

Organic Chemistry

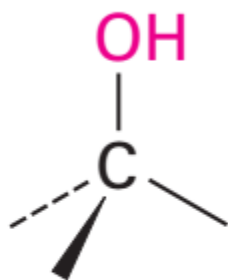
CHE 203

Lecture 13: Alcohols and Phenols

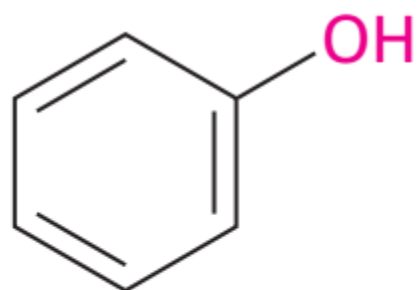
Le Quoc Chon – Duy Tan University



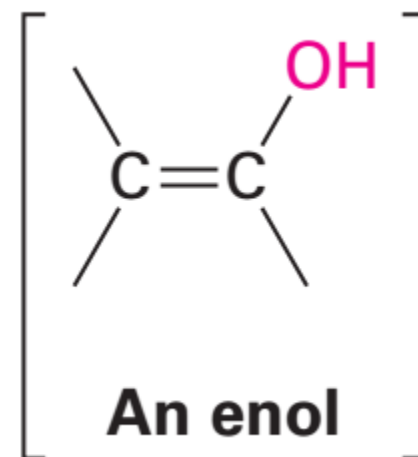




An alcohol

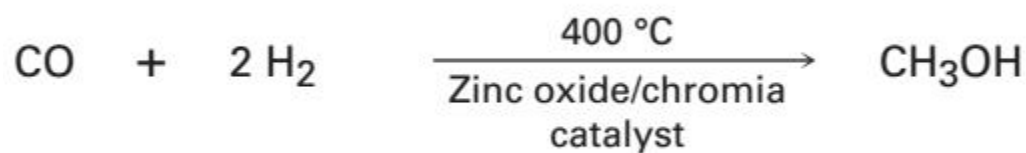


A phenol



An enol

Điều chế methanol



Oxidation
250-400 °C

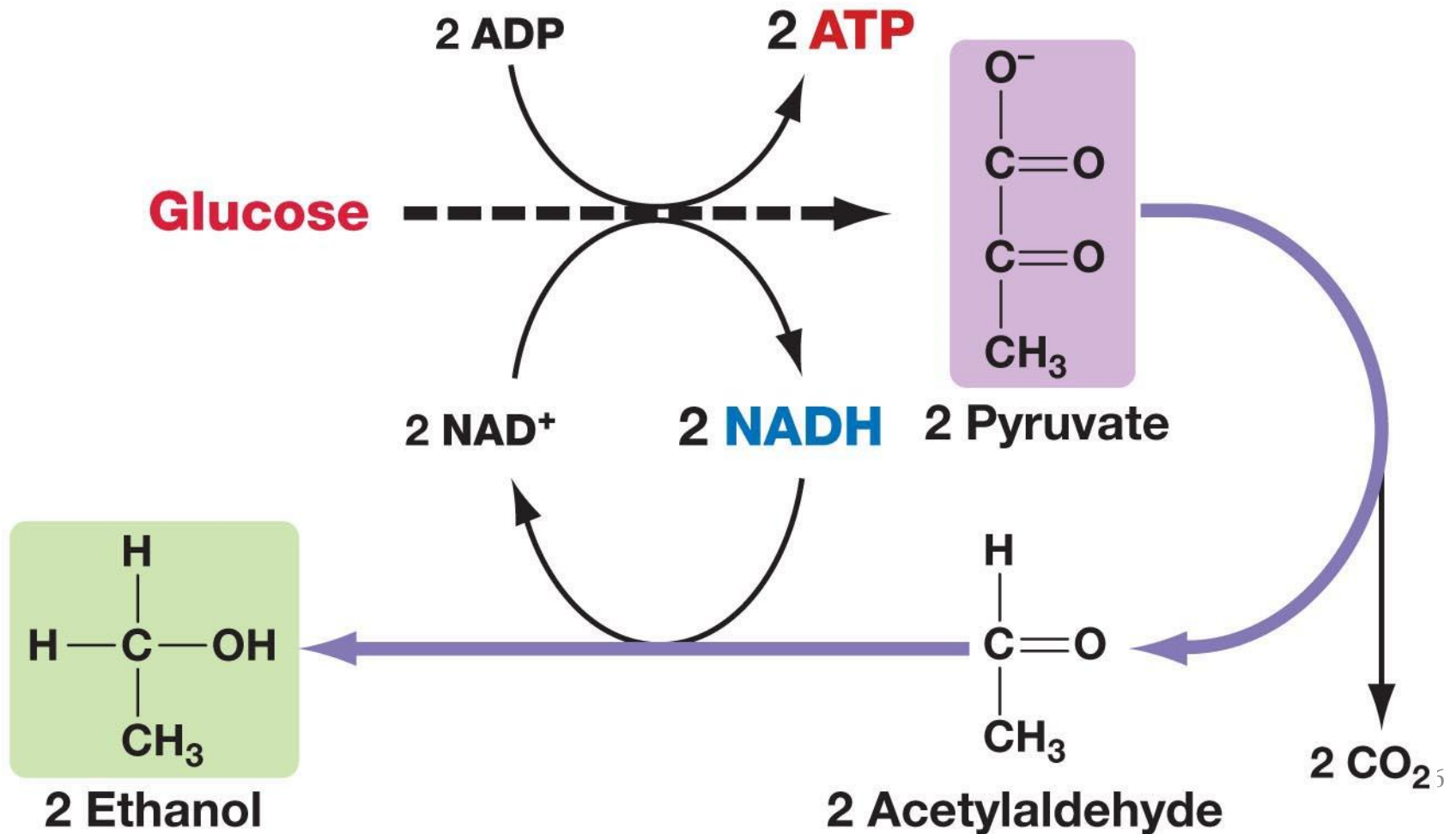


Formaldehyde & acetic acid

Ethanol

Produced by fermentation: 9000 years ago

Alcohol fermentation occurs in yeast.



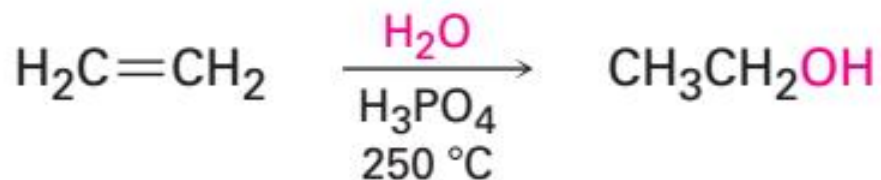
Bread making



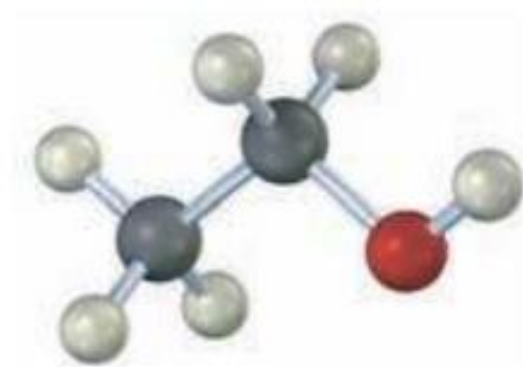
How often do you eat bread?

Ethanol

For industrial use



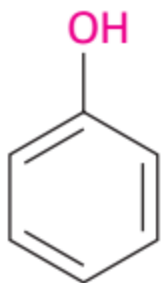
adsorbed onto a porous support such as silica gel or diatomaceous earth



Phenol

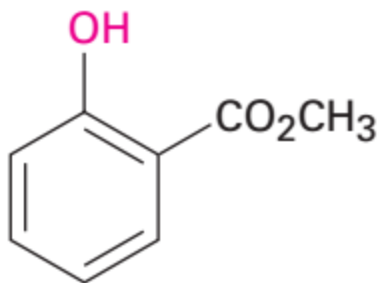


Poison ivy during autumn



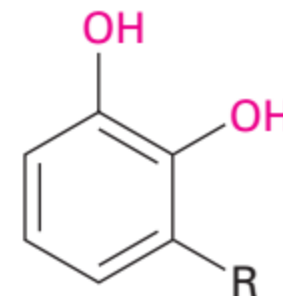
Phenol
(also known as
carbolic acid)

Dùng trong sx
chất kết dính



Methyl salicylate

Chất tạo mùi/vị

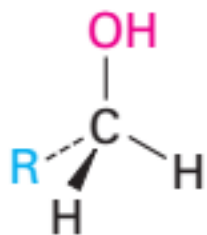


Urushiols
(R = different C₁₅ alkyl
and alkenyl chains)

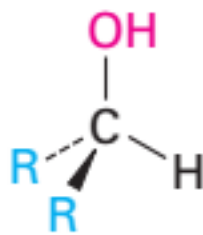
Một chất gây dị
ứng

Naming alcohols and phenols

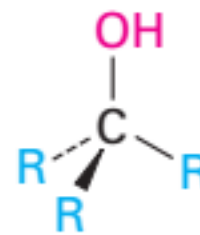
Đọc tên



A primary (1°) alcohol



A secondary (2°) alcohol



A tertiary (3°) alcohol

Naming alcohols and phenols

Đọc tên

RULE 1 Chọn mạch chính chứa nhóm -OH

Select the longest carbon chain containing the hydroxyl group, and derive the parent name by replacing the *-e* ending of the corresponding alkane with *-ol*. The *-e* is deleted to prevent the occurrence of two adjacent vowels: propanol rather than propaneol, for example.

RULE 2 Đánh số thứ tự bắt đầu từ phía sao cho nhóm -OH ở vị trí thấp nhất.

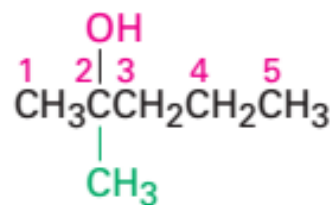
Number the alkane chain beginning at the end nearer the hydroxyl group.

RULE 3 Đánh số vị trí nhóm thế và đọc theo thứ tự alphabe.

Number the substituents according to their position on the chain, and write the name, listing the substituents in alphabetical order and identifying the position to which the -OH is bonded. Note that in naming *cis*-1,4-cyclohexanediol, the final *-e* of cyclohexane is not deleted because the next letter, *d*, is not a vowel; that is, cyclohexanediol rather than cyclohexandiol. Also, as with alkenes (**Section 7-3**), newer IUPAC naming recommendations place the locant immediately before the suffix rather than before the parent.

Naming alcohols and phenols

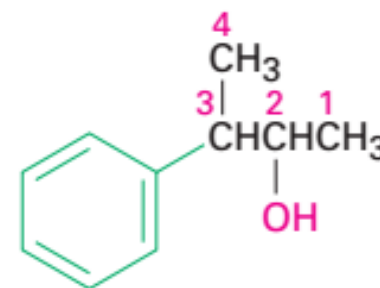
Đọc tên



2-Methyl-2-pentanol
(New: **2-Methylpentan-2-ol**)



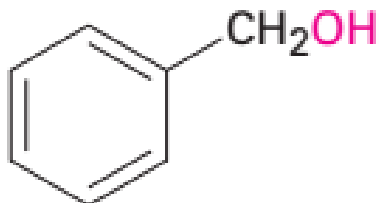
cis-1,4-Cyclohexanediol
(New: **cis-Cyclohexane-1,4-diol**)



3-Phenyl-2-butanol
(New: **3-Phenylbutan-2-ol**)

Naming alcohols and phenols

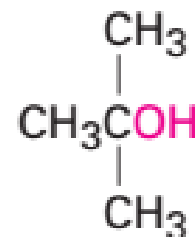
Đọc tên



Benzyl alcohol
(phenylmethanol)



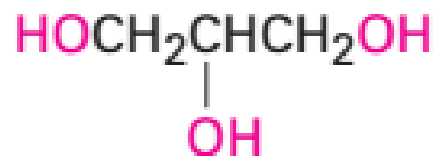
Allyl alcohol
(2-propen-1-ol)



***tert*-Butyl alcohol**
(2-methyl-2-propanol)



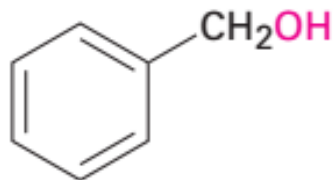
Ethylene glycol
(1,2-ethanediol)



Glycerol
(1,2,3-propanetriol)

Naming alcohols and phenols

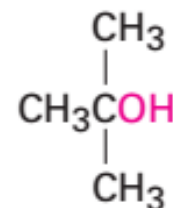
Đọc tên



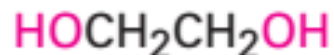
Benzyl alcohol
(phenylmethanol)



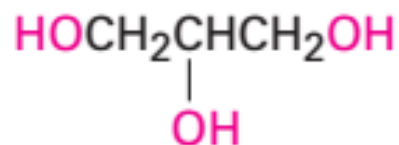
Allyl alcohol
(2-propen-1-ol)



***tert*-Butyl alcohol**
(2-methyl-2-propanol)



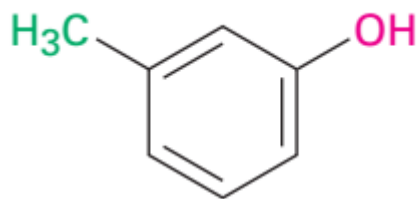
Ethylene glycol
(1,2-ethanediol)



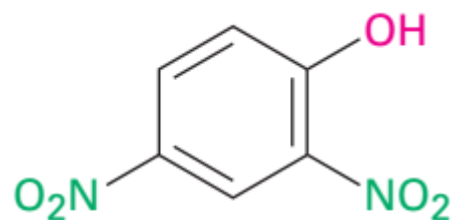
Glycerol
(1,2,3-propanetriol)

Naming alcohols and phenols

Đọc tên



***m*-Methylphenol**
(*m*-Cresol)

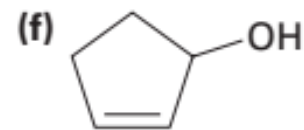
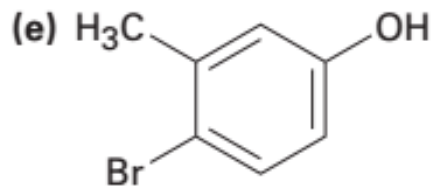
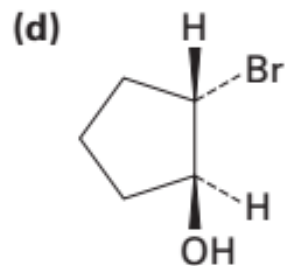
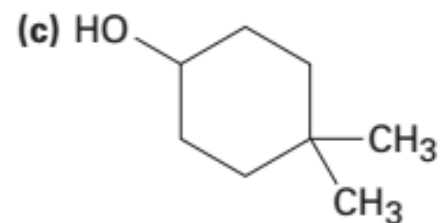
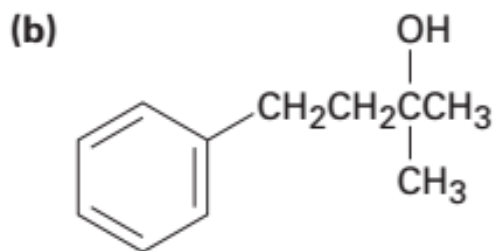
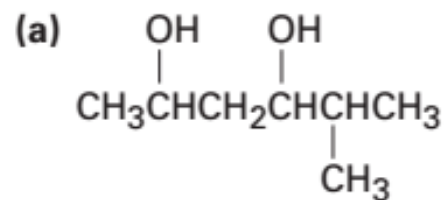


2,4-Dinitrophenol

Problem

PROBLEM 17-1

Give IUPAC names for the following compounds:



Problem

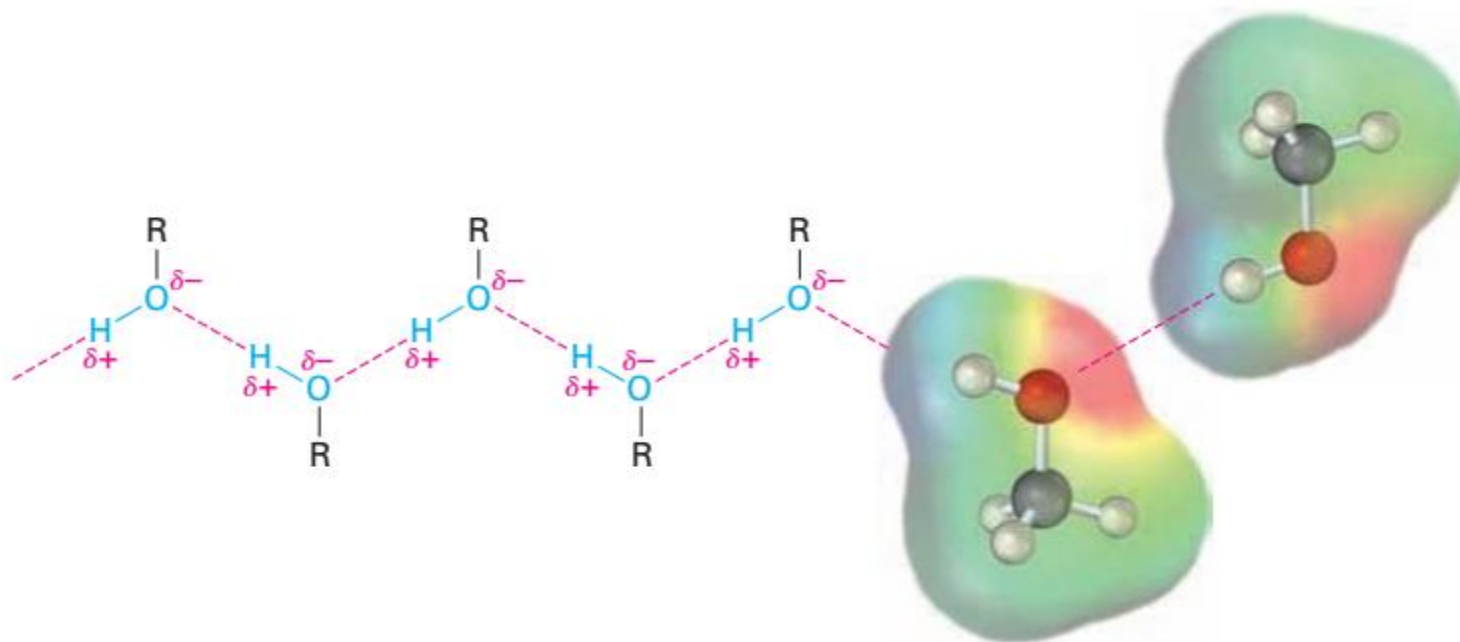
PROBLEM 17-2

Draw structures corresponding to the following IUPAC names:

- | | |
|---|--------------------------------------|
| (a) (<i>Z</i>)-2-Ethyl-2-buten-1-ol | (b) 3-Cyclohexen-1-ol |
| (c) <i>trans</i> -3-Chlorocycloheptanol | (d) 1,4-Pentanediol |
| (e) 2,6-Dimethylphenol | (f) <i>o</i> -(2-Hydroxyethyl)phenol |

Properties of alcohols and phenols

Độc tên

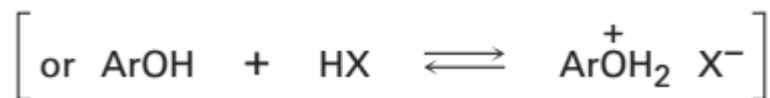
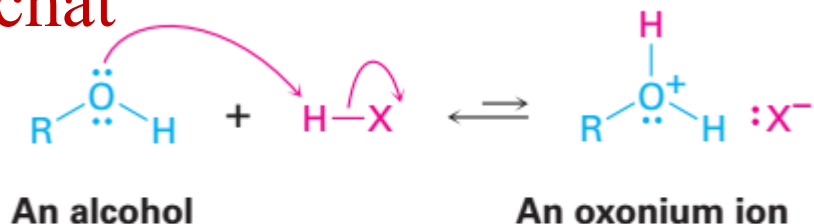


Hydrogen bonds => high boiling point

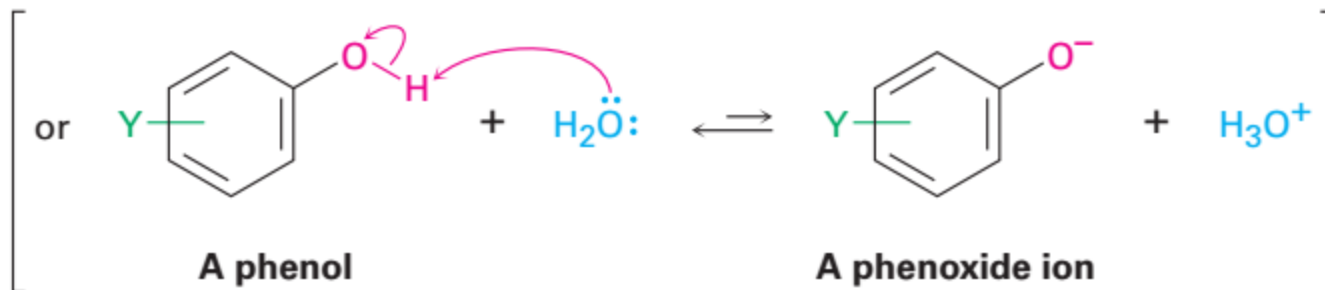
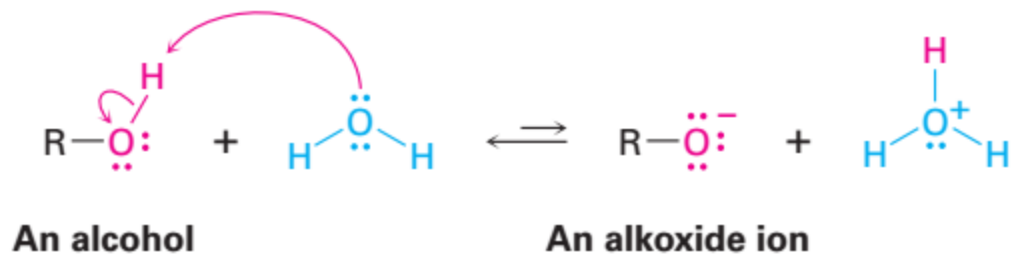
Properties of alcohols and phenols

Những tính chất

Weak base



Weak acid

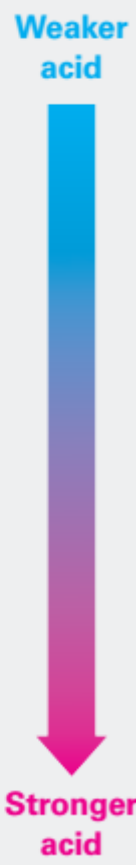


Properties of alcohols and phenols

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

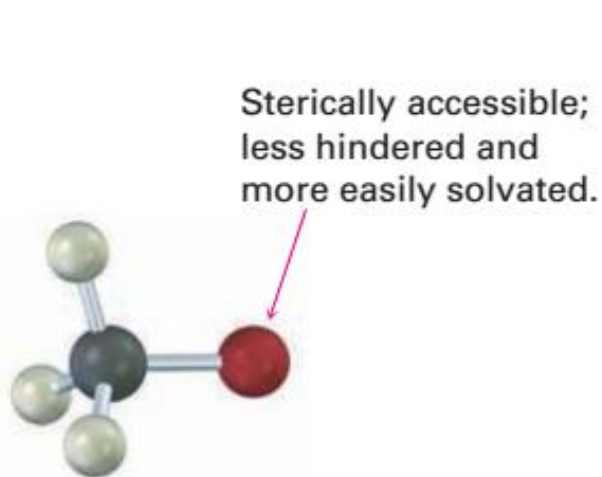
$$pK_a = -\log K_a$$

TABLE 17-1 Acidity Constants of Some Alcohols and Phenols

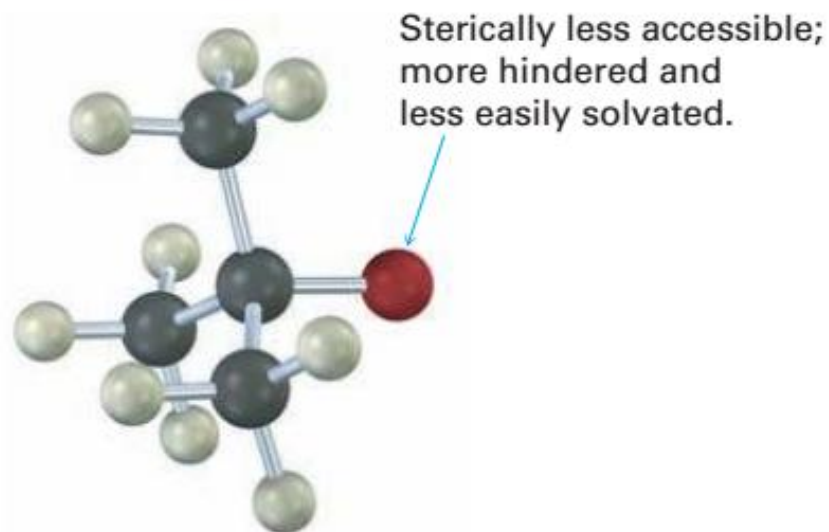
Compound	pK _a	
(CH ₃) ₃ COH	18	 <p>Weaker acid</p> <p>Stronger acid</p>
CH ₃ CH ₂ OH	16	
H ₂ O	15.74	
CH ₃ OH	15.54	
CF ₃ CH ₂ OH	12.43	
<i>p</i> -Aminophenol	10.46	
CH ₃ SH	10.3	
<i>p</i> -Methylphenol	10.17	
Phenol	9.89	
<i>p</i> -Chlorophenol	9.38	
<i>p</i> -Nitrophenol	7.15	

Properties of alcohols and phenols

Acidity: tính acid



Methoxide ion, CH_3O^-
($\text{p}K_a = 15.54$)



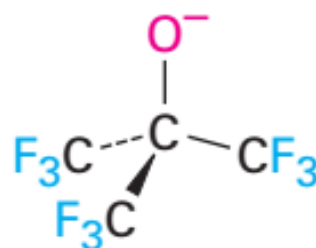
tert-Butoxide ion, $(\text{CH}_3)_3\text{CO}^-$
($\text{p}K_a = 18$)

Ảnh hưởng của kích thước nhóm alkyl lên tính acid

Properties of alcohols and phenols

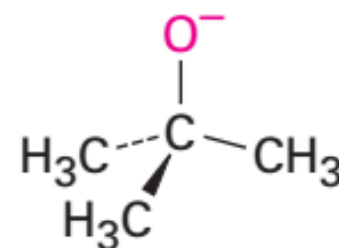
Acidity: tính acid

Electron-withdrawing groups stabilize the alkoxide ion and lower the pK_a of the alcohol.



$$pK_a = 5.4$$

versus

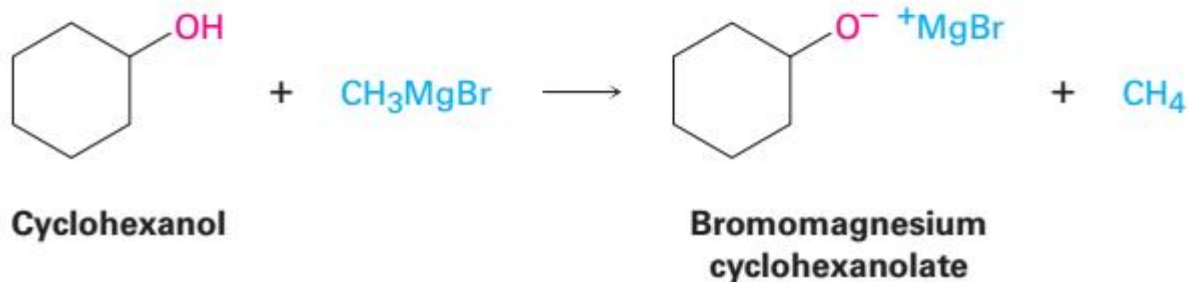
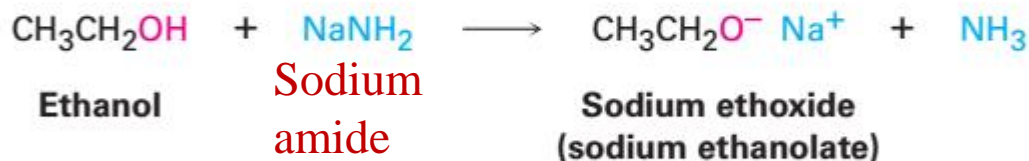
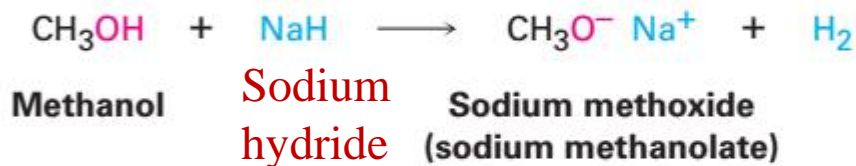
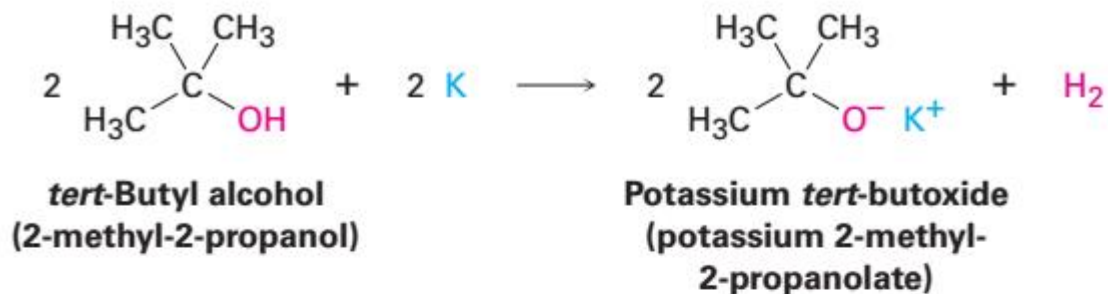


$$pK_a = 18$$

Ảnh hưởng của nhóm hút điện tử lên tính acid

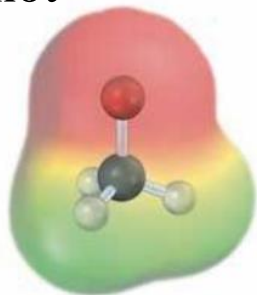
Properties of alcohols and phenols

Alcohol reacts with alkali metal, strong bases

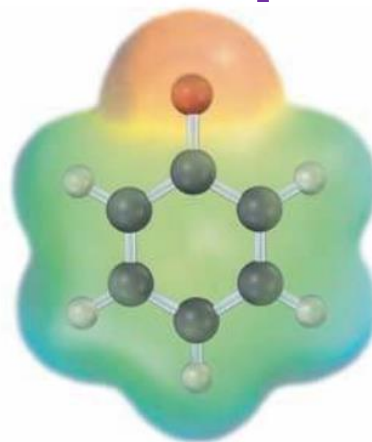


Properties of alcohols and phenols

Electron is not delocalized

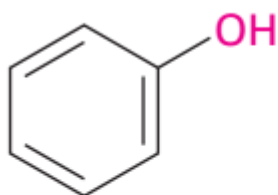


CH_3O^-



$\text{C}_6\text{H}_5\text{O}^-$

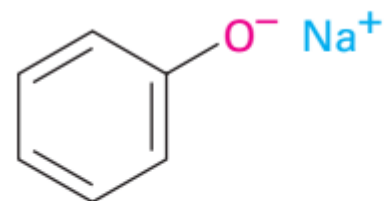
Resonance stabilized electron at ortho and para position



Phenol

+

NaOH



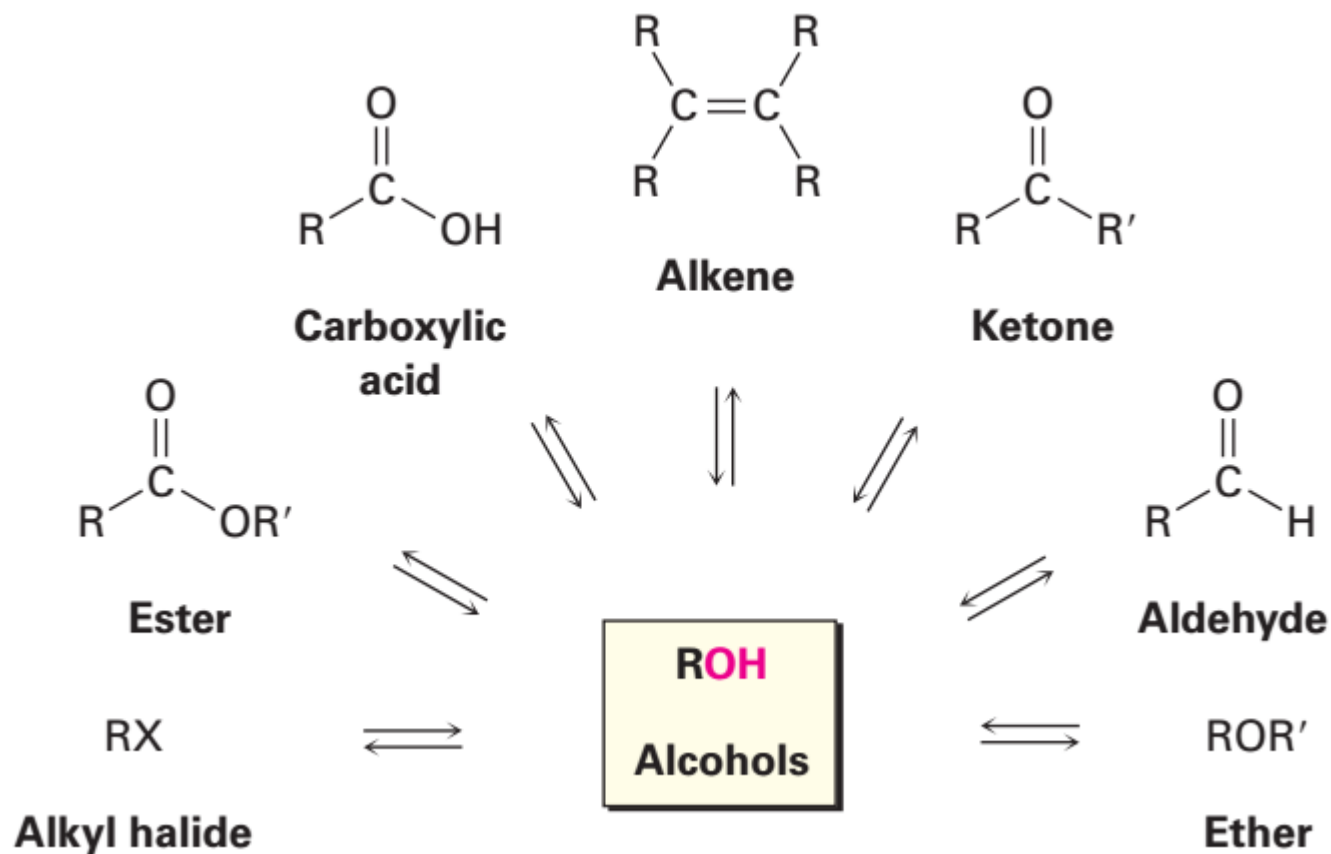
Sodium phenoxide
(sodium phenolate)

+

H_2O

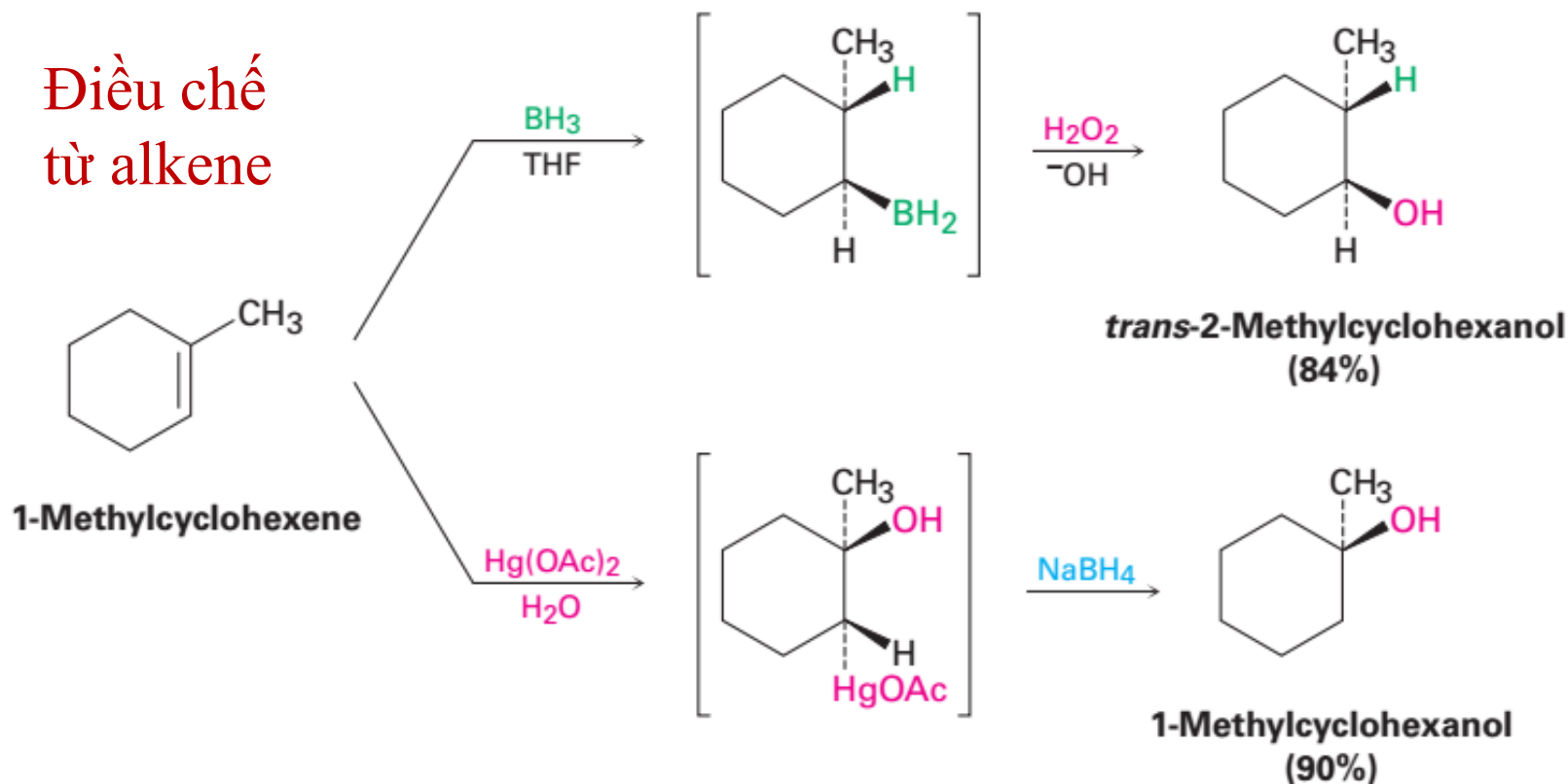
Phenol is million time more acidic than alcohol.

Preparation of alcohols



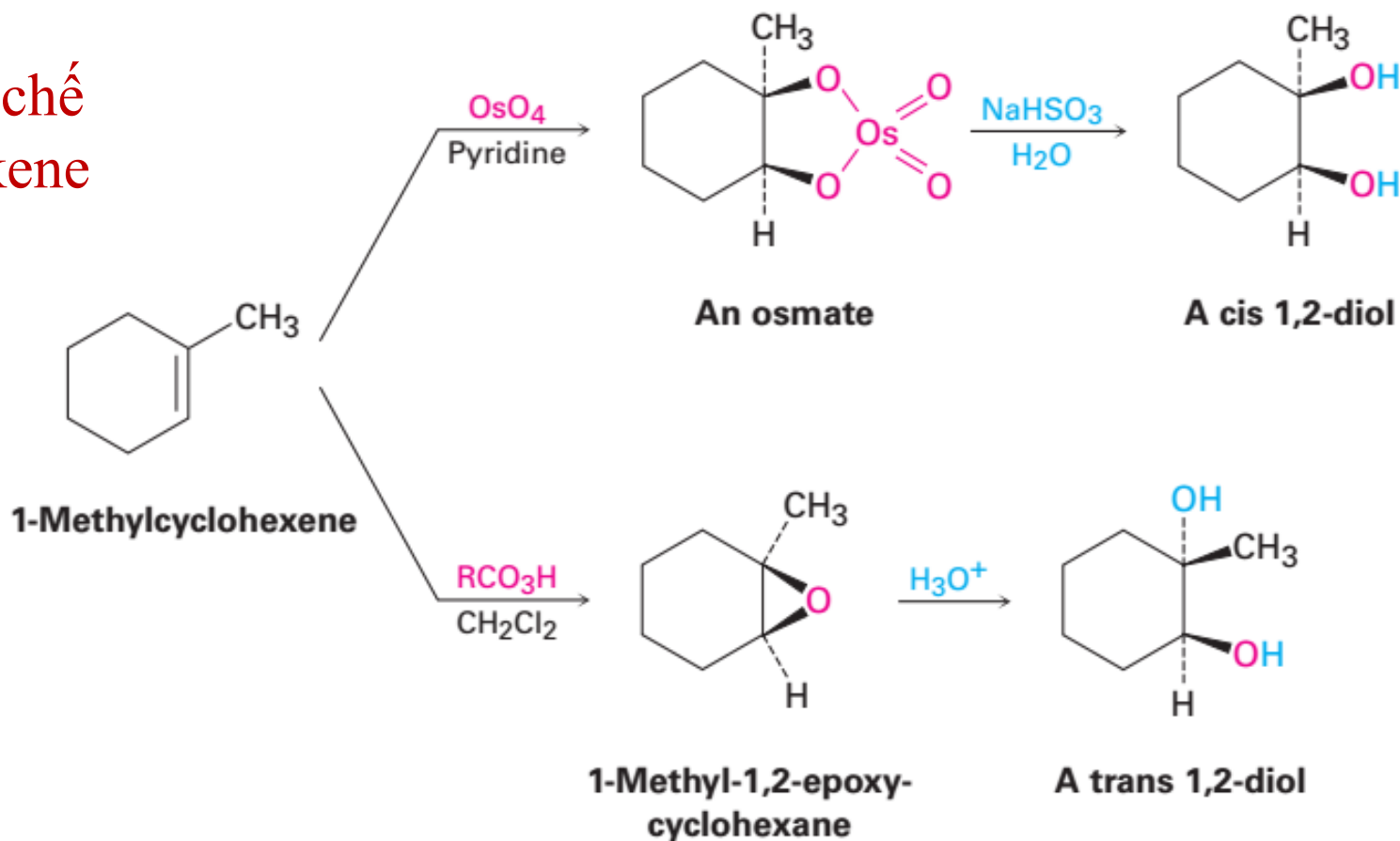
Preparation of alcohols

Điều chế
từ alkene



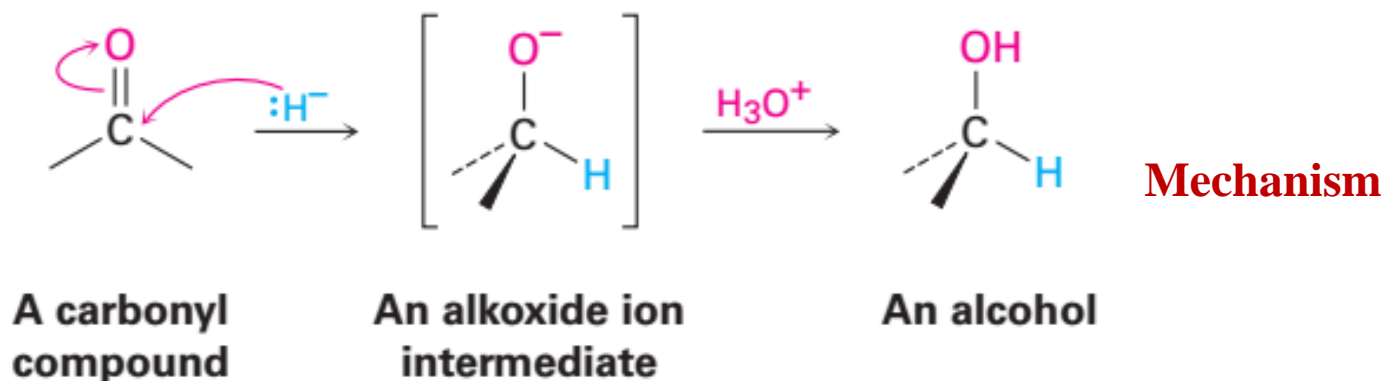
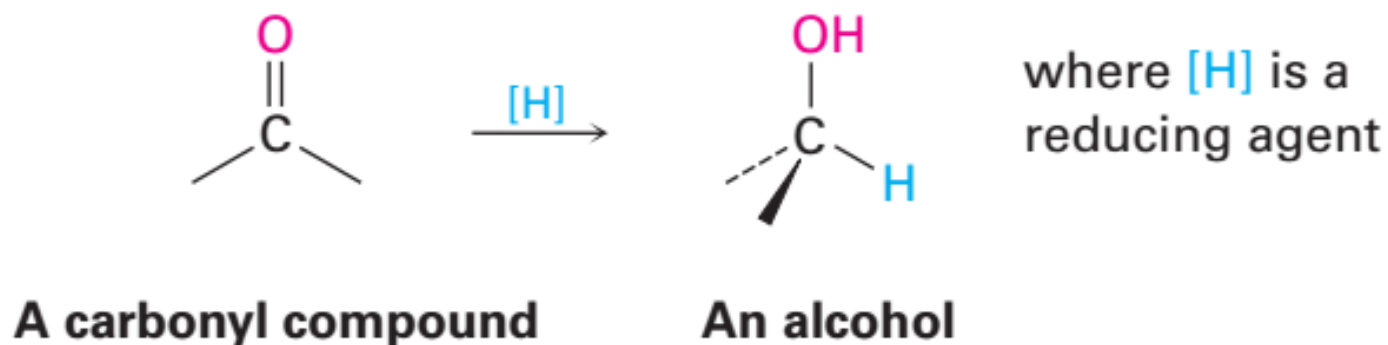
Preparation of alcohols

Điều chế
từ alkene



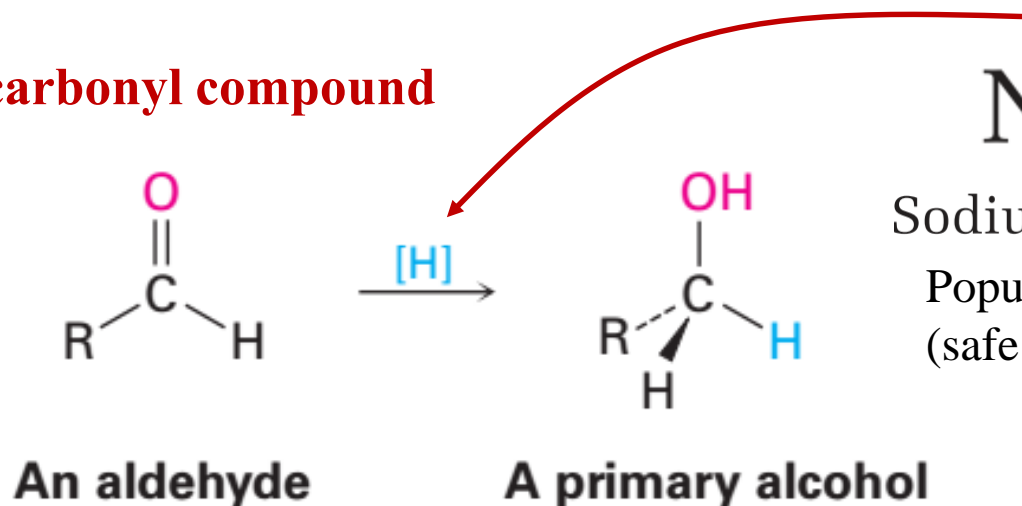
Preparation of alcohols

Điều chế từ carbonyl compound

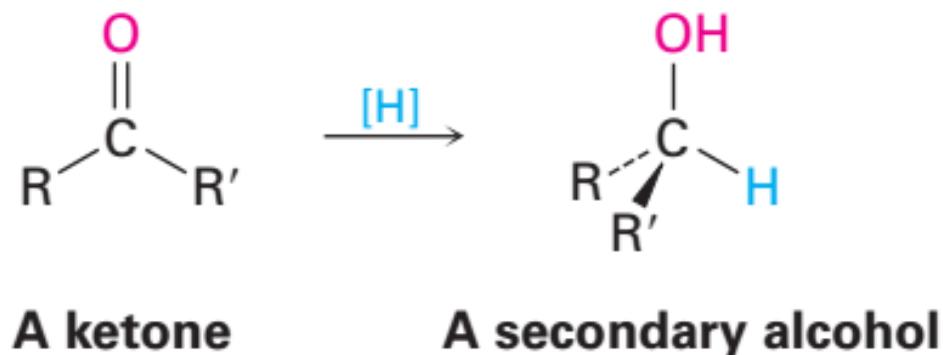


Preparation of alcohols

Điều chế từ carbonyl compound



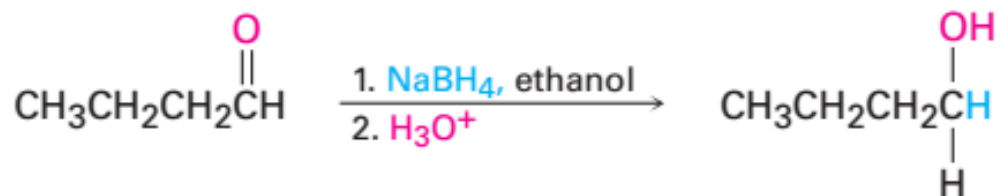
Sodium borohydride
Popular reducing agent
(safe and easy to handle)



Preparation of alcohols

Điều chế từ carbonyl compound

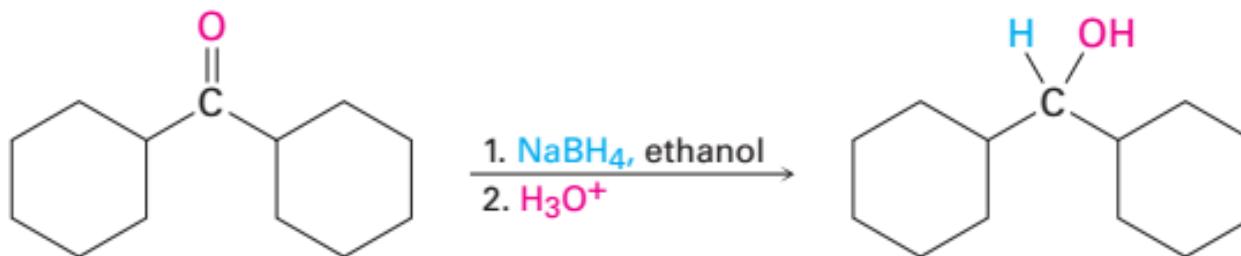
Aldehyde reduction



Butanal

1-Butanol (85%)
(a 1° alcohol)

Ketone reduction

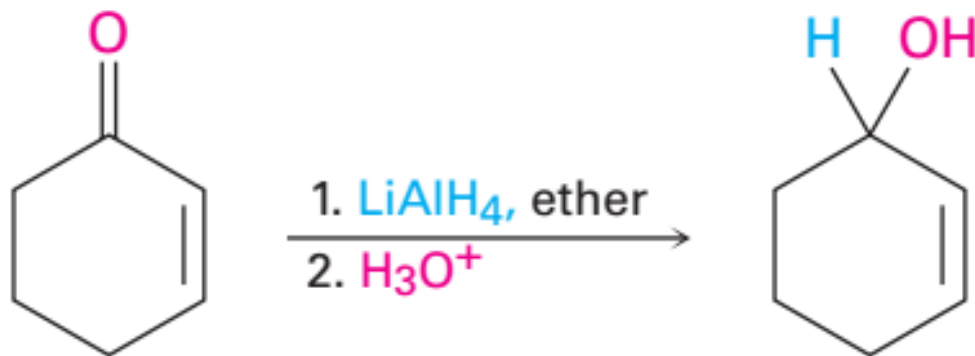


Dicyclohexyl ketone

Dicyclohexylmethanol (88%)
(a 2° alcohol)

Preparation of alcohols

Điều chế từ carbonyl compound



2-Cyclohexenone

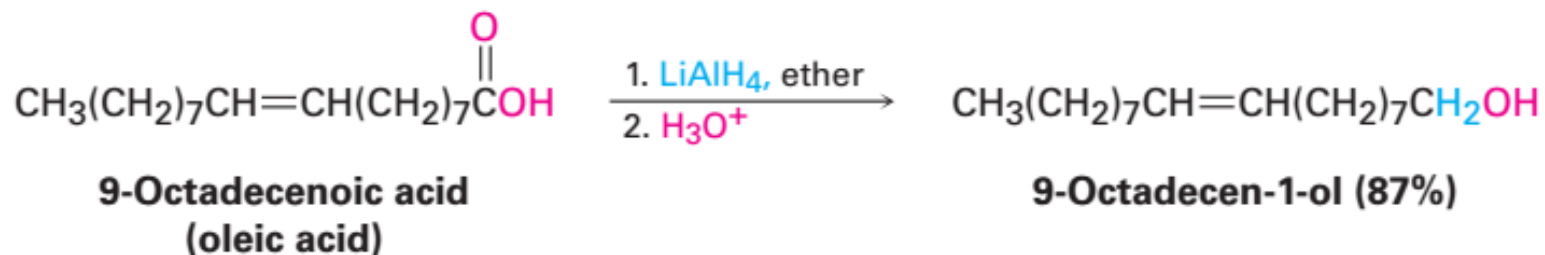
2-Cyclohexenol (94%)

Lithium aluminum hydride, LiAlH_4
A reducing agent, stronger than NaBH_4
Soluble in ether, tetrahydrofuran

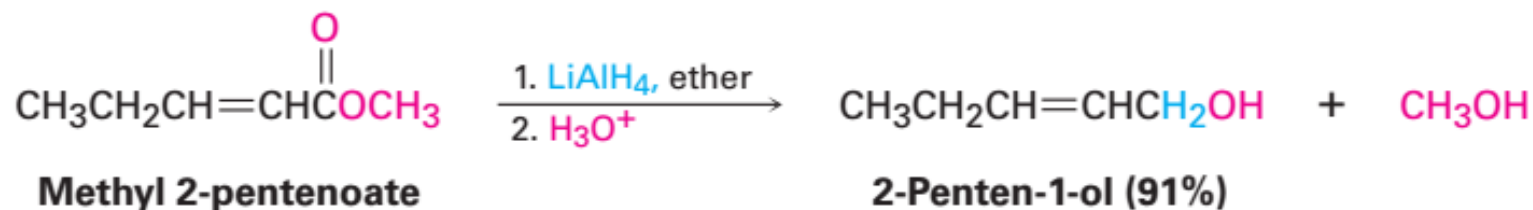
Preparation of alcohols

Reduction of carboxylic and ester

Carboxylic acid reduction

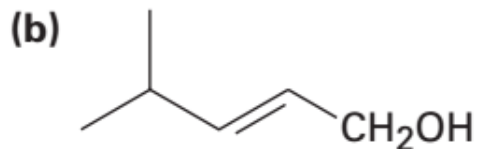
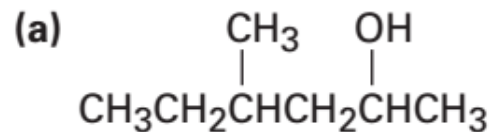


Ester reduction



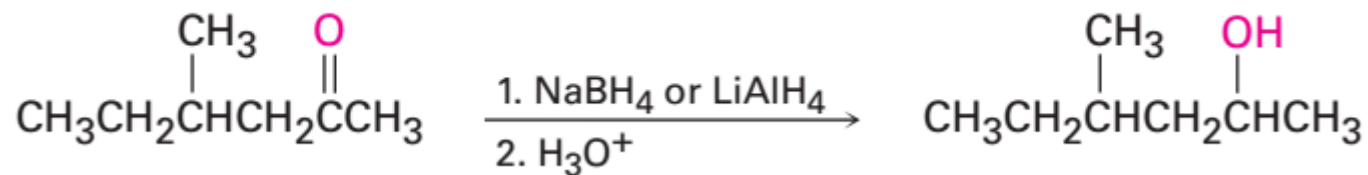
Problem

What carbonyl compounds would you reduce to obtain the following alcohols?

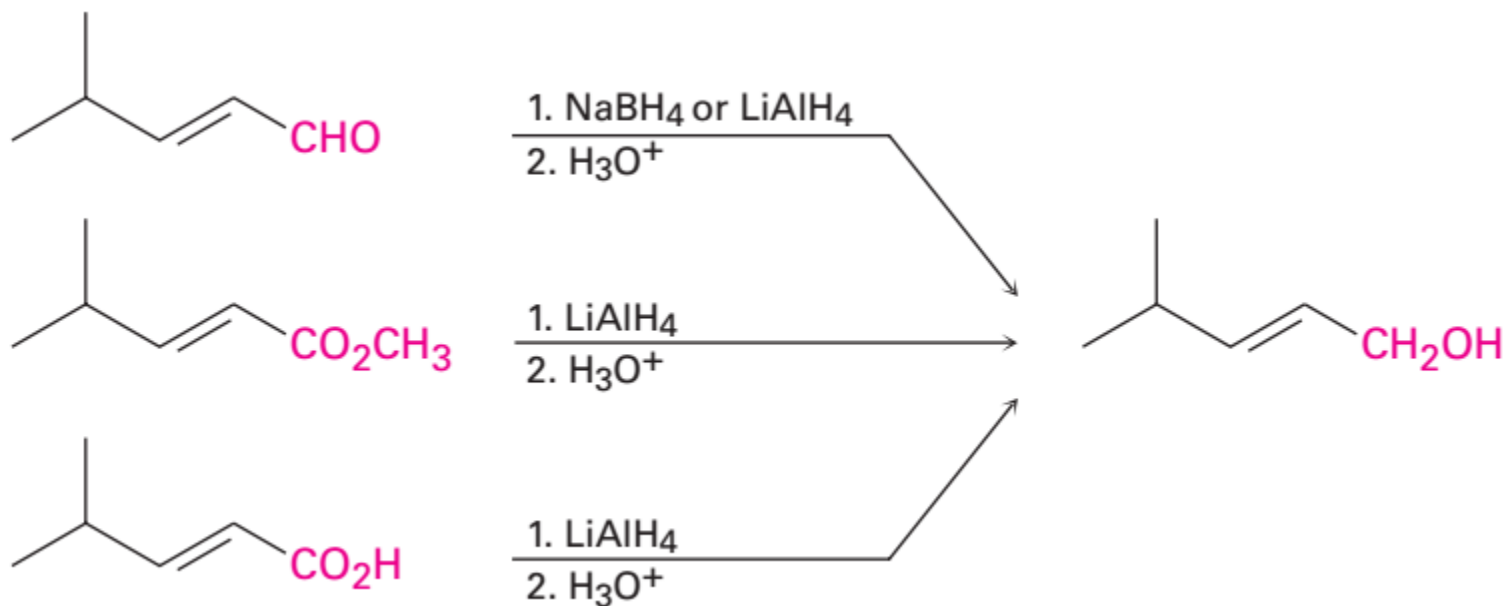


Solution

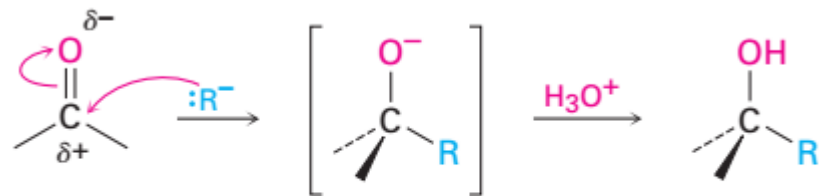
a



b



Grignard reagents

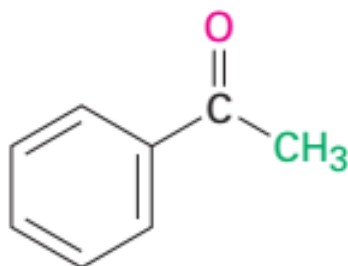


A carbonyl compound

An alkoxide ion intermediate

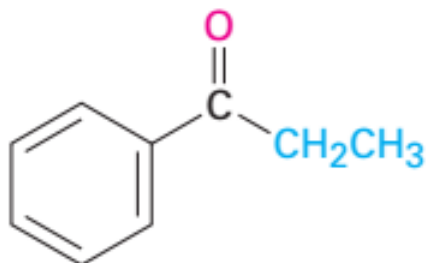
An alcohol

Acetophenone



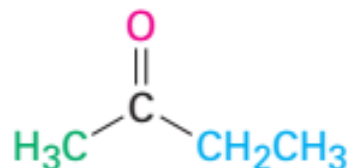
1. CH_3CH_2MgBr
2. H_3O^+

Propiophenone

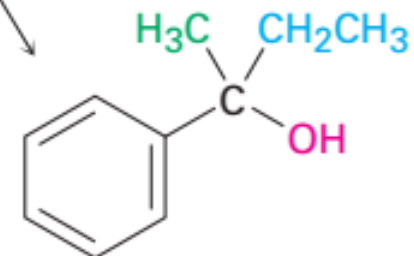


1. CH_3MgBr
2. H_3O^+

2-Butanone



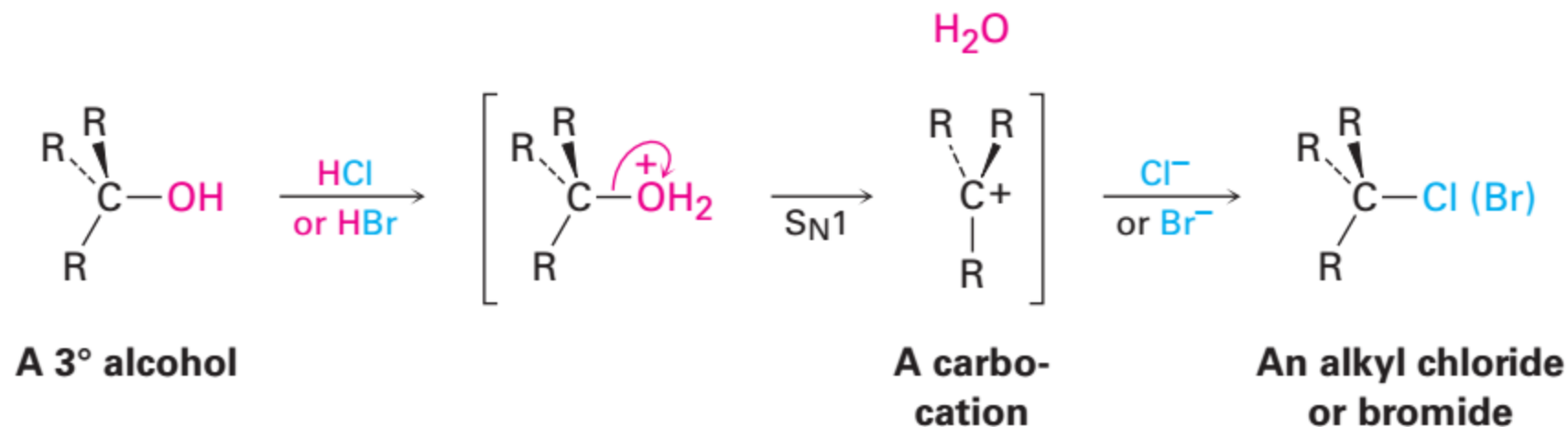
1. C_6H_5MgBr
2. H_3O^+



2-Phenyl-2-butanol

Reaction of alcohols

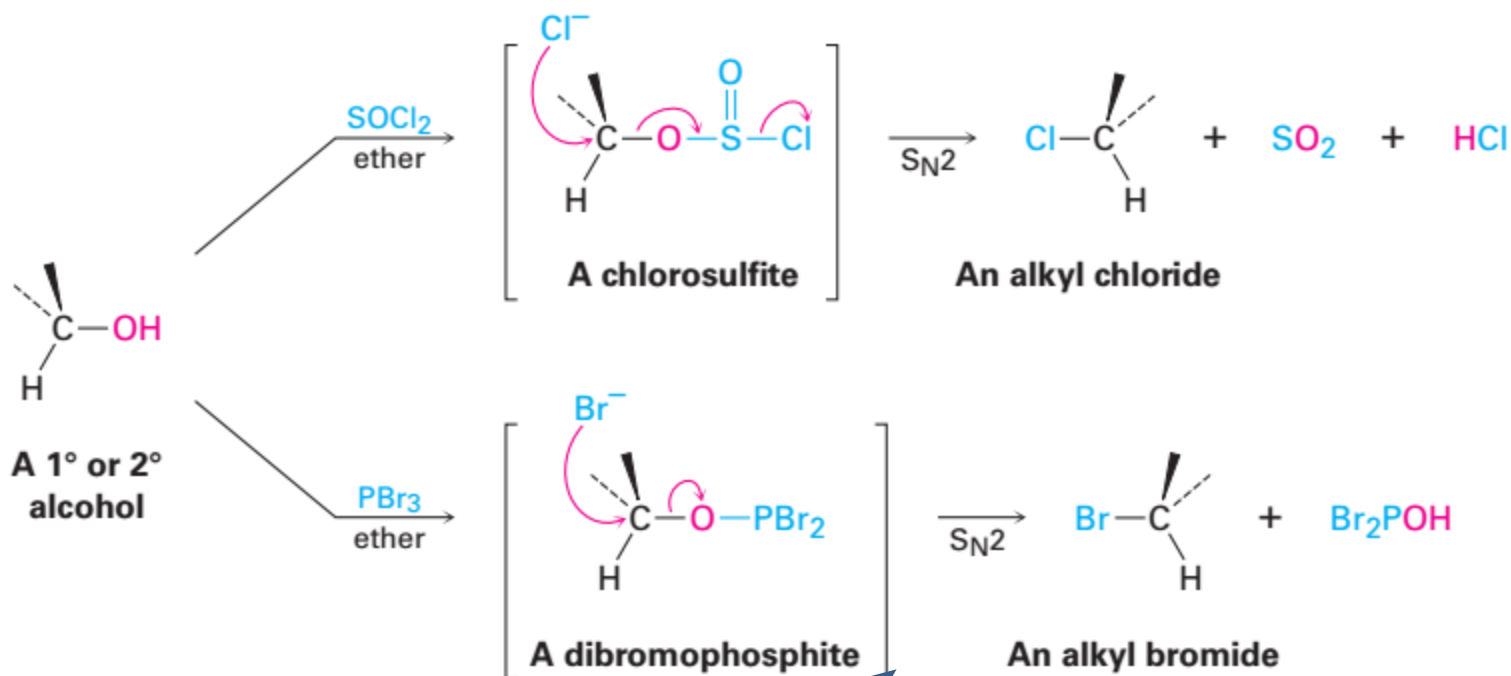
Conversion into alkyl halide



**This only works
with tertiary alcohol**

Reaction of alcohols

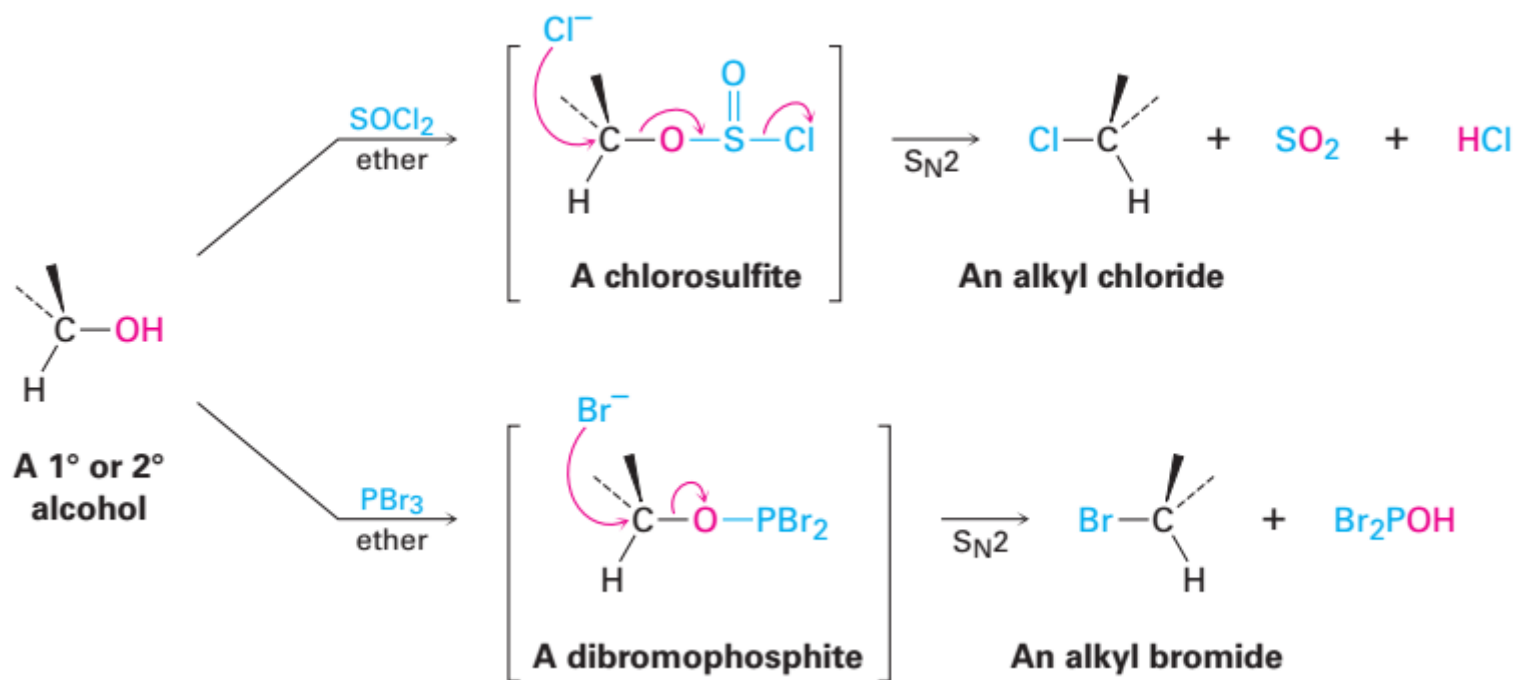
Conversion into alkyl halide



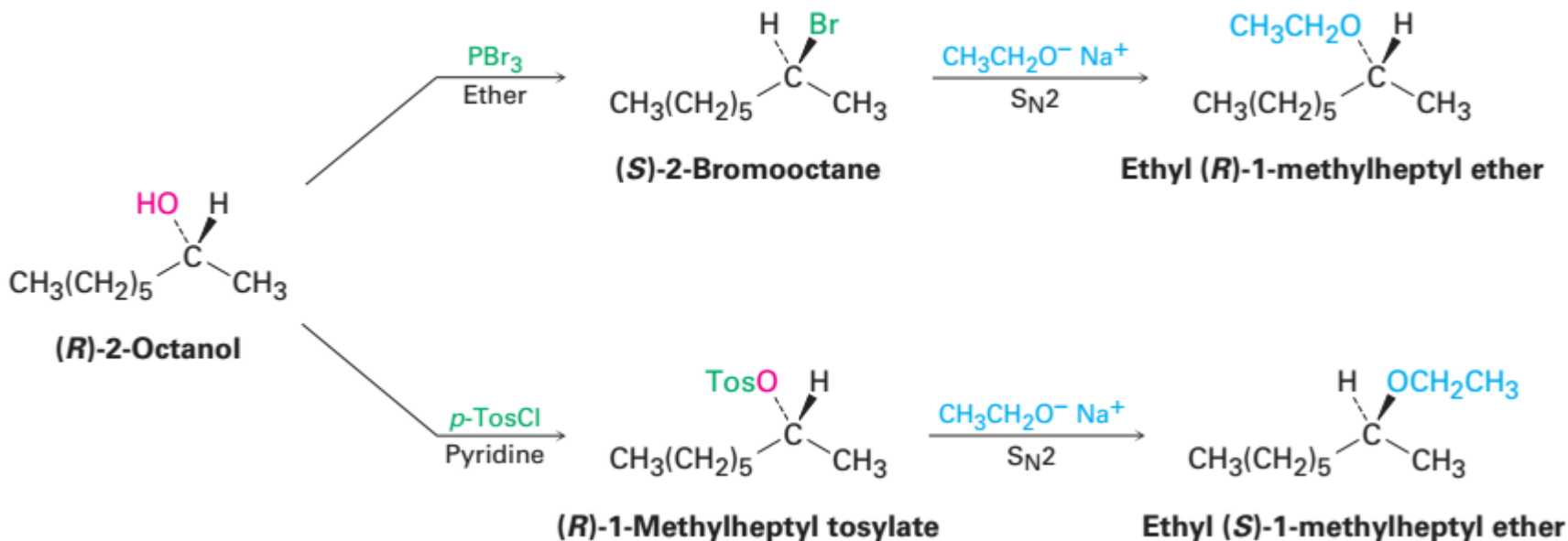
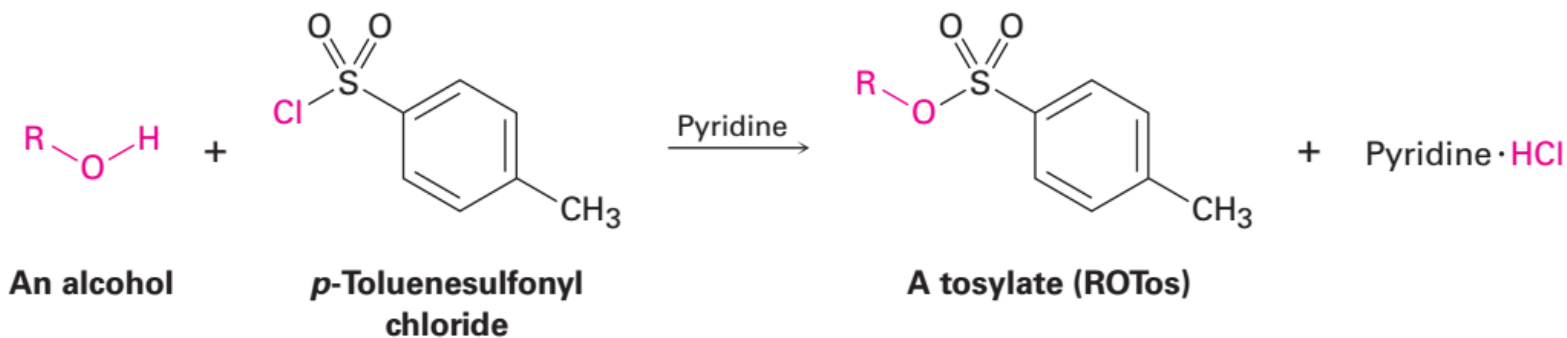
This works primary and secondary alcohol

**Better leaving group
And easier to expel by backside nucleophilic substitution**

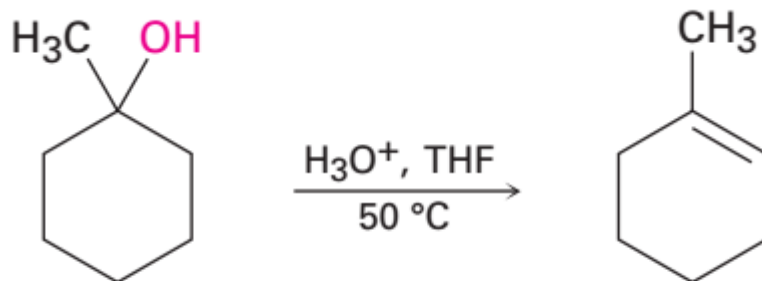
Conversion of alcohol into alkyl halide



Conversion of alcohol into tosylates

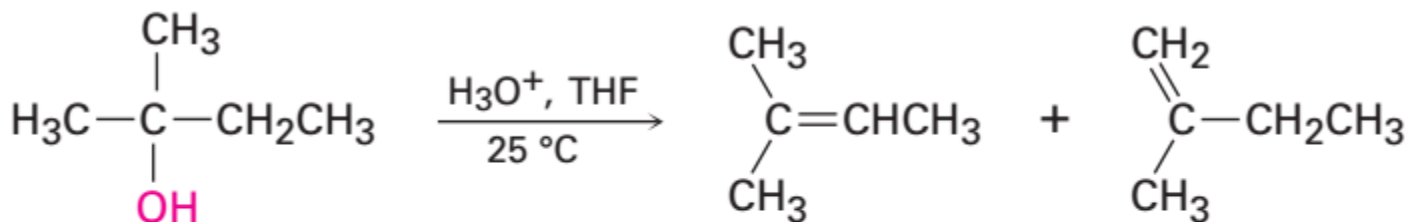


Conversion of alcohol into alkene



1-Methylcyclohexanol

1-Methylcyclohexene (91%)



2-Methyl-2-butanol

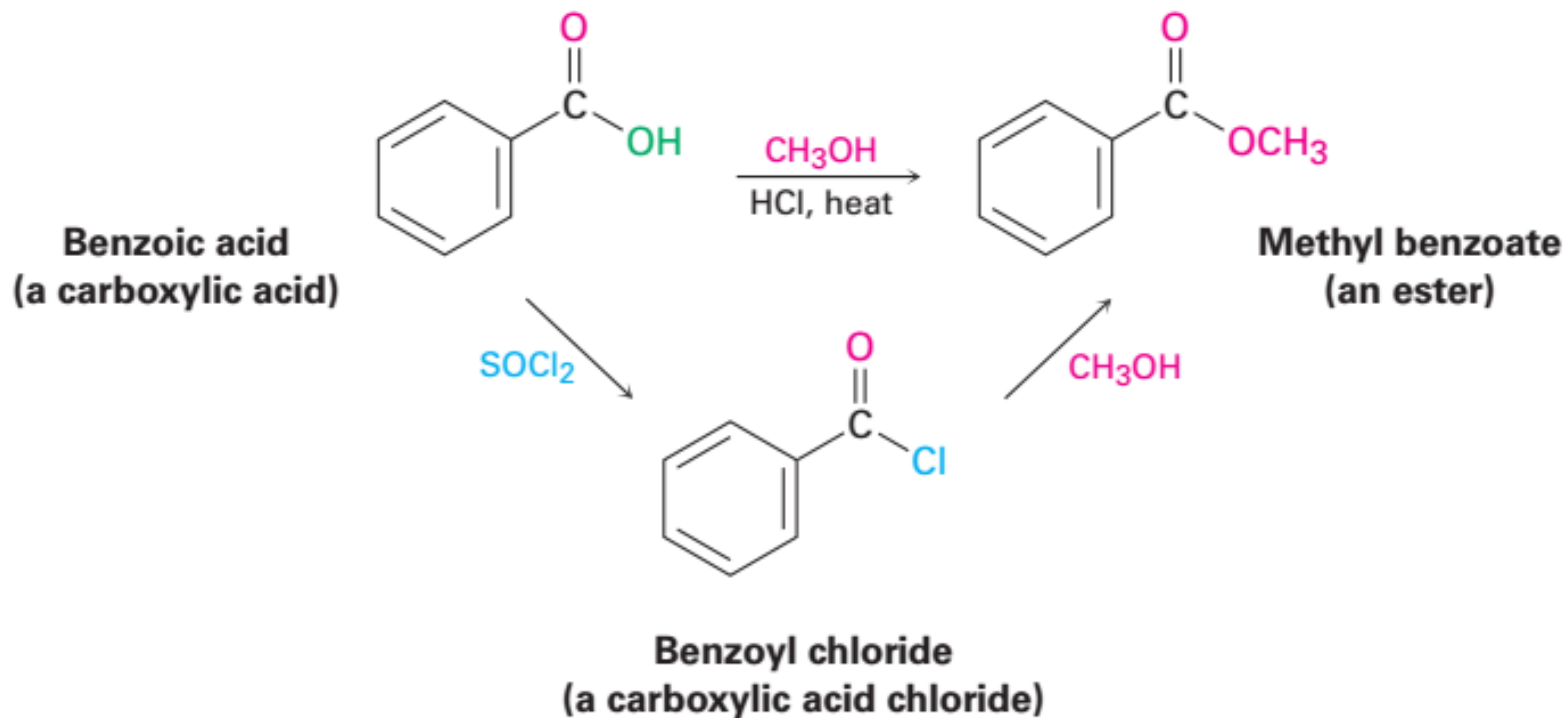
**2-Methyl-2-butene
(trisubstituted)**

**2-Methyl-1-butene
(disubstituted)**

Major product

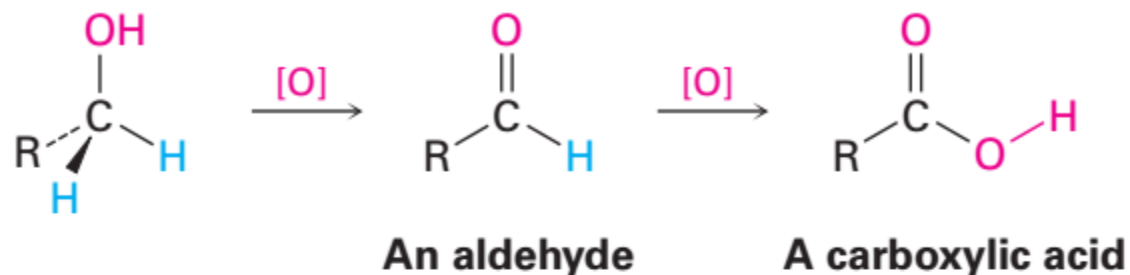
Minor product

Conversion of alcohol into ester

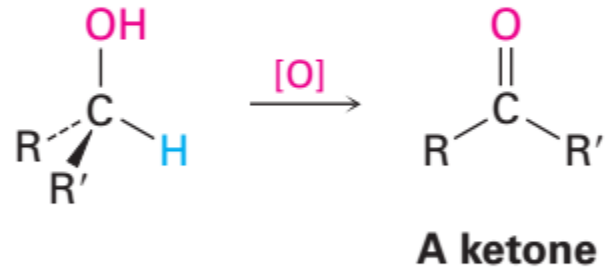


Oxidation of alcohols

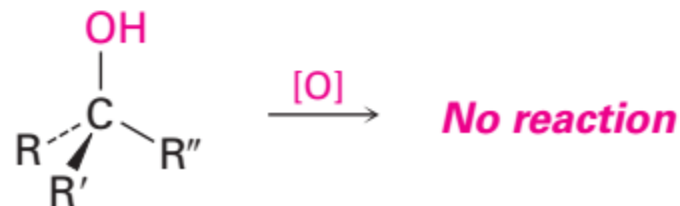
Primary alcohol



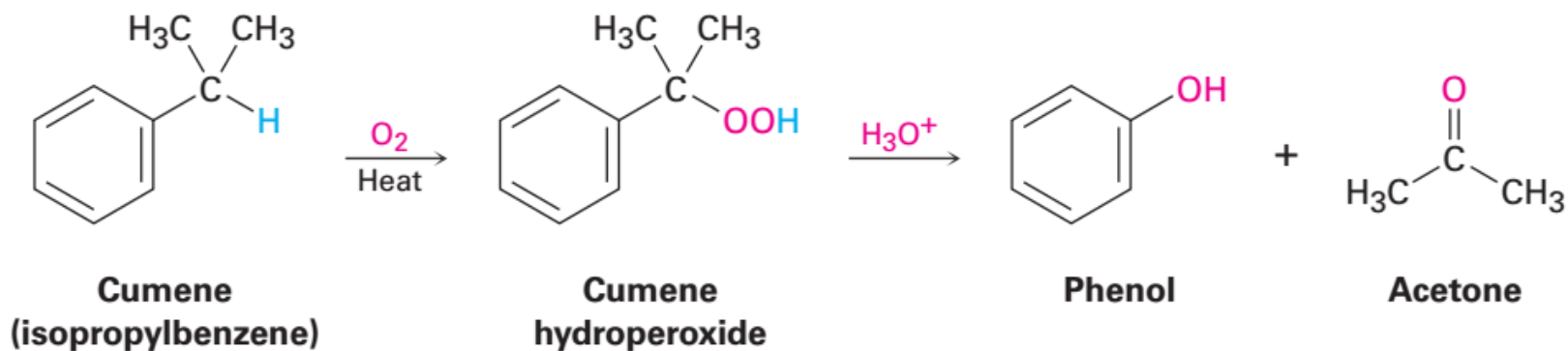
Secondary alcohol



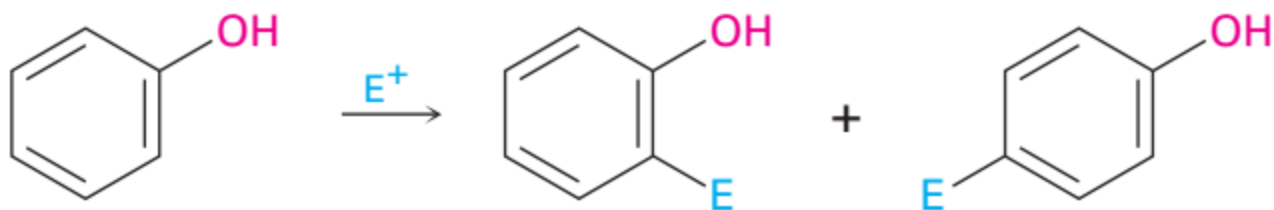
Tertiary alcohol



Production of Phenols



Reaction of Phenols



Electrophilic Aromatic Substitution Reactions