ORGANIC CHEMISTRY

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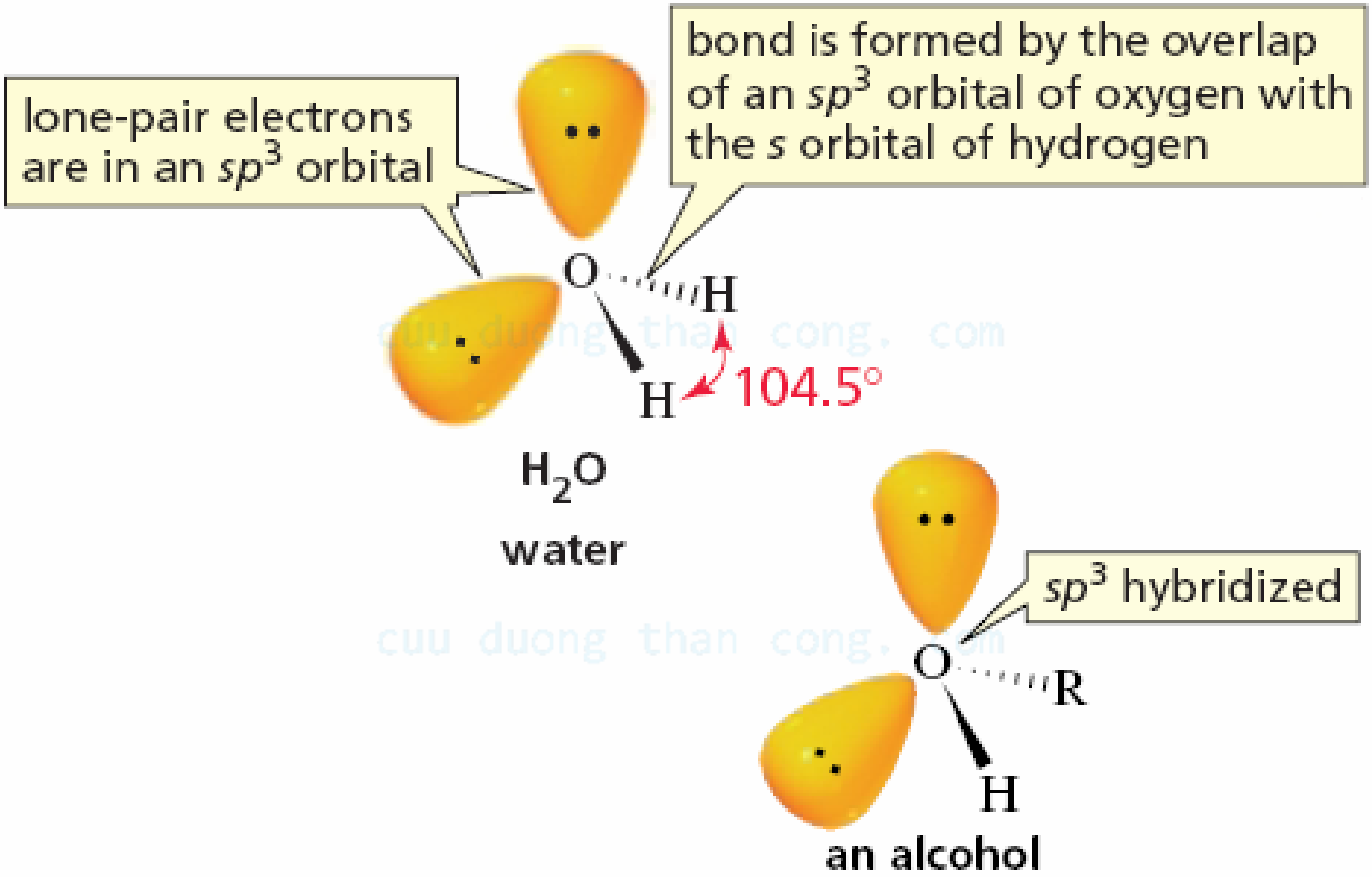
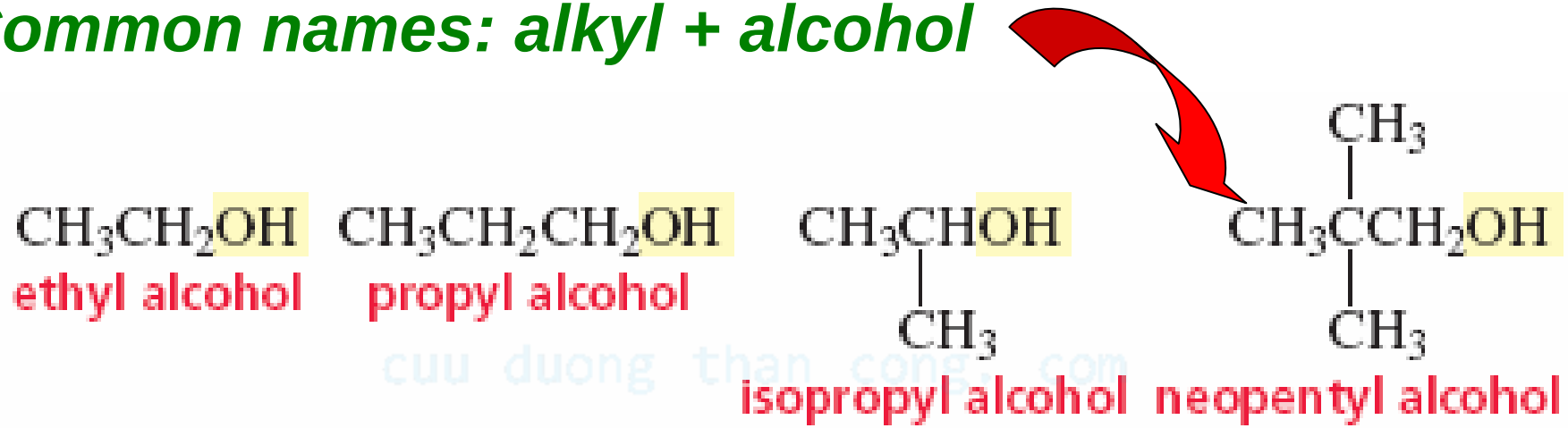
Chapter 10: ALCOHOLS-PHENOLS

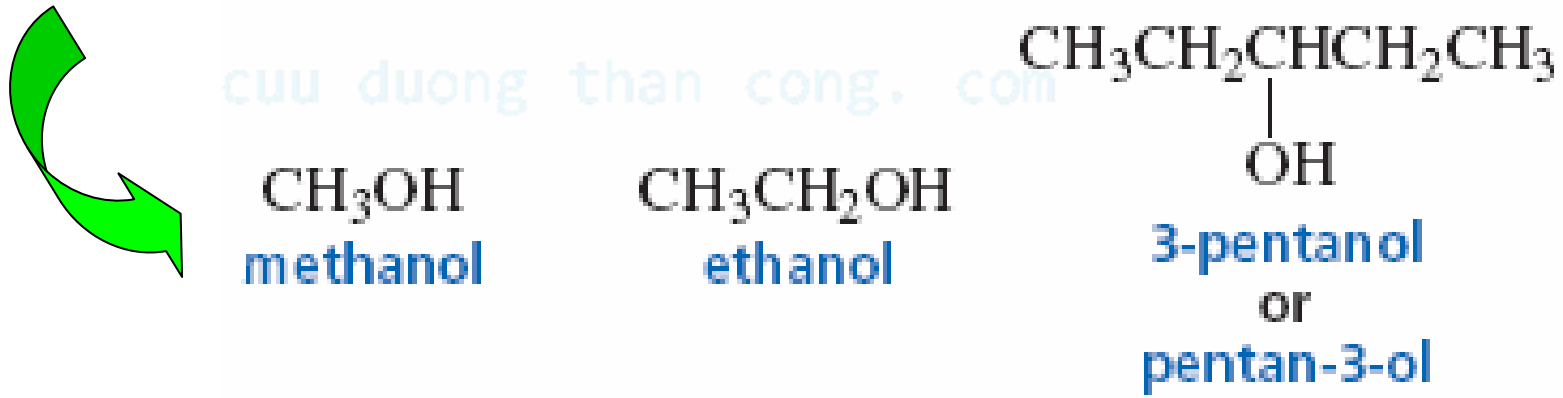


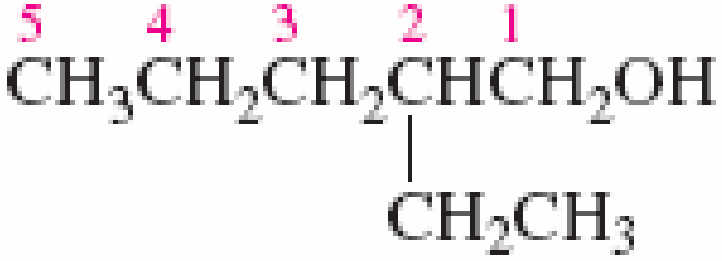
NOMENCLATURE OF ALCOHOLS

Common names: alkyl + alcohol



IUPAC names: hydrocarbon + ol

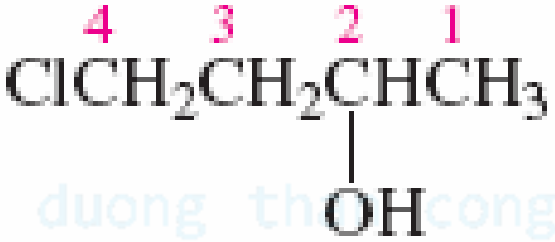




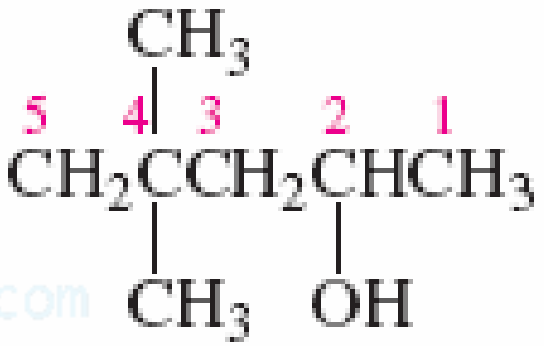
2-ethyl-1-pentanol
or
2-ethylpentan-1-ol

3-butoxy-1-propanol
or
3-butoxypropan-1-ol

3-bromo-1-propanol



4-chloro-2-butanol

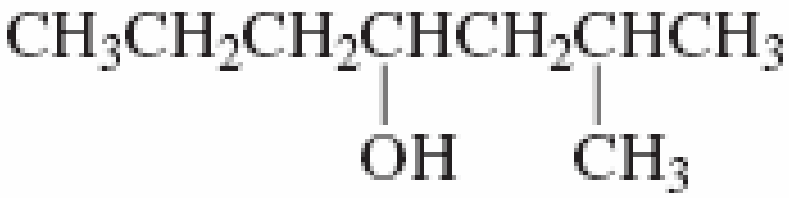


4,4-dimethyl-2-pentanol

2-chloro-3-pentanol

not

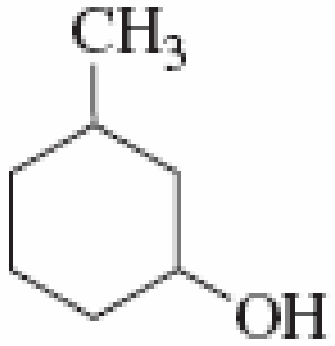
4-chloro-3-pentanol



2-methyl-4-heptanol

not

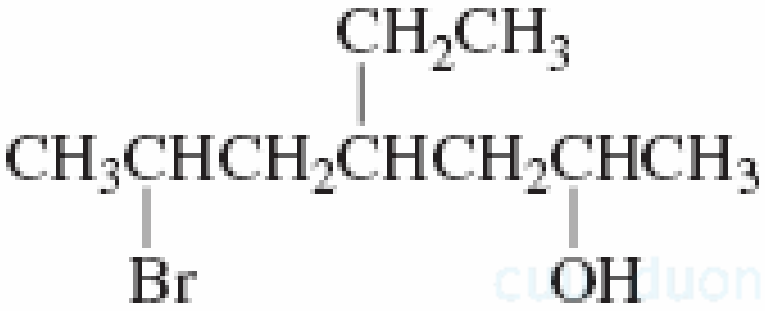
6-methyl-4-heptanol



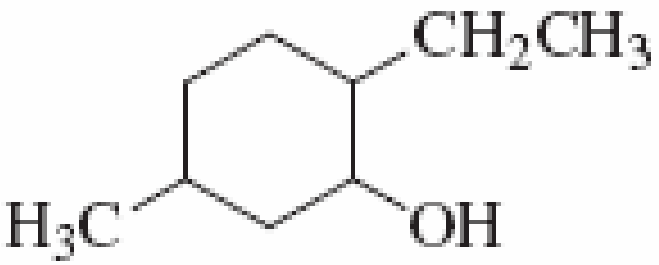
3-methylcyclohexanol

not

5-methylcyclohexanol



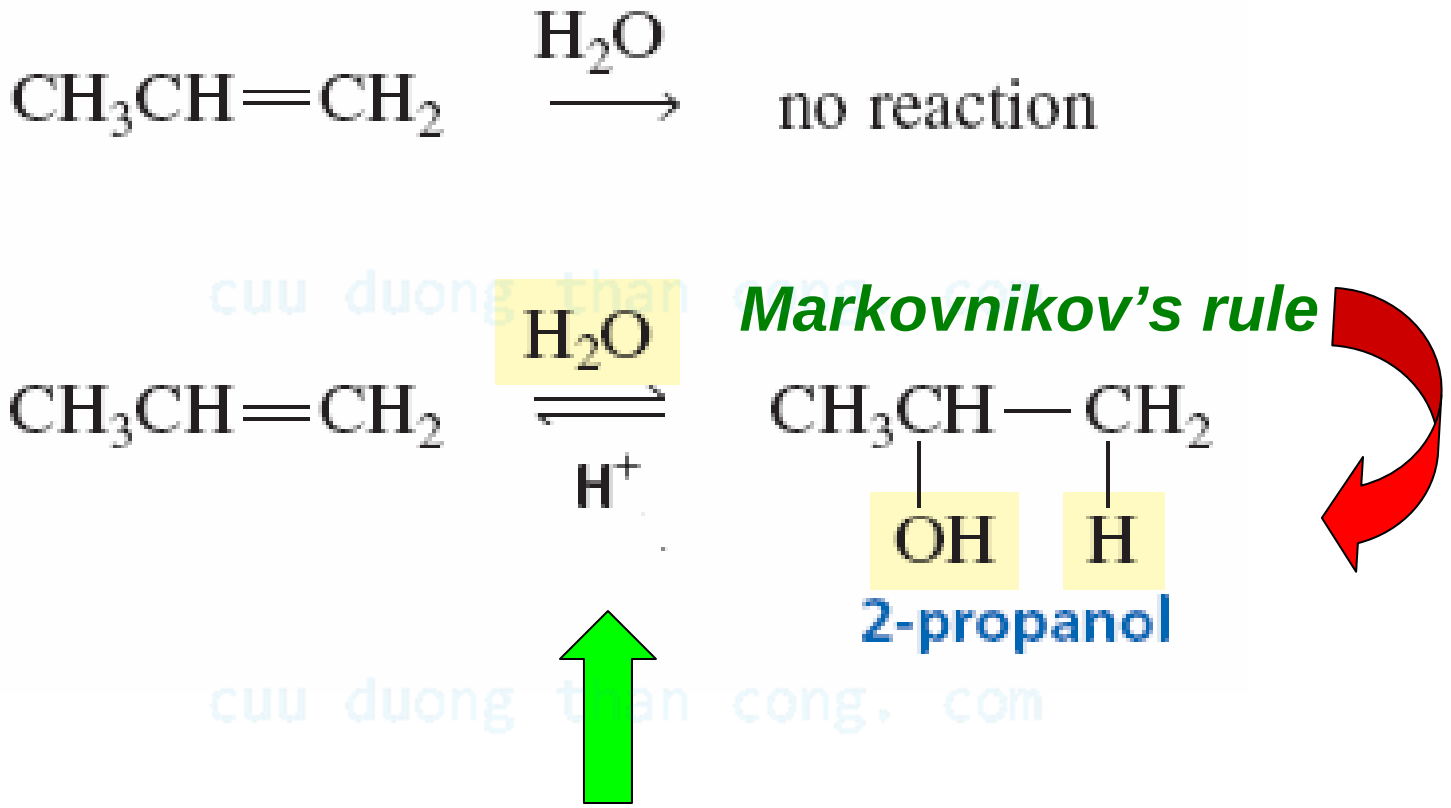
6-bromo-4-ethyl-2-heptanol

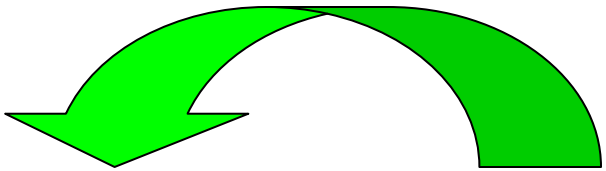


2-ethyl-5-methylcyclohexanol

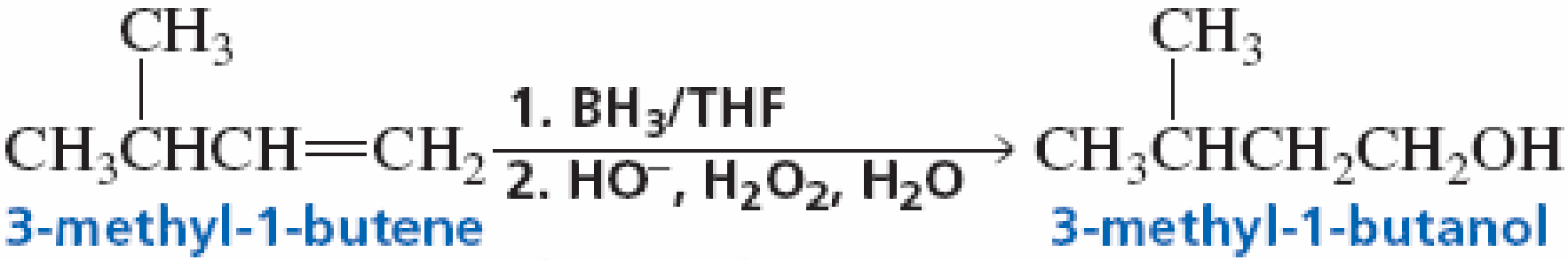
PREPARATION OF ALCOHOLS

Alcohols from alkenes

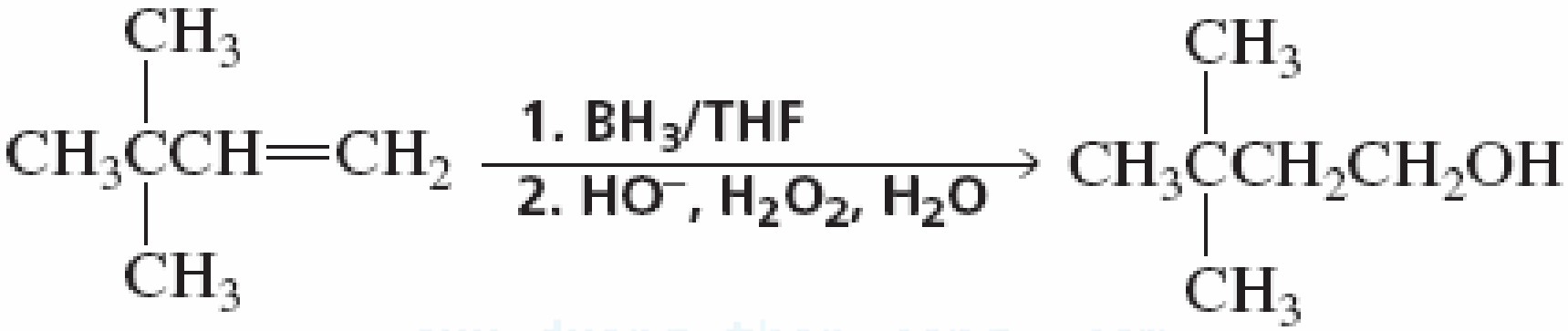




Anti-Markovnikov

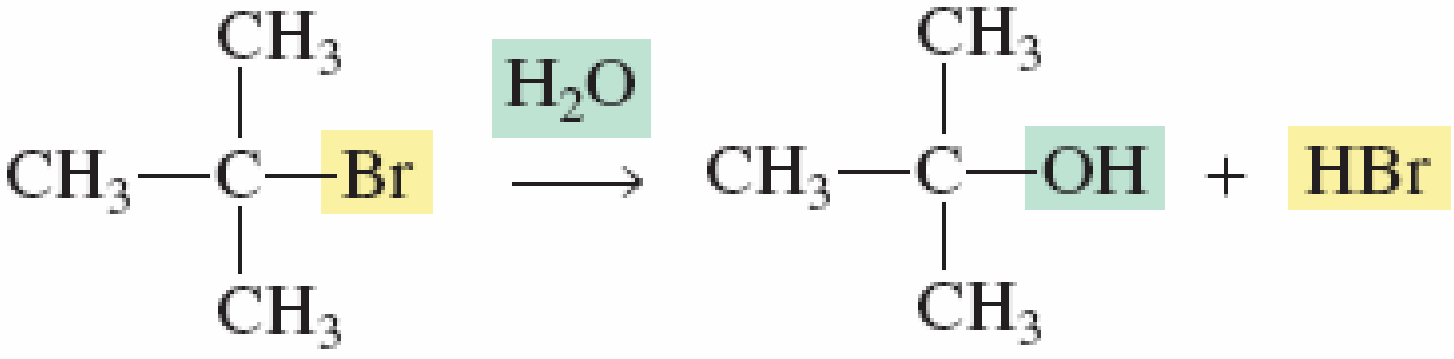


3-methyl-1-butene **3-methyl-1-butanol**

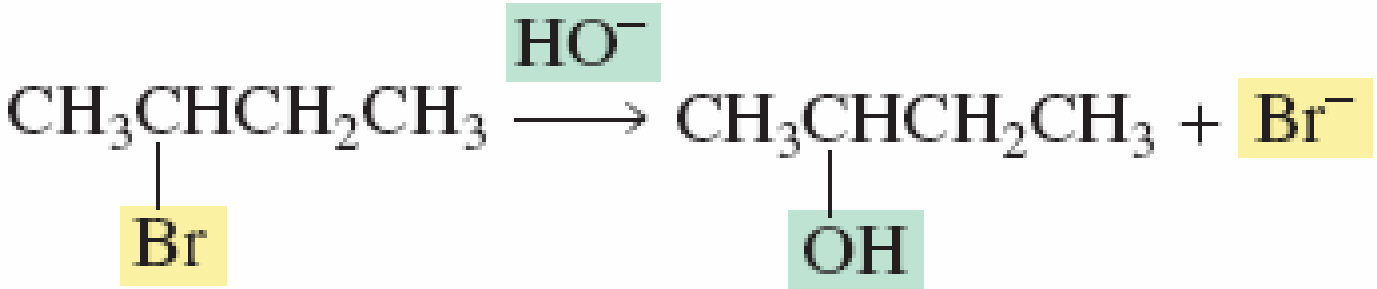


3,3-dimethyl-1-butene **3,3-dimethyl-1-butanol**

Alcohols from alkyl halides



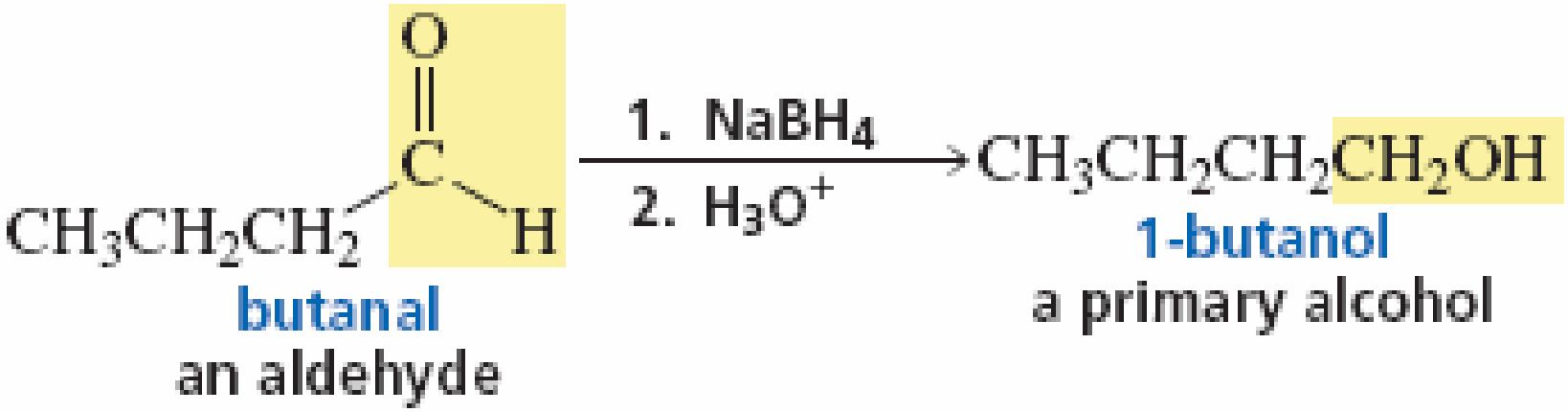
tert-butyl bromide *tert*-butyl alcohol

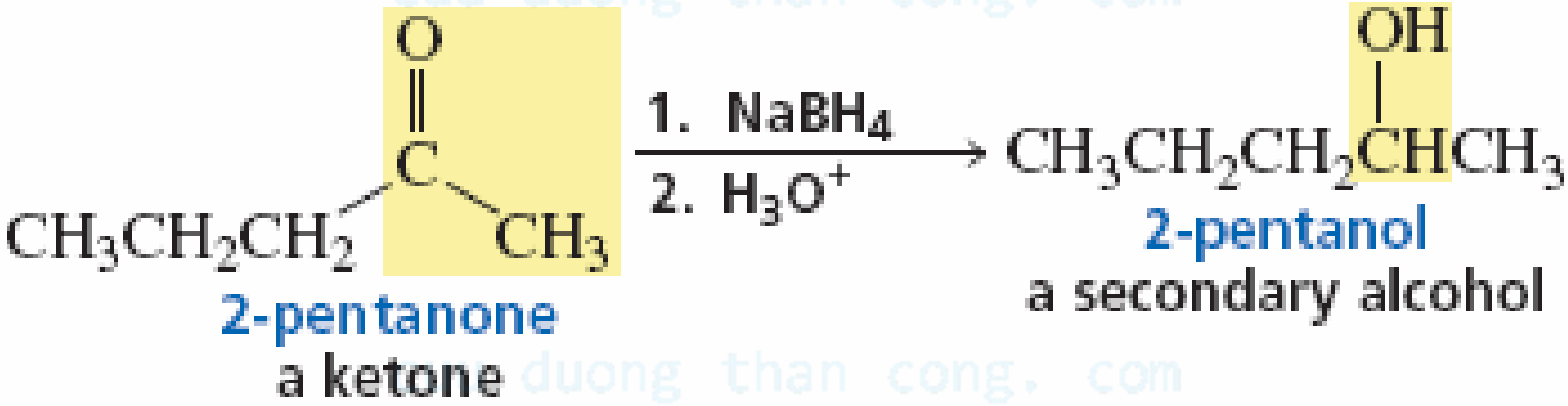


2-bromobutane 2-butanol

Carbocation rearrangements may occur

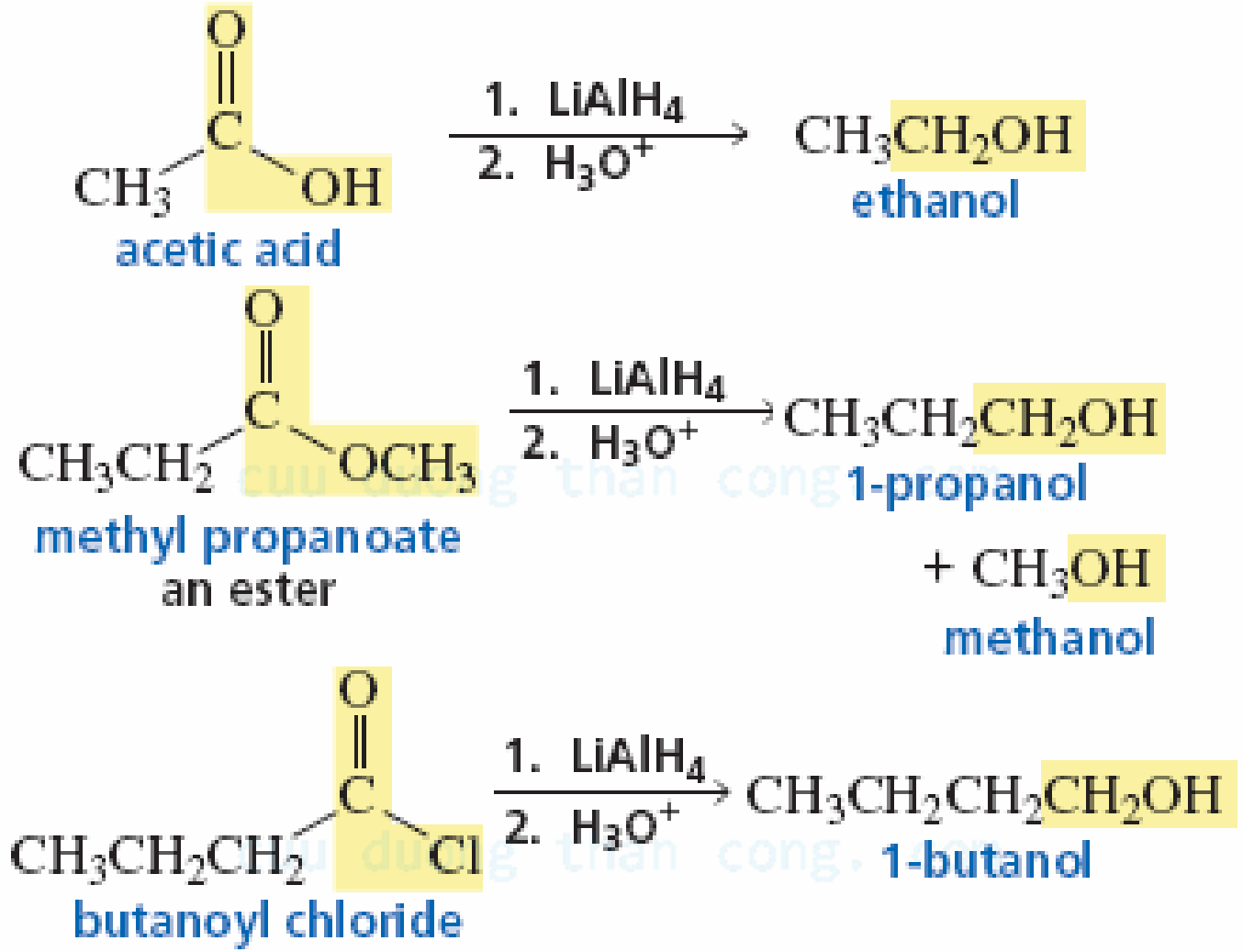
Alcohols from aldehydes & ketones





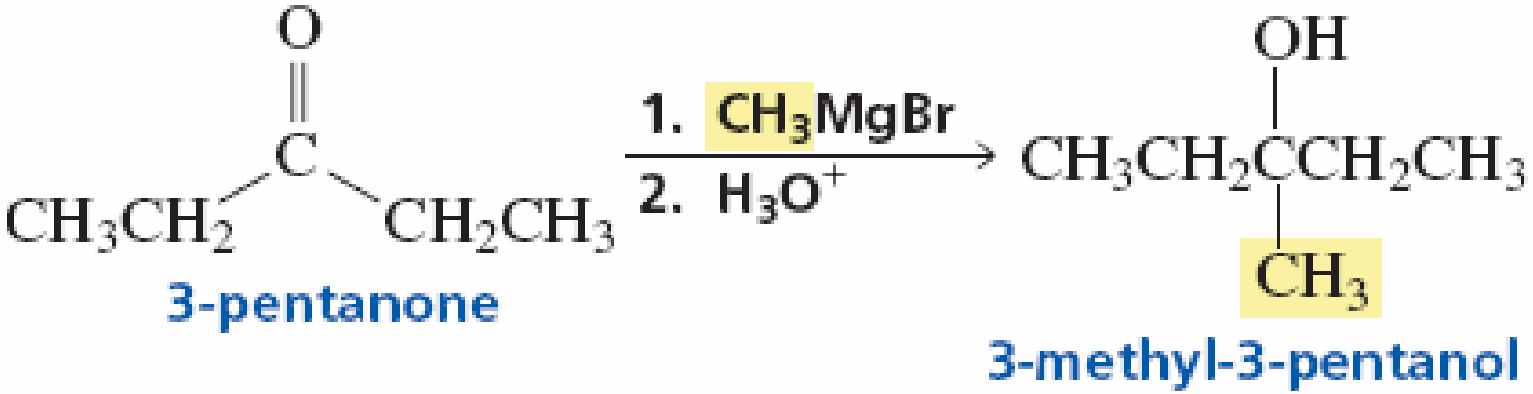
Aldehydes & ketones can also be reduced using $LiAlH_4$, H_2/Pt, Pd, Ni, Ru …

Alcohols from carboxylic acids & derivatives



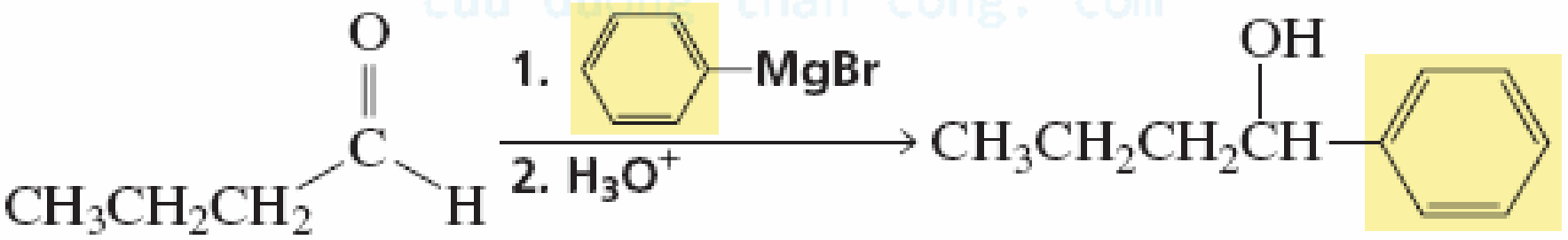
Can NOT use $NaBH_4$, H_2/Pt, Pd, Ni, Ru… for acids

Alcohols from Grignard reagents



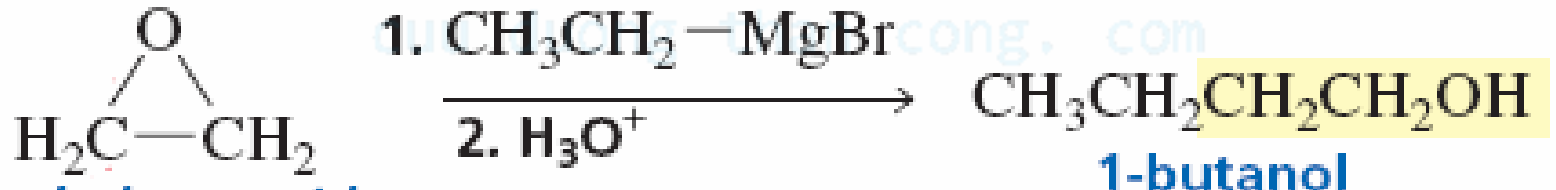
3-pentanone

3-methyl-3-pentanol



butanal

1-phenyl-1-butanol



ethylene oxide

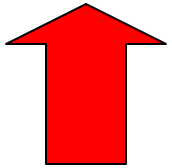
1-butanol

REACTIONS OF ALCOHOLS

Reactions of proton in -OH

$$ROH + Na \longrightarrow RO^- + Na^+ + \frac{1}{2}H_2$$

$$ROH + NaH \longrightarrow RO^- + Na^+ + H_2$$

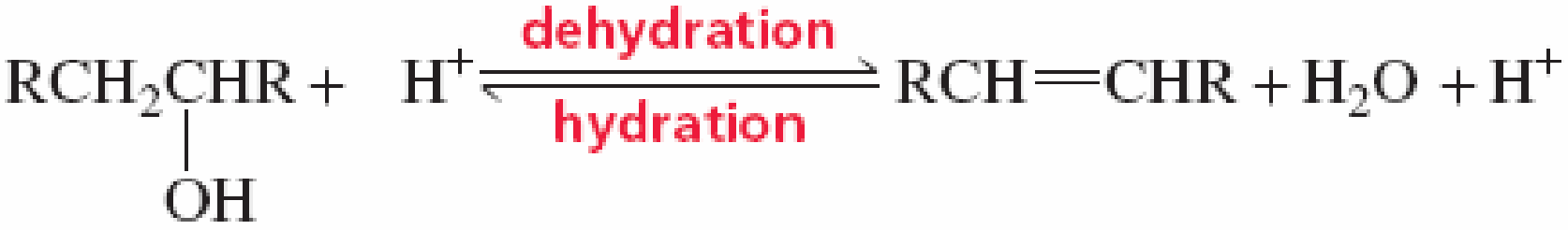


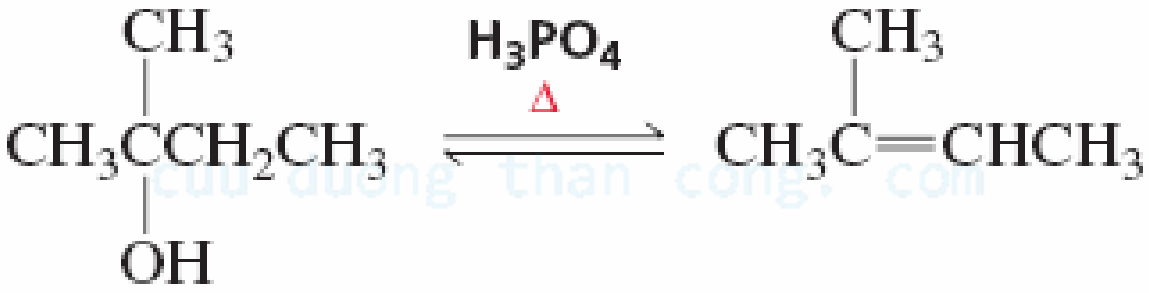
Can NOT react with NaOH

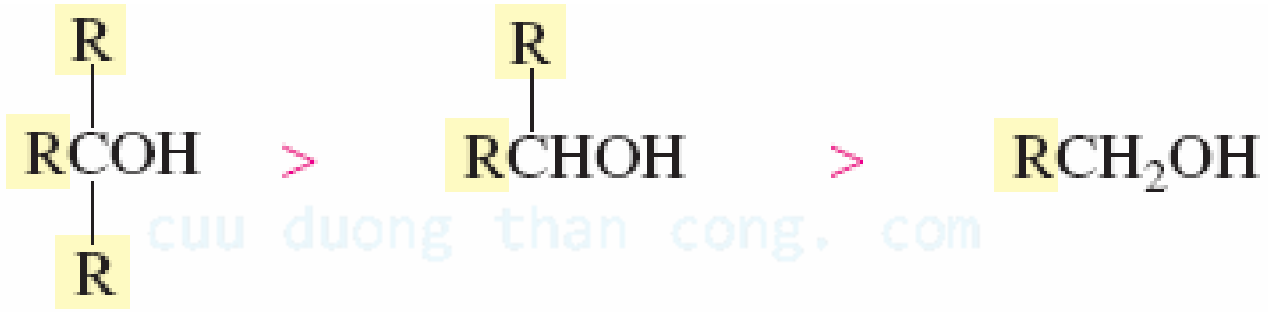
Relative Acidity

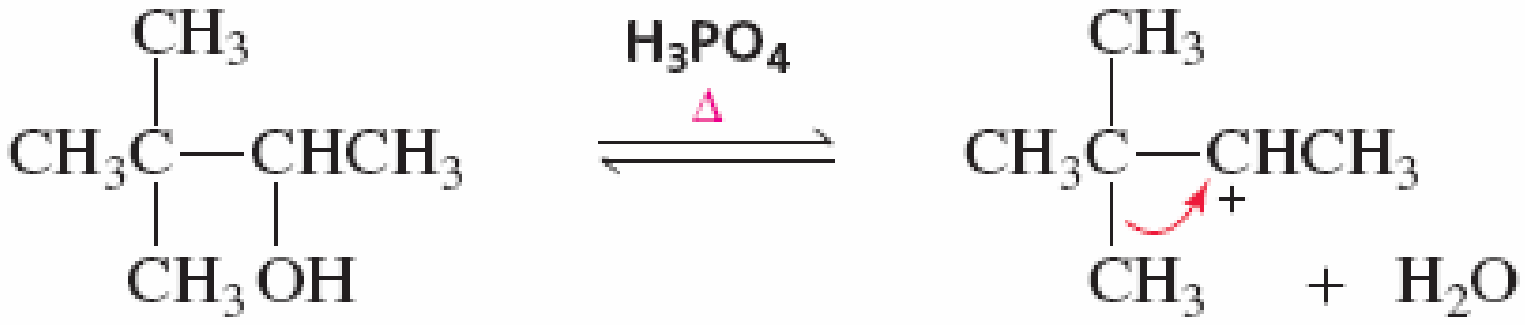
$H_2O > ROH > RC{\equiv}CH > H_2 > NH_3 > RH$

Dehydration reactions





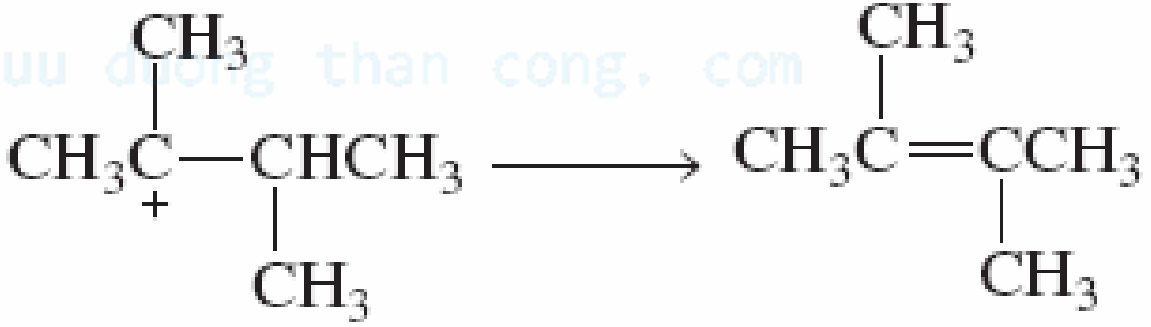




3,3-dimethyl-2-butanol

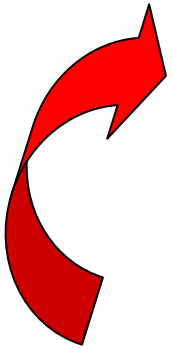
secondary carbocation + H_2O

1,2-methyl shift



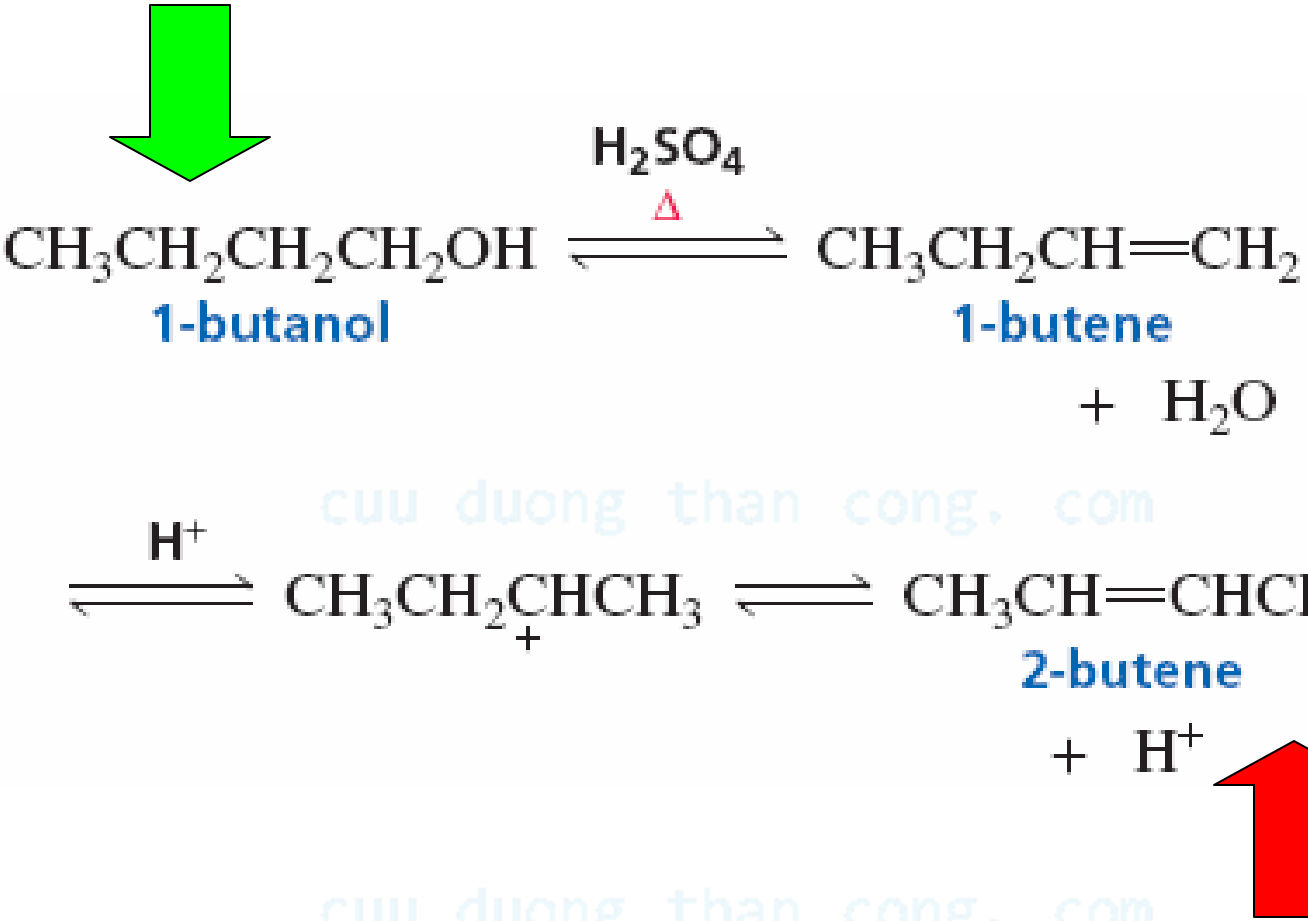
tertiary carbocation

2,3-dimethyl-2-butene



isomerization

Primary alcohol



Internal alkene

1-alkenes can NOT be prepared using the dehydration reaction

Conversion of alcohols to alkyl halides

Only in acidic conditions

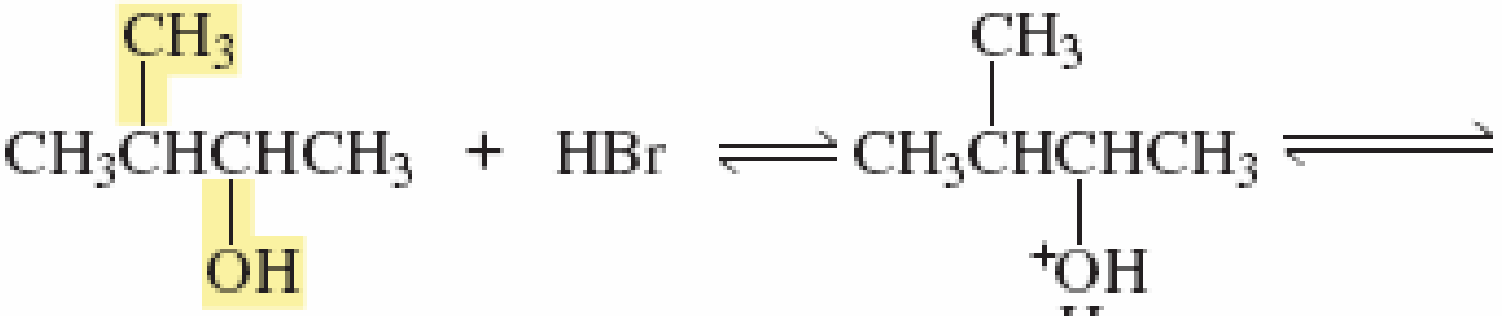
$$CH_3OH + Br^- \not\longrightarrow CH_3Br + HO^-$$

strong base

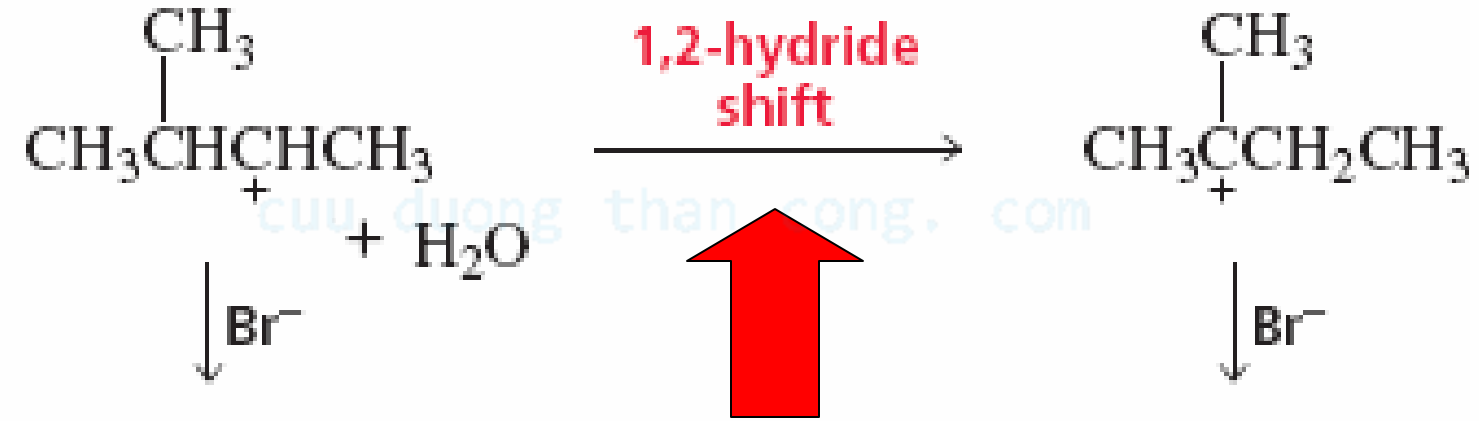
$$CH_3OH + HBr \rightleftharpoons CH_3\overset{H}{\overset{|}{O}}H^+ \xrightarrow{\Delta} CH_3Br + Br^- + H_2O$$

weak base

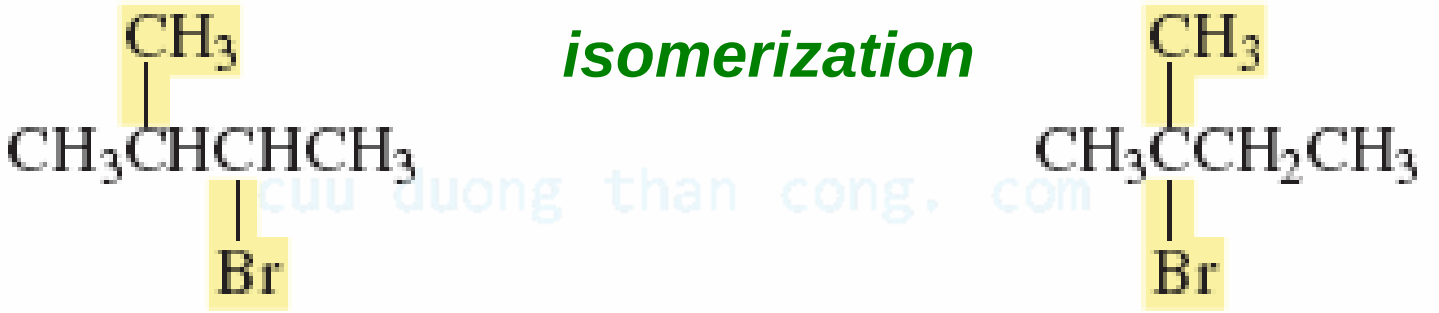
$$CH_3CH_2CH_2OH \xrightarrow[\Delta]{ZnCl_2} CH_3CH_2CH_2Cl + H_2O + HCl$$



3-methyl-2-butanol

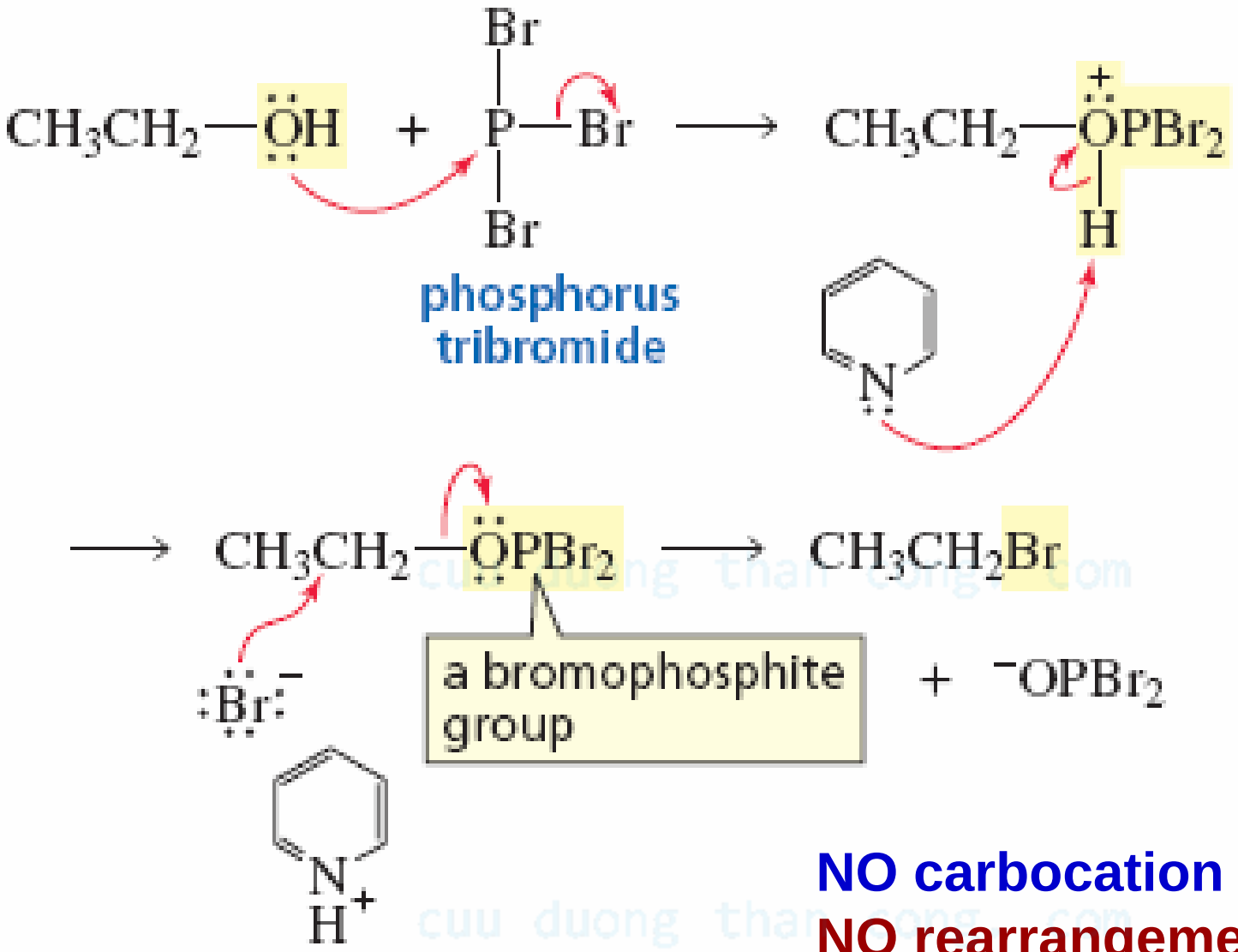


isomerization



2-bromo-3-methyl-butane
minor product

2-bromo-2-methyl-butane
major product

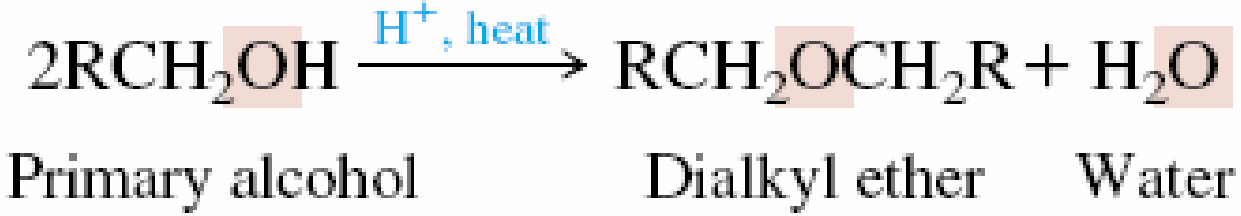


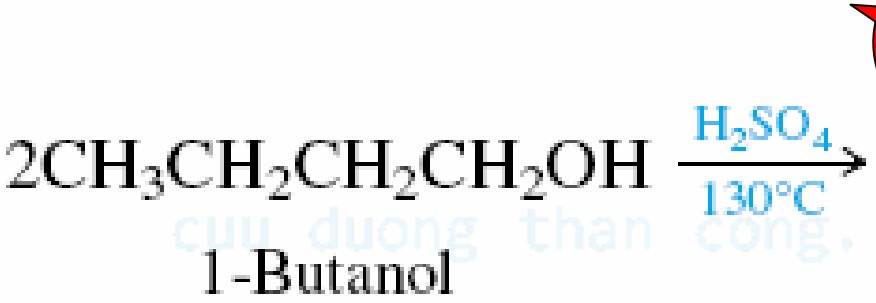
PCl_3, $SOCl_2$ … can also be used

NO carbocation formation,
NO rearrangement

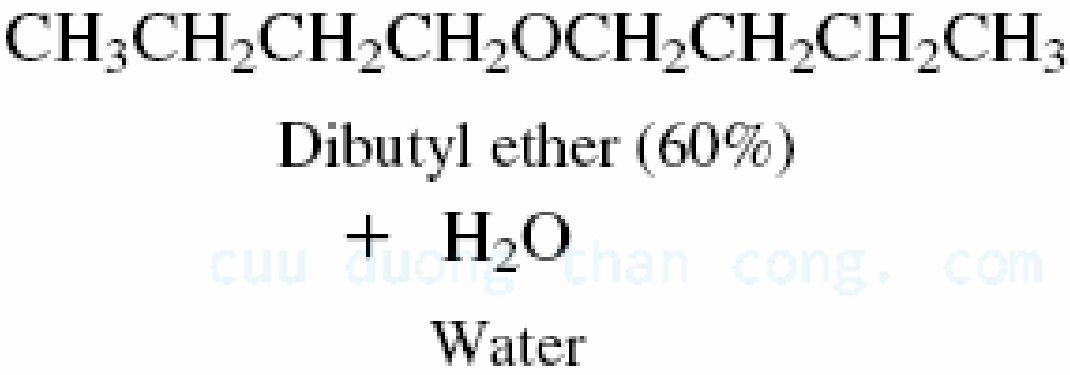
Can NOT work for tertiary alcohols due to steric hindrance

Conversion of alcohols to ethers





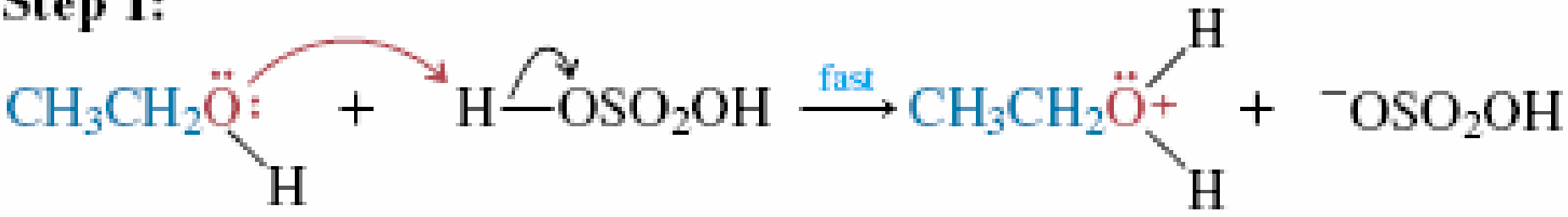
Only for symmetric ether



Only effective for primary alcohols

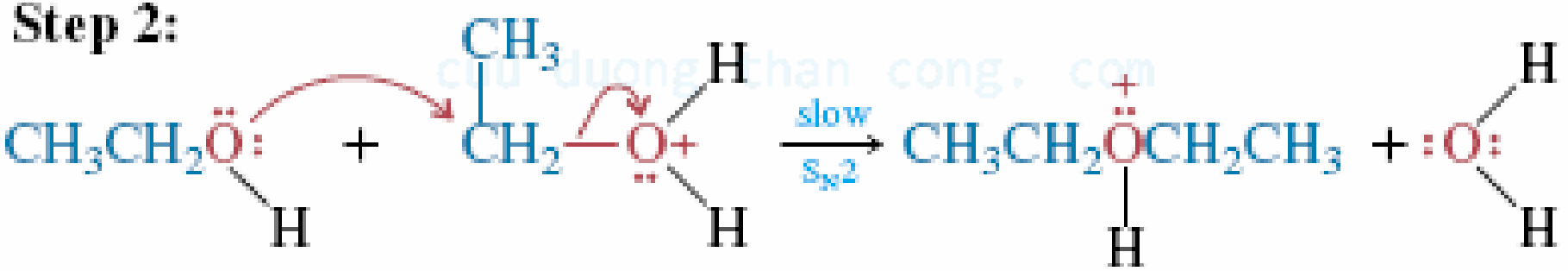
Reaction mechanism:

Step 1:



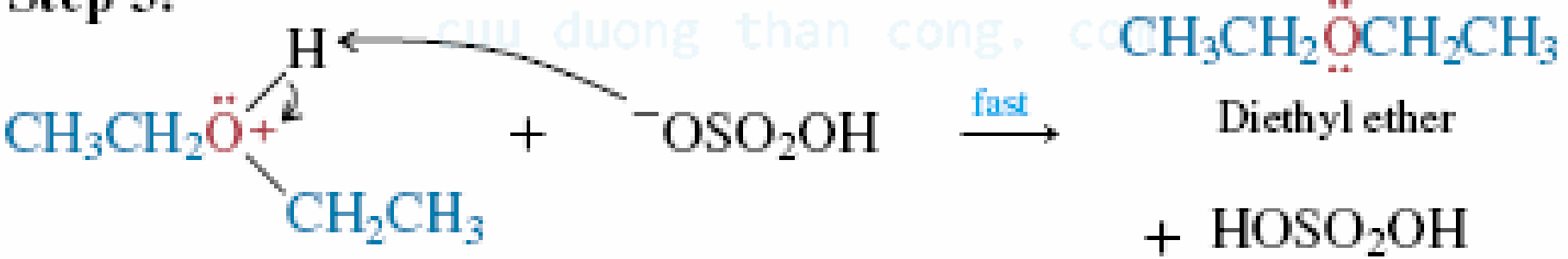
Ethyl alcohol — Sulfuric acid — Ethyloxonium ion — Hydrogen sulfate ion

Step 2:



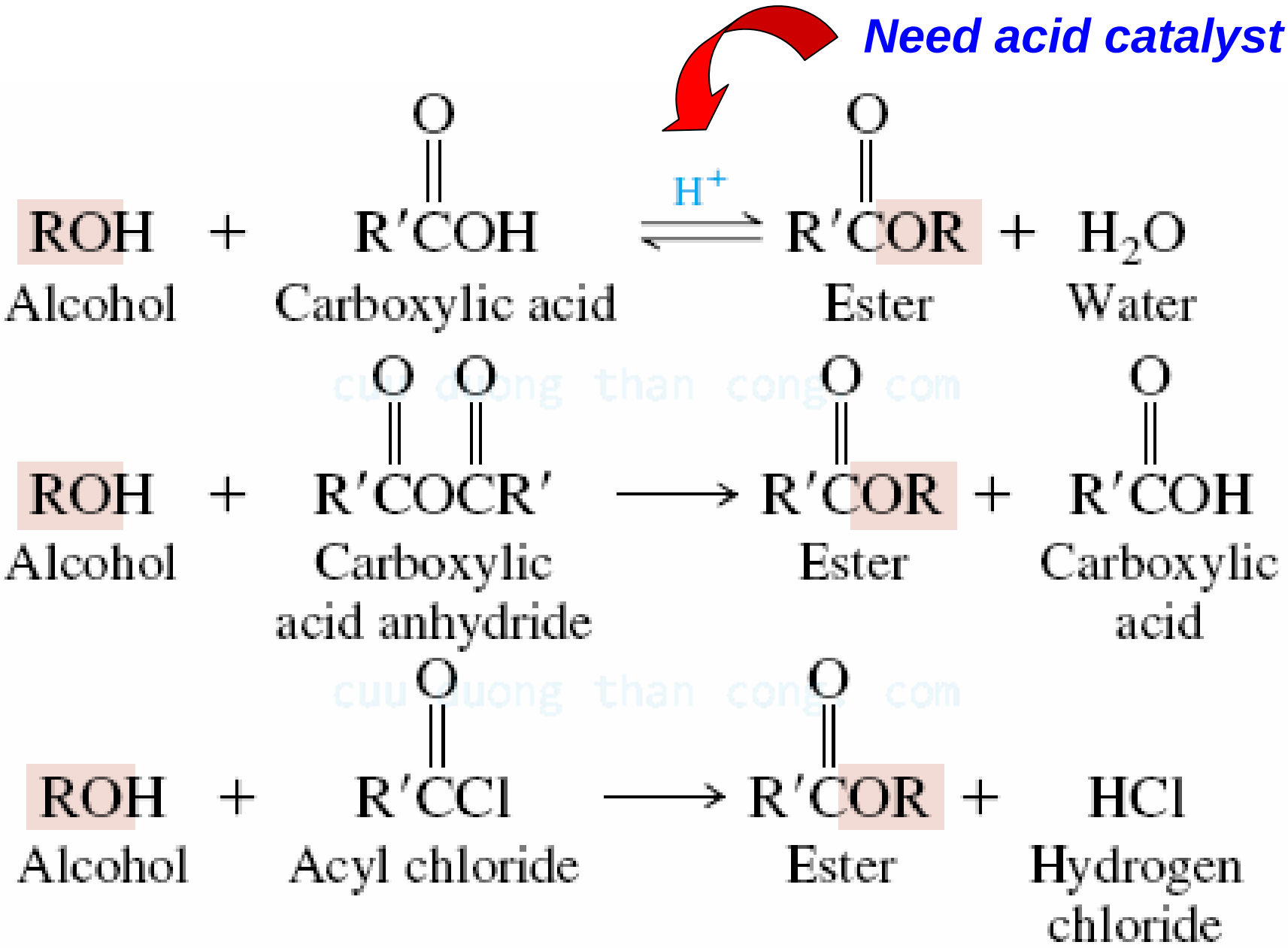
Ethyl alcohol — Ethyloxonium ion — Diethyloxonium ion — Water

Step 3:

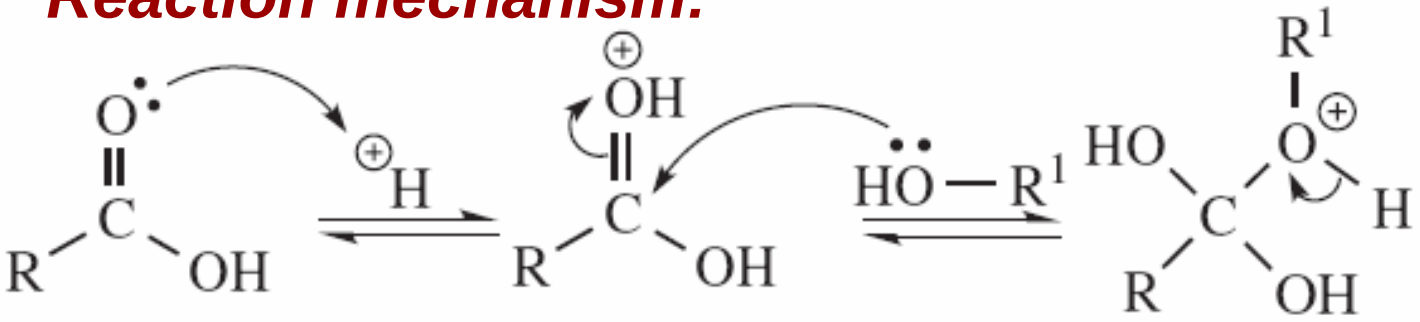


Diethyloxonium ion — Hydrogen sulfate ion — Diethyl ether — Sulfuric acid

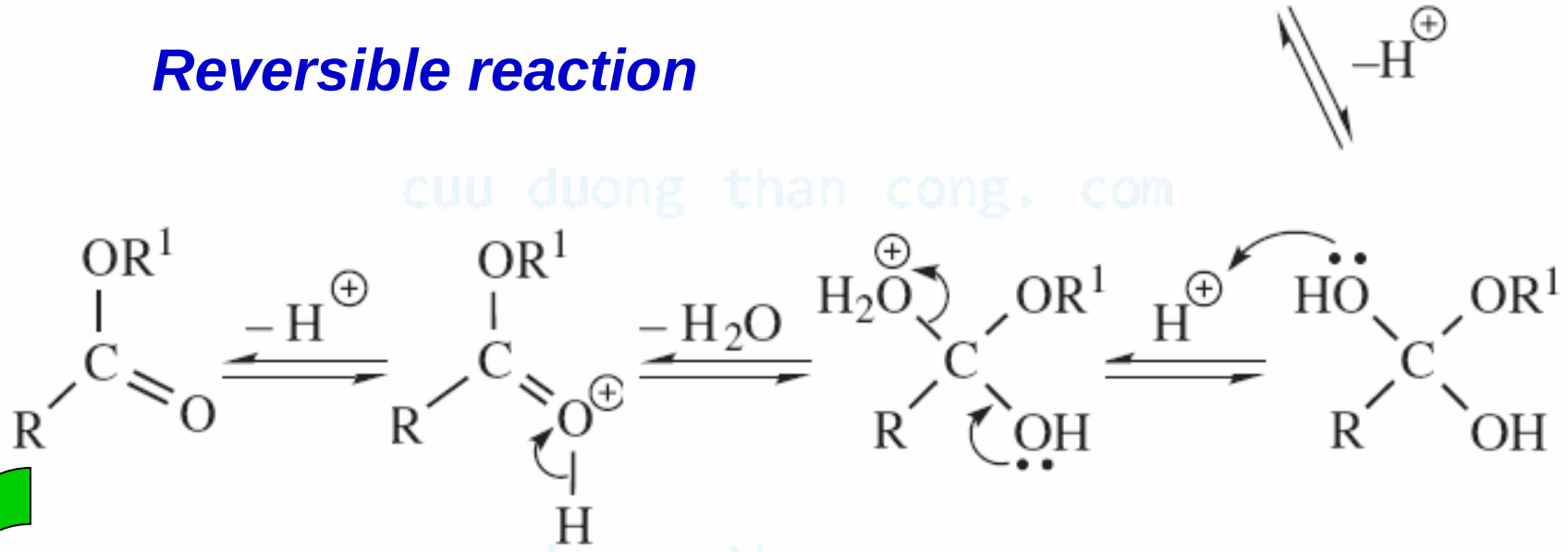
Fisher esterification reactions

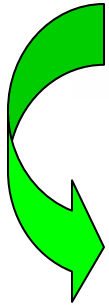


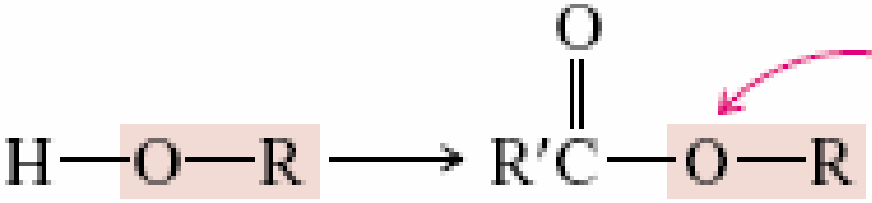
Reaction mechanism:



Reversible reaction

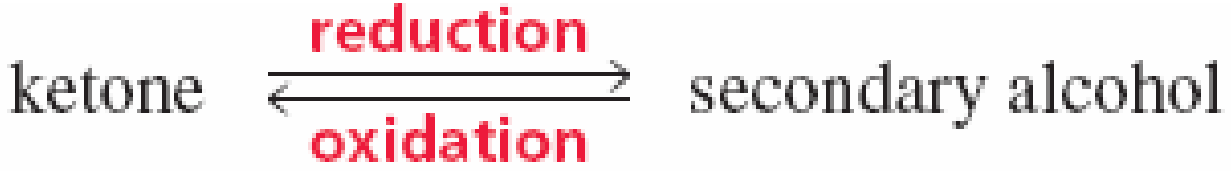


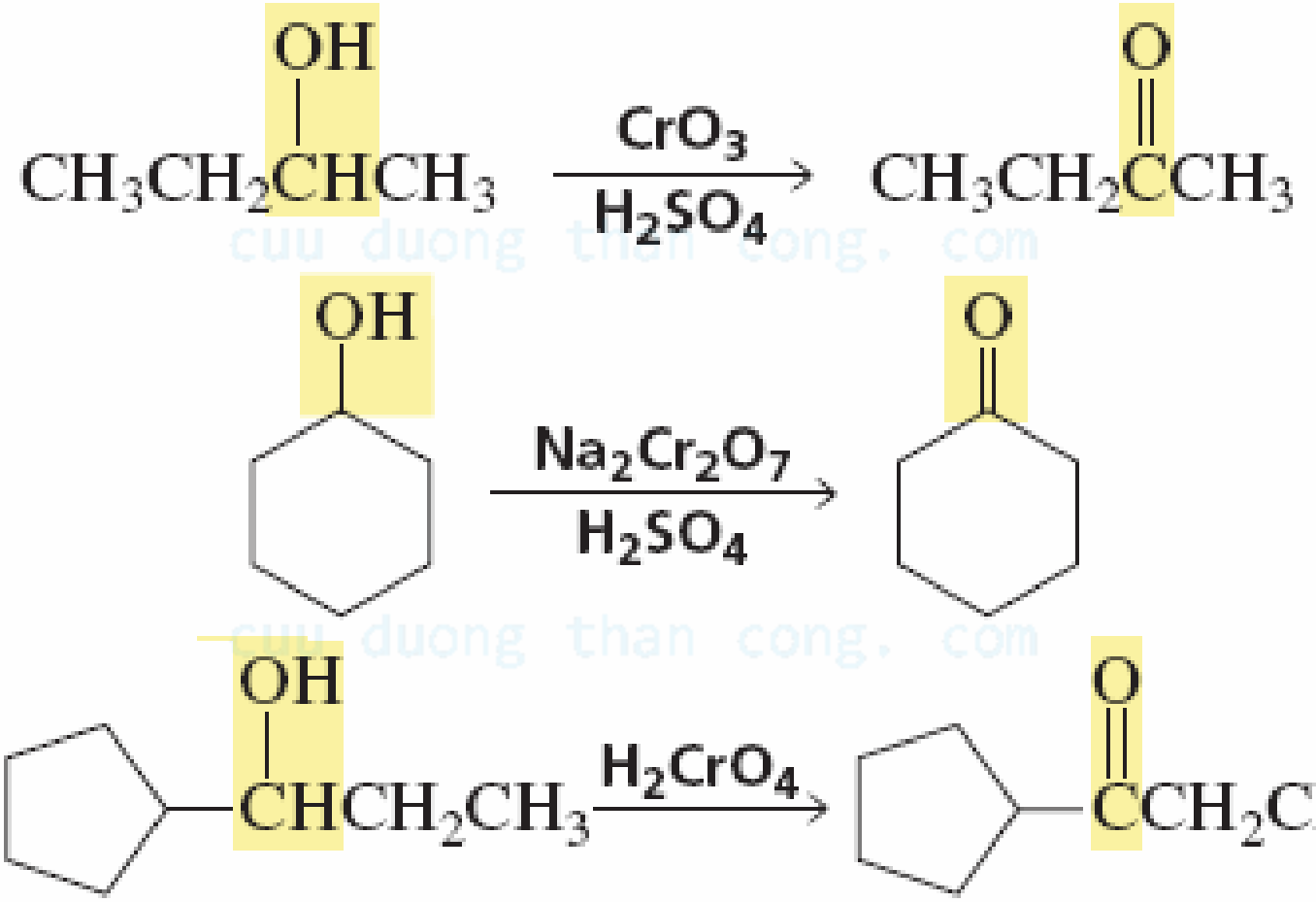




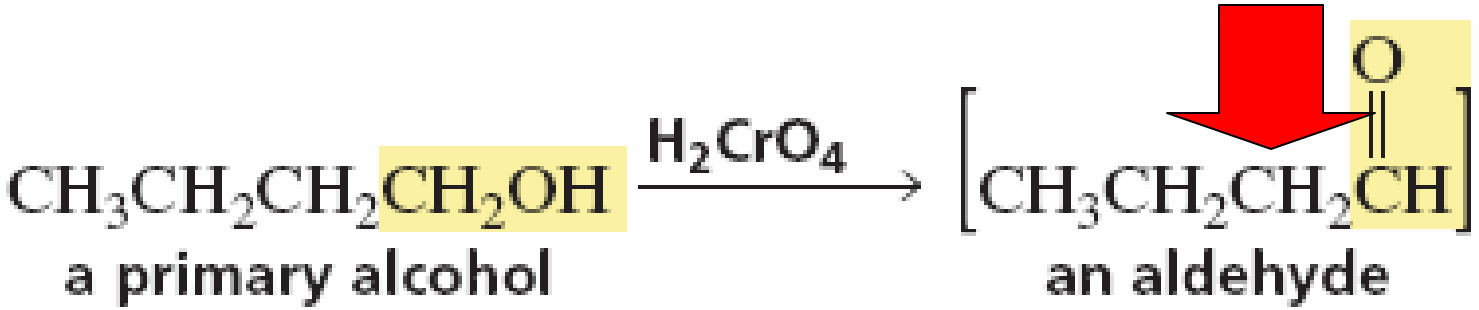
This is the same oxygen that was attached to the group R in the starting alcohol.

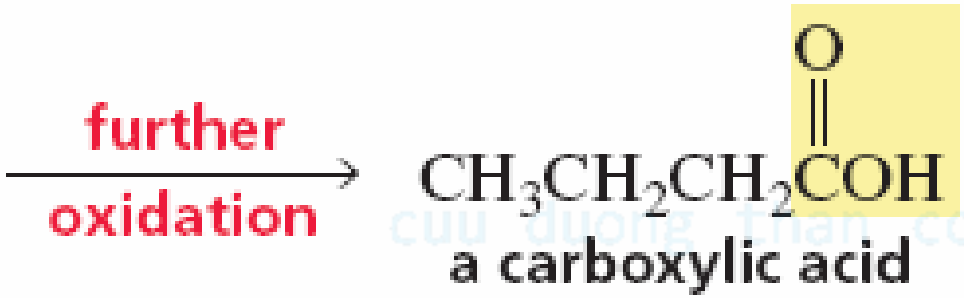
Oxidation reactions

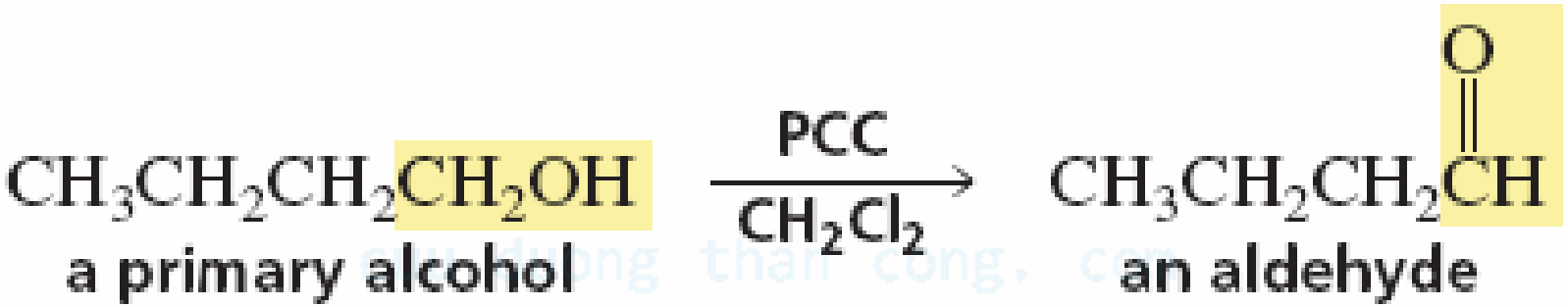




Can NOT be isolated



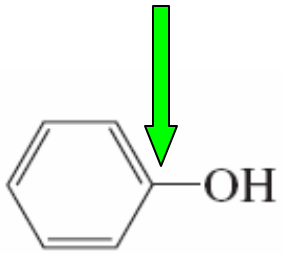




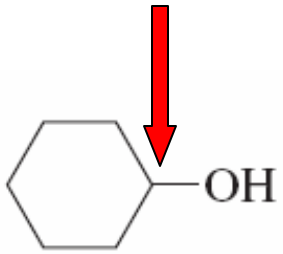
PCC: pyridinium chlorochromate

PHENOLS

SP² Carbon ***SP³ Carbon***



phenol
$pK_a = 10$

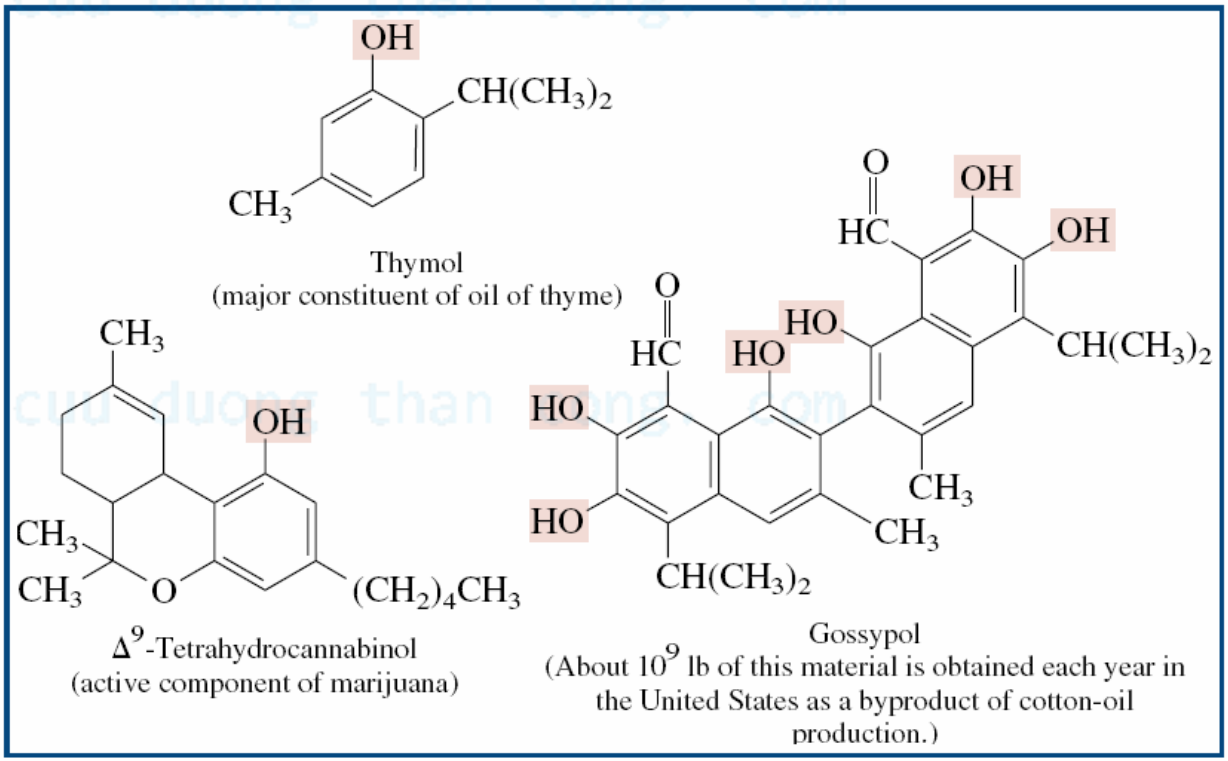


cyclohexanol
$pK_a = 16$

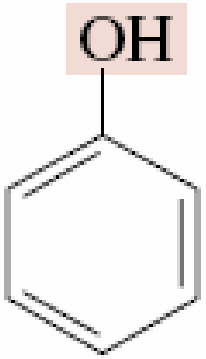
CH_3CH_2OH

ethanol
$pK_a = 16$

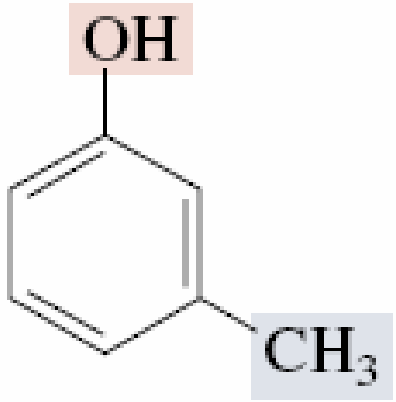
Some naturally occurring phenols



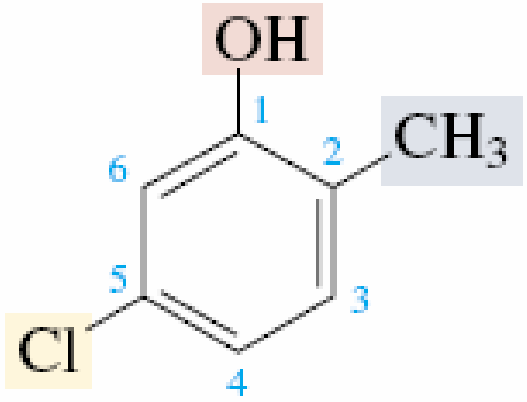
NOMENCLATURE OF PHENOLS



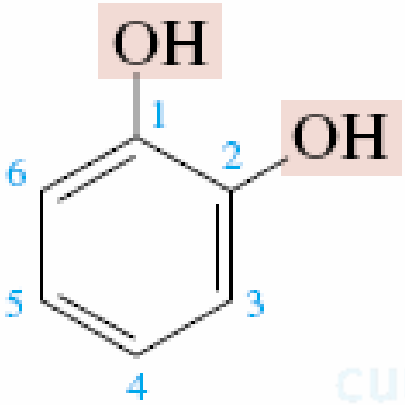
Phenol



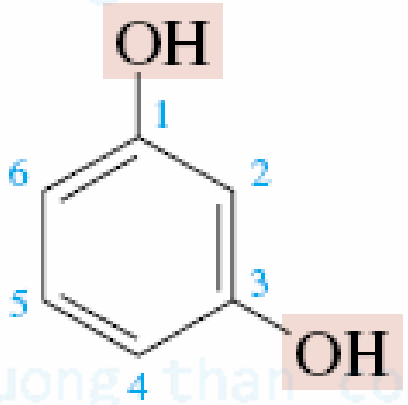
m-Cresol



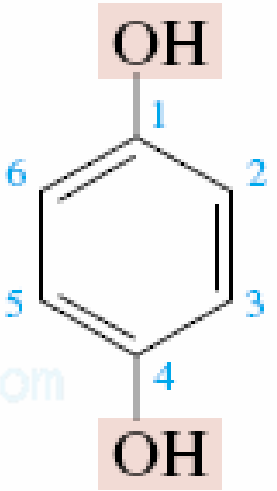
5-Chloro-2-methylphenol



1,2-Benzenediol
(pyrocatechol)

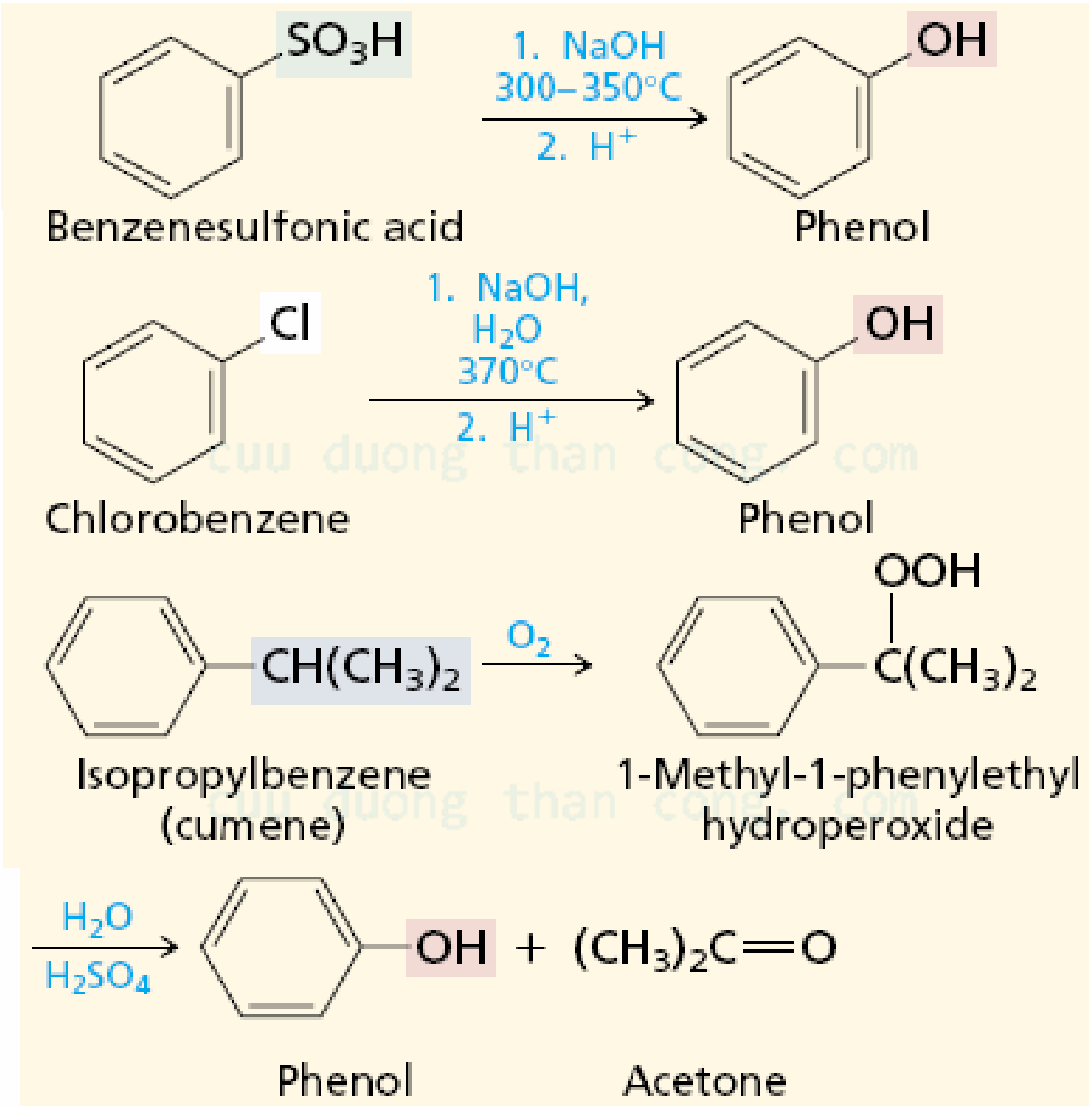


1,3-Benzenediol
(resorcinol)



1,4-Benzenediol
(hydroquinone)

PREPARATION OF PHENOLS

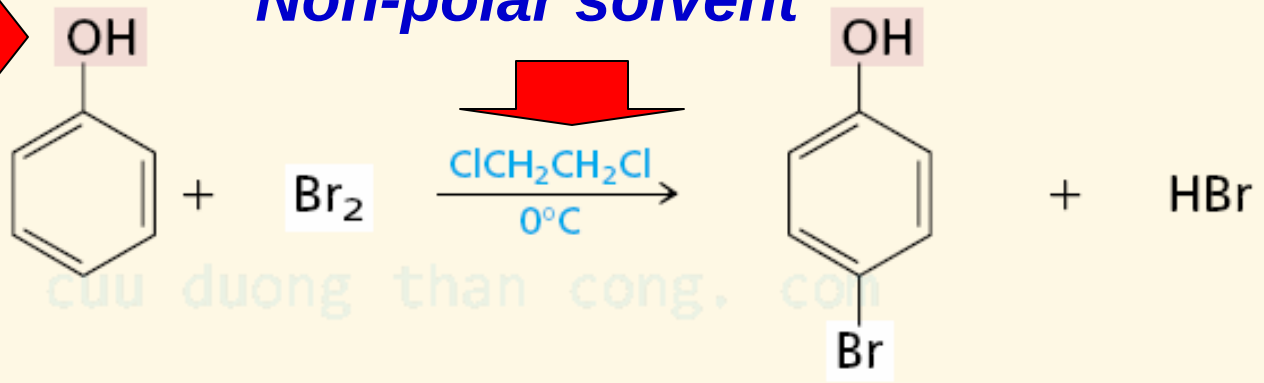


REACTIONS OF PHENOLS

Halogenation reactions

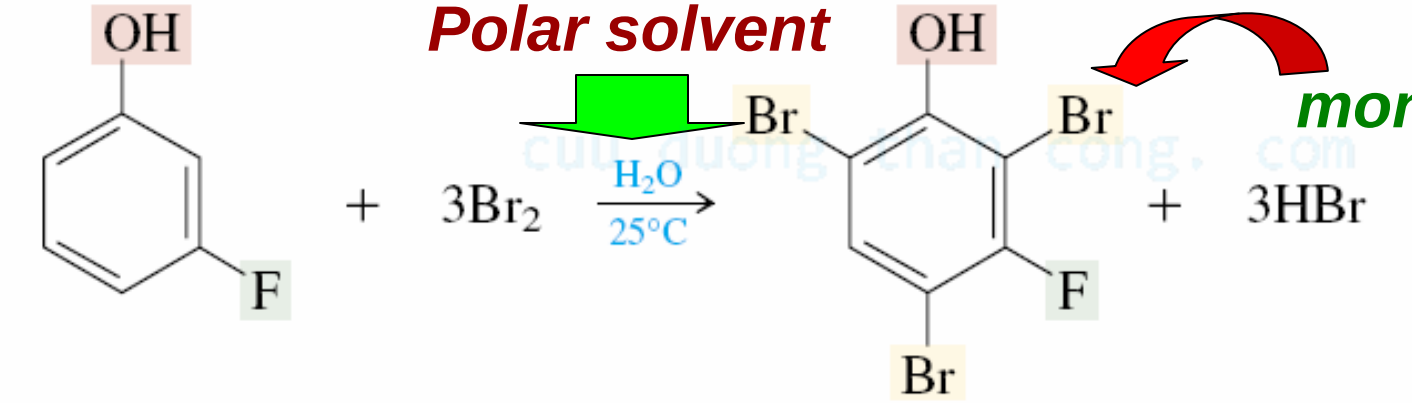
Strong activating group

Non-polar solvent



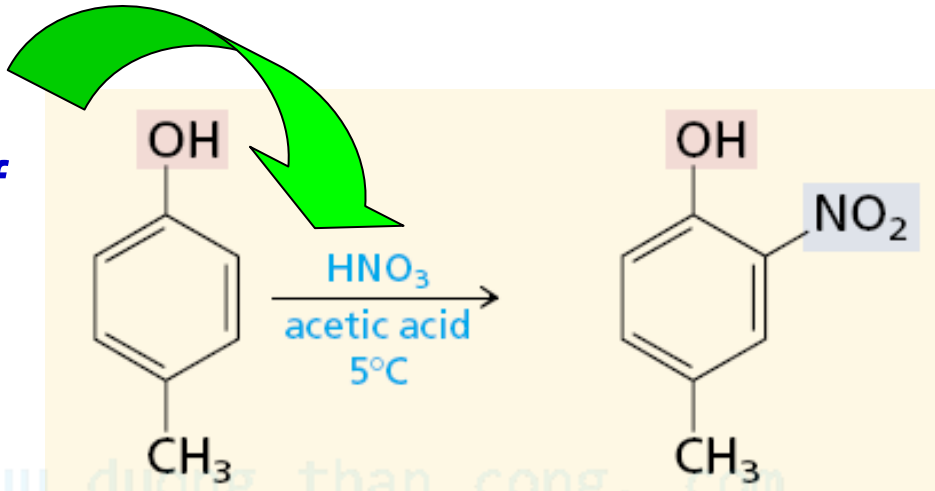
Polar solvent

NO monobromination



Nitration reactions

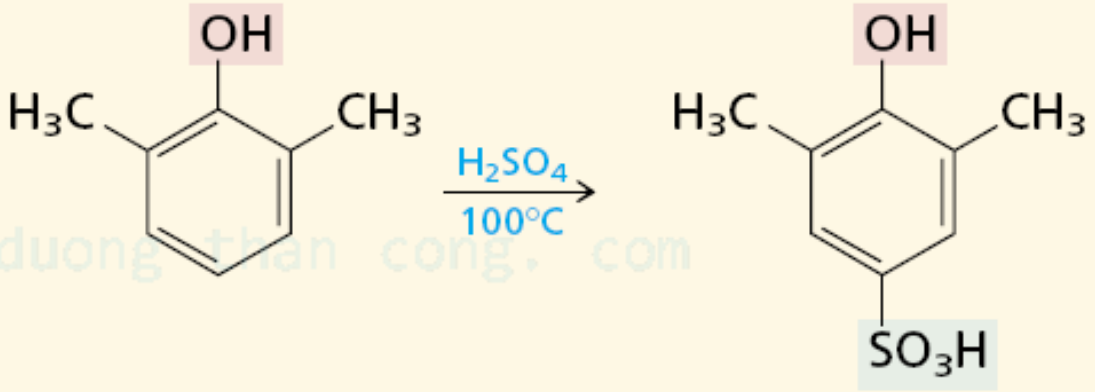
NOT necessary to use mixture of concentrated HNO_3 & H_2SO_4



p-Cresol

4-Methyl-2-nitrophenol (73–77%)

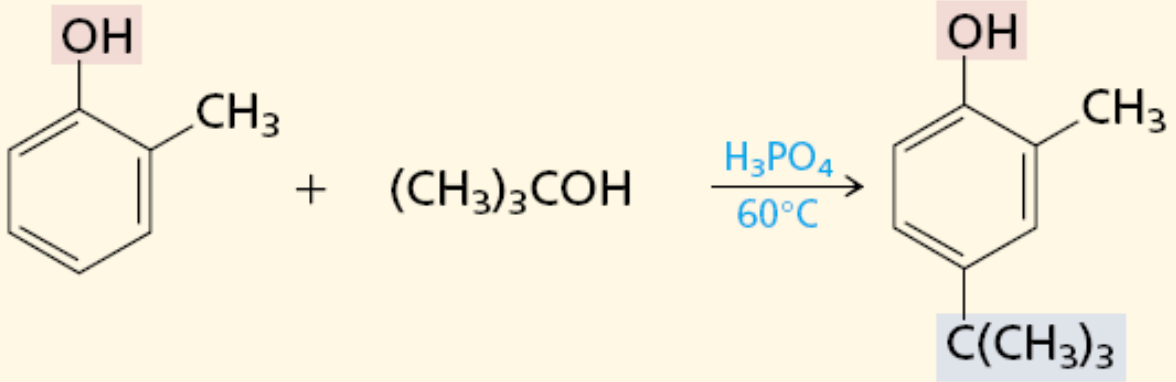
Sulfonation reactions



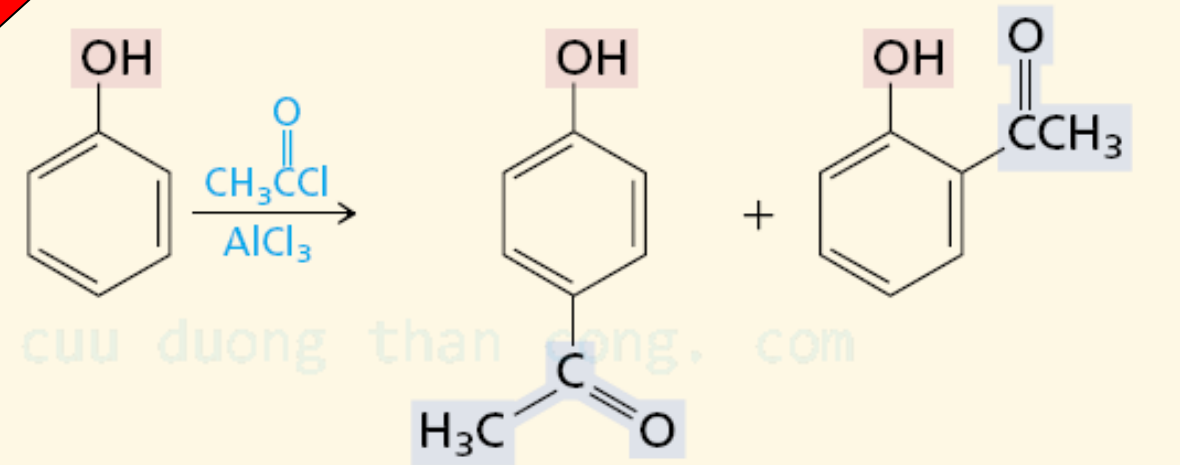
2,6-Dimethylphenol

4-Hydroxy-3,5-dimethylbenzenesulfonic acid (69%)

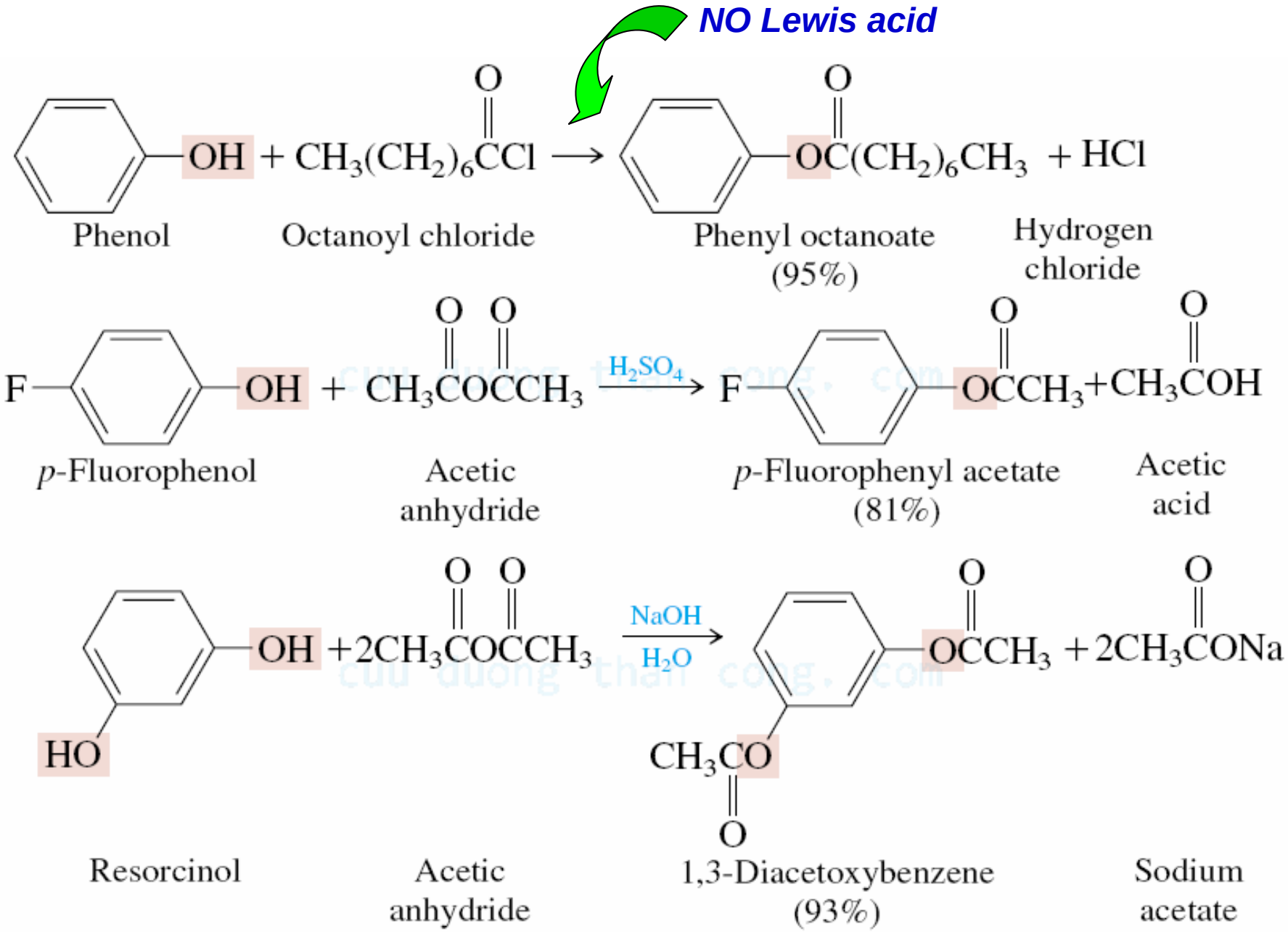
Friedel-Crafts Alkylation reactions



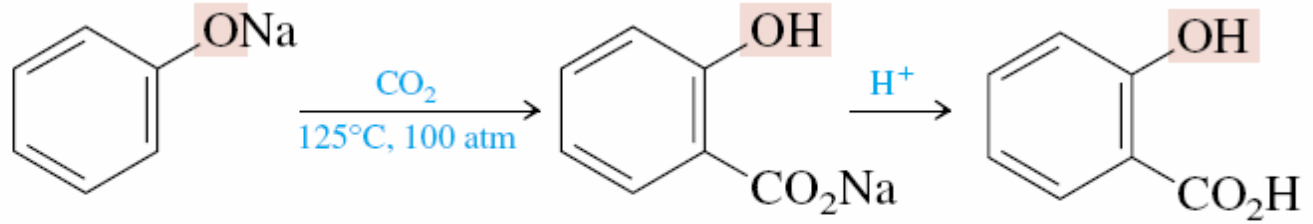
Friedel-Crafts Acylation reactions



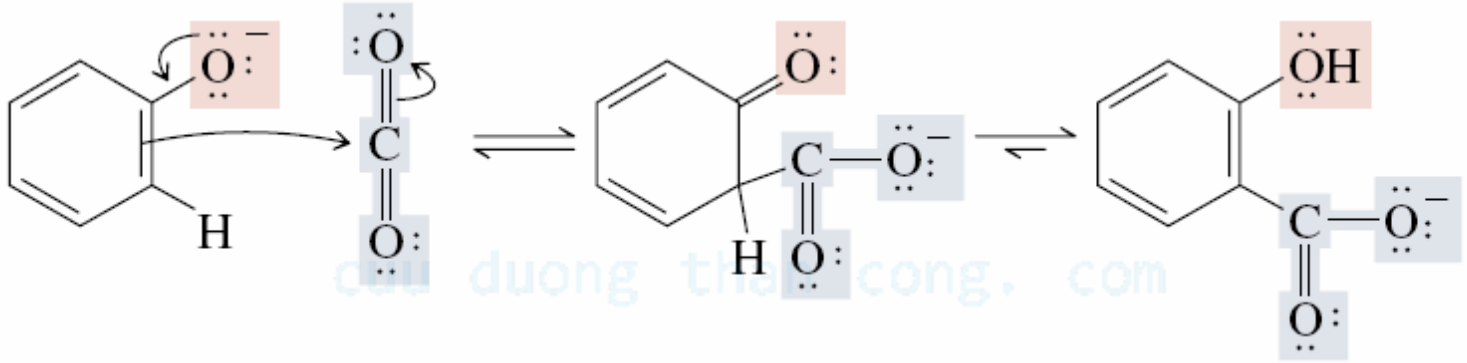
O-acylations of phenols



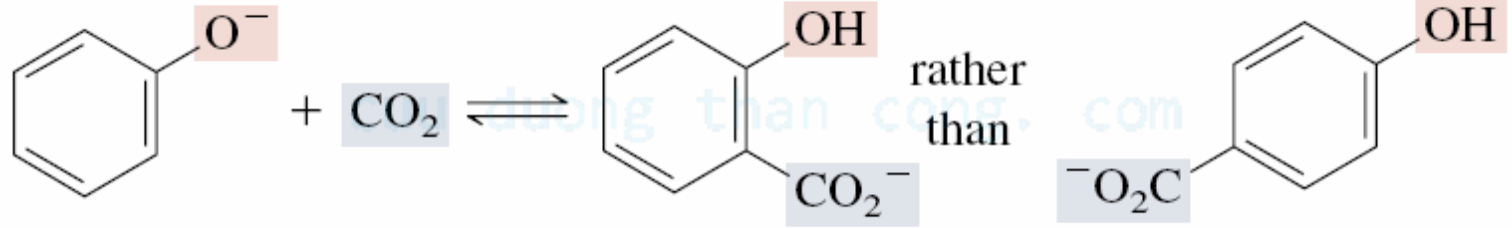
The Kolbe-Schmitt reaction



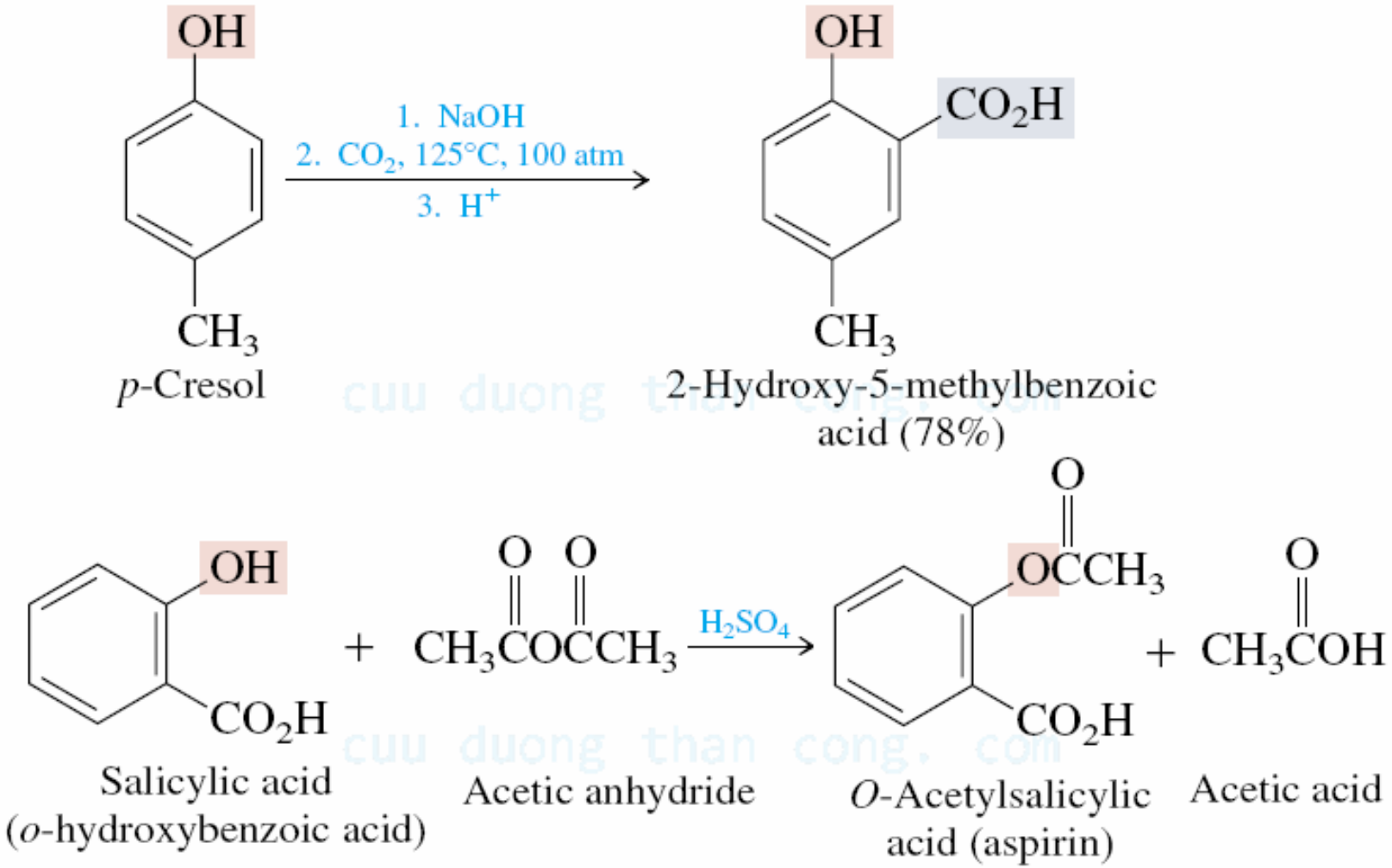
Sodium phenoxide — Sodium salicylate — Salicylic acid (79%)



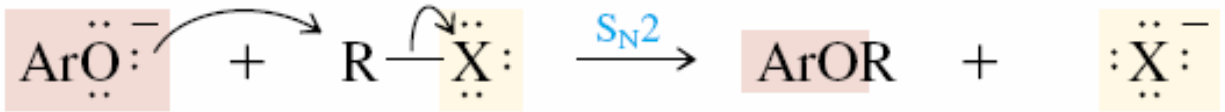
Phenoxide anion (stronger base) — Carbon dioxide — Cyclohexadienone intermediate — Salicylate anion (weaker base)



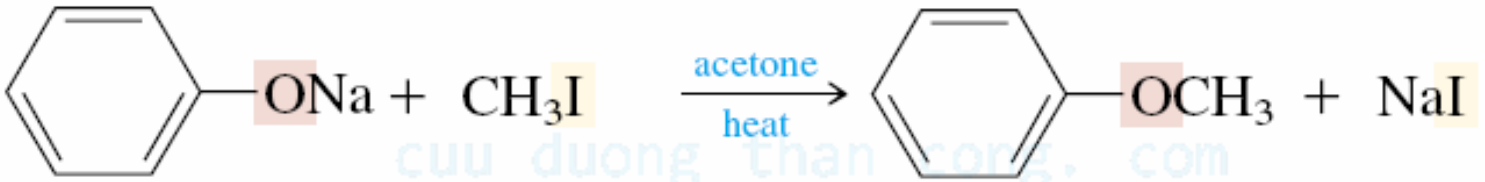
Phenoxide ion (strongest base; K_a of conjugate acid, 10^{-10}) — Carbon dioxide — Salicylate anion (weakest base; K_a of conjugate acid, 1.06×10^{-3}) — *p*-Hydroxybenzoate anion (K_a of conjugate acid, 3.3×10^{-5})


OH
CH3
p-Cresol
1. NaOH
2. CO2, 125°C, 100 atm
3. H+
OH
CO2H
CH3
2-Hydroxy-5-methylbenzoic acid (78%)
OH
CO2H
Salicylic acid (o-hydroxybenzoic acid)
+
O O
CH3COCCH3
Acetic anhydride
H2SO4
O
OCCH3
CO2H
O-Acetylsalicylic acid (aspirin)
+
O
CH3COH
Acetic acid

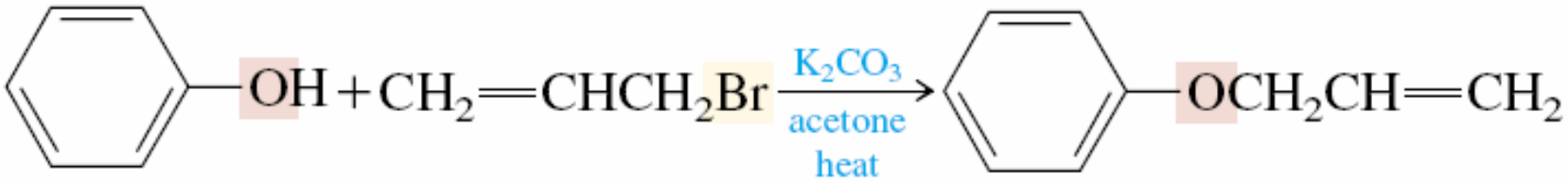
Preparation of aryl ethers



Phenoxide anion | Alkyl halide | Alkyl aryl ether | Halide anion



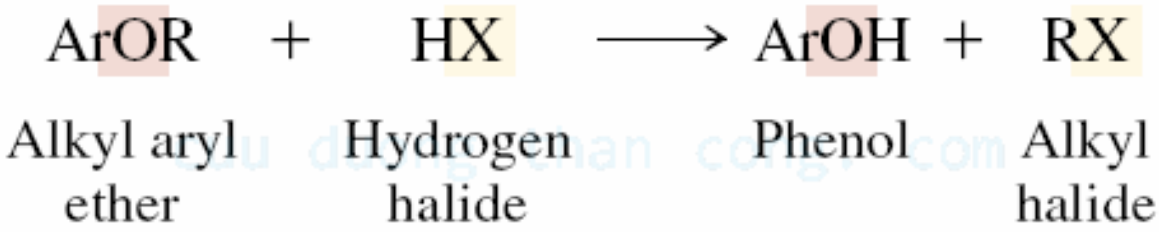
Sodium phenoxide | Iodomethane | Anisole (95%) | Sodium iodide

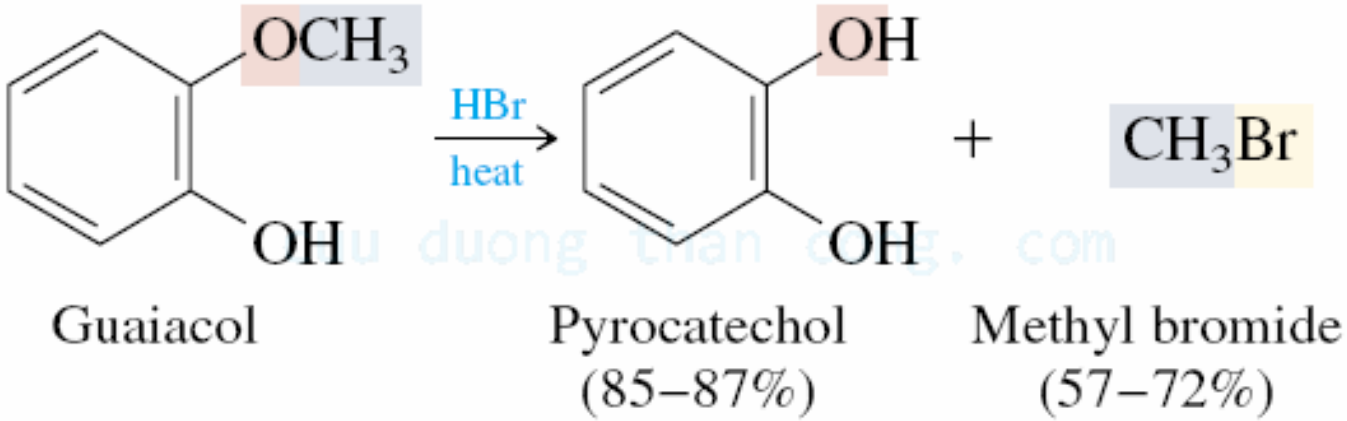


Phenol | Allyl bromide | Allyl phenyl ether (86%)

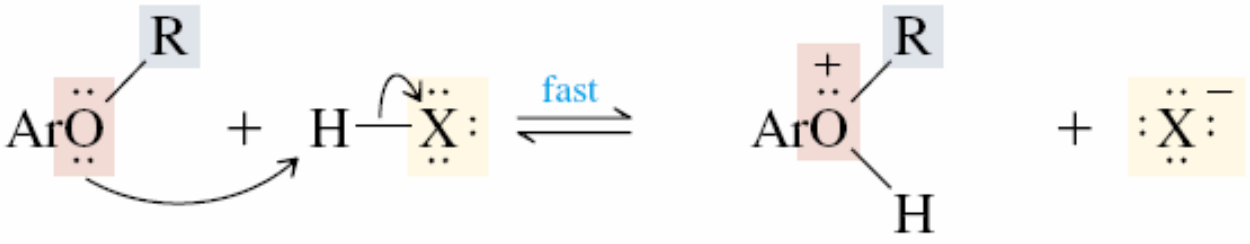
Can NOT prepare aryl ether directly from the reaction of phenol & alcohol in the presence of acid catalyst

Cleavage of aryl ethers by hydrogen halides



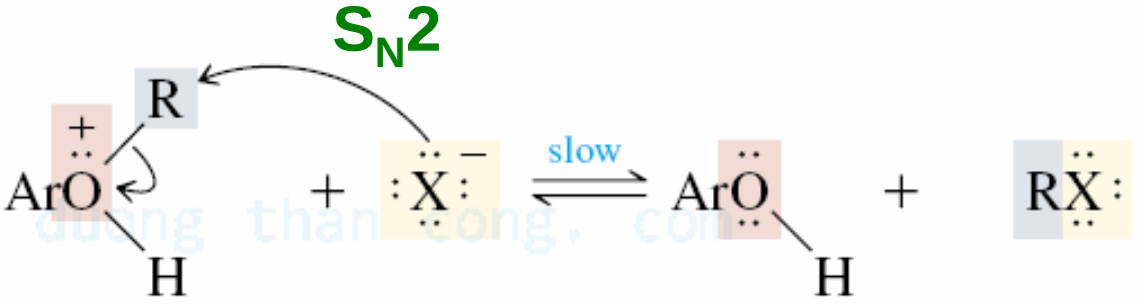


Reaction mechanism:



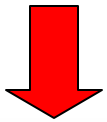
Alkyl aryl ether + Hydrogen halide ⇌ Alkylaryloxonium ion + Halide ion

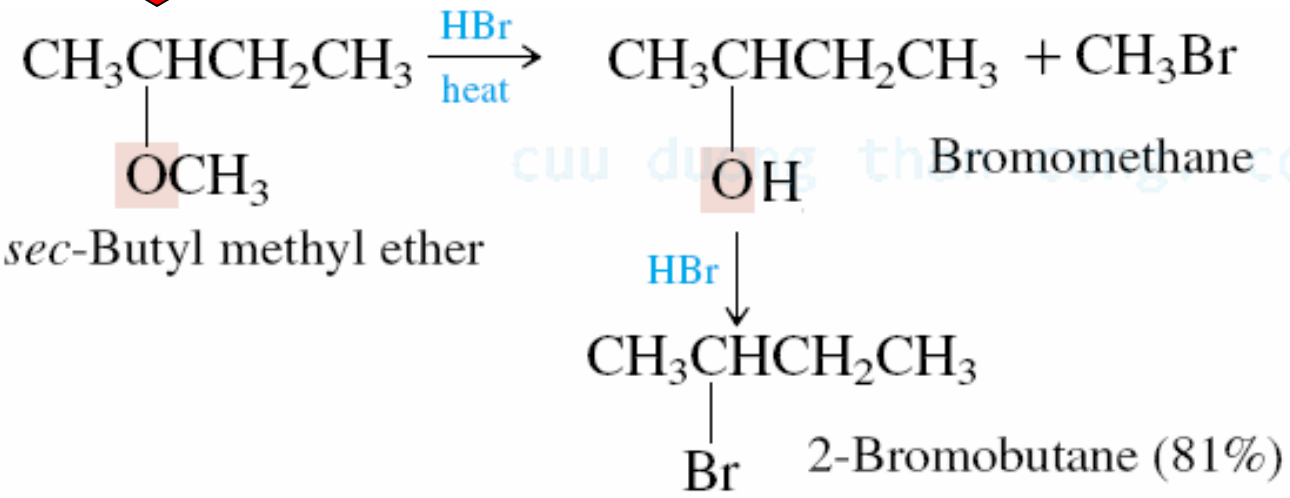
S_N2



Alkylaryloxonium ion + Halide ion ⇌ Phenol + Alkyl halide

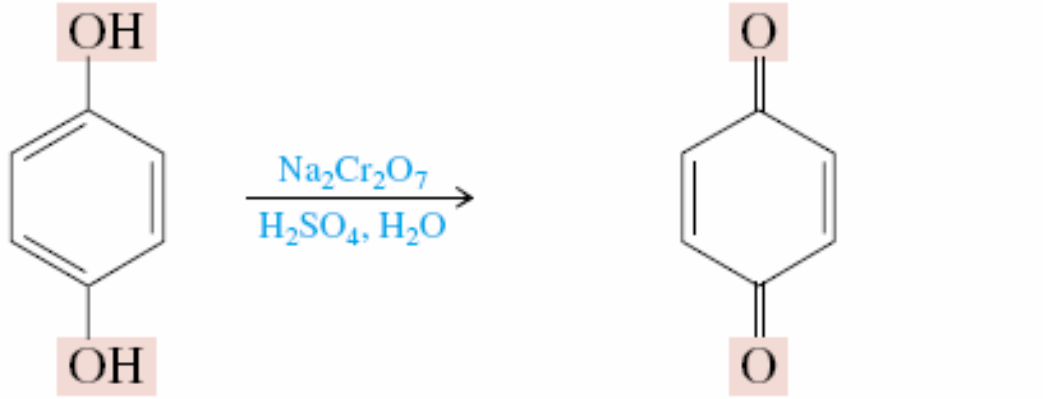
NOTE:





sec-Butyl methyl ether

Oxidation of phenols

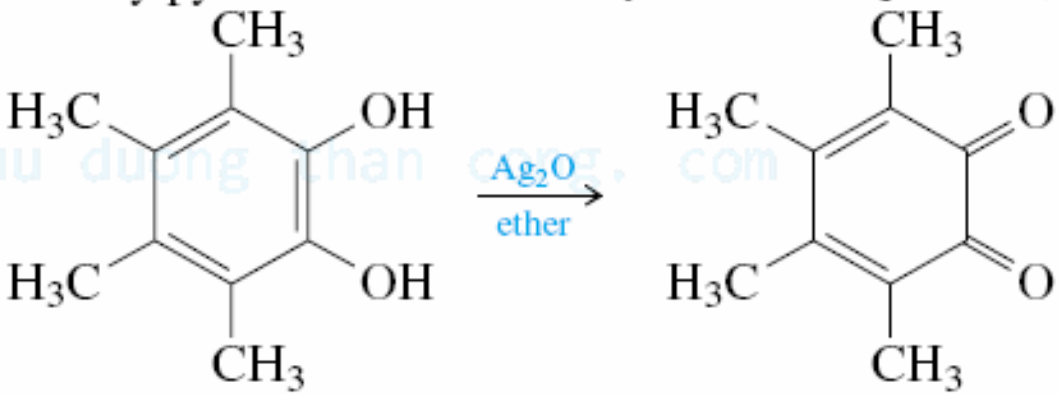


Hydroquinone

p-Benzoquinone (76–81%)

4-Methylpyrocatechol

4-Methyl-1,2-benzoquinone (68%)

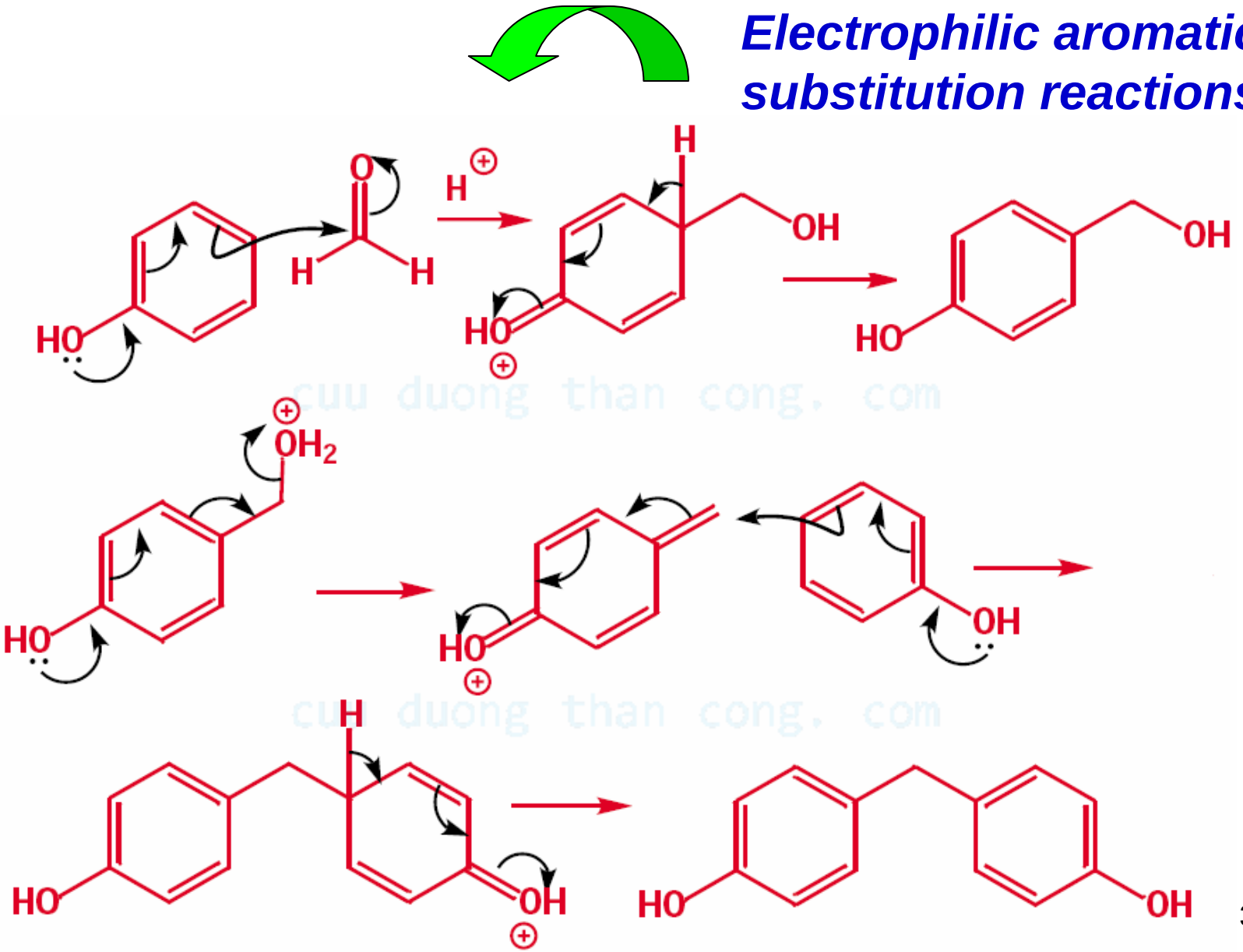


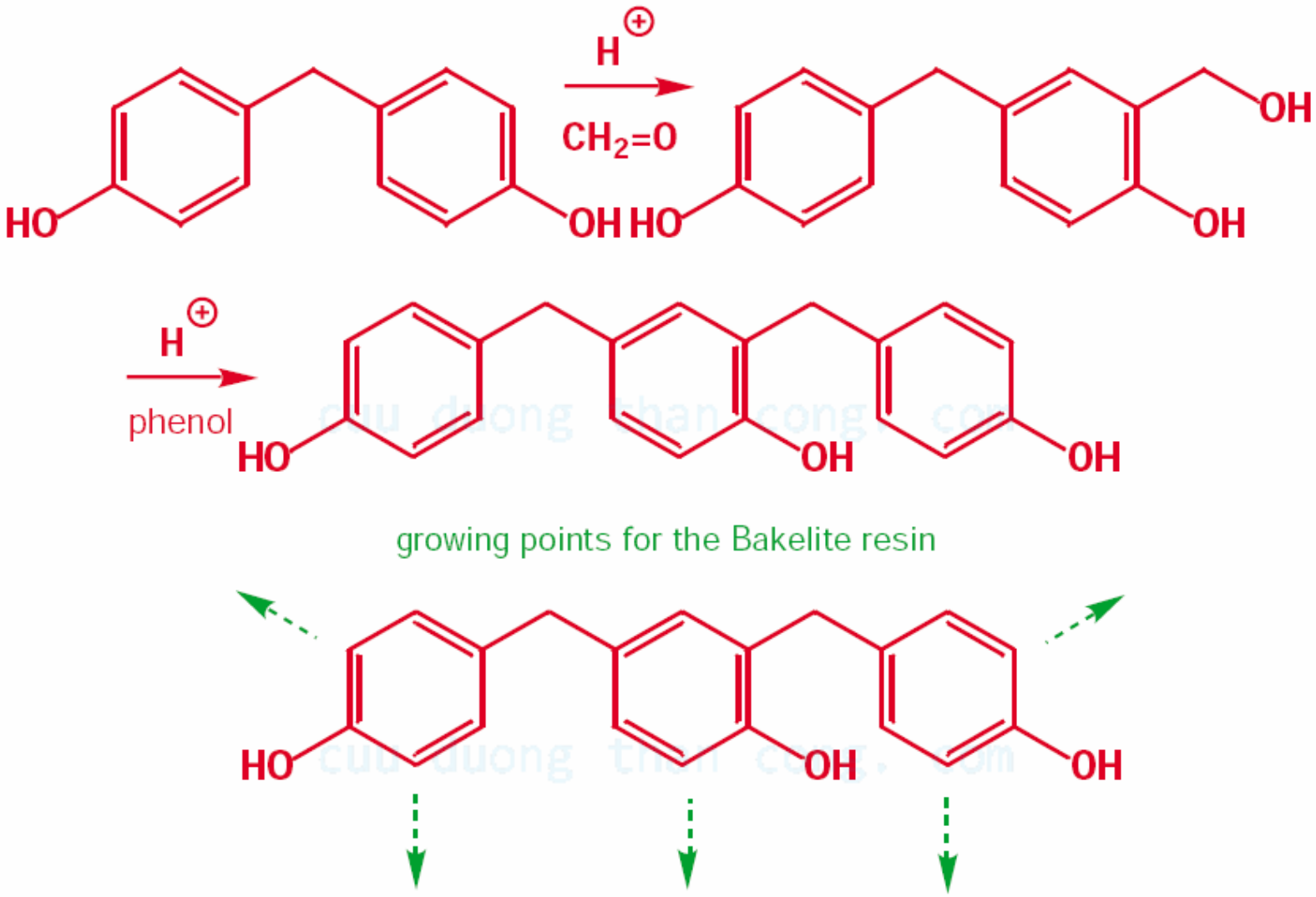
3,4,5,6-Tetramethyl-1,2-benzenediol

3,4,5,6-Tetramethyl-1,2-benzoquinone (81%)

Polymerization with formaldehyde

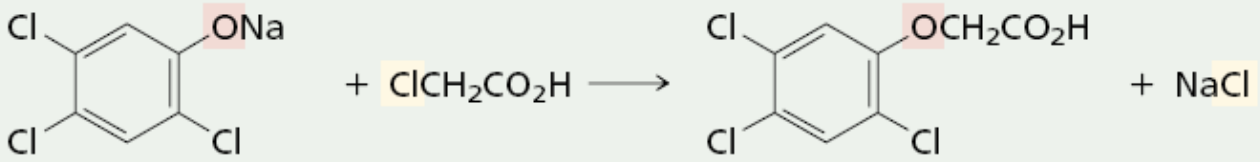
Electrophilic aromatic substitution reactions




H⊕
CH2=O
HO
OH
HO
OH
OH
H⊕
phenol
HO
OH
OH
growing points for the Bakelite resin
HO
OH
OH

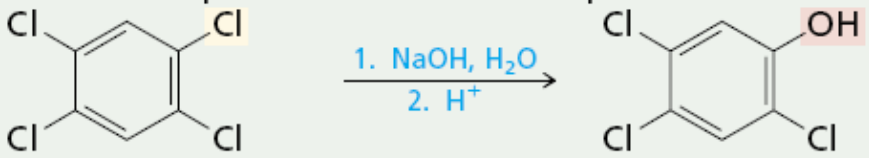
AGENT ORANGE AND DIOXIN

The once widely used herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) is prepared by reaction of the sodium salt of 2,4,5-trichlorophenol with chloroacetic acid:



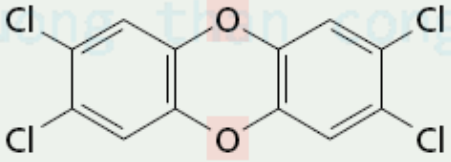
Sodium 2,4,5-trichlorophenolate — Chloroacetic acid — 2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)

The starting material for this process, 2,4,5-trichlorophenol, is made by treating 1,2,4,5-tetrachlorobenzene with aqueous base. Nucleophilic aromatic substitution of one of the chlorines by an addition–elimination mechanism yields 2,4,5-trichlorophenol:



1,2,4,5-Tetrachlorobenzene — 2,4,5-Trichlorophenol

In the course of making 2,4,5-trichlorophenol, it almost always becomes contaminated with small amounts of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, better known as *dioxin*.



2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (dioxin)