

HALOARENES

Dr. Anand Gupta

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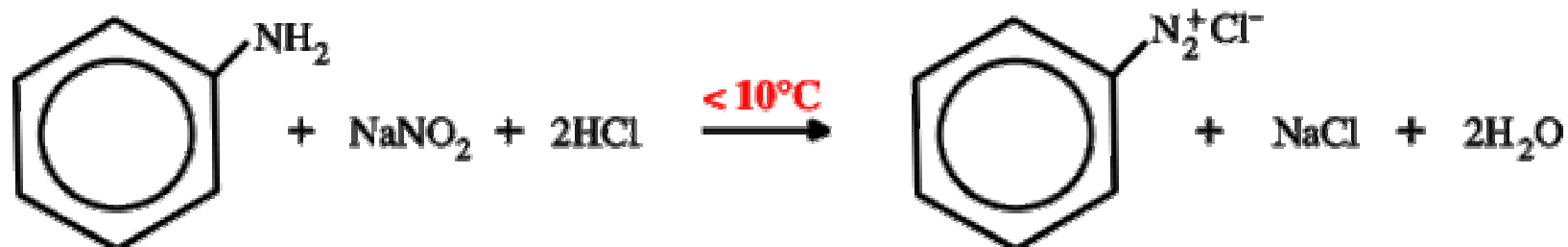
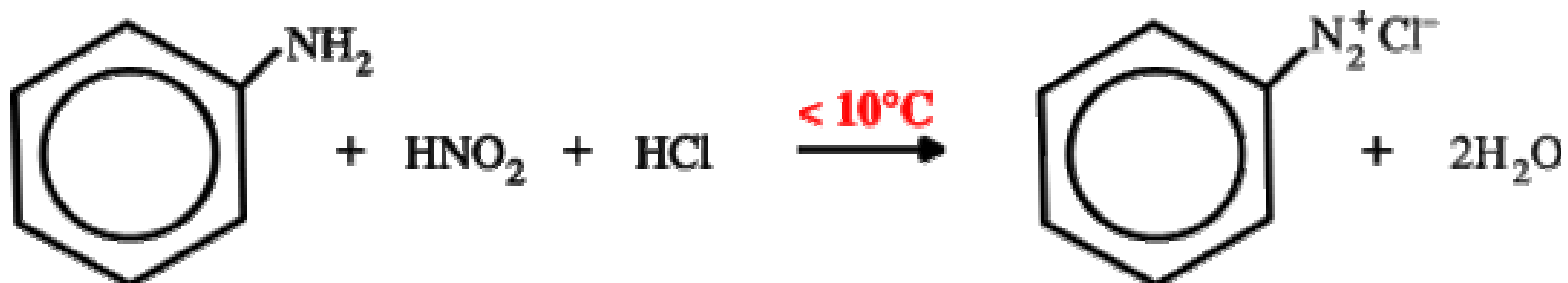
anandu71@yahoo.com

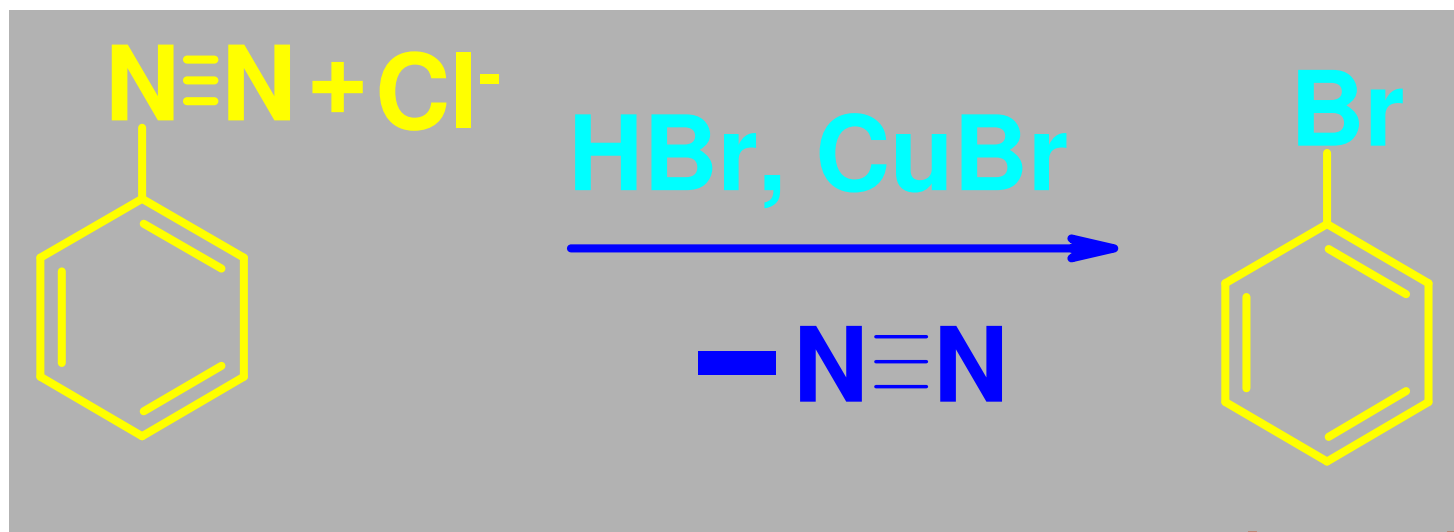
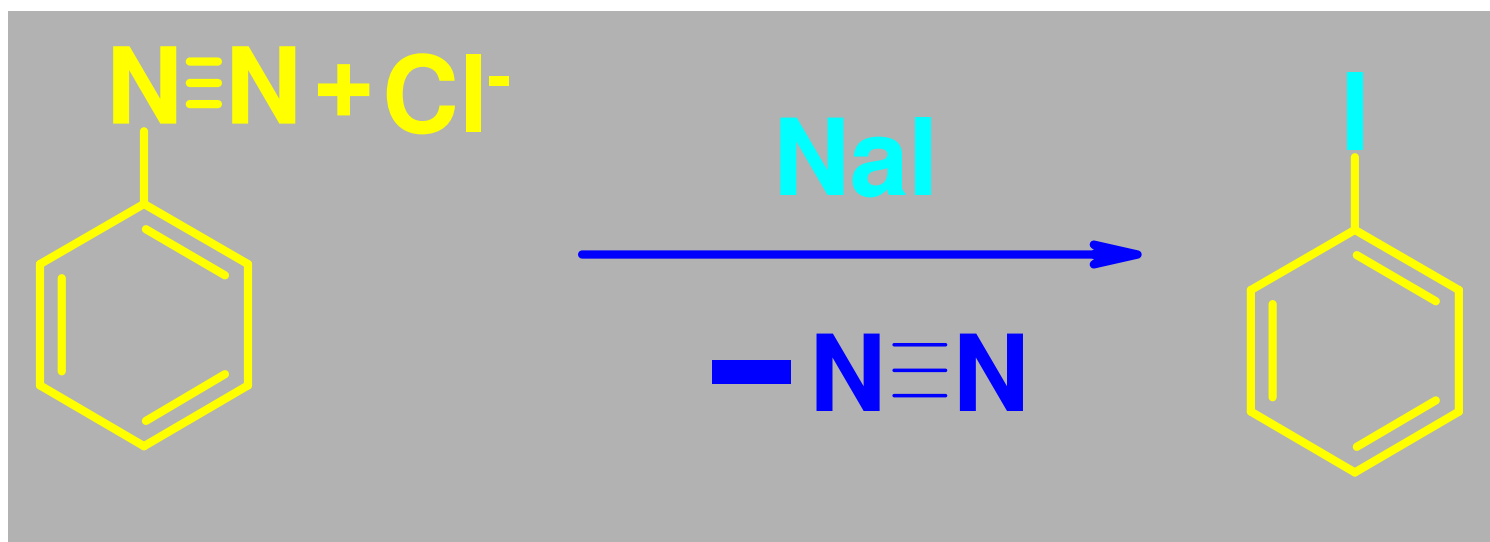
Mr Mahesh Kapil

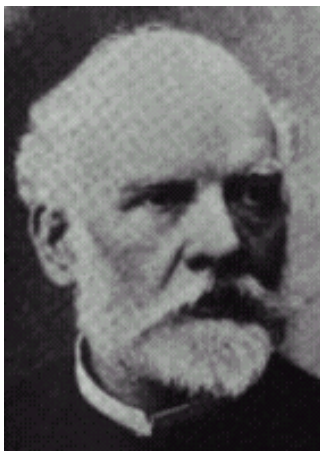
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mkapil_foru@yahoo.com

Preparation of Diazonium salts

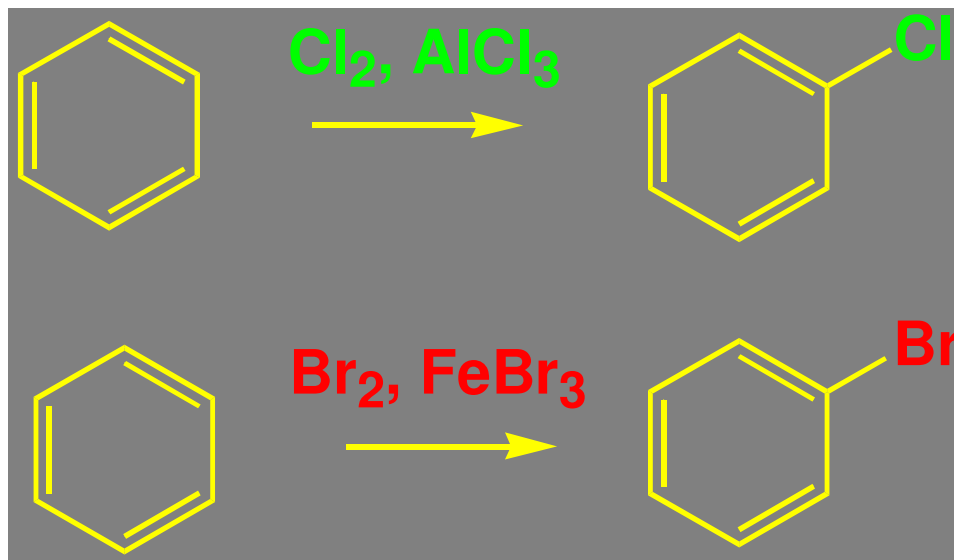




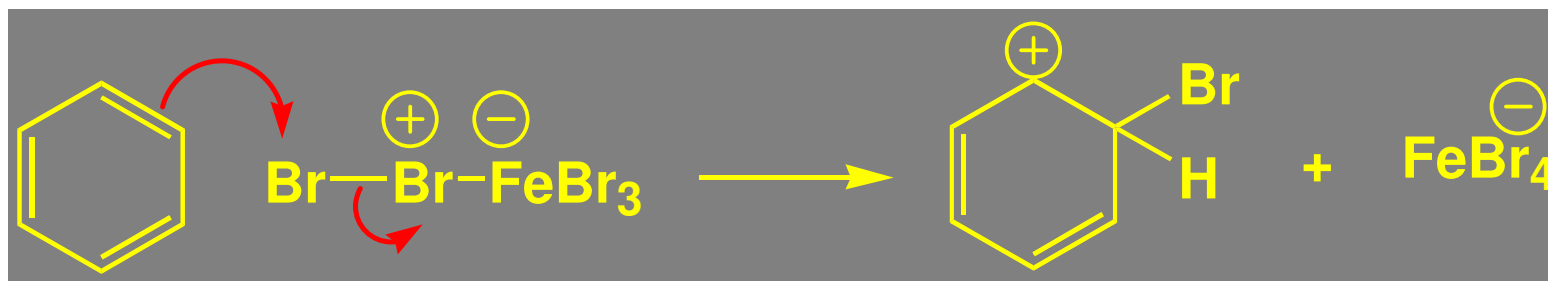


Professor Charles Friedel
and Professor James Crafts

HALOGENATION



The Halogen is polarised

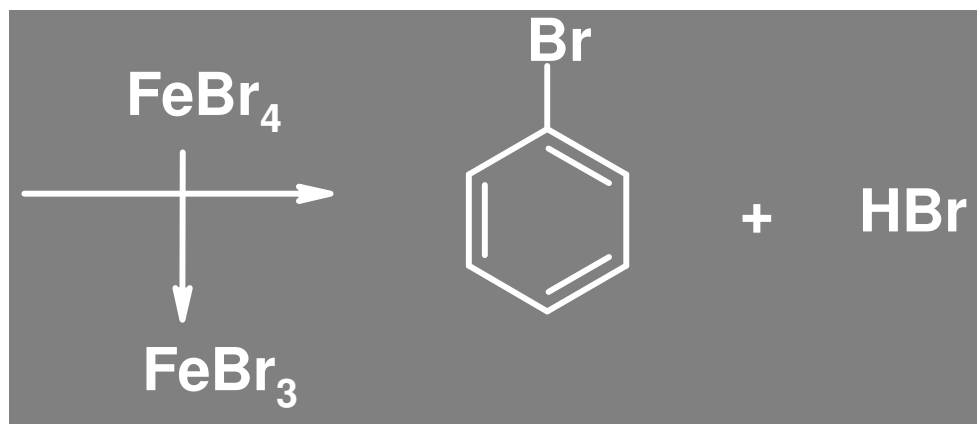
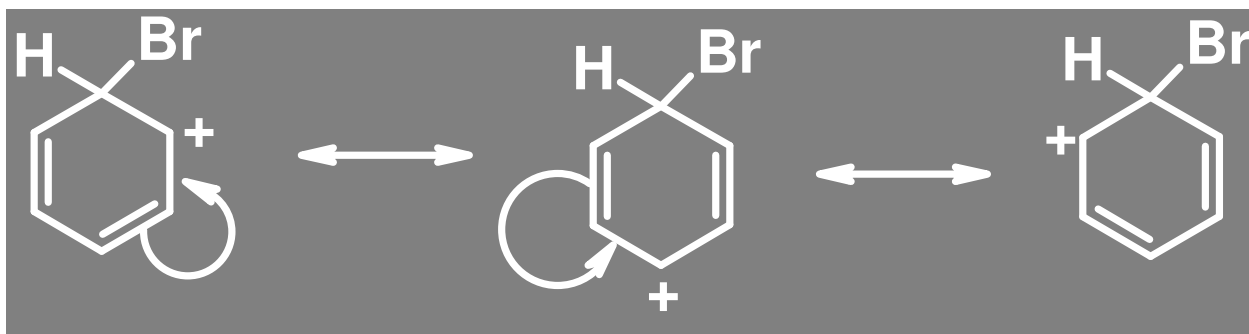


Aromatic Compounds are resonance stabilized

This gives them added stability

They undergo Electrophilic Substitution Reactions

Upon substitution, the fast step is the loss of a proton to regenerate aromaticity



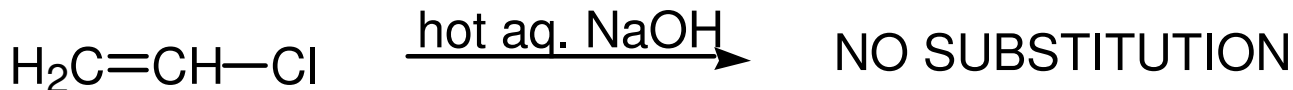
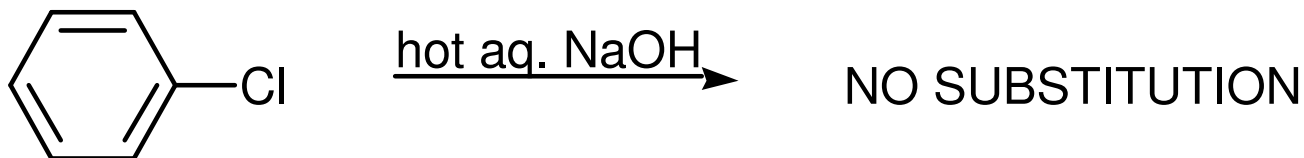
Regenerate the catalyst – so only a small amount is required

Reactions of arylhalides

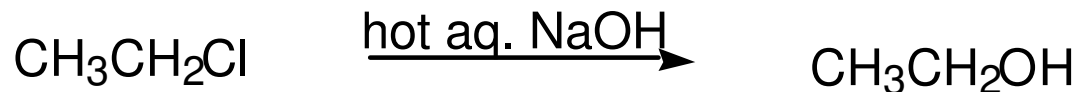
- Reactions

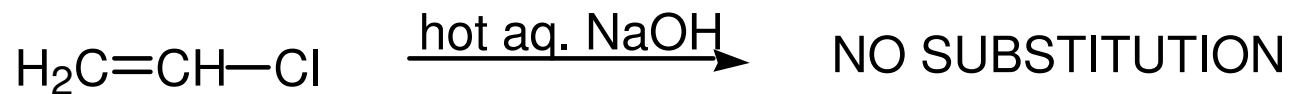
Alkyl halides react by S_N1 and S_N2 mechanisms

Simple aryl halides (and vinyl halides) are unreactive towards nucleophilic substitution e.g.

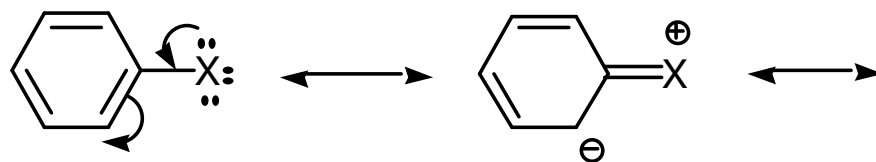


But

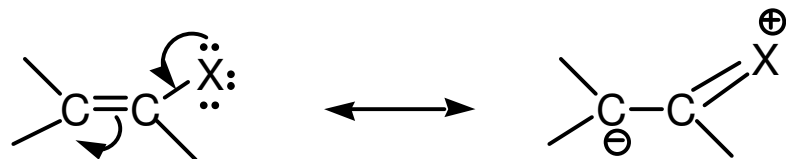




C – Halogen bonds of aryl (and vinyl) halides are shorter and stronger than those of alkyl, allylic and benzylic halides



(and other resonance forms)



Note the double-bond character of the C – X bond of aryl and vinyl halides.

Aryl halides and vinylic halides are relatively unreactive toward nucleophilic substitution under conditions that give facile nucleophilic substitution with alkyl halides.

Reason:

- (1) Phenyl cations are very unstable.
- (2) Halogen bonds of aryl (and vinylic) halides are shorter and stronger than those of alkyl, allylic, and benzylic halides because of the hybridized state and the resonance.

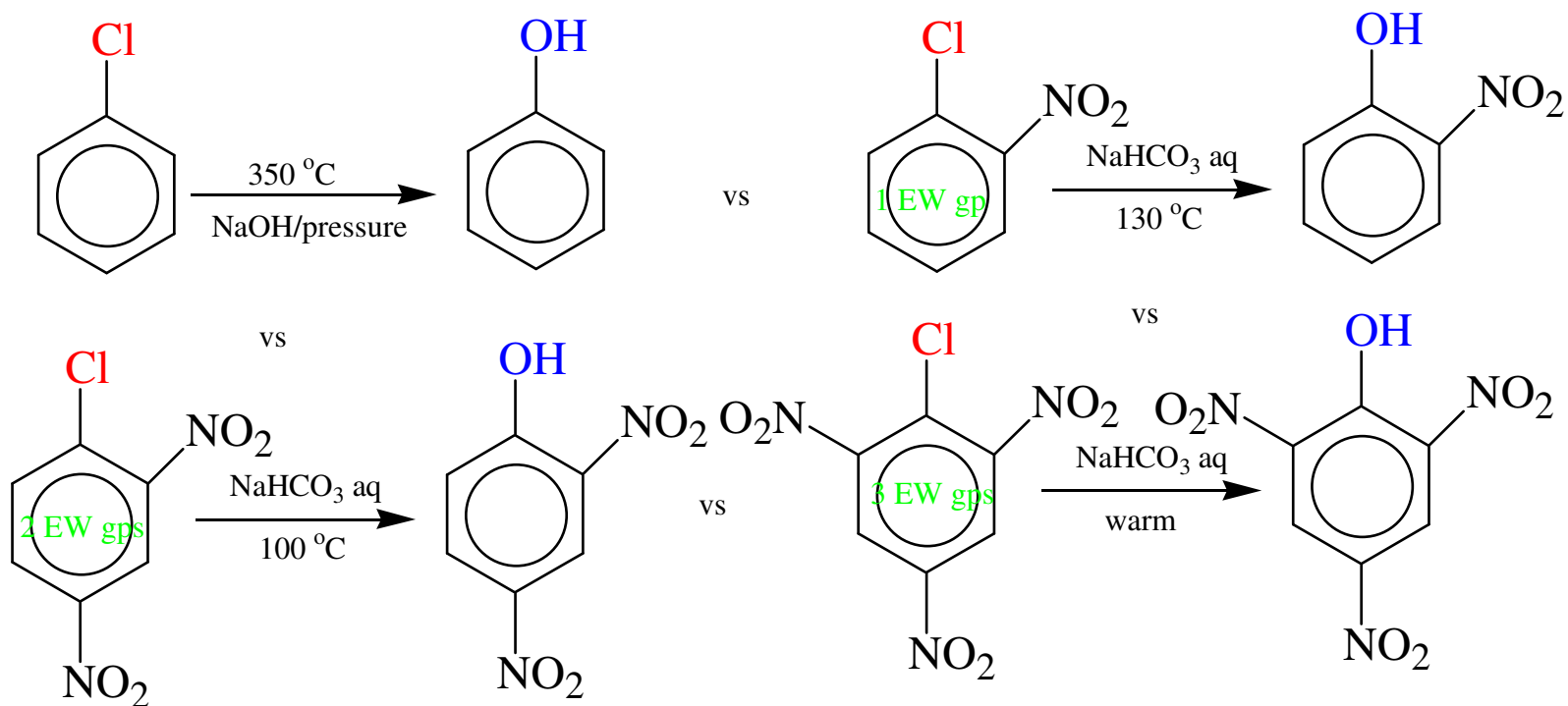
But aryl halides can be remarkably reactive toward nucleophiles if they bear certain substituents or when we allow them to react under the proper conditions.

So NORMALLY, aryl halides will not undergo nucleophilic aromatic substitution.

Some factors/conditions which allow aryl halides to undergo nucleophilic substitution

- A. When strong electron-withdrawing groups, (e.g. NO_2) are ortho- or para- to the halogen atom.
- B. When the aryl halides are allowed to react under forcing conditions e.g. aqueous NaOH , high P and $T \sim 350^\circ\text{C}$.

Nucleophilic Aromatic Substitution



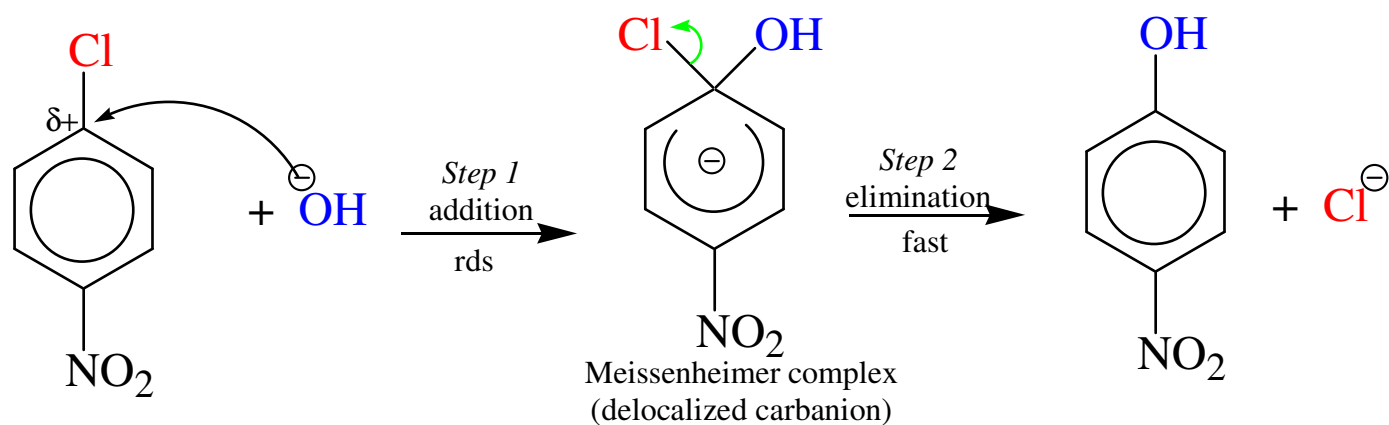
NB as EW gps are increased, milder rxn conditions suffice.
EW gps therefore activate the ring towards NAS

Nucleophilic aromatic substitution

There are two possible mechanism for NAS:

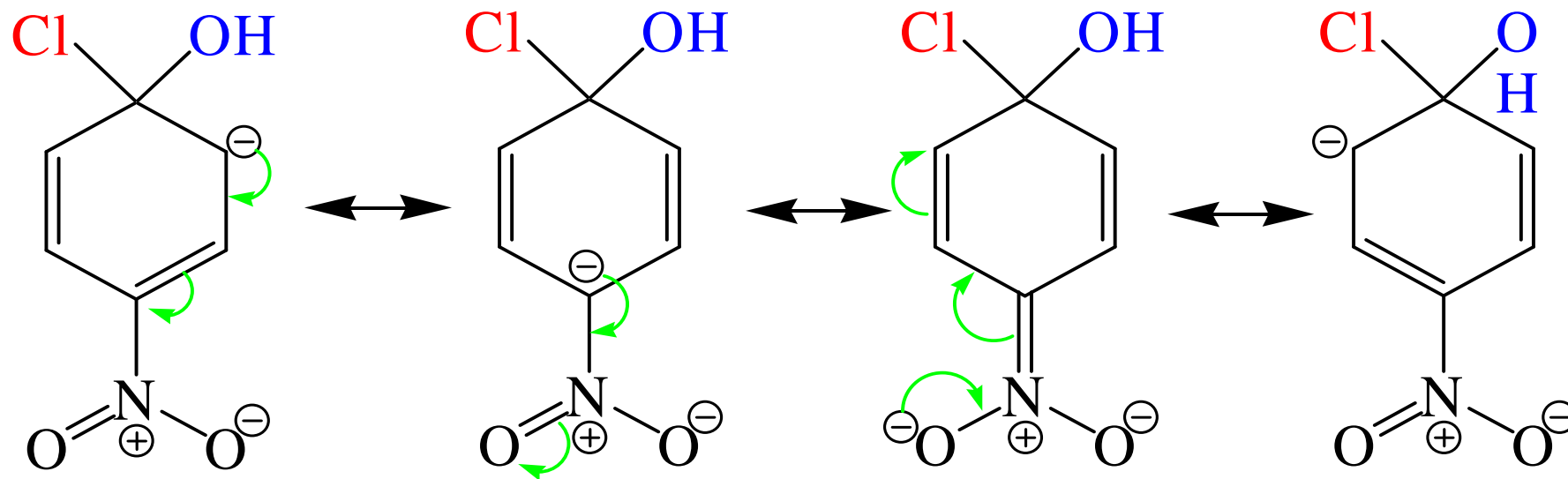
- A) Bimolecular Displacement mechanism (BDM) or the *addition-elimination* or S_NAr mechanism or the occurs when powerful EW substituents are on the ring. BDM results in *ipso* substitution, i.e., substitution at an atom that already had a substituent.
- B) **Elimination-addition mechanism**

A) For the BDM



Nucleophilic Aromatic Substitution

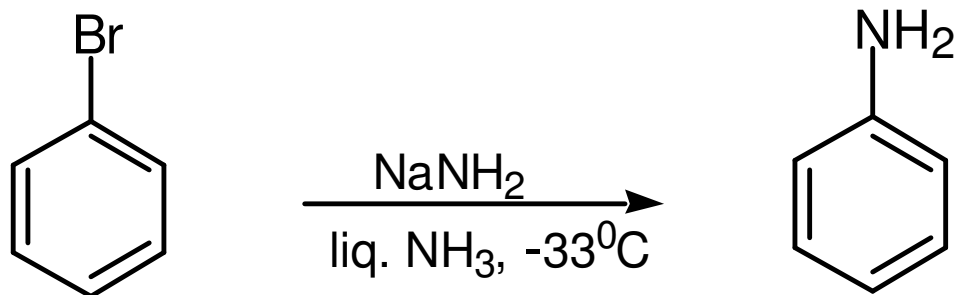
The *Meissenheimer complex* is stabilized by EW gps *o* or *p* to the halogen.



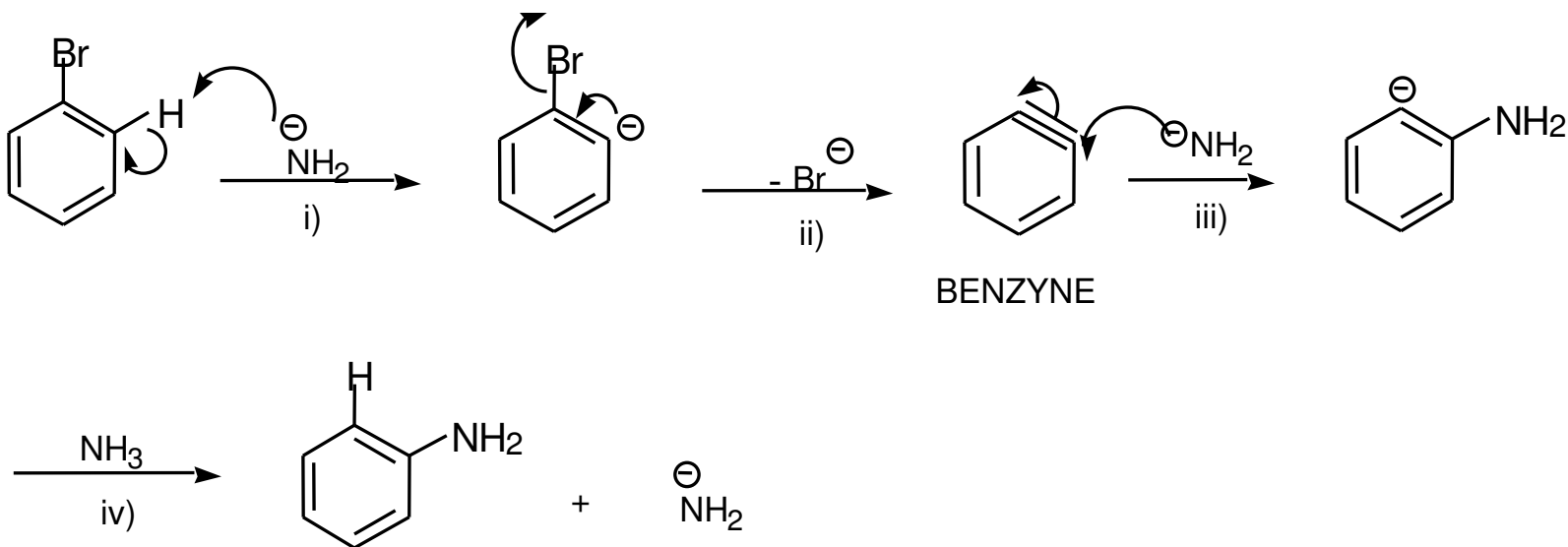
Especially stable.
-ve charges are on the O-atoms

In the last step the C-Cl bond is cleaved because it is more polar, making Cl⁻ a better leaving gp.

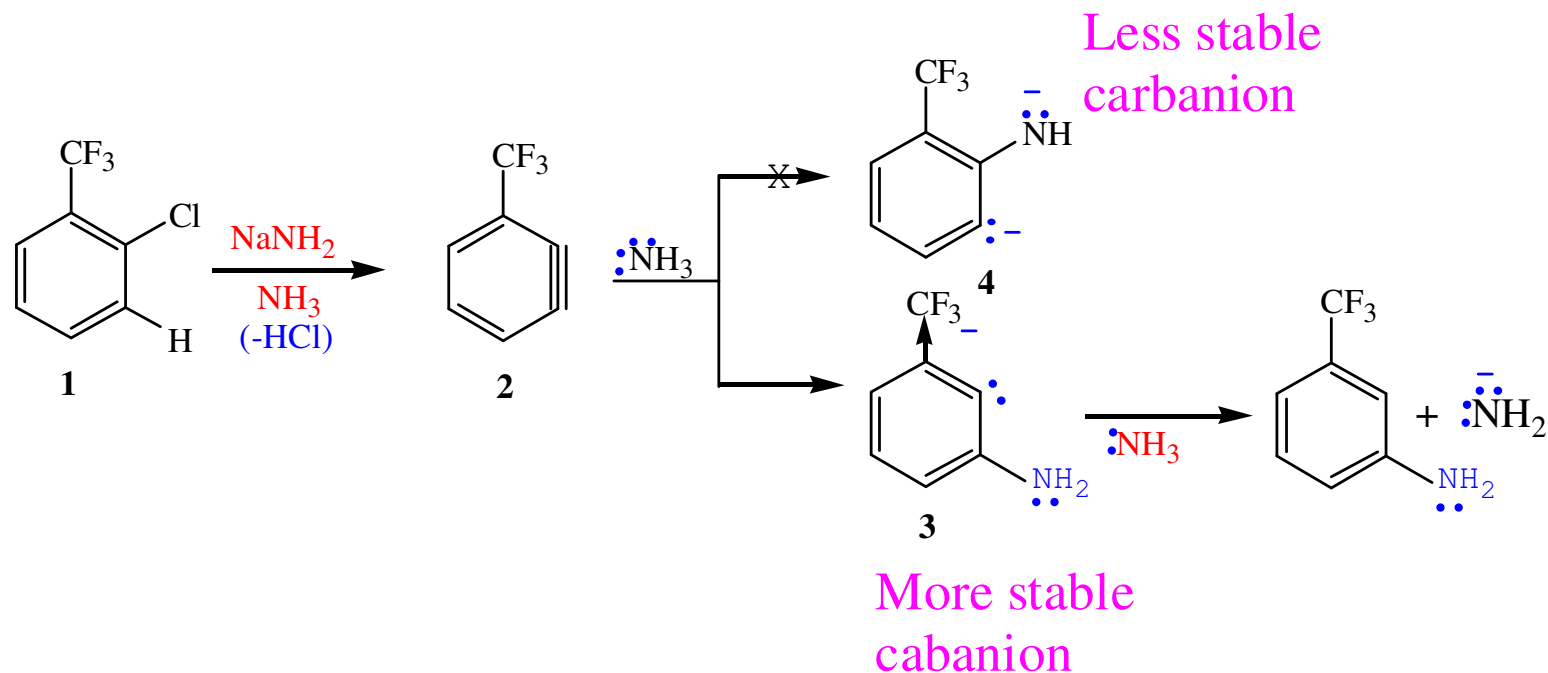
Benzyne Mechanism



Benzyne - unstable. 3rd bond is due to $\text{sp}^2 - \text{sp}^2$ overlap of orbitals which are perpendicular to the π - orbitals of the aromatic ring.



Mechanism:



Carbanion 3 is more stable than 4 because the carbon atom bearing the negative charge is closer to the highly electronegative trifluoromethyl group.

Electrophilic Substitution Reactions

- Halogenation
- Nitration
- Sulphonation
- Friedel Craft Acylation
- Friedel Craft Alkylation

Reaction With Metals

- Wurtz Reaction
- Wurtz Fittig Reaction
- Fittig Reaction
- Frankland Reaction
- Ullman Reaction
- Reaction with Magnesium

Questions

Q 1: How will you distinguish between Chlorobenzene & benzyl chloride and Chloroethane & bromoethane

Q 2 Why R-I becomes violet or brown on long standing in presence of light.

Q 3: Convert

- i) Bromomethane into propanone.
- ii) 2-bromobutane to 1-bromobutane
- iii) Benzene into biphenyl

Q4: Which reagent can be converted in ethane and methane in single step reactions. Give reactions.

USES OF HALOGENOALKANES

Synthetic

The reactivity of the C-X bond means that halogenoalkanes play an important part in synthetic organic chemistry. The halogen can be replaced by a variety of groups via nucleophilic substitution.

Polymers

Many useful polymers are formed from halogeno hydrocarbons

| Monomer | Polymer | Repeating unit |
|-------------------|------------------------------|---|
| chloroethene | poly(chloroethene) PVC | - (CH ₂ - CHCl) _n - |
| tetrafluoroethene | poly(tetrafluoroethene) PTFE | - (CF ₂ - CF ₂) _n - |

Chlorofluorocarbons - CFC's

| | | |
|----------------------------|-------------------------------------|--|
| dichlorofluoromethane | CHCl ₂ | refrigerant, aerosol propellant, blowing agent |
| trichlorofluoromethane | CF ₃ Cl | refrigerant, aerosol propellant, blowing agent |
| bromochlorodifluoromethane | CBrClF ₂ | fire extinguishers |
| | CCl ₂ FCClF ₂ | dry cleaning solvent, degreasing agent |

PROBLEMS WITH CFC's AND THE OZONE LAYER

CFC's have been blamed for damage to the environment by thinning the ozone layer

Ozone absorbs a lot of harmful UV radiation

However it breaks down more easily in the presence of CFC's

CFC's break up in the atmosphere to form radicals



Free radicals catalyse the breaking up of ozone



CFC's were designed by chemists to help people

Chemists are now having to synthesise alternatives to CFC's to protect the environment

This will allow the reversal of the ozone layer problem



PROBLEMS WITH CFC's AND THE OZONE LAYER

There is a series of complex reactions but the basic process • ozone in the atmosphere breaks down naturally



• CFC's break down in UV light to form radicals



• chlorine radicals then react with ozone



• chlorine radicals are regenerated



Overall, chlorine radicals are not used up so a small amount of CFC's can destroy thousands of ozone molecules before they take part in a termination stage.

ALCOHOLS

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Alcohols

 Nomenclature

 Isomerism

 Preparation

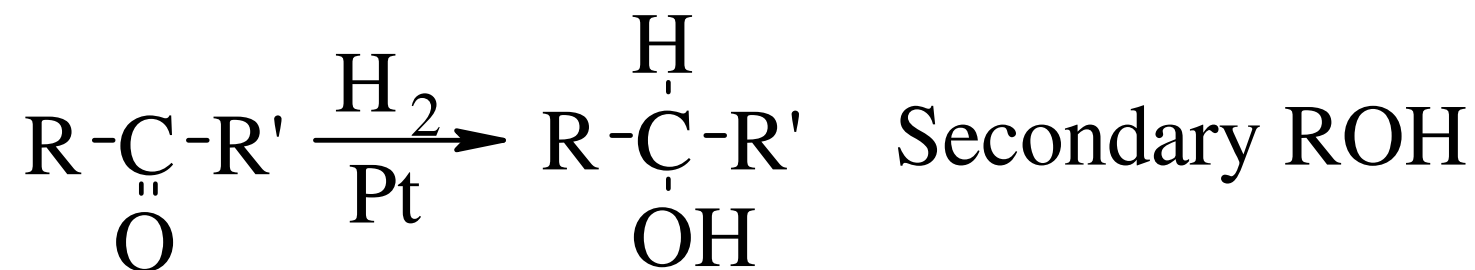
 Properties

Preparation Reactions

- 👍 Reduction of carbonyl compounds
- 👍 Reduction of Carboxylic acids/Esters
- 👍 Hydration of Alkenes
- 👍 Grignard reactions

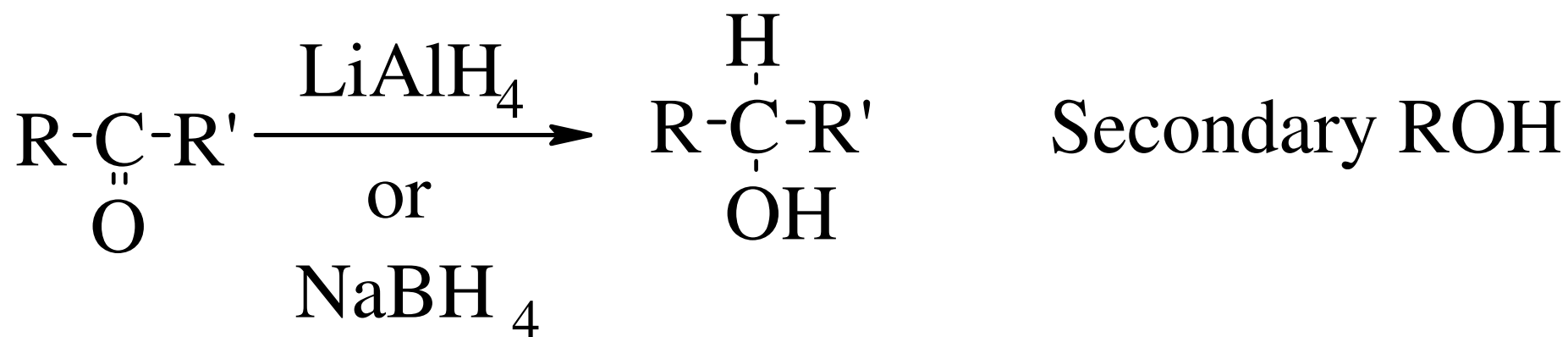
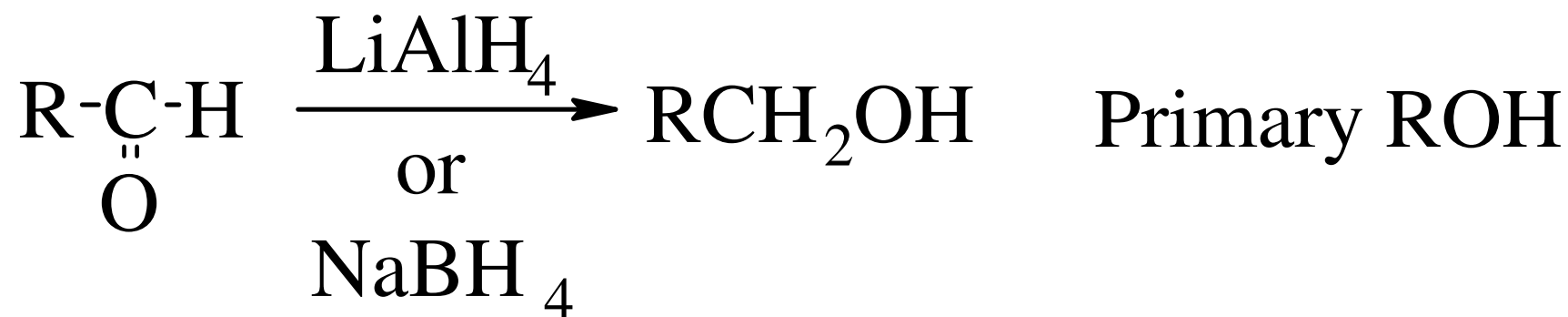
Reduction of Aldehydes/Ketones

Hydrogenation



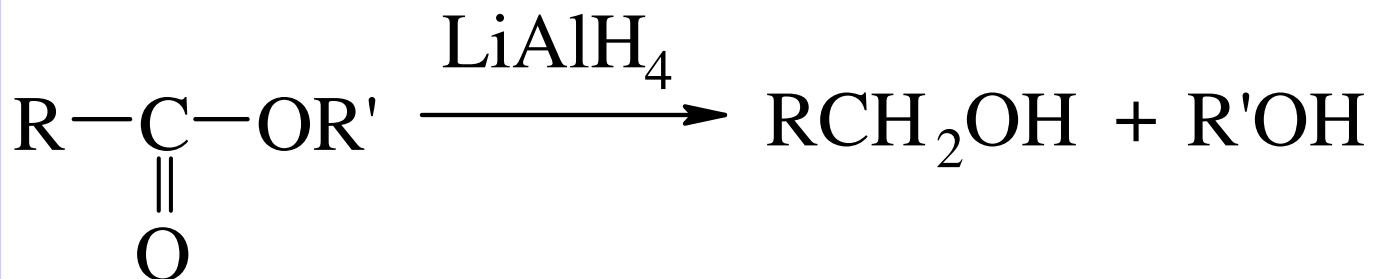
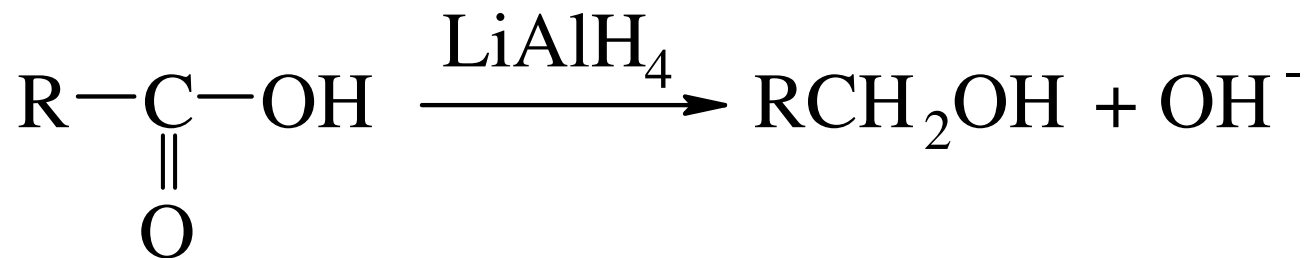
Reduction of Aldehydes/Ketones

Hydride Reductions



Reduction of Carboxylic Acids and Esters

Lithium Aluminum Hydride Reduction

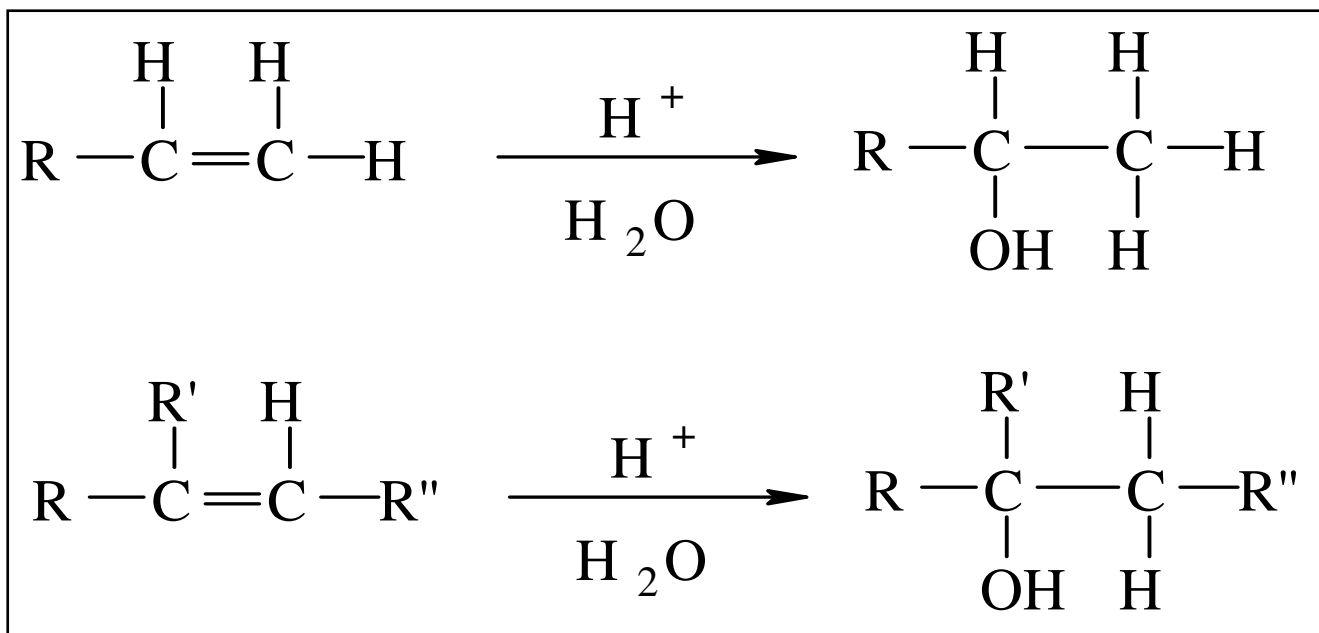


Hydration of Alkenes

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

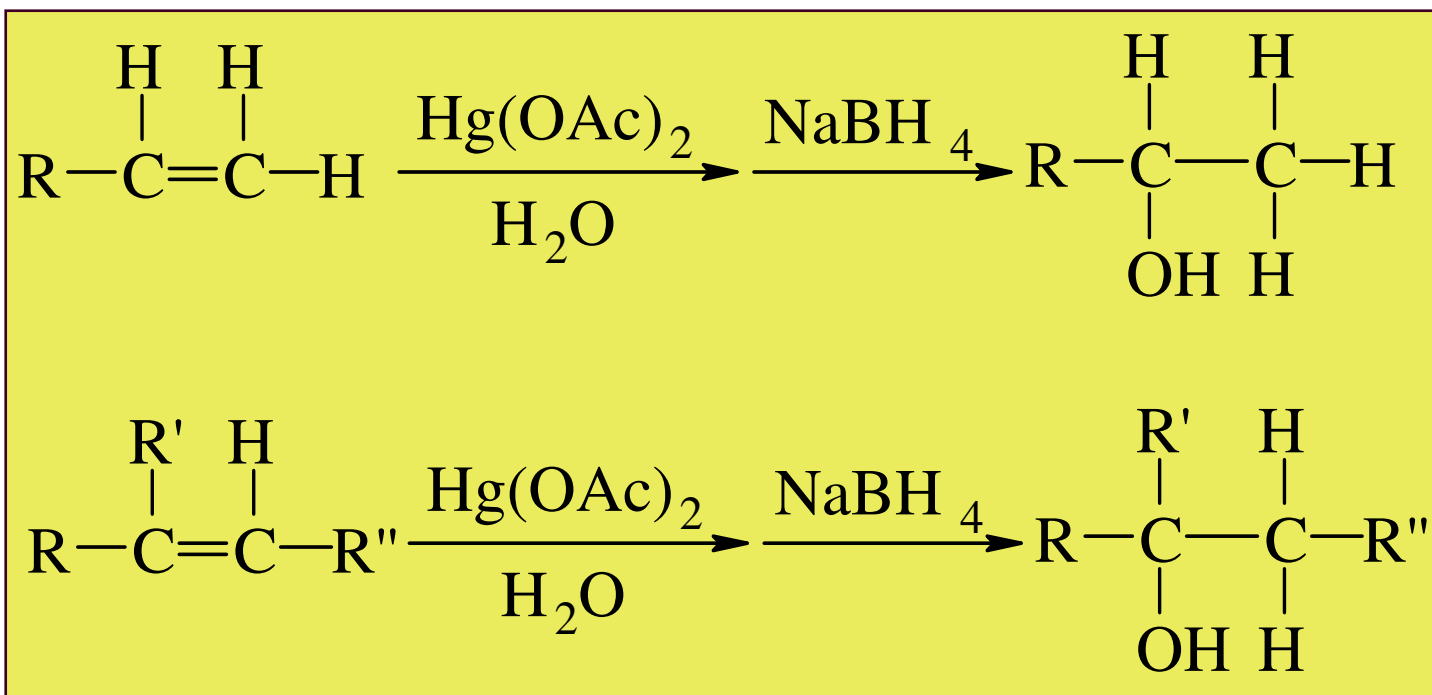
Acid-Catalyzed Hydration of Alkenes

- ✍ 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

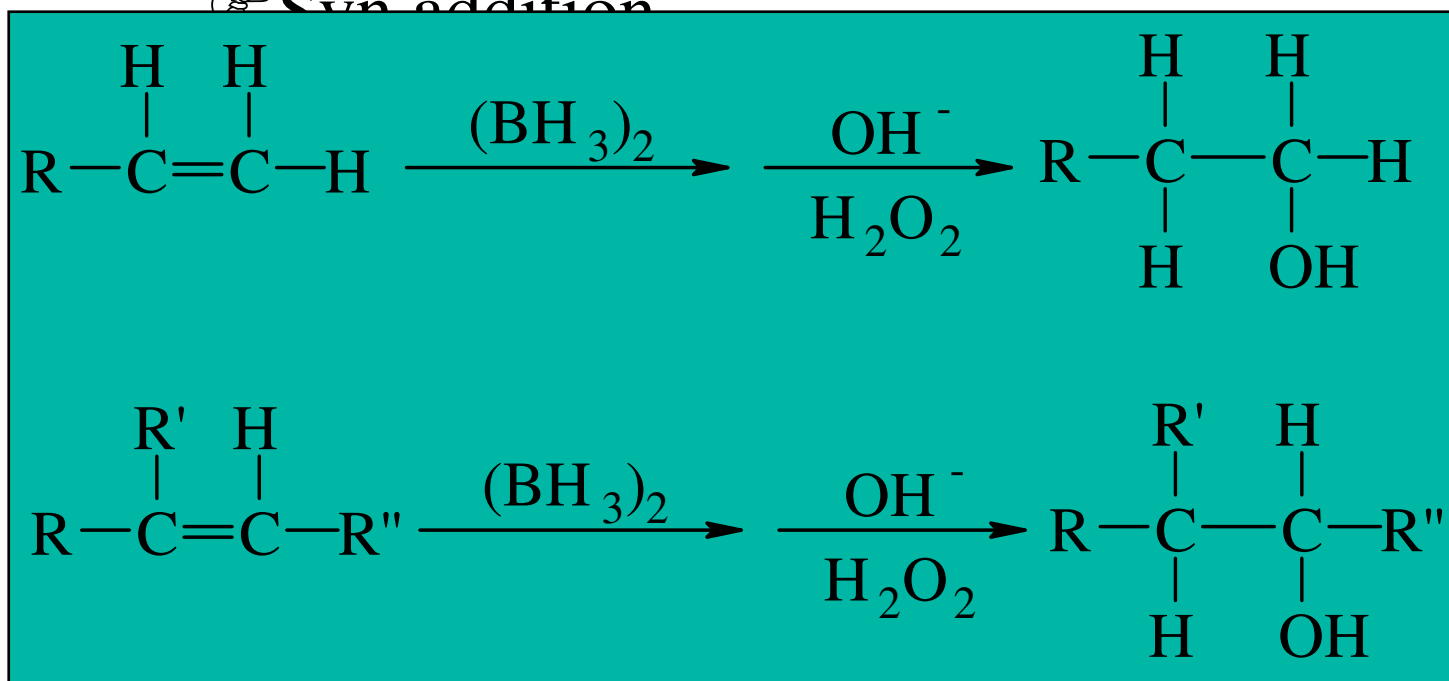


Hydroboration-Oxidation of Alkenes

☞ Anti-Markovnikov addition

☞ No shifts/rearrangements

☞ Syn addition

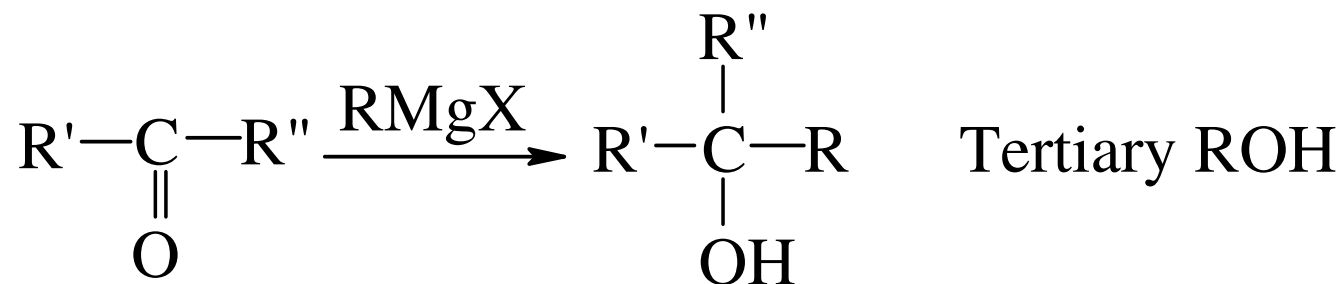
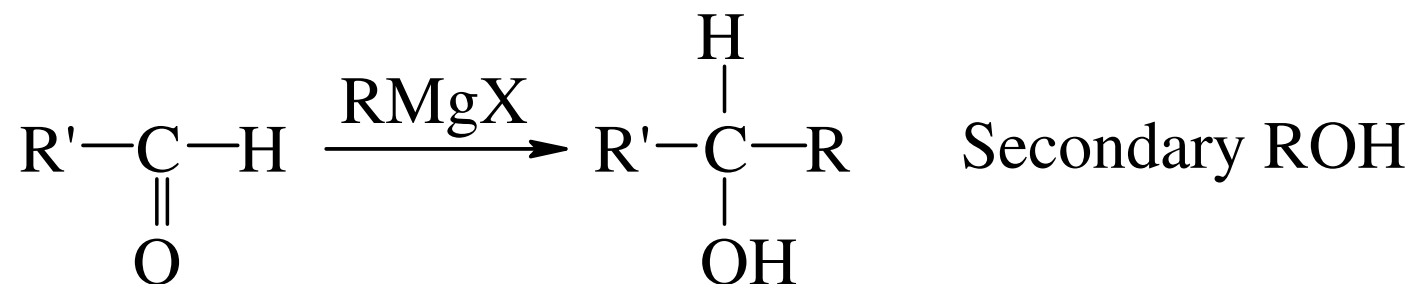
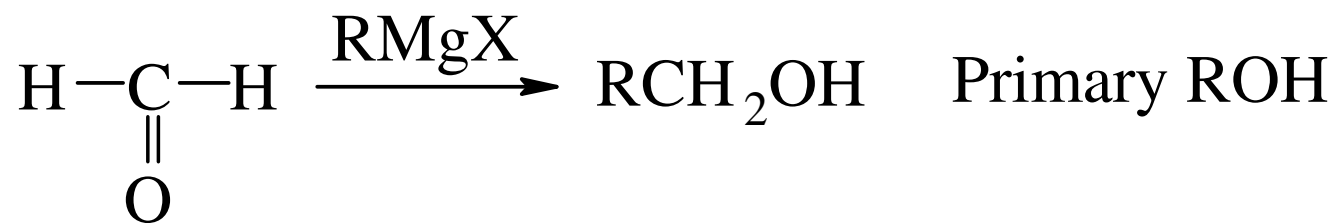


Grignard Addition Reactions

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

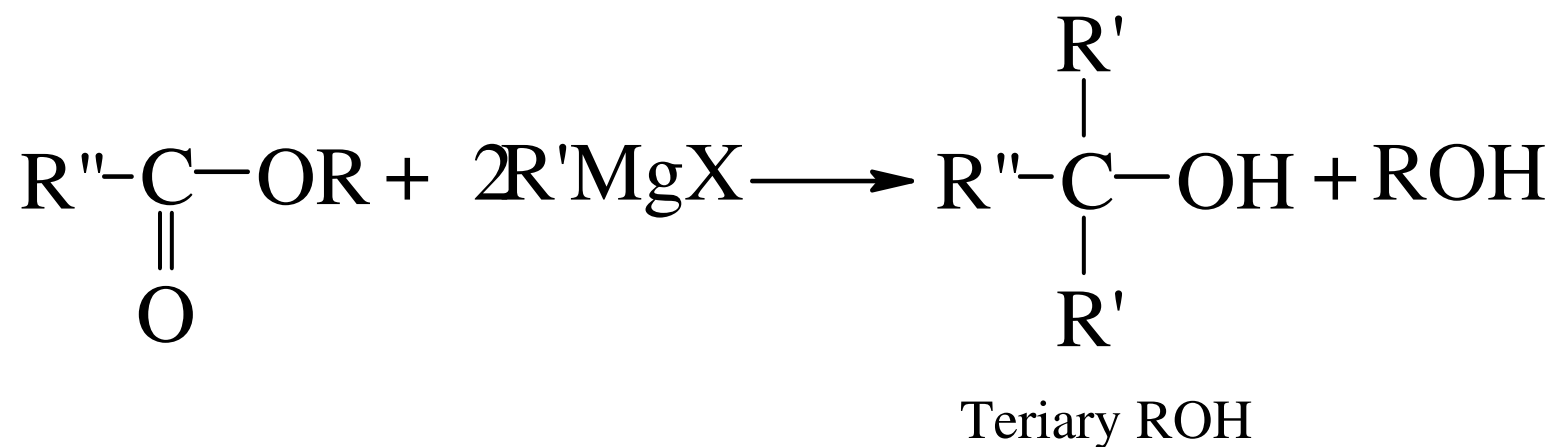
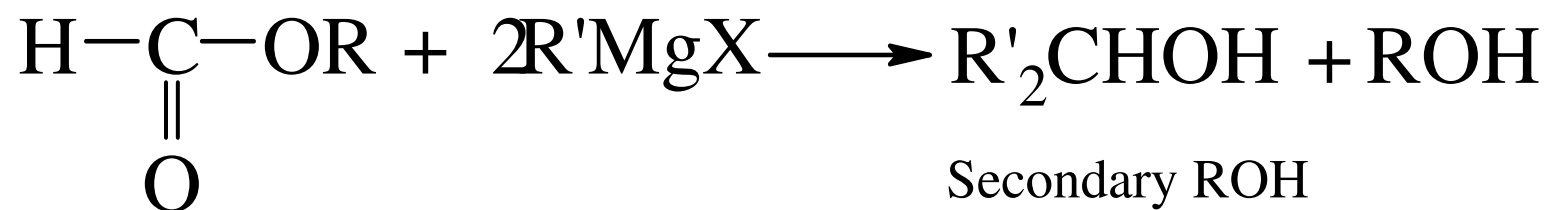
Grignard Additions to Aldehydes/Ketones

Formation of primary, secondary, and tertiary alcohols

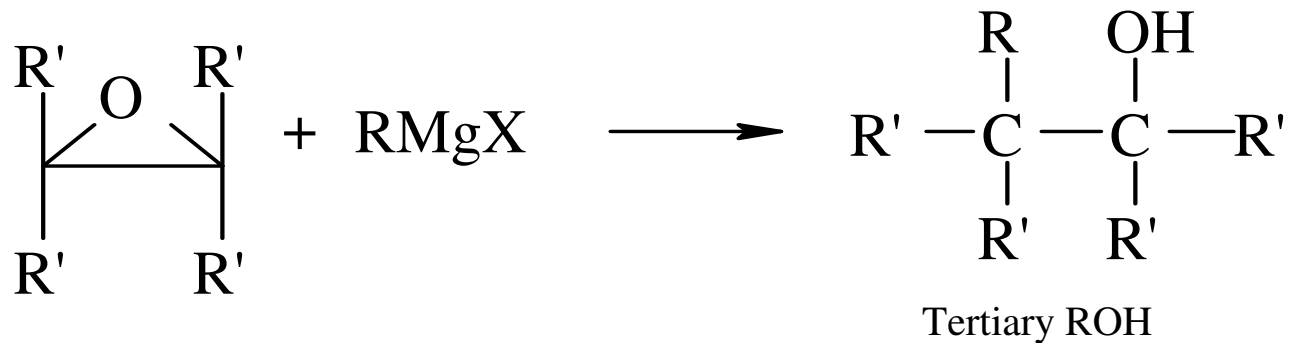
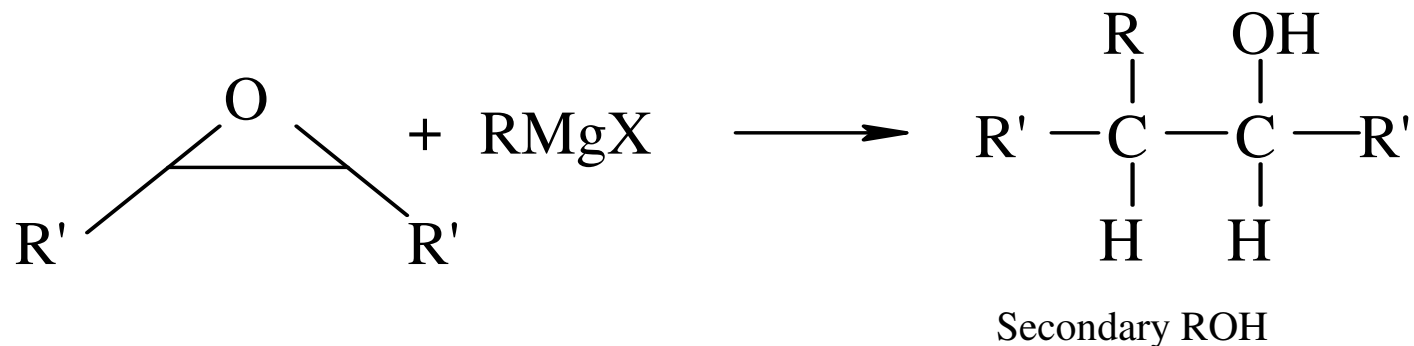
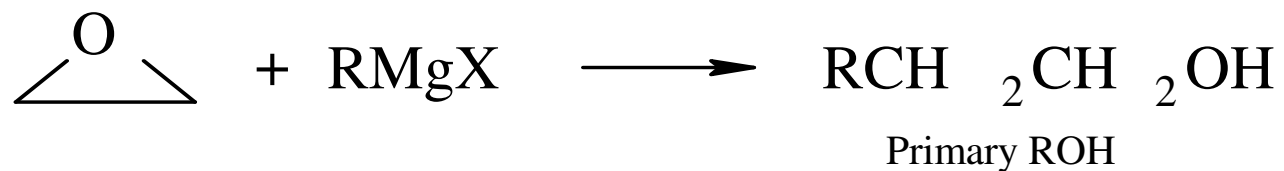


Grignard Additions to Esters

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

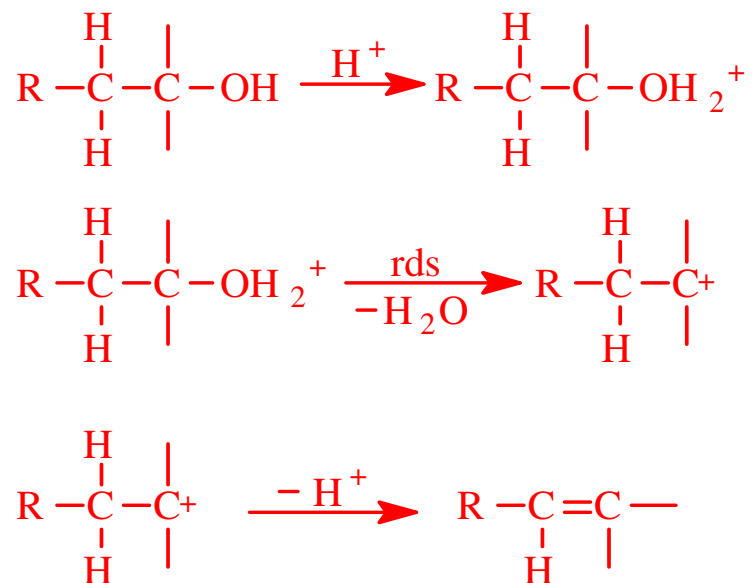
Conversion of Alcohols to Salts

Reaction with Active Metals



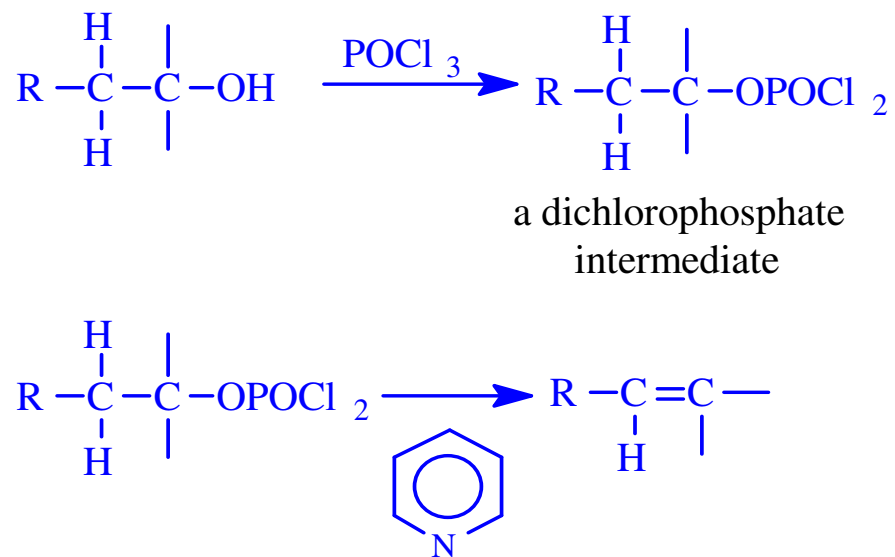
Dehydration of Alcohols

E-1



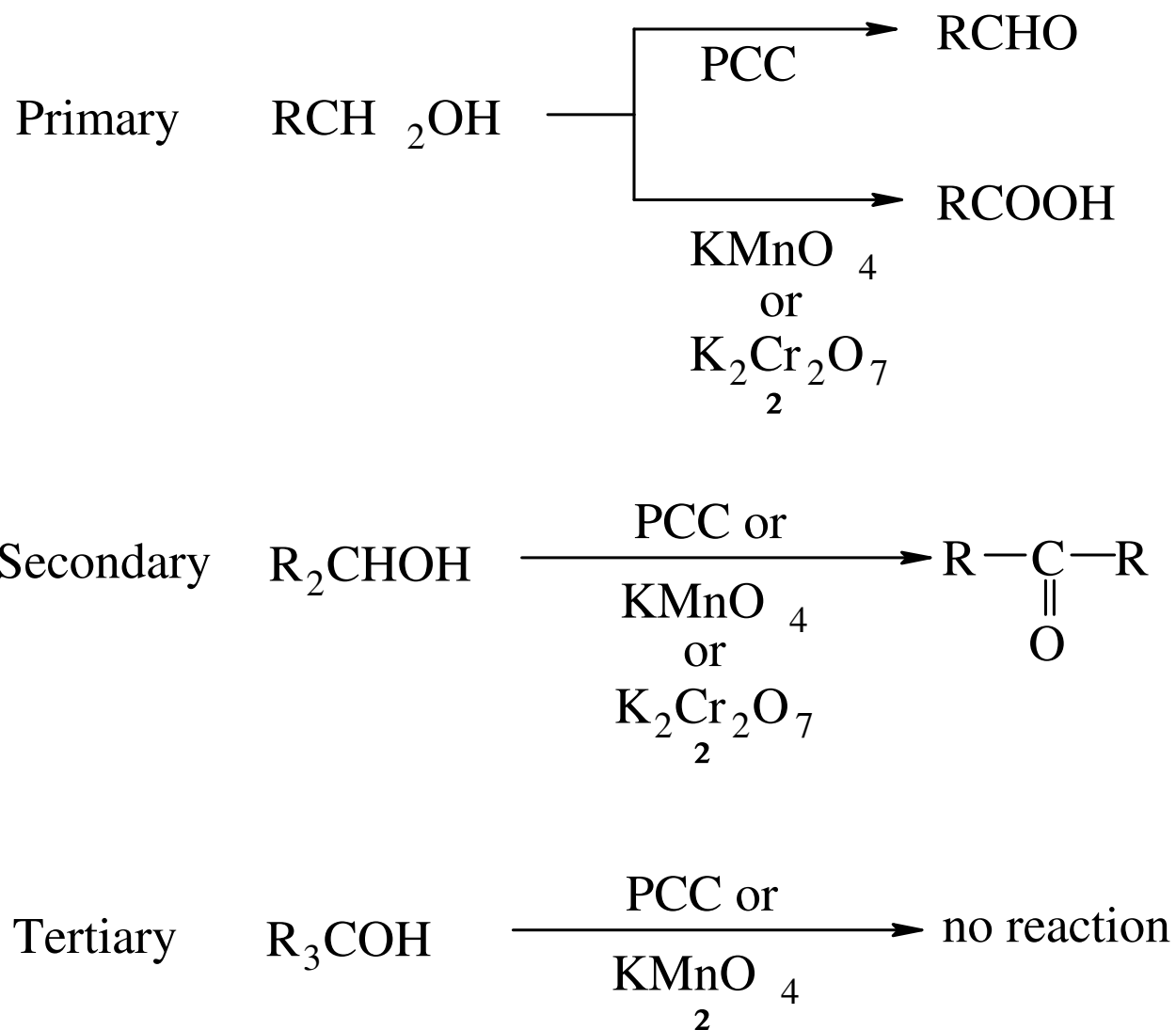
1,2-shifts/rearrangements possible

E-2



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

Oxidation of Alcohols



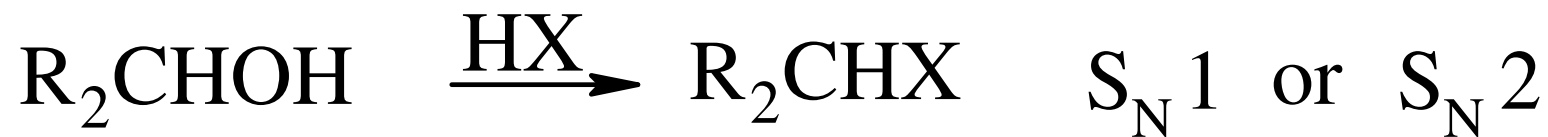
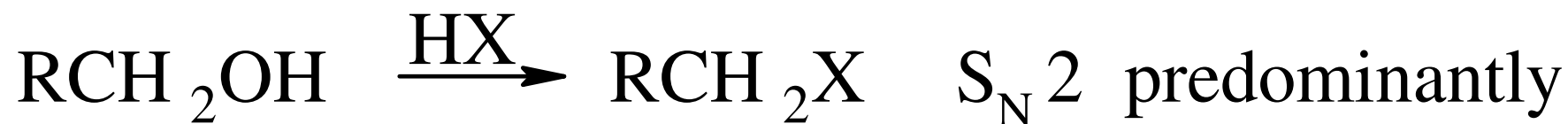
Alcohol Conversion to Alkyl Halides

⌘ **Reaction with Hydrogen halides**

⌘ **Reaction with Thionyl chloride**

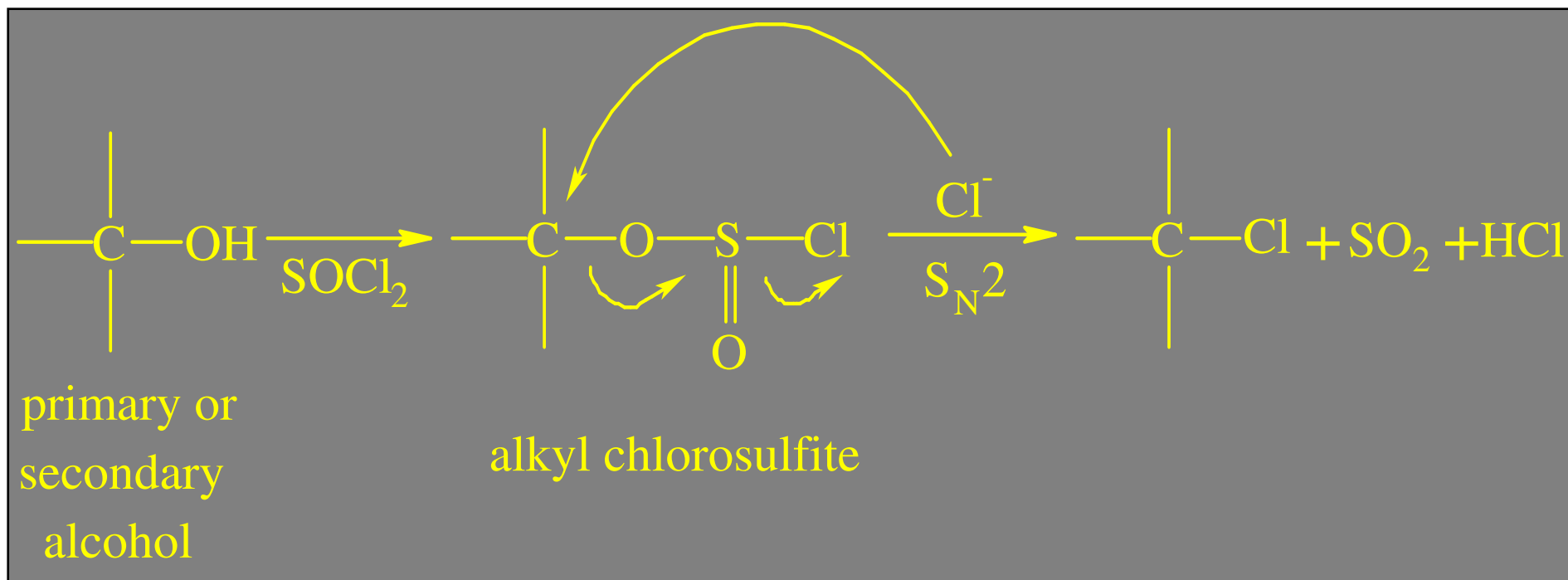
⌘ **Reaction with Phosphorus trihalides or pentahalides**

Hydrogen Halide Conversion of Alcohols to Alkyl Halides

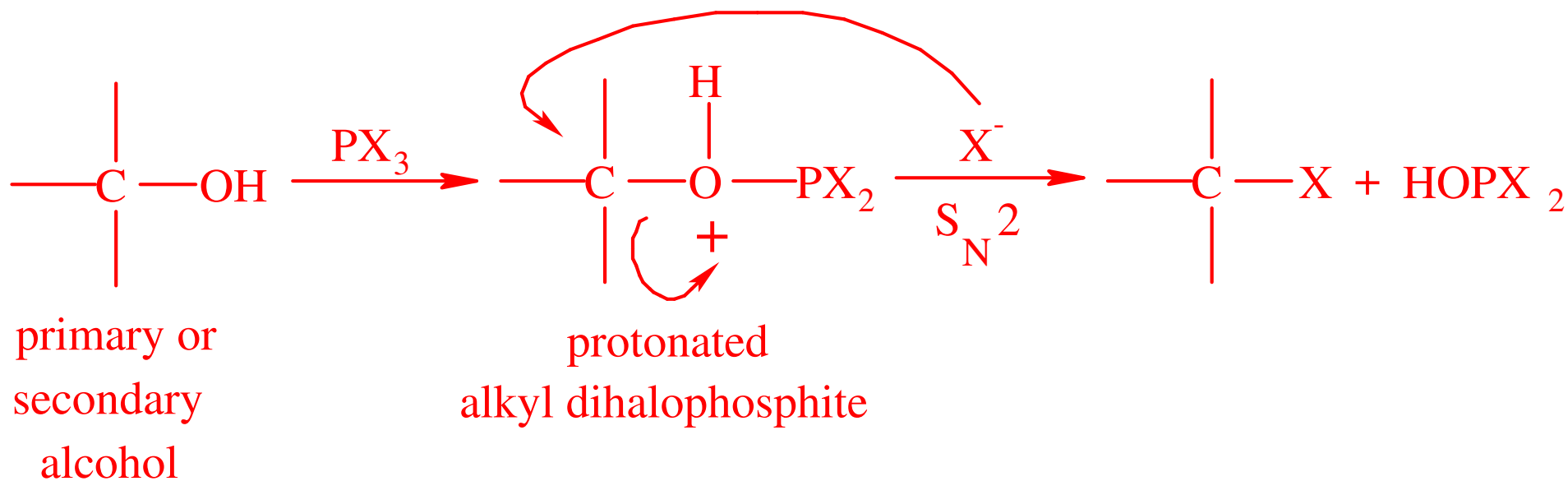


where HX = HI, HBr, or HCl

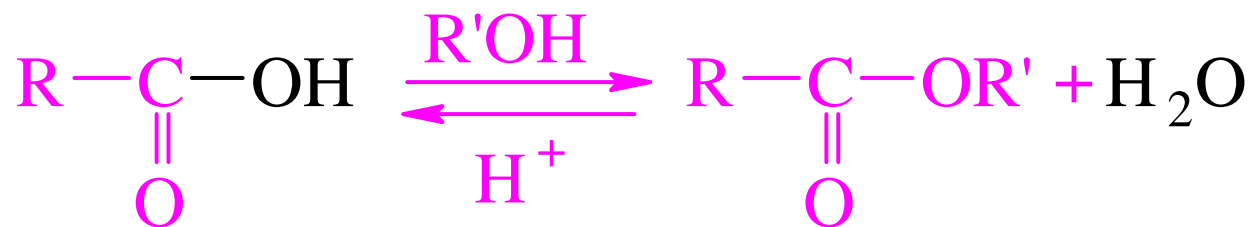
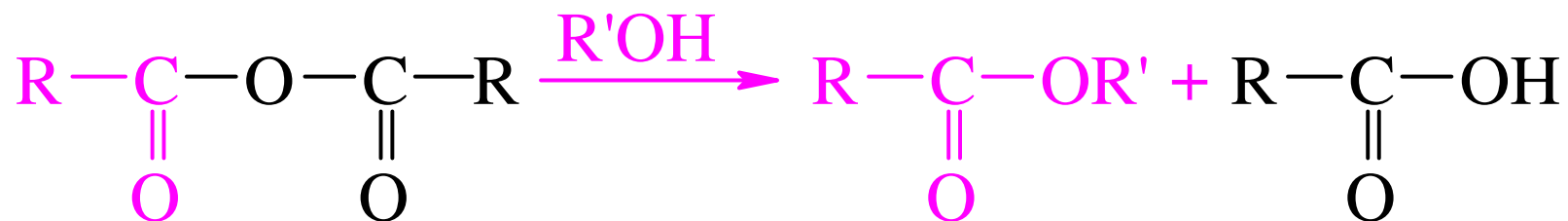
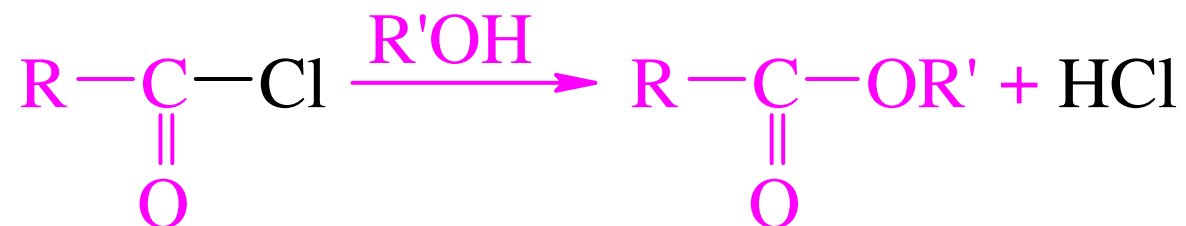
Conversion of Alcohols to Alkyl Chlorides via Thionyl Chloride



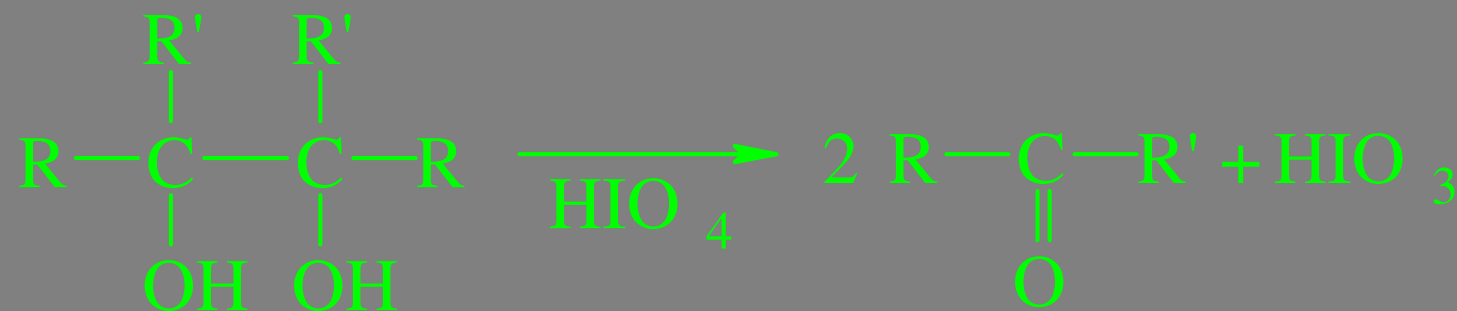
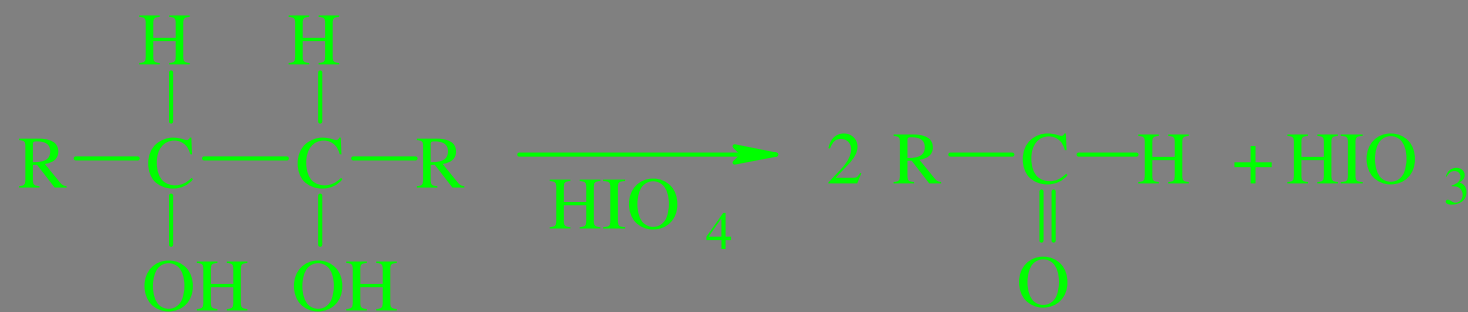
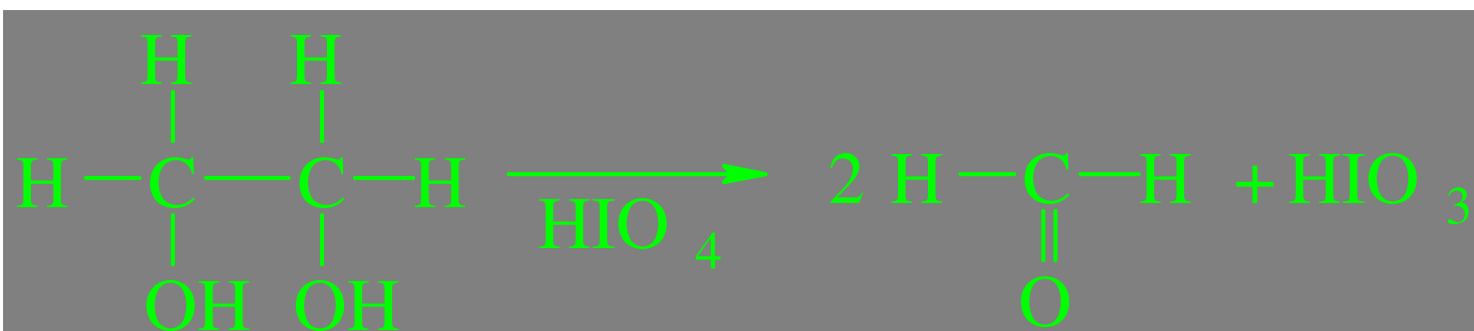
Conversion of Alcohols to Alkyl Halides via Phosphorus Halides



Ester Formation from Alcohols

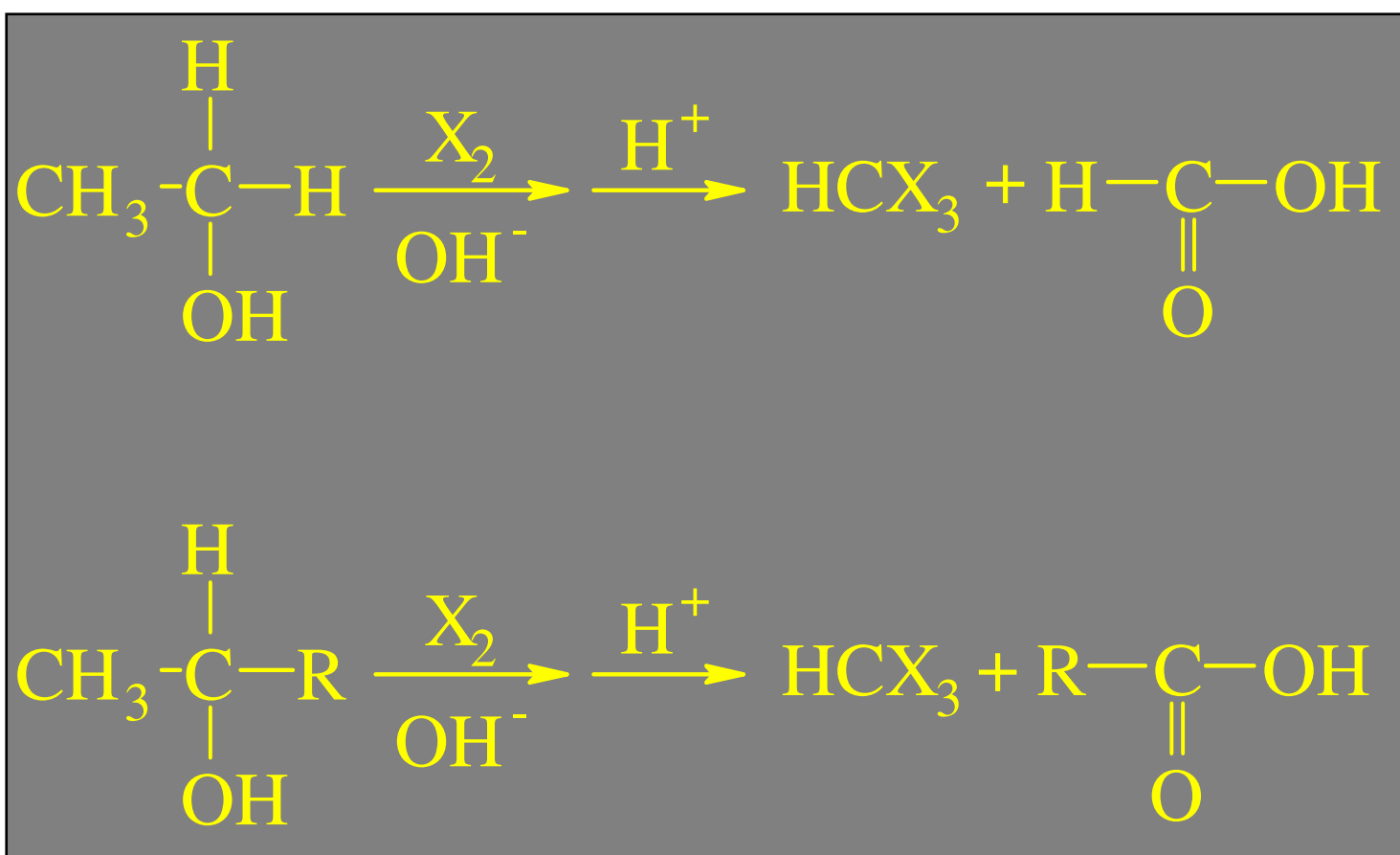


Periodic Acid Cleavage of Glycols



Haloform Reaction

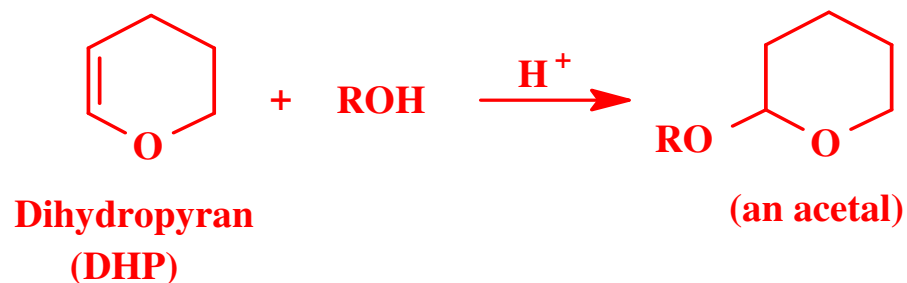
**Methyl carbinol cleavage to give
Carboxylic acids and Haloform**



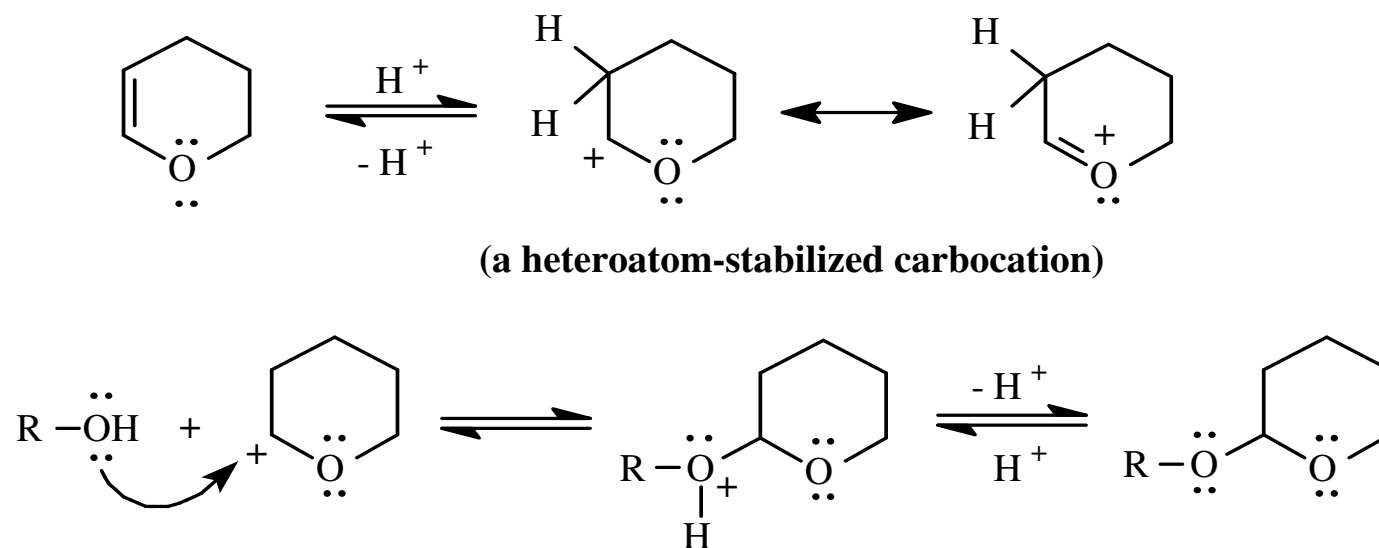
Disguising an Alcohol

Creating a tetrahydropyranyl acetal

Overall Transformation



Mechanism



Ethers



Nomenclature



Properties



Preparation



Reactions

Preparation of Ethers

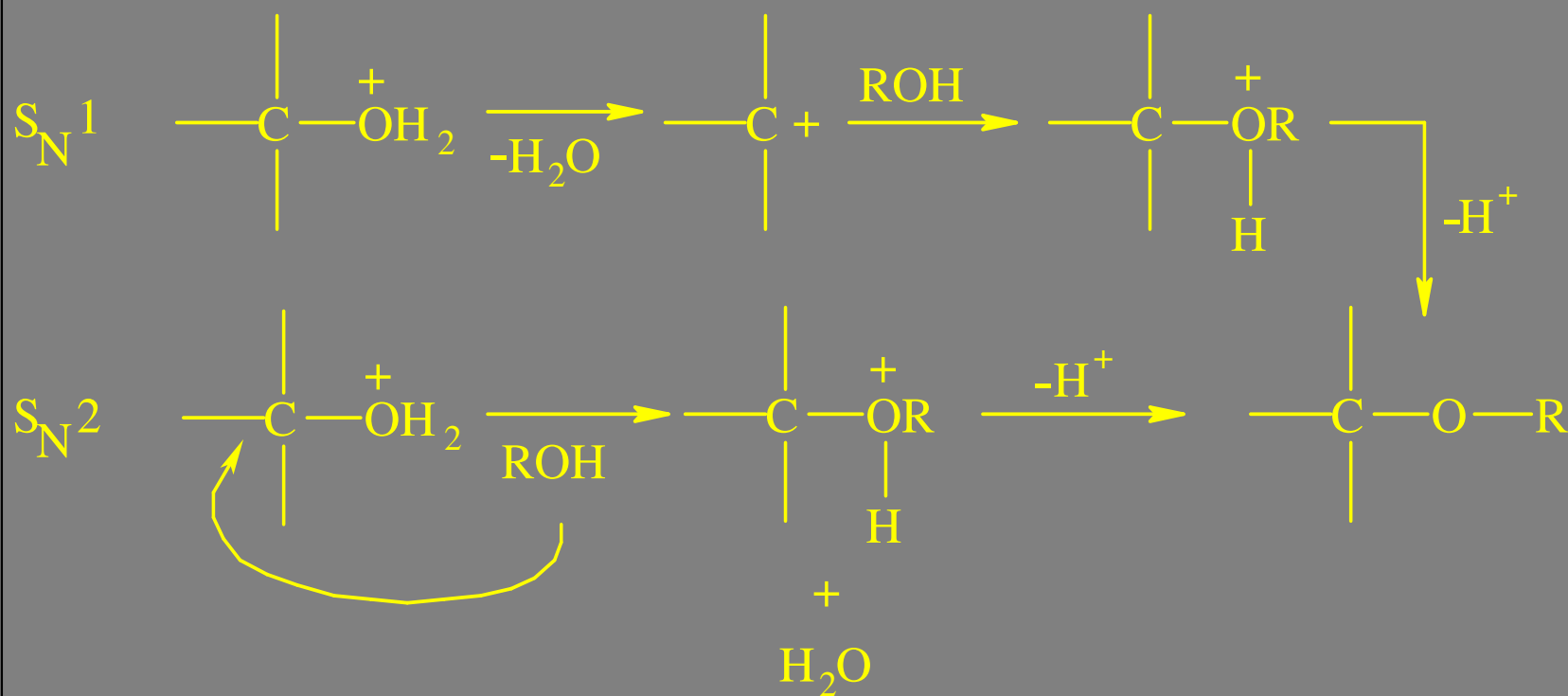
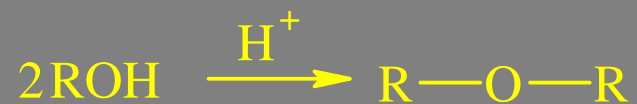
Dehydration of Alcohols

Williamson synthesis

Alkoxymercuration- Demercuration

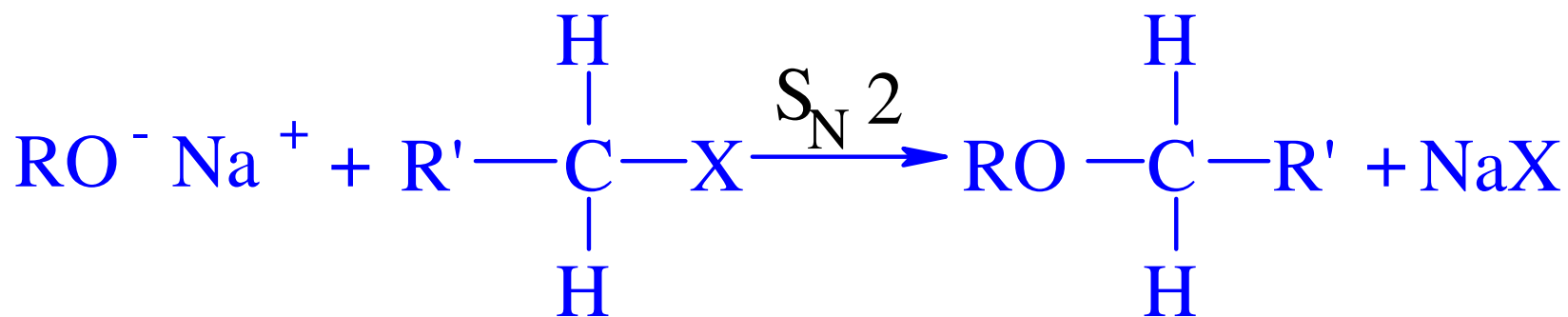
Peroxyacid Epoxidation of Alkenes

Ether Formation via Acid Catalyzed Dehydration of Alcohols



Williamson Synthesis of Ethers

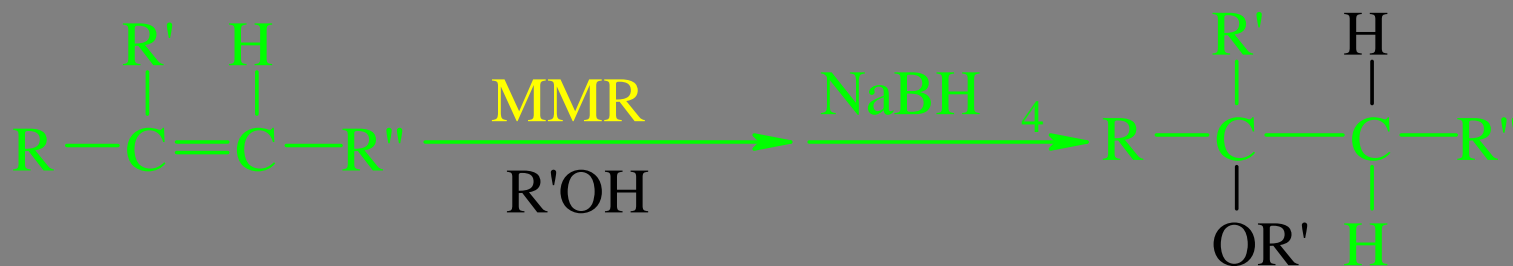
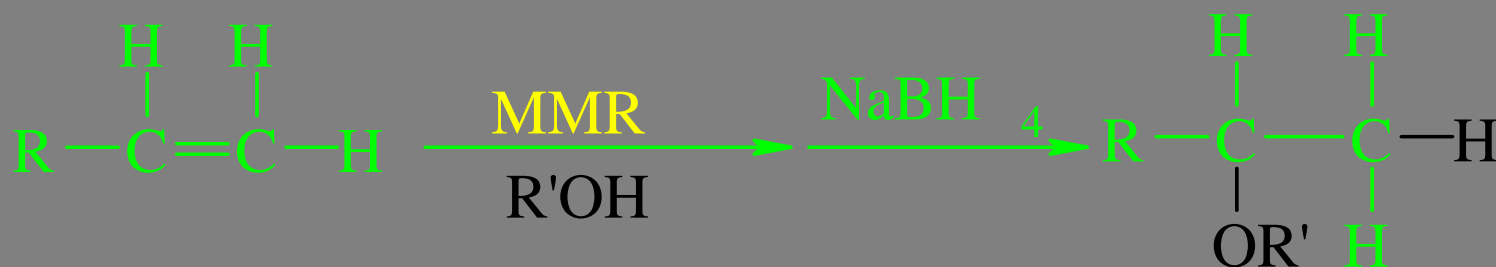
Bimolecular Substitution by Alkoxide on a suitable substrate



Primary
Alkyl Halide

Alkoxymercuration-Demercuration of Alkenes

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

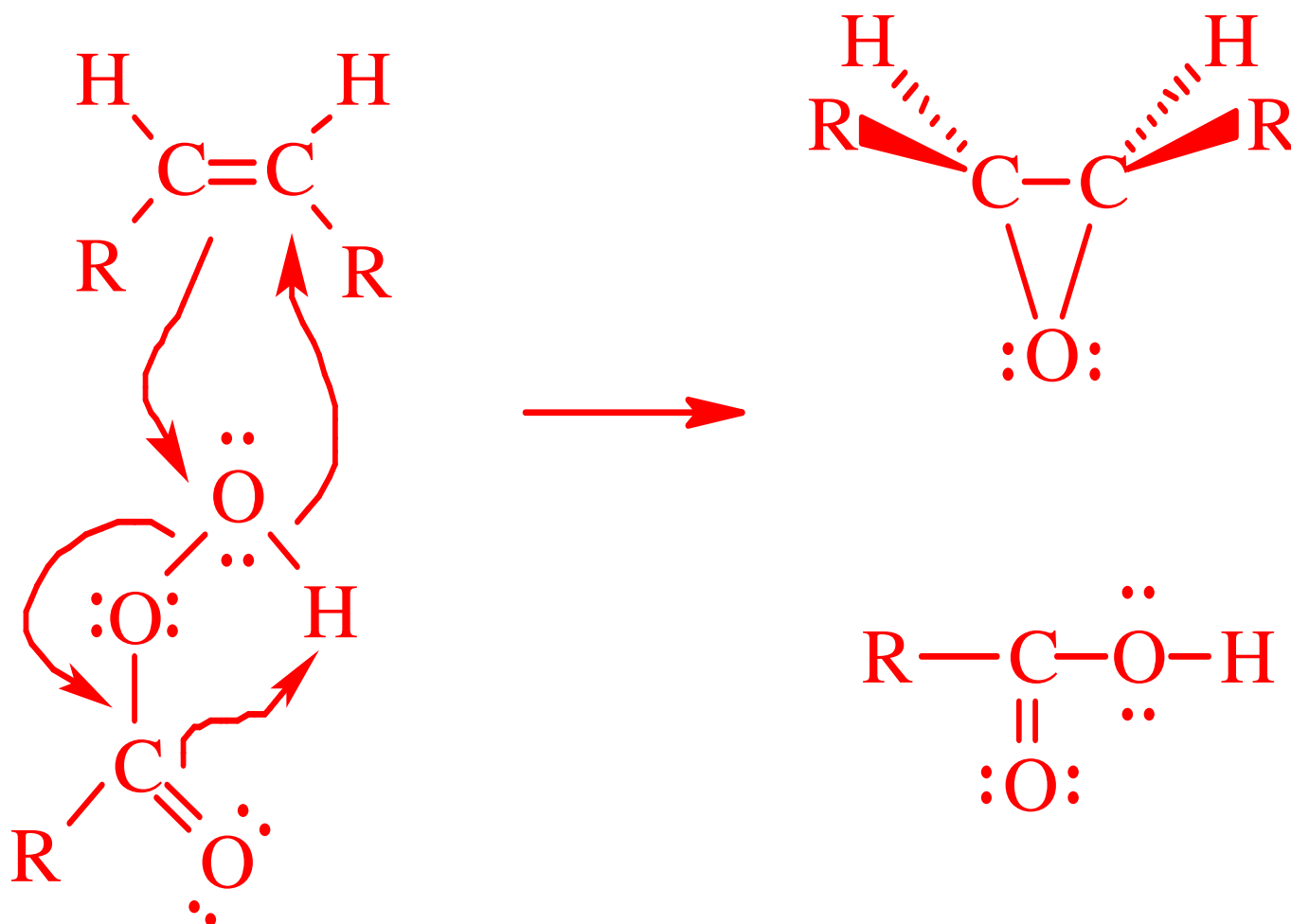


Where MMR = modified mercury reagent

= Mercury trifluoroacetate

Epoxidation of Alkenes

Prilezhaev reaction



Ether Reactions



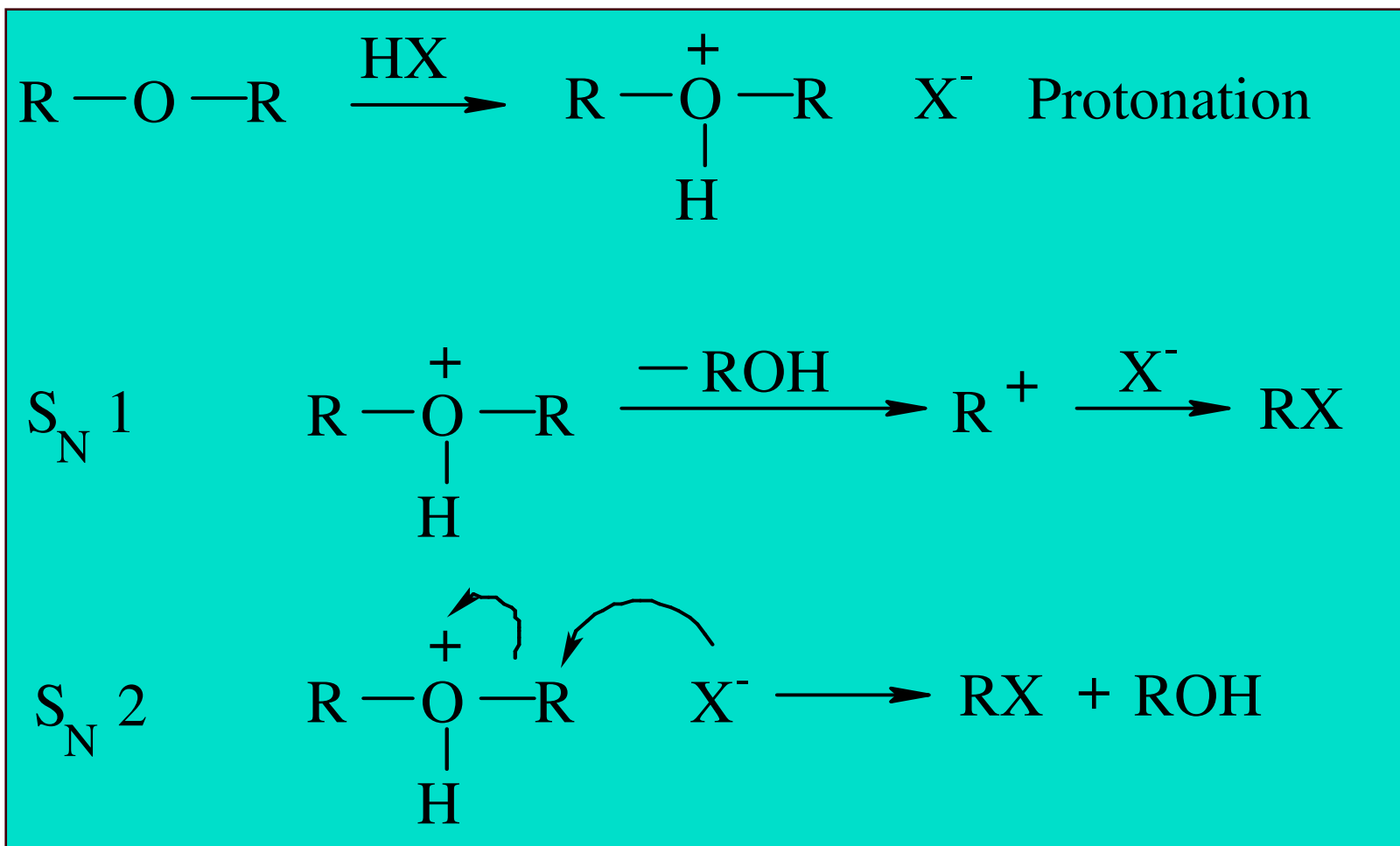
HX Cleavage



Epoxide Ring Opening

HX Cleavage of Ethers

Unimolecular or Bimolecular Cleavage Pathways



Epoxide Ring Opening

Unimolecular or Bimolecular

