Course 345 Chem (Section 1) Lecturer Gellman

Day ~~1/27/17~~ Friday Date 1/27/17

Notes Taken By A. Brezny Total # of Pages 6

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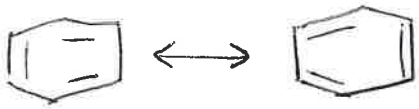
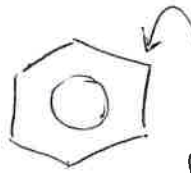
Ch. 16 Benzene + Derivatives

→ reactivity w/ electrophiles

Rec. Problems: 4-9, 12-27, 29-33, 35-37, 39-41, 43-46, 48-50, 52-54, 60-66

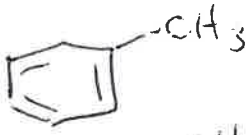
Recall: Aromaticity

1) cyclic
2) uninterrupted π system (sp^2-hybrid.)
3) $4n+2$ π e^-
4) Planar

Benzene:  =  useless for drawing mechanisms

Terms:

1) common names:

 toluene

 phenol

 anisol

 aniline

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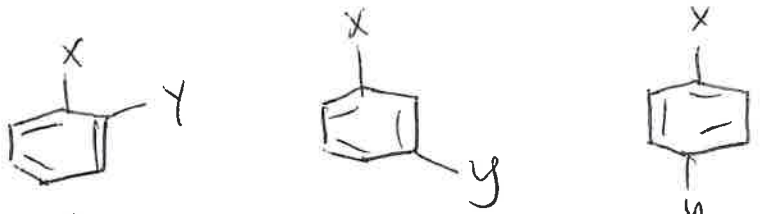
2) Disubstitute benzene

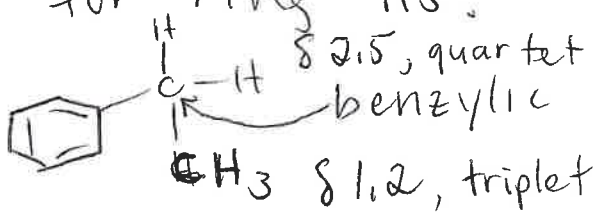


ortho o | meta m | para p

Spectroscopy

1) IR - see text
2) ^{1}H-NMR

Explanation (see figure 16.2)
- magnetic field induces motion of π-e⁻ that augments the external field for ring H's.



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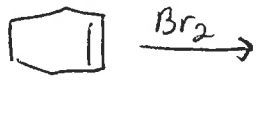
^{13}C NMR

δ 110–160

UV-Vis
- skip
16.3D

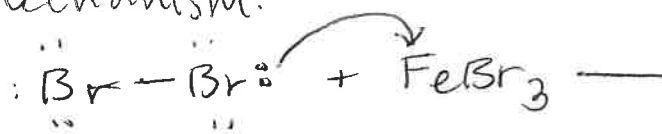
Electrophilic Aromatic Substitution (EAS)

- π system much less reactive than alkene
- Energy penalty to breaking aromaticity

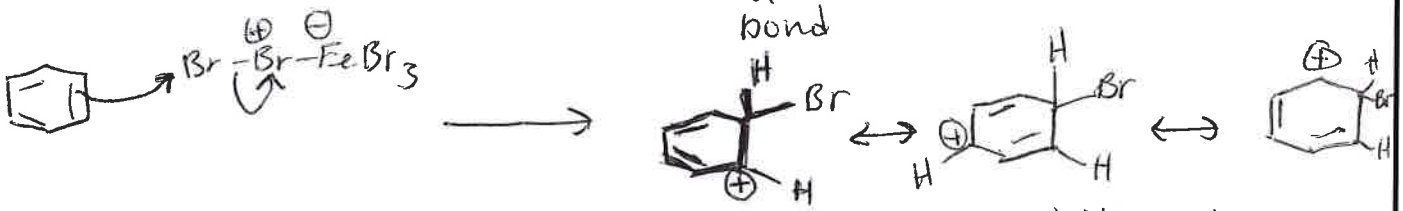
Example:  Very rapid

How to make electrophile more reactive?
↳ use a Lewis acid

Mechanism:



Br–Br much weaker bond



resonance stabilized

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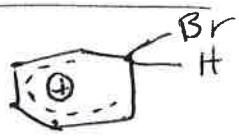
Breaking aromaticity is slowest (rate determining) step! Reforming aromaticity is downhill.

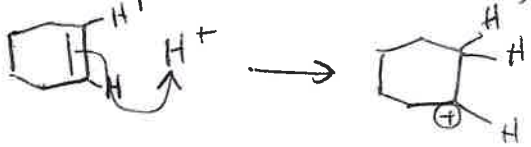
Intermediate



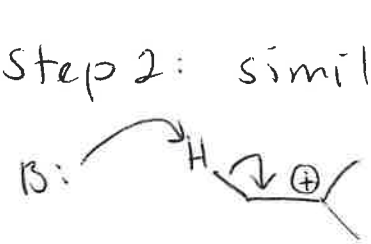
delocalized over 5 sp^2 carbons

Not aromatic
$4\pi e^-$
Not planar

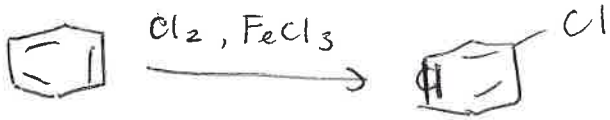
Step 1: similar to alkene π system attack on an electrophile (like H^+)



Step 2: similar to 2nd step of E1 elimination



Chlorination:



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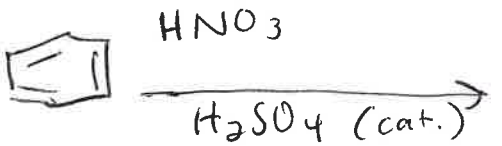
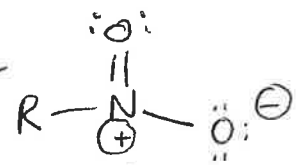
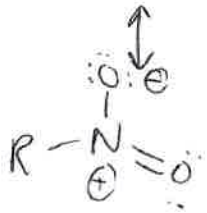
Nitration:

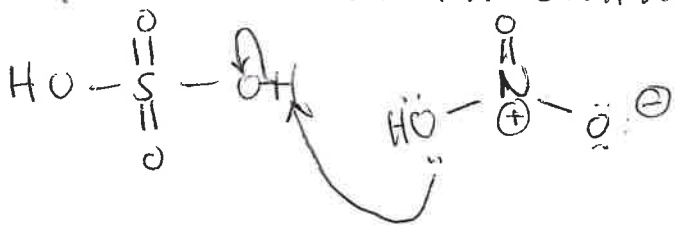


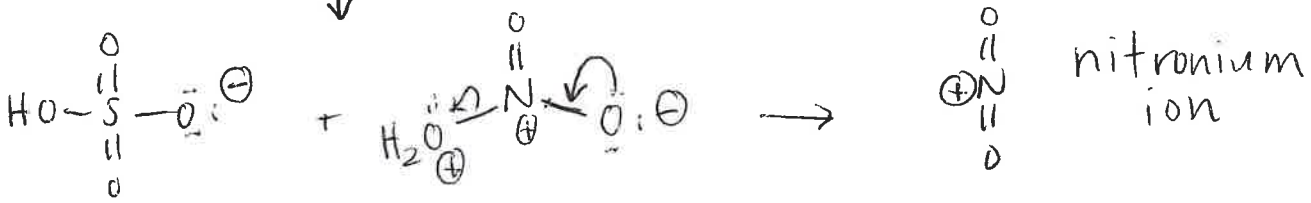
Nitro group



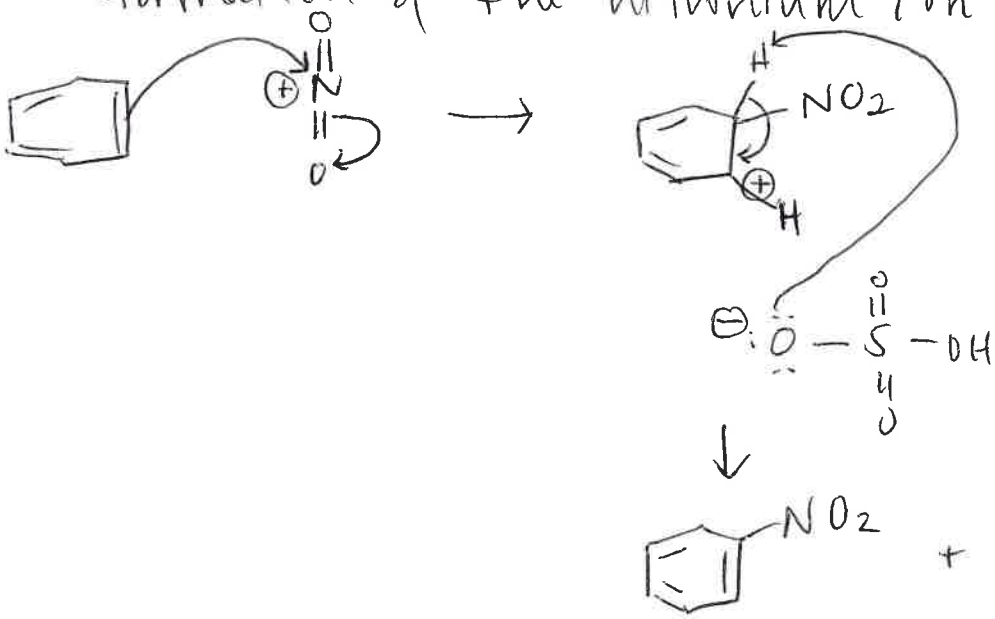


Why do we need the sulfuric acid?





(Sulfuric acid enables the dehydration for formation of the nitronium ion)



Draw all resonance structures for exams

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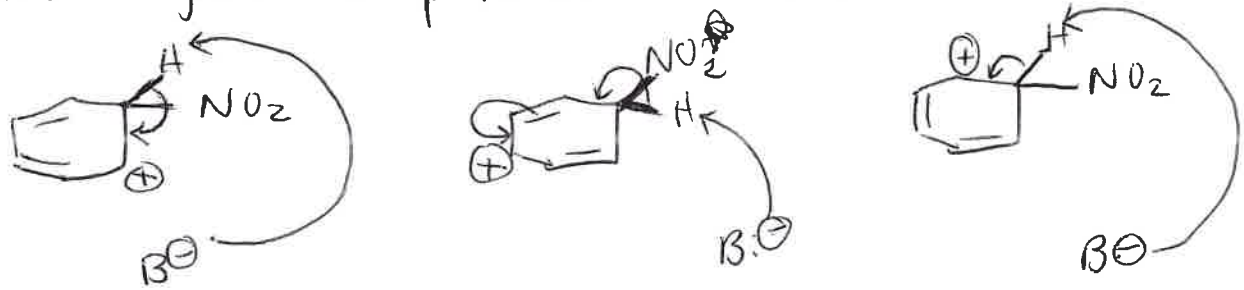
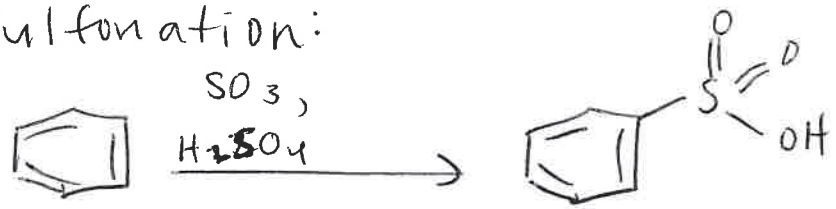
Note: the book does not show all 3 resonance structures, which is too bad...
Can get to product from any of them

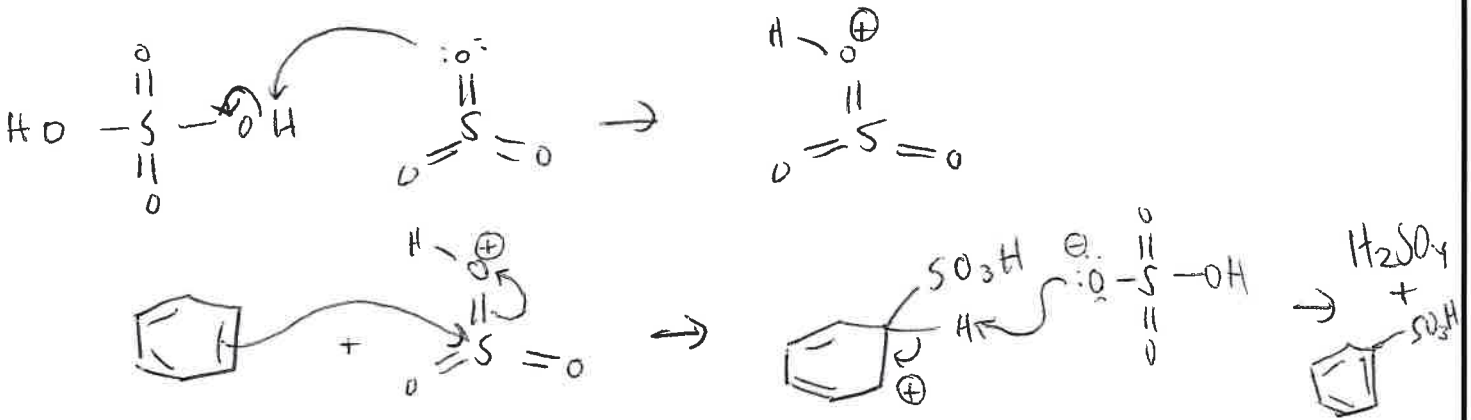


Draw all 3 on exams

Sulfonation:



sulfonic acid
(3 oxygens, 1 carbon)



practice other resonance structures