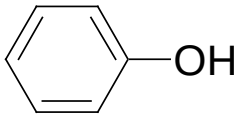
台灣大學開放式課程

有機化學乙

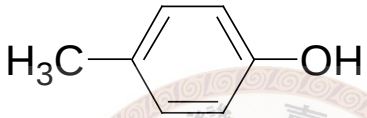
蔡蘊明　教授

Chapter 21
Phenols, aryl halides and sulfur compounds

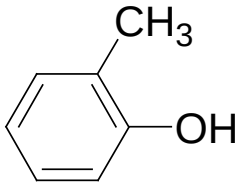
※ Structure and nomenclature of phenols



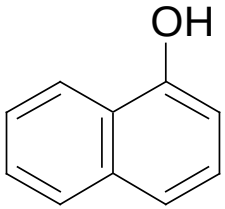
phenol



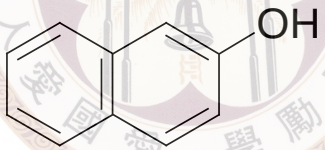
4-methylphenol
(*p*-cresol)



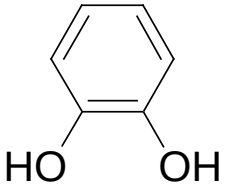
2-methylphenol
(*o*-cresol)



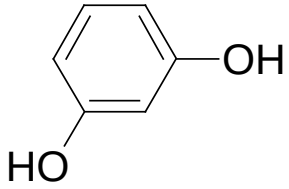
1-naphthol
(α-naphthol)



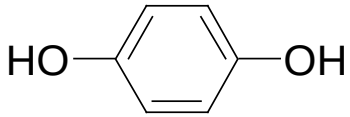
2-naphthol
(β-naphthol)



1,2-benzenediol
(catechol)



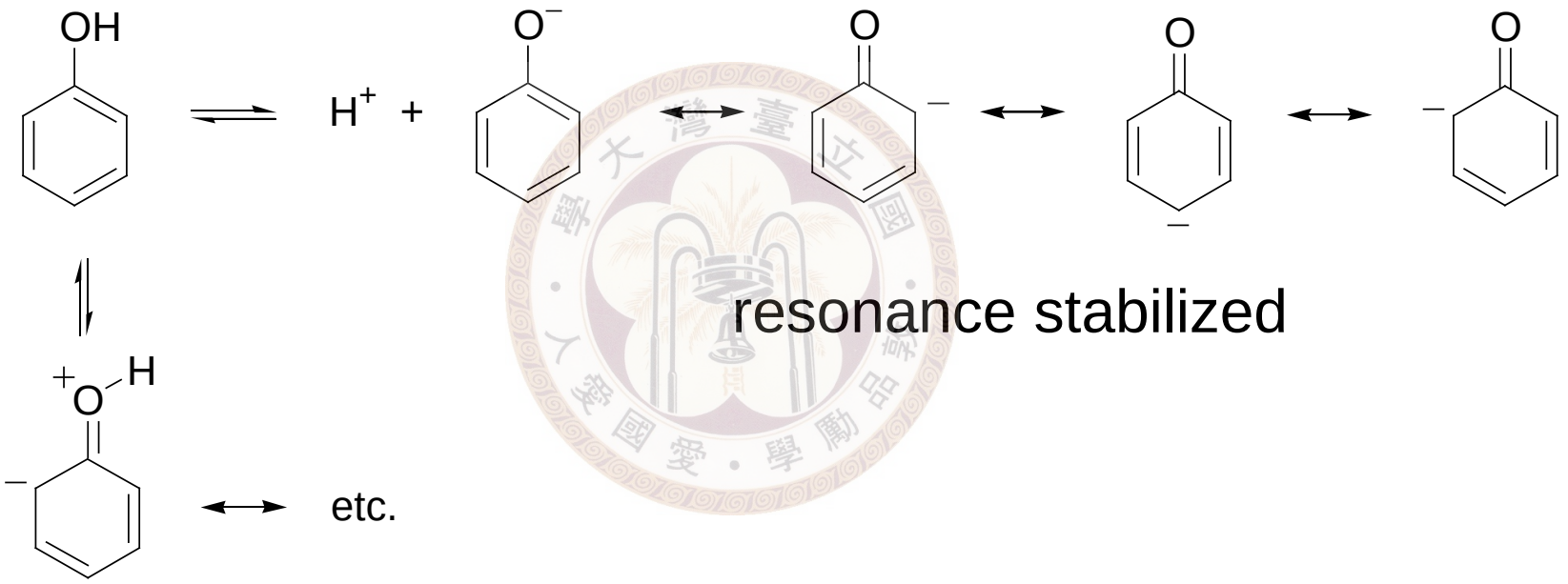
resorcinol



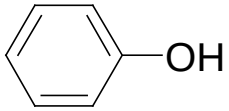
hydroquinone

※ Properties

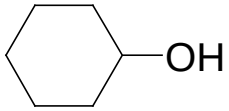
Alcohol like, but more acidic



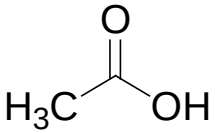
Not as stabilized
due to charge separation



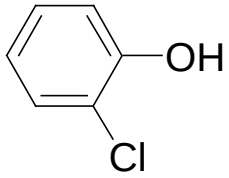
$pK_a = 9.89$



$pK_a = 18$



$pK_a = 4.74$



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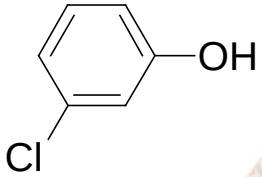

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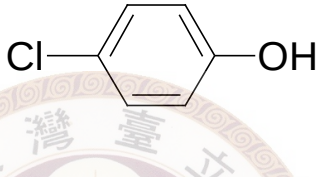

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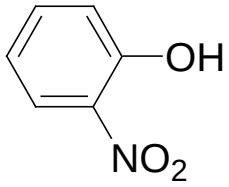
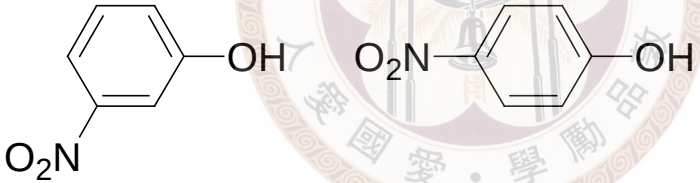
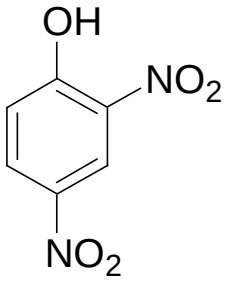


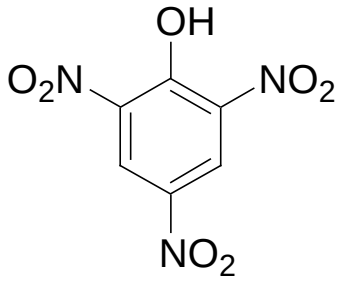
7.17



8.28 7.15



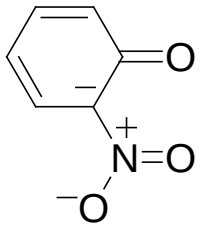
3.96

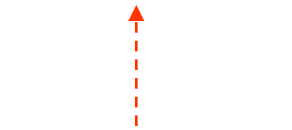


0.38

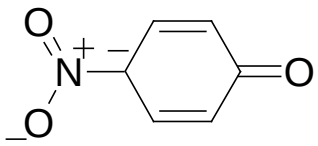
picric acid

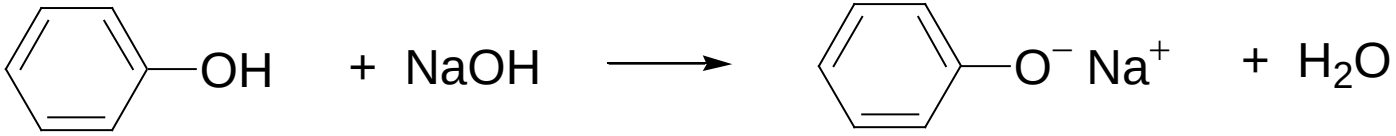
苦味酸





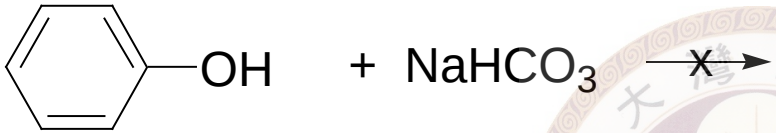
no such stabilization





water insoluble

water soluble

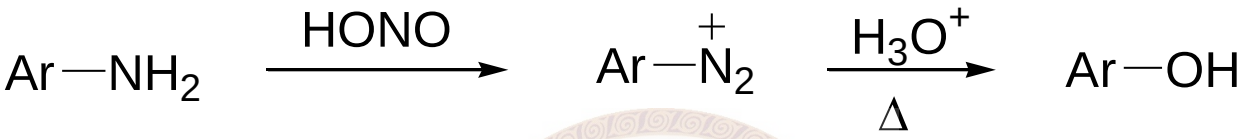


not basic enough

can be used to separate phenols from acids

※ Synthesis of phenol

✓ From diazonium salt



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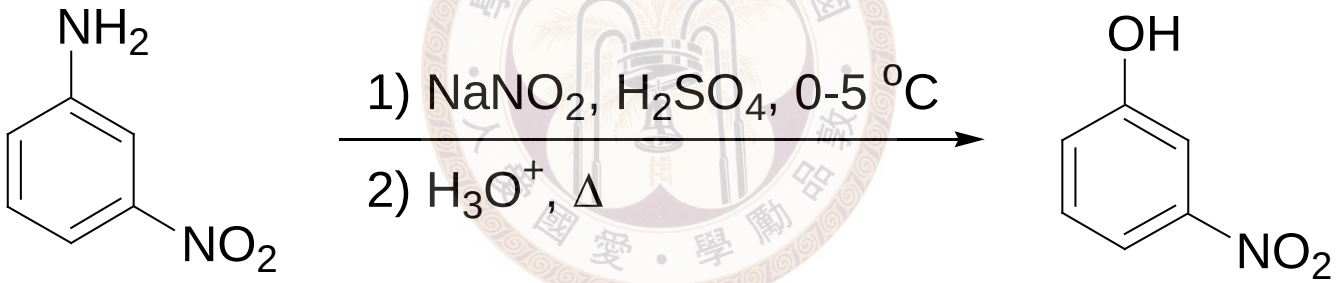
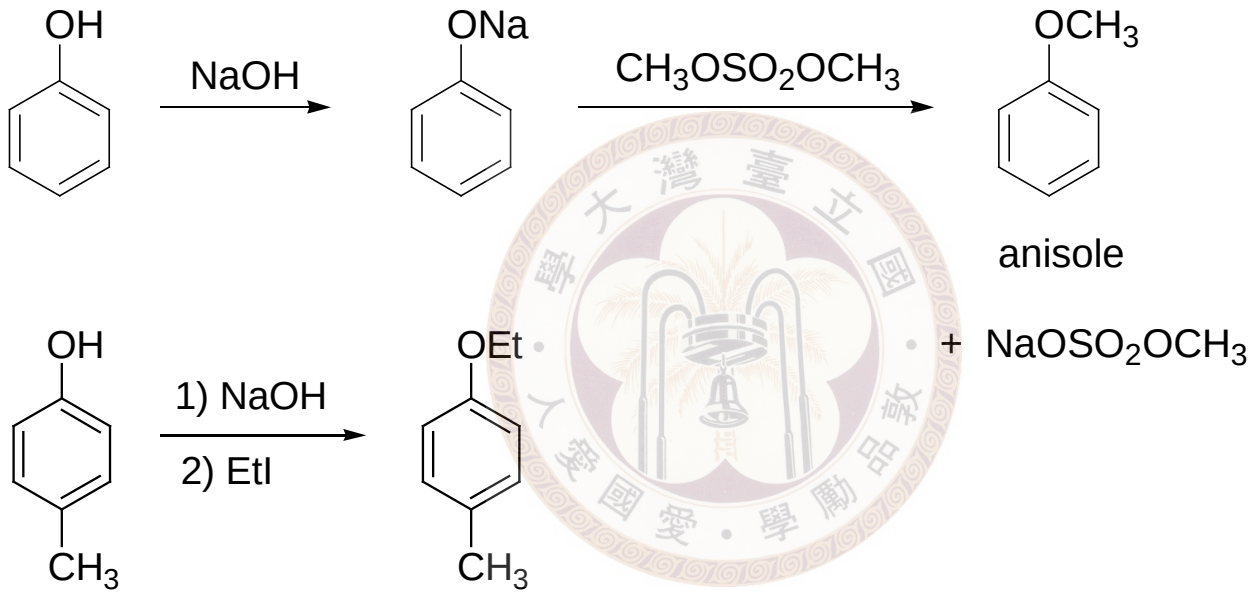
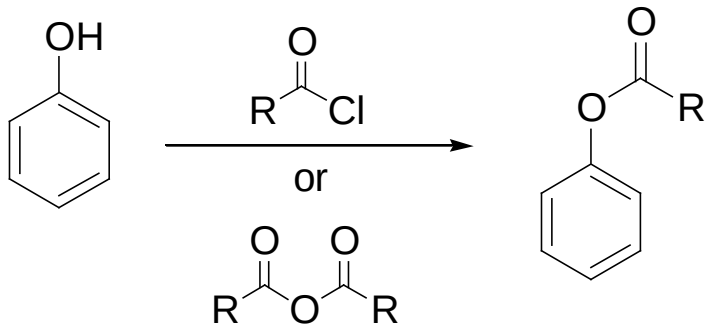
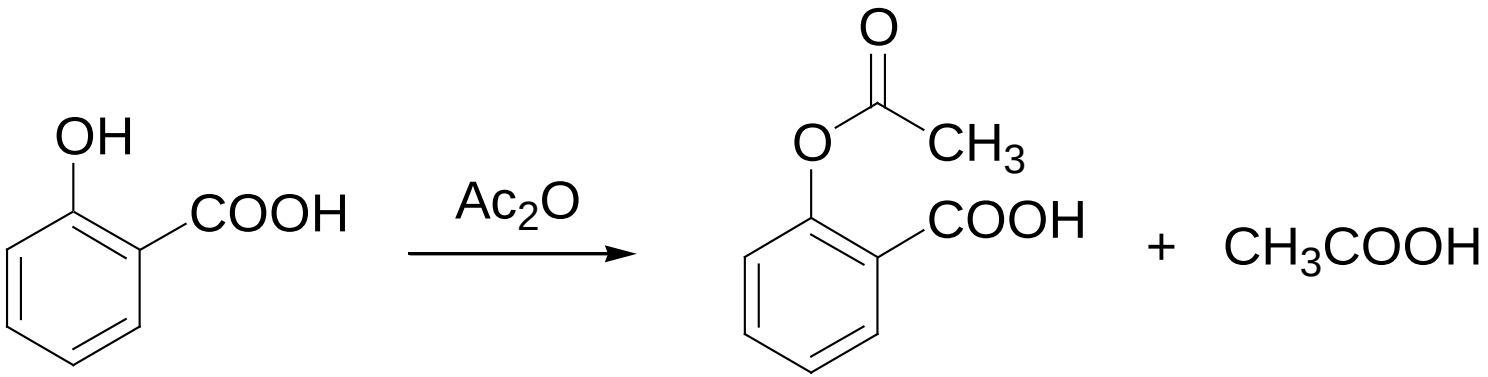


※ Reactions of the oxygen

◎ *O*-alkylation or acylation

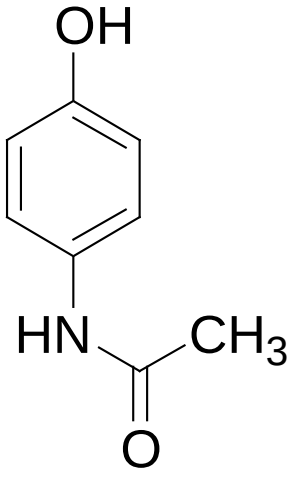




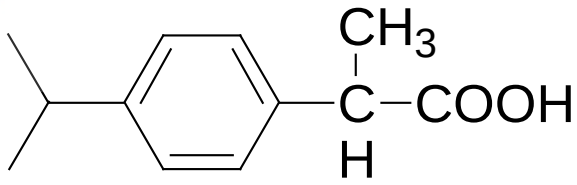


acetylsalicylic acid
(Aspirin)

cf.



acetaminophen
(Tylenol)

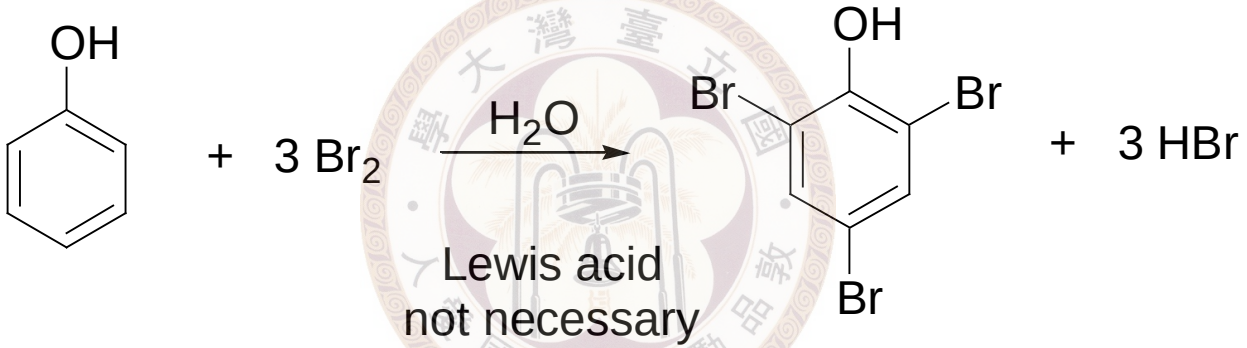


ibuprofen (Advil)

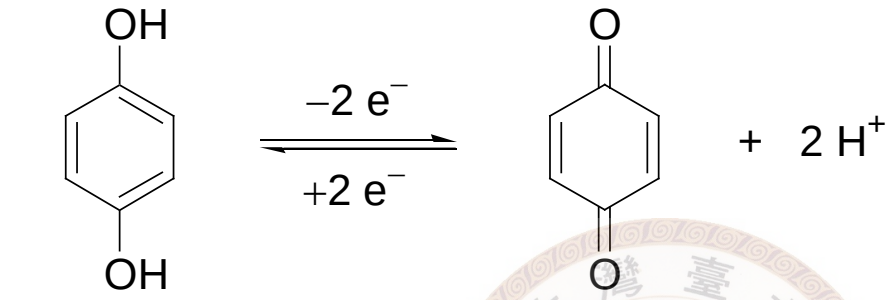
◎ Reactions of the ring

✓ Electrophilic aromatic substitution

Phenols are electron rich
→ highly reactive



※ Quinones

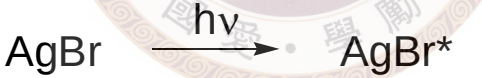


hydroquinone

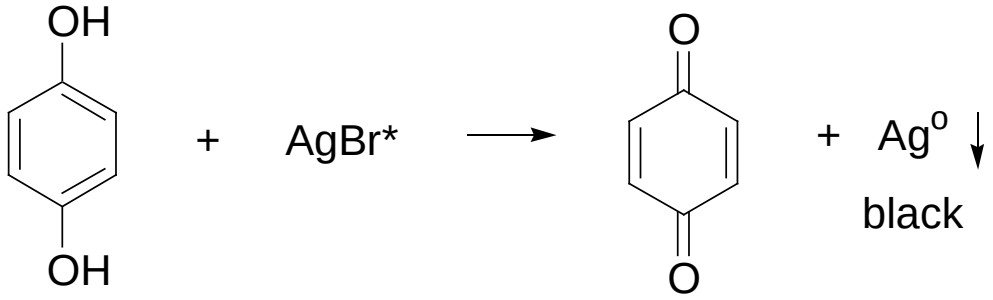
p-benzoquinone

Reduction potential: $E^o = 0.699$

✓ In photography

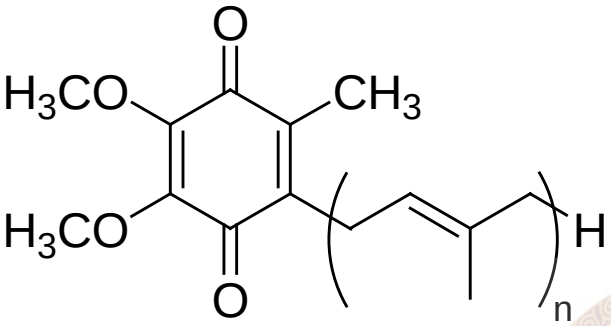


sesitized

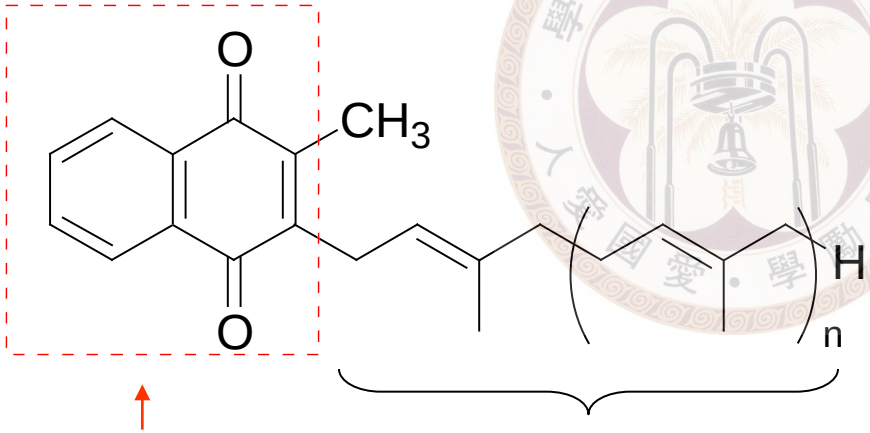


black

✓ Biological system



ubiquinones (n = 6-10) (coenzyme Q) involved in electron-transport systems

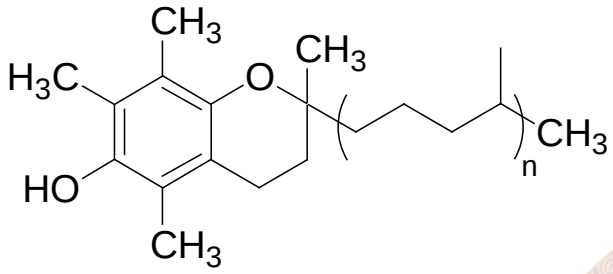


Vitamin K

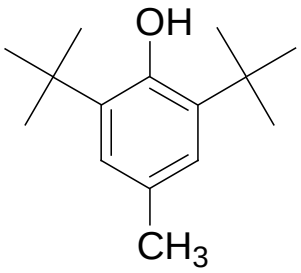
1,4-naphthoquinone structure (E^o = 0.47)

This part is to promote fat solubility

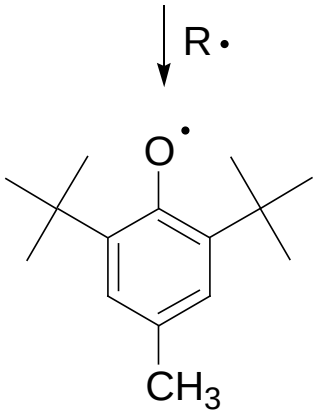
※ Antioxidant



α-tocopherol
(vitamin E)
a natural antioxidant

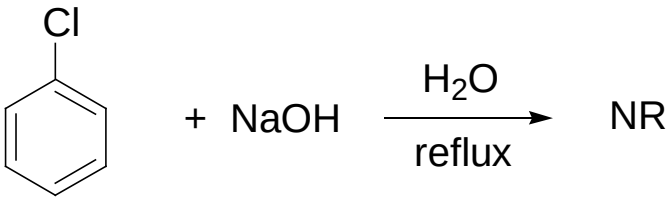


butylated hydroxytoluene
(BHT)
a food preservative

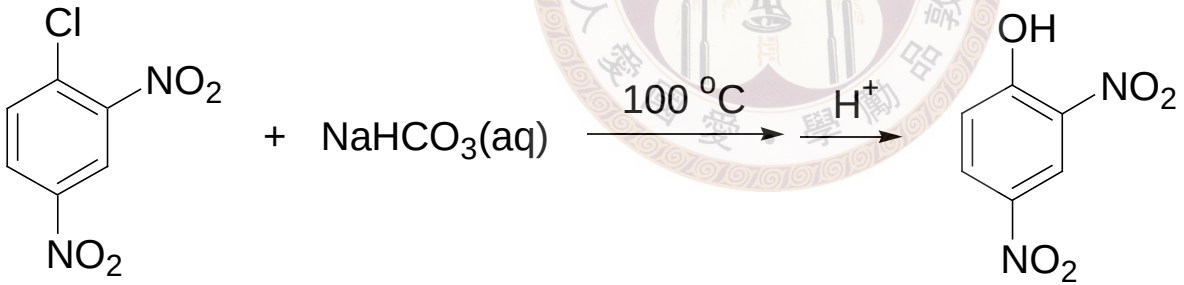


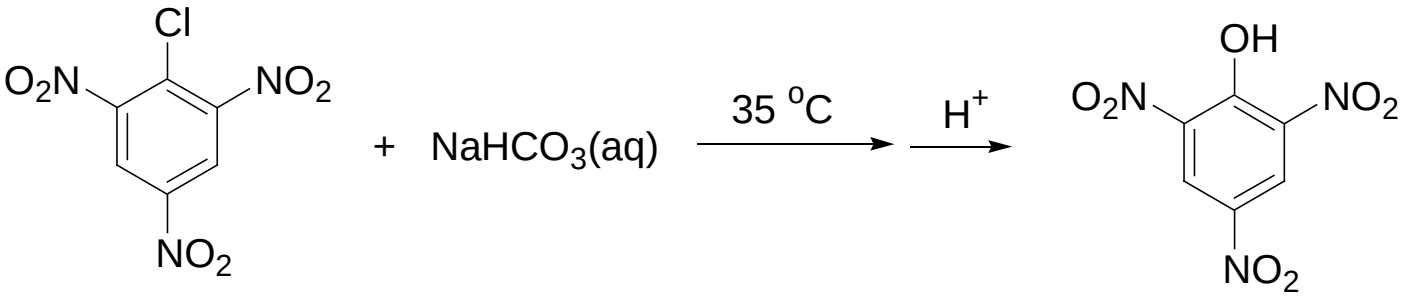
very unreactive
→ resonance stabilization and steric effect

※ Nucleophilic aromatic substitution

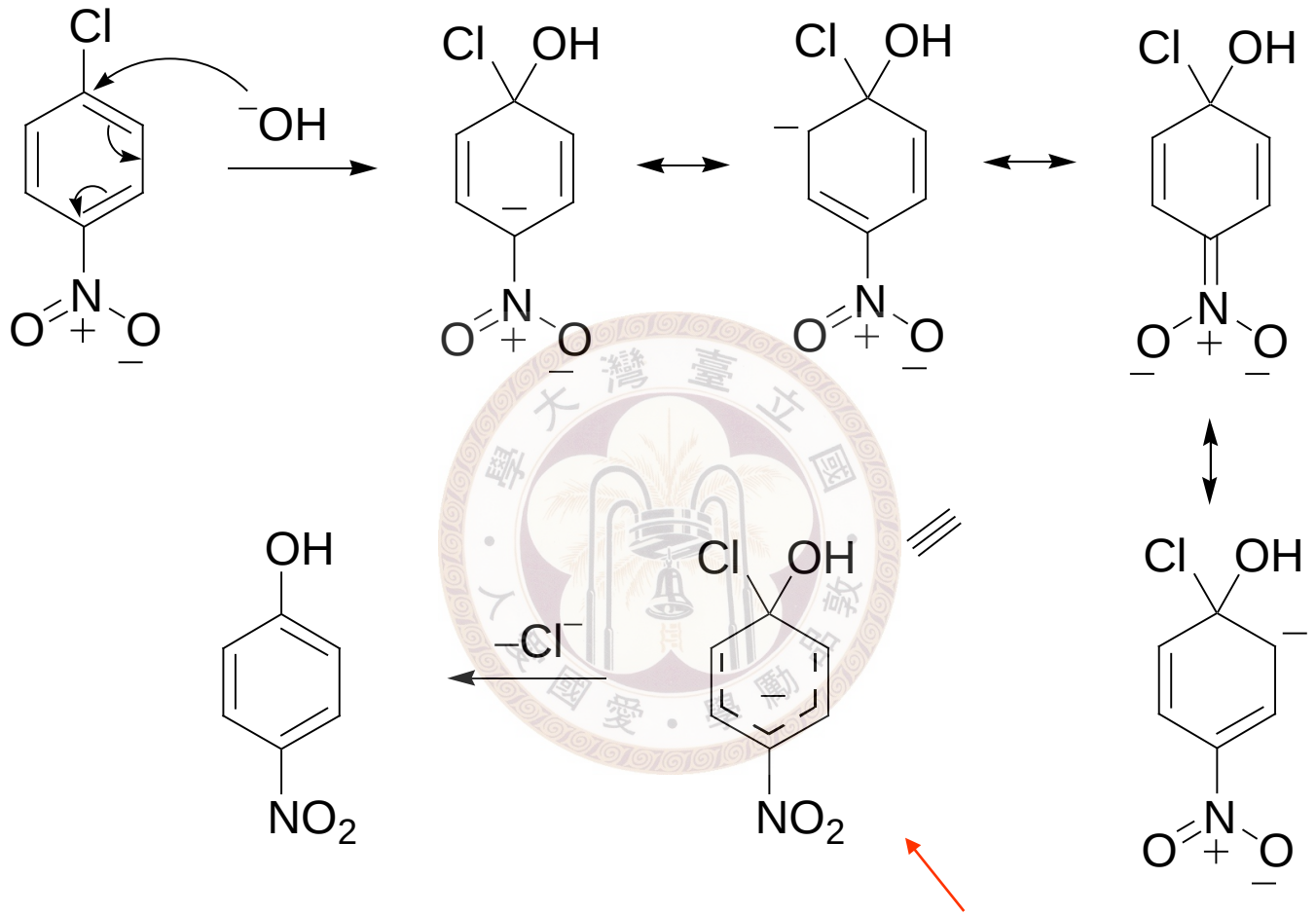


but





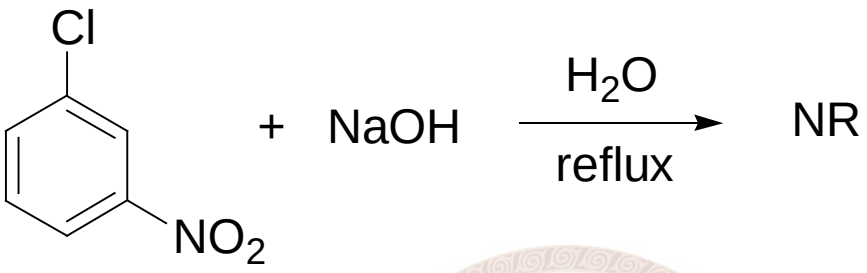
Reason: an addition followed by elimination mechanism



NO_2 at 2, 4 and 6 position
→ more effective
→ more NO_2, more stabilization

A resonance stabilized delocalized carbanion (Meisenheimer complex)

NO_2 at meta position:



※ Thiols, Thioethers and disulfides

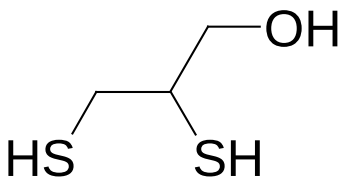
RSH thiols

RSR’ thioethers

RS-SR’ disulfides

✓Thiols

also called mercaptans



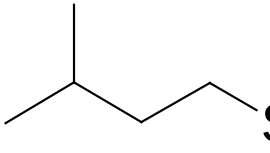
Used as antidote for mercury poisoning

CH_3CH_2SH

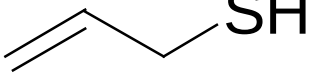
ethanethiol
(ethyl mercaptan)

PrSH

1-propanethiol
(in onion)



3-methyl-1-butanethiol
(in skunks)



2-propene-1-thiol
(in garlic)

※ Special feature of sulfur

✓ More polarizable than oxygen

$$RSH \rightleftharpoons RS^- + H^+$$

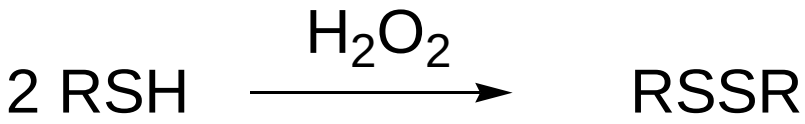
pK_a ~9-10

more stable than RO^-
→ RSH is more acidic than ROH

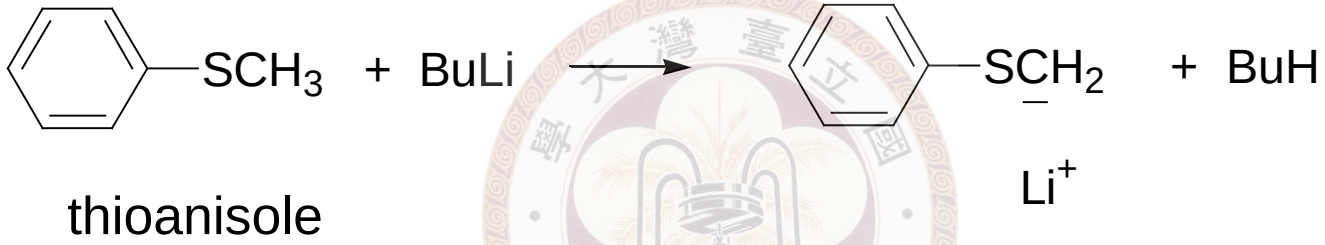
✓ RS^- is a stronger nucleophile than RO^-

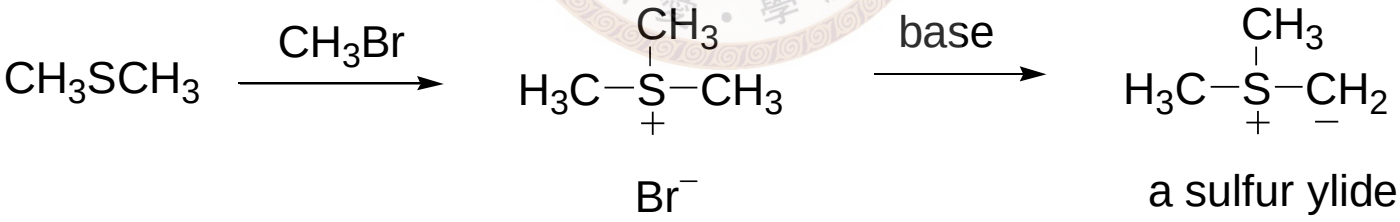
larger: less solvation
more polarizable: stabilizes transition state

✓ RSH oxidized easily

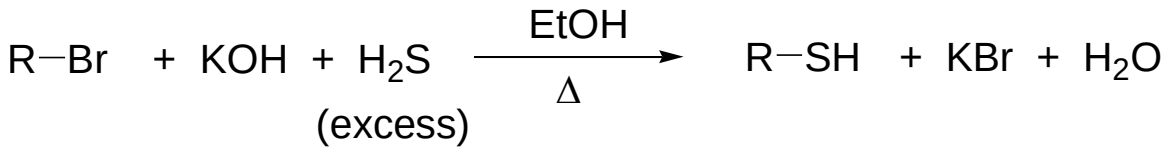


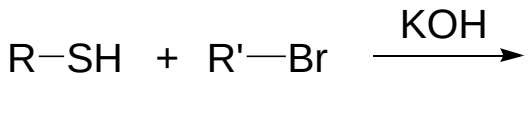
✓ Stabilizes negative charge on adjacent atom

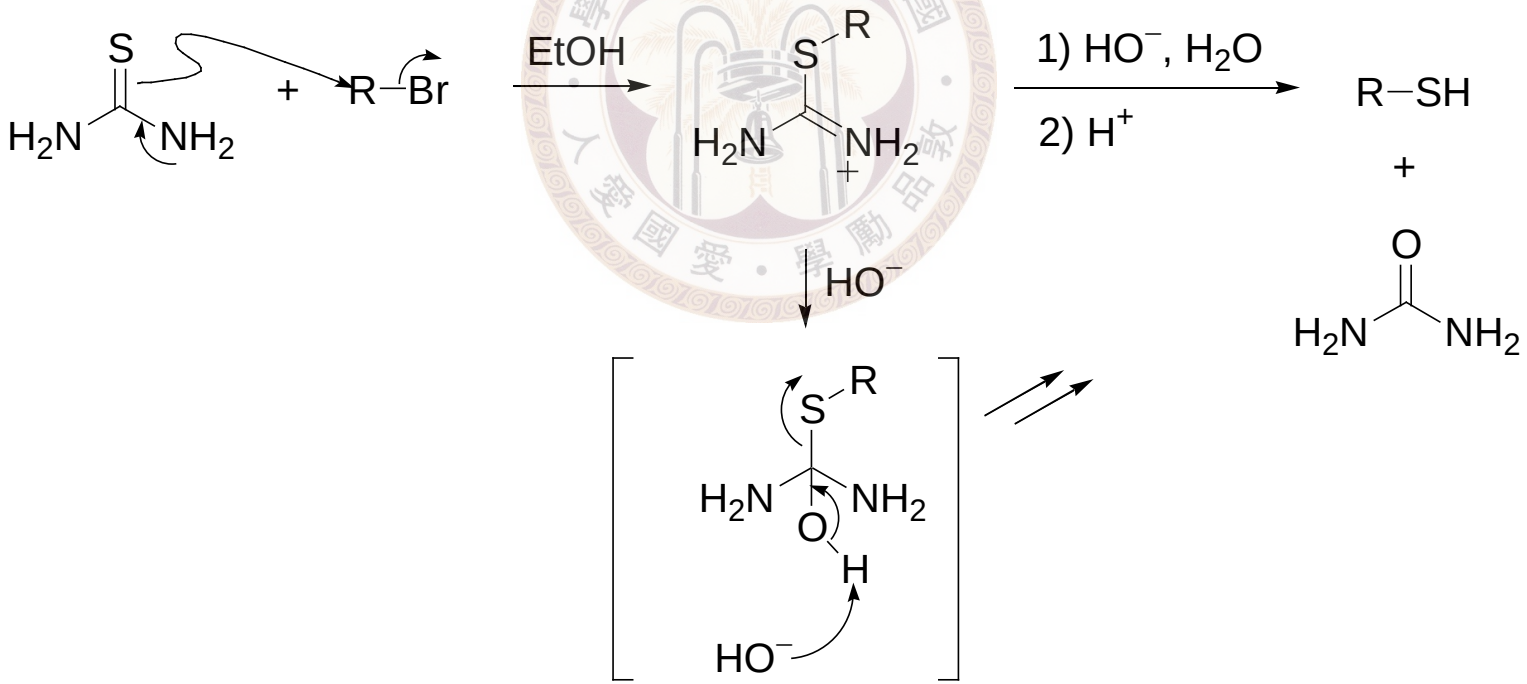




※ Preparation of thiols and sulfides







Chapter 23 Lipids

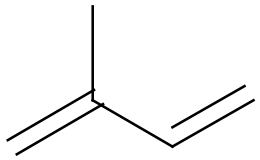
Compounds of biological origin

Insoluble in water
Soluble in organic solvent

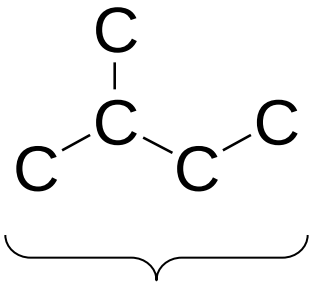
- Fats
- Oils
- Terpenoids and steroids

※ Terpenes and terpenoids

Structurally build up from C_5 units: isoprene units



isoprene
(2-methyl-1,3-butadiene)



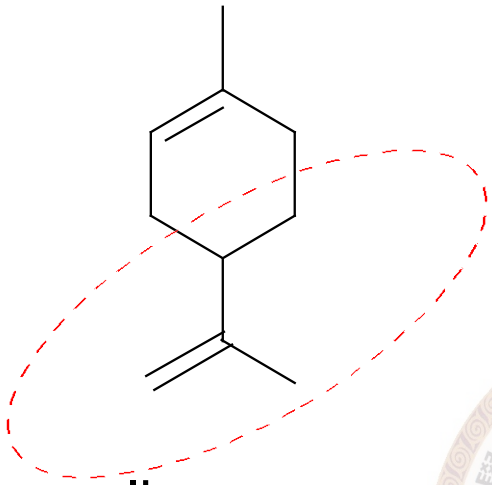
an isoprene unit

✓ Terpenes: hydrocarbons

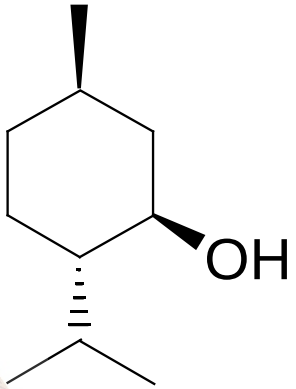
C_{10}	monoterpenes
C_{15}	sesquiterpenes
C_{20}	diterpenes
C_{30}	triterpenes

✓ Terpenoids: with extra oxygen functionalities

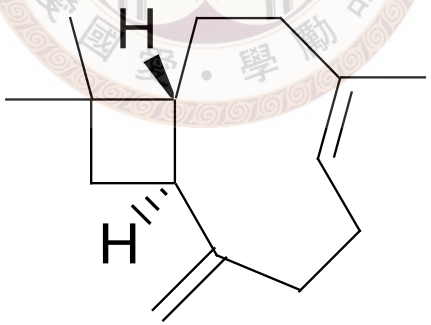
例



limonene



menthol



caryophyllene
(from cloves)

✓ Related biological chemistry