

C. Alkynes

Physical Properties

- Alkynes resemble alkanes and alkenes in their physical properties: low density and low water-solubility
- They are slightly more polar and generally have slightly higher boiling points than the corresponding alkanes and alkenes.
- Terminal alkynes are more acidic than alkenes and alkanes.

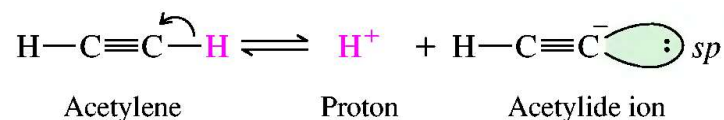
Table 8.1 Acidity of Simple Hydrocarbons			
Family	Example	K_a	pK_a
Alkyne	$\text{HC}\equiv\text{CH}$	10^{-25}	25
Alkene	$\text{H}_2\text{C}=\text{CH}_2$	10^{-44}	44
Alkane	CH_4	10^{-60}	60

Stronger acid

↑

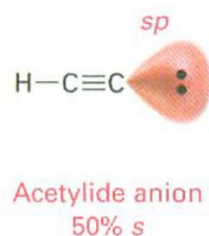
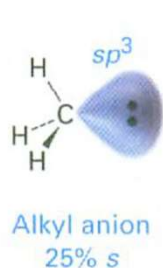
Weaker acid

Why Terminal alkynes are more acidic than alkenes and alkanes? In other words, why are acetylide anions more stable than vinylic or alkyl anions?

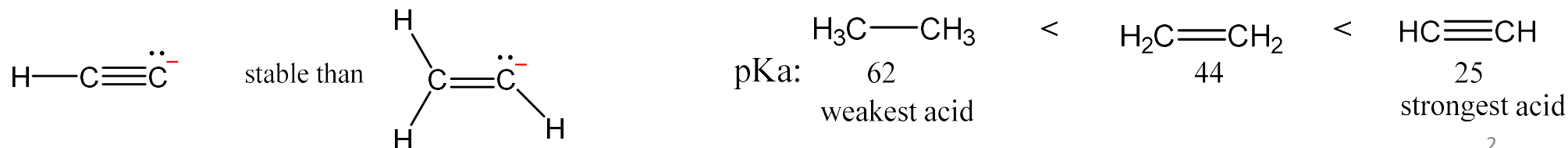


The simplest explanation involves the hybridization of the negatively charged carbon atom.

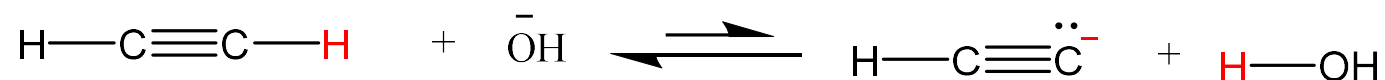
An acetylide anion has an sp -hybridized carbon, so the negative charge resides in an orbital that has 50 % s character.



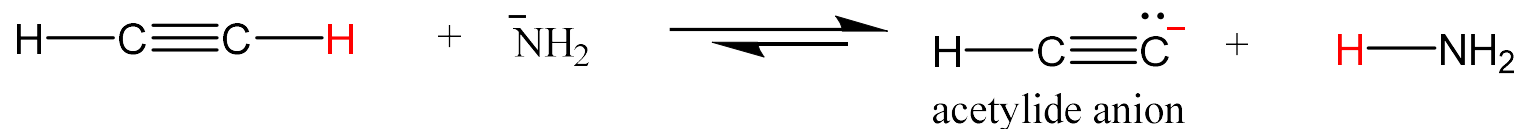
Because s orbitals are nearer to the positive nucleus and lower in energy than p orbitals, the negative charge is stabilized to a greater extent in an orbital with higher s character.



- Although acetylene and terminal alkynes are far stronger acids than other hydrocarbons, they are very weak acids-much weaker than water and alcohols, for example.
- Hydroxide ion is too weak a base to convert acetylene to its anion in meaningful amounts.

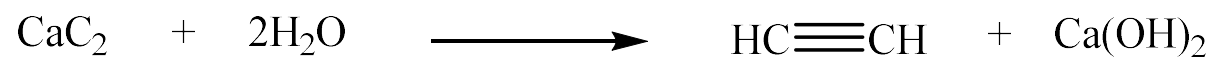


- *Amide* ion is a much stronger base than acetylide ion and converts acetylene to its conjugate base .



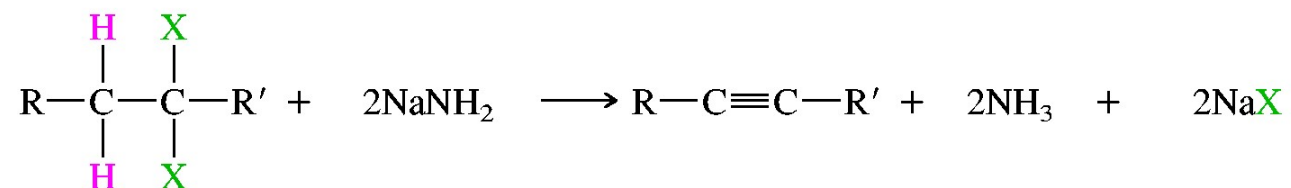
Preparation of Alkynes

A. Lab preparation of acetylene

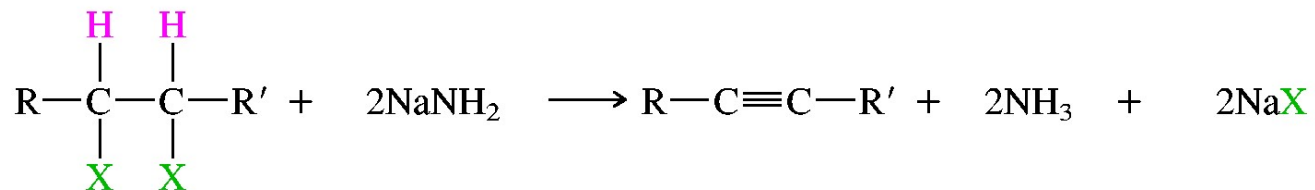


B. By Elimination Reactions

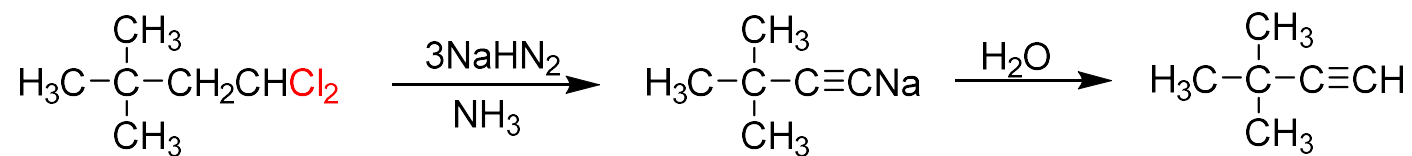
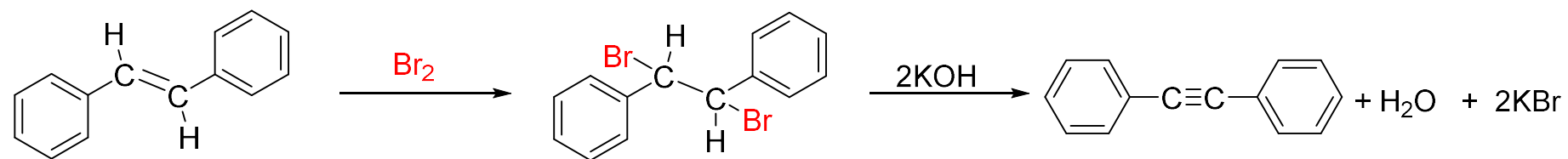
Double dehydrohalogenation of a geminal dihalide



Double dehydrohalogenation of a vicinal dihalide

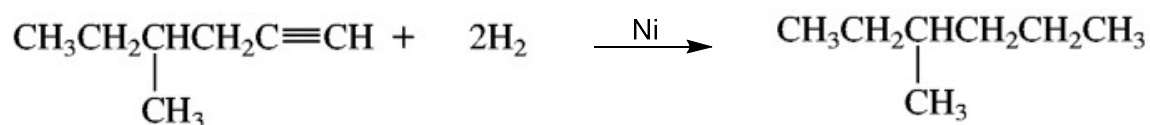
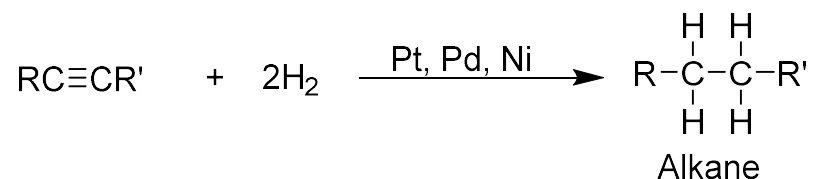


E.g



REACTIONS OF ALKYNES

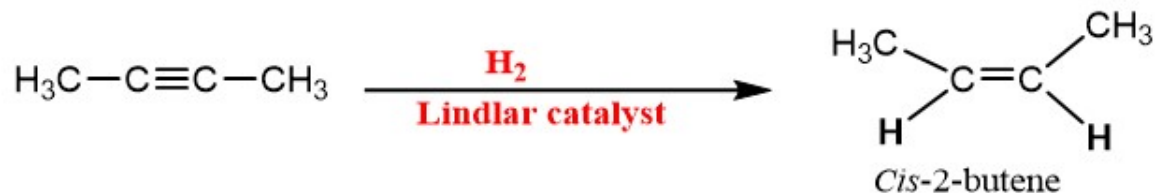
A . Hydrogenation of Alkynes



Partial hydrogenation of an alkyne to produce alkene could be achieved using Lindlar catalyst.

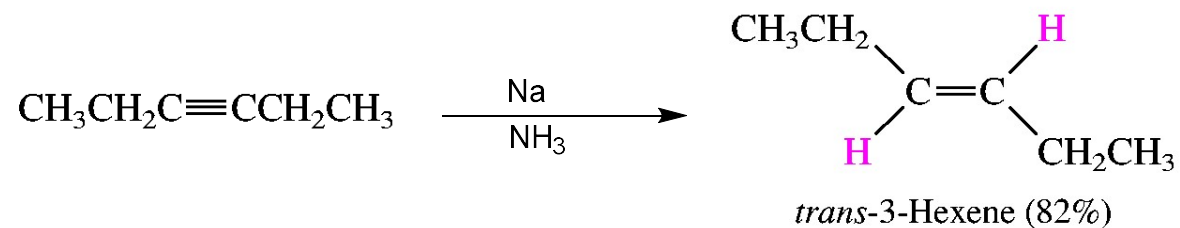
Lindlar catalyst = palladium on CaCO_3 combination to which lead acetate and quinoline have been added.

Hydrogenation of alkynes with internal triple bonds gives cis alkenes



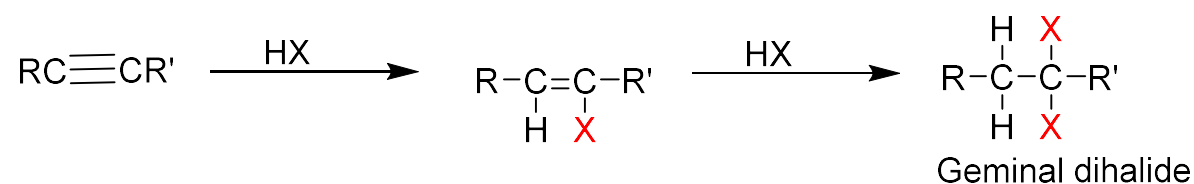
B. Metal-ammonia reduction of alkynes

- A useful alternative to catalytic partial hydrogenation for converting alkynes to alkenes is reduction by a Group I metal (lithium, sodium, or potassium) in liquid ammonia.
- The unique feature of metal-ammonia reduction is that it converts alkynes to *trans* alkenes.

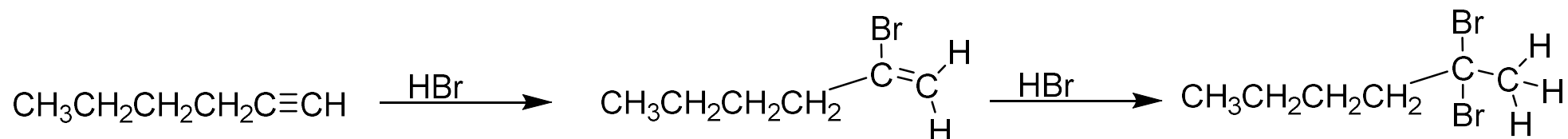


C. Addition of Hydrogen Halides (HX)

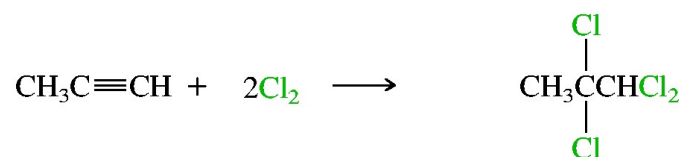
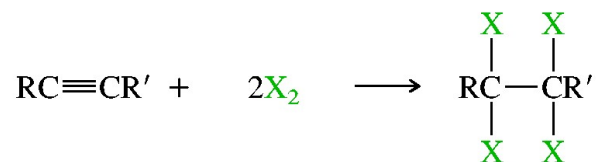
Reaction with an excess of HX lead to a dihalides product



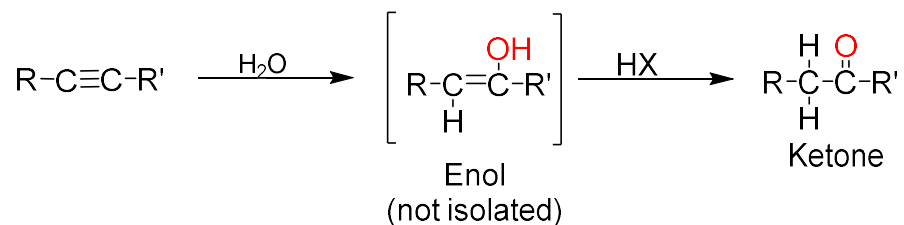
It follows Markovnikov's addition: halogen adds to more highly substituted side of the alkyne bond.



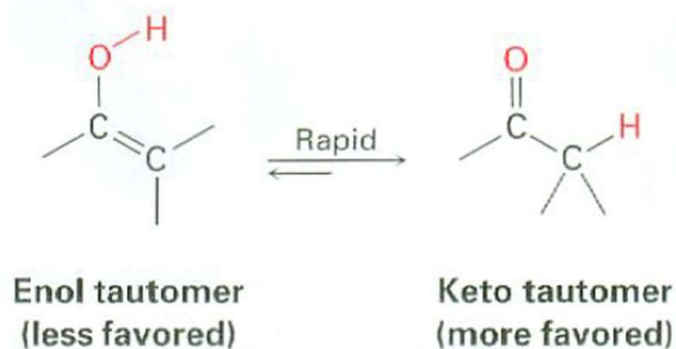
D. Addition of Halogens (X₂)



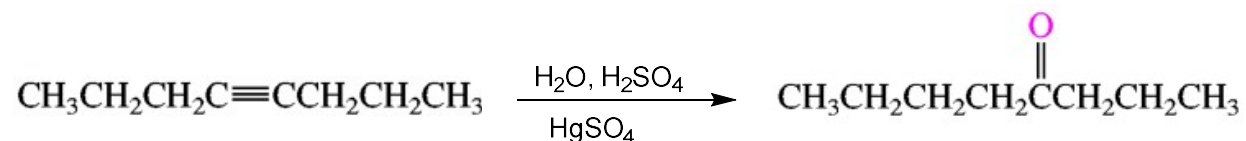
E. Hydration of Alkynes



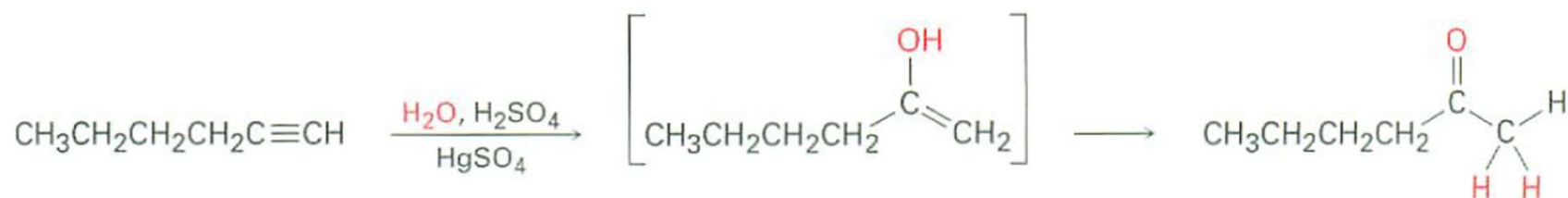
- The product actually isolated is a ketone, not the enol.
- Although the enol is an intermediate in the reaction, it immediately rearranges to a ketone by a keto-enol tautomerism
- Tautomers are constitutional isomers that equilibrate by migration of an atom or group, and their equilibration is called tautomerism.
- In general, ketones are more stable than their enol precursors.



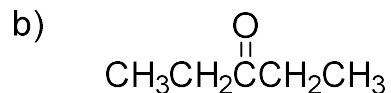
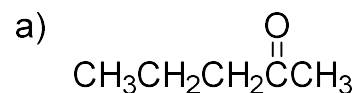
- Alkynes don't react directly with aqueous acid but will undergo hydration in the presence of mercury (II) sulfate as a Lewis acid catalyst.
- The reaction follows Markovnikov rule.



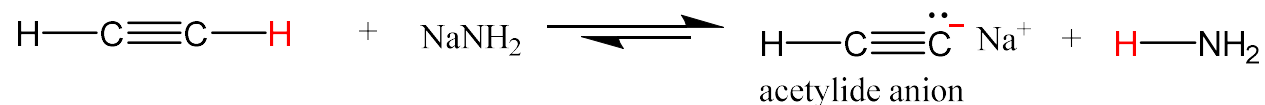
Terminal alkynes yield methyl substituted ketones.



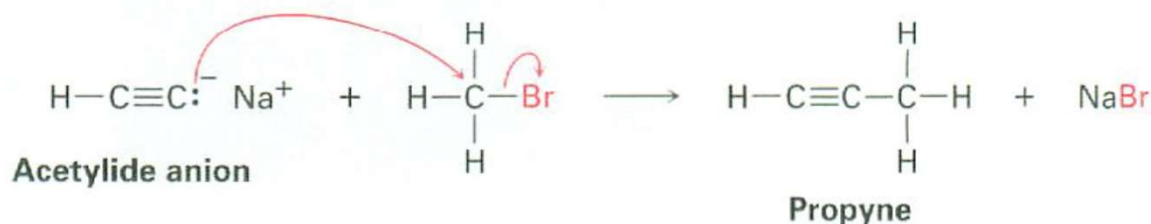
Ex. What alkynes would you start with to prepare the following ketones?



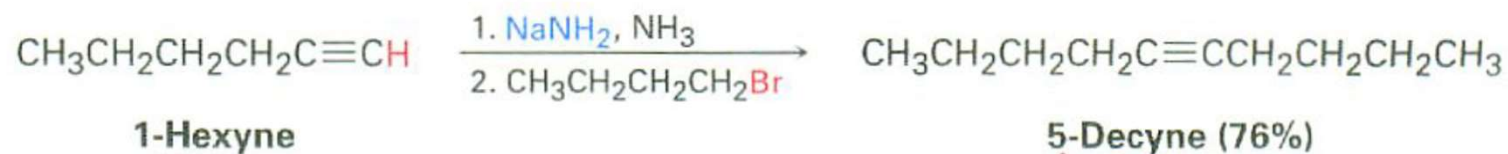
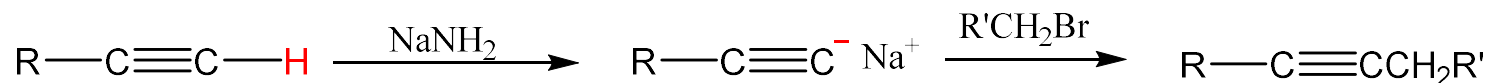
F. Alkylation of Alkynes



Acetylide anion can react with an alkyl halide to substitute for the halogen and yield a new alkyne product.

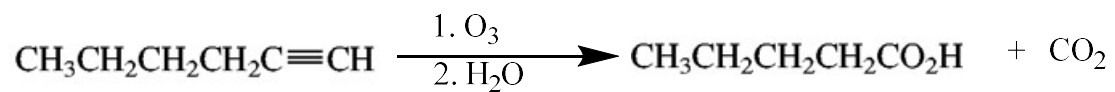
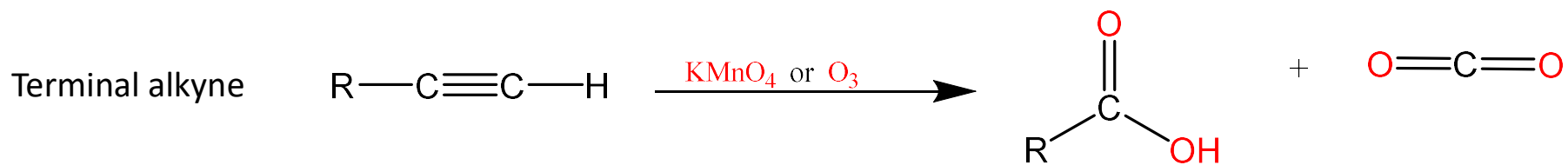
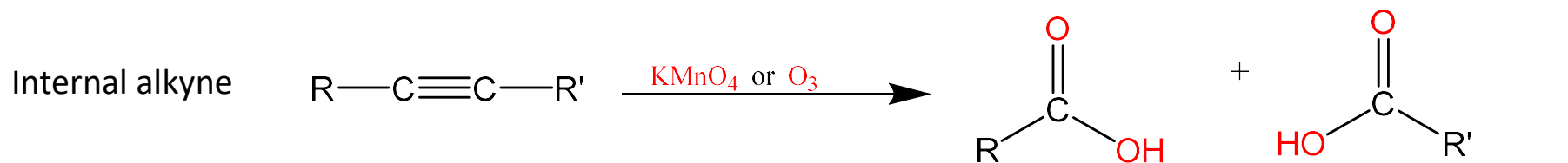


Any terminal alkyne can be alkylated by treatment with an alkyl halide, yielding an internal alkyne.



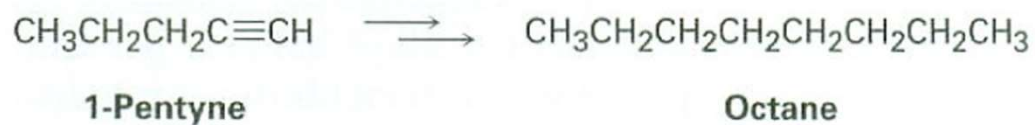
G. Oxidative cleavage of Alkynes

Alkynes, like alkenes, can be cleaved by reaction with powerful oxidizing agents such as O_3 or $KMnO_4$

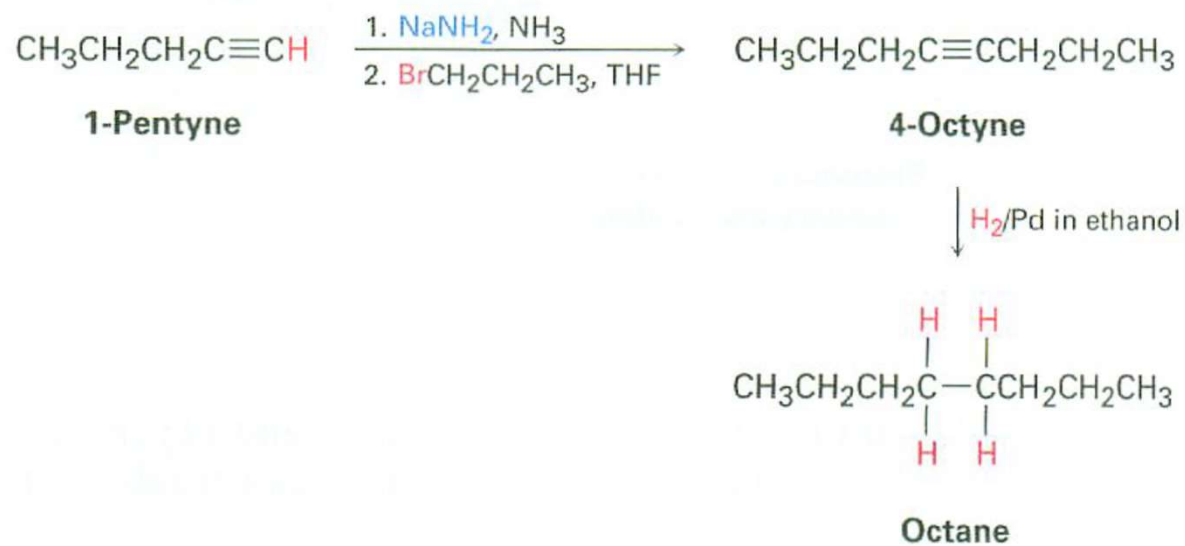


Devising a Synthesis Route

Prepare octane from 1-pentyne



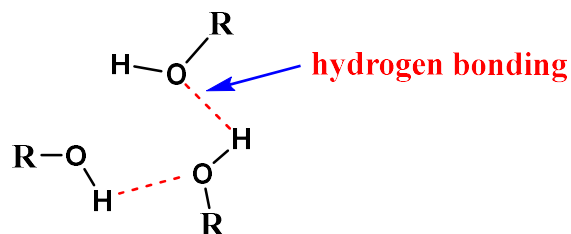
Solution:



D. Alcohols

- Most of the common alcohols are liquids at room temperature, the higher alcohols are somewhat viscous, and some of the highly branched isomers are solid at normal temperature

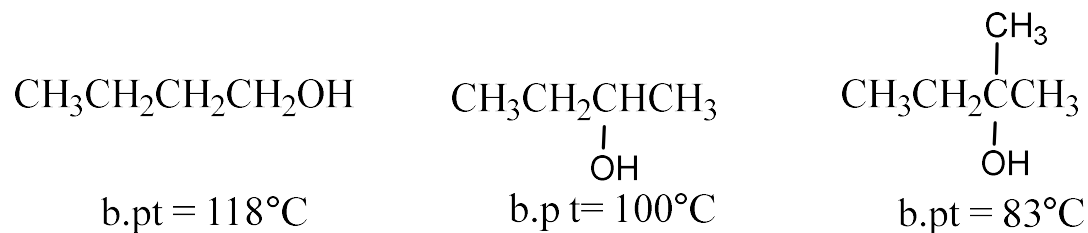
- Alcohols form hydrogen bonding



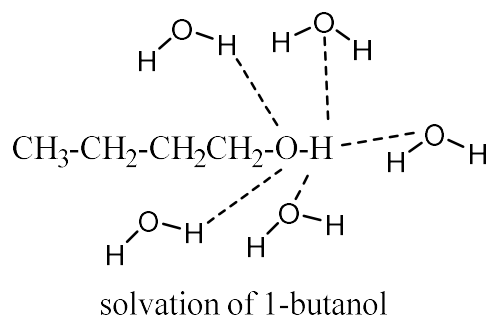
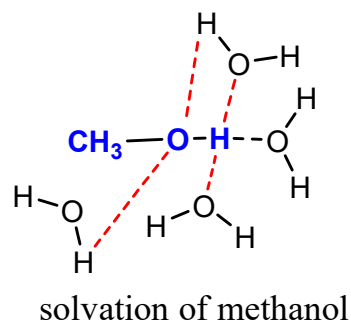
- The boiling points of alcohols are in general much higher than comparably sized hydrocarbon, alkyl halide, ethers and carbonyl compounds.

	Ethanol CH ₃ CH ₂ OH	Dimethylether CH ₃ —O—CH ₃	Propane CH ₃ CH ₂ CH ₃
Mol wt	46	46	44
b.pt	+ 78°C	-24°C	-42°C

- Branching tend to decrease the boiling point since a more symmetrical molecules have less Dispersion forces



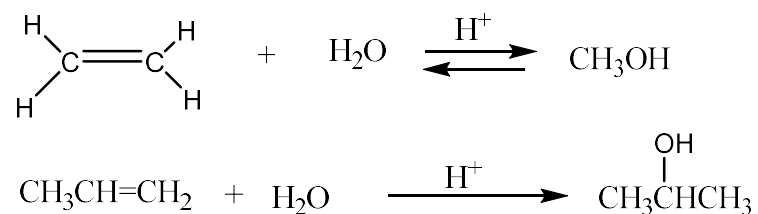
- Low molecular weight alcohols (methyl, ethyl, n-propyl, and isopropyl alcohol) are soluble in water in all proportions.
- With smaller molecules water can more easily surround the alcohol molecules effectively separating them from one another (solvation).



Preparation of alcohols

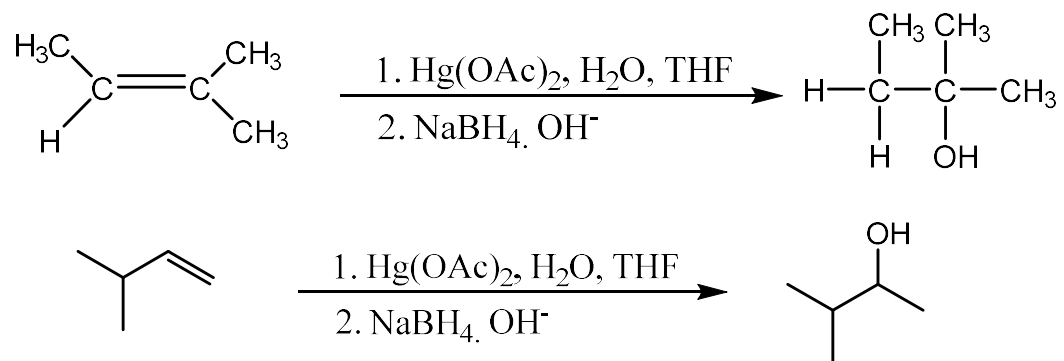
1. By Hydration of Alkenes

a. Acid Catalyzed Hydration of Alkenes



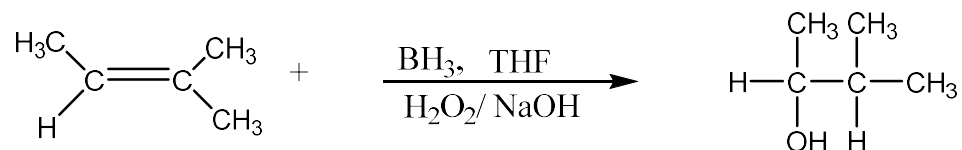
b. Oxymercuration-demercuration.

Alkenes add water in the presence mercury acetate, the reaction follow Markovnikov's rule.

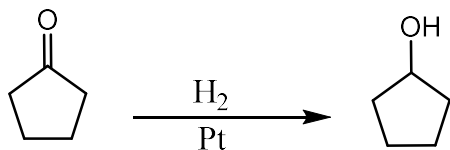
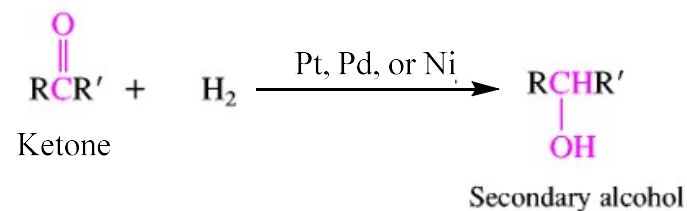
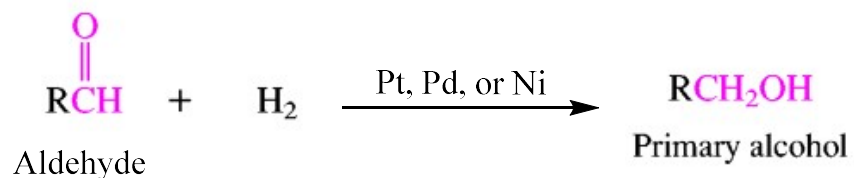


c. Hydroboration-oxidation

follows anti-Markovnikov rule

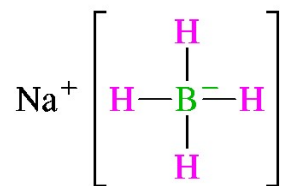


2. By Reduction of Aldehydes and ketones

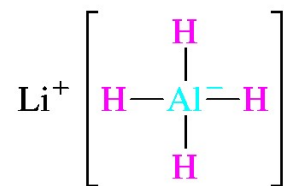


For most laboratory-scale reductions of aldehydes and ketones, catalytic hydrogenation has been replaced by methods based on metal hydride reducing agents.

The two most common reagents are sodium borohydride (NaBH_4) and lithium aluminum hydride (LiAlH_4).

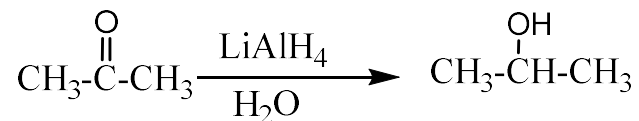
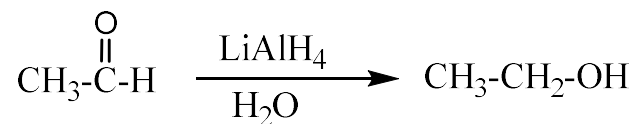


Sodium borohydride (NaBH_4)

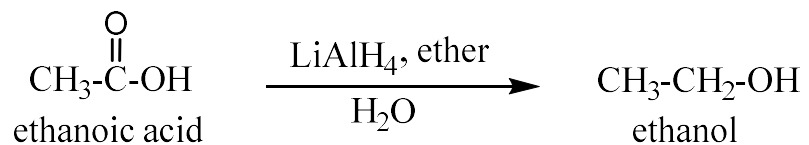


Lithium aluminum hydride (LiAlH_4)

E.g.

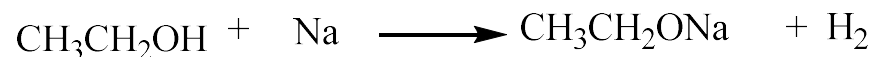


By Reduction of carboxylic acid and ester using lithium aluminum hydride (LiAlH_4)



Reaction of Alcohols

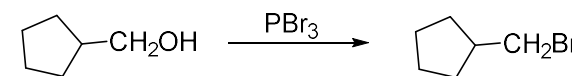
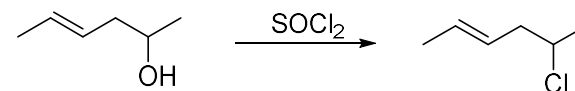
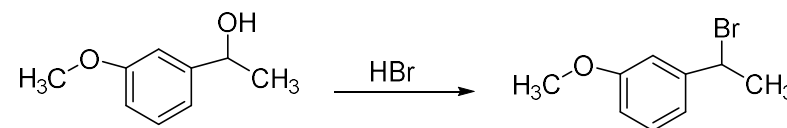
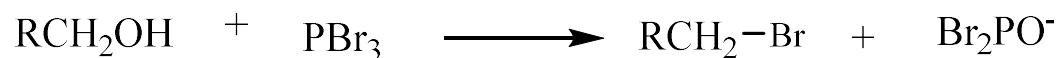
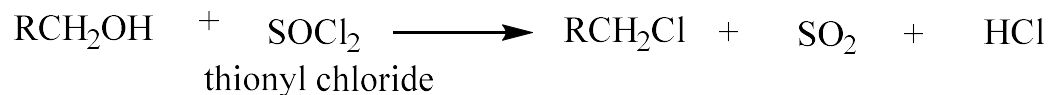
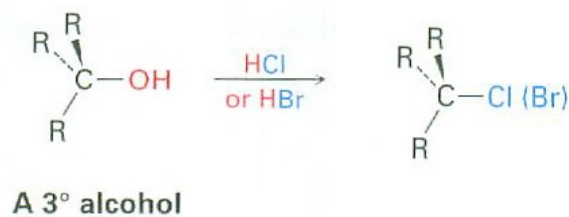
Alcohols are slightly less acidic than water and react readily with group I metals to liberate hydrogen and to form metal alkoxide



A. Conversion of alcohols into alkyl halides

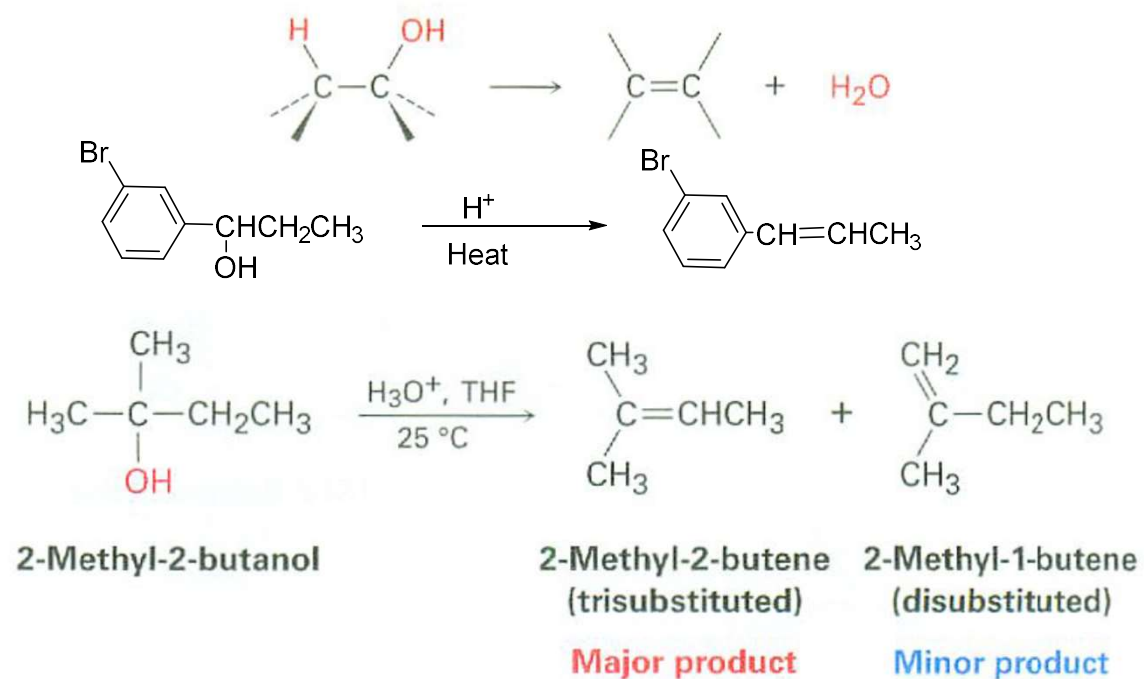
Primary and secondary alcohols are best converted into halides by treatment with SOCl_2 or PBr_3

Tertiary alcohols react with HCl or HBr



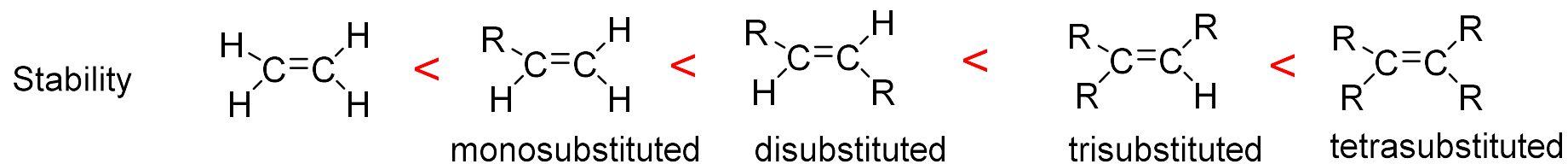
B. Acid catalyzed dehydration of alcohol

In the presence of acid catalyst water is eliminated from the adjacent carbon to form alkene

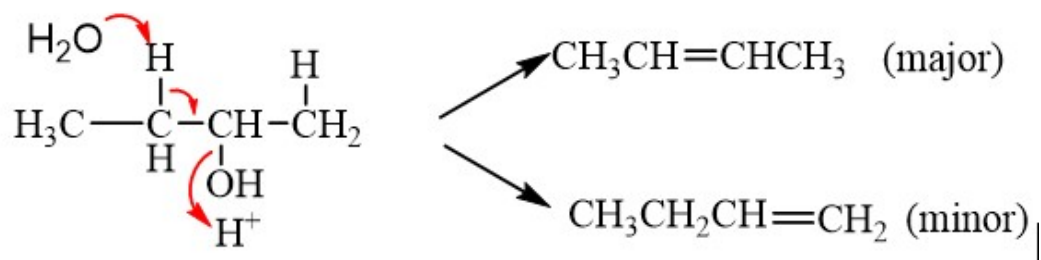


- The reaction follows Zaitsev's rule (Saytzeff's rule)

Saytzeff's rule: in an elimination reaction the most substituted product will be the most stable, and therefore the most favoured.



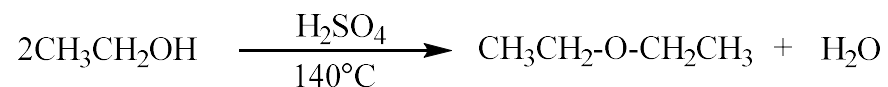
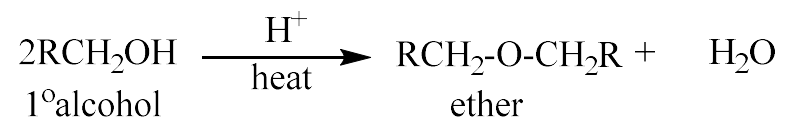
- more highly substituted C=C double bond is more stable due to the electron donating properties of the alkyl group



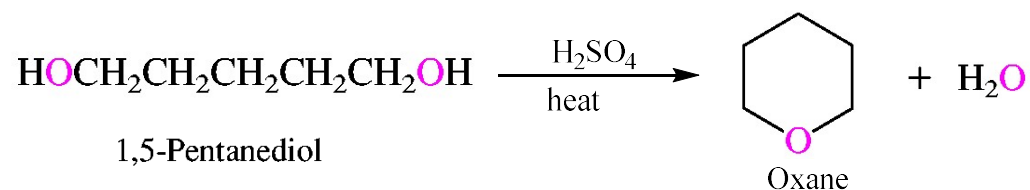
more stable alkene is the major product

C. Conversion of alcohols to ether

Primary alcohols are converted to ethers on heating in the presence of an acid catalyst.

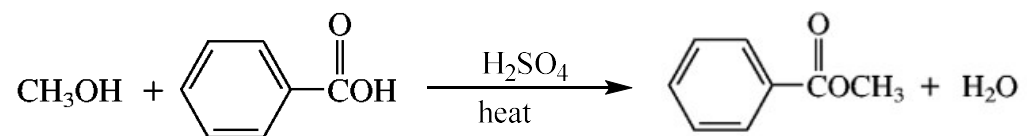
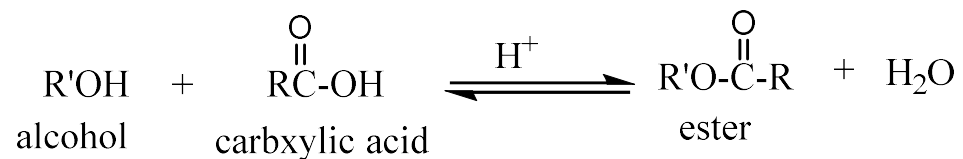


Diols react intramolecularly to form cyclic ethers.



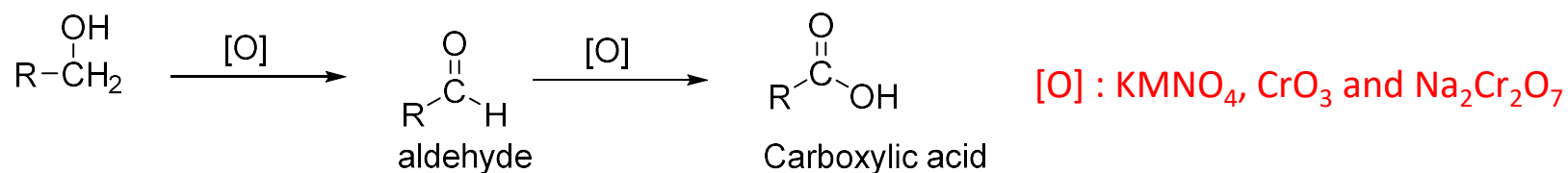
D. Esterification

In the presence of acid catalyst alcohols react with carboxylic acid to form ester

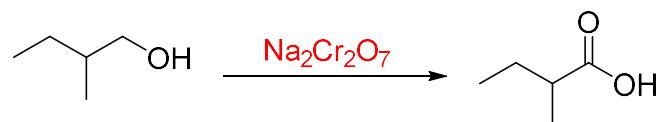


E. Oxidation of alcohol

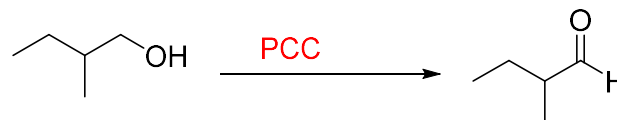
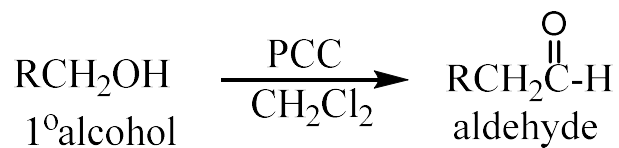
Primary alcohols may be oxidized either to an aldehyde or to a carboxylic acid



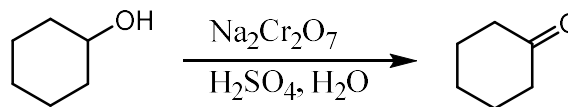
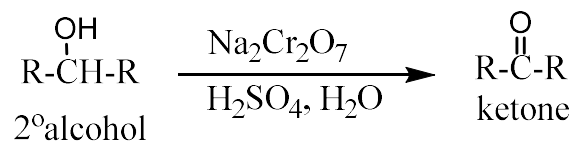
With vigorous oxidizing agent such as chromic acid it gives carboxylic acid



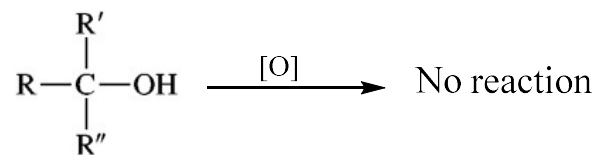
With mild oxidizing agent such as pyridinium chlorochromate (pcc) primary alcohol is oxidized to an aldehyde



Secondary alcohol is oxidized to ketone



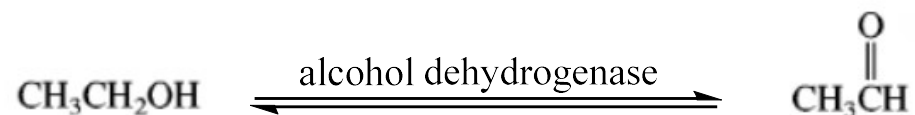
Tertiary alcohols have no hydrogen on their hydroxyl-bearing carbon and do not undergo oxidation.



Biological Oxidation of Alcohols

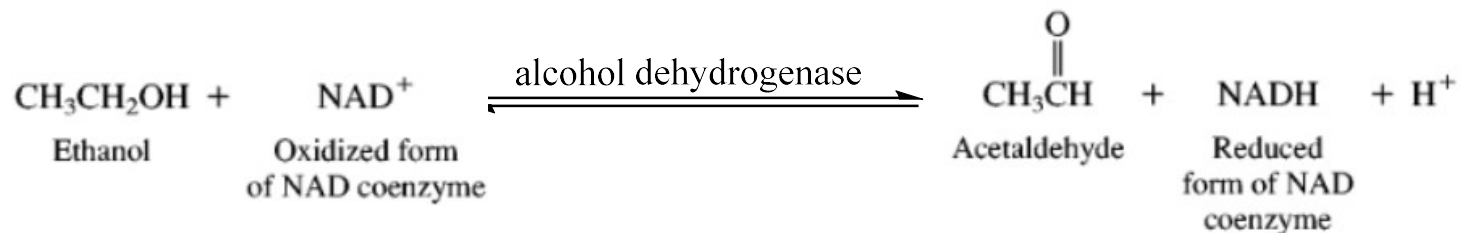
Many biological processes involve oxidation of alcohols to carbonyl compounds or the reverse process, reduction of carbonyl compounds to alcohols.

Ethanol, for example, is metabolized in the liver to acetaldehyde. Such processes are catalyzed by an enzymes called [alcohol dehydrogenase](#).



- In addition to enzymes, biological oxidations require substances known as co-enzymes.
- If ethanol is oxidized, some other substance must be reduced. This other substance is the oxidized form of the coenzyme [nicotinamide adenine dinucleotide](#) (NAD). The oxidized form of this coenzyme abbreviate as NAD^+ and its reduced form as NADH.

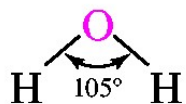
More completely, the chemical equation for the biological oxidation of ethanol may be written:



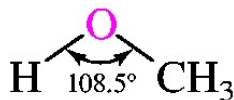
E. Ethers and Epoxides

Ethers

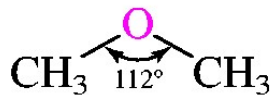
- Bonding in ethers is readily understood by comparing ethers with water and alcohols
- Van der Waals strain involving alkyl groups causes the bond angle at oxygen to be larger in ethers than in alcohols, and larger in alcohols than in water



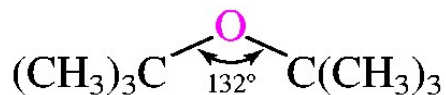
Water



Methanol

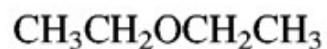


Dimethyl ether



Di-*tert*-butyl ether

- With respect to boiling point, ethers resemble alkanes more than alcohols. With respect to solubility in water the reverse is true; ethers resemble alcohols more than alkanes.



Diethyl ether



Pentane



1-Butanol

Boiling point: 35°C
Solubility in water: 7.5 g/100 mL

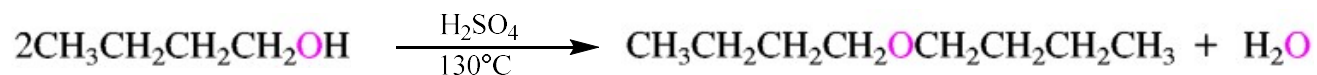
36°C
Insoluble

117°C
9 g/100 mL

In general, the boiling points of alcohols are unusually high because of hydrogen bonding.

Preparation of Ethers

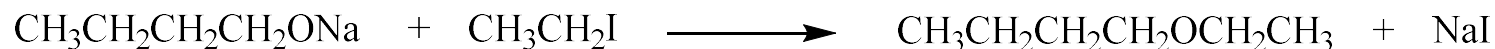
1. By acid catalyzed condensation of alcohols



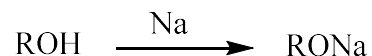
- In general, this method is limited to the preparation of symmetrical ethers in which both alkyl groups are primary.
- Isopropyl alcohol is readily available at low cost and gives high enough yields of diisopropyl ether making $(\text{CH}_3)_2\text{CHOCH}(\text{CH}_3)_2$ by this method on an industrial scale.

2. Williamson ether synthesis.

Involve the reaction of sodium alkoxide with alkylhalide.

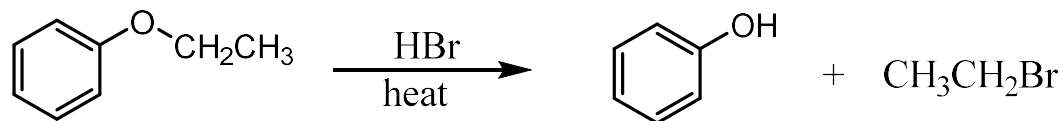
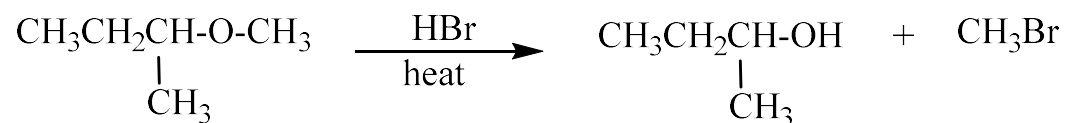


Sodium alkoxide is prepared by the reaction of alcohol with sodium metal.



Reactions of ethers

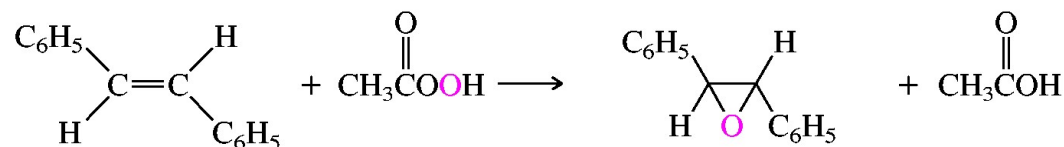
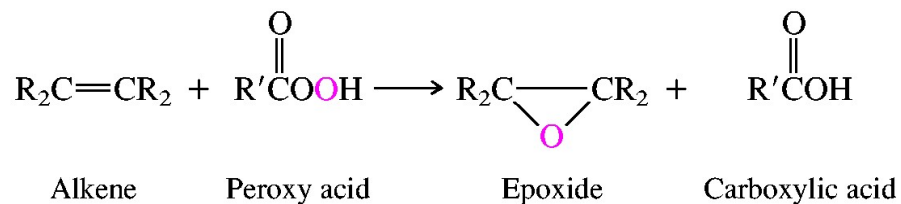
- Ethers are one of the unreactive functional group compounds; it is this low reactivity that makes ethers most often to use as a solvent in many organic reactions.
- Ethers react with strong acids such as hydrogen halides to undergo acidic cleavage to form alkylhalide. Both aqueous HBr and HI work well, but HCl doesn't cleave ethers.



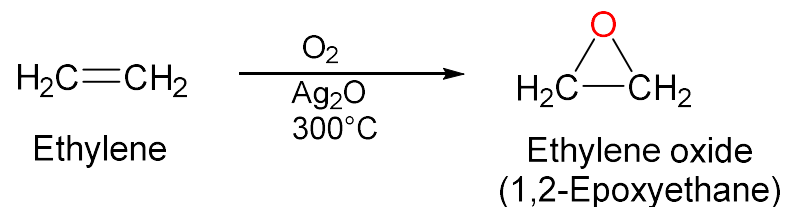
Epoxides

Preparation of Epoxides:

Epoxidation of alkenes by reaction with peroxy acids



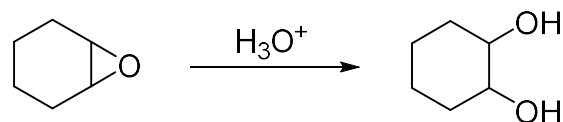
Ethylene oxide, the simplest epoxide, is used for automobile antifreeze and polyester polymers, is produced by air oxidation of ethylene over a silver oxide catalyst at 300 °C. This method is not useful for other epoxides.



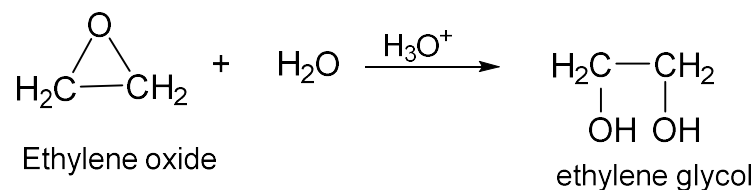
Reactions of Epoxides- Ring opening

1. Acid-Catalyzed Ring-Opening of Epoxides

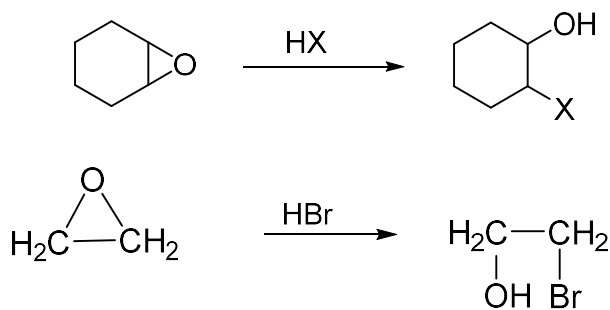
Epoxides are cleaved by treatment with acid to produce diols.



The industrial preparation of ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) by hydrolysis of ethylene oxide in dilute H_2SO_4 .



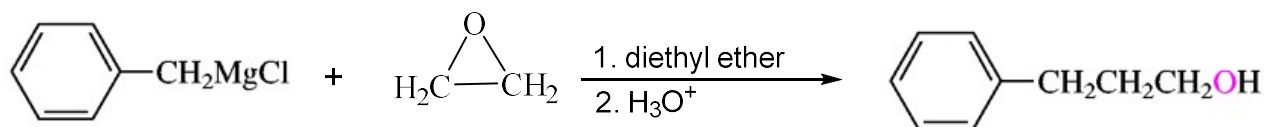
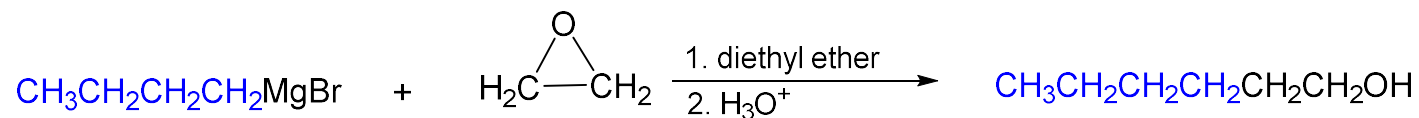
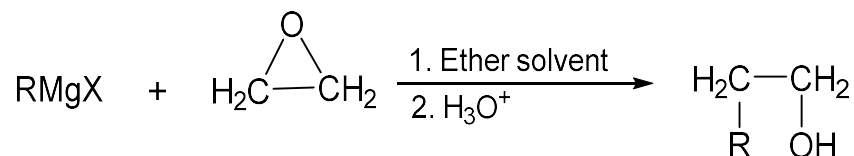
Epoxides can also be opened by reaction with acids other than H_3O^+ . If anhydrous HX is used, an epoxide is converted into halohydrin



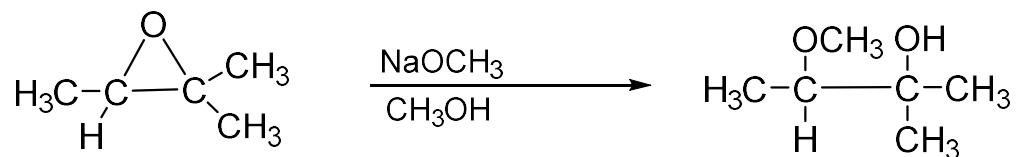
- The regiochemistry of acid-catalyzed ring-opening depends on the epoxide's structure, and a mixture of products often formed.



2. Ring opening of epoxides using Grignard reagents



3. Nucleophilic Ring-Opening of Epoxides



Unsymmetrical epoxides are attacked at the less substituted, less sterically hindered carbon

