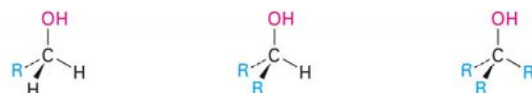
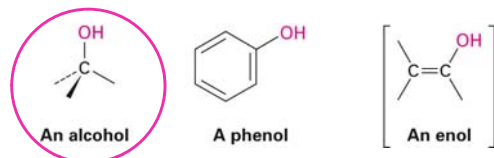
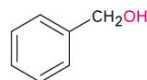


## Naming Alcohols

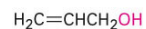


### alcohols with common names:

IUPAC names?



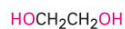
Benzyl alcohol



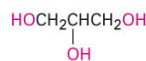
Allyl alcohol



tert-Butyl alcohol



Ethylene glycol



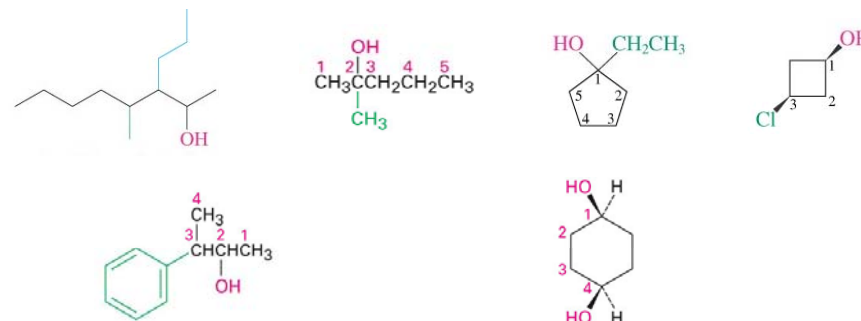
Glycerol

13-1

## Systematic Nomenclature of Alcohols

Simple alcohols are named by the IUPAC system as derivative of alkanes:

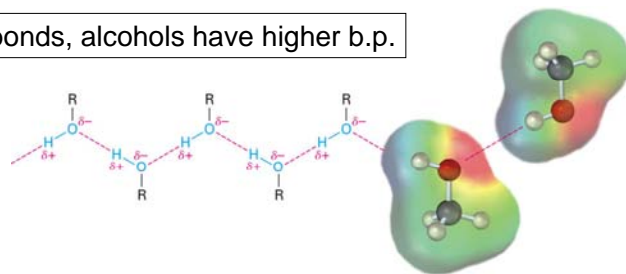
- Select the longest carbon chain containing the hydroxyl group, and replace the *-e* ending with *-ol*.
- Number the parent chain beginning at the end nearer the  $-\text{OH}$  group.
- Number the substituents according to their position on the chain, and write the name listing the substituents in alphabetic order and identifying the position of the  $-\text{OH}$ .



13-2

## Properties of Alcohols

Due to H-bonds, alcohols have higher b.p.



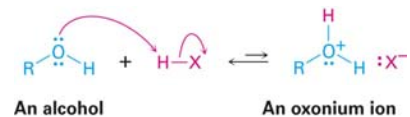
Short-chain alcohols are miscible with water, also due to H-bonds; alcohols bearing longer alkyl chains become less soluble in water.

Compound	IUPAC name	Common name	Melting point (°C)	Boiling point (°C)	Solubility in H <sub>2</sub> O at 23°C
$\text{CH}_3\text{OH}$	Methanol	Methyl alcohol	-97.8	65.0	Infinite
$\text{CH}_3\text{Cl}$	Chloromethane	Methyl chloride	-97.7	-24.2	0.74 g/100 mL
$\text{CH}_4$	Methane		-182.5	-161.7	3.5 mL (gas)/100 mL
$\text{CH}_3\text{CH}_2\text{OH}$	Ethanol	Ethyl alcohol	-114.7	78.5	Infinite
$\text{CH}_3\text{CH}_2\text{Cl}$	Chloroethane	Ethyl chloride	-136.4	12.3	0.447 g/100 mL
$\text{CH}_3\text{CH}_3$	Ethane		-183.3	-88.6	4.7 mL (gas)/100 mL

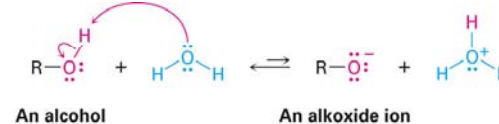
13-3

## Alcohols as Acids and Bases

Alcohols are weak bases:

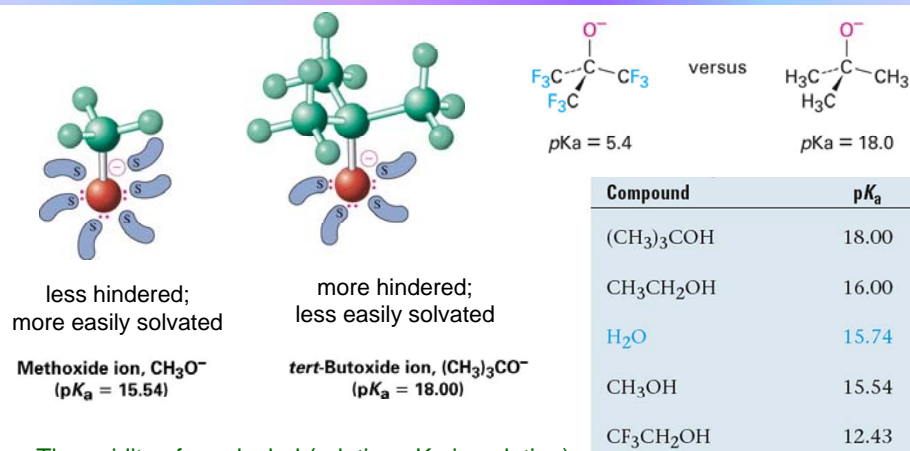


Alcohols as acids:



13-4

## Solvation and Inductive Effect on the Acidity of Alcohols



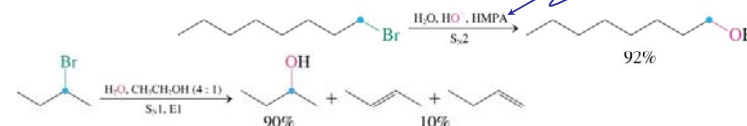
The acidity of an alcohol (relative  $pK_a$  in solution):

**Strongest acid**  $\longleftrightarrow$  **Weakest acid**  
 $\text{CH}_3\text{OH} < \text{primary} < \text{secondary} < \text{tertiary}$

13-5

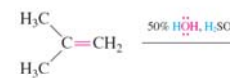
## Preparation of Alcohols: a Review

By nucleophilic substitution of alkyl halides:  $\swarrow$  an aprotic polar solvent



Direct hydration:

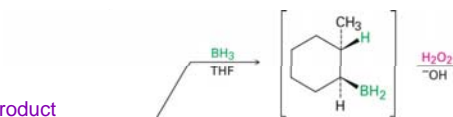
- acidic conditions;
- carbocation intermediate
- Markovnikov product



2-Methylpropene

Hydroboration/oxidation:

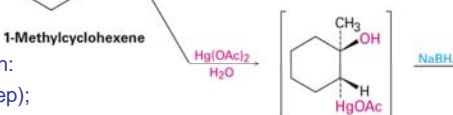
- syn-addition;
- anti-Markovnikov product



1-Methylcyclohexene

Oxymercuration/reduction:

- anti-addition (1<sup>st</sup> step);
- Markovnikov product

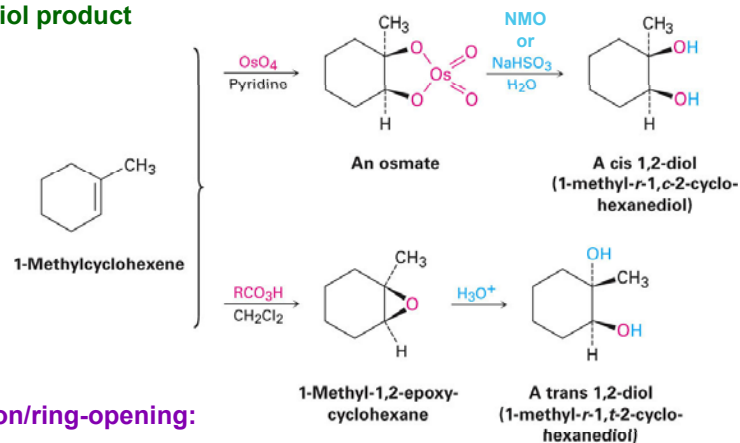


13-6

## Preparation of Alcohols from Alkenes: a Review

Oxidation with  $\text{OsO}_4$ :

- syn-addition;
- cis-diol product

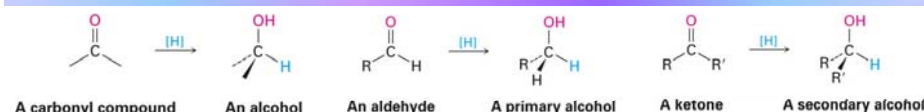


Epoxidation/ring-opening:

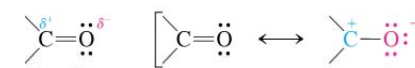
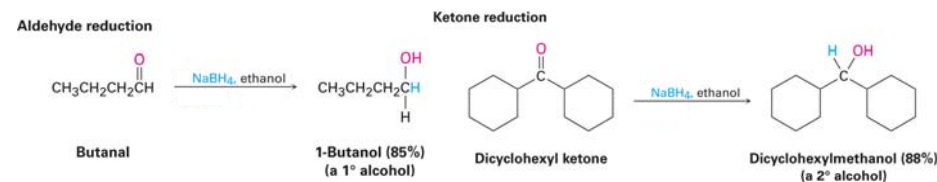
- anti-addition

13-7

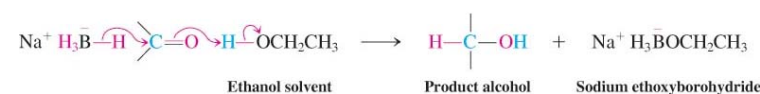
## Alcohols from Reduction of Carbonyl Compounds



Using  $\text{NaBH}_4$  (with alcohol as solvent)



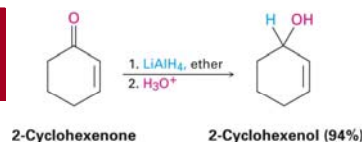
Mechanism of  $\text{NaBH}_4$  Reduction



13-8

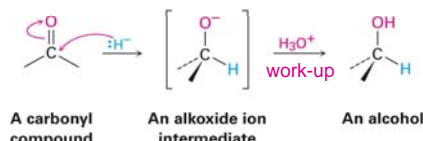
## Reduction of Aldehydes and Ketones with $\text{LiAlH}_4$

with  $\text{LiAlH}_4$   
(anhydrous aprotic solvent)

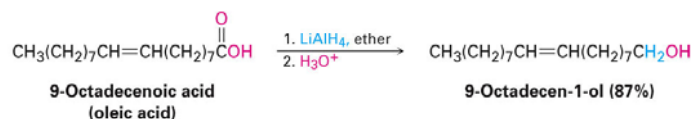


$\text{LiAlH}_4$  even reduces carboxylic acids and esters into alcohols

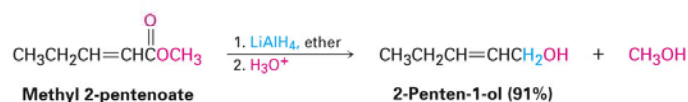
### Reaction of Lithium Aluminum Hydride with Protic Solvents



### Carboxylic acid reduction

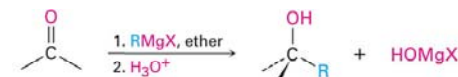


### Ester reduction



13-9

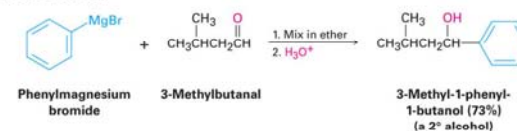
## Reaction of Grignard Reagents with Carbonyl Compounds



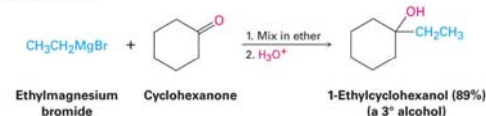
### Formaldehyde reaction



### Aldehyde reaction



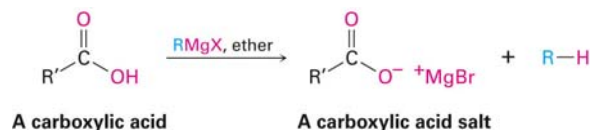
### Ketone reaction



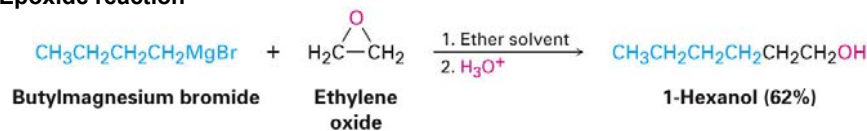
13-10

## Reactions of Grignard Reagents with Carbonyl Compounds and Epoxides

### Ester reaction



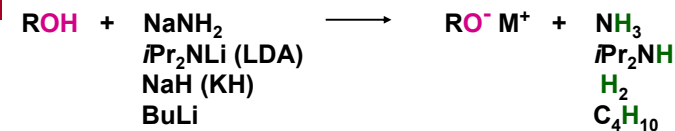
### Epoxide reaction



13-11

## Reactions of Alcohols: with Bases and Alkali Metals

with base



with alkali metals



### Relative Reactivity of ROH with Alkali Metals

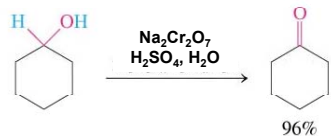
$\text{R} = \text{CH}_3 > 1^\circ > 2^\circ > 3^\circ \text{ alkyl groups}$

Alkoxides ( $\text{RO}^-$ ) are useful nucleophiles or bases in nucleophilic substitution and elimination reactions.

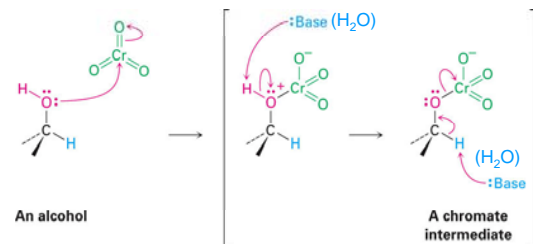
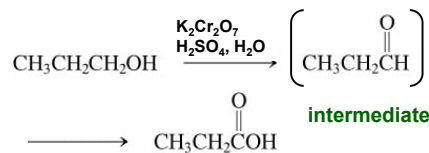
13-12

## Oxidation of Alcohols

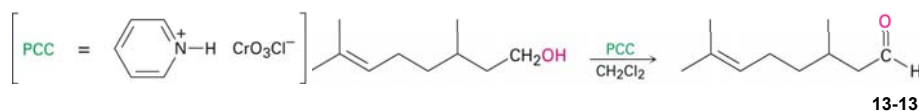
Oxidation of a 2° alcohol with chromic acid yields a ketone:



Oxidation of a 1° alcohol with chromic acid results in an acid:

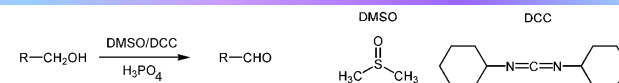


Oxidation of a 1° alcohol with PCC gives aldehyde:

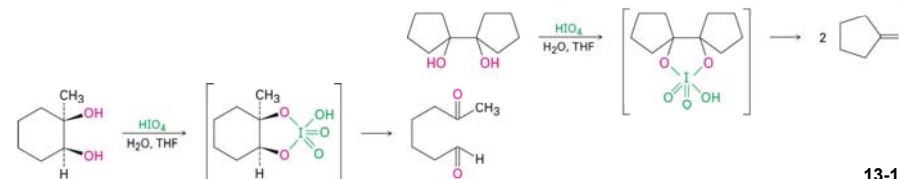
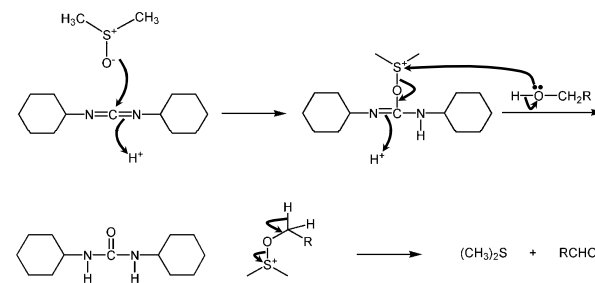


13-13

## Oxidation of Alcohols



Mechanism:



13-14

## Substitution and Elimination Reactions of Alcohols

In this section we apply what we've learned - to reason by analogy - so that we can predict the outcome of new reactions (e.g., predictions of leaving group ability)

Breaking C-O bonds

-OH is a poor leaving group and does NOT directly participate in S<sub>N</sub>1, S<sub>N</sub>2, E1 or E2 reactions.

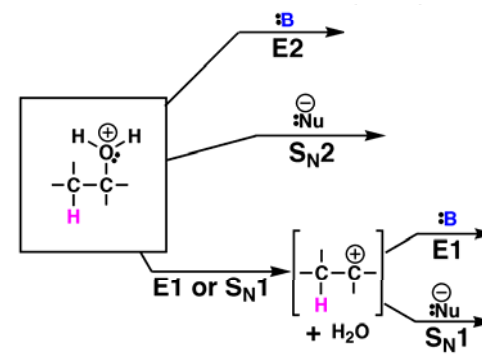
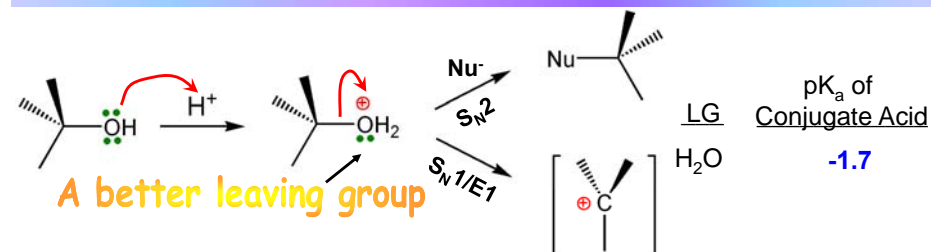


Why is -OH a poor leaving group?

LG <sup>⊖</sup>	Conjugate Acid	pK <sub>a</sub> of Conjugate Acid
$\text{I}^-$	HI	-10.0
$\text{Br}^-$	HBr	-9.0
$\text{H}_2\text{O}$	HOH	15.7

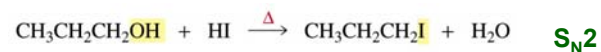
13-15

## Protonation of an Alcohol Improves the Leaving Ability

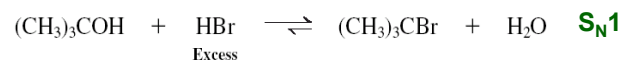


13-16

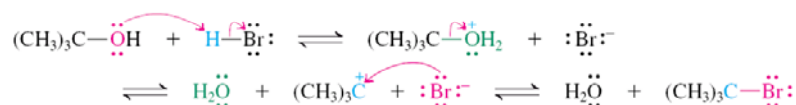
## Examples – Nucleophilic Substitution



a primary alcohol

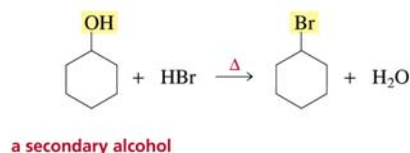


a tertiary alcohol



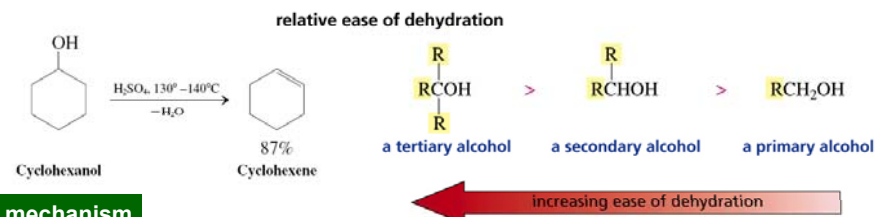
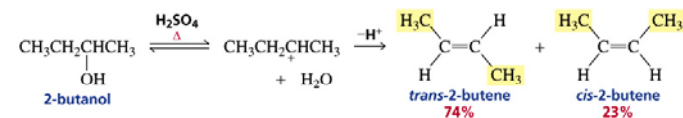
stable carbocation facilitates S<sub>N</sub>1 reaction

Secondary alcohols show complex behavior when treated with HX, following S<sub>N</sub>2, S<sub>N</sub>1, and E1 pathways.

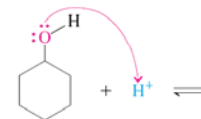


13-17

## Dehydration of Alcohols into Alkenes - Elimination

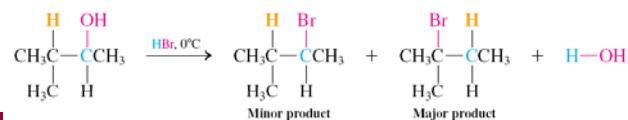


mechanism

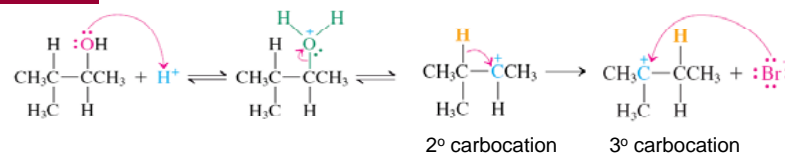


13-18

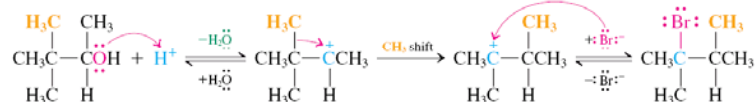
## Carbocation Rearrangement



Hydride Shift

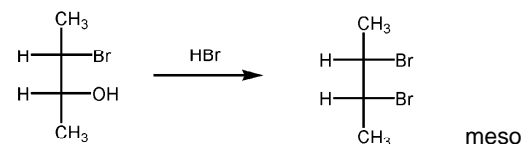
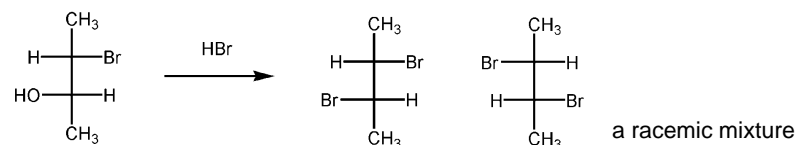


Alkyl Shift:



13-19

## Neighboring-Group Effect

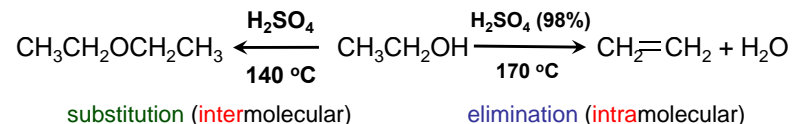
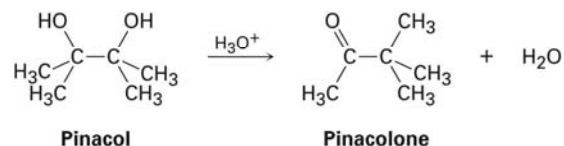


13-20

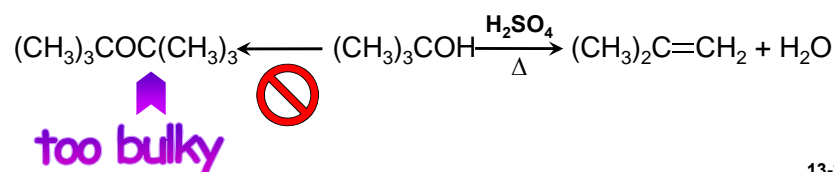


## Pinacol Rearrangement and Intermolecular vs. Intramolecular Dehydrations

Suggest a mechanism:

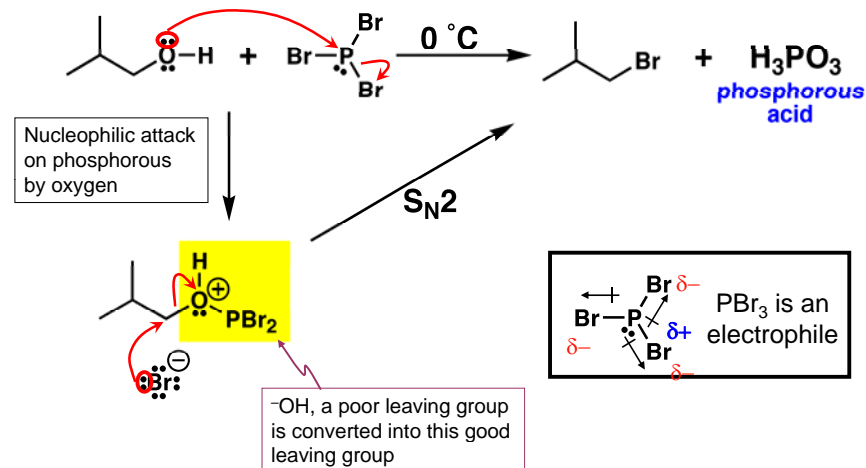


Write out the mechanism for this reaction.



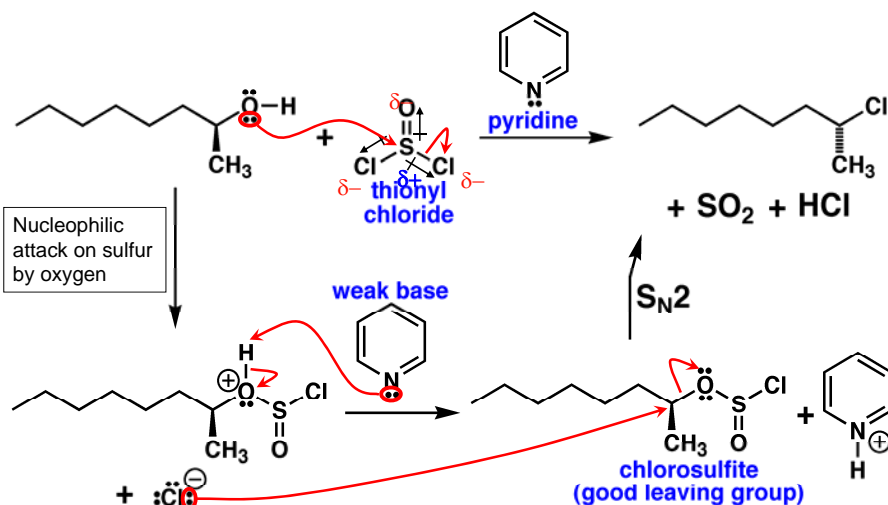
13-21

## Activate Alcohols with $\text{PBr}_3$



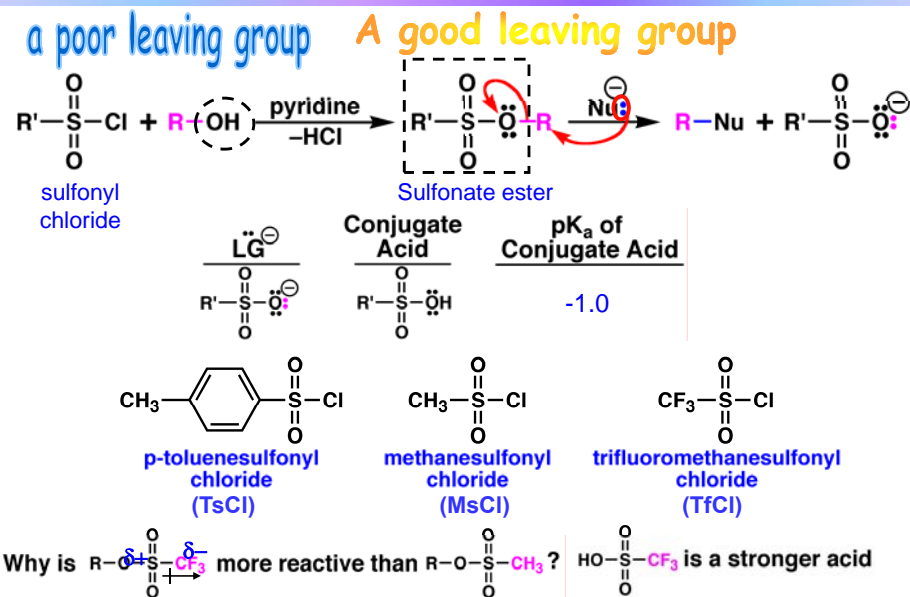
13-22

## Activated Alcohols Based on $\text{SOCl}_2$



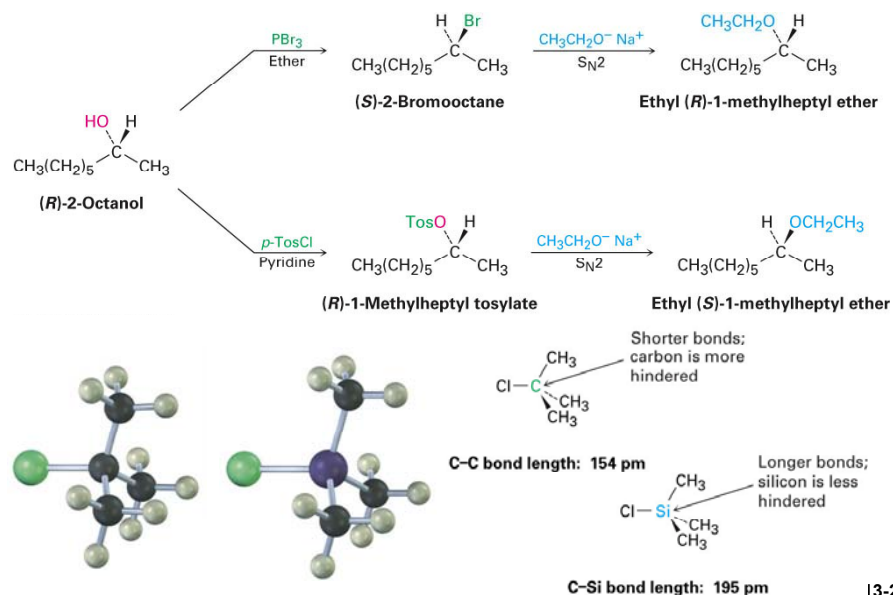
13-23

## Activated Alcohols Based on Sulfonate Esters



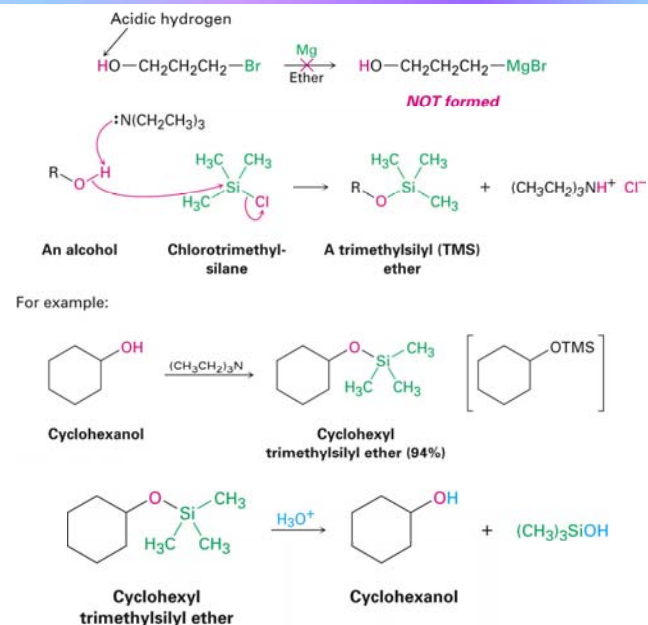
13-24

## Stereochemistry of Activated Alcohols



13-25

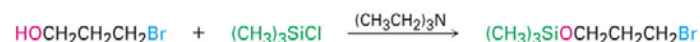
## Protection and Deprotection of Alcohols



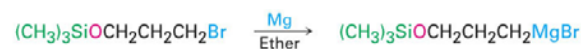
13-26

## Example of Protection and Deprotection

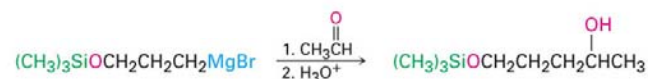
**Step 1** Protect alcohol:



**Step 2a** Form Grignard reagent:



**Step 2b** Do Grignard reaction:

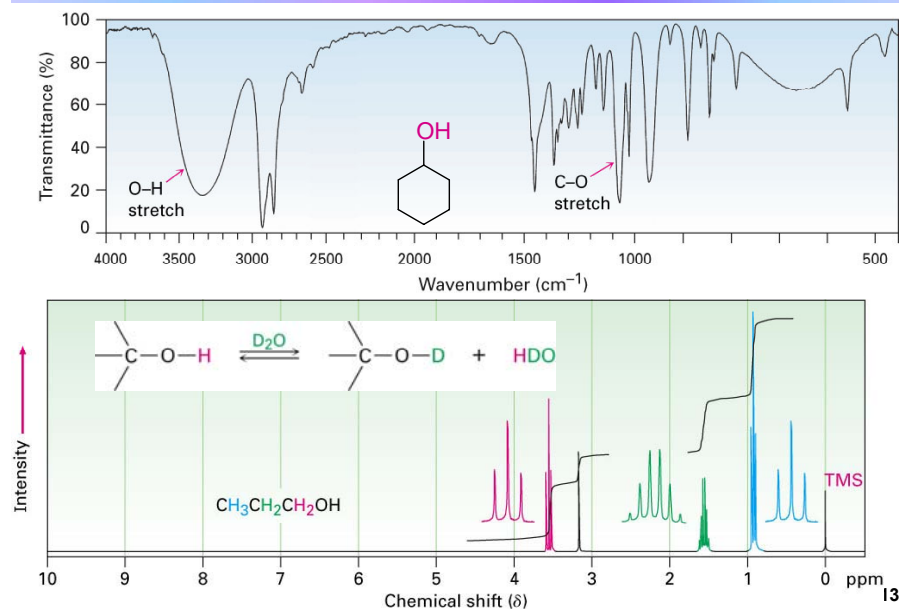


**Step 3** Remove protecting group:



13-27

## Spectroscopies of Alcohols



13-28