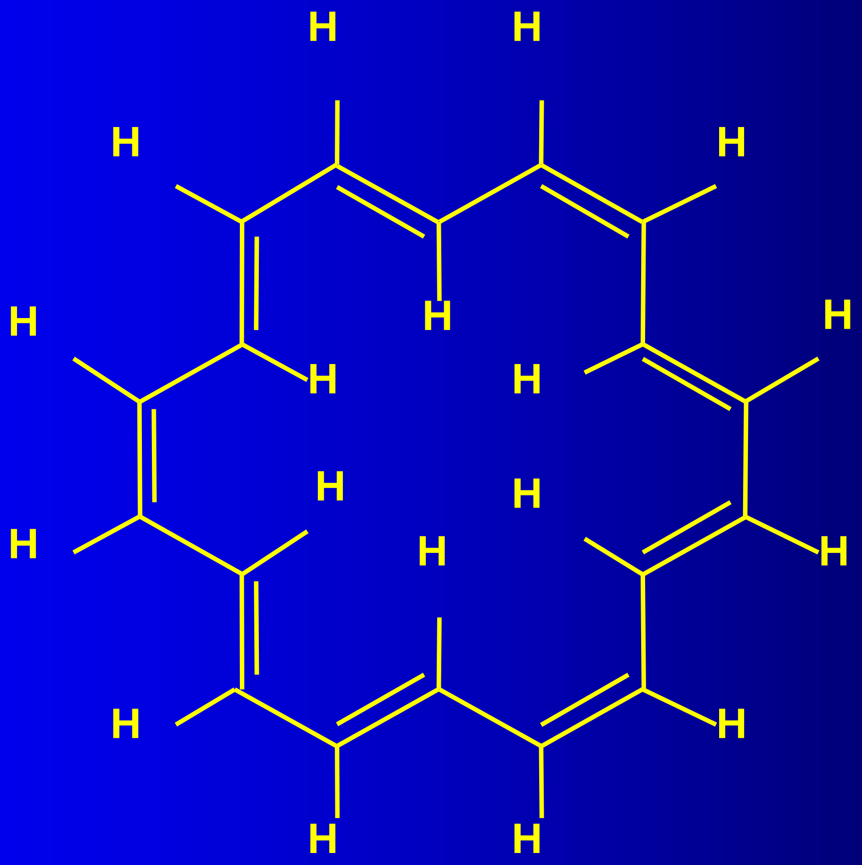
Lecture 10

More Aromatics

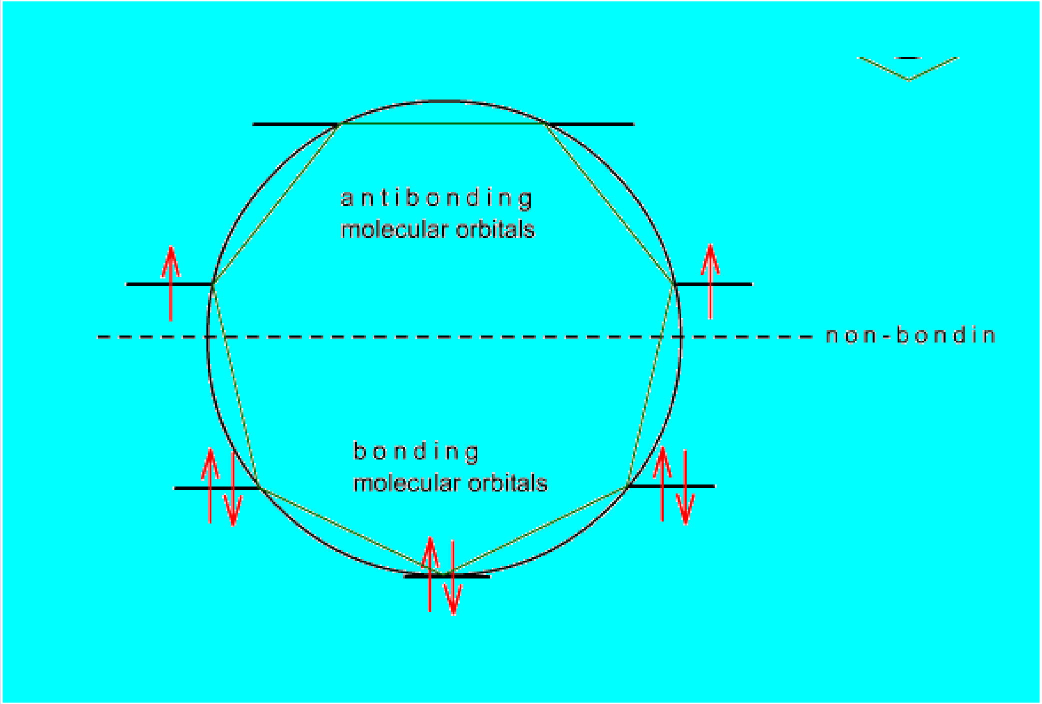


February 21, 2019

Chemistry 328N

From Lecture 9

Erich Armand Arthur Joseph Hückel
1896 - 1980



Arthur Atwater Frost
1909 - 2002

Hückel's Rule for Aromaticity

To be Aromatic …a compound must :

1. be Cyclic
2. have one P orbital on each atom in the ring
3. be planar or nearly so to give orbital overlap
4. have a closed loop of 4n+2 pi electrons in the cyclic arrangement of p orbitals

Hückel's Rule

Among planar, monocyclic, completely conjugated polyenes, only those with $4n + 2\pi$ electrons possess special stability (are aromatic)

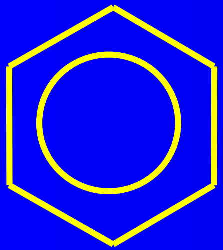
Magic Numbers

n	$4n+2$	
0	2	
1	6	benzene!
2	10	
3	14	
4	18	

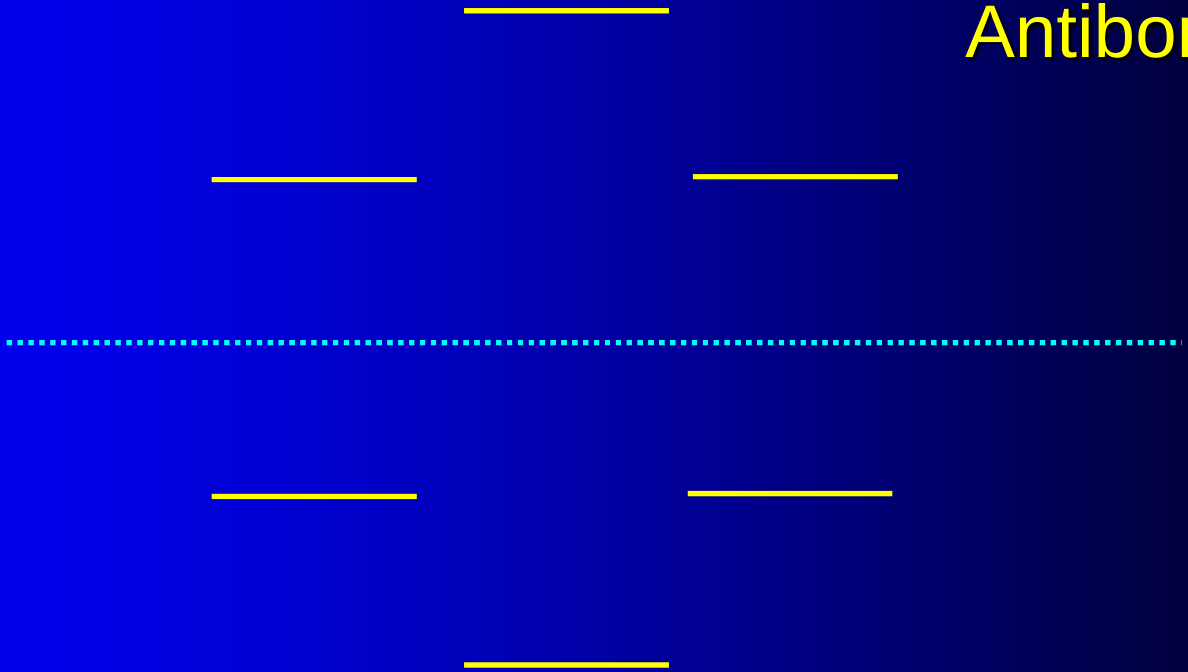
Hückel's Rule

Actually and inadvertently defines a condition for cyclic molecules in which the bonding molecular orbitals are filled and there are no electrons in non-bonding or antibonding orbitals …. roughly analogous to the “rare gas” condition for atomic orbitals…

π-MOs of Benzene



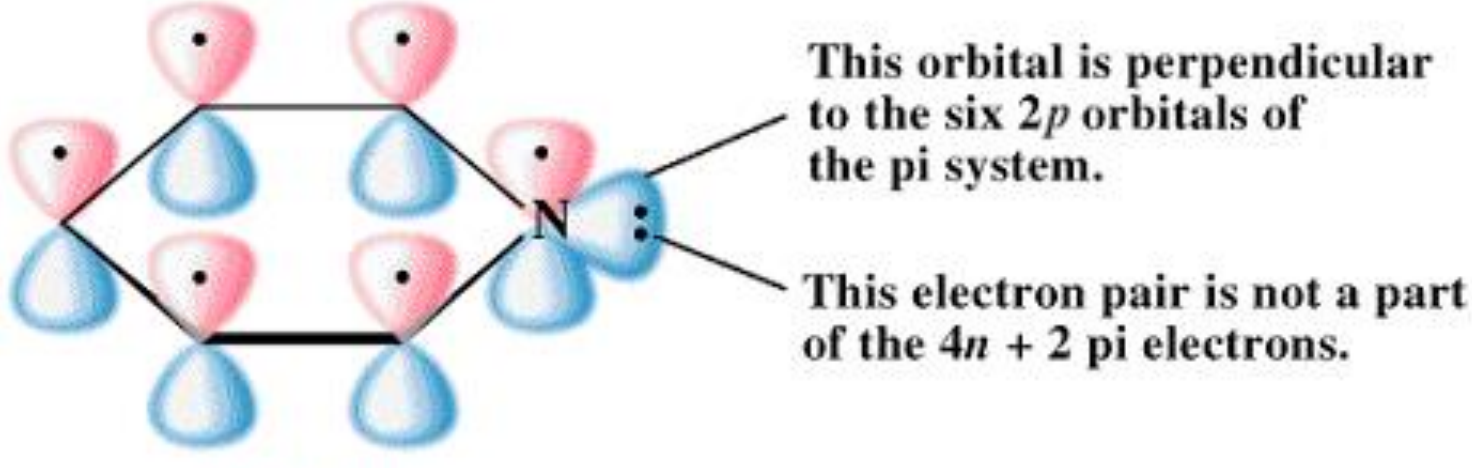
Benzene



6 π electrons fill all of the bonding orbitals

all π antibonding orbitals are empty

Hückel and Pyridine

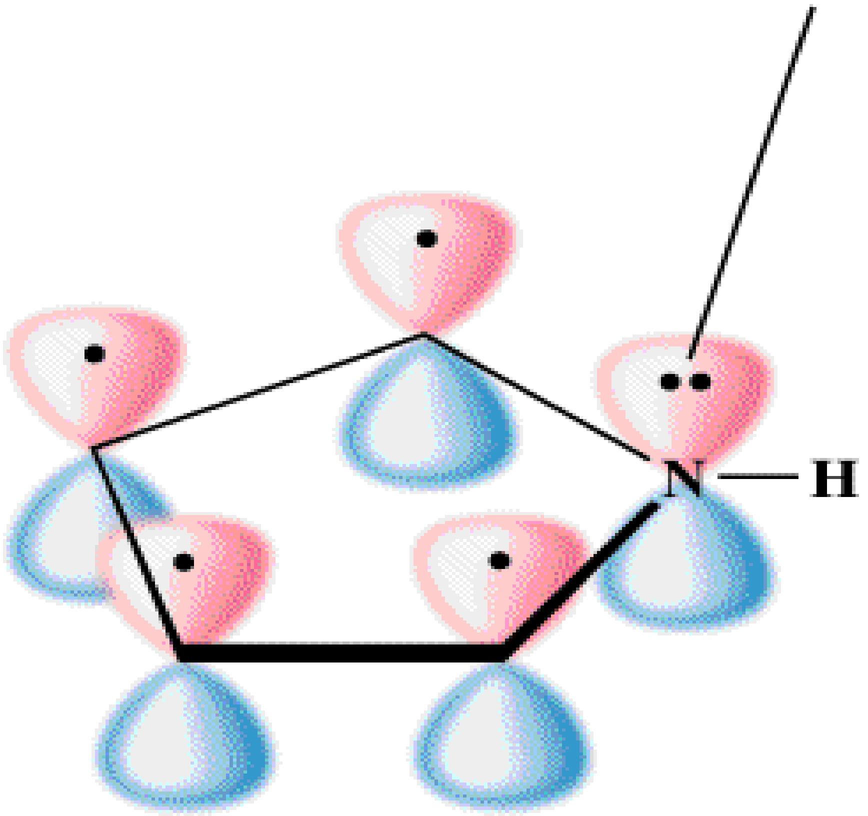


This orbital is perpendicular to the six 2*p* orbitals of the pi system.

This electron pair is not a part of the 4*n* + 2 pi electrons.

Pyridine

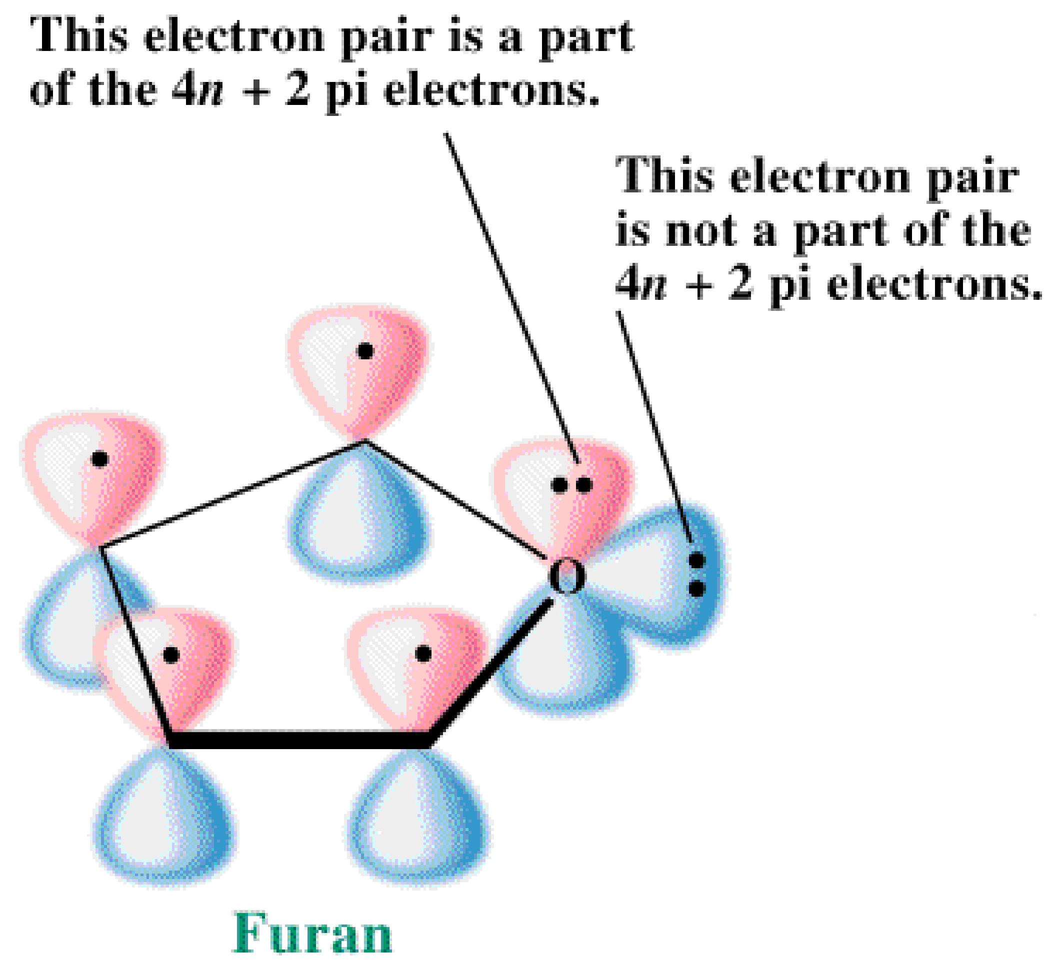
Hückel and Pyrrole



This electron pair is a part of the 4*n* + 2 pi electrons.

Pyrrole

Huckel and Furan



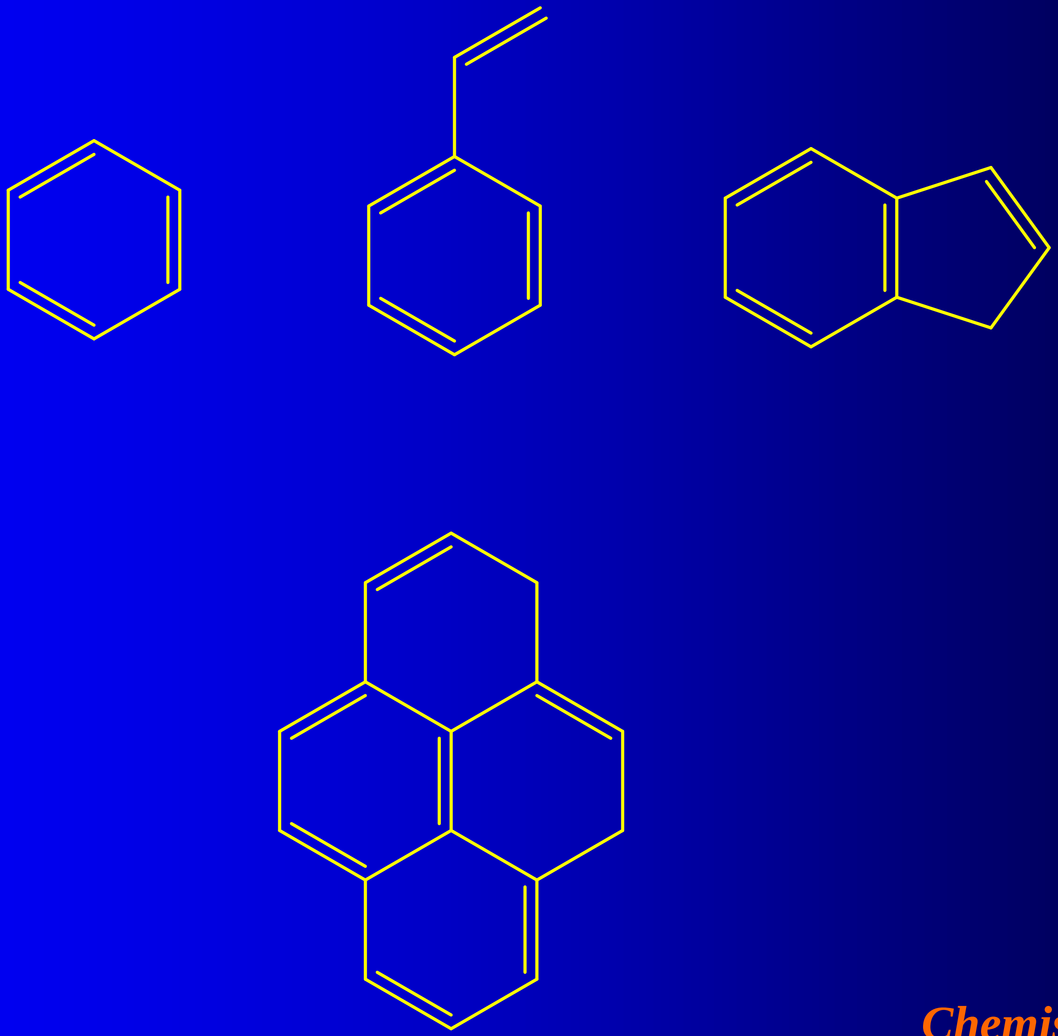
This electron pair is a part of the $4n + 2$ pi electrons.

This electron pair is not a part of the $4n + 2$ pi electrons.

Furan

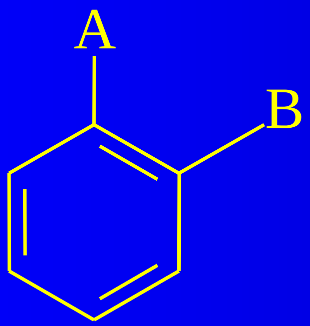
Recognizing Aromatic Compounds

Be careful with Huckel’s Rule

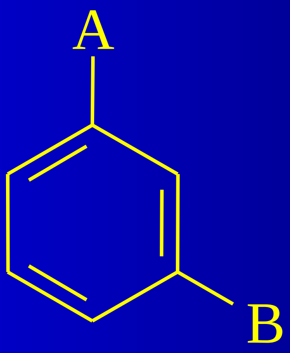


Some Nomenclature

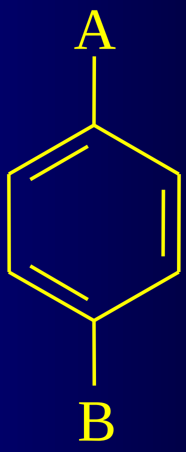
http://www.word-origins.com/definition/benzene.html



Ortho
or 1,2



Meta
or 1,3

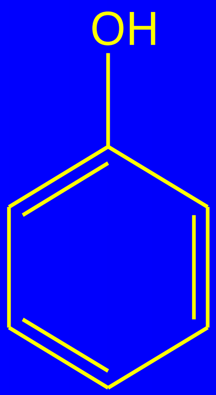


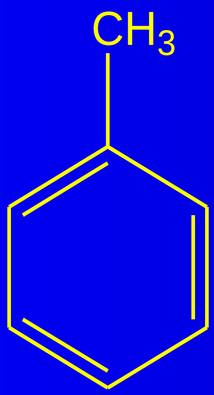
Para
or 1,4

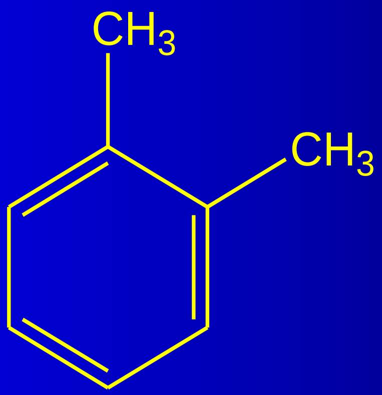
Please read about naming in Chapter 21!

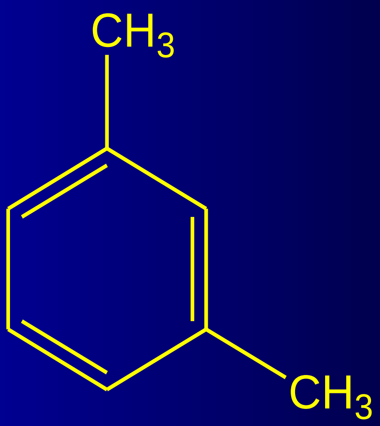
Some Nomenclature

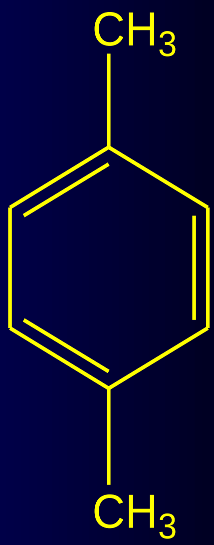
Please read about naming in Chapter 21.3. Many substituted benzenes are so old and so common that they have been given “nick” names!



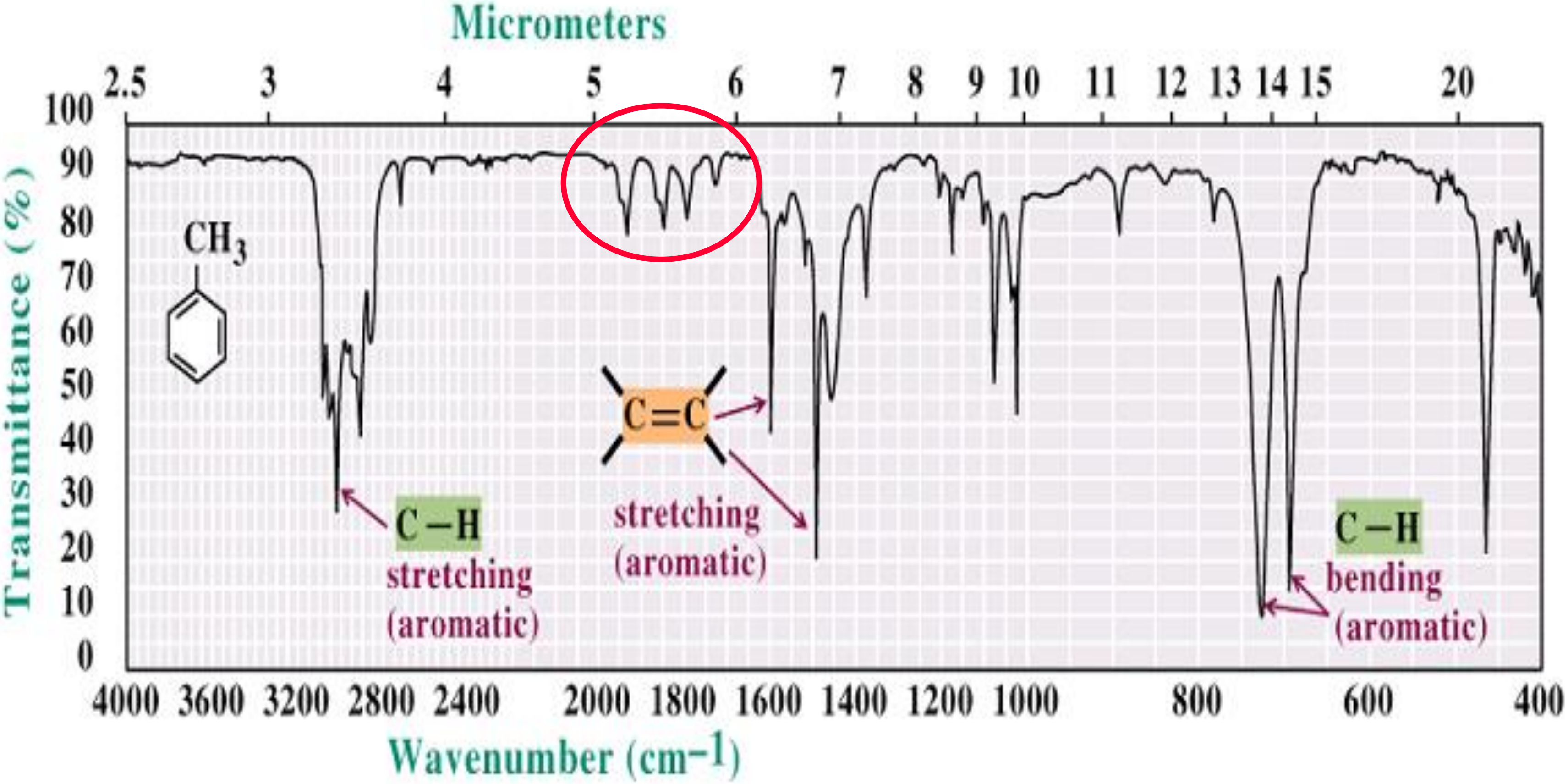




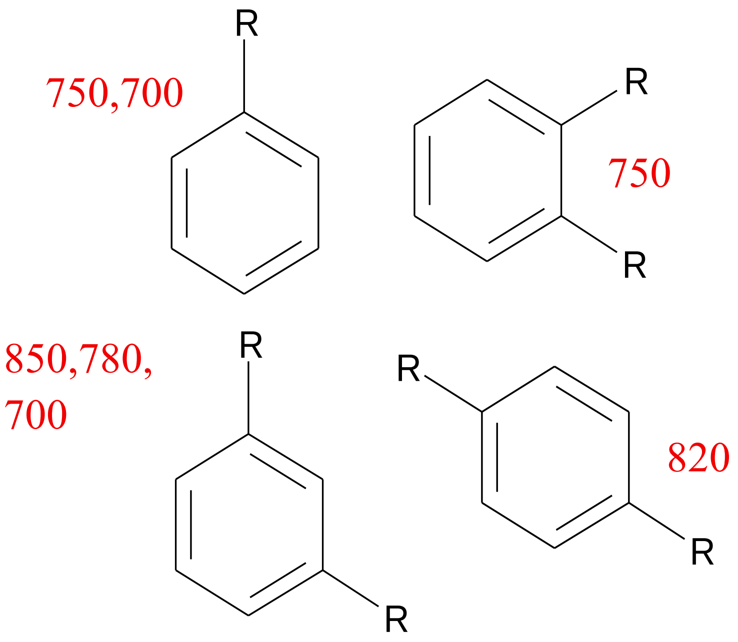




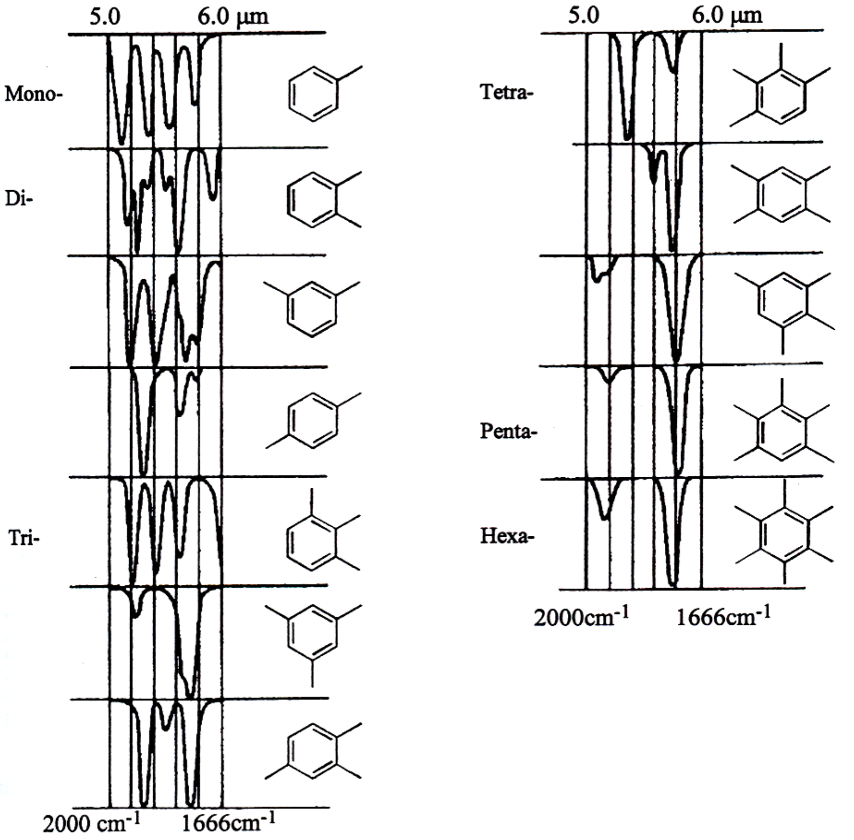
IR spectrum of toluene



Benzene rings--substitution patterns



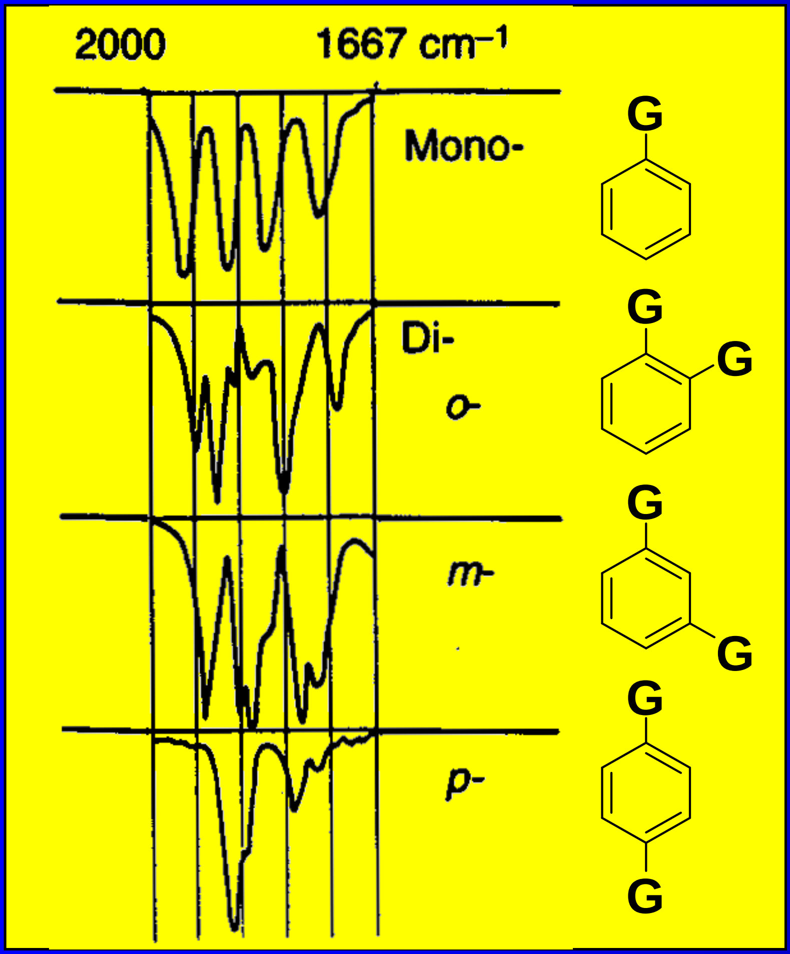
Unreliable with NO_2, CO_2H subs

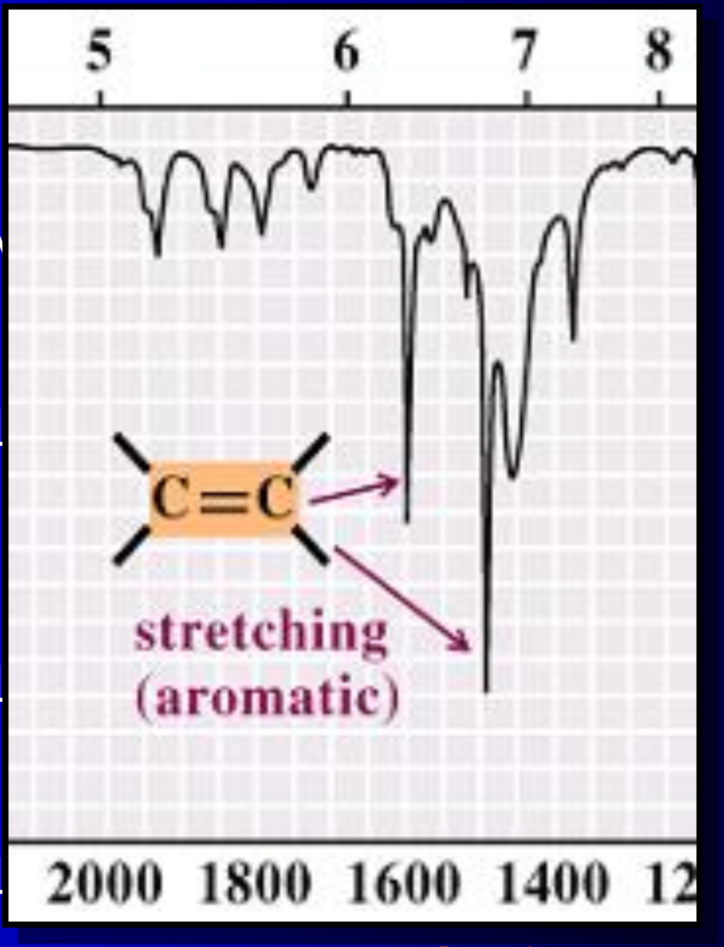


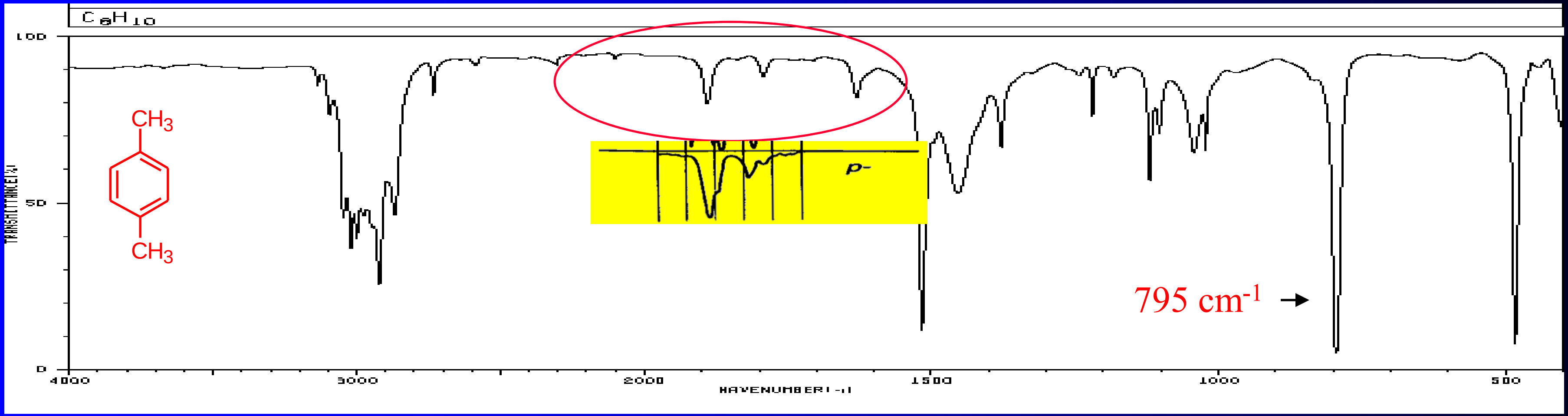
From Crewes, Rodriguez and Jaspars, ch 8

Out-of-plane bending *combinations*, quite small, but in a normally clean region of IR. Reliable even with nitro or carboxyl substitution

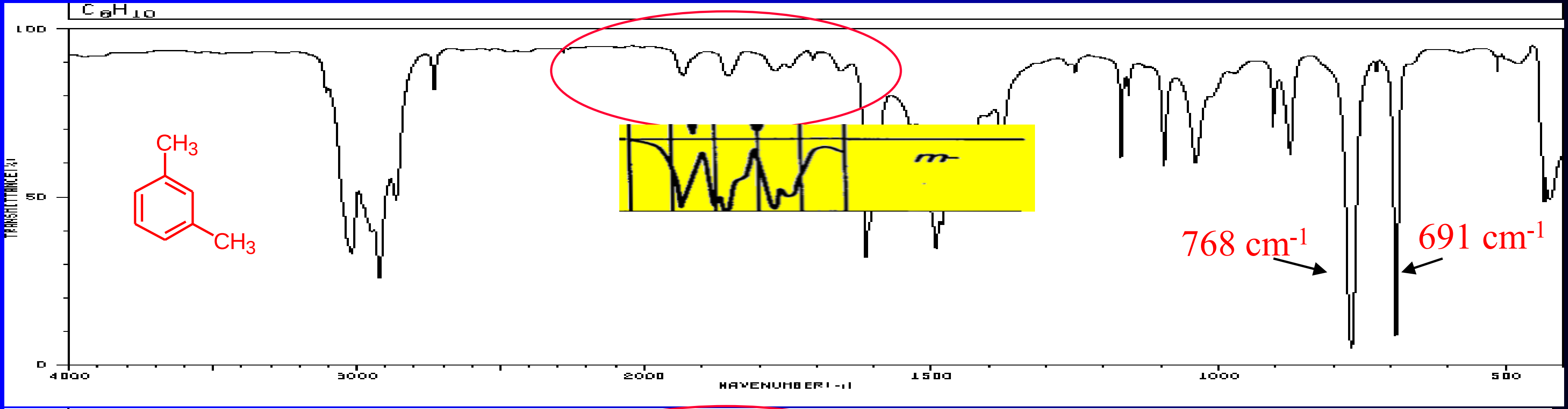
If the region between 1667-2000 cm^{-1} (w) is free of interference (C=O stretching frequency) a weak grouping of peaks is observed for aromatic systems. Analysis of this region can lead to a determination of the substitution pattern on the aromatic ring





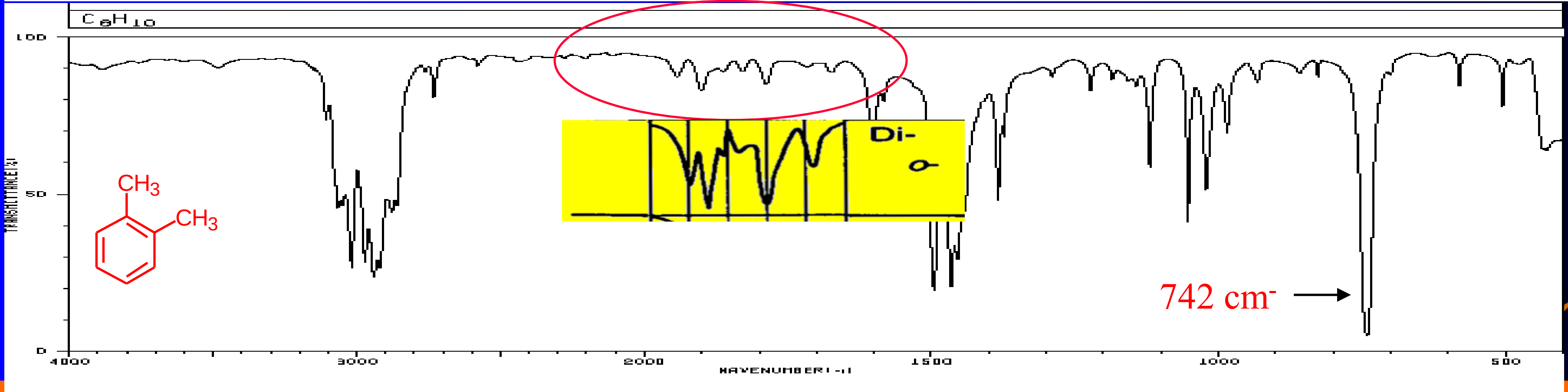


795 cm^{-1} →



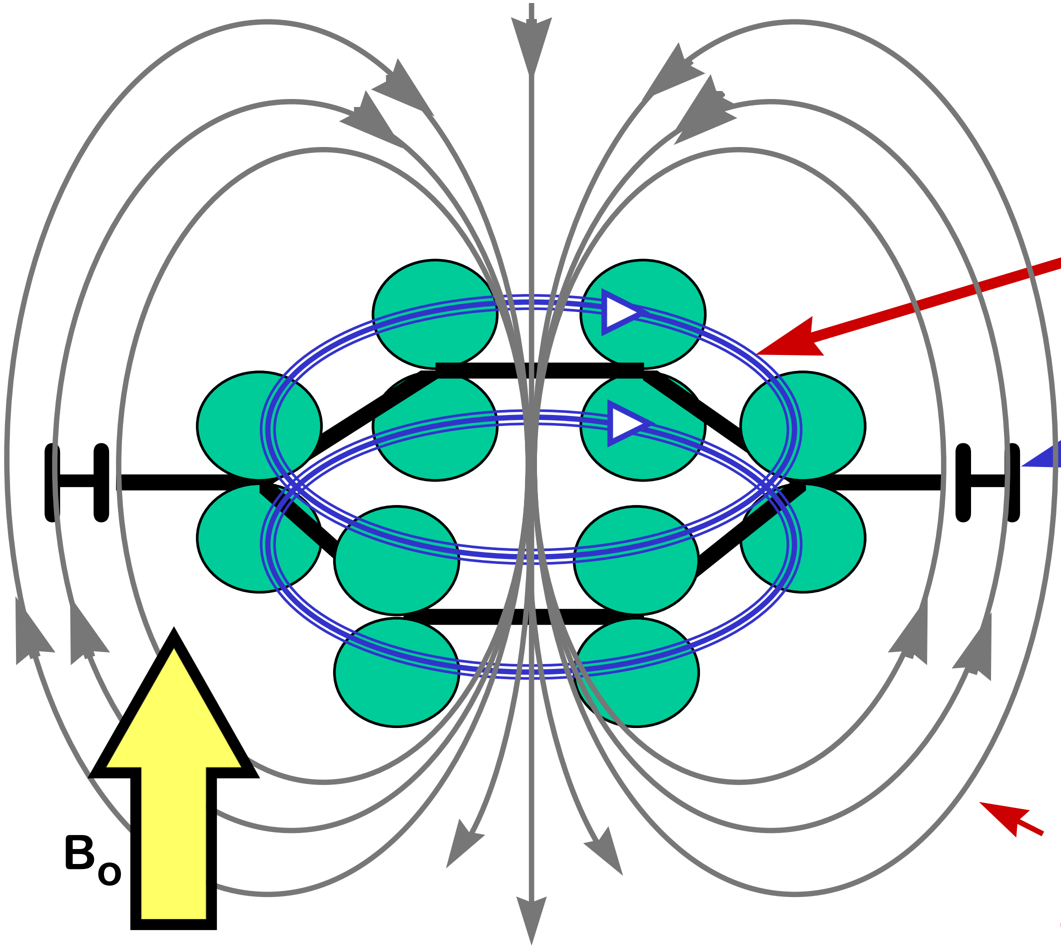
768 cm^{-1}

691 cm^{-1}



742 cm^{-} →

Ring Current in Benzene

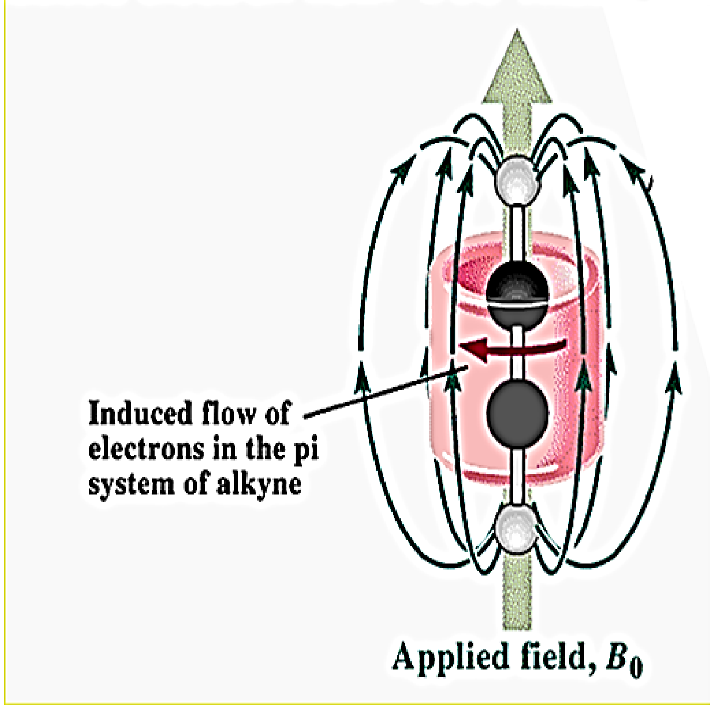


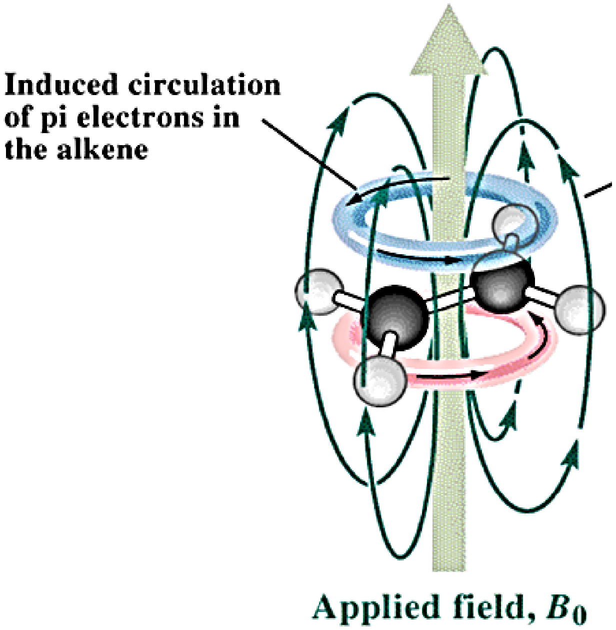
Circulating π electrons

Deshielded

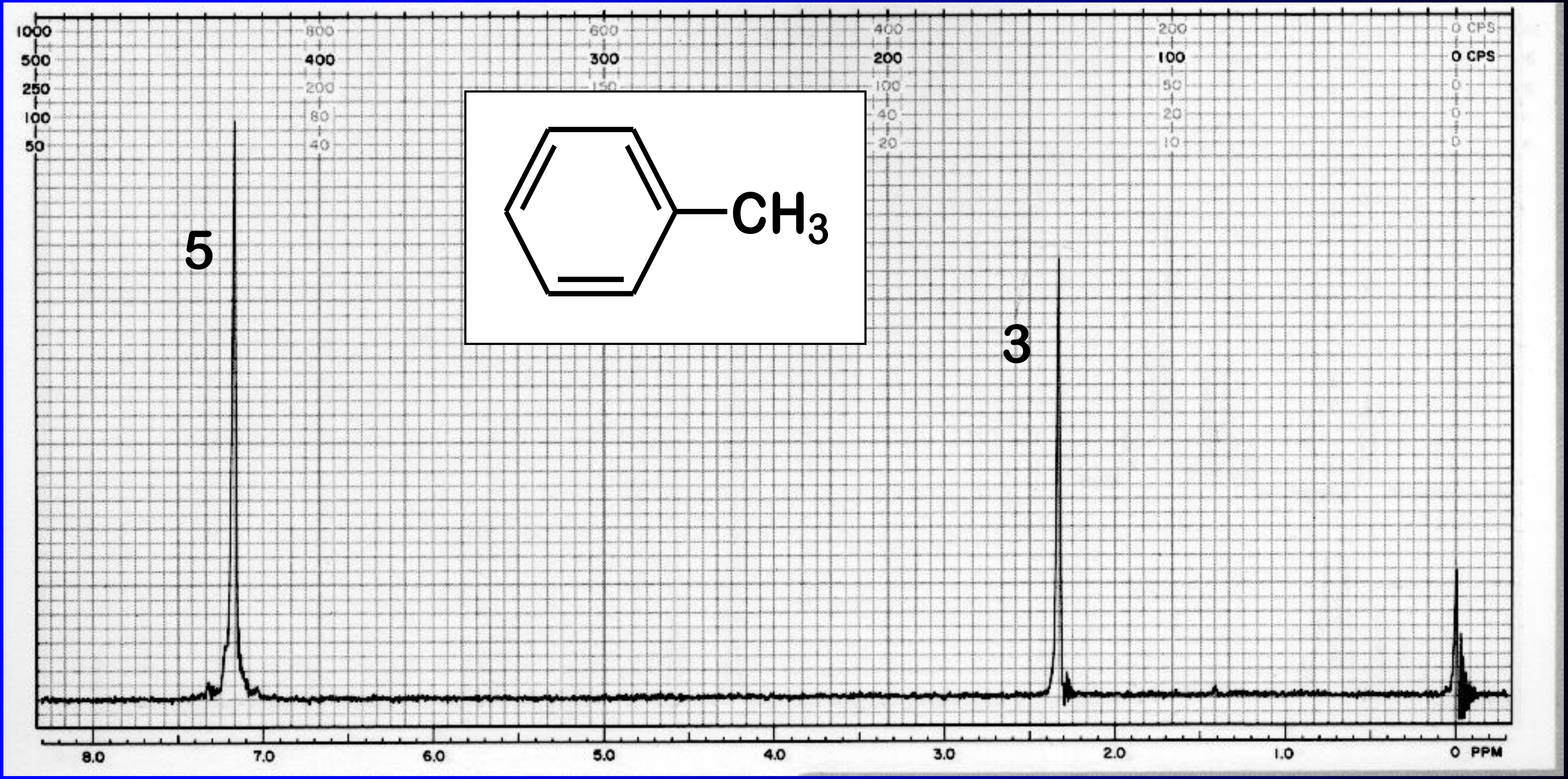
Secondary magnetic field generated by circulating π electrons deshields aromatic protons

5. (pts) These figures from the book show field induced electron flow in the pi system of an alkyne and an alkene. The captions state clearly that the arrow designates induced *electron flow*. Are These figures accurate? If not why not??

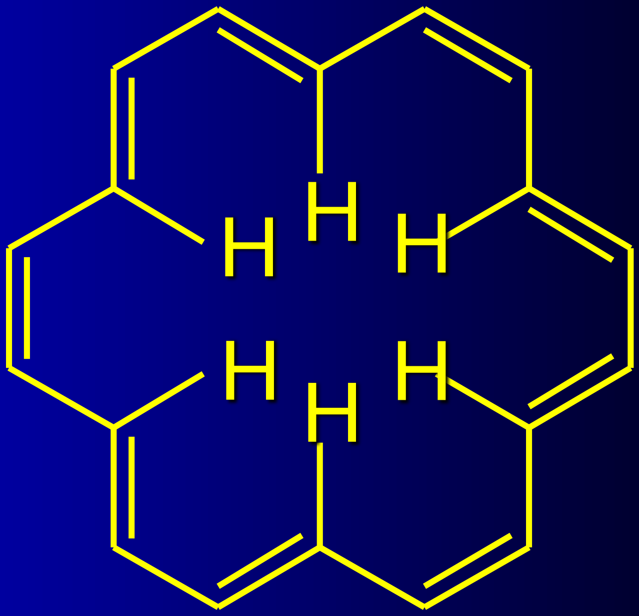




NMR Spectrum of Toluene



[18]Annulene



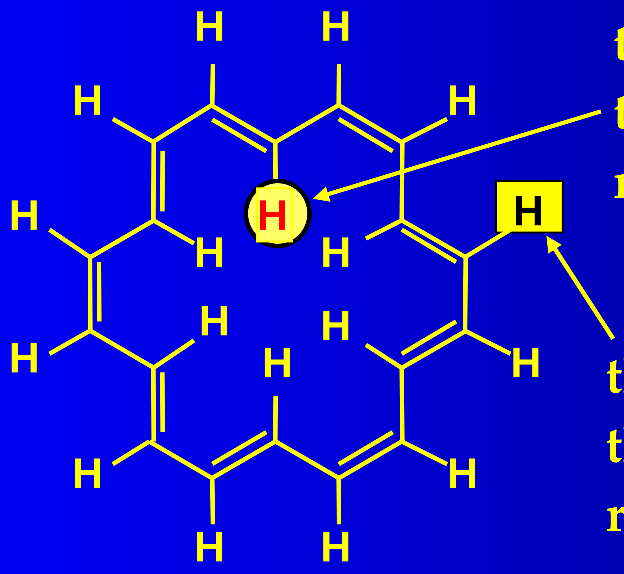
18 π electrons satisfies Hückel's rule

resonance energy = 418 kJ/mol

bond distances range between 137-143 pm

nmr Spectroscopy

- Ring Current effect is massive in the larger annulenes, for example for [18]annulene



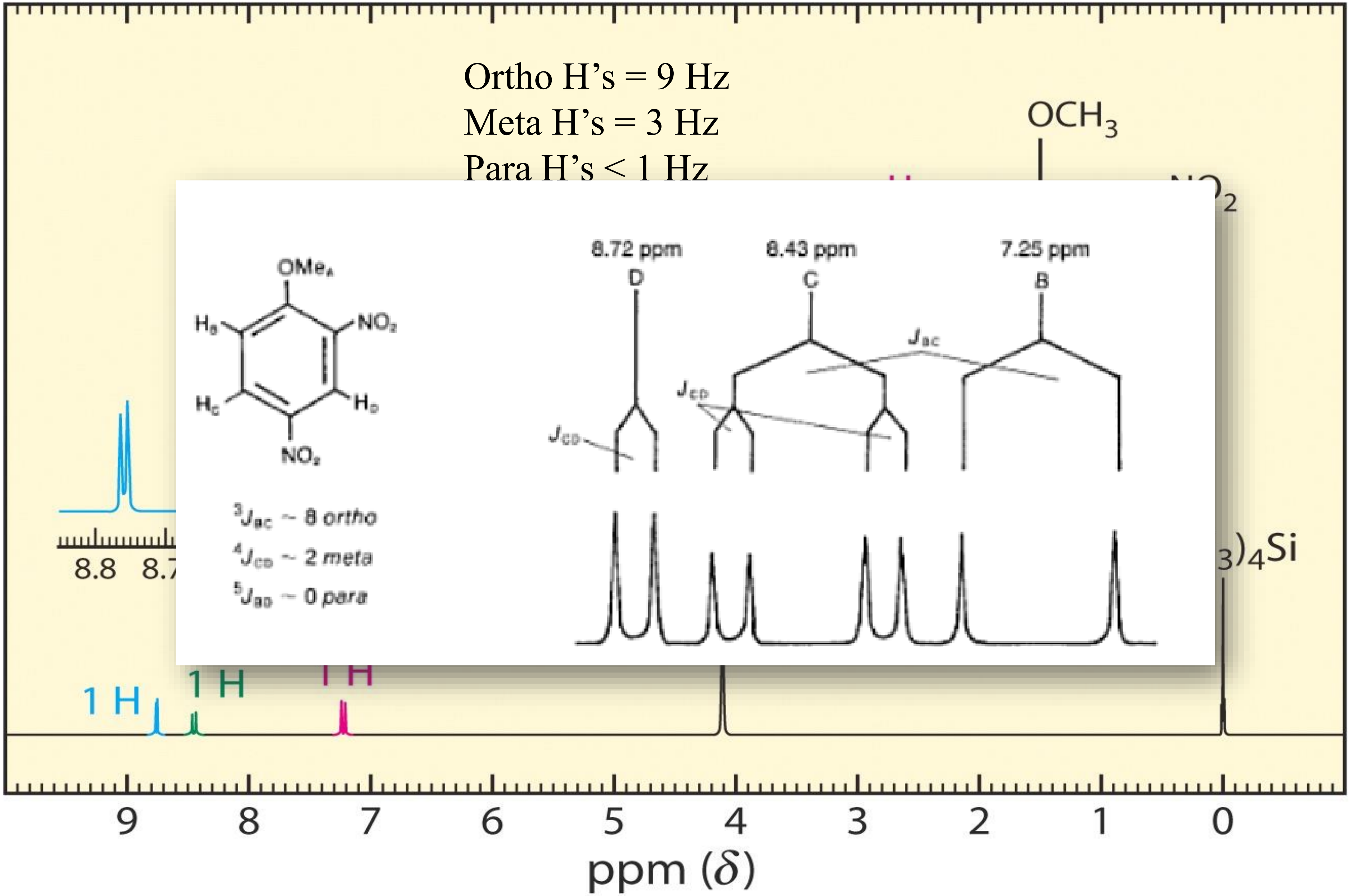
the six hydrogens on the inside of the ring resonate at δ - 3.00!!

<u>Up field of TMS!!</u>

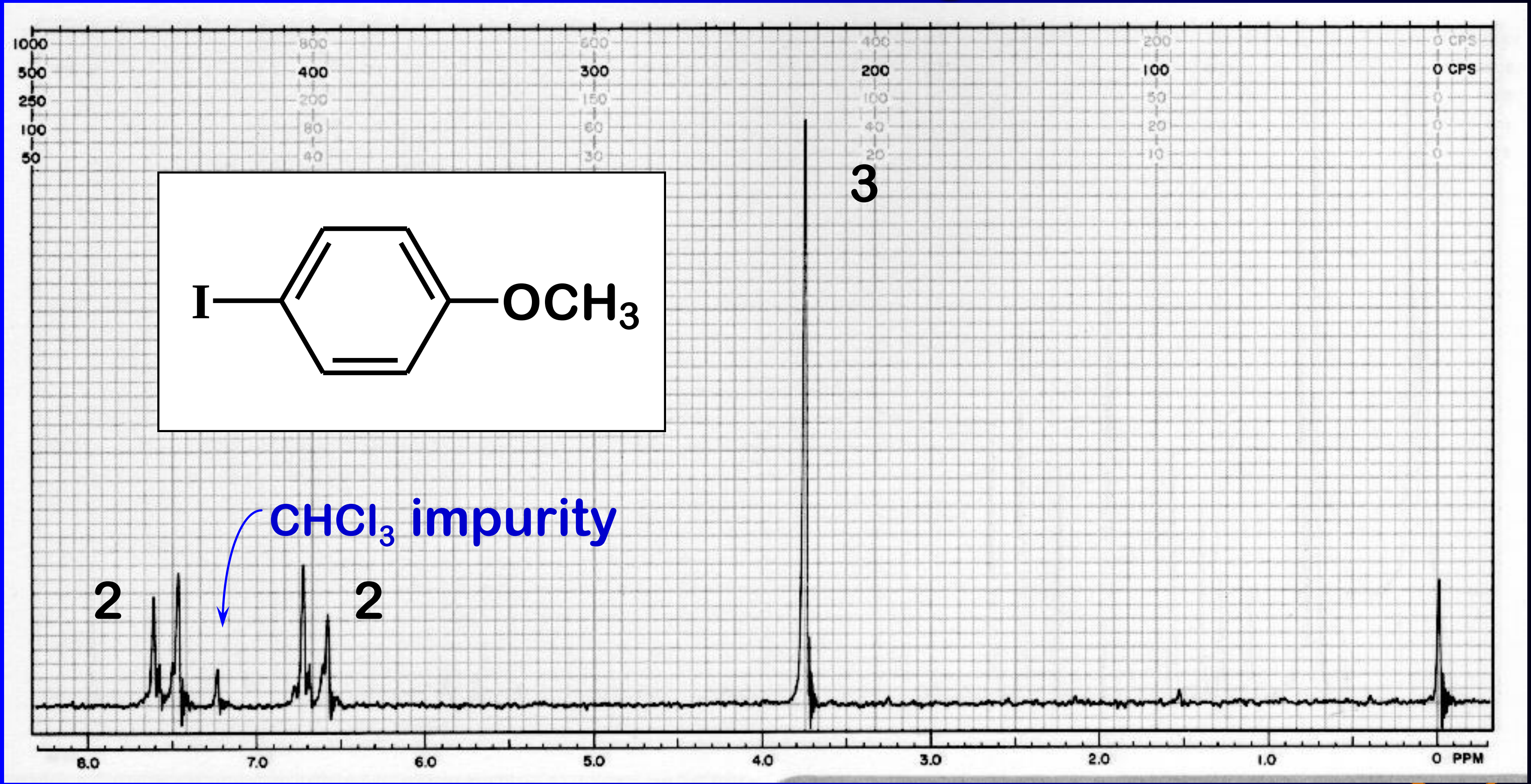
the twelve hydrogens on the outside of the ring resonate at δ 9.3

Coupling Constants - Aromatics

Ortho H’s = 9 Hz
Meta H’s = 3 Hz
Para H’s < 1 Hz



NMR Spectrum of 1-iodo-4-methoxybenzene



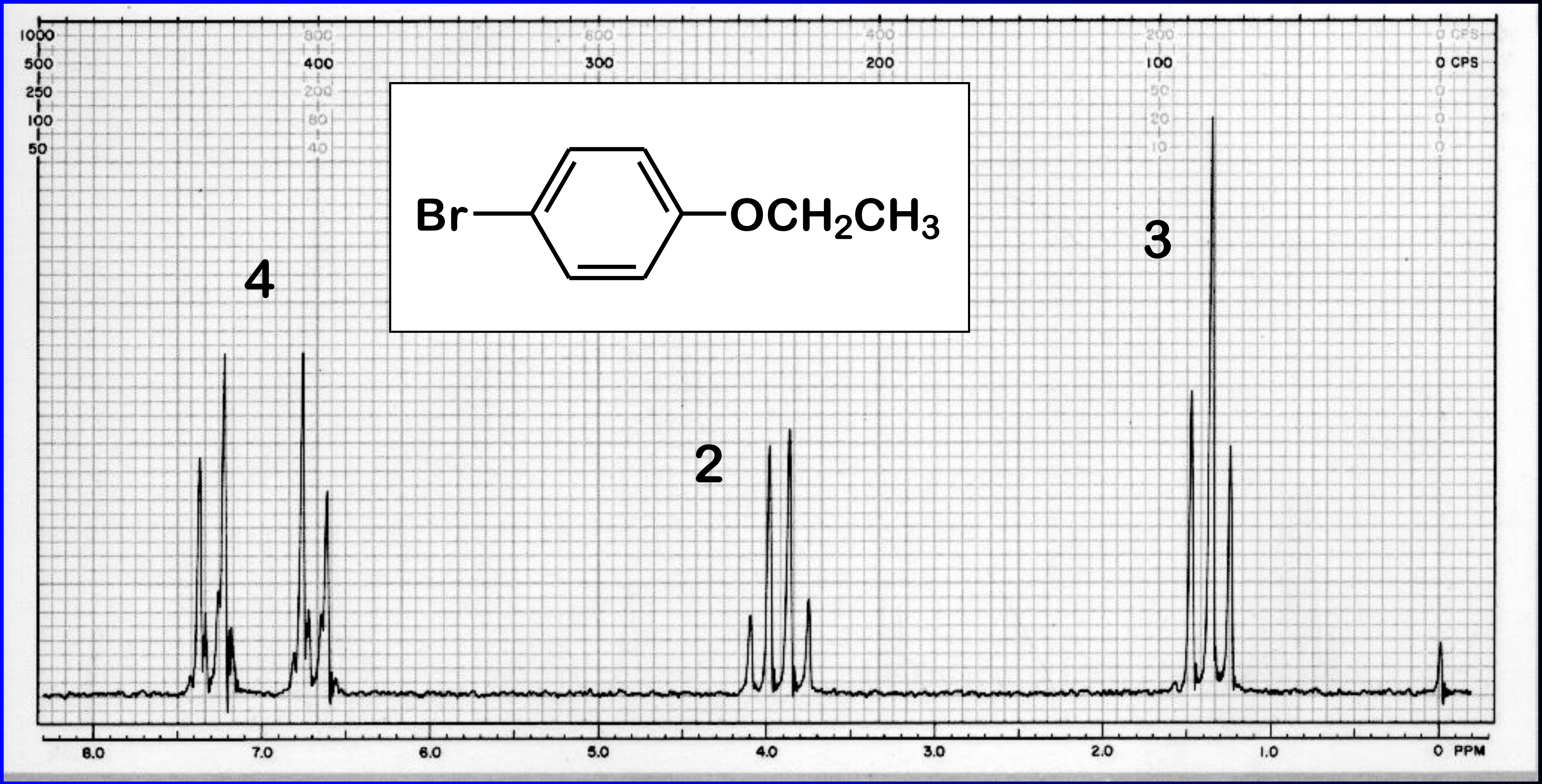
3

$CHCl_3$ impurity

2

2

NMR Spectrum of 1-bromo-4-ethoxybenzene

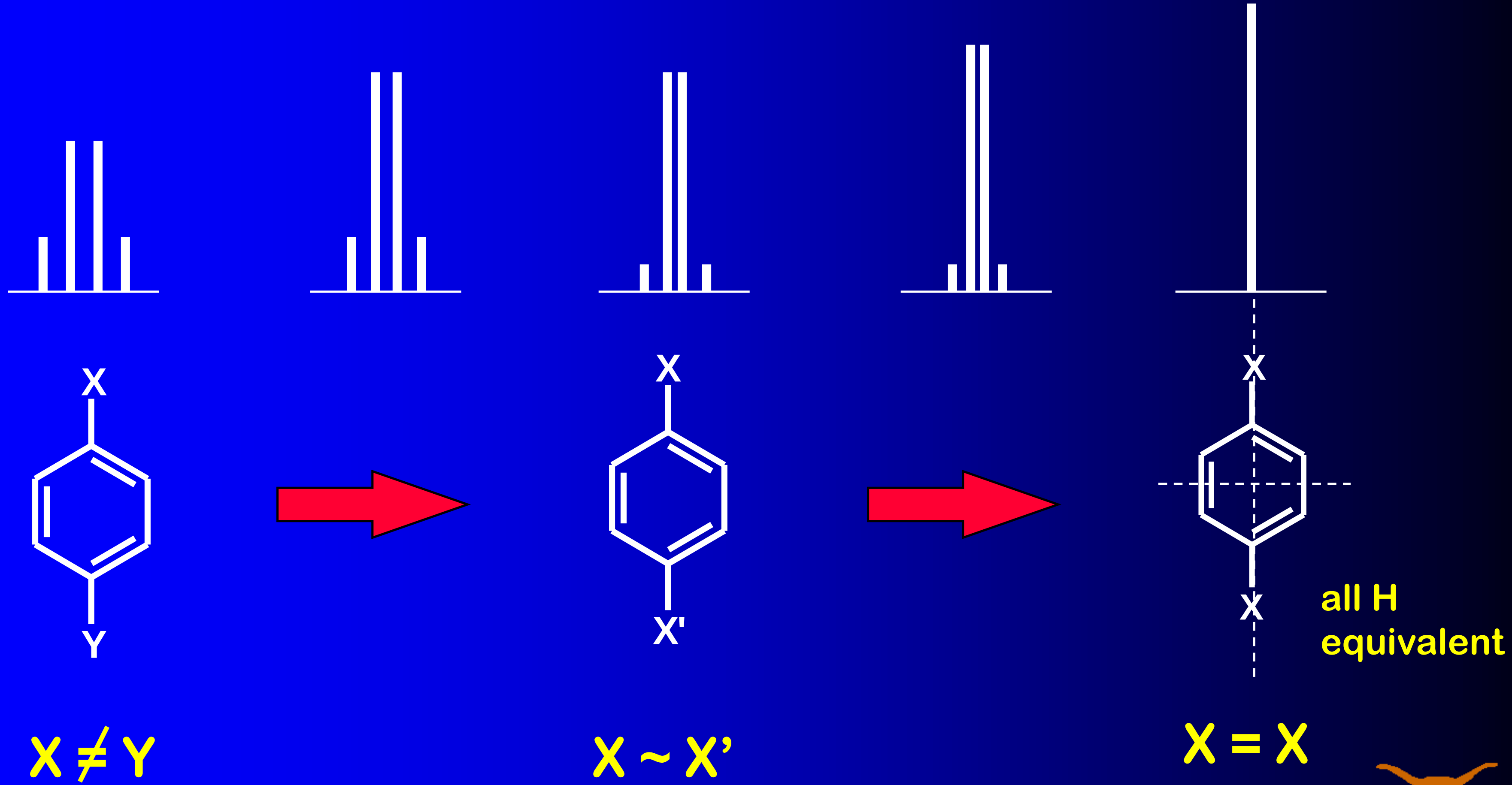


THE p-DISUBSTITUTED PATTERN CHANGES AS THE TWO GROUPS BECOME MORE AND MORE SIMILAR

All peaks move closer.

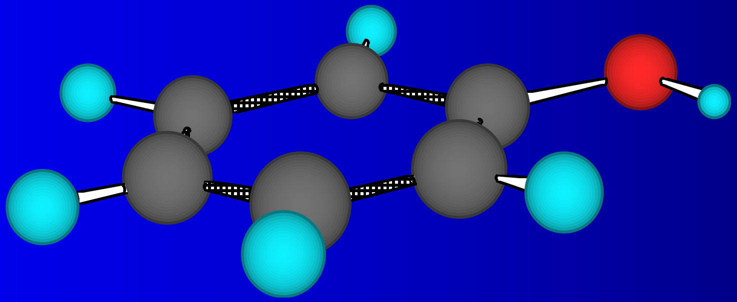
Outer peaks get smaller .... and finally disappear.

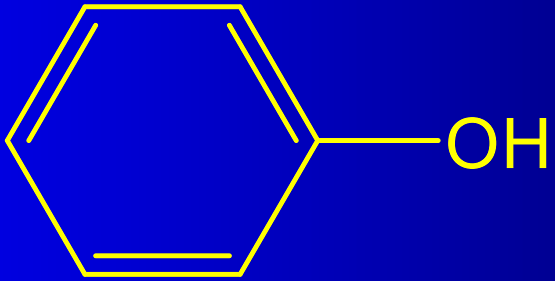
Inner peaks get taller.............................. and finally merge.



Phenols

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

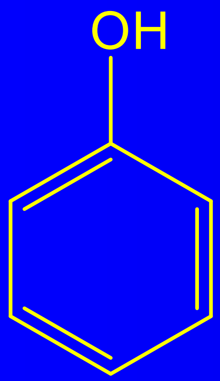




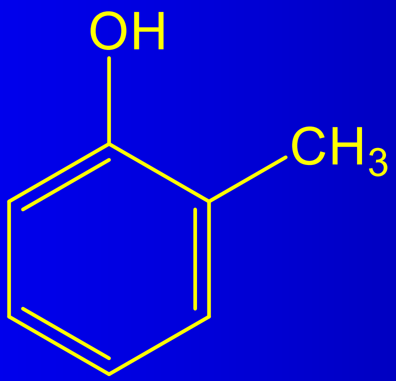
Phenol

Phenols

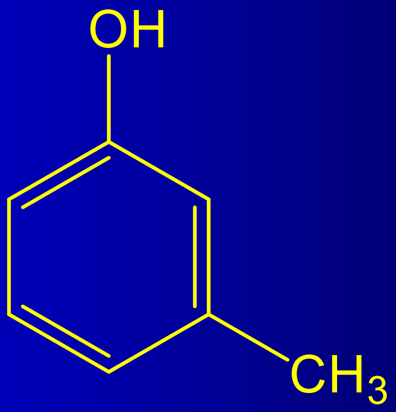
- Cresols



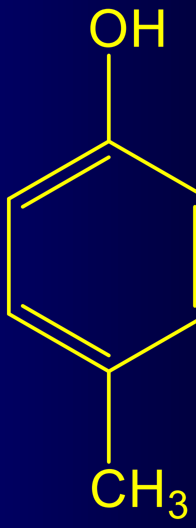
Phenol



o-cresol



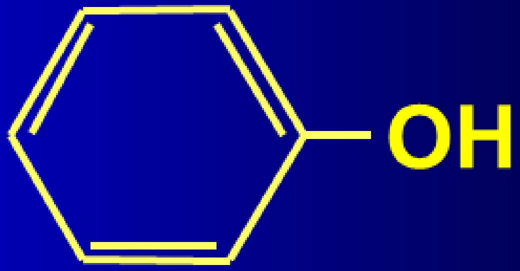
m-cresol



p-cresol

La Brea Tar Pits

Phenol

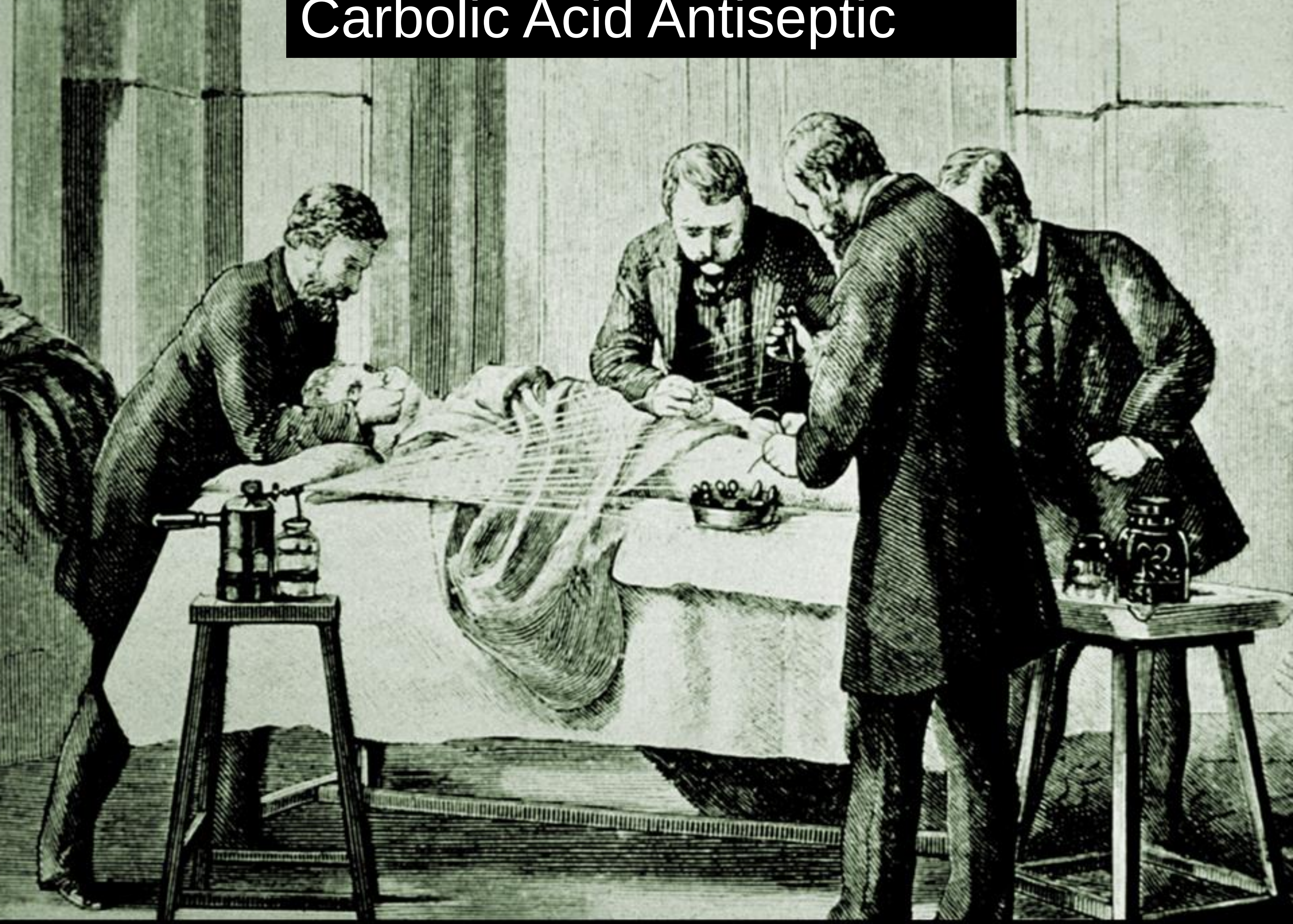


Joseph Lister

1827 - 1909

A British surgeon and a pioneer of antiseptic surgery, who successfully introduced carbolic acid (now known as phenol) to sterilize surgical instruments and to clean wounds, which led to reducing post-operative infections and made surgery safer for patients.

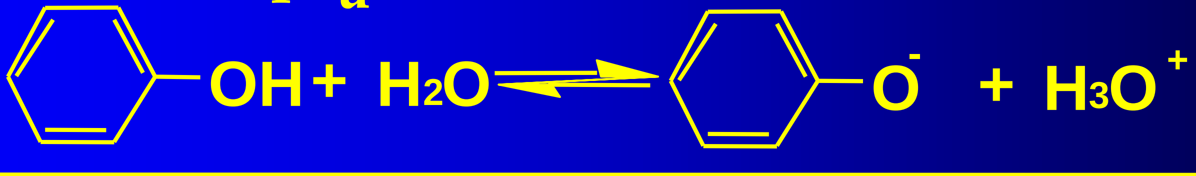
Carbolic Acid Antiseptic



Acidity of Phenols

- Phenols are much more acidic than aliphatic alcohols that also contain the -OH group

Phenol: $pK_a = 9.95$



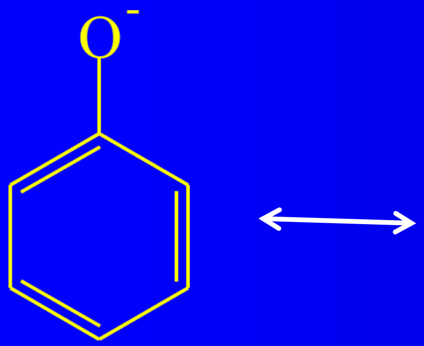
Ethanol: $pK_a = 15.9$

$$CH_3CH_2OH + H_2O \rightleftharpoons CH_3CH_2O^- + H_3O^+$$

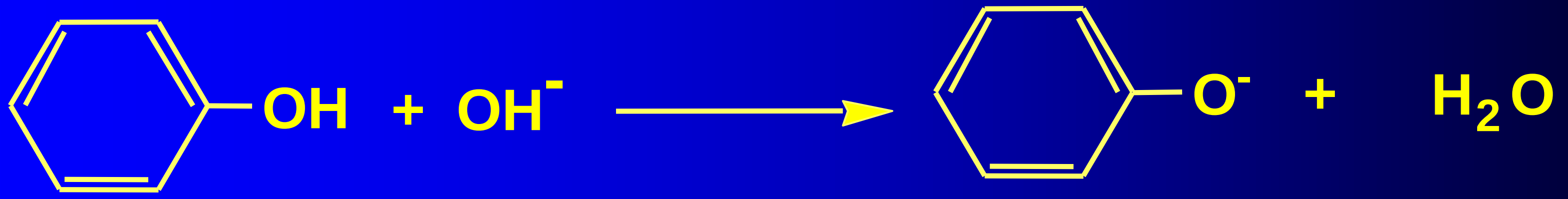
- delocalization of the negative charge by resonance stabilizes the phenoxide ion relative to the alkoxide ion

Lets move electrons together!!

PLEASE FOLLOW ME STEP BY STEP



Acidity of Phenols



pKa 9.95

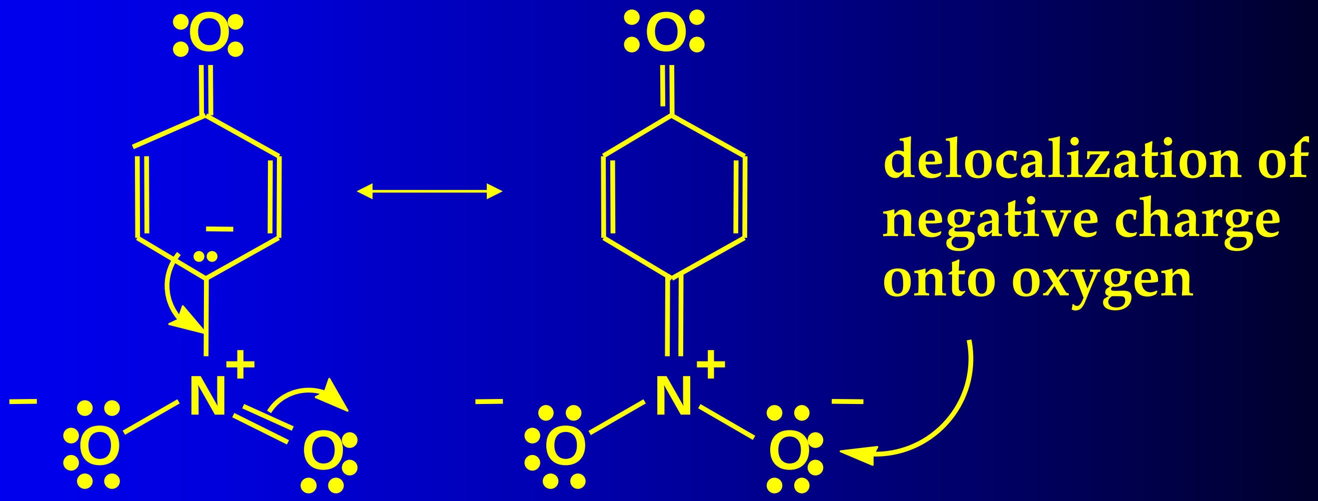
pKa 15.7

Strong acid + Strong base → Weak base + Weak acid

- Strong acids have weak conjugate bases
- Stabilization of anions leads to weak/stable conjugate bases!

Acidities of Phenols

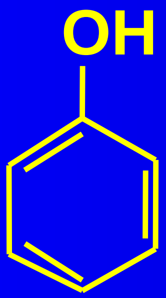
- Part of the acid-strengthening effect of -NO_2 is due to its electron-withdrawing inductive effect
- In addition, -NO_2 substituents in the ortho and para positions help to delocalize the negative charge by Resonance



delocalization of negative charge onto oxygen

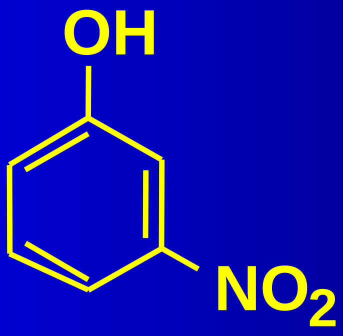
Acidities of Phenols

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



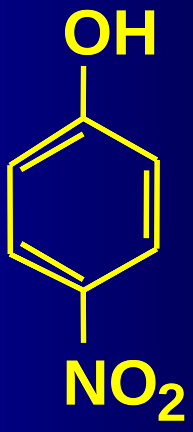
Phenol

pK_a 9.95



m-Nitrophenol

pK_a 8.28

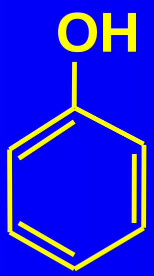


p-Nitrophenol

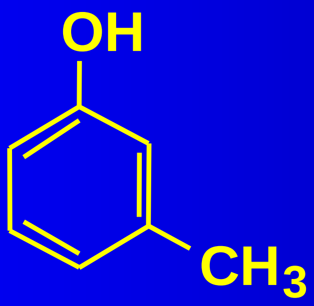
pK_a 7.15

Acidity of Phenols

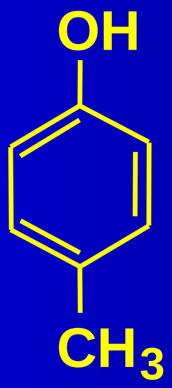
- Alkyl and halogen substituents effect acidities by inductive effects
  - alkyl groups are electron-releasing by “induction”
  - halogens are electron-withdrawing by “induction”



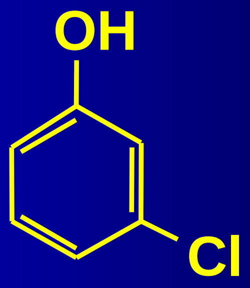
Phenol
pK_a 9.95



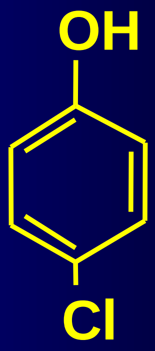
m-Cresol
pK_a 10.01



p-Cresol
pK_a 10.17



m-Chloro phenol
pK_a 8.85



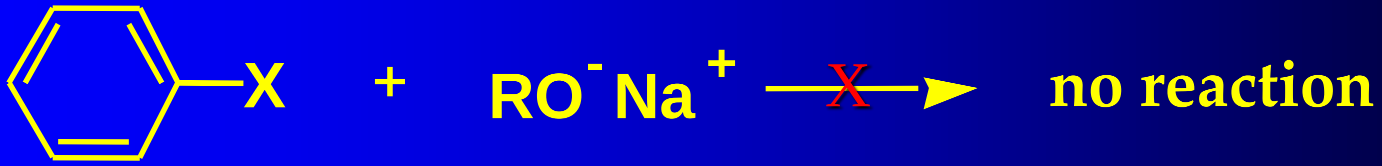
p-Chloro-phenol
pK_a 9.18

Finally….Chemistry!!

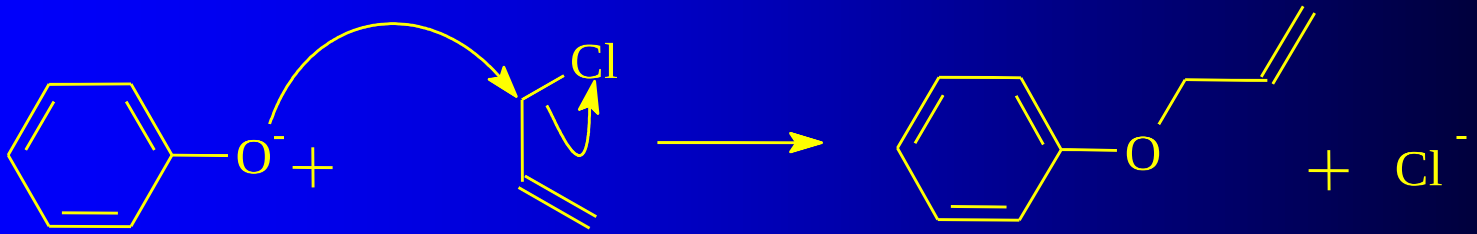
$$A + B \longrightarrow C$$

Synthesis: Alkyl-Aryl Ethers

- Alkyl-aryl ethers can be prepared by the Williamson ether synthesis
  - but only using phenoxide salts and alkyl halides
  - aryl halides are unreactive to S_N2 reactions



Alkyl-Aryl Ethers



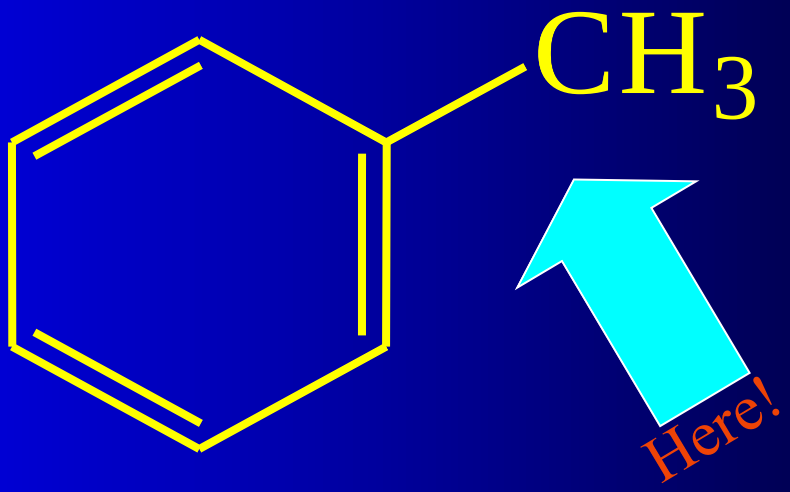
S_n2 reactions are accelerated by:

- polar aprotic solvents
- phase transfer catalysis
- crown ethers

Remember: methyl > 1^0 >2^0 and 3^0 is a no go!

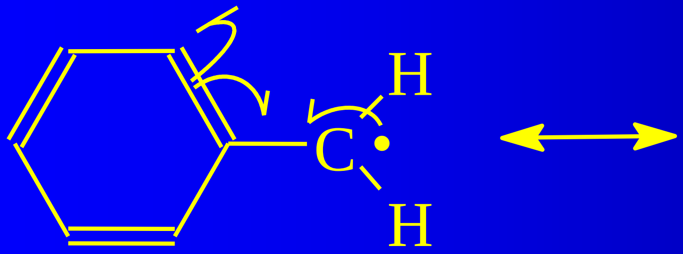
{Review chapter 8??}

Reactions at Benzyl Carbons



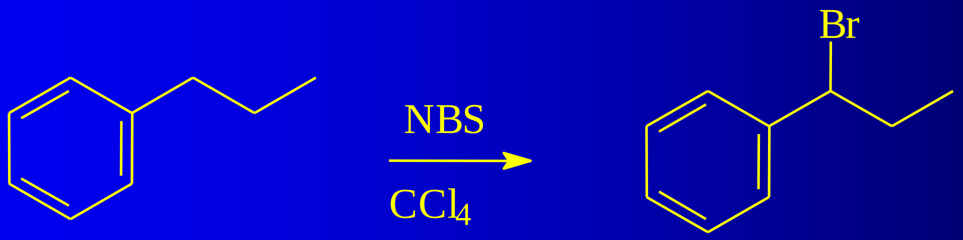
Benzylic Reactions

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

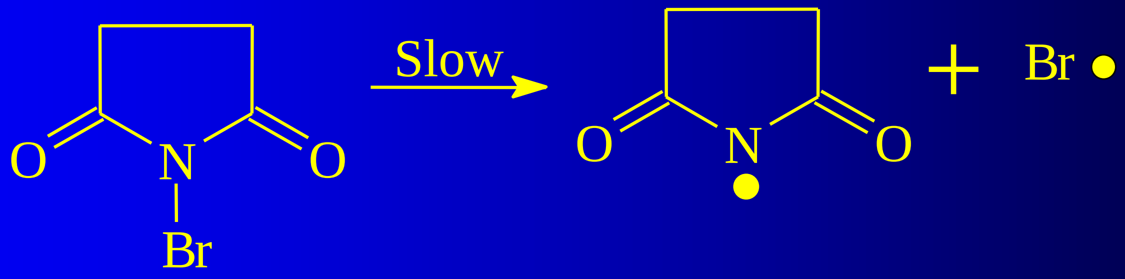


Benzylic Bromination

- Bromination proceeds by a radical mechanism



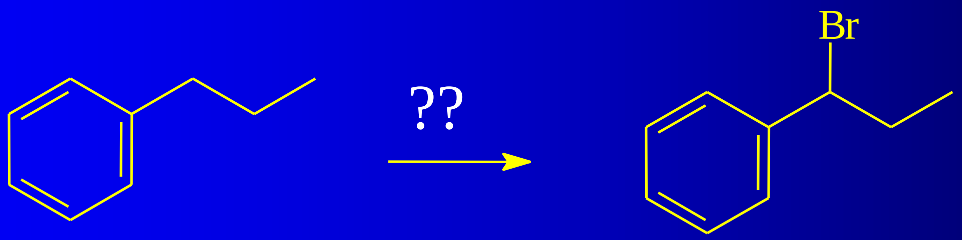
A Regioselective reaction ! !



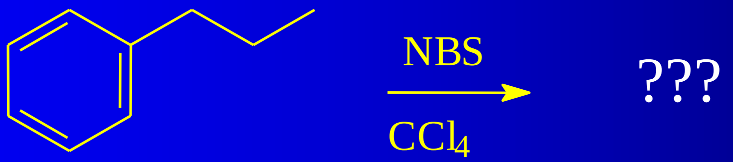
NBS = N-bromosuccinimide

Flash Card Tricks

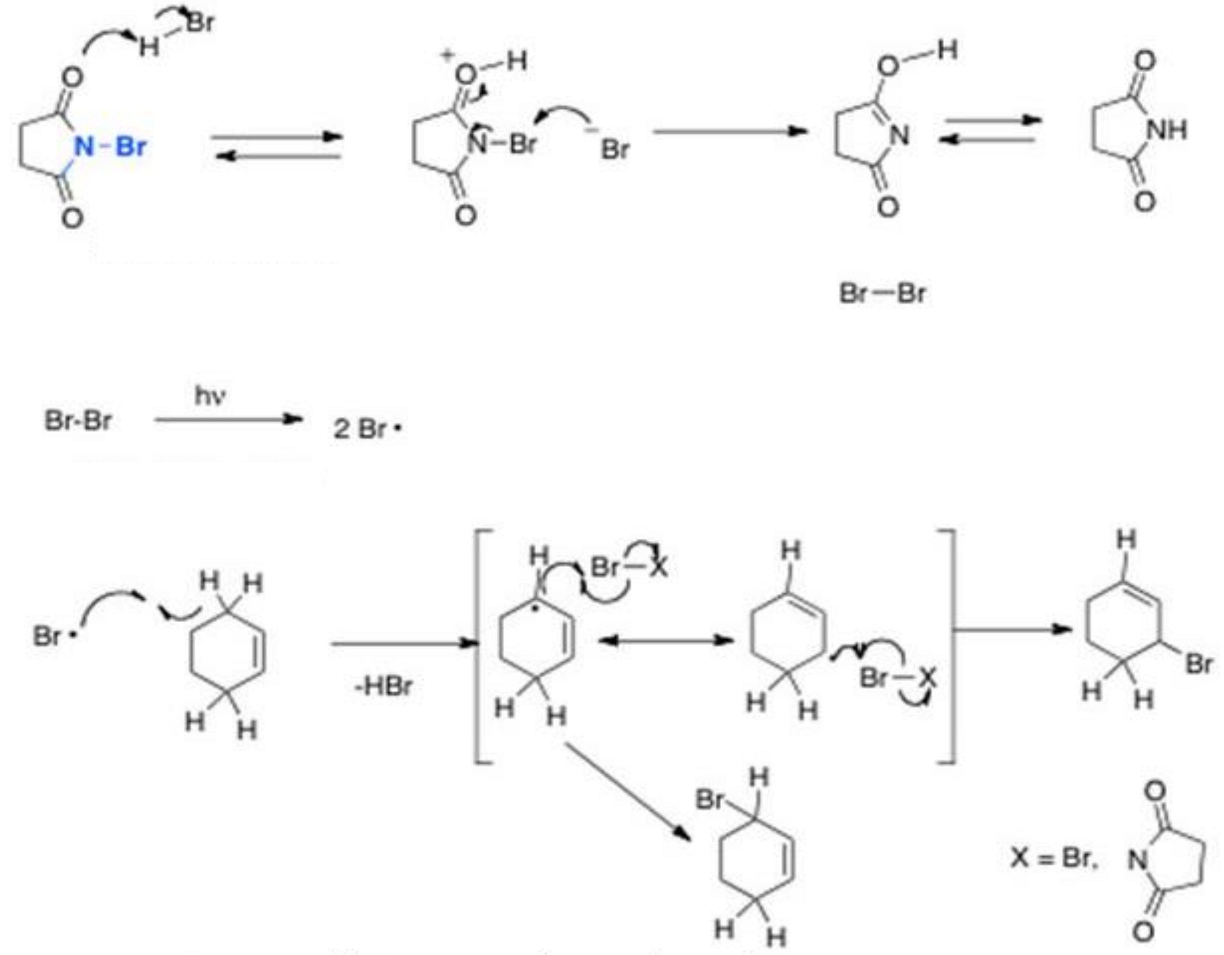
- front



- Back



Allylic and benzylic bromination with NBS



NBS: keeps concentration of Br_2 too low for slower electrophilic bromiation of alkene to compete