

CH 310 N

TH 2-3:30

LECTURE 20

Textbook Assignment: Chapter 21 & 22

Homework (for credit): POW 10 posted

Today's Topics: Benzene & Reactions of Its Derivatives

Notice & Announcements:

ORGANIC LECTURE SERIES

Benzene & Aromaticity

Concept of Aromaticity

The underlying criteria for aromaticity were recognized in the early 1930s by Erich Hückel, based on molecular orbital (MO) calculations

To be aromatic, a compound must:

1. be cyclic
2. have one p orbital on each atom of the ring
3. be planar or nearly planar so that there is continuous or nearly continuous overlap of all p orbitals of the ring
4. have a closed loop of $(4n + 2) \pi$ electrons in the cyclic arrangement of p orbitals

3

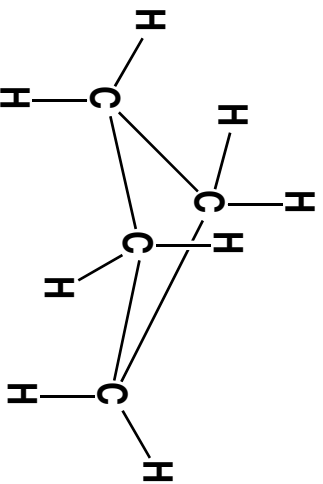
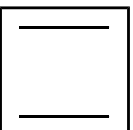
Antiaromatic Hydrocarbons

- **Antiaromatic hydrocarbon:** a monocyclic, planar, fully conjugated hydrocarbon with $4n \pi$ electrons (4, 8, 12, 16, 20...)
 - an antiaromatic hydrocarbon is especially unstable relative to an open-chain fully conjugated hydrocarbon of the same number of carbon atoms

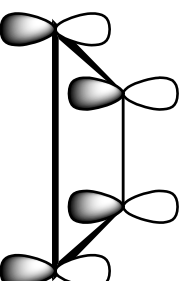
E.G. Cyclobutadiene is antiaromatic

- in the ground-state electron configuration of this molecule, two electrons fill the π_1 bonding MO
- the remaining two electrons lie in the π_2 and π_3 nonbonding MOs

4



Cyclobutane can adopt a "puckered" conformation

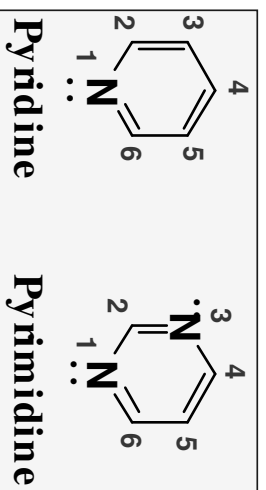


Cyclobutadiene is strained and has electrons in nonbonding orbitals

5

Heterocyclic Aromatics

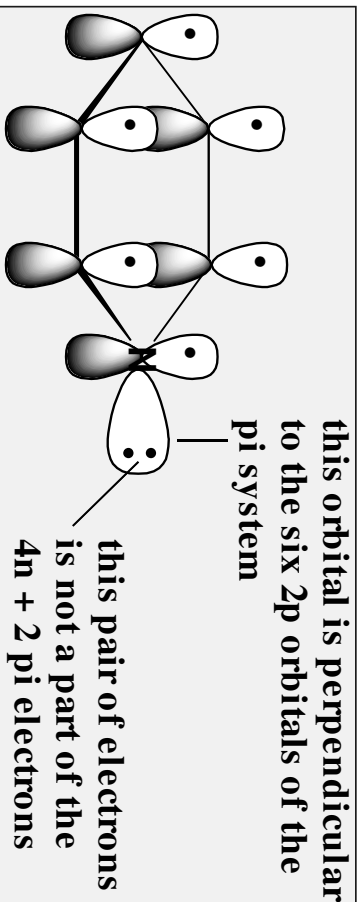
- Heterocyclic compound: a compound that contains more than one kind of atom in a ring
 - in organic chemistry, the term refers to a ring with one or more atoms are other than carbon
- Pyridine and pyrimidine are heterocyclic analogs of benzene; each is aromatic.



6

Pyridine

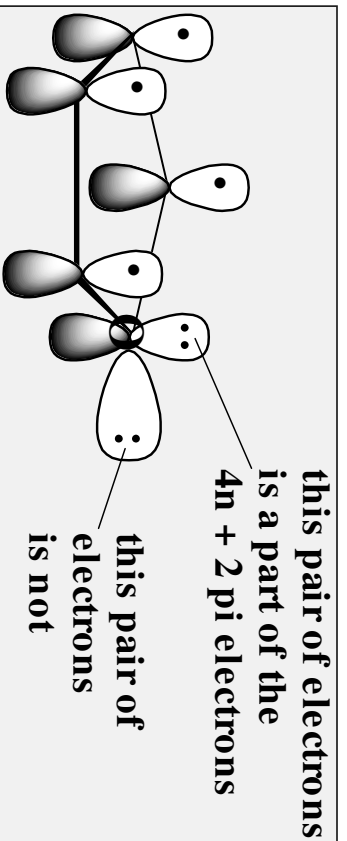
- the nitrogen atom of pyridine is sp^2 hybridized
- the unshared pair of electrons lies in an sp^2 hybrid orbital and is not a part of the six π electrons of the aromatic system
- pyridine has a resonance energy of 134 kJ (32 kcal)/mol, slightly less than that of benzene



7

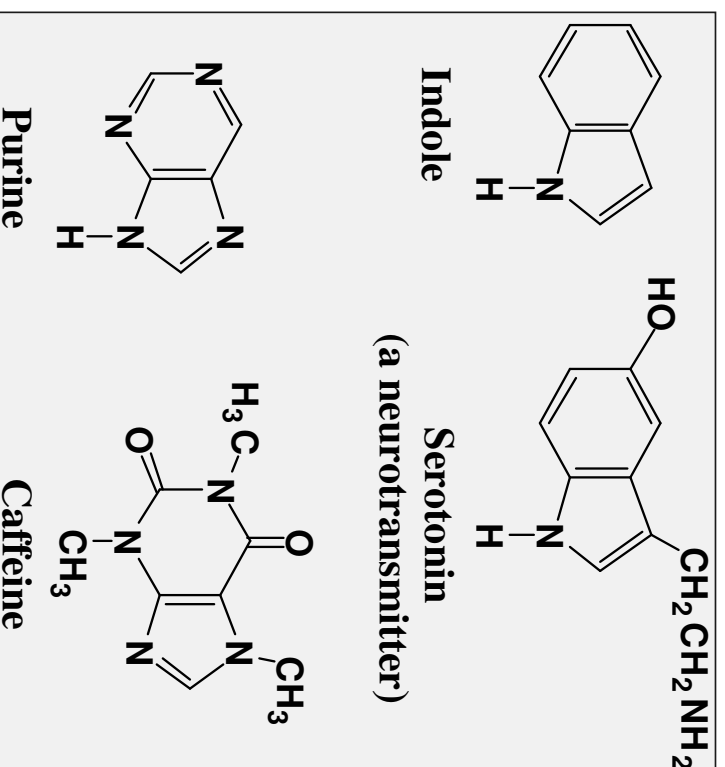
Furan

- the oxygen atom of furan is sp^2 hybridized
- one unshared pair of electrons on oxygen lies in an unhybridized 2p orbital and is a part of the aromatic sextet
- the other unshared pair lies in an sp^2 hybrid orbital and is not a part of the aromatic system
- the resonance energy of furan is 67 kJ (16 kcal)/mol



8

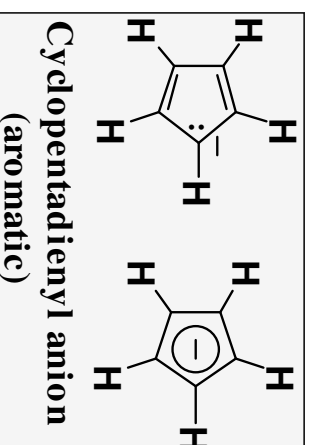
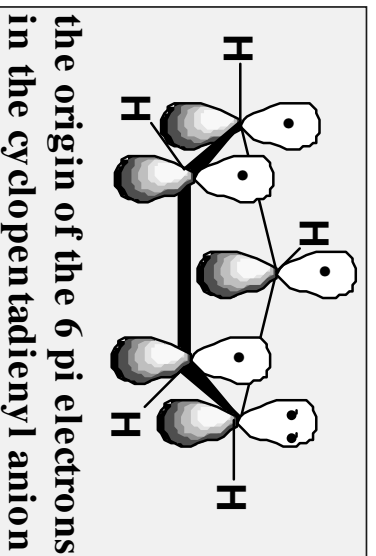
Other Heterocyclics



9

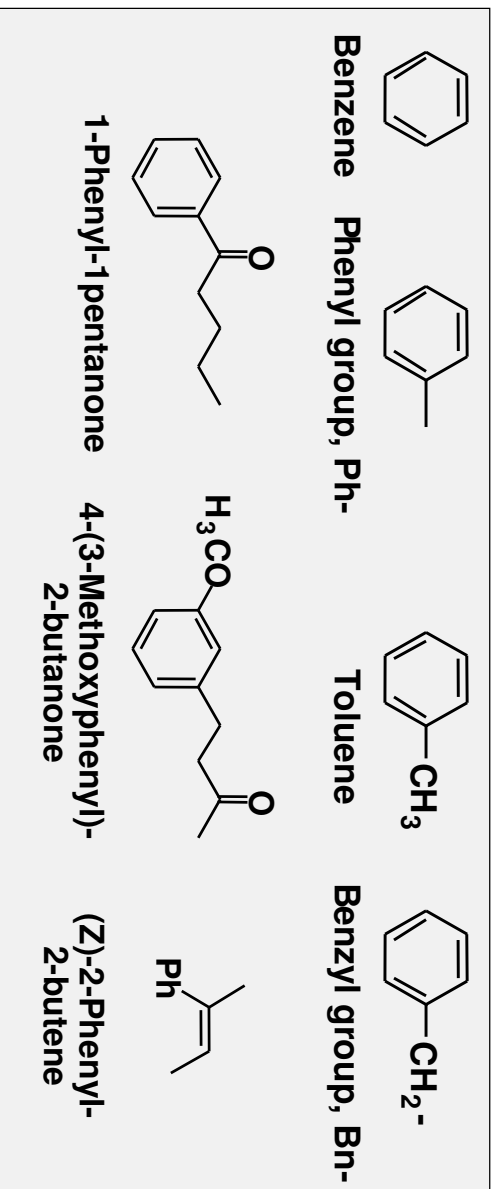
- To convert cyclopentadiene to an aromatic ion, it is necessary to convert the CH_2 group to a CH group in which carbon becomes sp^2 hybridized and has 2 electrons in its unhybridized $2p$ orbital

Cyclopentadienyl Anion



10

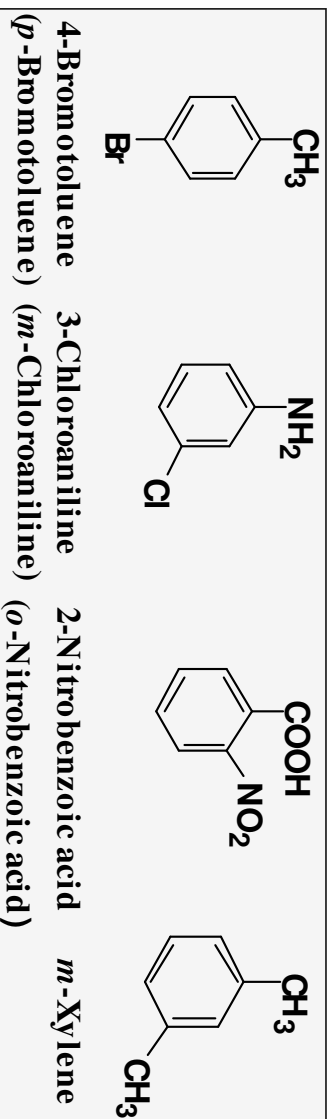
Benzyl and phenyl groups:



13

Disubstituted Benzenes

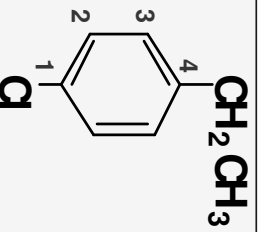
- Locate two groups by numbers or by the locators ortho (1,2-), meta (1,3-), and para (1,4-)
 - where one group imparts a special name, name the compound as a derivative of that molecule



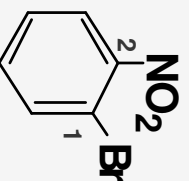
14

Disubstituted Benzenes

where neither group imparts a special name, locate the groups and **list them in alphabetical order**



1-Chloro-4-ethylbenzene
(*p*-Chloroethylbenzene)

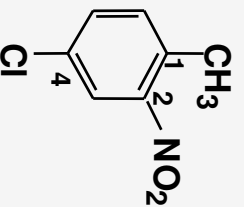


1-Bromo-2-nitrobenzene
(*o*-Bromonitrobenzene)

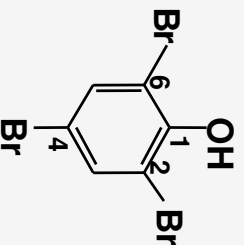
15

Polysubstituted Derivatives

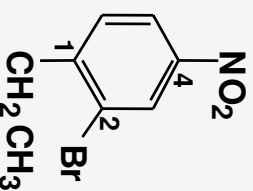
- if one group imparts a special name, name the molecule as a derivative of that compound
- if no group imparts a special name, list them in alphabetical order, giving them the lowest set of numbers



4-Chloro-2-nitro-toluene



2,4,6-Tribromophenol

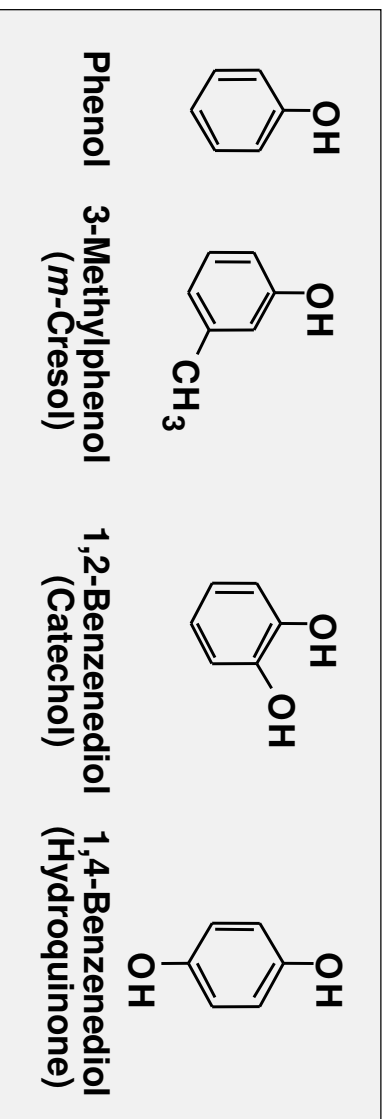


2-Bromo-1-ethyl-4-nitrobenzene

16

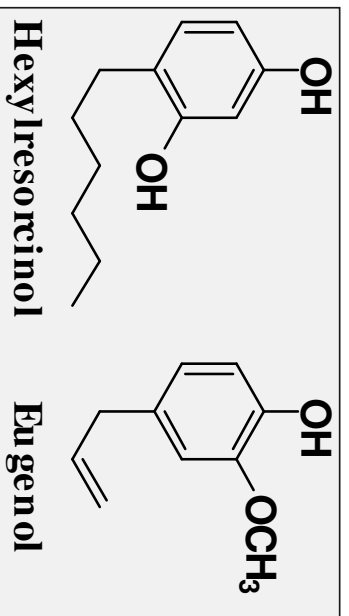
Phenols

- The functional group of a phenol is an -OH group bonded to a benzene ring



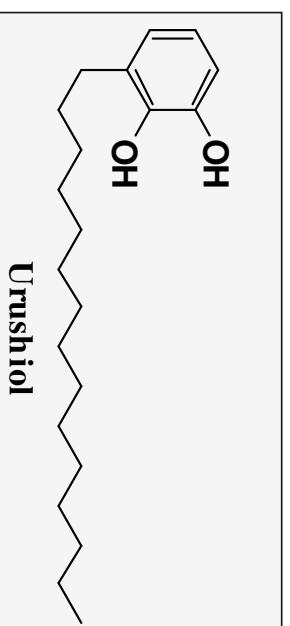
17

Phenols



- hexylresorcinol is a mild antiseptic and disinfectant
- eugenol is used as a dental antiseptic and analgesic

–urushiol is the main component of the oil of poison ivy

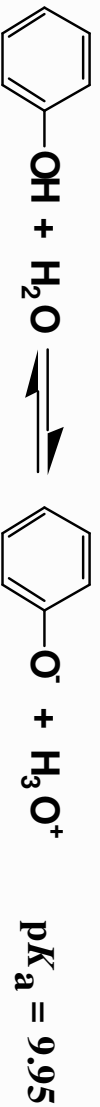


18

Acidity of Phenols

- Phenols are significantly more acidic than alcohols, compounds that also contain the OH group

Phenoxide:

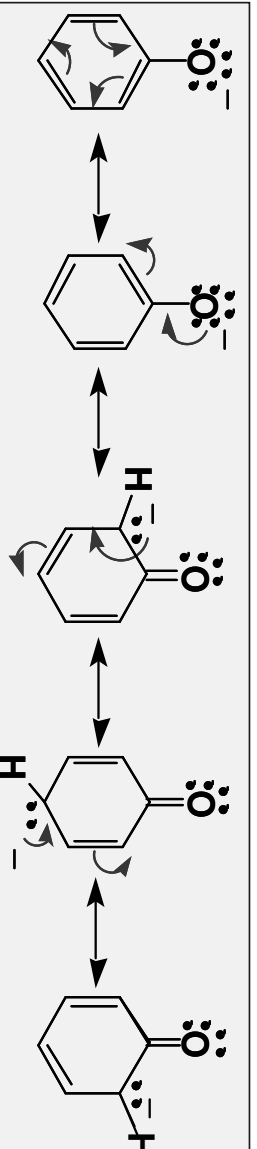


Ethoxide

19

Acidity of Phenols

—the greater acidity of phenols compared with alcohols is due to the greater stability of the phenoxide ion relative to an alkoxide ion



These 2 Kekulé structures are equivalent

These three contributing structures delocalize the negative charge onto carbon atoms of the ring

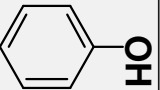
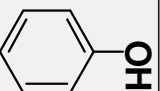
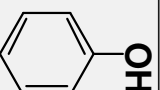
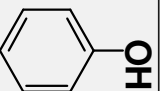
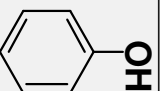
20

Acidity of Phenols

Alkyl and halogen substituents effect

acidities by inductive effects:

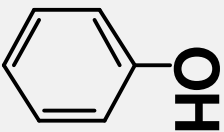
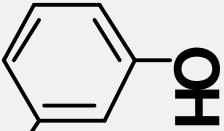
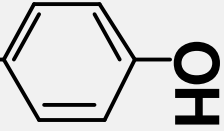
- alkyl groups are electron-releasing
- halogens are electron-withdrawing

				
Phenol pK_a 9.95	<i>m</i> -Cresol pK_a 10.01	<i>p</i> -Cresol pK_a 10.17	<i>m</i> -Chlorophenol pK_a 8.85	<i>p</i> -Chlorophenol pK_a 9.18

21

Acidity of Phenols

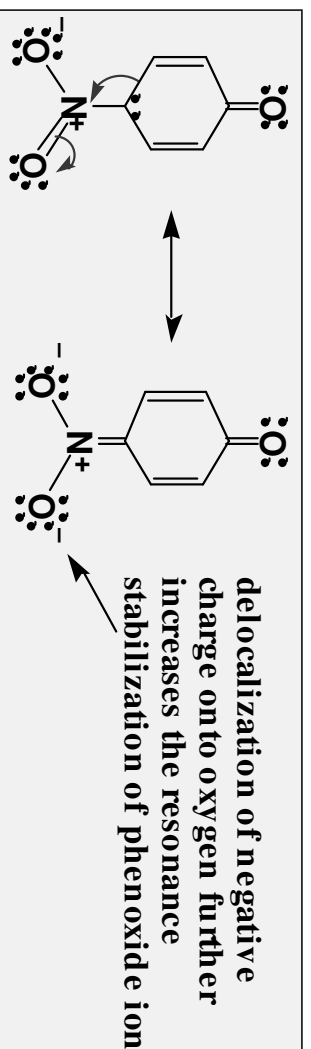
- nitro groups increase the acidity of phenols by both an electron-withdrawing inductive effect and a resonance effect

		
Phenol pK_a 9.95	<i>m</i> -Nitrophenol pK_a 8.28	<i>p</i> -Nitrophenol pK_a 7.15

22

Acidity of Phenols

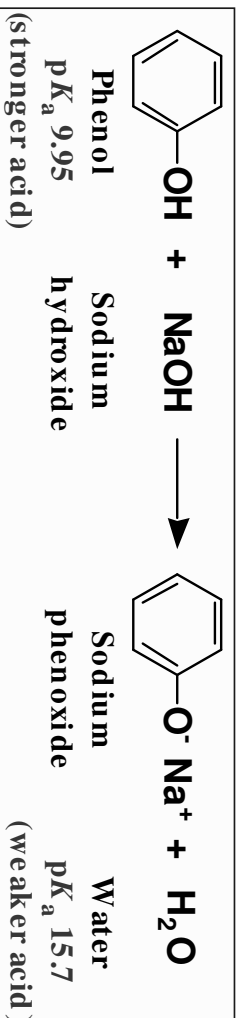
- part of the acid-strengthening effect of $-\text{NO}_2$ is due to its electron-withdrawing inductive effect
- in addition, $-\text{NO}_2$ substituents in the ortho and para positions help to delocalize the negative charge



23

Acidity of Phenols

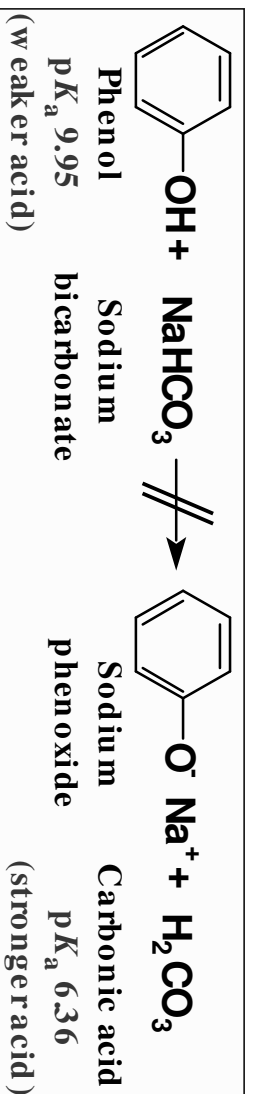
- Phenols are weak acids and react with strong bases to form water-soluble salts
 - water-insoluble phenols dissolve in $\text{NaOH}(\text{aq})$



24

Acidity of Phenols

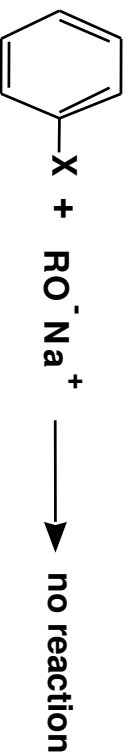
–most phenols do not react with weak bases such as NaHCO_3 ; they do not dissolve in aqueous NaHCO_3



25

Alkyl-Aryl Ethers

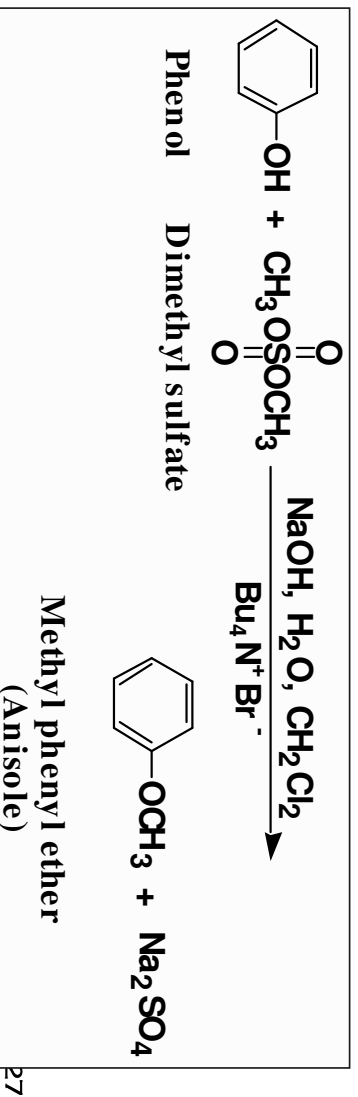
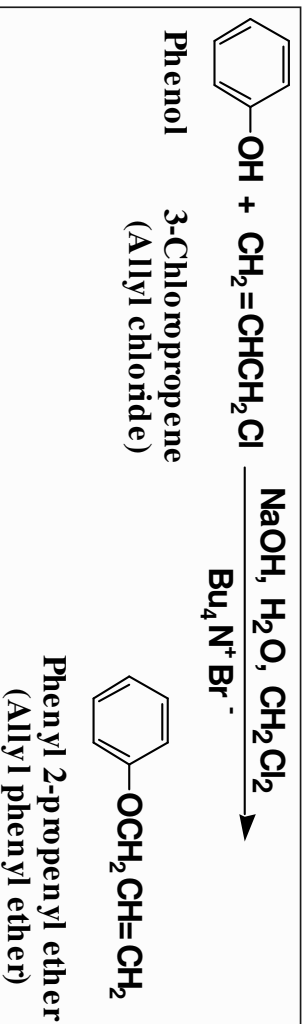
- Alkyl-aryl ethers can be prepared by the Williamson ether synthesis
 - but only using phenoxide salts and haloalkanes
 - haloarenes are unreactive to $\text{S}_{\text{N}}2$ reactions



- The following two examples illustrate
 - the use of a phase-transfer catalyst
 - the use of dimethyl sulfate as a methylating agent

26

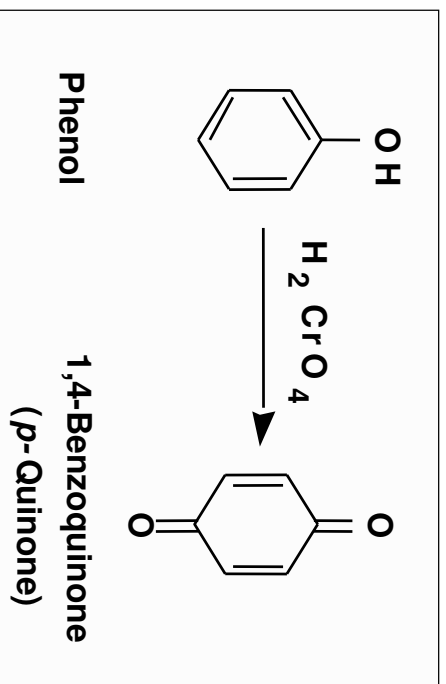
Alkyl-Aryl Ethers



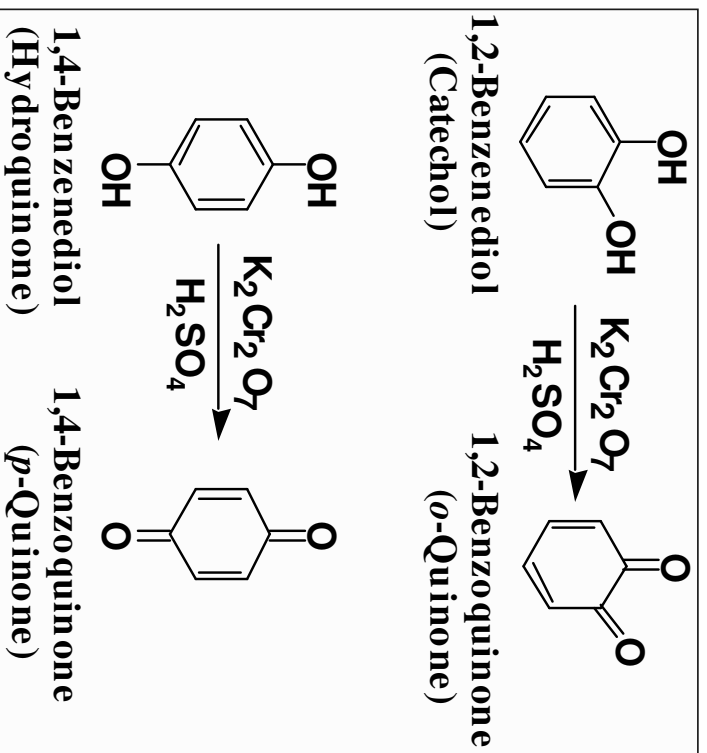
27

Quinones

- Because of the presence of the electron-donating -OH group, phenols are susceptible to oxidation by a variety of strong oxidizing agents



Quinones

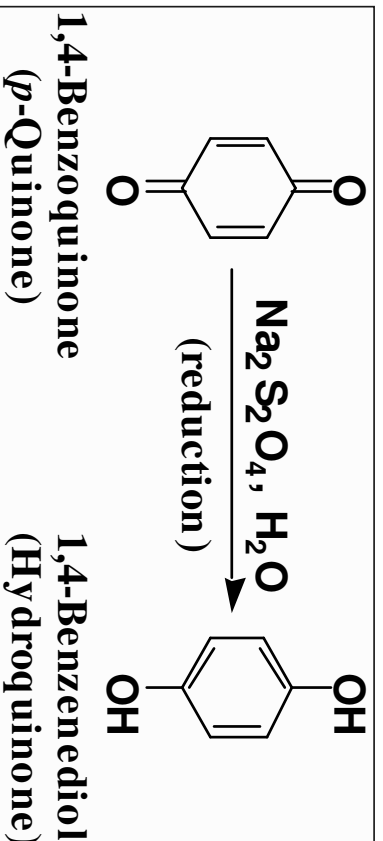


Not responsible for mechanism

29

Quinones

- Perhaps the most important chemical property of quinones is that they are readily reduced to hydroquinones:

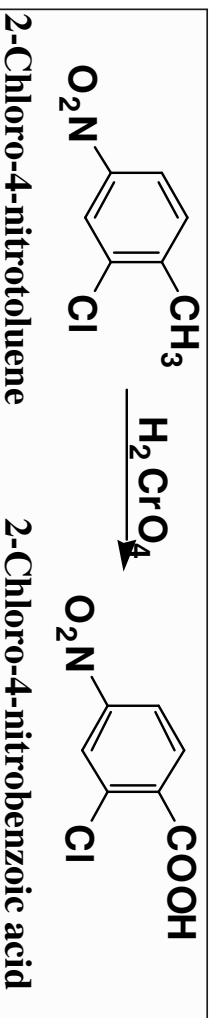


Not responsible for mechanism

30

Benzylic Oxidation

- Benzene is unaffected by strong oxidizing agents such as H_2CrO_4 and KMnO_4
 - halogen and nitro substituents are also unaffected by these reagents
 - an alkyl group with at least one hydrogen on its benzylic carbon is oxidized to a carboxyl group

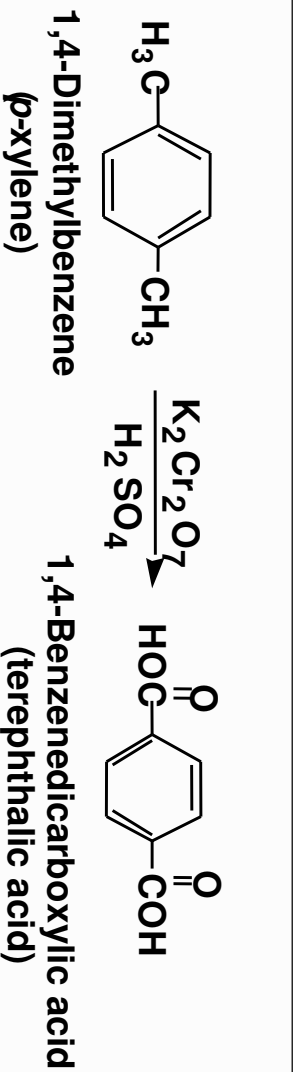


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31

Benzylic Oxidation

- if there is more than one alkyl group on the benzene ring, each is oxidized to a -COOH group

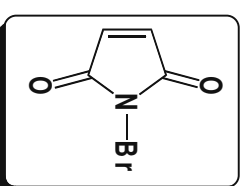
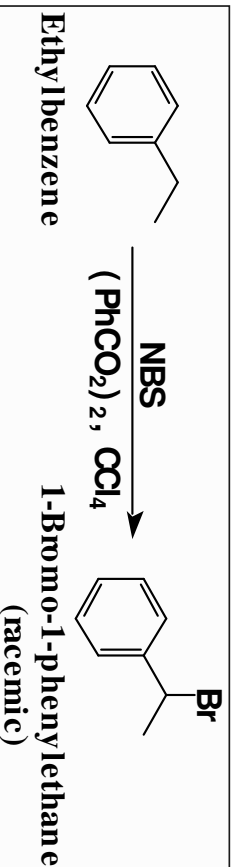
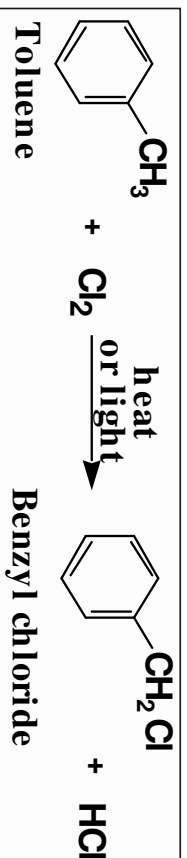


Not responsible for mechanism

32

Benzylic Chlorination

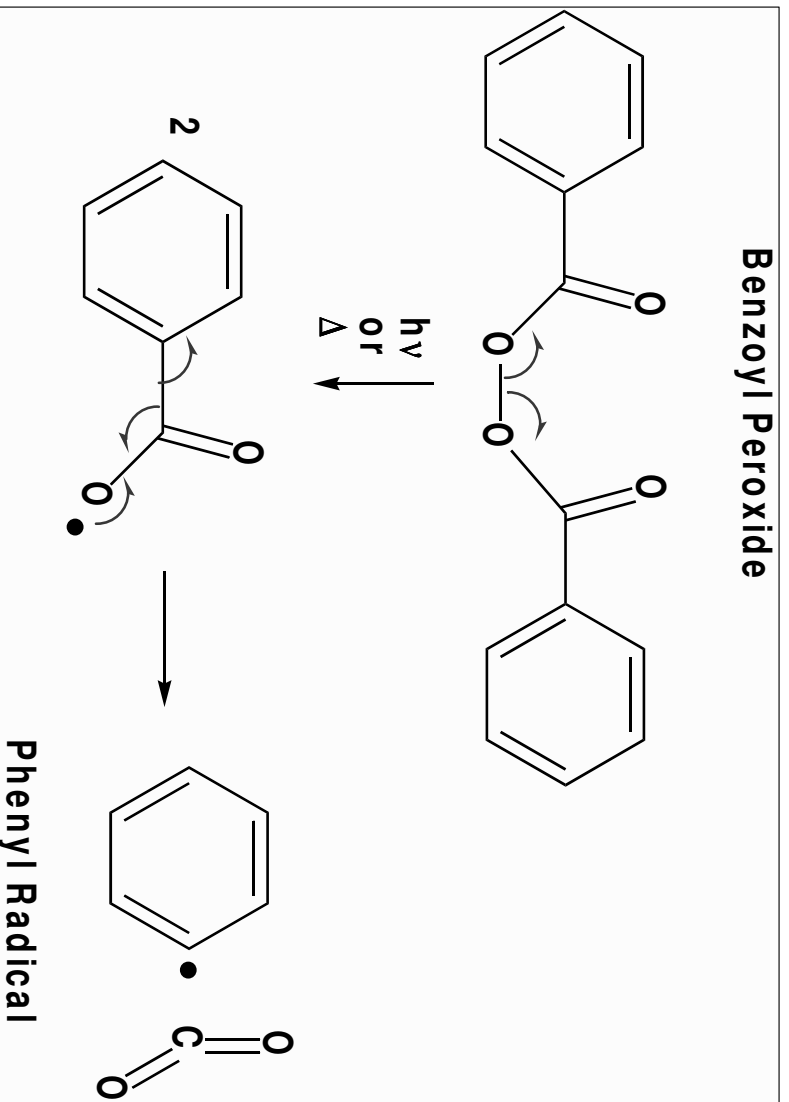
- Chlorination (and bromination) occurs by a radical mechanism



33

Benzoyl Peroxide as a Radical initiator

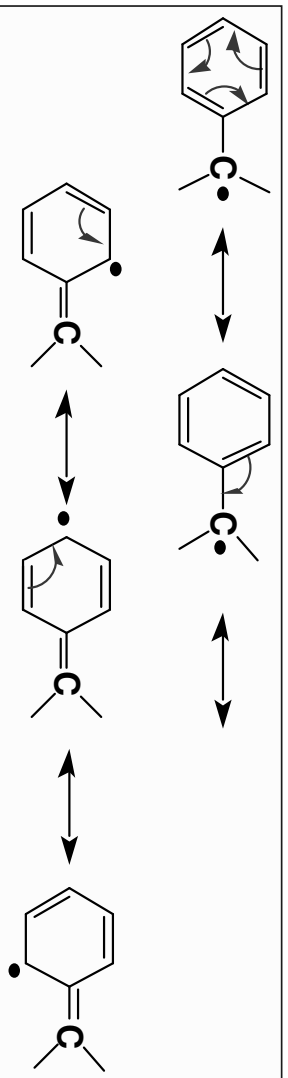
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4

Benzylic Reactions

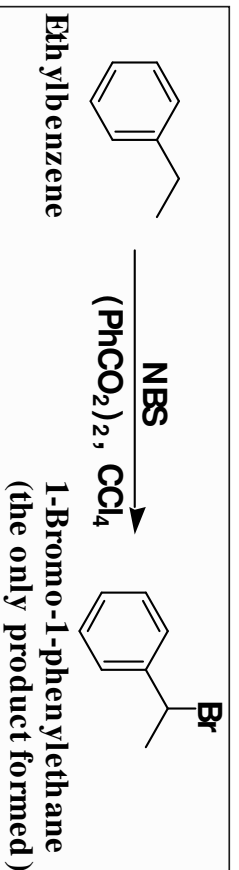
- **Benzylic radicals** (and cations also) are easily formed because of the resonance stabilization of these intermediates
 - the benzyl radical is a hybrid of five contributing structures



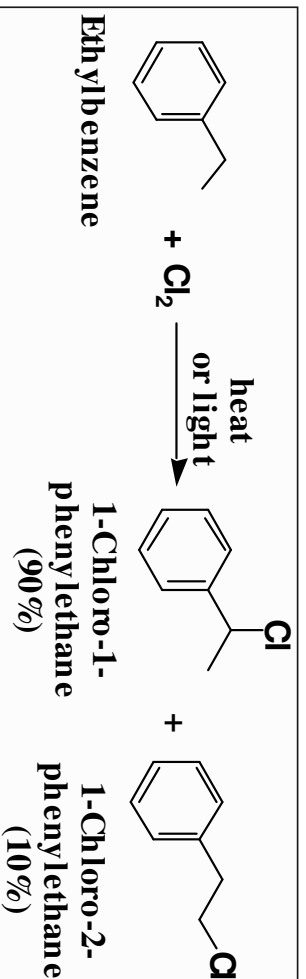
35

Benzylic Halogenation

- benzylic bromination is highly regioselective



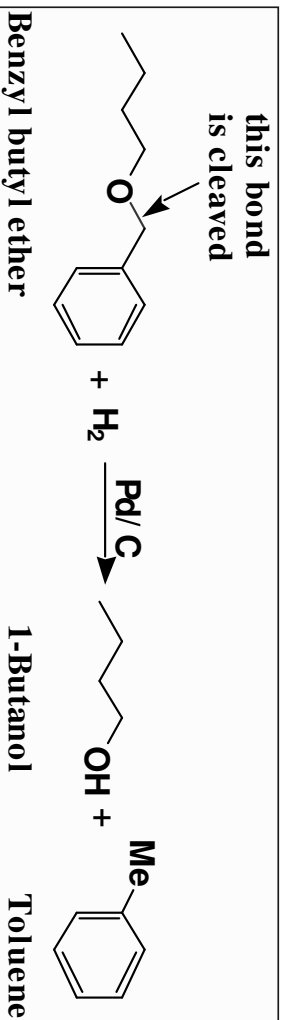
- benzylic chlorination is less regioselective



36

Hydrogenolysis

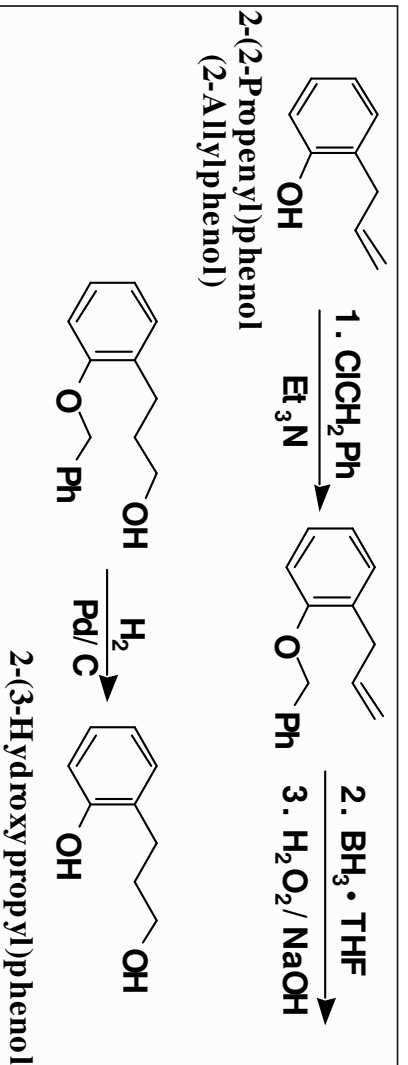
- Hydrogenolysis: cleavage of a single bond by H_2
 - among ethers, benzylic ethers are unique in that they are cleaved under conditions of catalytic hydrogenation



37

Benzyl Ethers

- The value of benzyl ethers is as protecting groups for the OH groups of alcohols and phenols
 - to carry out hydroboration/oxidation of this alkene, the phenolic -OH must first be protected; it is acidic enough to react with BH_3 and destroy the reagent



38