CHEM 222 section 01

LECTURE #14   Thurs., Oct.18, 2007

Lecture topics & readings

Today's class
- stability & reactions of dienes: Ch.7

Before next class
- practice determining structures from spectral data
- relate diene material to UV/Vis spectroscopy

Next class
- aromaticity & rxns of benzene: Ch. 14.1-

| Problem set quiz: due on Tues. Oct. 23 |
| Midterm exam: on Tues. Oct. 30 |

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BACK TO STUDYING REACTIONS
Ch.7,14,15: Delocalized e⁻s & rxns of dienes & aromatics

Chapter Goals & hints
   Understand the impact of e⁻ delocalization on stability & reactivity.
- Understand the enhanced stability of delocalized π-electrons.
- *Learn the typical reactions of dienes.*
- *Learn the typical reactions of aromatic compounds.*

Topics Outline:

Topics from Ch.7 (much of this is 221 review, but read it all):

| Delocalization of e⁻s, resonance - REVIEW on your own | 7.1-6, 9 |
| Dienes: stability & typical reactions | 7.7-12 |

Topics from Ch.14-15 (not all of Ch.15):

Aromaticity: why benzene is so stable	14.1-7
Rxns of benzene: electrophilic aromatic substitution	14.8-17, 19
i.e., adding substituents onto Ph rings	
Rxns of substituted benzenes: regio effects of EDG/EWG	15.1-9

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Dienes: alkenes with two π-systems

$$CH_2=CH-CH_2-CH=CH_2 \qquad CH_3CH=CH-CH=CHCH_3$$

What is the difference?

Conjugated dienes:

- Stronger single C-C bonds

1.34 Å
1.33 Å in $H_2C=CH_2$
...Why longer?

1.47 Å
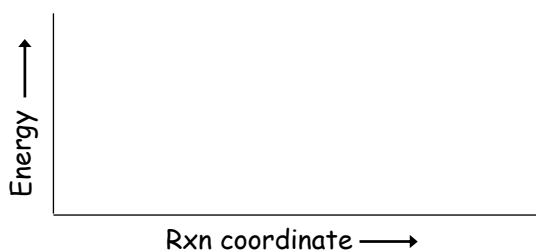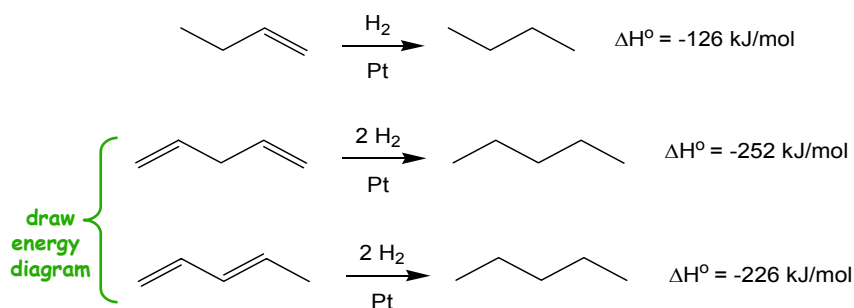sp^3C-sp^3C 1.54 Å
...Why shorter?
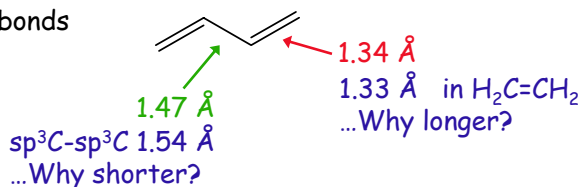
- Release less heat when hydrogenated...

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Conjugated dienes: more stable than isolated dienes (7.7)

- Experimental evidence:
  - **lower enthalpy of hydrogenation if conjugated**

$\xrightarrow[\text{Pt}]{H_2}$ ΔH^o = -126 kJ/mol

draw energy diagram

$\xrightarrow[\text{Pt}]{2 H_2}$ ΔH^o = -252 kJ/mol

$\xrightarrow[\text{Pt}]{2 H_2}$ ΔH^o = -226 kJ/mol

Implication:
- conjugated π-systems are more stable
- BUT WHY?

Energy ⟶

(4)   Rxn coordinate ⟶

Dienes: a resonance view showing e⁻ delocalization (7.6)

"Bond / no-bond" resonance:

$$\overset{\ominus}{\underset{\cdot\cdot}{CH_2}}-CH=CH-\overset{\oplus}{CH_2} \longleftrightarrow CH_2=CH-CH=CH_2 \longleftrightarrow$$
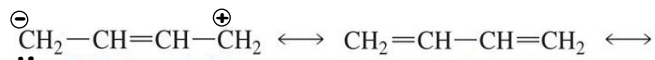
Resonance hybrid: $CH_2\text{---}CH\text{---}CH\text{---}CH_2$

most contribution from which contributor(s)?
WHY?

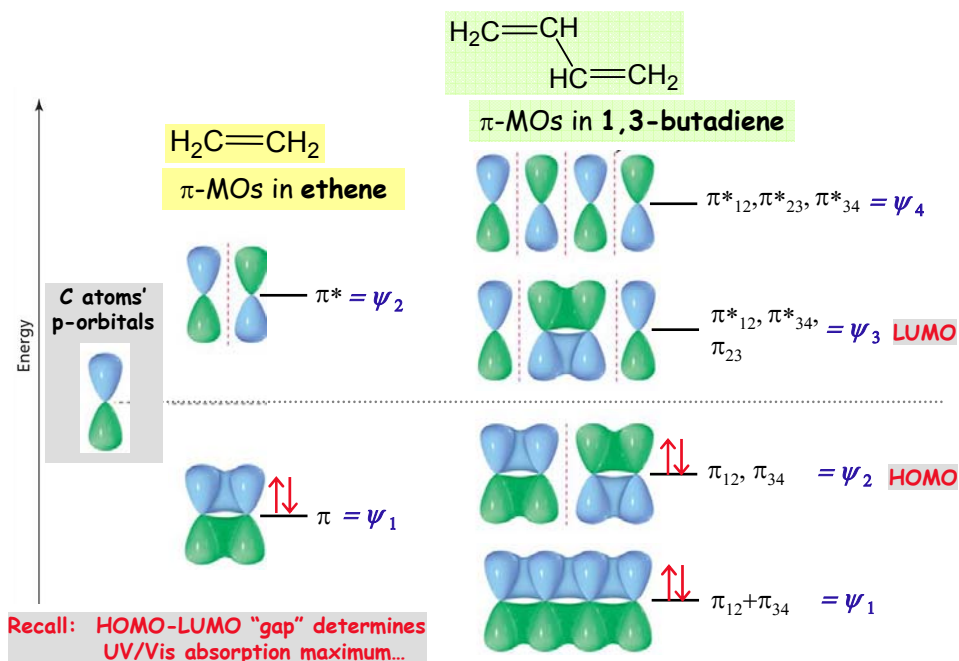**IMPORTANT: Review & practice resonance structures yourselves**
- only π-e⁻s & lone pairs move ⇨ nuclei & σ-bonds do **not** move
- most stable contributors have: full octets & minimal charge separation
- Bruice 7.1-7.5 AND Study Guide/Solutions Manual – Special Topic II

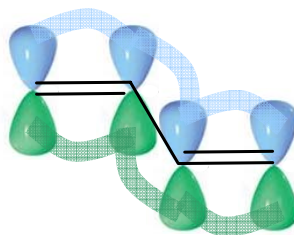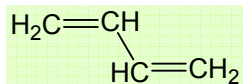**& Remember what you've already learned about resonance effects:**
- resonance-stabilized carbocations form more easily / faster…
- conjugated products form preferentially in reactions (if possible)

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Dienes: a molecular orbital view (7.8)   note: 2e⁻ / MO (ψ)

$H_2C=CH$
$HC=CH_2$

π-MOs in **1,3-butadiene**

$H_2C=CH_2$

π-MOs in **ethene**

C atoms' p-orbitals

Energy

$\pi^*_{12}, \pi^*_{23}, \pi^*_{34} = \psi_4$

$\pi^* = \psi_2$

$\pi^*_{12}, \pi^*_{34}, \pi_{23} = \psi_3$ LUMO

$\pi = \psi_1$

$\pi_{12}, \pi_{34} = \psi_2$ HOMO

$\pi_{12}+\pi_{34} = \psi_1$

Recall: HOMO-LUMO "gap" determines
UV/Vis absorption maximum…

1,3-butadiene H$_2$C=CH
HC=CH$_2$

IMPORTANT CONSEQUENCES for conjugated dienes:

1. **σ-bond with partial double-bond character**
   ⇨ shorter, stronger bond

2. **π-electrons are spread out (delocalized)**
   ⇨ enhanced stability

3. **Conjugated dienes must be planar to maintain overlap**
   ⇨ two preferred conformations: *s-cis*   *vs.*   *s-trans*

Which is more stable?

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Dienes: how can they be prepared (simply…)?

1.) From an alkene: brominate at allylic position, then eliminate HBr

*See section 11.8
for how N-bromosuccinimide works…*

2.) From an α,β-unsaturated carbonyl compound: via Wittig rxn
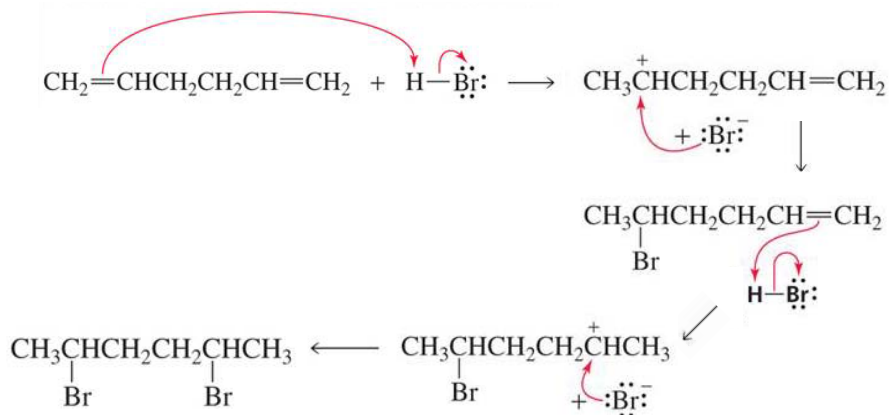
See later in Ch.17 section 17.13 (carbonyl compounds II)

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Dienes: addition rxns & effects of delocalization (7.10)

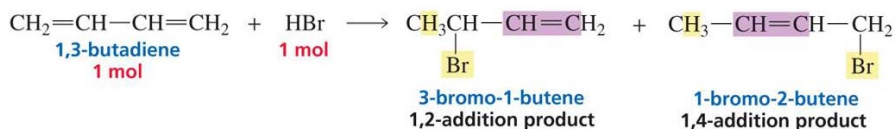**Isolated diene + HBr:** two 1,2 additions (= typical regiochemistry...)

$$CH_2{=}CHCH_2CH_2CH{=}CH_2 \; + \; HBr \; \longrightarrow \; CH_3CHCH_2CH_2CHCH_3$$

1,5-hexadiene   excess   Br   Br

Mechanism:

$$CH_2{=}CHCH_2CH_2CH{=}CH_2 \; + \; H{-}\ddot{B}r{:} \; \longrightarrow \; CH_3\overset{+}{C}HCH_2CH_2CH{=}CH_2$$

$$+ \; {:}\ddot{B}\ddot{r}{:}^-$$

$$CH_3CHCH_2CH_2CH{=}CH_2$$
Br

$$H{-}\ddot{B}r{:}$$

$$CH_3CHCH_2CH_2CHCH_3 \; \longleftarrow \; CH_3CHCH_2CH_2\overset{+}{C}HCH_3$$
Br   Br   Br

$$+ \; {:}\ddot{B}\ddot{r}{:}^-$$

Dienes: effect of delocalization on addition rxns (7.10)

Conjugated diene + excess HBr:

$$CH_2{=}CH{-}CH{=}CH_2 \; + \; HBr \; \longrightarrow \; CH_3CH{-}CH{=}CH_2 \; + \; CH_3{-}CH{=}CH{-}CH_2$$

1,3-butadiene   1 mol   Br   Br
1 mol

                                        3-bromo-1-butene   **1-bromo-2-butene**
                                     1,2-addition product   **1,4-addition product**

Mechanism to form each product...?

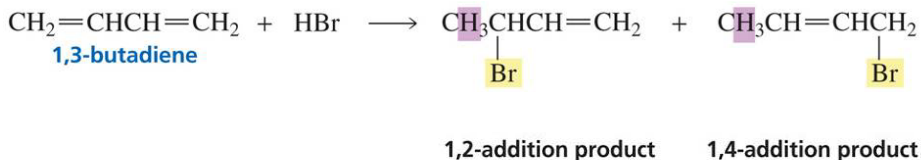(10)

Thermodynamic control: yields more stable product
- if reactions are reversible (forward & reverse E_as are accessible)…
- reactions reach equilibrium
- formation of product driven by stability of final products
- *How can we deliberately make this happen?*
    - perform reaction at elevated temperature

Kinetic control: easiest product to form (lowest E_a)
- if reaction is irreversible (reverse E_a is inaccessible)
- don't get most stable product
- formation of product is driven by stability of transition state
- *How can we deliberately make this happen?*
   - perform reaction at lower temperatures

Powerful tool: choose rxn conditions that favour desired product

Example: Thermodynamic *vs.* kinetic control

$$CH_2=CHCH=CH_2 + HBr \longrightarrow CH_3CHCH=CH_2 + CH_3CH=CHCH_2$$

1,3-butadiene   Br   Br

1,2-addition product   1,4-addition product

	Kinetic product	Thermodynamic product
Rxn at –80°C	80%	20%
Rxn at 45°C	15%	85%

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Draw this yourselves too – <u>beside</u> the mechanisms…
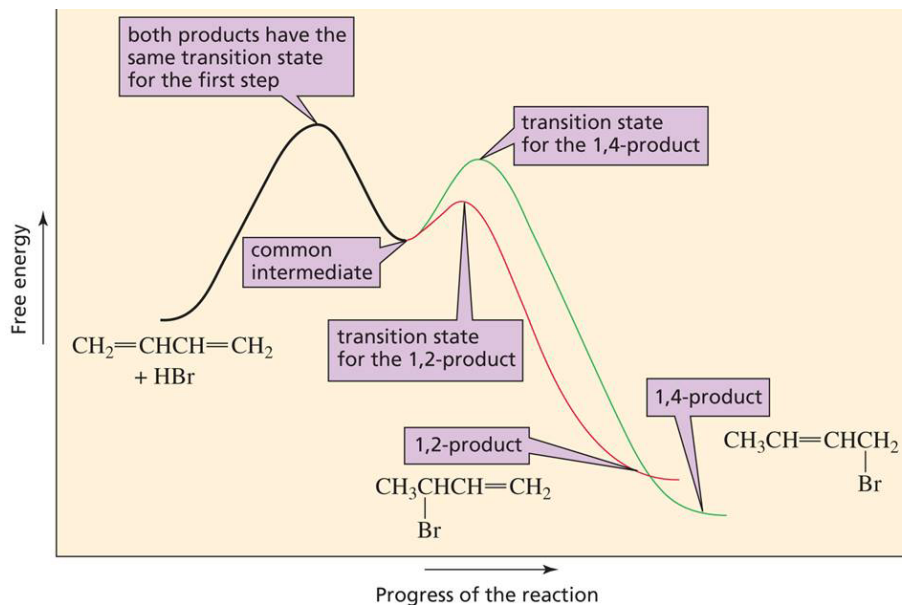
Dienes: other reactions…

1.) Ozonolysis: similar to regular alkenes (section 19.7)
- cleave C=C
- functionalize the new "ends" with C=O and O=C…
- route to carbonyl compounds…
  - reductive workup (Zn, H_2O or $(CH_3)_2S$) ⇨ aldehydes & ketones
  - oxidative workup (H_2O_2)   ⇨ carboxylic acids

2.) Diels-Alder reaction: special reaction of dienes

See next…