Course 343-3 Lecturer Gellman

Day Wednesday Date 12/12/12

Notes Taken By Matt Aronoff Total # of Pages 4

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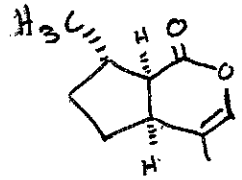
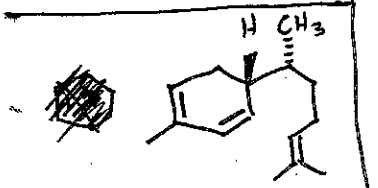
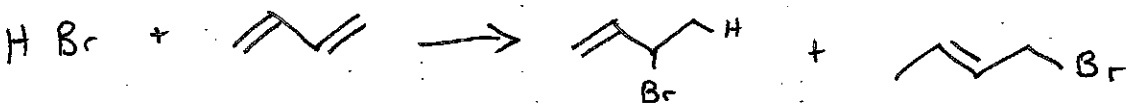




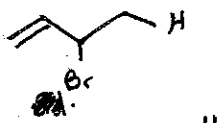
Recall: Distinctive rxns of conjugated dienes ( , etc.)

→ Diels-Alder

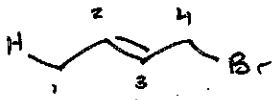
HX addition...



Nomenclature:

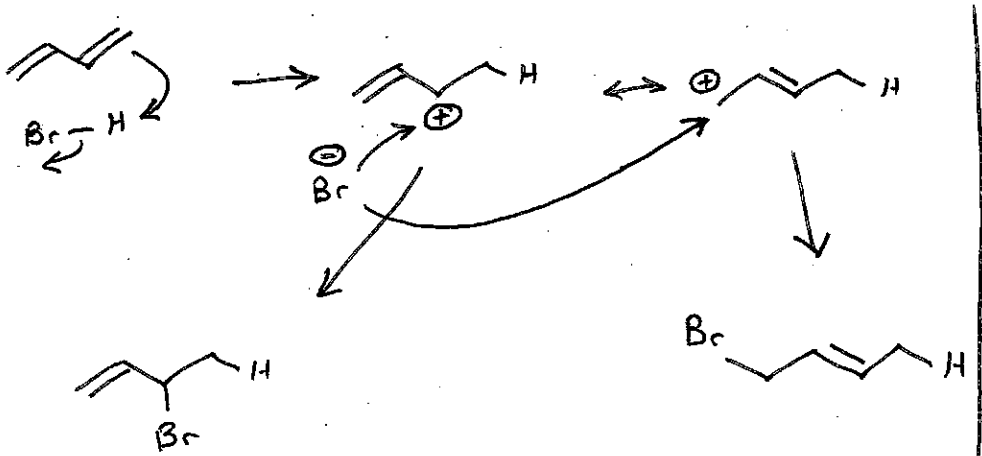


"1,2-addition"

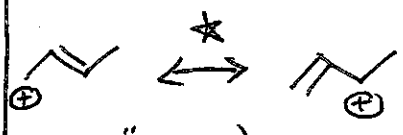


"1,4-addition"

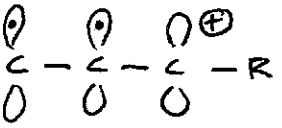
Mech:



Delocalized carbocation; allylic carbocation ("resonance structures")



see text for M.O.



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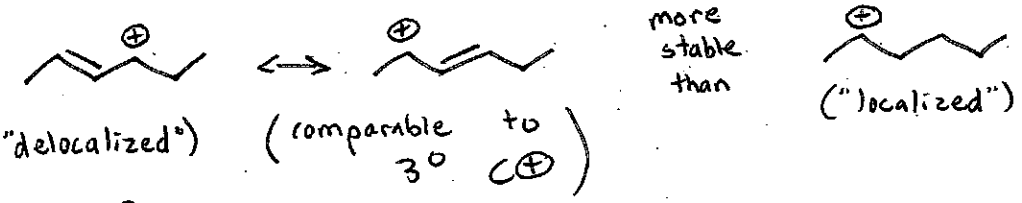
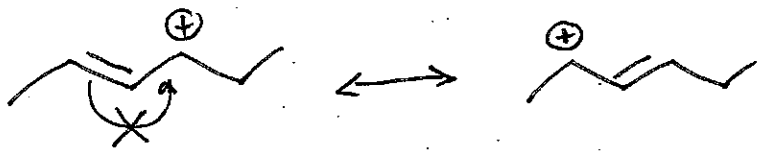
Resonance delocalization of ⊕ (or ⊖ or •) is stabilizing!

Ex:



See § 15.6 on drawing proper resonance structures.... BUT

DO NOT USE CURVED ARROWS TO INTERCONVERT RES. STRUCTURES!



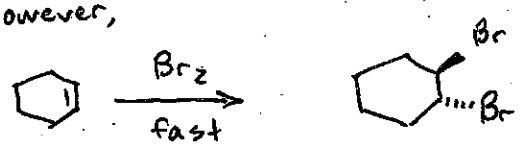
Aromaticity in organic molecules - a dramatic example of e⁻ delocalization.

Benzene ≡ C_6H_6

∴ 4 degrees of unsat.

∴ Alkene... ?

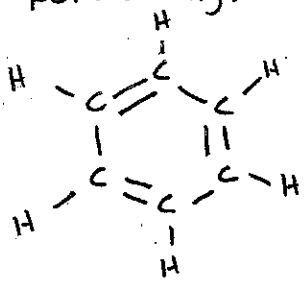
However,



vs.

Benzene $\xrightarrow{Br_2}$ No Rxn

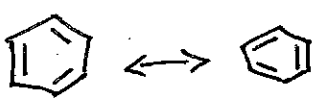
Kekulé hypothesis.



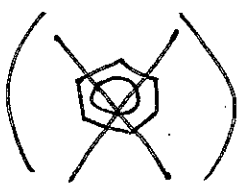
A triene?

Aromaticity - special stabilization in the π-system of benzene (rel. to alkenes)

π-system in benzene is fully delocalized:



(all bonds equivalent)



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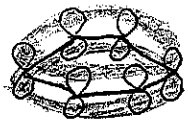
Another view:

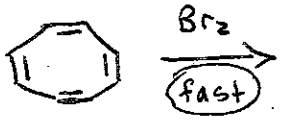


cyclic delocalization

Aromatic benzene vs "triene benzene"

~ 34 kcal/mol

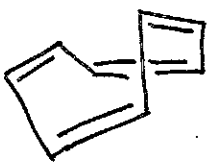
∴ must recognize when molecules are aromatic!



many products

"a typical alkene" ⟹ not aromatic

not planar!



Defining characteristics for aromaticity:

1) Proper # of e⁻'s in π-system

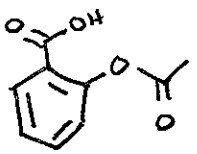
Hückel rule: 2, 6, 10, ...

$(4n + 2$, where n = integer$)$

2) Closed loop of p-orbitals

3) Planarity - to allow full p-overlap

We must be able to recognize molecules that are aromatic, or that have aromatic sub-structures.



Aspirin

Heterocycles - rings in which at least one atom is not carbon. E.g.)

pyridine

Is pyridine aromatic? (Yes)

If so, is N lone pair involved in aromatic π-system (NO)

pyridinium

pka ~ 5

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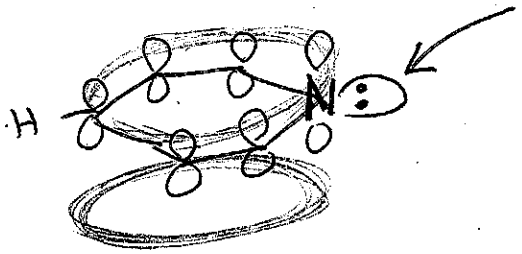
e- accounting



lone pair not involved in π- system