

Course Chem 343 11 AM Lecturer Gellman
Day Monday Date 12/12/11
Notes Taken By Herndon Total # of Pages 5

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This week...

Office hours - today 5 pm

Wed. as usual

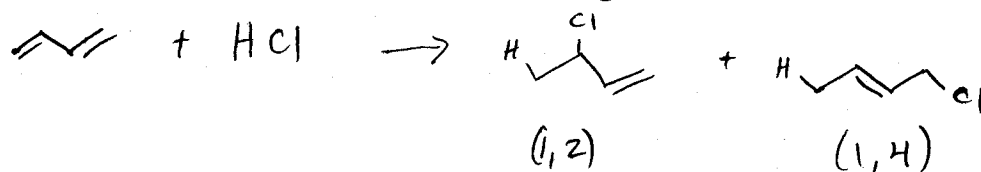
Fri - 1-3 pm

~~Next week~~

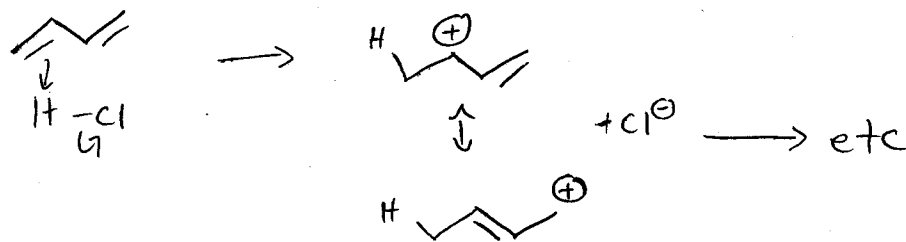
Review - Tues + Thurs 5 pm. B371

Final: 10⁰⁵ AM Mon 19 Dec Ingraham B10

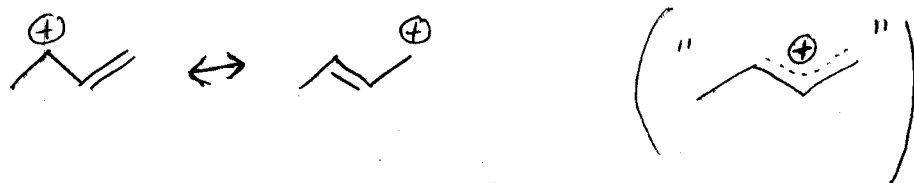
Recall: HX addn to conjugated diene...



Mech.

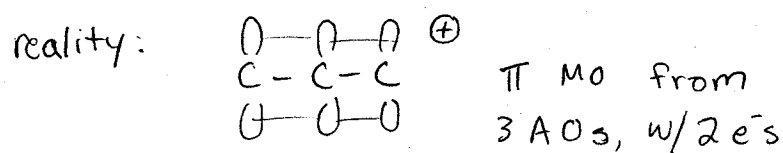


Closer look @ C+



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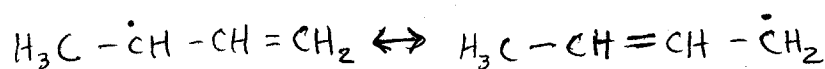
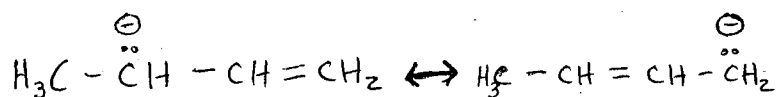
Consider an MO view...



Allylic carbocation

reacts w/ nucleophiles at only the ends (NOT middle c)

Allylic stabilization observed for anions + for radicals (as well as for cations): Resonance delocalization in each case.



Resonance delocalization of $\oplus$, $\ominus$ or $\cdot$ leads to stabilization

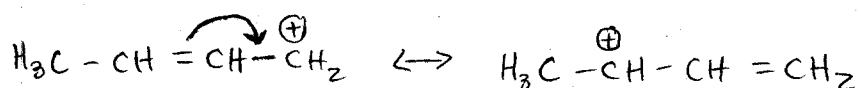


Read § 15.6 carefully on drawing + interpretation of res. structures

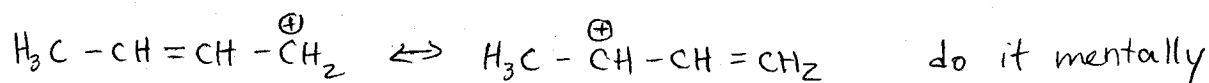
* Strongly advise against using curved arrow formalism to relate resonance structures to one another.

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Book:



I suggest:

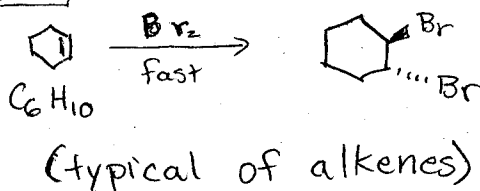


Aromatic molecules - dramatic example of the effects of electronic delocalization.

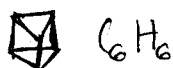
Benzene: C_6H_6

4 degrees of unsaturation
 $\Rightarrow$ suggests "alkene"

BUT



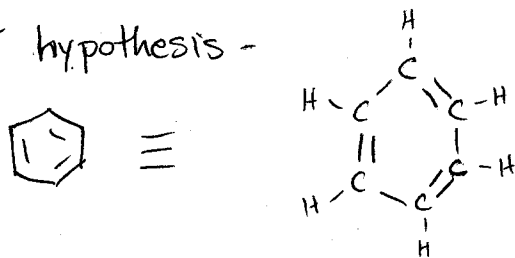
One proposal:



Contrast

benzene $\xrightarrow{\text{Br}_2}$ No rxn!

Kekulé hypothesis -



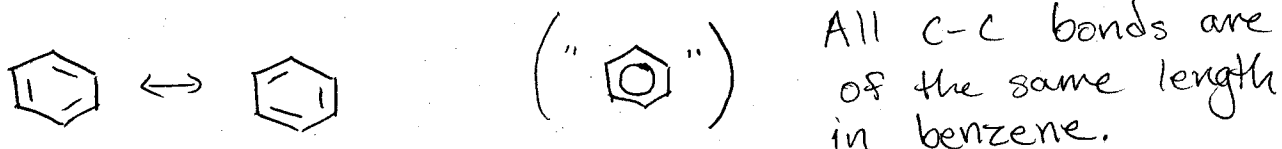
... and, must propose that this particular π bonding situation has unusual stability.

Special stability = "aromaticity"

We now understand that the special stability arises from cyclic delocalization of π e^- s

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thus:

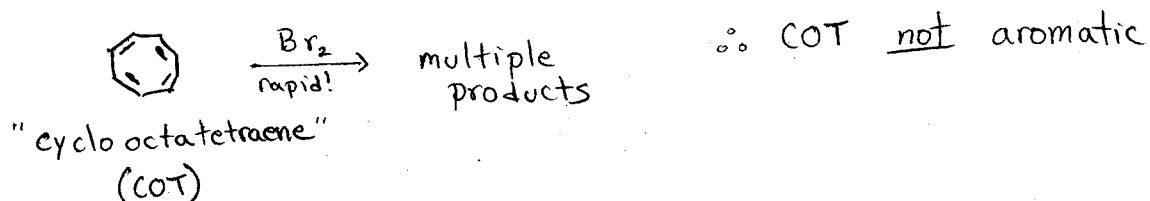


One can estimate that benzene is
 ~ 34 kcal/mol more stable than "cyclohexatriene"

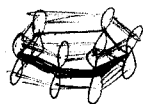
Defining characteristics of aromatic systems?

cyclic arrangements of π bonds are necessary but not sufficient.

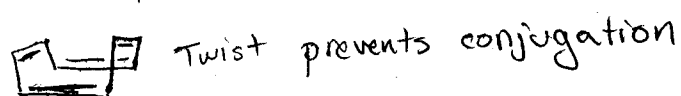
Ex:



This conclusion is consistent with structural results:
benzene is perfectly planar, as required for cyclic conjugation



COT is not planar (see p. 719)



Hückel's Rule -

Aromatic π systems contain only certain $\#$ s of electrons

$$2, 6, 10, \dots (4n+2) \quad n = \text{any integer}$$

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Note: $4n + 2$ π e's = "antiaromatic" -destabilizing

Two other requirements:

- closed loop of π electrons
- planarity, to allow π conjugation (cyclic)