Course Chem 343 Lecturer Gellman

Day Wed. Date 12/12/12

Notes Taken By Brian Total # of Pages 5

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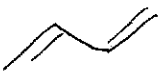
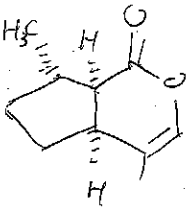
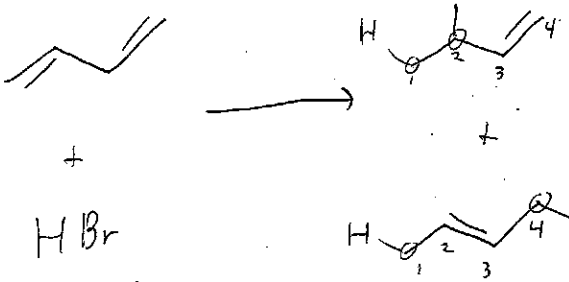
Reall: distinctive reactivity of conjugated dienes





Active ingredient of catnip ⇒ Organic chemistry is fun! (for cats and humans)

- HX addition to dienes

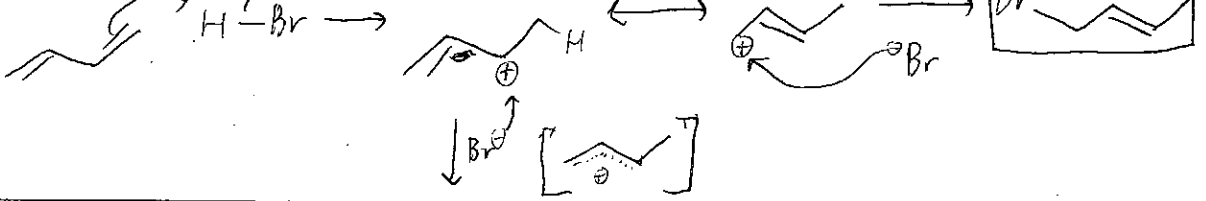


"Typical" Markovnikov addition prod. = 1,2-addition

Looks odd... = 1,4-addition

- Nomenclature: #'s indicate relative positions of added atoms (H & Br)

Mech



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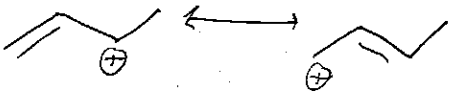
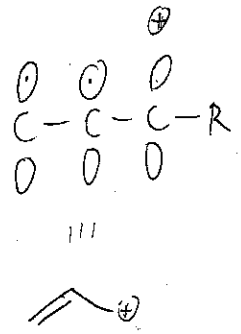
- Intermediate is an allylic carbocation
  - ↳ "next to double bond"



delocalized

- MO view

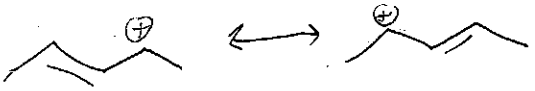


← see text for full description. But this case is very similar to that of  (see prev. day's notes), except w/ 3 orbitals instead of 4.

- Neither structure alone perfectly describes the molecules e⁻ distribution. The reality is really a superposition of the two. So it's more like:

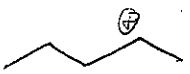
a resonance hybrid.

- Delocalization profoundly stabilized $C^{\oplus}$

ex 

2°, allylic $C^{\oplus}$

- similarly stable to 3° $C^{\oplus}$ 

vs. 

2° $C^{\oplus}$

so, stability: $3°C^{\oplus} \approx 2°$ allylic $C^{\oplus} > 2° >> 1°$

- Read section 15.6 for resonance structures

Course Chem 343 Lecturer Gellman

Day Wed. Date 12/12/12

Notes Taken By Brian. Total # of Pages 5

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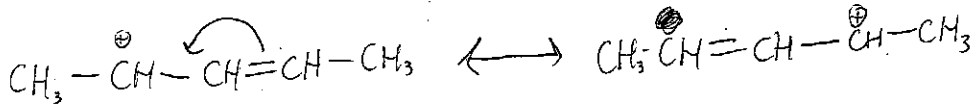
- Prof. Gellman thinks something the book does is dumb.

Using curved arrows for resonance structures: bad



don't do this!

Why?

- This convention implies that these are two different molecules. But they're the same.
- Can't distinguish between these curved arrows and ones that actually are important in a mechanism

• Aromaticity

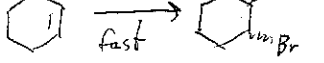
1800's: Quandary: what is up with benzene?

↳ they knew the formula: C_6H_6 ∴ 4 degrees of unsaturation

- How is this distributed — rings, double bonds — how many of each?

- was it an alkene?

↳ didn't behave like one.

ex. 

test for alkene. This reaction is visibly apparent. Br_2 is orange, and the alkene would remove this color. ⇒ Benzene does not decolorize Br_2.

Course Chem 343 Lecturer Gellman

Day Wed. Date 12/12/12

Notes Taken By Brian Total # of Pages 5

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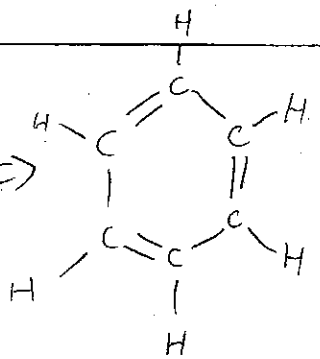
• August Kekulé

Chemist. Had a dream!

Ouroboros

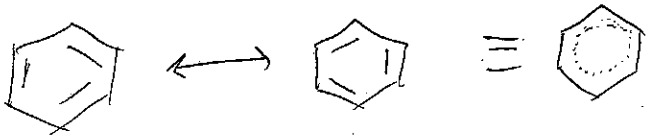
Snake eating its tail

=> cyclic?! =>



benzene structure

- But benzene still doesn't act like an alkene. Why?
  - ↳ This "triene" has an extra source of stabilization → aromaticity
  - ↳ aromaticity → cyclic delocalization of e^- → greatly stabilizing



∴ All C–C bonds are identical in benzene

- Aromatic molecules have very distinct reactivity compared to normal alkenes.
  - ↳ How can we ID aromatic molecules?
    - Just having ~~cyclic conjugated~~ cyclic π-bonds isn't sufficient

ex.  $\xrightarrow{Br_2}$ decolorizes (reacts like alkene)

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• Characteristics of aromatic systems

1) Correct # of π-electrons

Hückel's rule: $\#\pi e^- = 4n+2$ where $n = 0, 1, 2, \ldots$

ex.  $\#\pi e^- = 6$

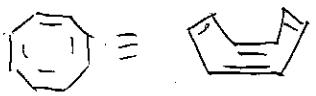
$4(1)+2 = 6$ ✓

2) Closed loop of π-bonds or p-orbitals

• benzene is planar

not planar

flat

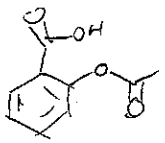


"tub-shaped"

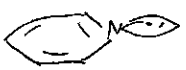
slightly better drawing

• Many important organic molecules have aromatic rings.

ex.



aspirin



• Aromaticity w/ heteroatoms

'heteroatom': atom that is not C or H

ex. N, O, S, etc.

'heterocycle': cyclic molecule w/ heteroatom

pyridine

ex.

• Aromatic

↳ but the N's lone pair is not involved in the π-system ∴ it is able to act as a base.