

8/1/20
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no 81
1/20...

Phenols Ar-OH

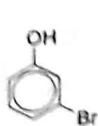
Phenols are compounds with an -OH group attached to an aromatic carbon. Although they share the same functional group with alcohols, where the -OH group is attached to an aliphatic carbon, the chemistry of phenols is very different from that of alcohols.

Nomenclature.

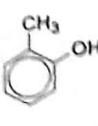
Phenols are usually named as substituted phenols. The methylphenols are given the special name, cresols. Some other phenols are named as hydroxy compounds.



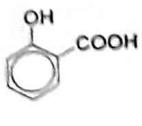
phenol



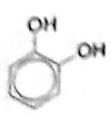
m-bromophenol



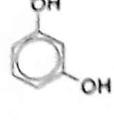
o-cresol



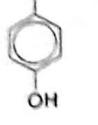
salicylic acid



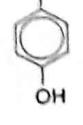
catechol



resorcinol



hydroquinone



p-hydroxybenzoic acid

physical properties

phenols are polar and can hydrogen bond

phenols are water insoluble

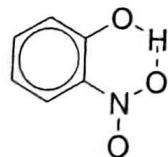
phenols are stronger acids than water and

will dissolve in 5% NaOH

phenols are weaker acids than carbonic acid and

do not dissolve in 5% NaHCO₃

Intramolecular hydrogen bonding is possible in some ortho-substituted phenols. This intramolecular hydrogen bonding reduces water solubility and increases volatility. Thus, *o*-nitrophenol is steam distillable while the isomeric *p*-nitrophenol is not.



o-nitrophenol

bp 100°C at 100 mm

0.2 g / 100 mL water

volatile with steam

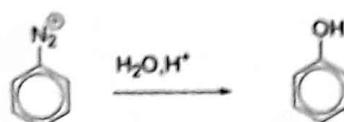
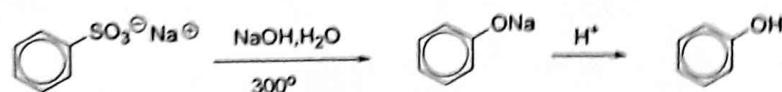


p-nitrophenol

bp decomposes

1.69 g / 100 mL water

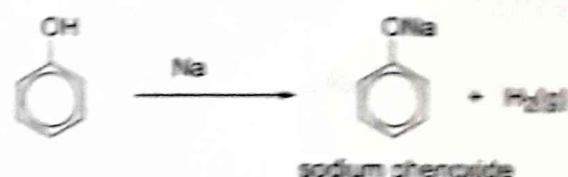
non-volatile with steam

phenols, syntheses:**1. From diazonium salts****2. Alkali fusion of sulfonates****Reactions:**

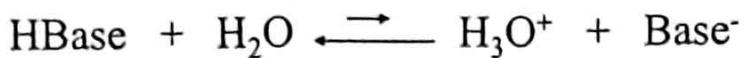
| alcohols | phenols |
|--------------------|-------------------------|
| 1. HX | NR |
| 2. PX_3 | NR |
| 3. dehydration | NR |
| 4. as acids | phenols are more acidic |
| 5. ester formation | similar |
| 6. oxidation | NR |

Phenols, reactions:

1. as acids
2. ester formation
3. ether formation
4. EAS
 - a) nitration
 - b) sulfonation
 - c) halogenation
 - d) Friedel-Crafts alkylation
 - e) Friedel-Crafts acylation
 - f) nitrosation
 - g) coupling with diaz. salts
 - h) Kolbe
 - i) Reimer-Tiemann

as acids:**with active metals:****with bases:**

We use the ionization of acids in water to measure acid strength (K_a):

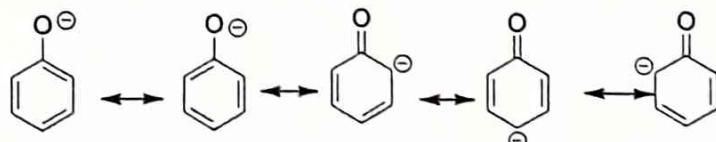
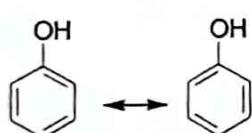
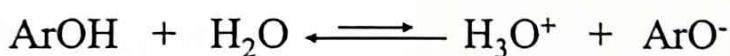
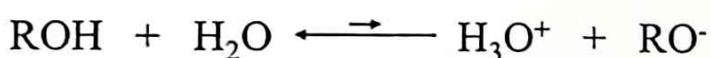


$$K_a = [\text{H}_3\text{O}^+][\text{Base}]/[\text{HBase}]$$

$$\text{ROH } K_a \sim 10^{-16} - 10^{-18}$$

$$\text{ArOH } K_a \sim 10^{-10}$$

Why are phenols more acidic than alcohols?



Resonance stabilization of the phenoxide ion, lowers the PE of the products of the ionization, decreases the ΔH , shifts the equil farther to the right, makes phenol more acidic than an alcohol

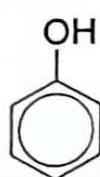
effect of substituent groups on acid strength?



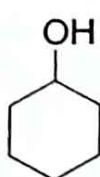
Electron withdrawing groups will decrease the negative charge in the phenoxide, lowering the PE, decreasing the ΔH , shifting the equil farther to the right, **stronger acid**.

Electron donating groups will increase the negative charge in the phenoxide, increasing the PE, increasing the ΔH , shifting the equilibrium to the left, **weaker acid**.

Number the following acids in decreasing order of acid strength (let # 1 = most acidic, etc.)



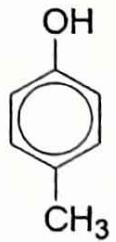
3



5



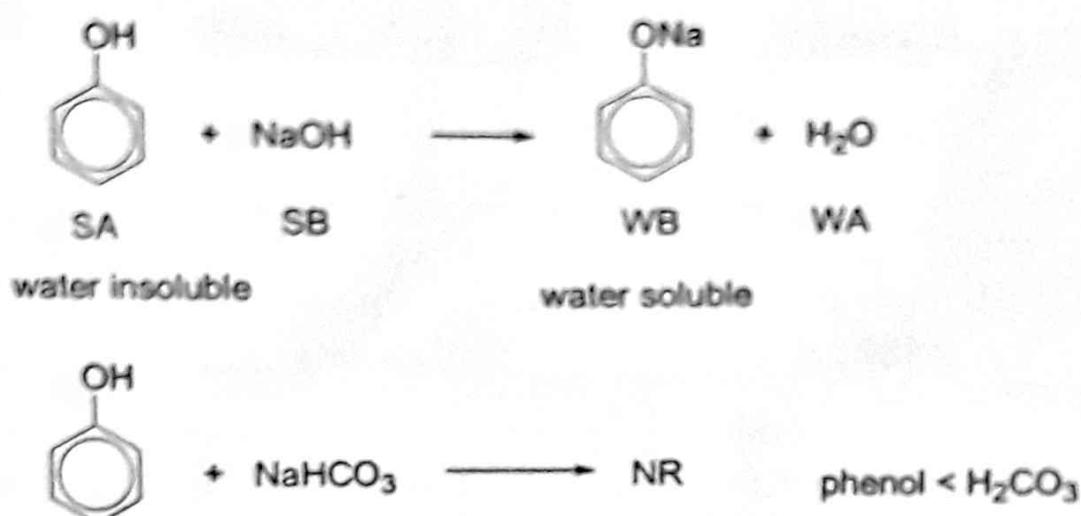
1



4



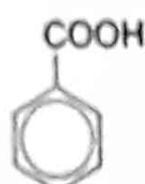
2



| | water | 5% NaOH | 5% NaHCO ₃ |
|------------------|-----------|---------|-----------------------|
| phenols | insoluble | soluble | insoluble |
| carboxylic acids | insoluble | soluble | soluble |



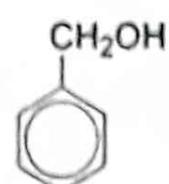
1



2

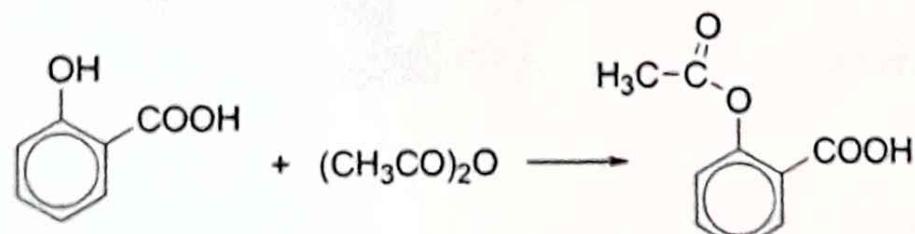
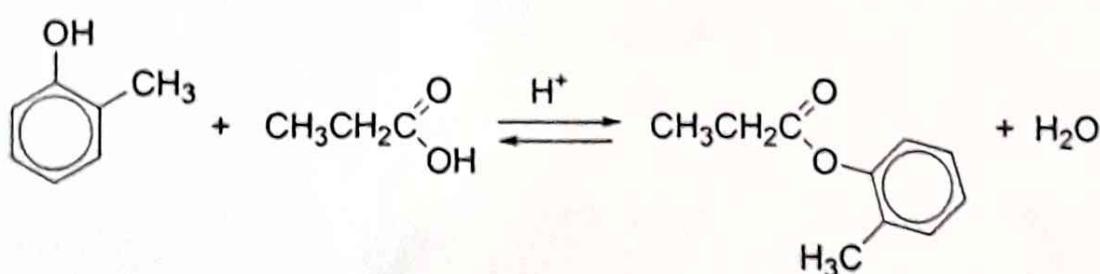


3



4

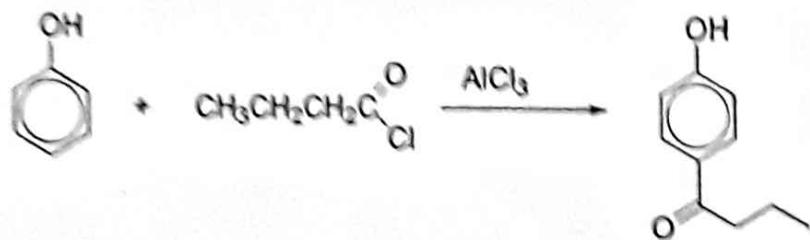
2. ester formation (similar to alcohols)



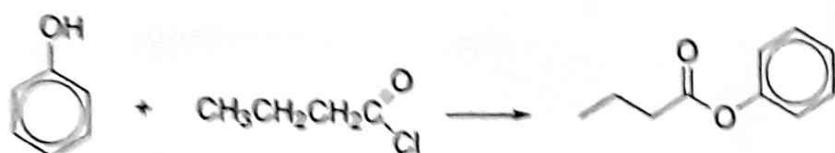
salicylic acid

aspirin

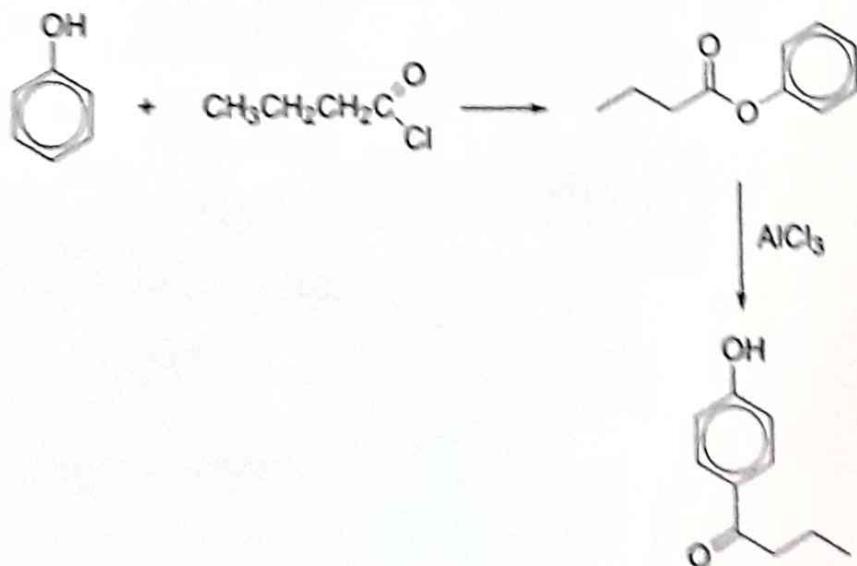
e) Friedel-Crafts acylation



Do not confuse FC acylation with esterification:



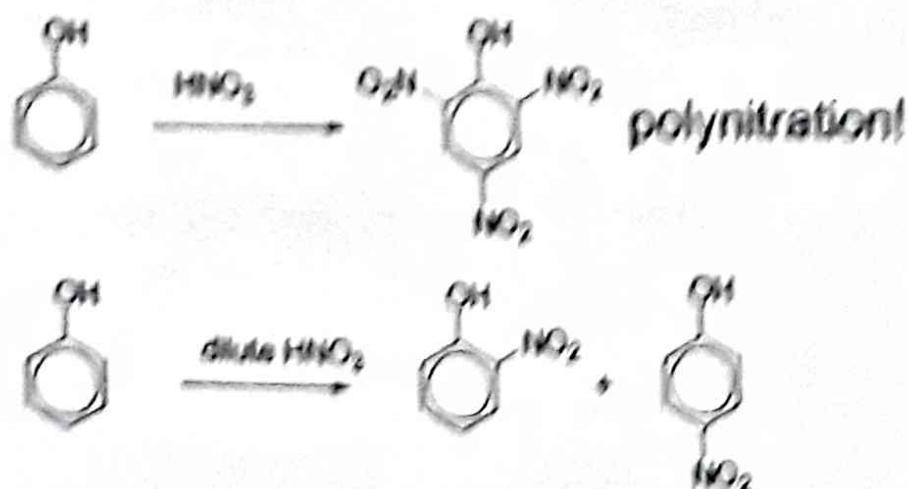
Fries rearrangement of phenolic esters.



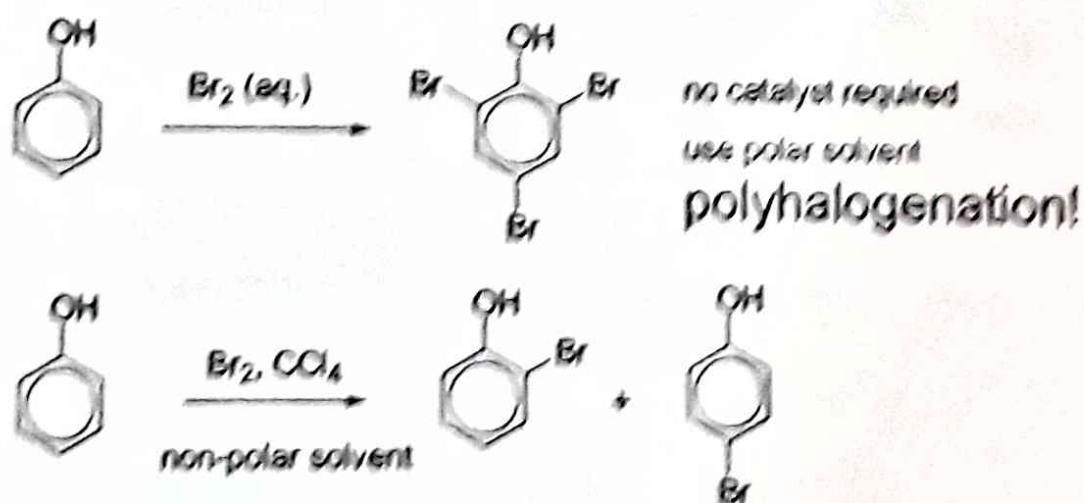
4. Electrophilic Aromatic Substitution

The -OH group is a powerful activating group in EAS and an *ortho/para* director.

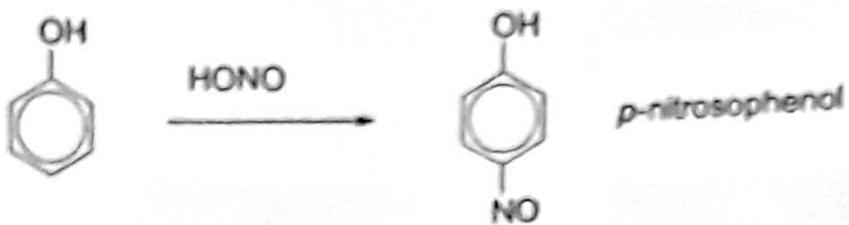
a) nitration



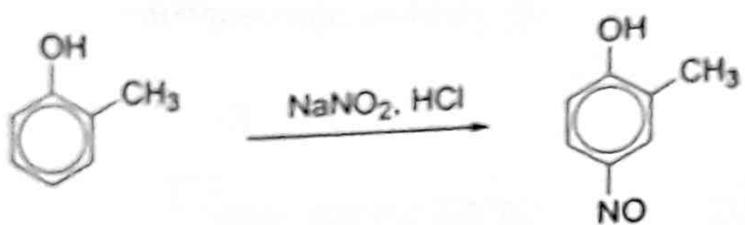
b) halogenation



f) nitrosation

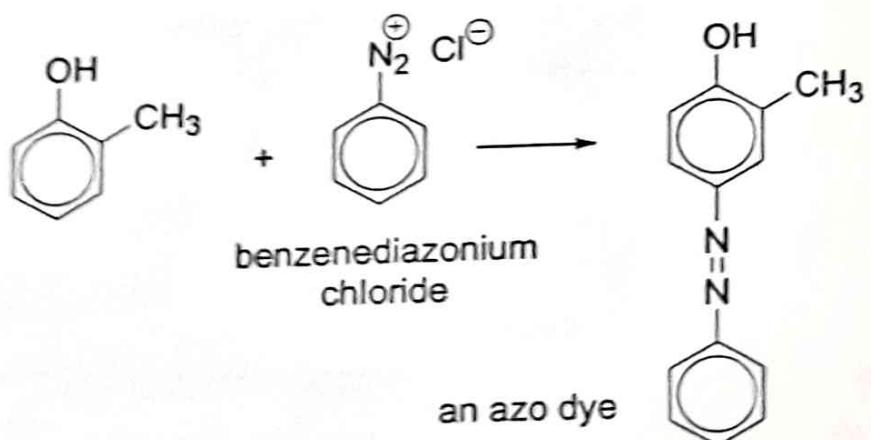


EAS with very weak electrophile NO^+

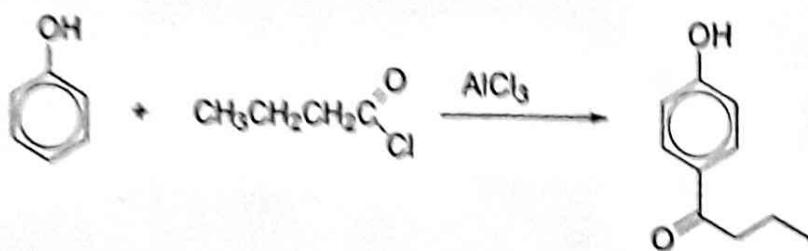


g) coupling with diazonium salts

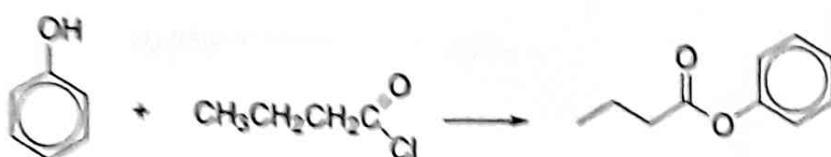
(EAS with the weak electrophile diazonium)



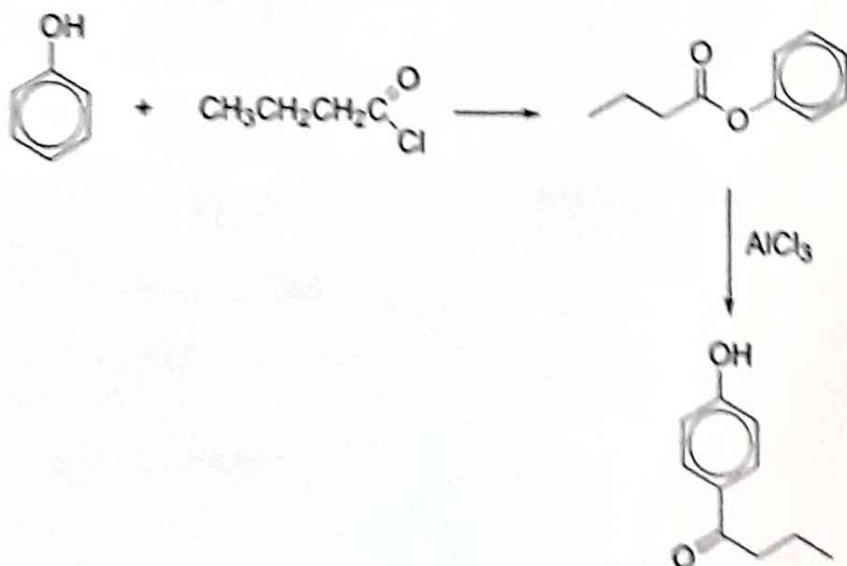
e) Friedel-Crafts acylation



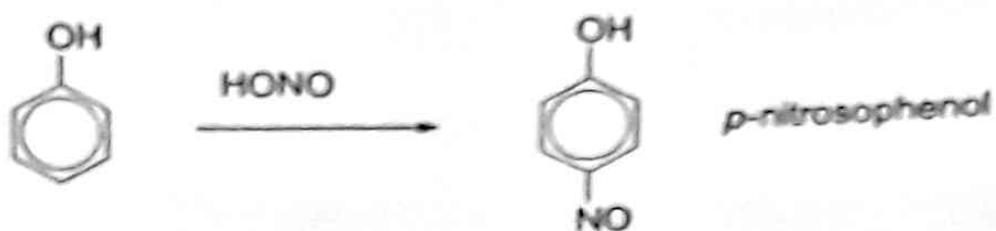
Do not confuse FC acylation with esterification:



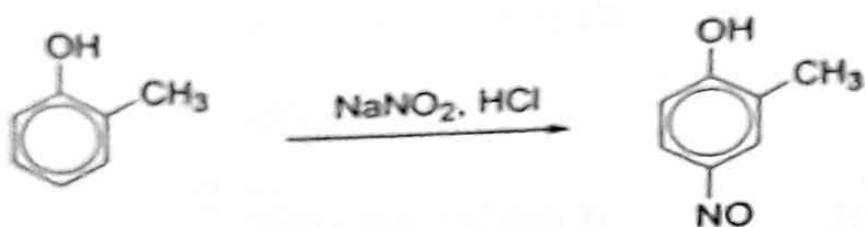
Fries rearrangement of phenolic esters.



f) nitrosation

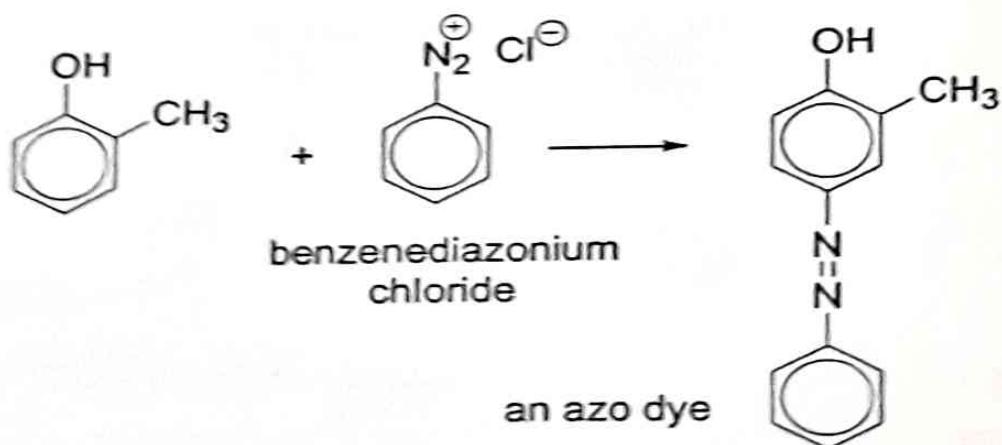


EAS with very weak electrophile NO⁺

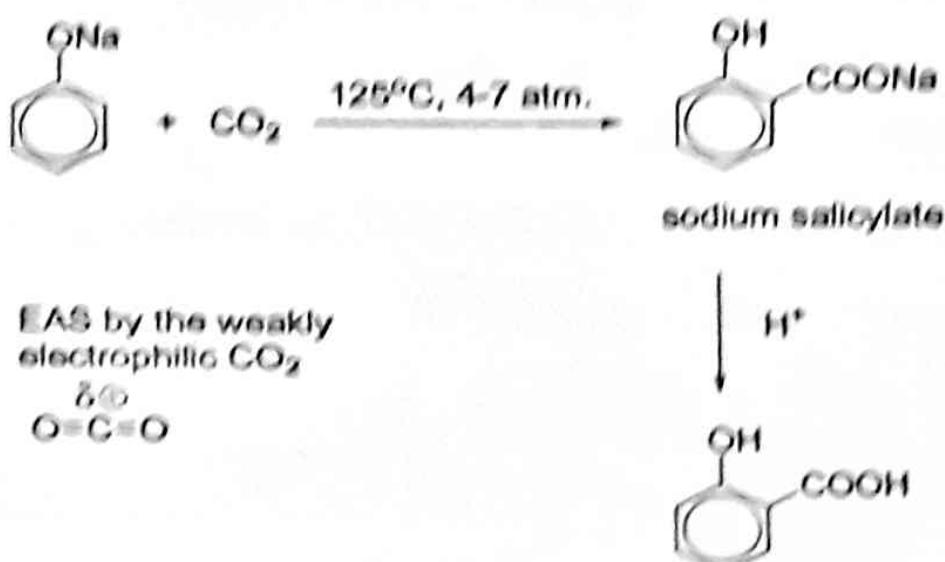


g) coupling with diazonium salts

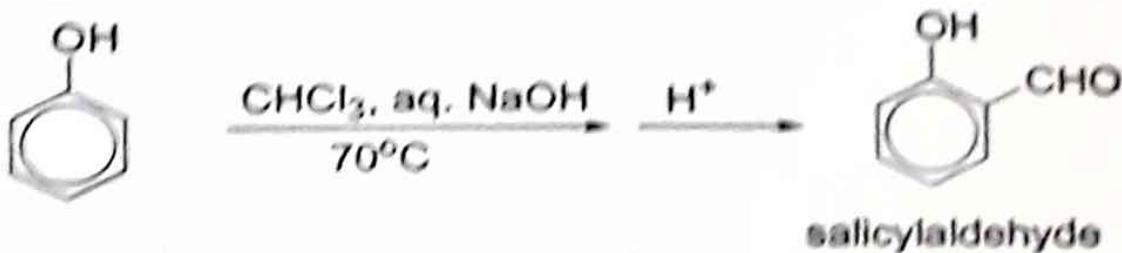
(EAS with the weak electrophile diazonium)



h) Kolbe reaction (carbonation)



i) Reimer-Tiemann reaction



The salicylaldehyde can be easily oxidized to salicylic acid

Spectroscopy of phenols:

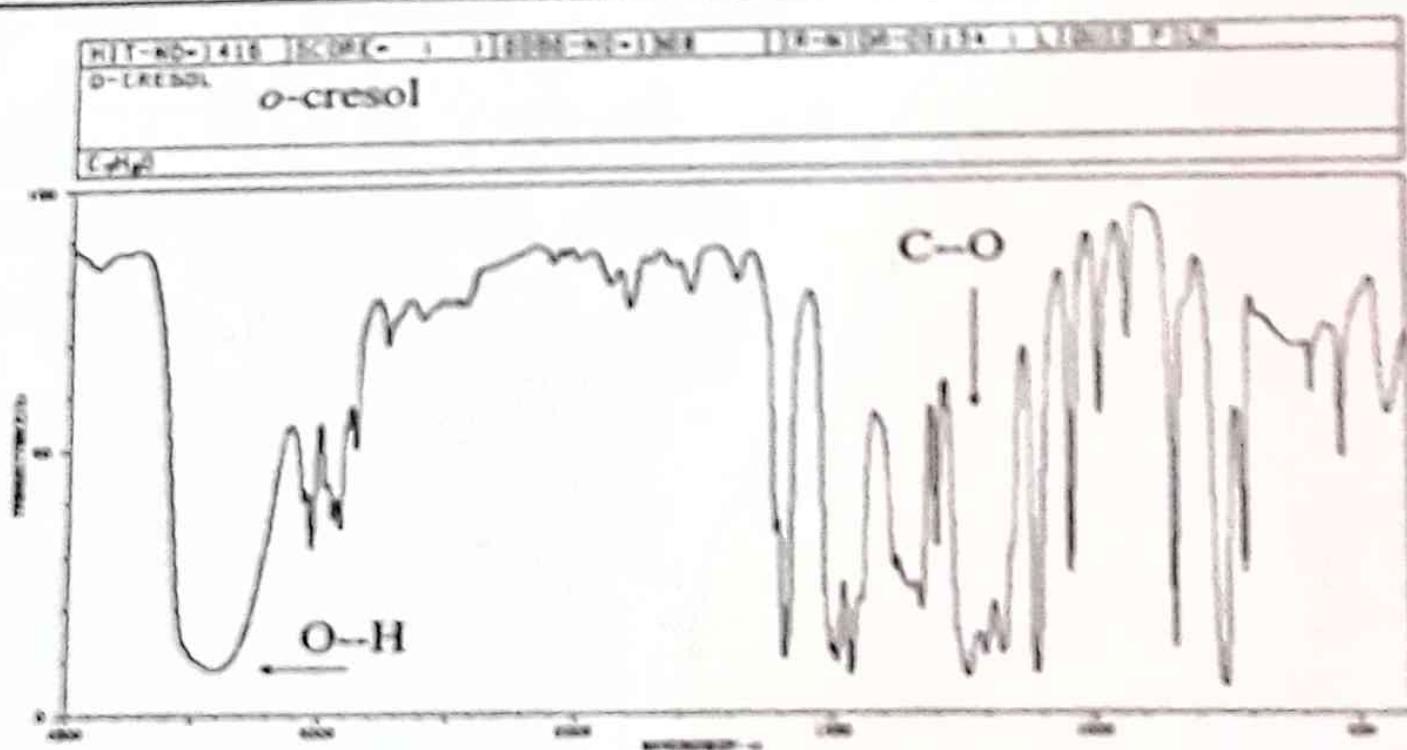
Infrared:

O—H stretching, strong, broad $3200\text{-}3600\text{ cm}^{-1}$

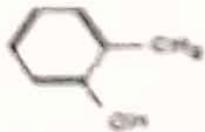
C—O stretch, strong, broad $\sim 1230\text{ cm}^{-1}$

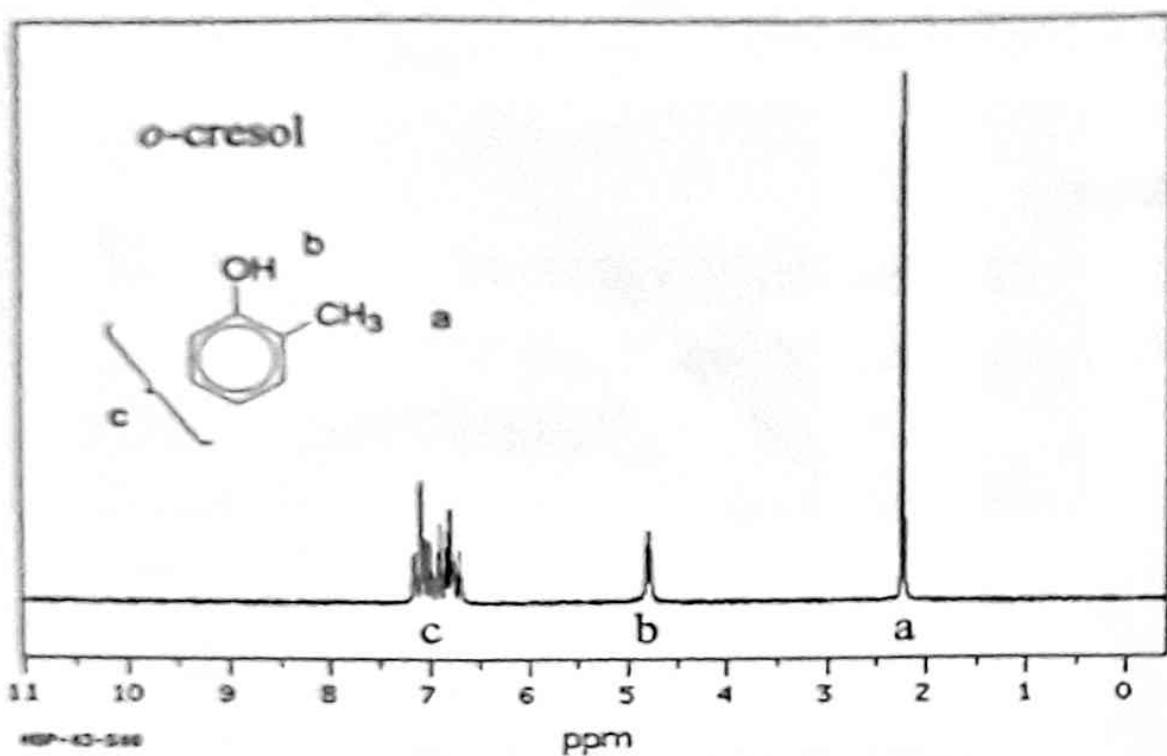
(alcohols $\sim 1050\text{ - }1200$)

nmr: O—H 4-7 ppm (6-12 ppm if intramolecular hydrogen bonding)

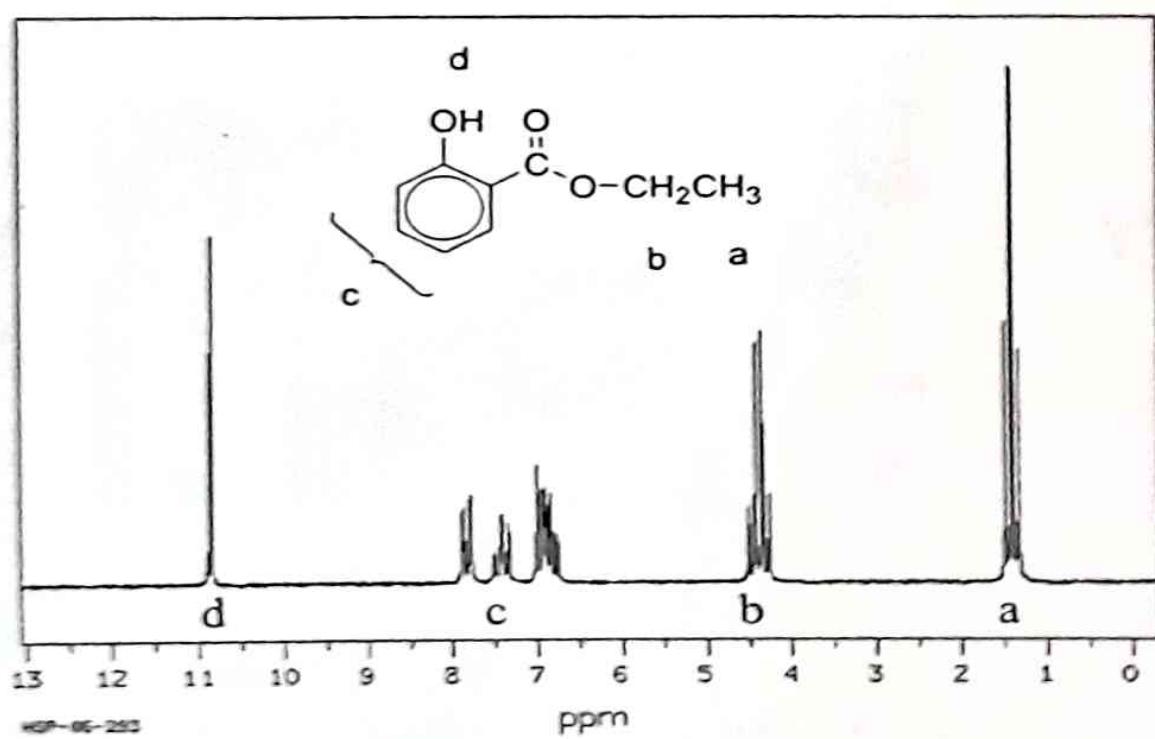


| | | | | | | | | | | | | |
|------|------|------|------|------|------|------|------|------|------|-----|-----|-----|
| 3430 | 3380 | 3080 | 2950 | 2850 | 1900 | 1700 | 1500 | 1300 | 1100 | 900 | 700 | 500 |
| 3420 | 3370 | 3070 | 2940 | 2840 | 1890 | 1690 | 1490 | 1390 | 1190 | 990 | 790 | 590 |
| 3410 | 3360 | 3060 | 2930 | 2830 | 1880 | 1680 | 1480 | 1380 | 1180 | 980 | 780 | 580 |
| 3400 | 3350 | 3050 | 2920 | 2820 | 1870 | 1670 | 1470 | 1370 | 1170 | 970 | 770 | 570 |
| 3390 | 3340 | 3040 | 2910 | 2810 | 1860 | 1660 | 1460 | 1360 | 1160 | 960 | 760 | 560 |
| 3380 | 3330 | 3030 | 2900 | 2800 | 1850 | 1650 | 1450 | 1350 | 1150 | 950 | 750 | 550 |





ethyl salicylate (intramolecular hydrogen bonding)



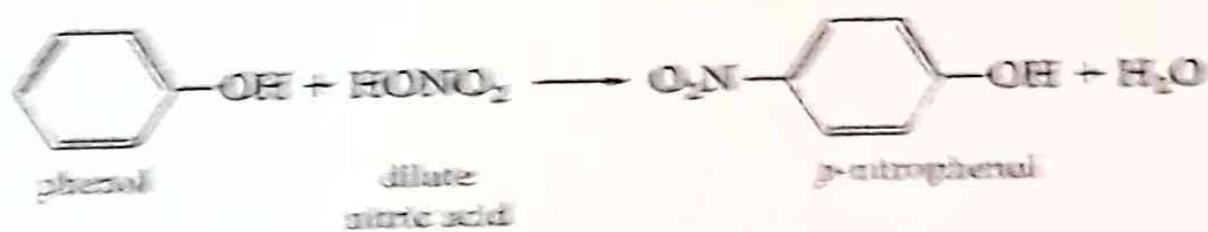
The Activity of Alcohols and Phenols



Residues with stronger positive charges usually have the corresponding phenoxide ions stabilized by resonance. The negative charge of the phenoxide ion is concentrated on the oxygen atom, while the negative charge on the phenoxide group is delocalized to the ortho and para positions (Scheme 1).

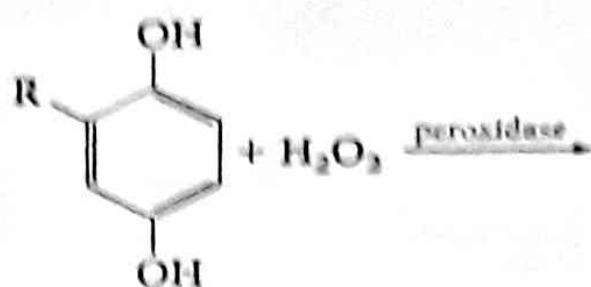


Aromatic Substitutions in Phenols

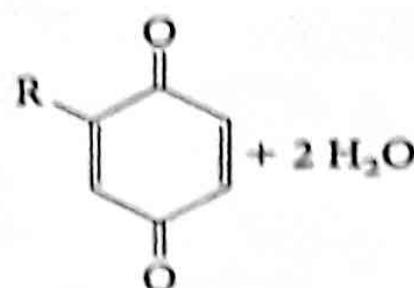




Dendrobium beetle spraying



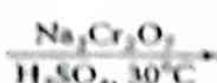
$\text{R} = \text{H}$ 1,4-hydroquinone
 $\text{R} = \text{CH}_3$ 2-methyl-1,4-hydroquinone



$\text{R} = \text{H}$ 1,4-benzoquinone
 $\text{R} = \text{CH}_3$ 2-methyl-1,4-benzoquinone



hydroquinone
colorless, mp 171°C



1,4-benzoquinone
yellow, mp 116°C

Phenols and Antioxidants



Reaction mechanism

Phenol is a strong reducing agent and can reduce many oxidants. It is also a strong antioxidant due to its ability to reduce radicals. Phenol is a good antioxidant because it is a strong reducing agent. It is also a good antioxidant because it is a strong reducing agent.



Reaction conditions

Phenol is a strong reducing agent and can reduce many oxidants. It is also a strong antioxidant due to its ability to reduce radicals. Phenol is a good antioxidant because it is a strong reducing agent. It is also a good antioxidant because it is a strong reducing agent.