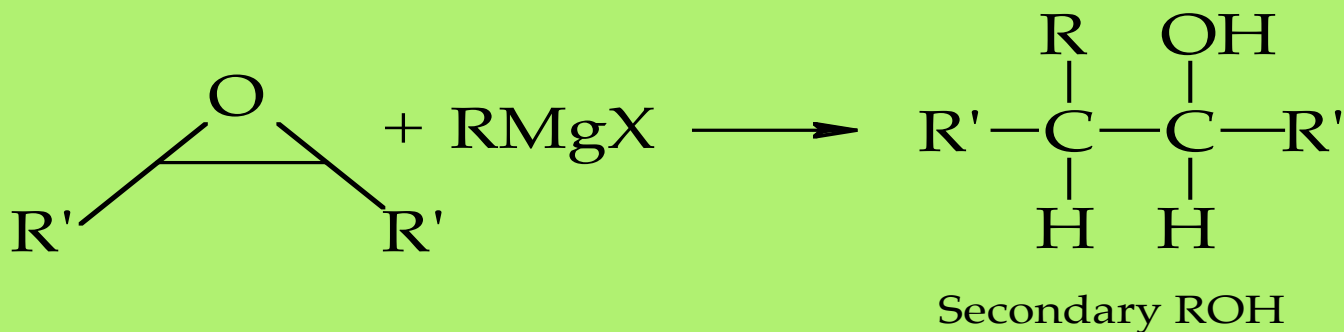
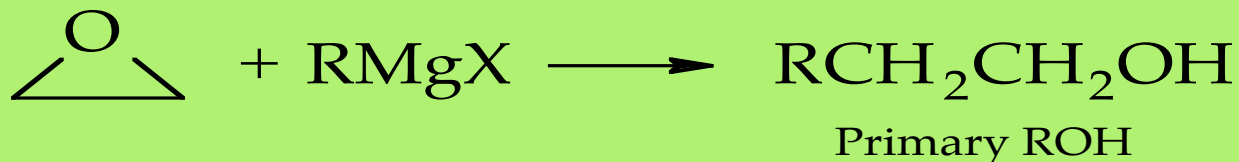


Grignard Additions to Esters

Formation of secondary and tertiary alcohols



Grignard Addition to Epoxides



Typical Alcohol Reactions

- ❖ **Salt formation**
- ❖ **Dehydration**
- ❖ **Oxidation**
- ❖ **Alkyl halide formation**
- ❖ **Ester formation**

- ❖ **Ether synthesis**
- ❖ **Periodic acid cleavage of glycols**
- ❖ **Haloform reaction of methyl carbinols**
- ❖ **THP acetal formation**

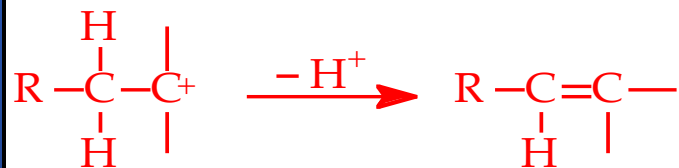
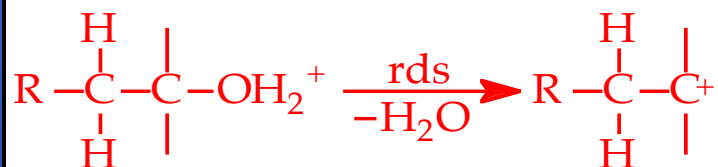
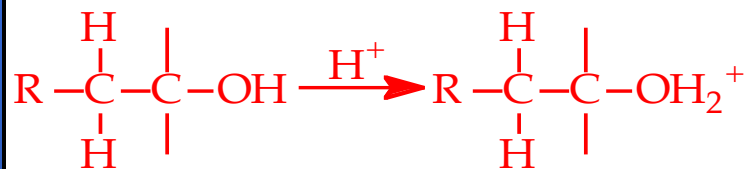
Conversion of Alcohols to Salts

Reaction with Active Metals



Dehydration of Alcohols

E-1

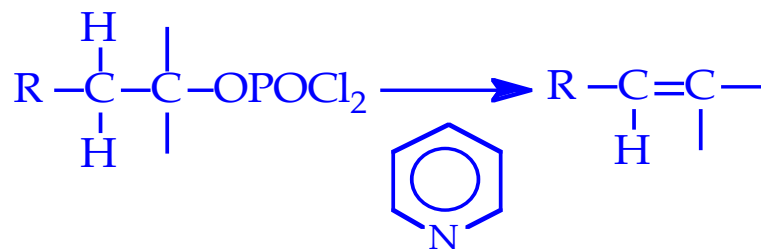


1,2-shifts/rearrangements possible

E-2

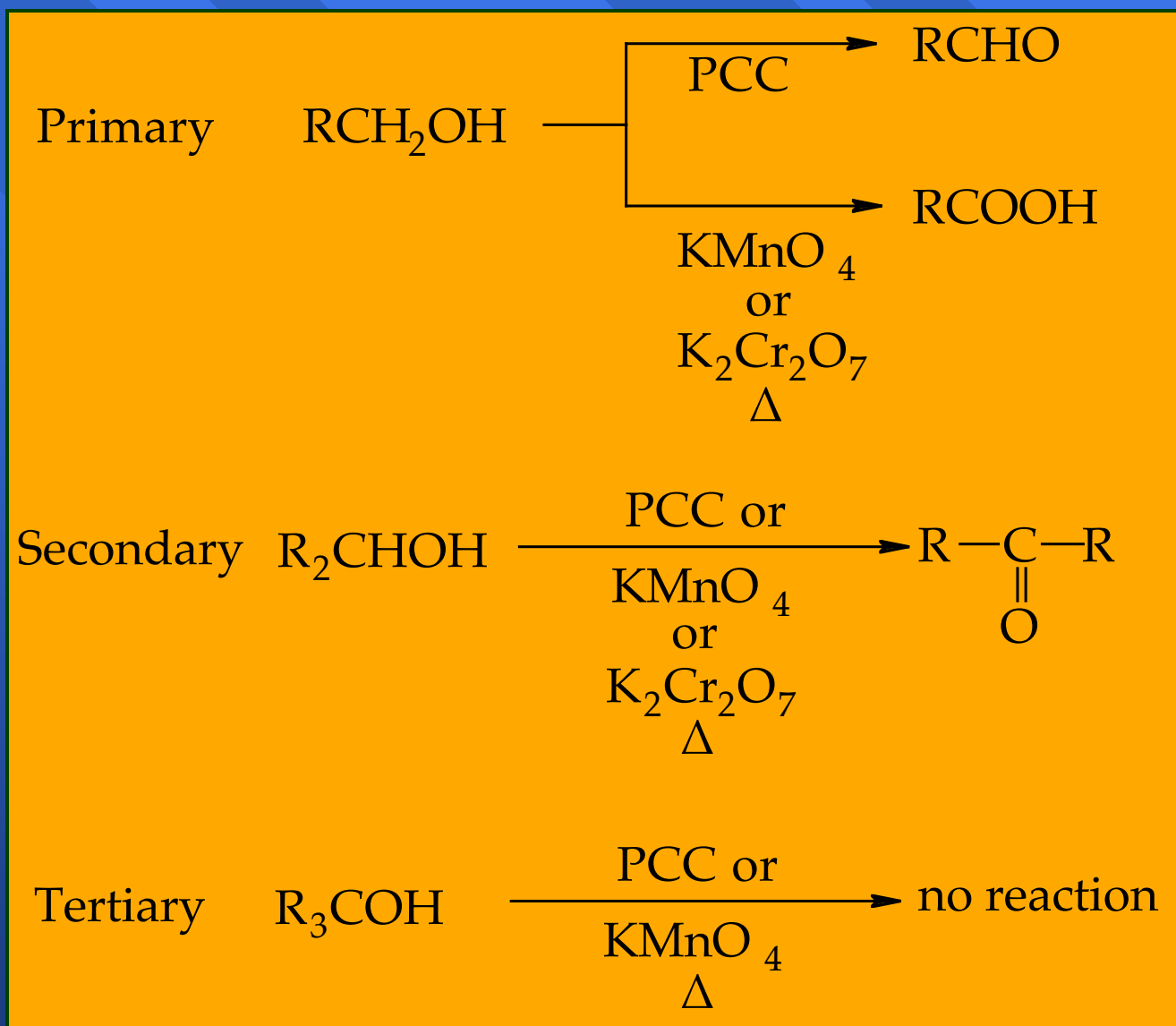


a dichlorophosphate
intermediate



Anti periplanar (coplanar) elimination
No 1,2-shifts/rearrangements possible

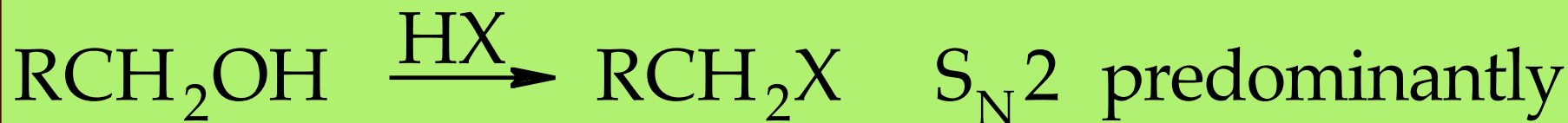
Oxidation of Alcohols



Alcohol Conversion to Alkyl Halides

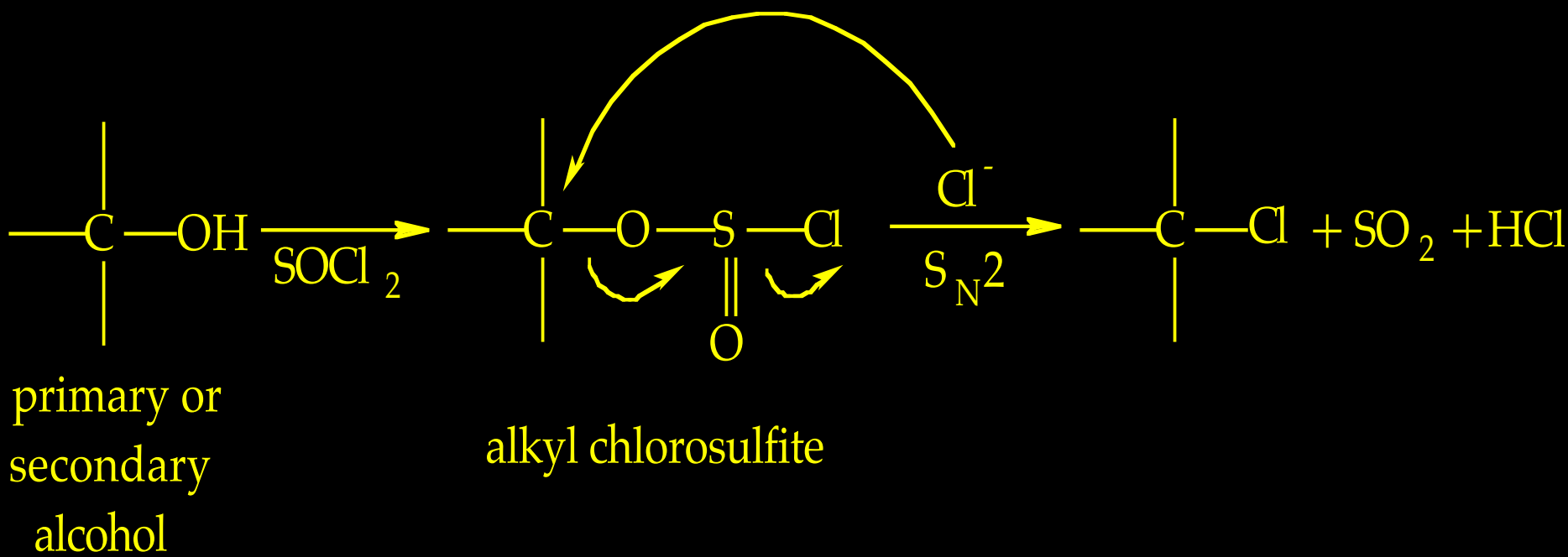
- * **Reaction with Hydrogen halides**
- * **Reaction with Thionyl chloride**
- * **Reaction with Phosphorus trihalides or pentahalides**

Hydrogen Halide Conversion of Alcohols to Alkyl Halides

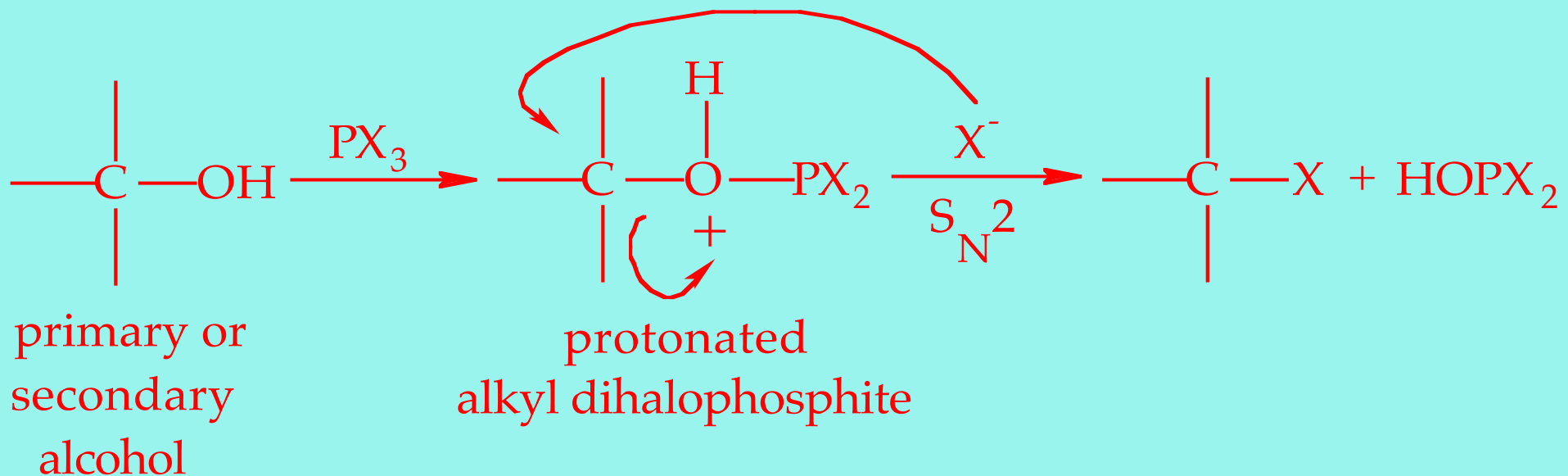


where HX = HI, HBr, or HCl

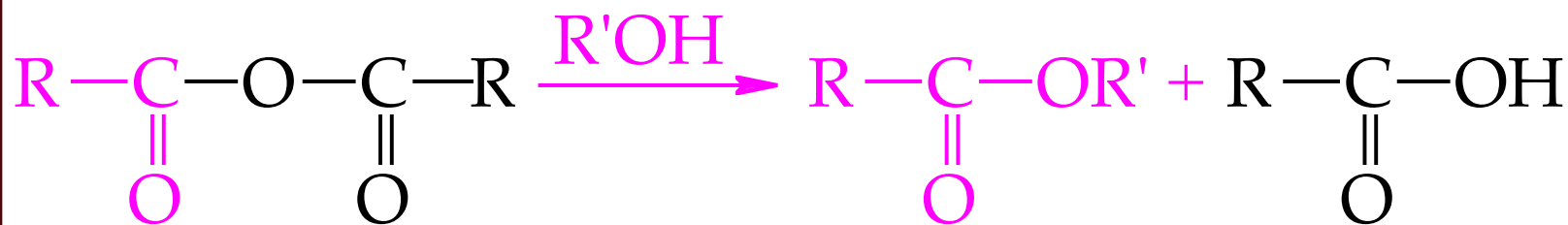
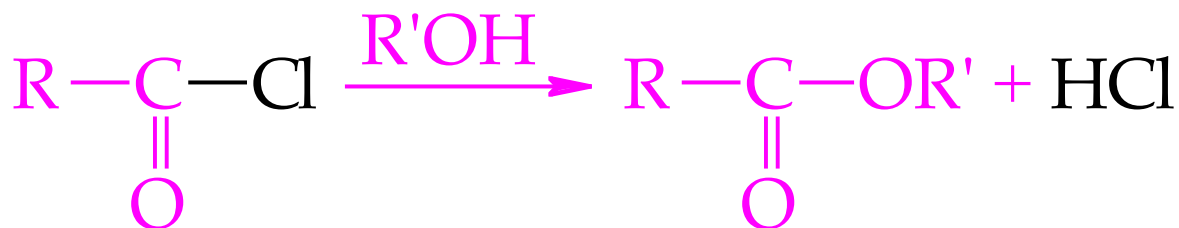
Conversion of Alcohols to Alkyl Chlorides via Thionyl Chloride



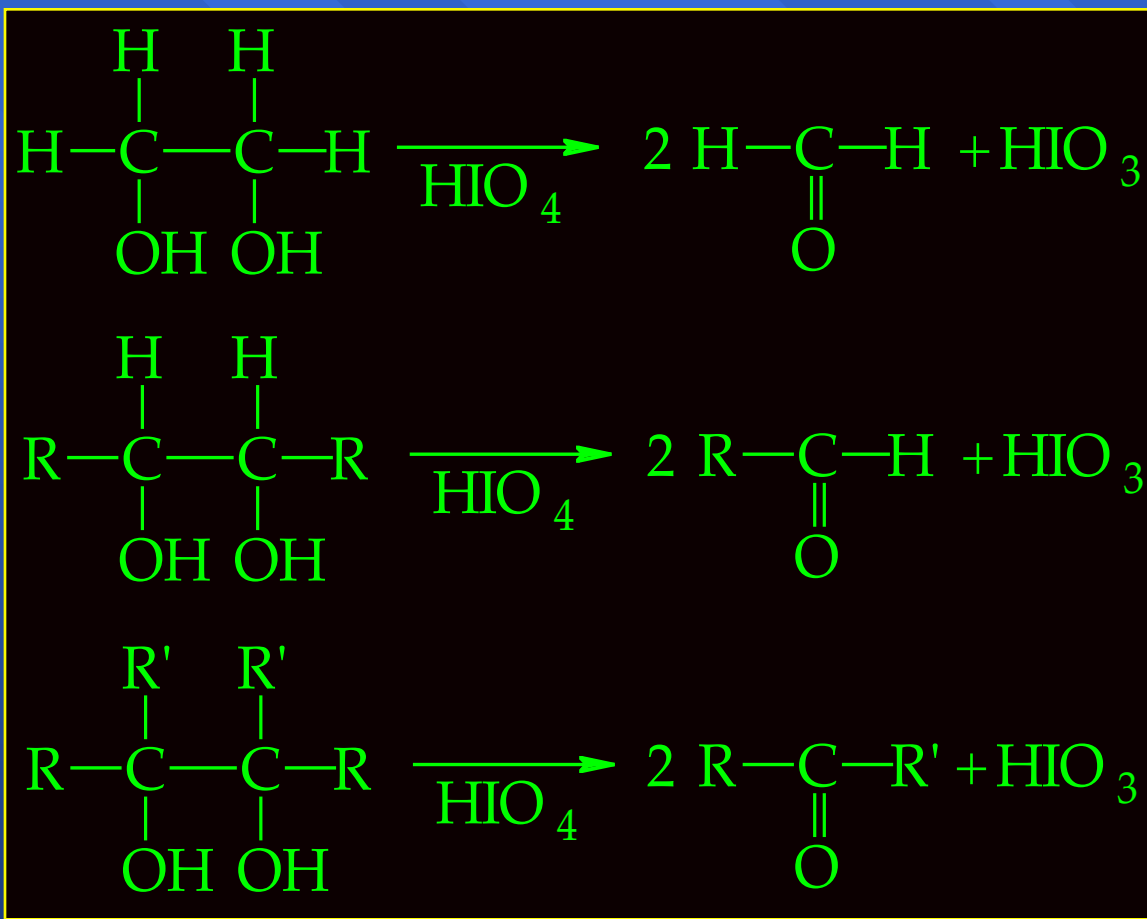
Conversion of Alcohols to Alkyl Halides via Phosphorus Halides



Ester Formation from Alcohols

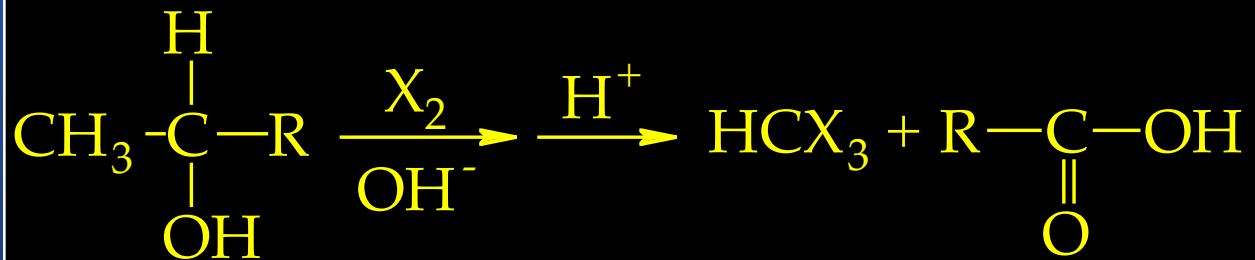
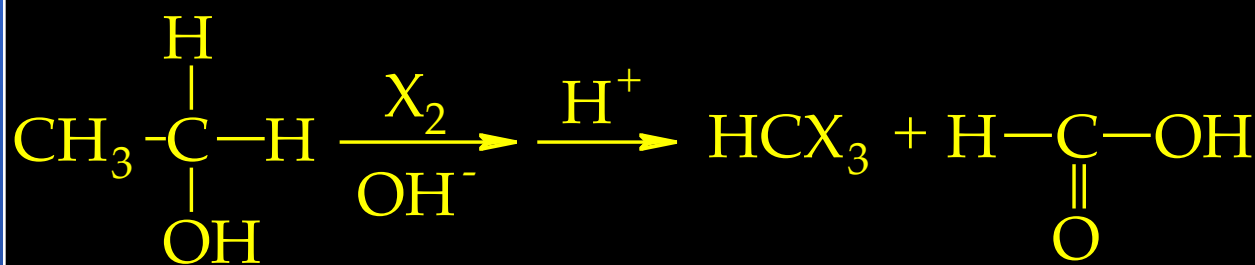


Periodic Acid Cleavage of Glycols



Haloform Reaction

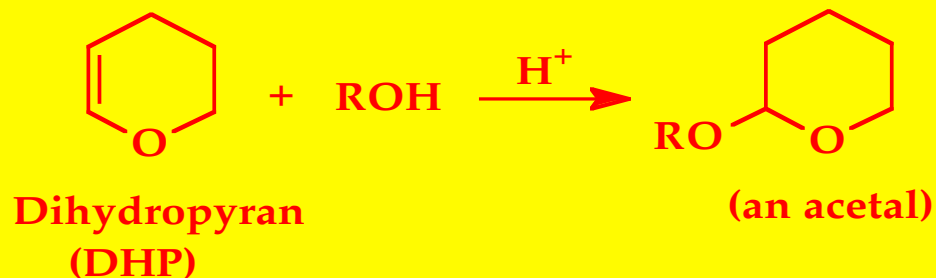
**Methyl carbinol cleavage to give
Carboxylic acids and Haloform**



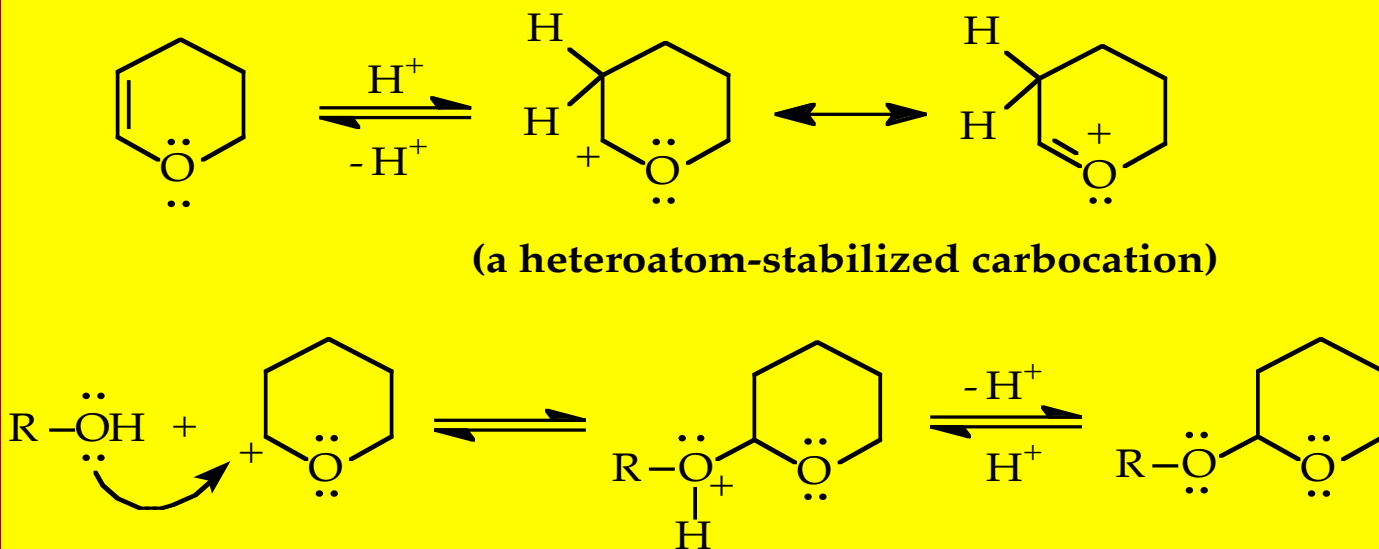
Disguising an Alcohol

Creating a tetrahydropyranyl acetal

Overall Transformation



Mechanism



Spectroscopic Characteristics of Alcohols

✦ Infrared

✦ Pmr

✦ Cmr

Ethers

- ★ **Nomenclature**
- ★ **Properties**
- ★ **Preparation**
- ★ **Reactions**

Ether

Nomenclature

Preparation of Ethers

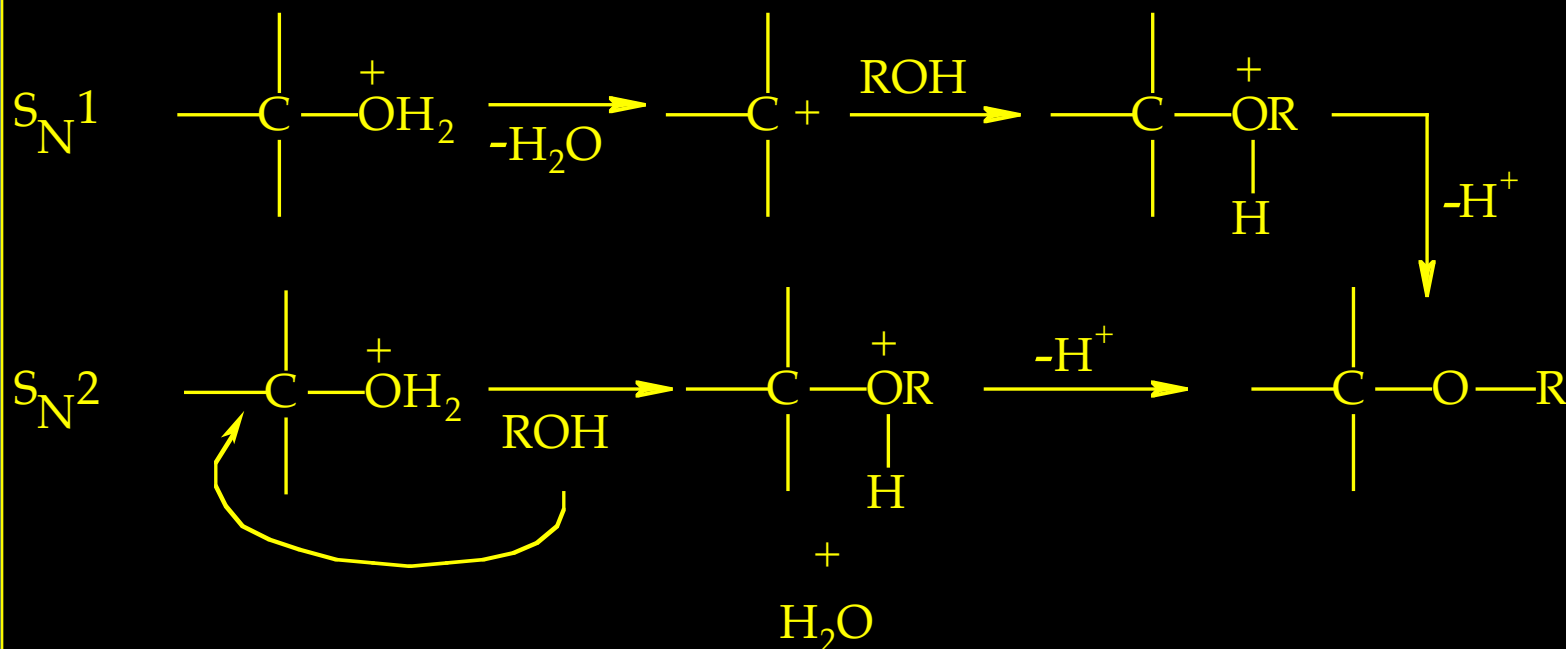
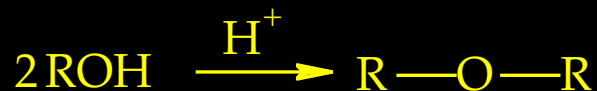
Dehydration of Alcohols

Williamson synthesis

**Alkoxymercuration-
Demercuration**

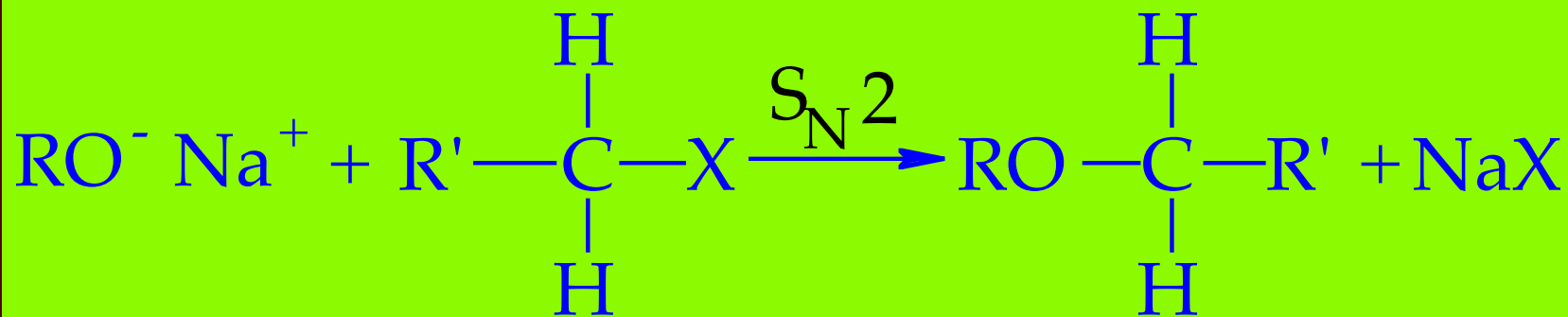
**Peroxyacid Epoxidation of
Alkenes**

Ether Formation via Acid Catalyzed Dehydration of Alcohols



Williamson Synthesis of Ethers

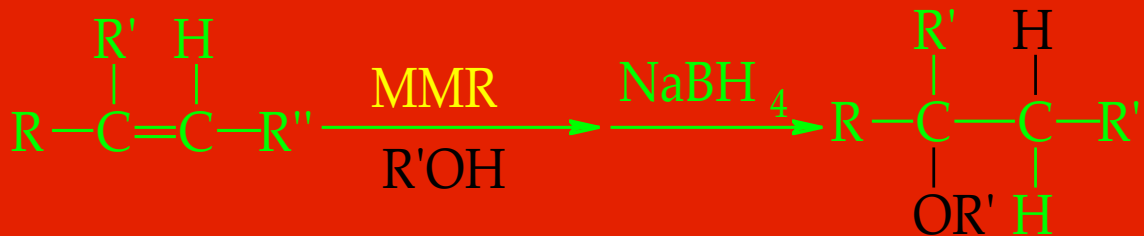
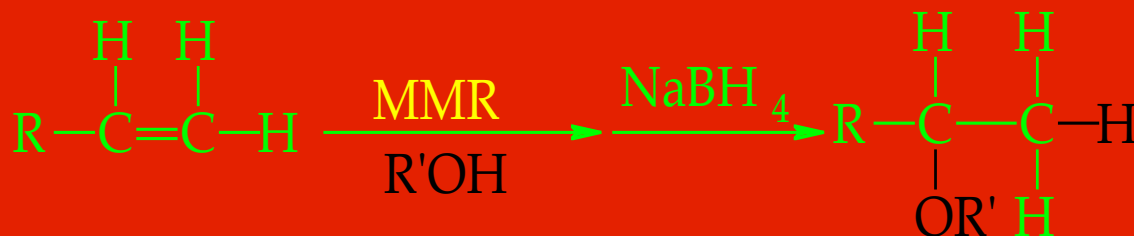
**Bimolecular Substitution by Alkoxide
on a suitable substrate**



Primary
Alkyl Halide

Alkoxymercuration-Demercuration of Alkenes

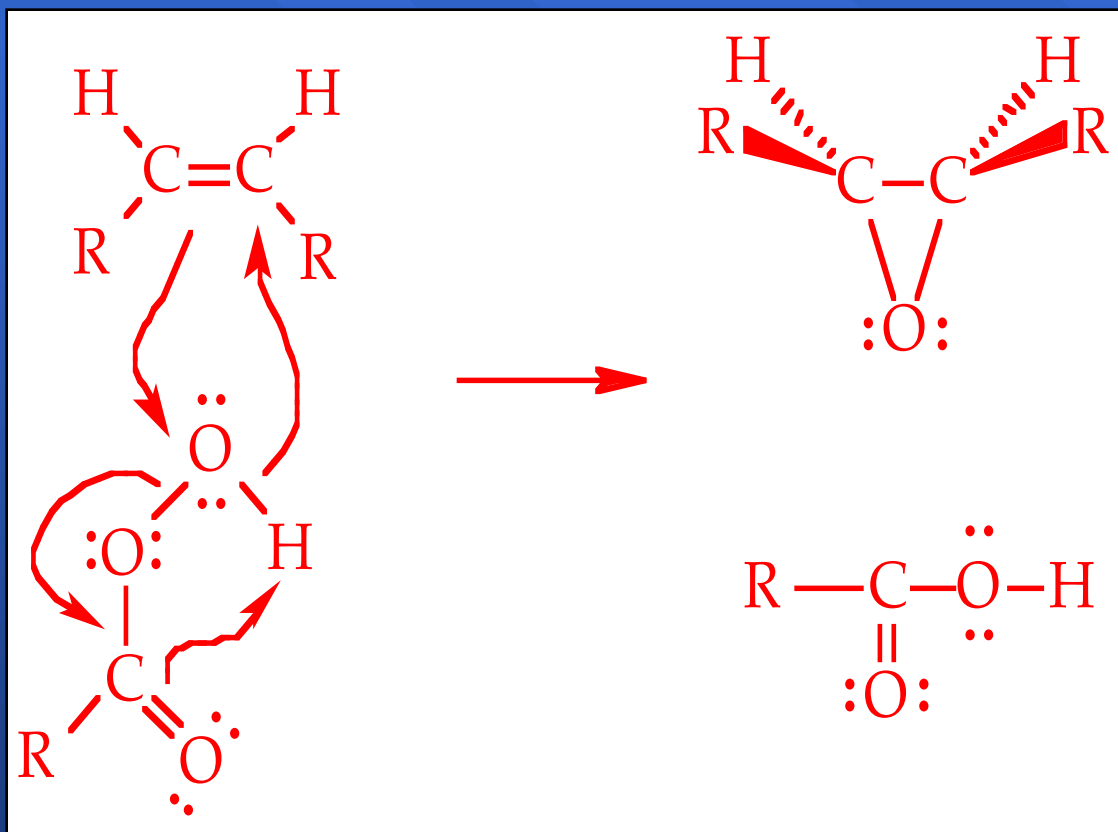
- * Markovnikov Addition
- * Typically no rearrangements/shifts
- * Mercurinium ion involvement



Where MMR = modified mercury reagent = Mercury trifluoroacetate

Epoxidation of Alkenes

Prilezhaev reaction

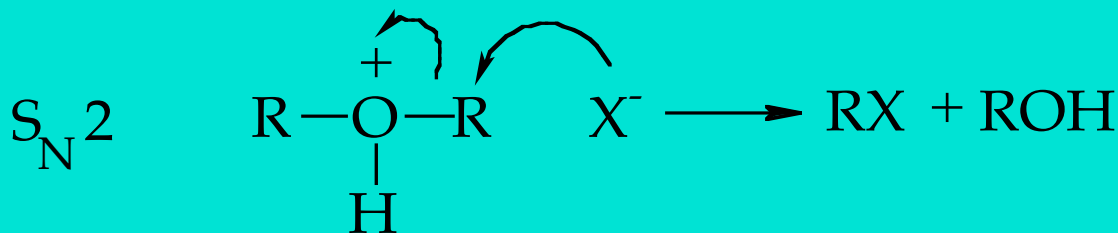
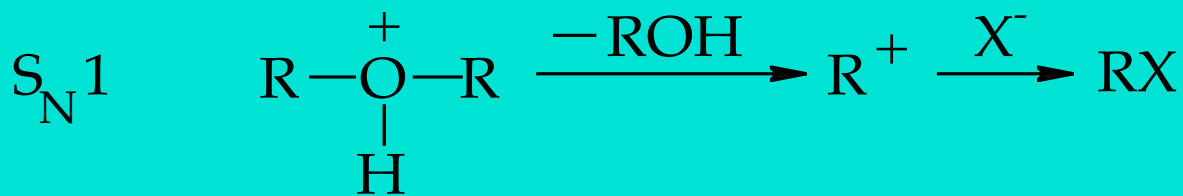
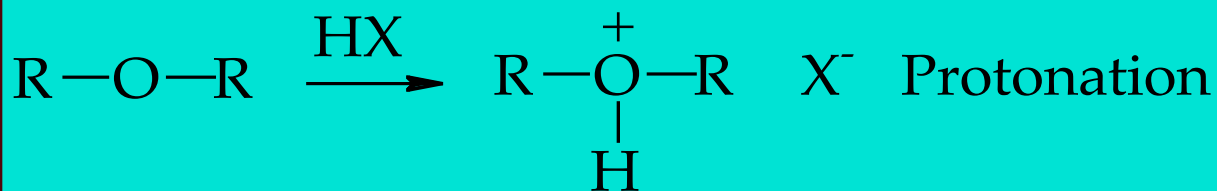


Ether Reactions

- * HX Cleavage
- * Epoxide Ring Opening

HX Cleavage of Ethers

Unimolecular or Bimolecular Cleavage Pathways



Epoxide Ring Opening

Unimolecular or Bimolecular

