

Chapter 7

Delocalized electrons

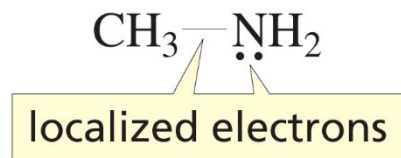
Resonance structure

Molecular orbital theory

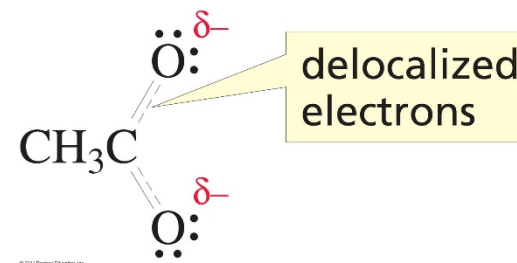
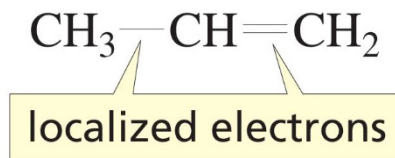
Diels-Alder reaction

Delocalized electrons

□ localized vs delocalized electrons



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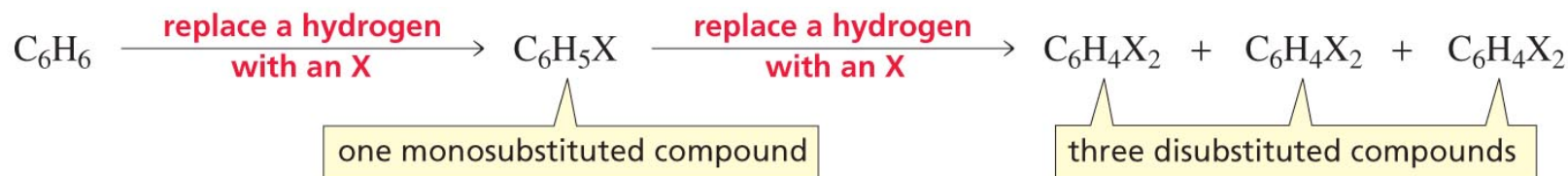
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□ structure of benzene ~ historical review



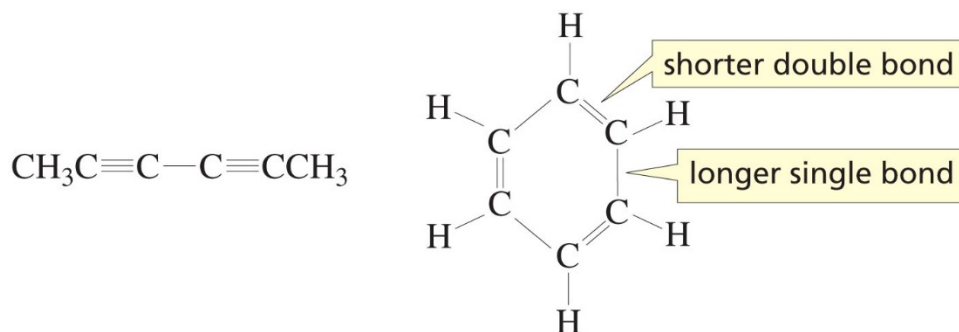
□ $\text{DU} = 4$

■ substitution reactions



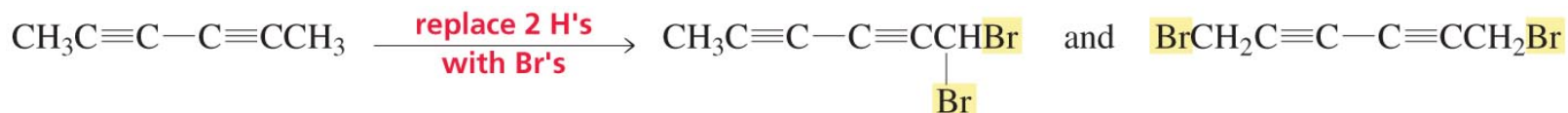
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- only 1 mono-substituted product, then either

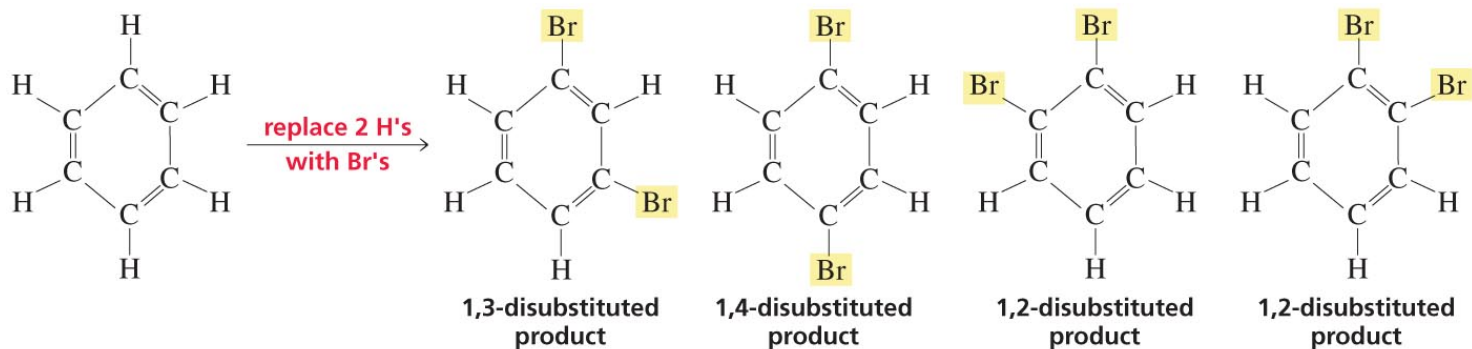


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- 2nd substitution \rightarrow 2 or 4, not 3

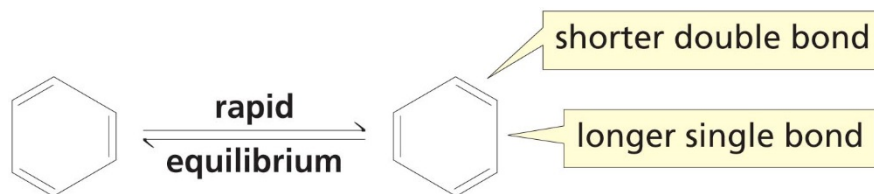


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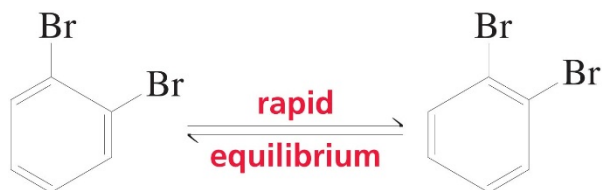
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■ Kekule (1865)

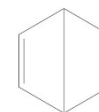


Kekulé structures of benzene

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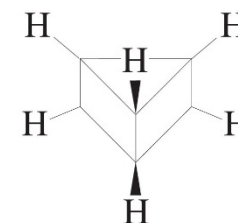


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Dewar benzene

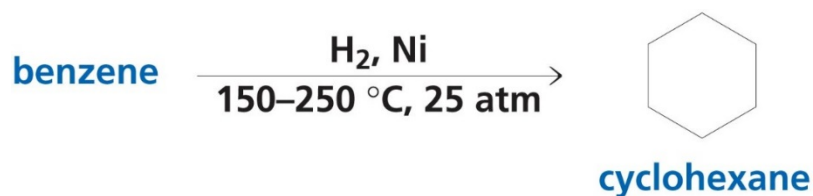
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Ladenburg benzene

□ Why not e-philic additions?

■ Sabatier (1901)

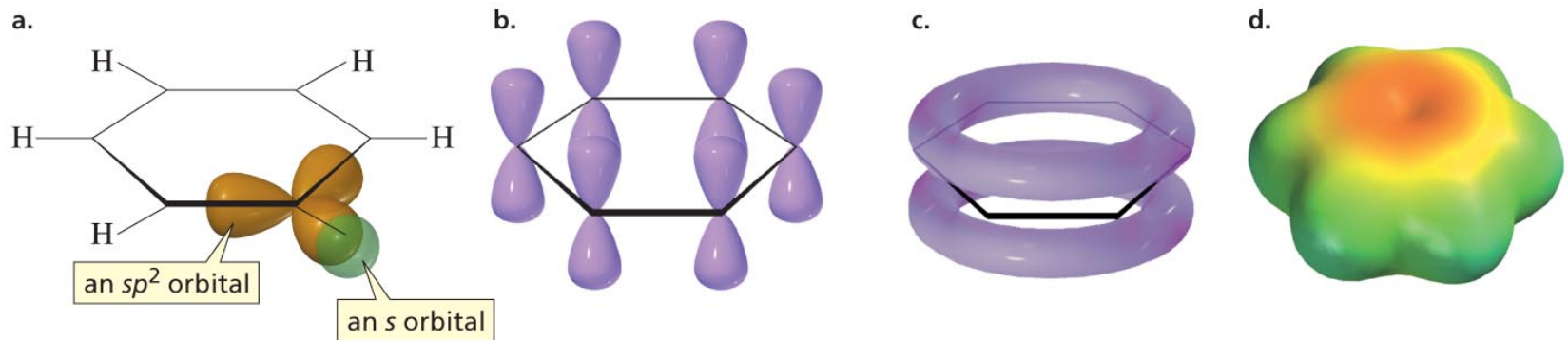


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□ Why so stable?

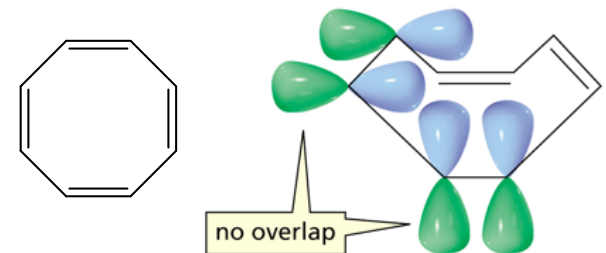
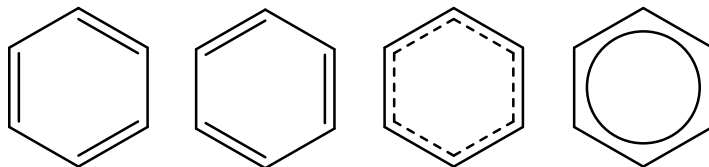
□ X-ray and electron diffraction

- locating atoms (in crystal)
- planar
- C-C with the same length ($1.33 < 1.4 < 1.54 \text{ \AA}$)



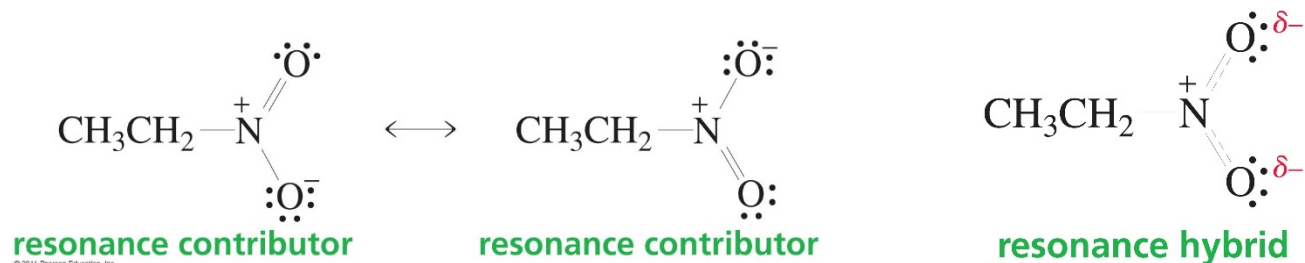
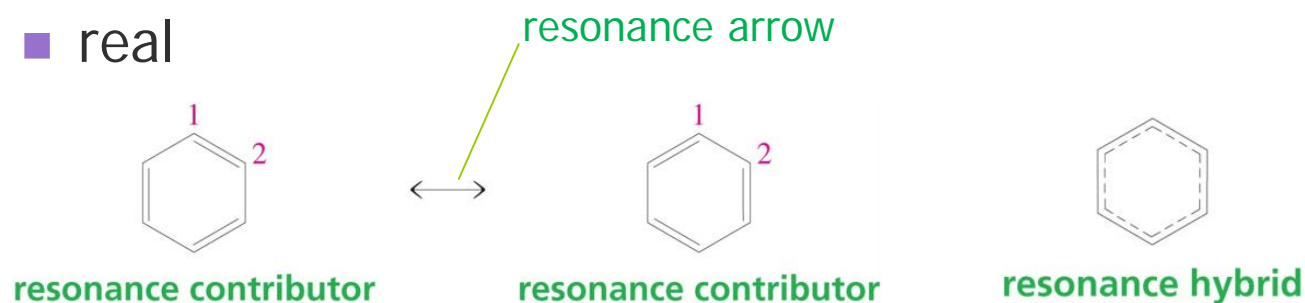
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- Electrons are delocalized.



Resonance [共鳴]

- = electron delocalization
- resonance contributors
 - = resonance structures = resonance forms
 - not real
- resonance hybrid
 - real



Rules for drawing resonance forms

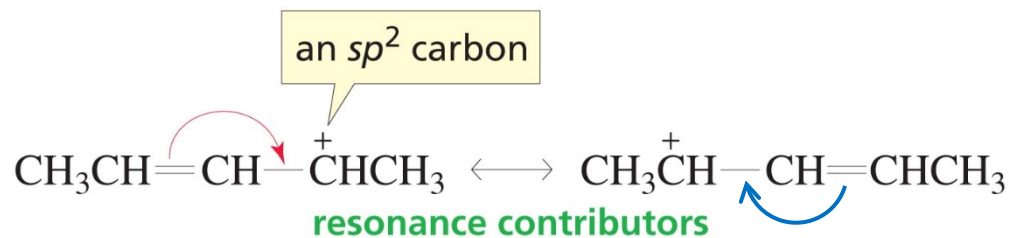
Ch 7 #7

1. Move electrons only.
 - Never move atoms [nuclei].
 2. Move π electrons and lone-pair electrons only.
 - Never move σ electrons.
 3. Do not change total # of electrons (in the molecule).
 - Never change total charge. May change formal charge.
 4. Move electrons to sp^2 or sp C (N, O), not to sp^3 C (N, O).
 - sp^2 C with = or (+); sp C with \equiv ; sp^3 with complete octet
 - May break π bond, not σ bond.
- Resonance not for actual movement of e's, but just for book-keeping.

Types of resonance

Ch 7 #8

□ π e's to sp^2 C



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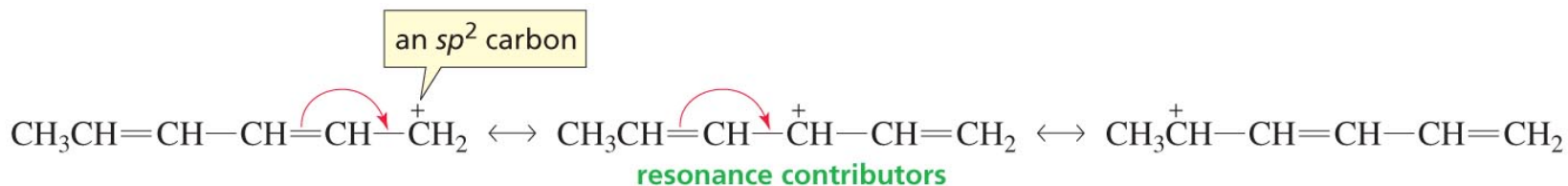
3-center resonance

an sp^3 carbon
cannot accept electrons

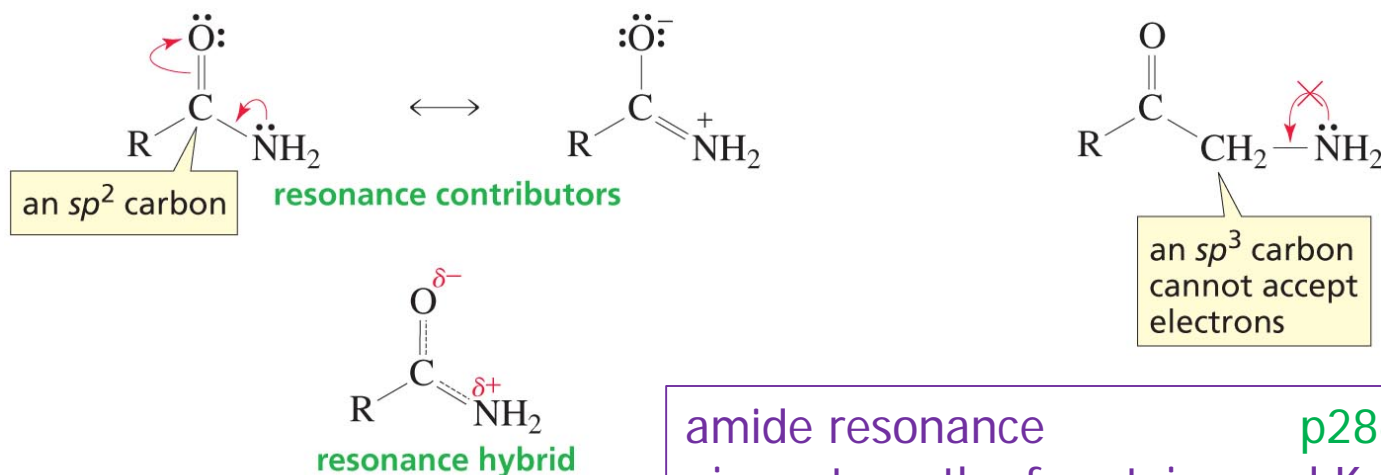


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5-center resonance

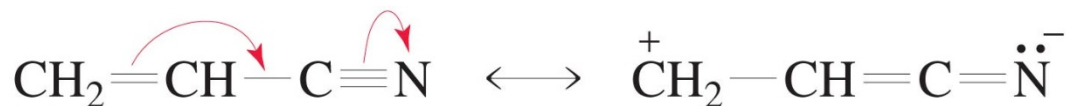
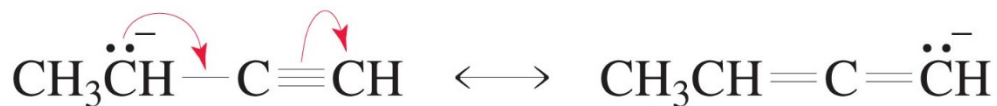


□ lone-pair e's to sp^2 C

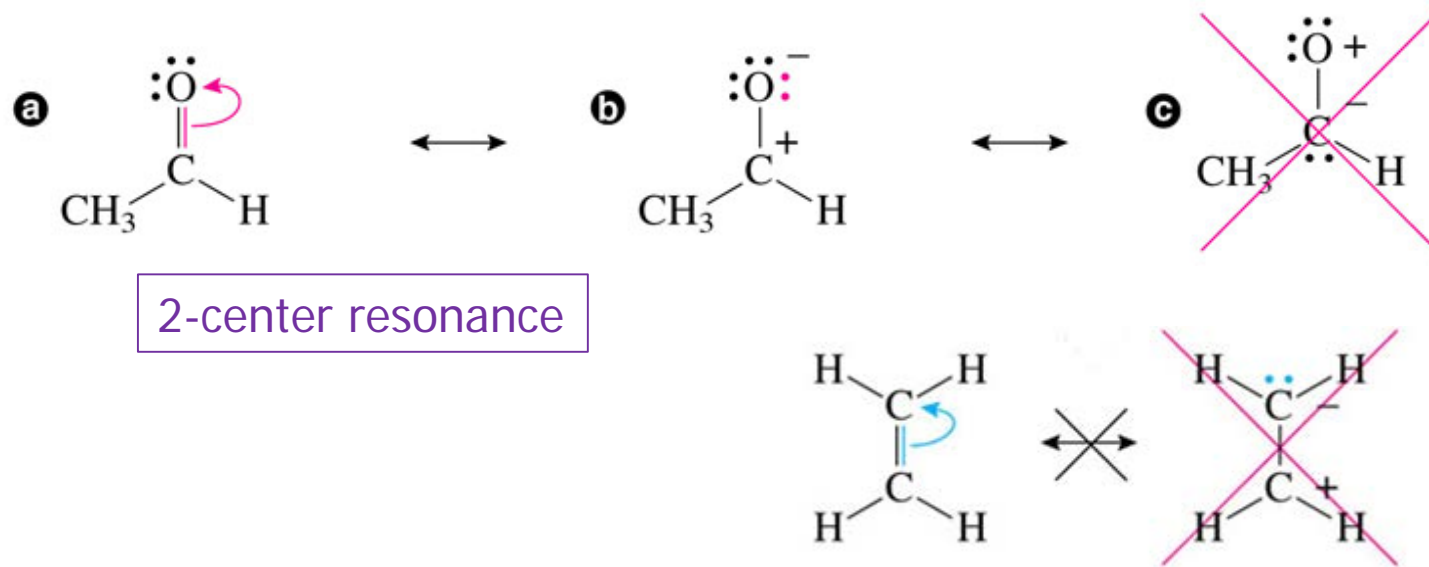


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□ lone-pair or π e's to sp C



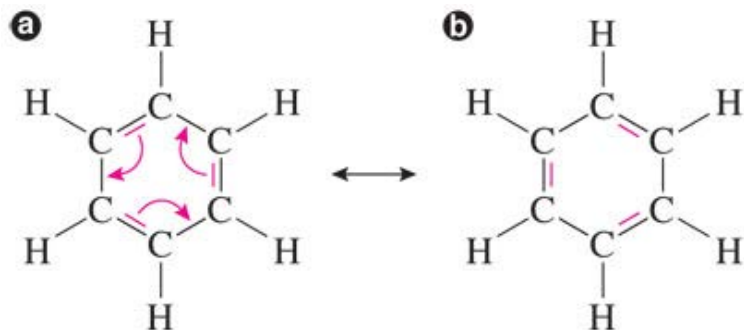
□ π e's to more e-negative atom



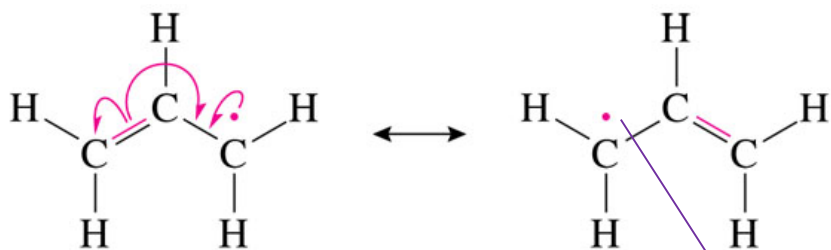
■ π e's to more e-positive atom, when it is the only way



□ cyclic (π e's to sp^2 C)



□ one e to sp^2 C



a π e (in p orbital)

Relative stabilities of contributors

Ch 7 #12

□ stability depends on

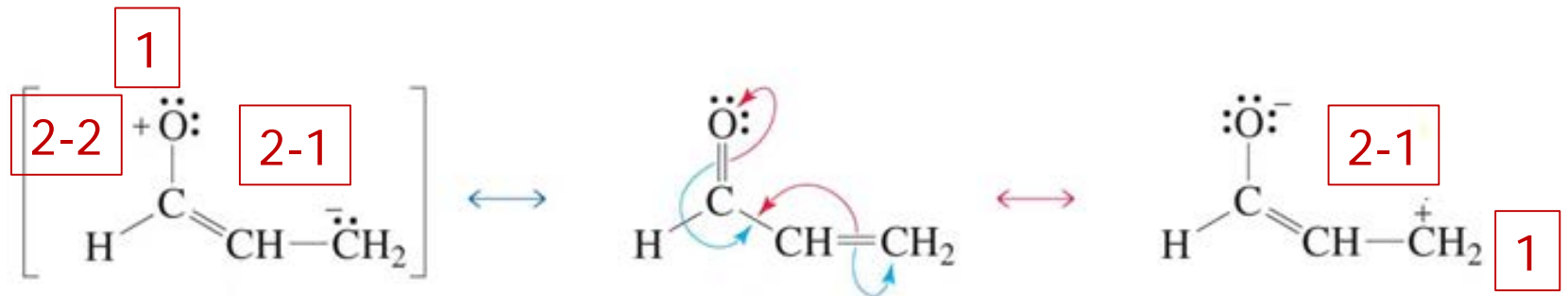
1. octet rule

2. formal charge

2-1. number ~ stable for no (or less) formal charge

▪ less stable for (separated) charge

2-2. location ~ stable for (-) on EN atom



not stable
not important [insignificant]
resonance contributor
should not draw

most stable
more important
resonance contributor
contribute more
closer to real structure

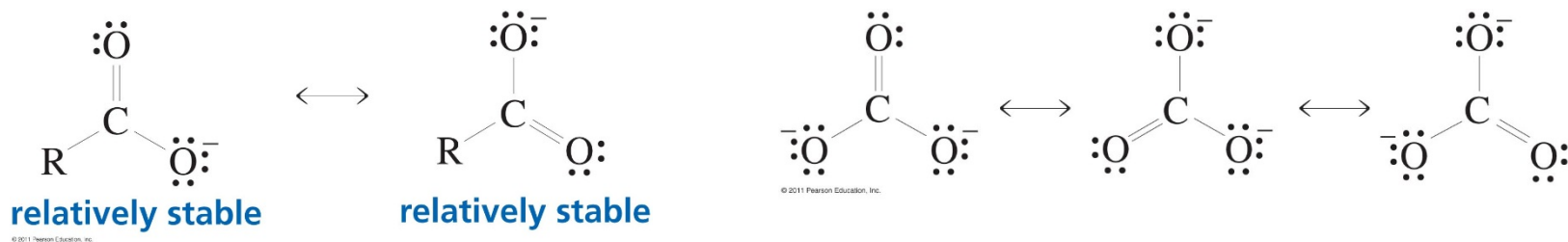
less stable
less important
resonance contributor

C=O ~ > 1.5 bond

Delocalization energy

Ch 7 #13

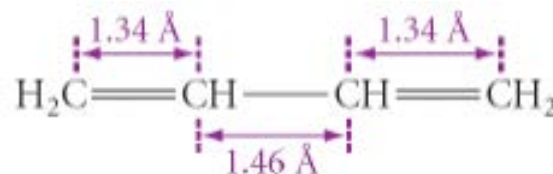
- = resonance (stabilization) energy
- extra stabilization gained by resonance
- larger stabilization with
 - larger # of 'relatively stable' [important] contributors



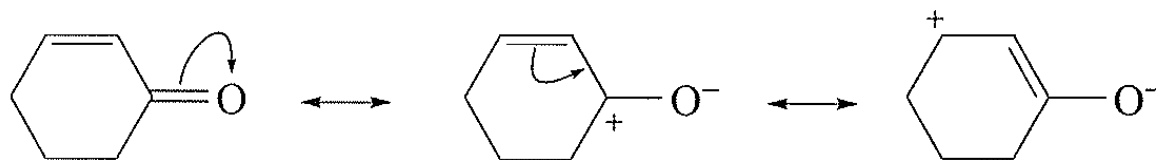
- more nearly equivalent contributors



C1-C2 ~ > 1.33 bond
C2-C3 ~ < 1.6 bond



Prob 4d

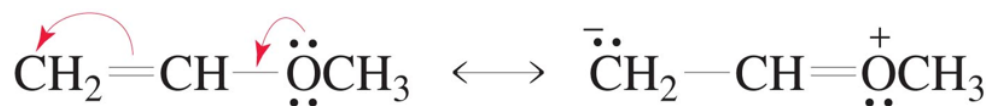


most stable
more important
contribute more
closer to hybrid

least stable
not important
may not draw

less stable
less important
contribute less

p287

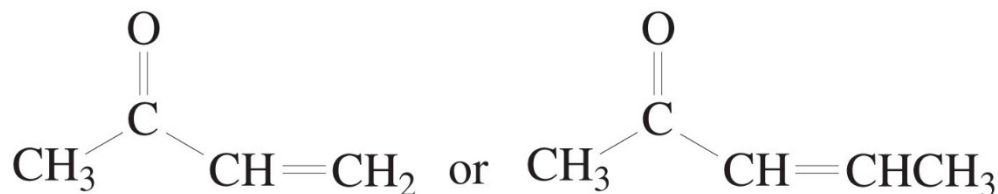


more stable
more important
contribute more
close to real

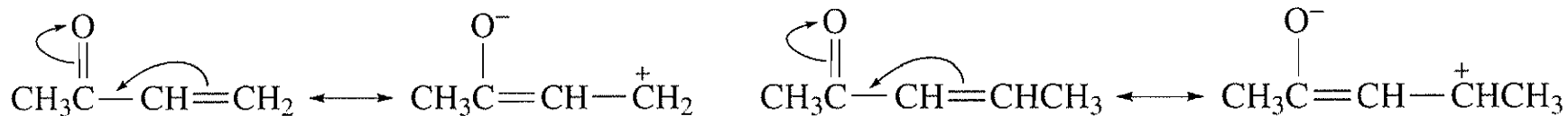
much less stable
much less important
contribute much less

less resonance-stabilized
lower resonance energy

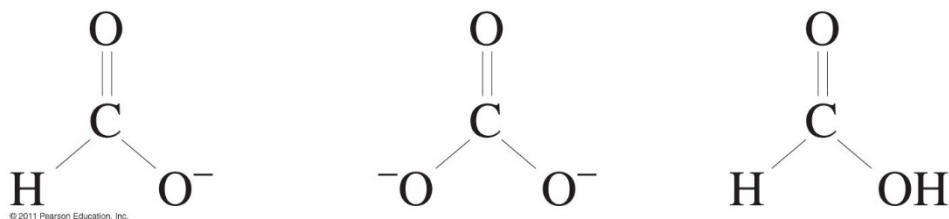
Prob 7b. Which is more stable?



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Prob 8. Which is more resonance-stabilized?



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Conjugation and resonance

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□ isolated vs conjugated double bonds



1,4-pentadiene
an isolated diene

Heat of
hydrogenation

60.2



1,3-pentadiene
a conjugated diene

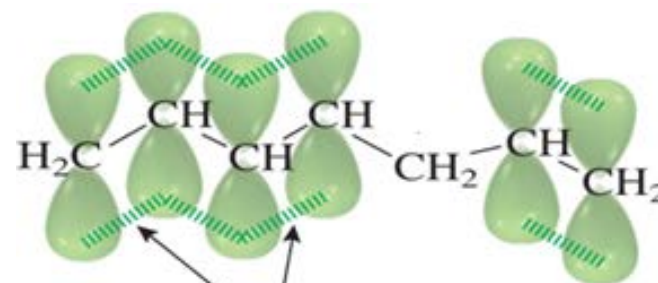
54.1

■ conjugated = 's ~ = 's separated by one single bond



conjugated
→ resonance

isolated
not conjugated



These two pi bonds
are conjugated.

□ A conjugated diene is more stable by

■ resonance



■ hybridization state

single bond formed by sp^2-sp^2 overlap



1,3-pentadiene

single bonds formed by sp^3-sp^2 overlap



1,4-pentadiene

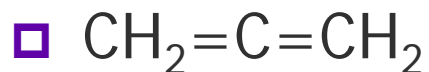
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Table 7.1 Dependence of the Length of a Carbon–Carbon Single Bond on the Hybridization of the Orbitals Used in Its Formation

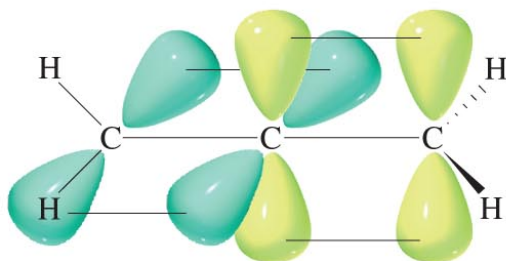
Compound	Hybridization	Bond length (Å)
$\text{H}_3\text{C}-\text{CH}_3$	sp^3-sp^3	1.54
$\begin{array}{c} \text{H} \\ \\ \text{H}_3\text{C}-\text{C}=\text{CH}_2 \end{array}$	sp^3-sp^2	1.50
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}_2\text{C}=\text{C}-\text{C}=\text{CH}_2 \end{array}$	sp^2-sp^2	1.47
$\text{H}_3\text{C}-\text{C}\equiv\text{CH}$	sp^3-sp	1.46
$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C}=\text{C}-\text{C}\equiv\text{CH} \end{array}$	sp^2-sp	1.43
$\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$	$sp-sp$	1.37

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Allene

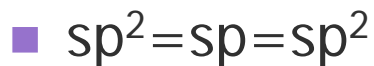
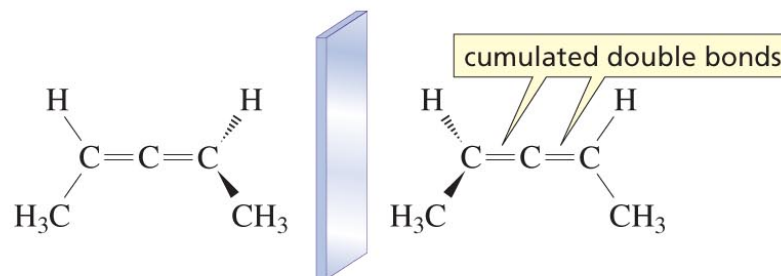


a.



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b.



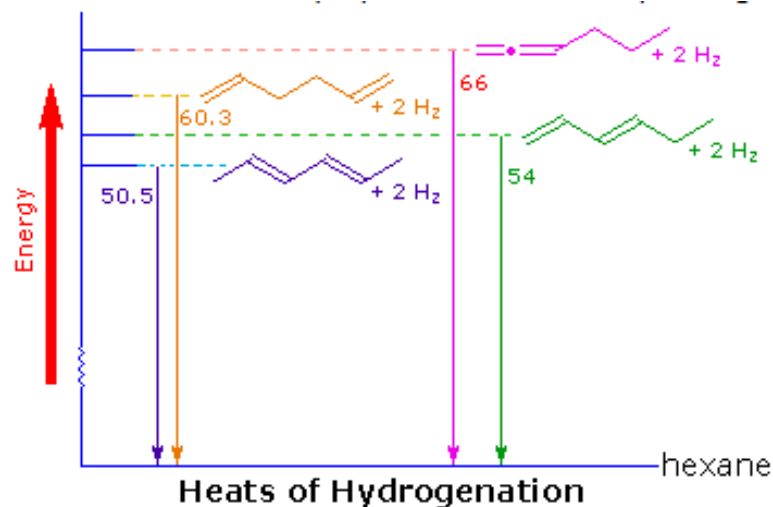
□ substituted allene is chiral (with no C^*)

□ a cumulated diene

■ more unstable than isolated diene

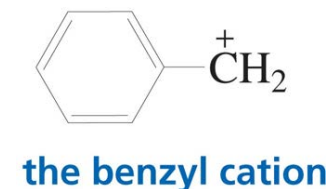
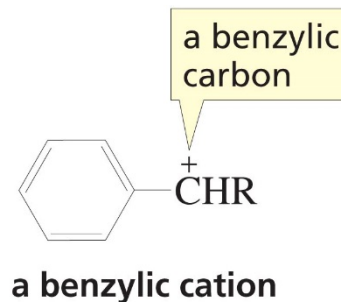
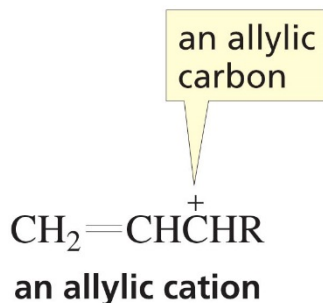
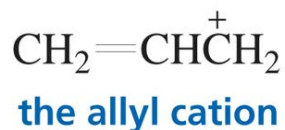
■ Prob 9 p292

■ cum < isol < conj

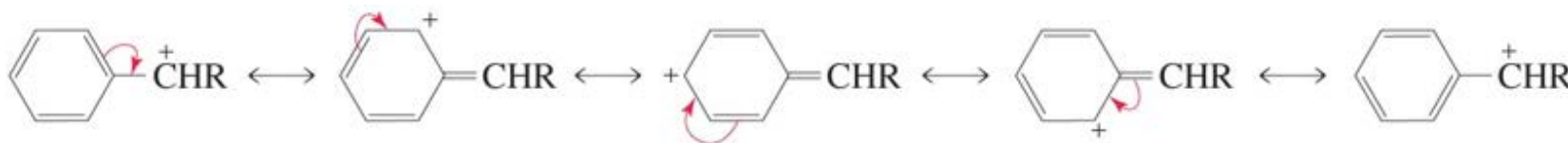


Allylic and benzylic cation

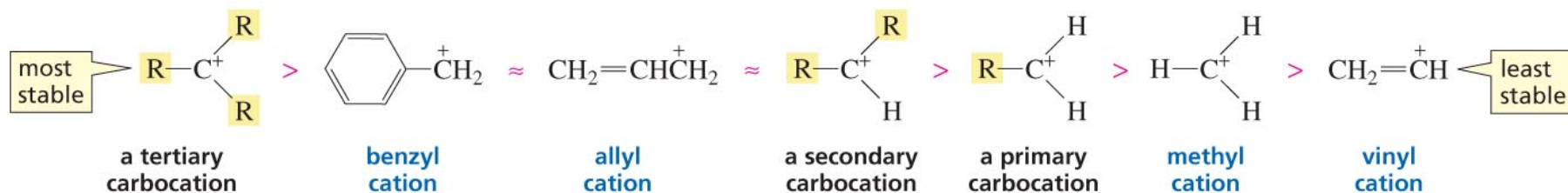
Ch 7 #19



□ resonance-stabilized



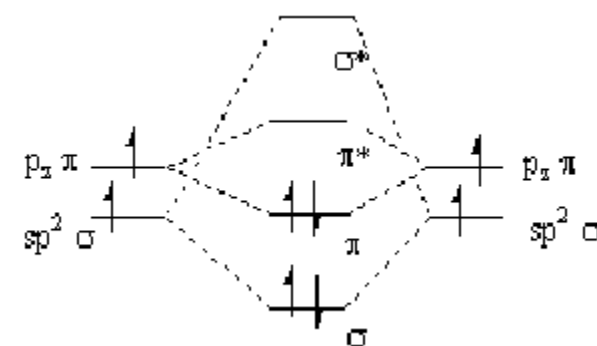
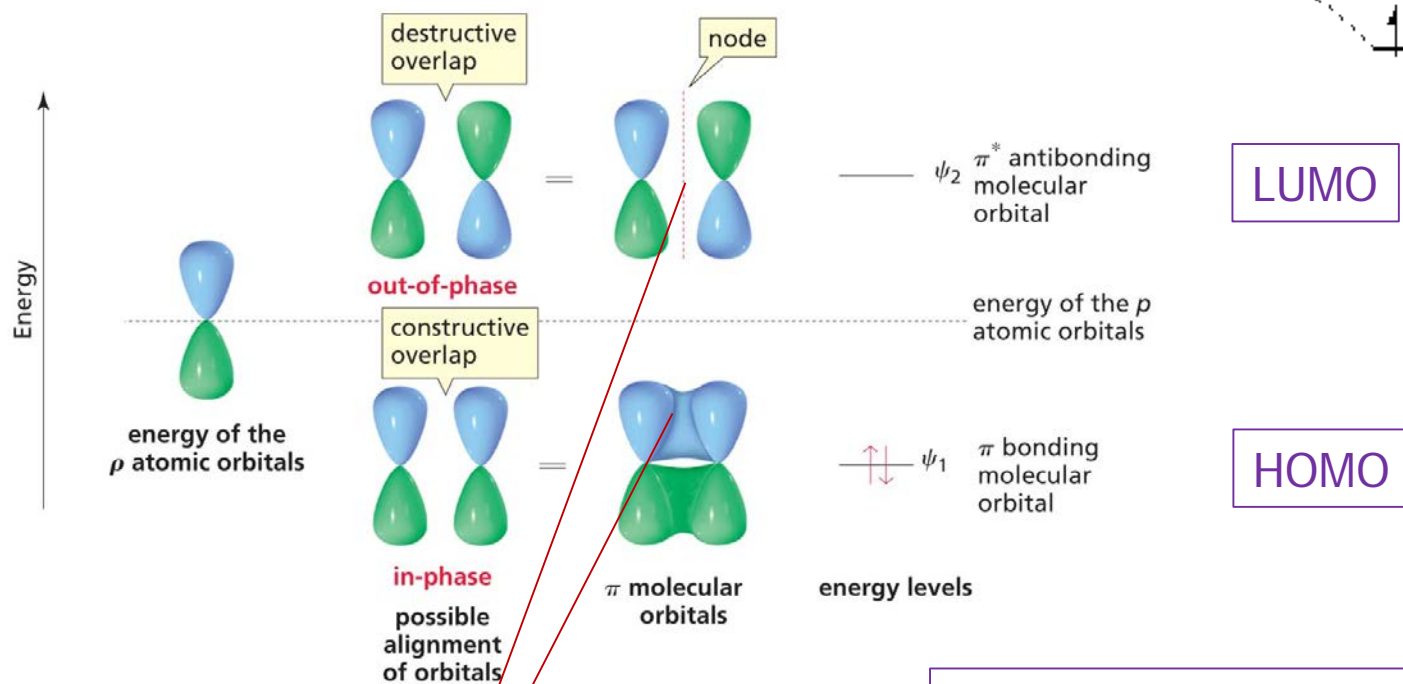
relative stabilities of carbocations



Molecular orbital and stability

Ch 7 #21

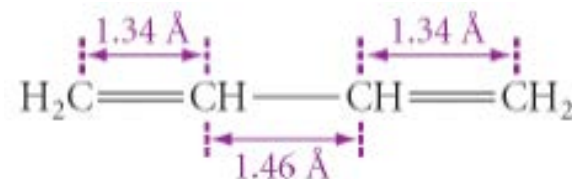
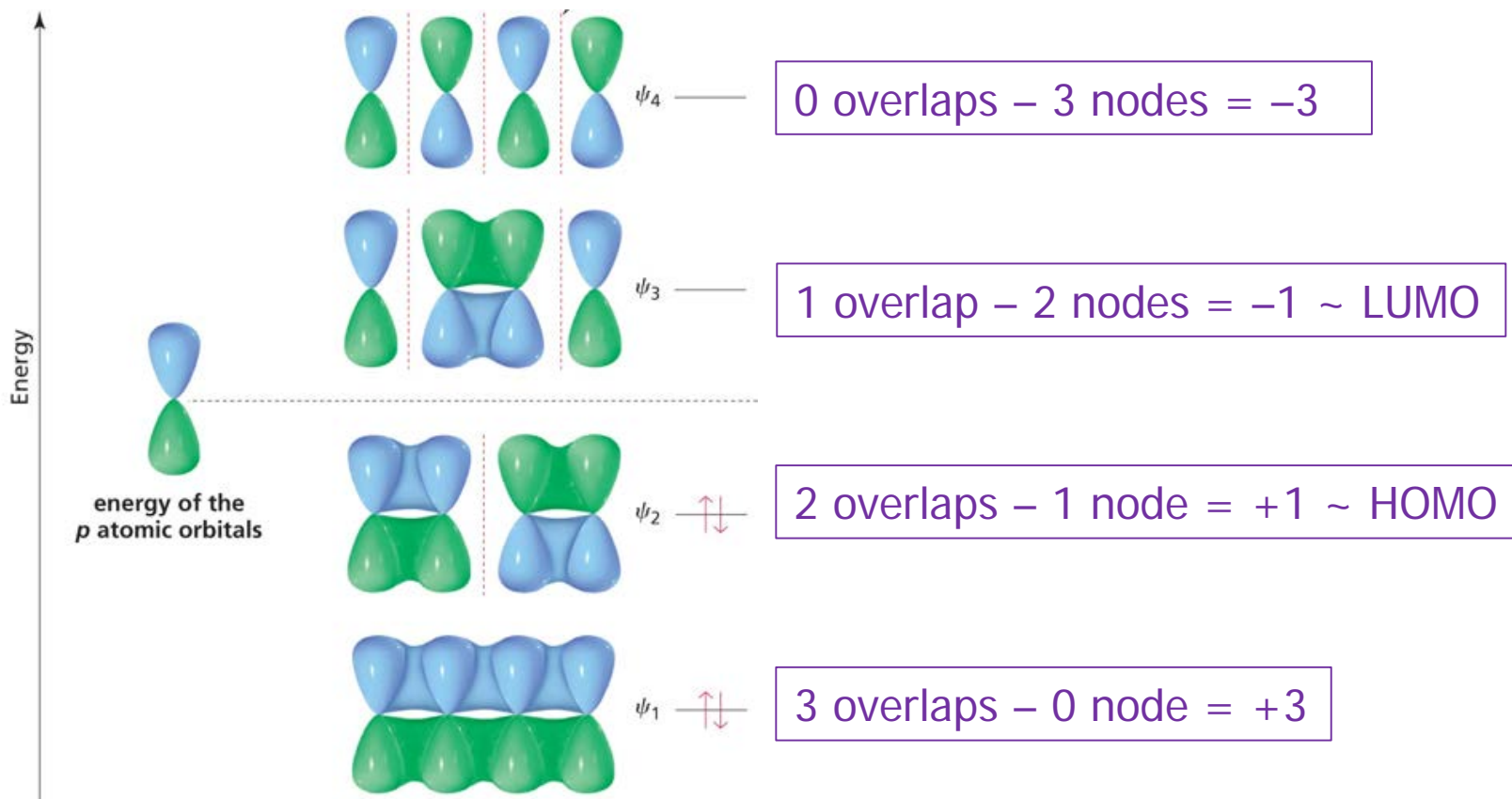
- MO from LCAO [linear combination of AO]
 - 2 AO \rightarrow 2 MO = 1 BMO + 1 AMO
- ethane (π e's of C-C only)



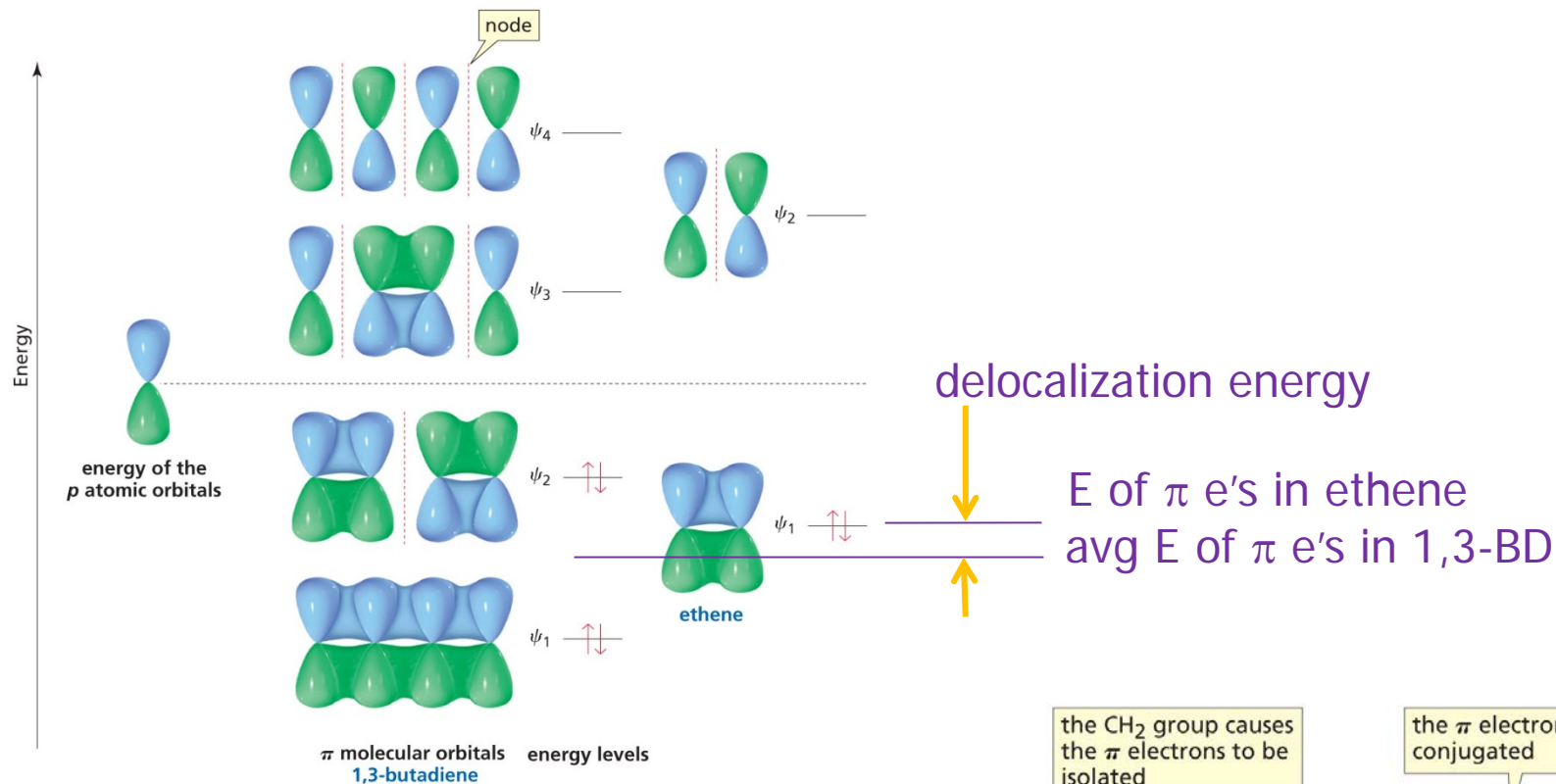
node = anti-bonding interaction
overlap = bonding interaction

LUMO = lowest unoccupied MO
HOMO = highest occupied MO

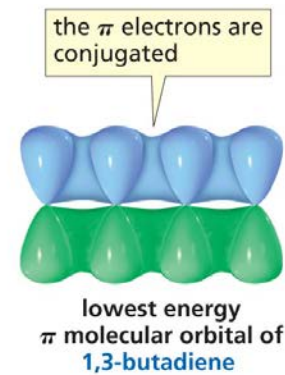
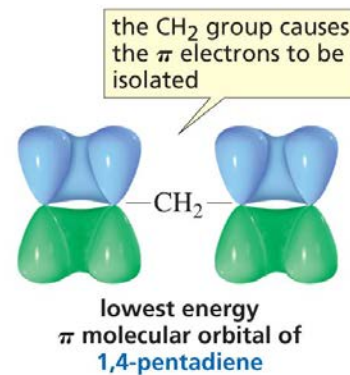
□ 1,3-butadiene



delocalization energy

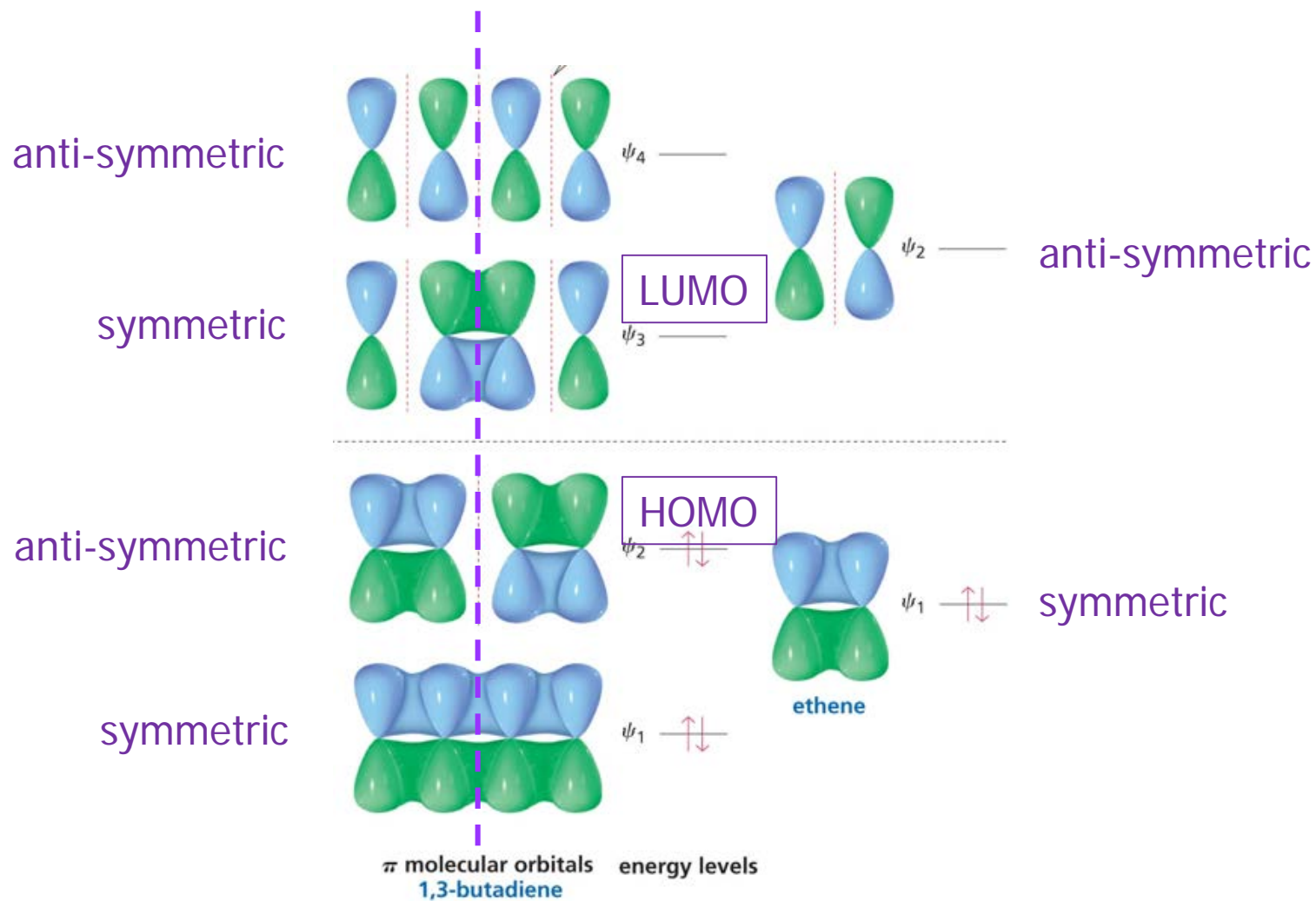


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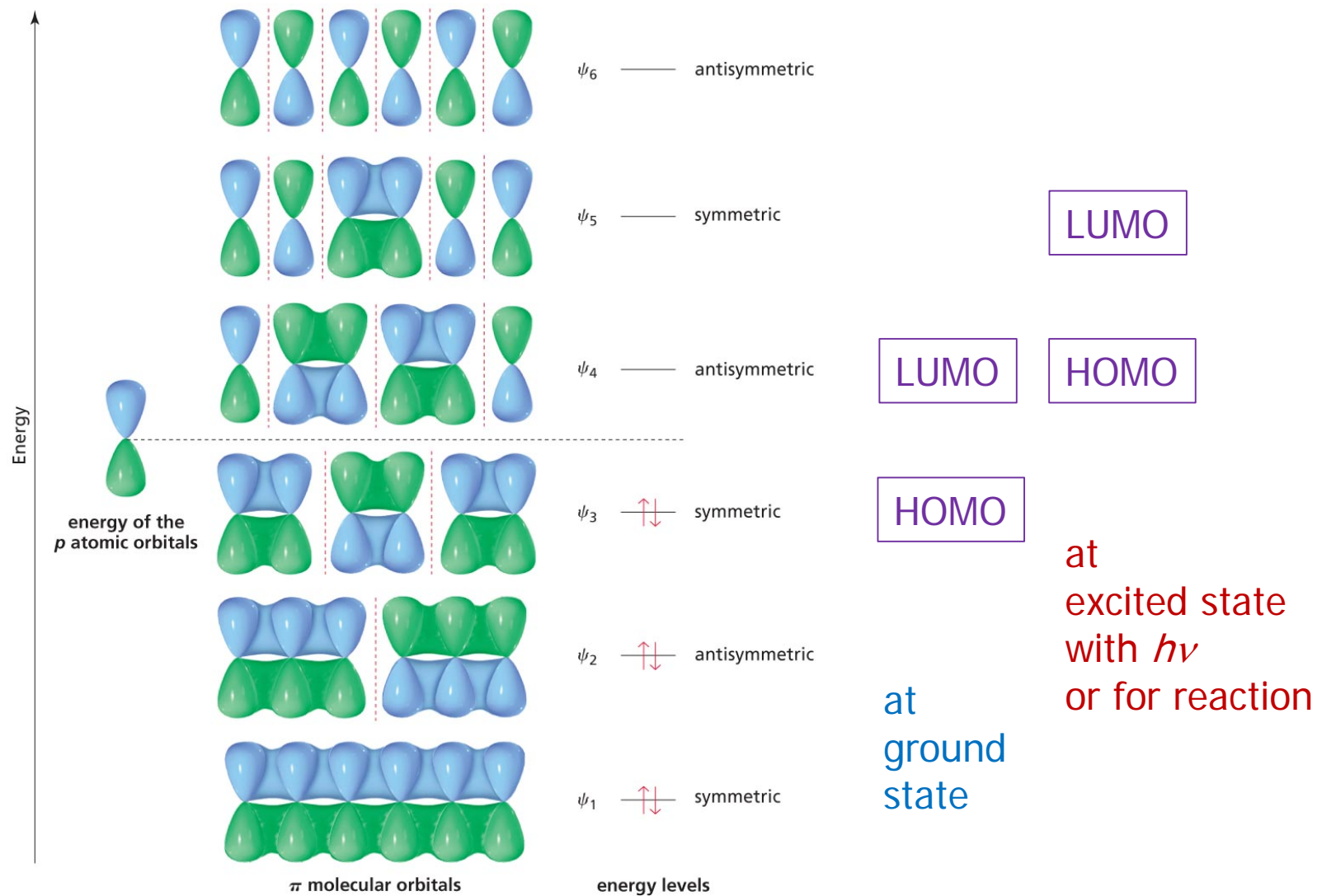


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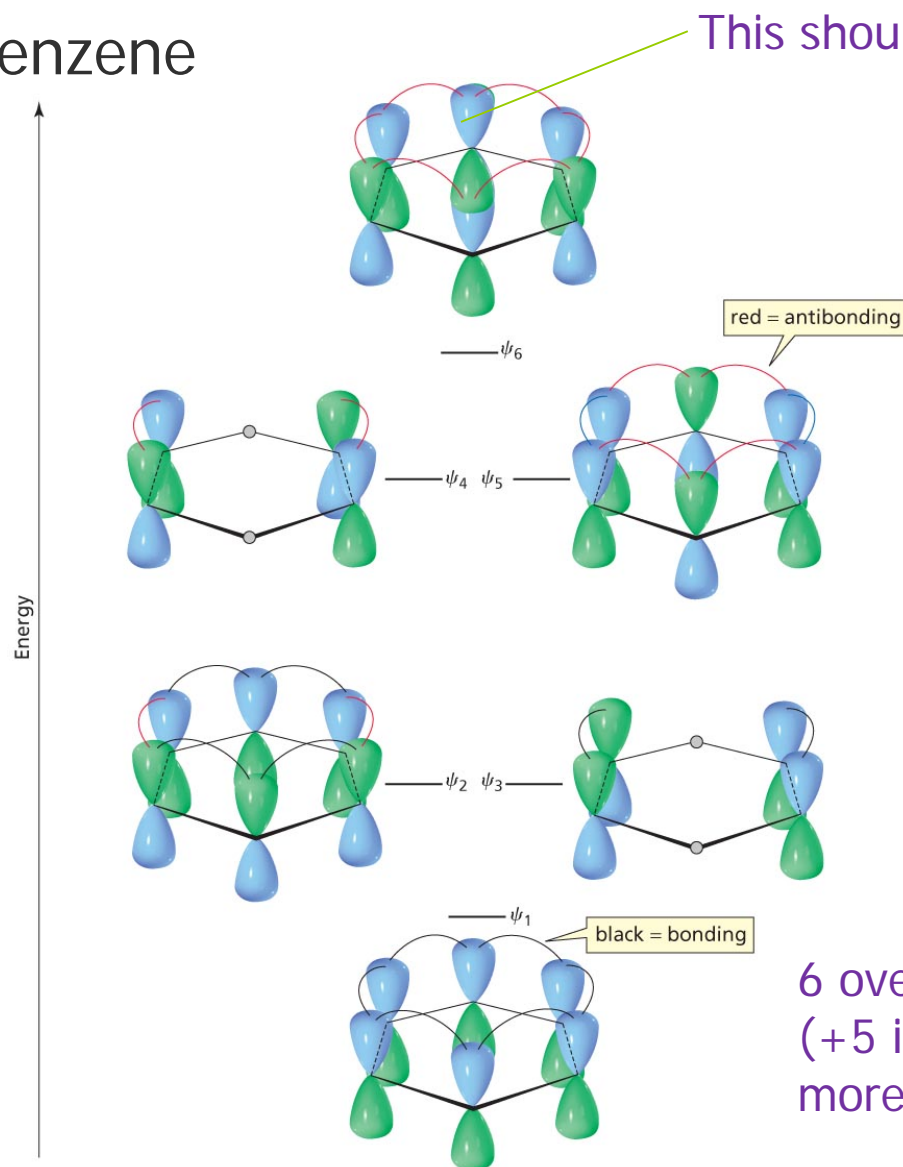
■ symmetric vs anti-symmetric MO



□ 1,3,5-hexatriene



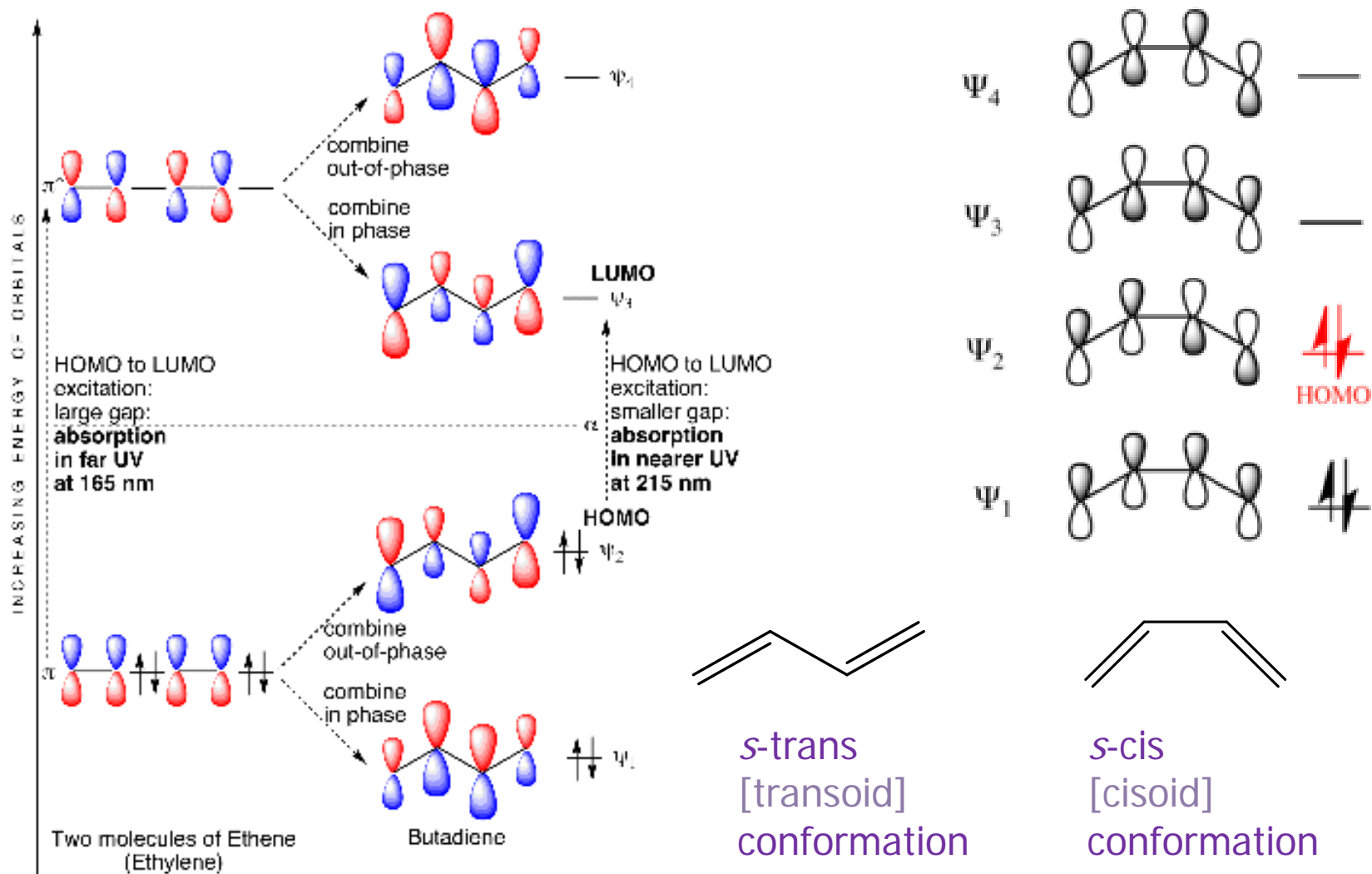
□ benzene



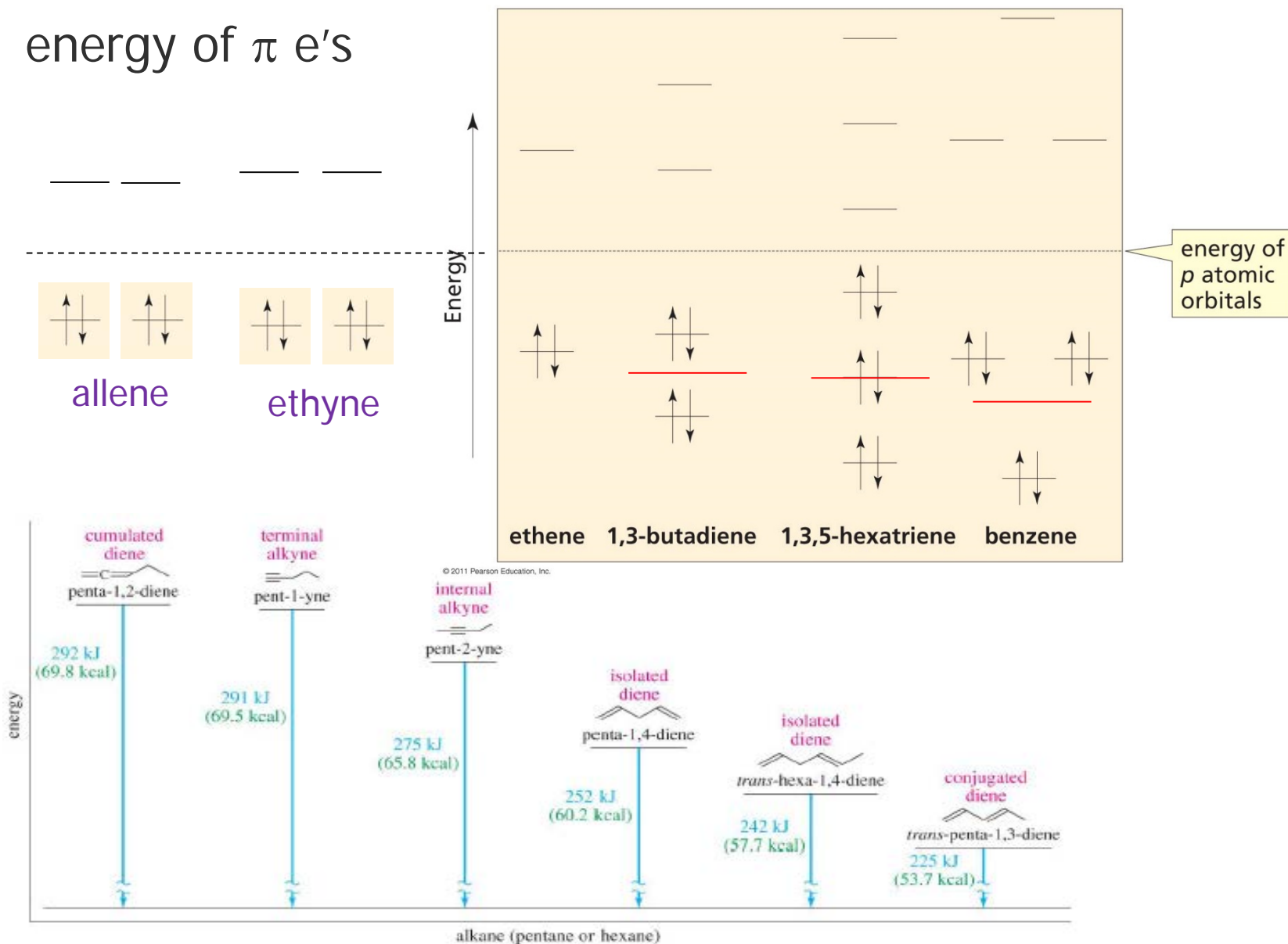
Ψ_2 and Ψ_3 degenerate
+2 bonding interactions

6 overlaps – 0 node = +6
(+5 in lowest-E MO of 1,3,5-hexatriene)
more resonance-stabilized ~ aromaticity

conformations of 1,3-butadiene



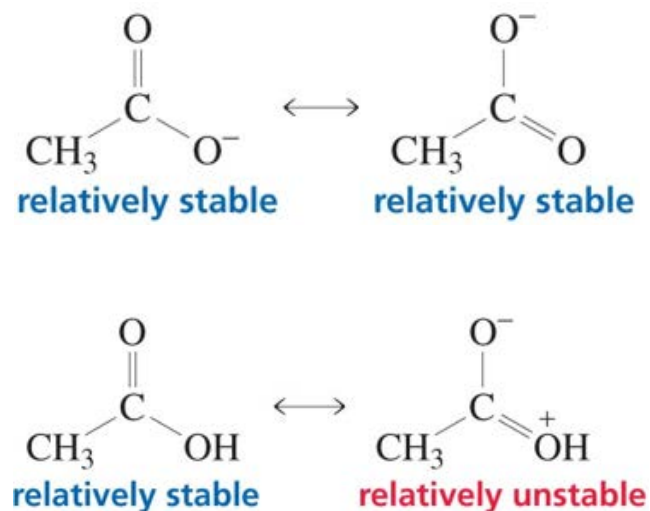
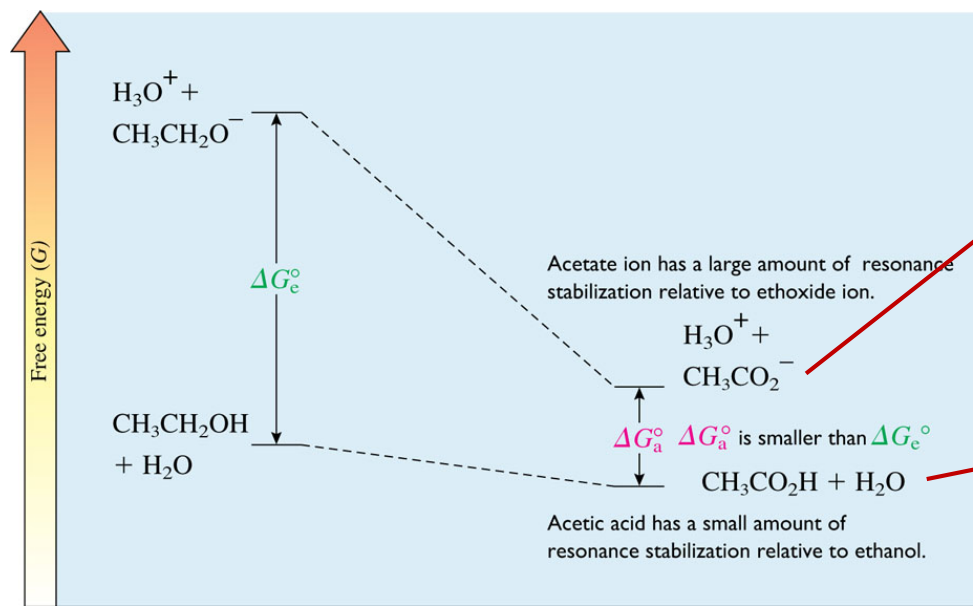
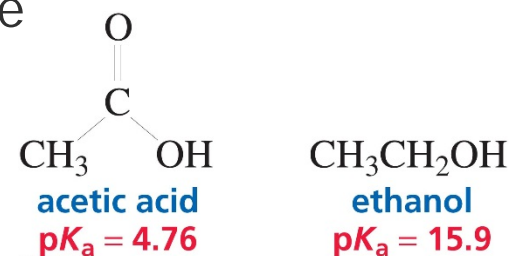
□ energy of π e's



Resonance and acidity

Ch 7 #29

- Carboxylic acids are (much) stronger acids than alcohols.
 - inductive effect (of e-withdrawing O)
 - account for the (smaller) part of the difference
 - resonance effect
 - stabilize conj base (more than acid)

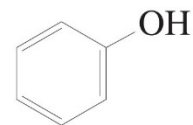


□ phenols vs cycloalkanols

■ inductive

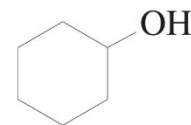
□ sp^2 C vs sp^3 C

■ resonance



phenol
 $pK_a = 10$

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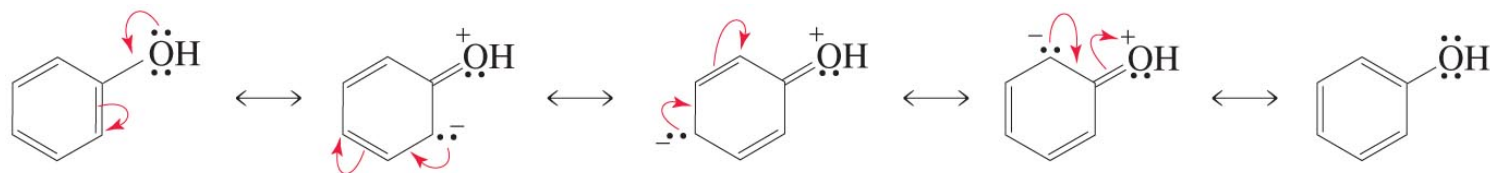


cyclohexanol
 $pK_a = 16$



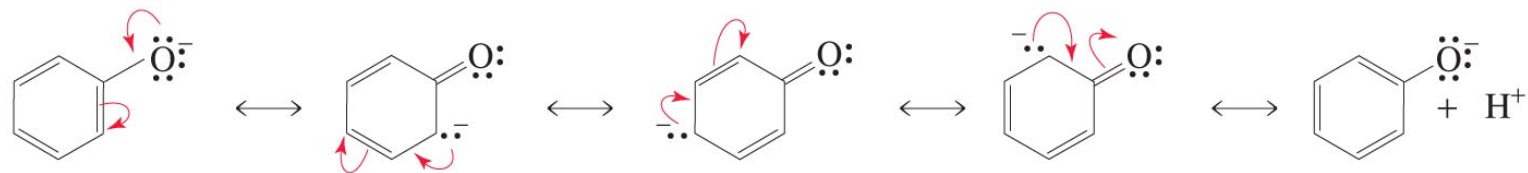
ethanol
 $pK_a = 16$

phenol = carboxylic acid



phenol

charge separation and O^+ (and C^-)
→ less important forms



phenolate ion

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C^- → less important forms

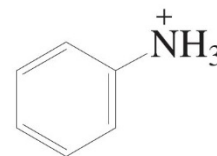
→ lower resonance energy (than carboxylic acid)

□ arylamine vs alkylamine

■ inductive

□ sp^2 C vs sp^3 C

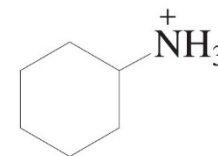
■ resonance



protonated aniline

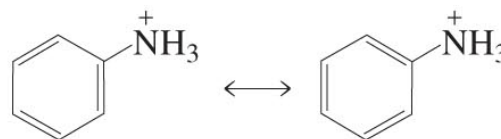
$pK_a = 4.60$

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protonated cyclohexylamine

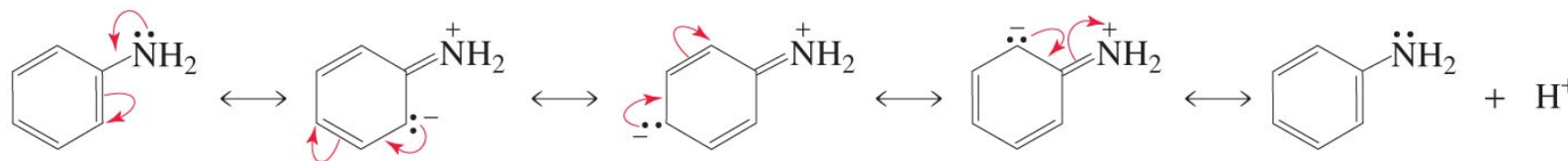
$pK_a = 11.2$



protonated aniline

no lone pair of N
cyclic resonance only

cyclic resonance +



aniline

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□ Arylamines are weaker base than alkylamines

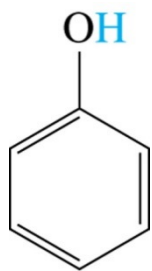
Organic acids (and bases)

Ch 7 #32

$pK_a < 0$	$pK_a \approx 5$	$pK_a \approx 10$	$pK_a \approx 15$
ROH^+ H	$\text{R}-\text{C}(=\text{O})-\text{OH}$	RNH_3^+	ROH
HO^+ $\text{C}=\text{O}$ $\text{R}-\text{C}-\text{OH}$	$\text{C}_6\text{H}_5\text{NH}_3^+$	$\text{C}_6\text{H}_5\text{OH}$	H_2O
H_3O^+			

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- acid stronger by
 - inductive effect
 - e-withdrawing through σ bonds
 - resonance effect
 - resonance-stabilizing (conj base)
 - resonance e-withdrawing (through π bonds)



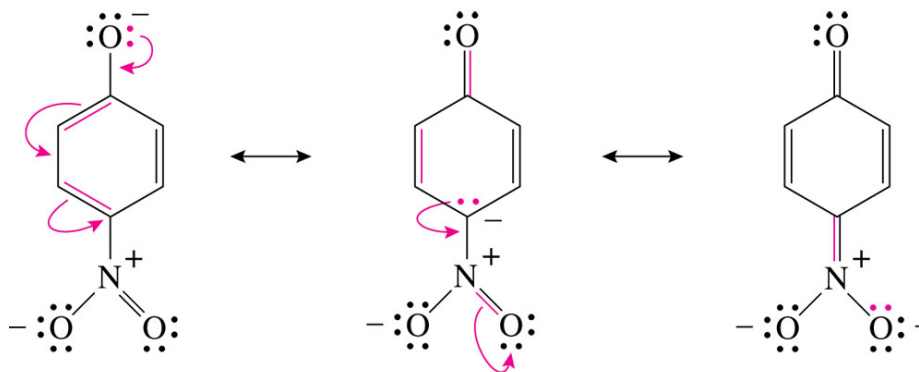
Phenol
 $pK_a = 10$

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p-Nitrophenol
 $pK_a = 7.15$

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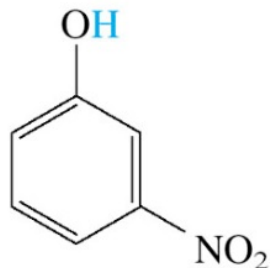
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- inductive effect of NO_2
- resonance effect
 - resonance-stabilizing conj base
 - additional resonance contributors due to NO_2
 - resonance e-withdrawing of NO_2



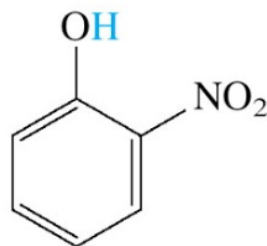
p-Nitrophenol
 $pK_a = 7.15$

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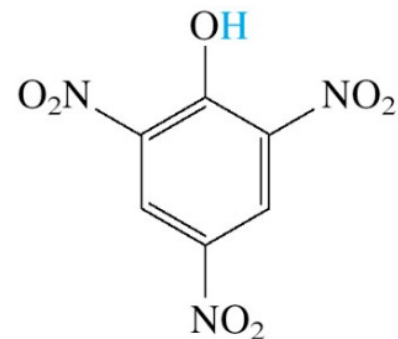


m-Nitrophenol
 $pK_a = 8.36$

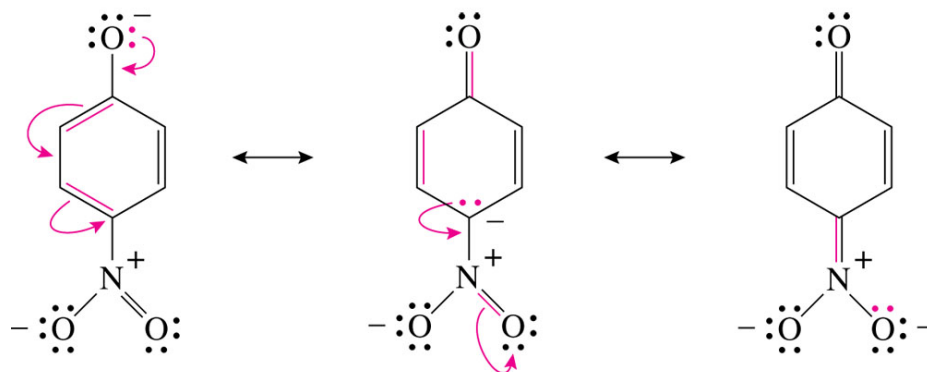
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o-Nitrophenol
 $pK_a = 7.22$



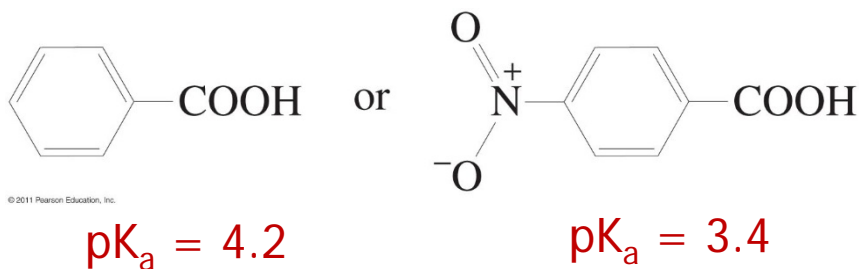
2,4,6-Trinitrophenol
 (picric acid)
 $pK_a = 0.42$



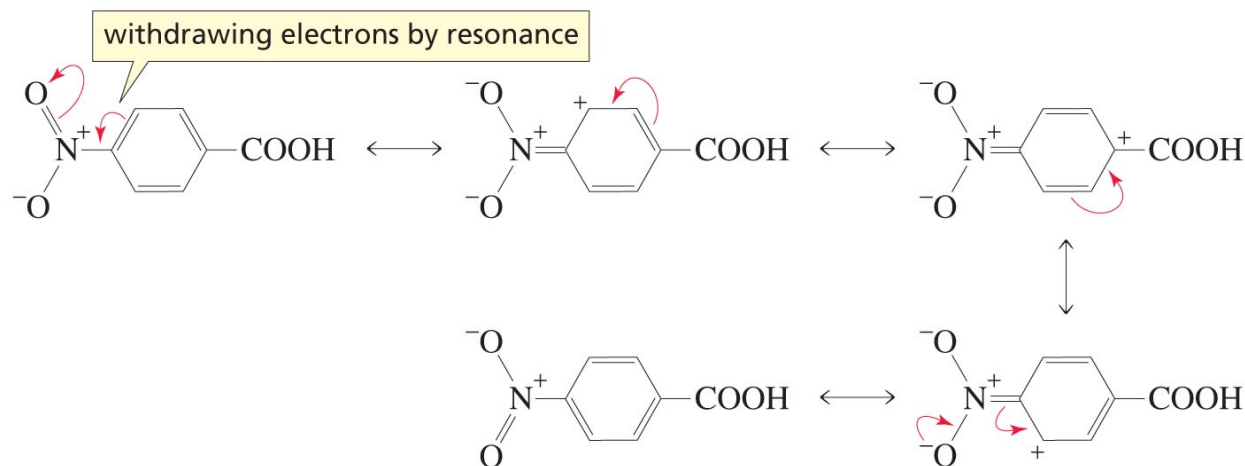
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Resonance e-withdrawing or donating Ch 7 #35

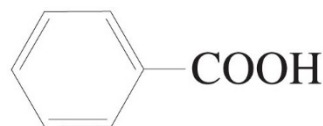
□ Prob 19 p304



- (additional) resonance stabilization effect (of NO_2)?
 - No. not with COO^- . same to acid and conj base.
- inductive effect of (e-withdrawing) NO_2
- resonance e-withdrawing NO_2



□ Prob 20 p305



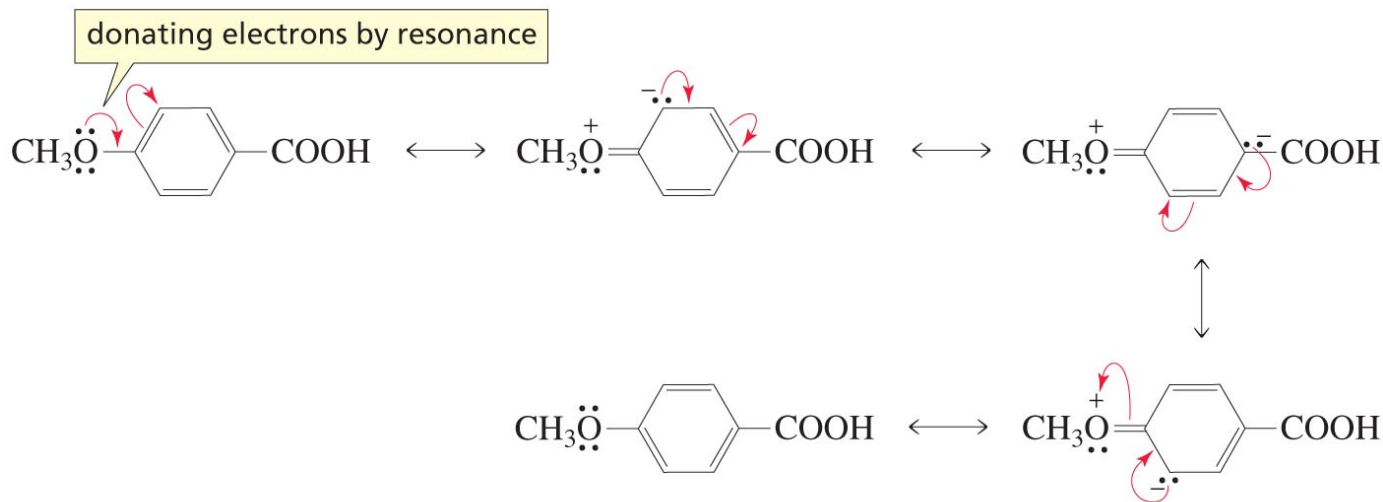
$pK_a = 4.20$

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$pK_a = 4.47$

- inductive e-withdrawing OCH_3
- resonance e-donating OCH_3

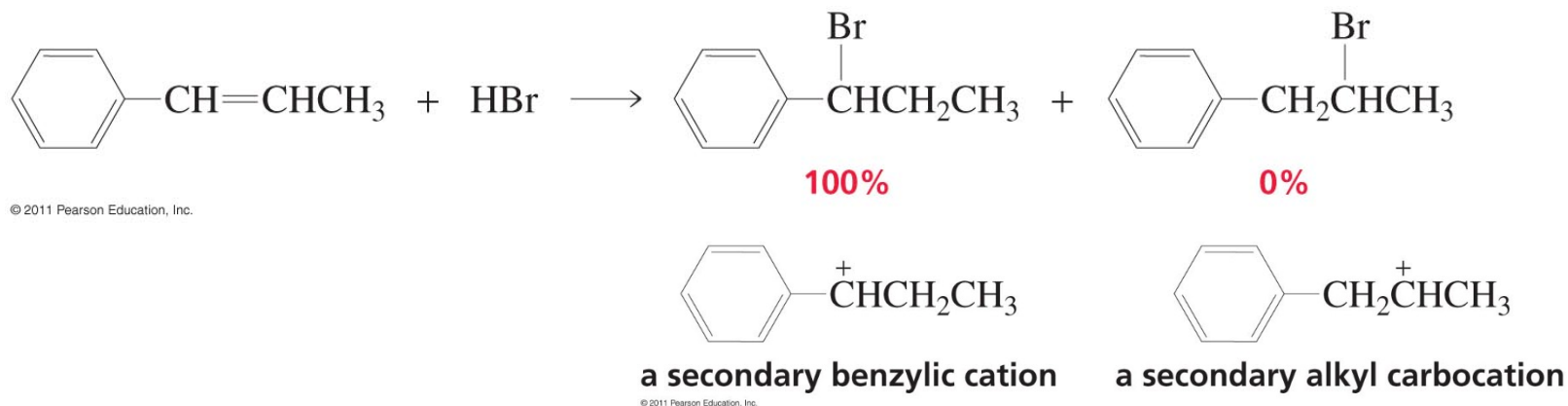


- resonance effect outweighs inductive effect

Resonance and rxn product

Ch 7 #37

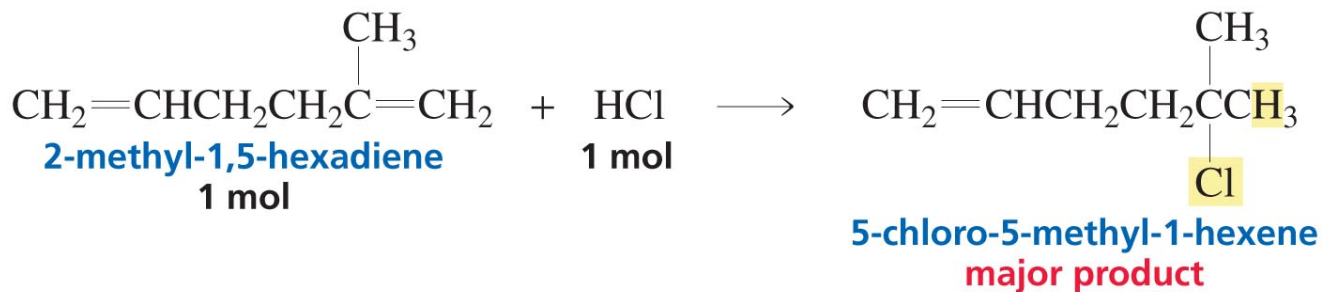
□ resonance-stabilized intermediate



□ reaction of isolated dienes



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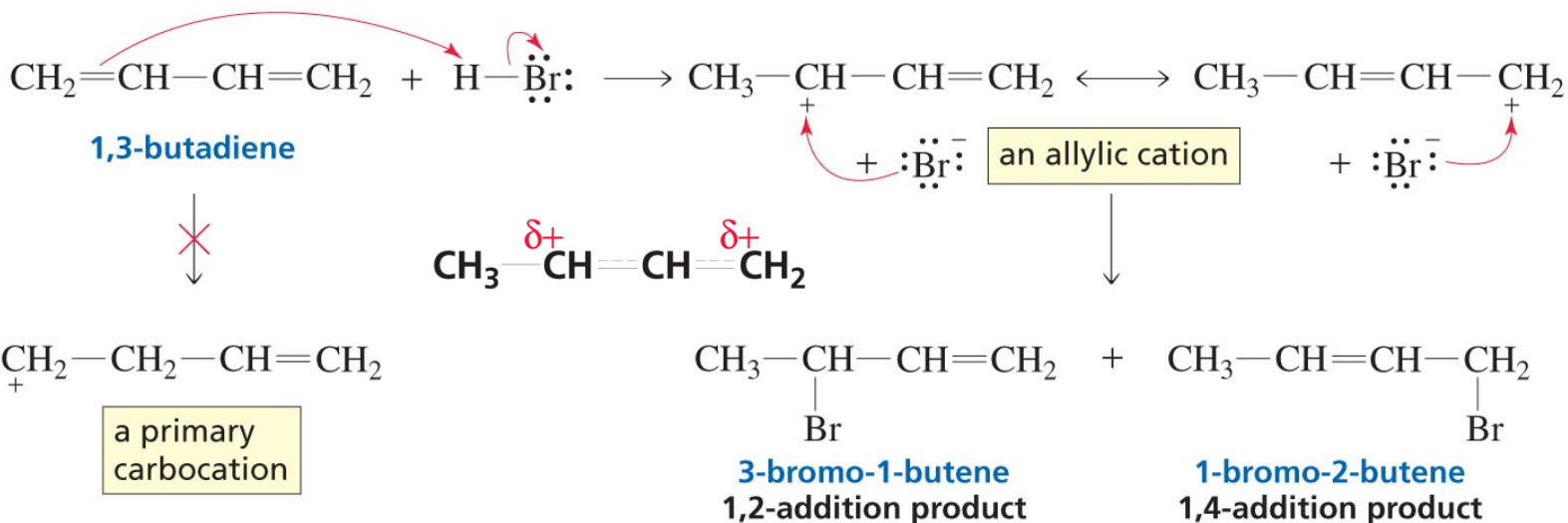
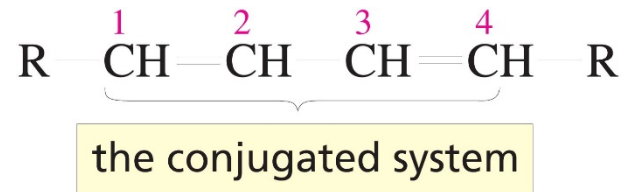
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Reaction of conjugated dienes

Ch 7 #38

□ addition to **symmetrical** conj diene

■ 1,2- and 1,4-addition



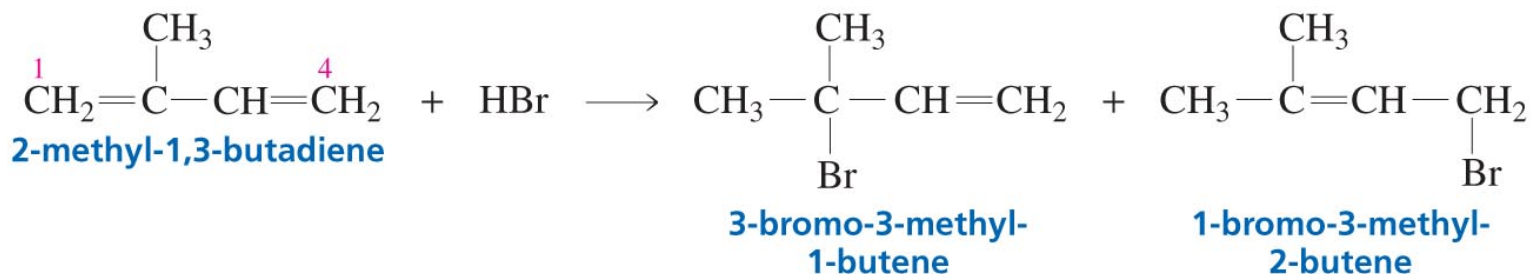
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■ H⁺ adds to C1 or C4, not to C2 or C3

□ 1° vs resonance hybrid

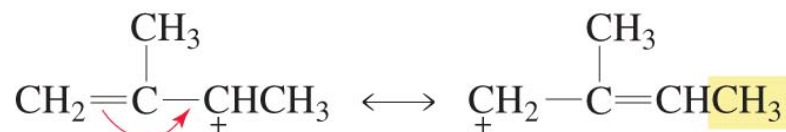
■ 1,2- > 1,4- ?

□ addition to **unsymmetrical** conj diene



carbocation formed by adding H⁺ to C-1

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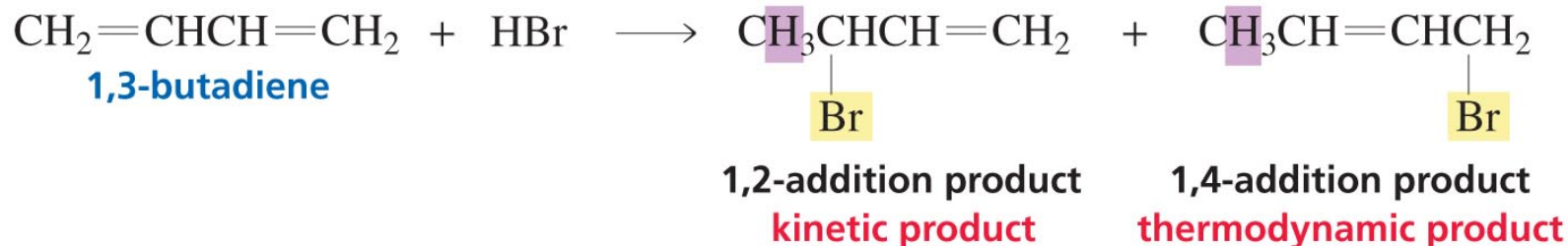


carbocation formed by adding H⁺ to C-4

- H⁺ adds not to C2 or C3
- H⁺ adds to C1 or C4
 - {1,2- + 1,4-addition} or {3,4- + 1,4-addition}
 - {3° + 1° C⁺} or {2° + 1° C⁺}
 - {mono- + tri-subst =} or {di- + tri-subst =}

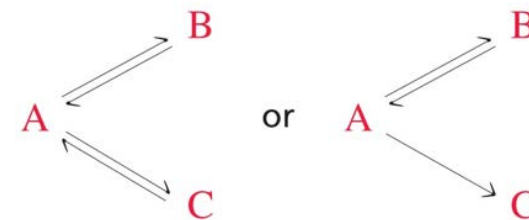
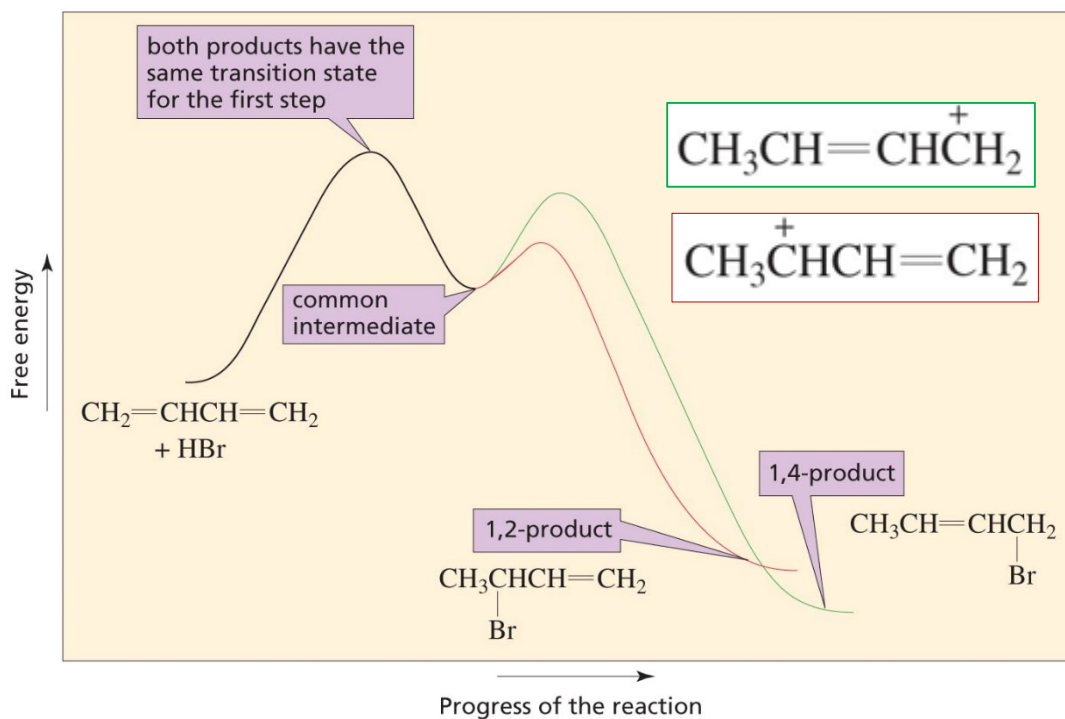
Kinetic vs thermodynamic control

Ch 7 #40

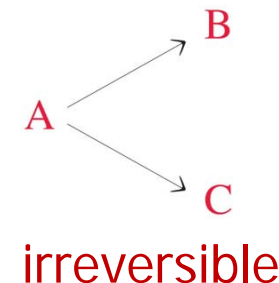


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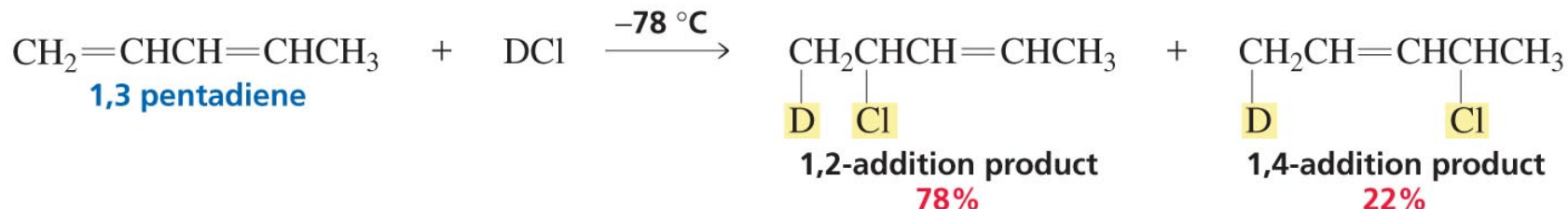
at -80 °C	80%	20%
at 45 °C	15%	85%



reversible

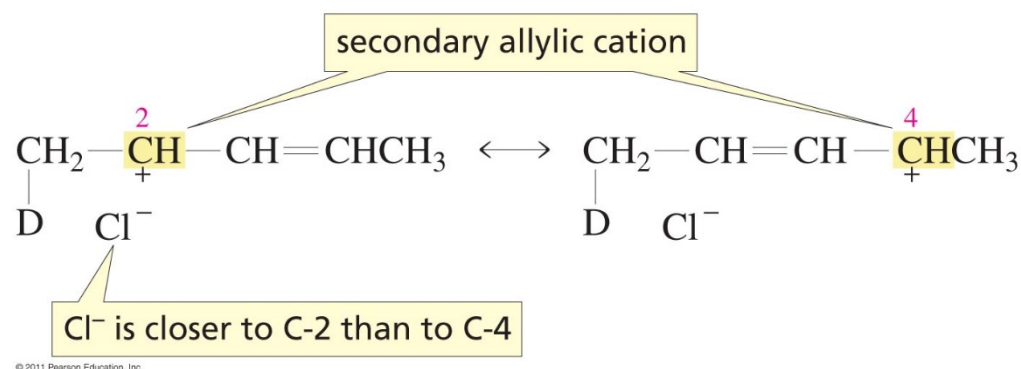


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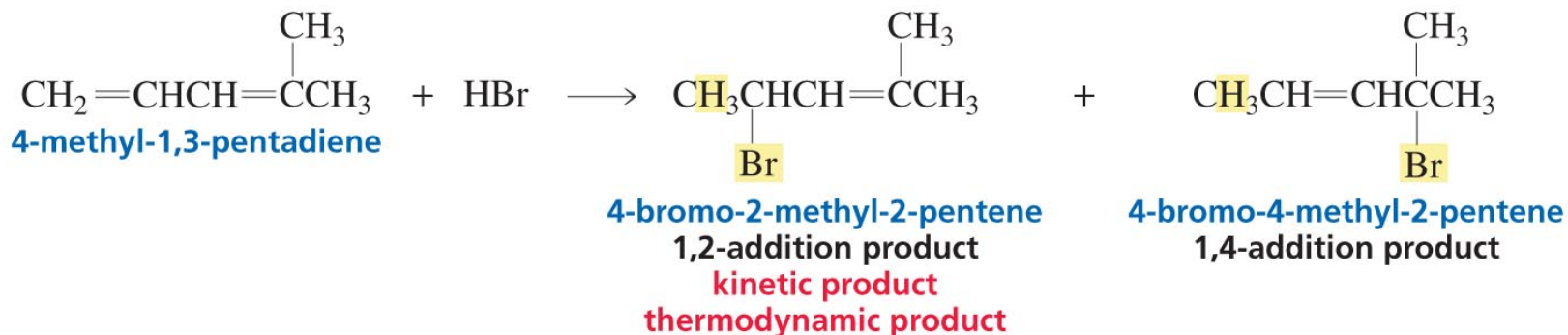


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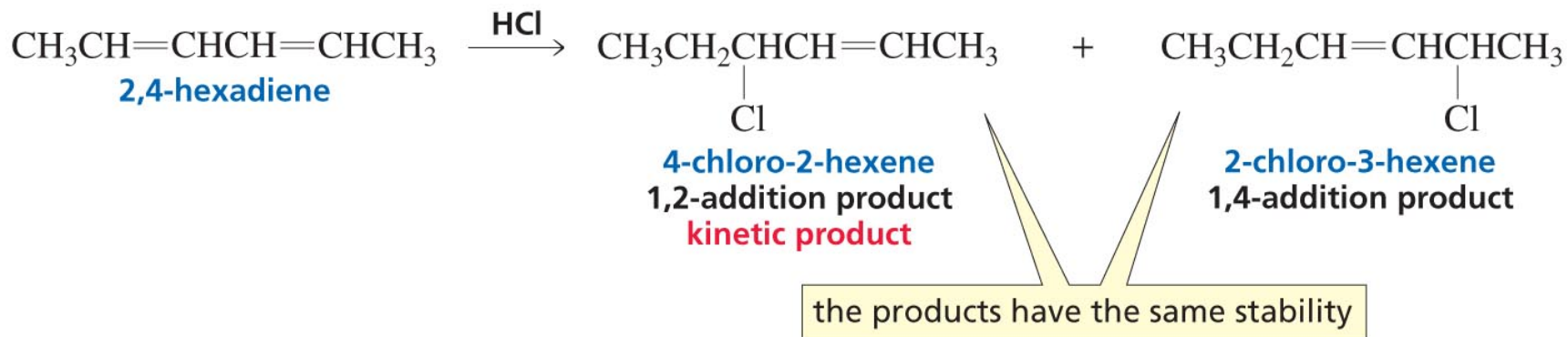
- Why not 50/50?
- proximity effect



□ Due to proximity effect, 1,2- is **always** the kinetic product.



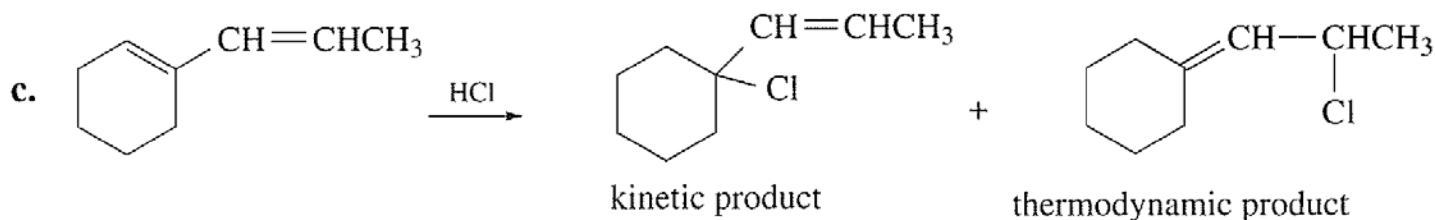
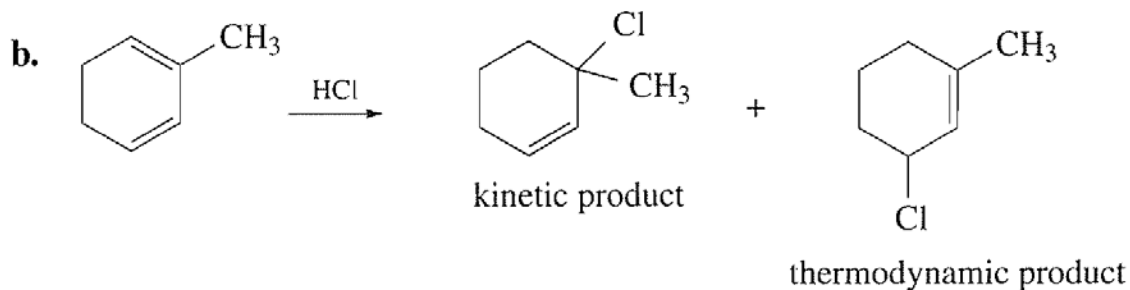
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- As temp up, reaction goes to 50/50.

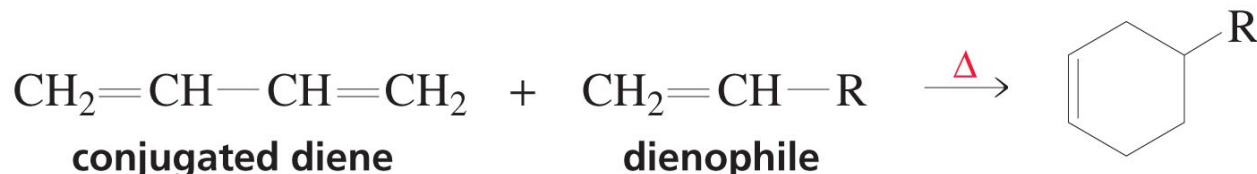
Prob 31 p314



Diels-Alder reaction

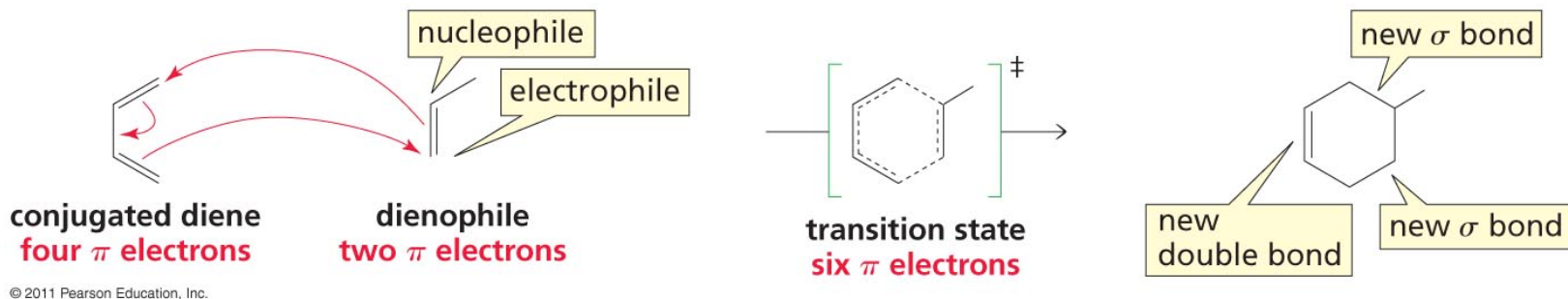
Ch 7 #43

- reaction of **conjugated diene** and alkene [**dienophile**]



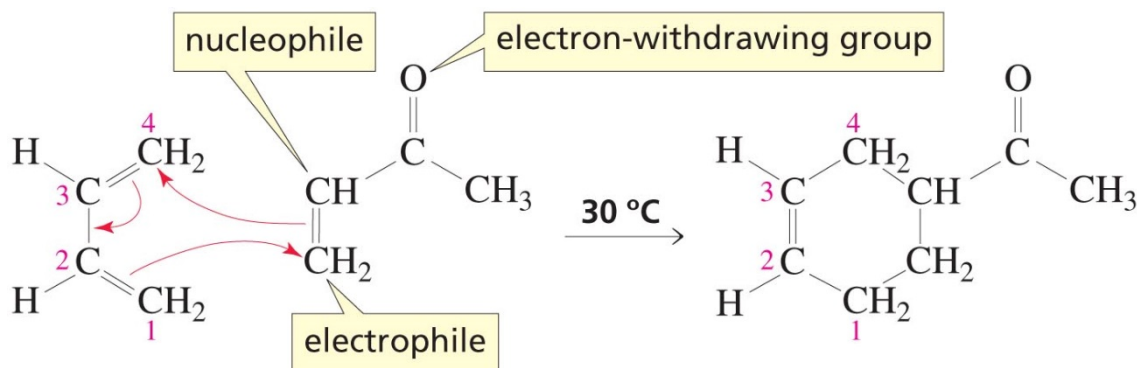
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- a pericyclic reaction
= **concerted** rxn thru cyclic TS



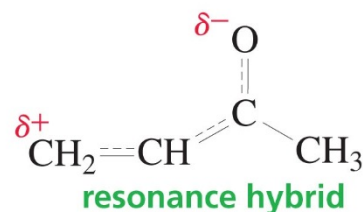
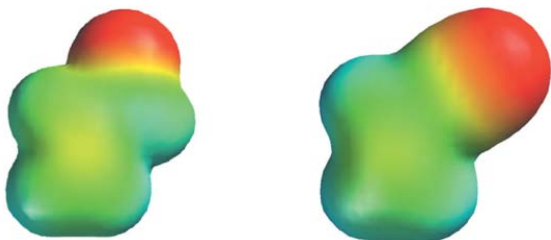
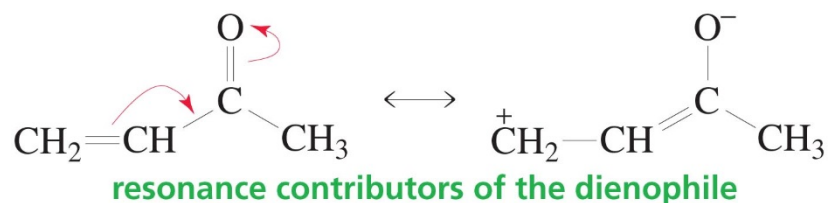
- a [4 + 2] **cycloaddition**
 - 4 π e's + 2 π e's from 3 π bonds of reactants
 - to form 6-π-e cyclic TS
 - and cyclic product with 1 π [2 e] and 2 σ [4 e] bonds

- a 1,4-addition reaction



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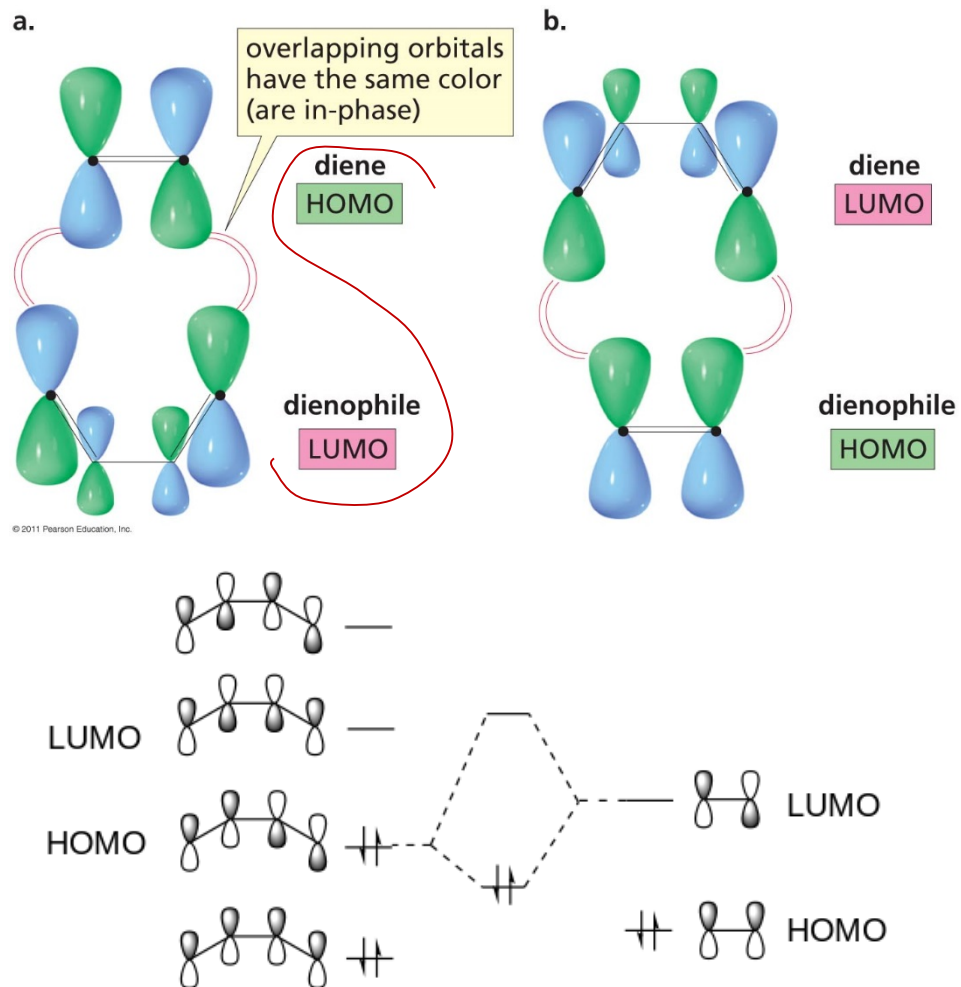
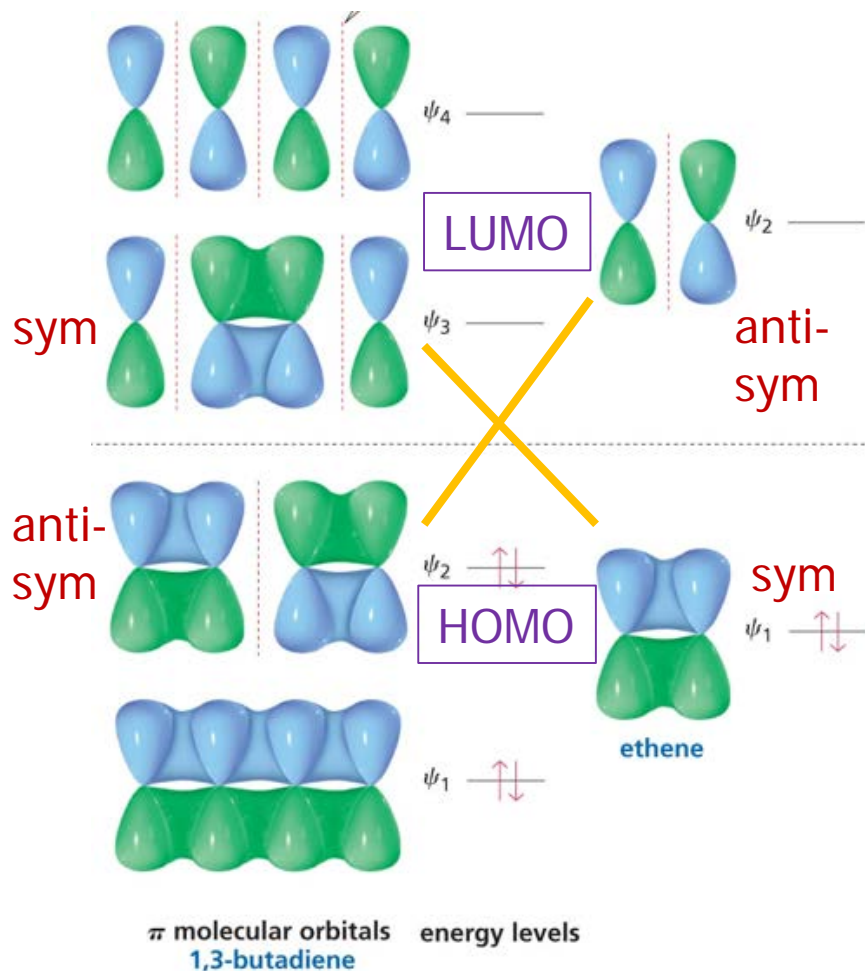
- e-withdrawing group (like C=O or C≡N) makes C of dienophile electrophilic

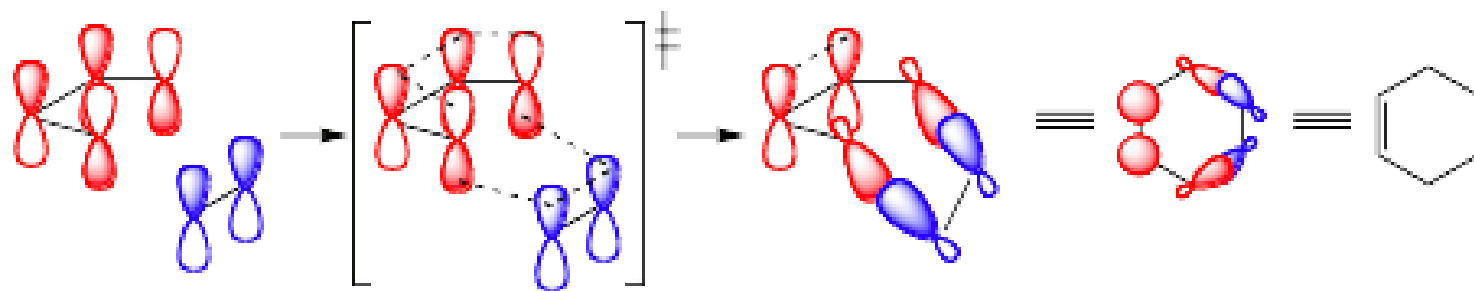
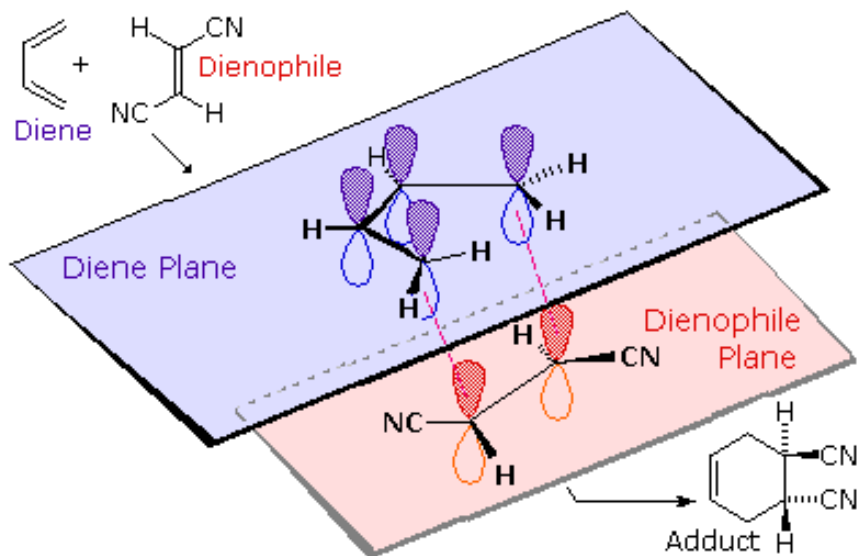


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MO view of D-A rxn

- to form bond, e transfer from HOMO to LUMO and overlap of orbitals

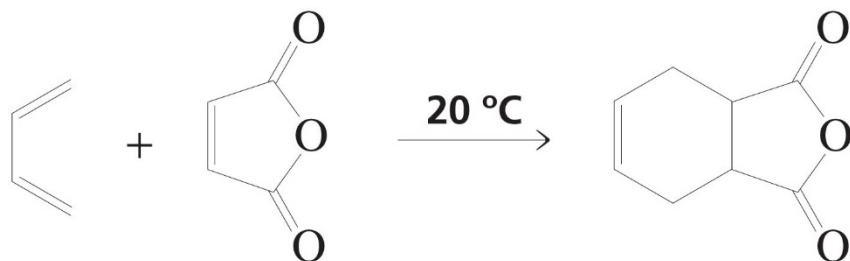




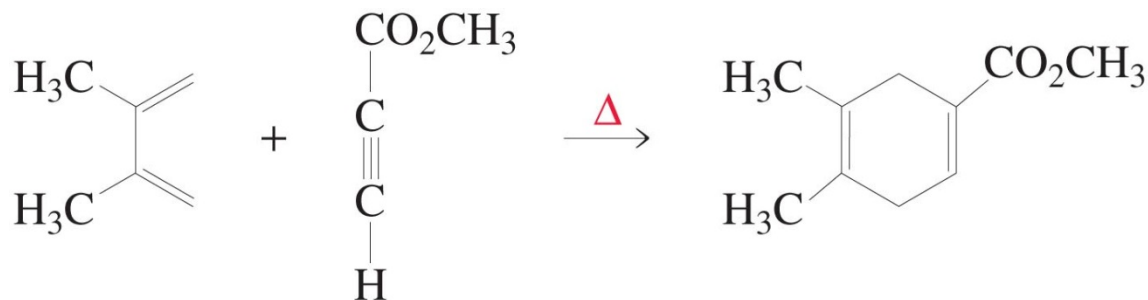
re-hybridization
from p to sp^3

D-A reaction: examples

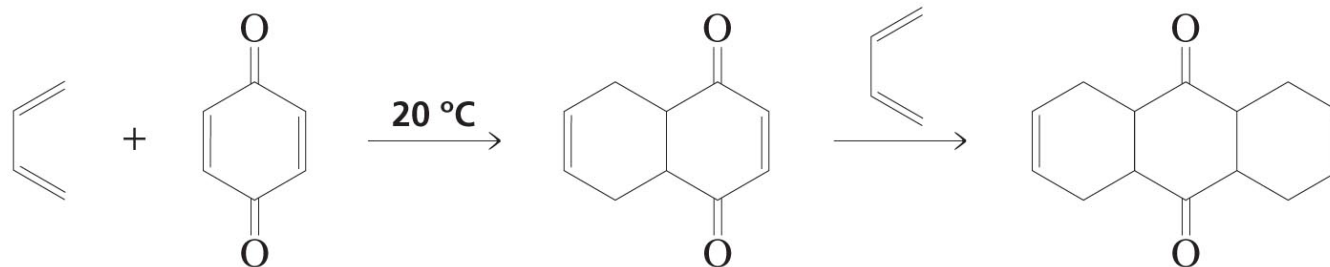
Ch 7 #47



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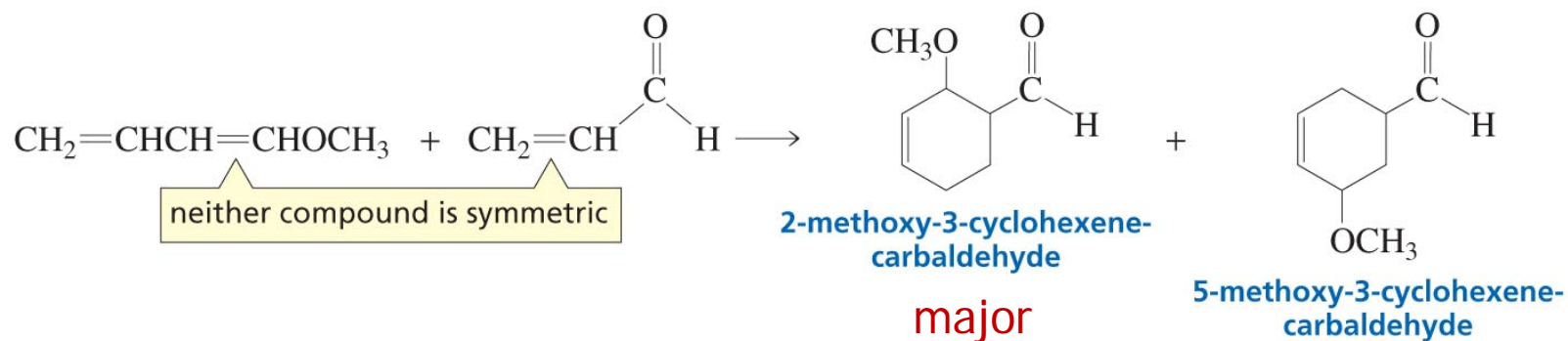
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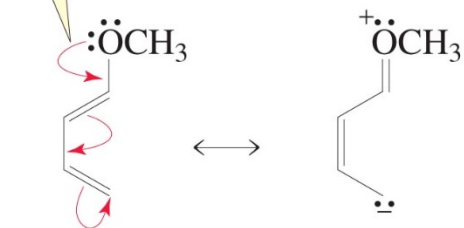
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D-A reaction: regioselectivity

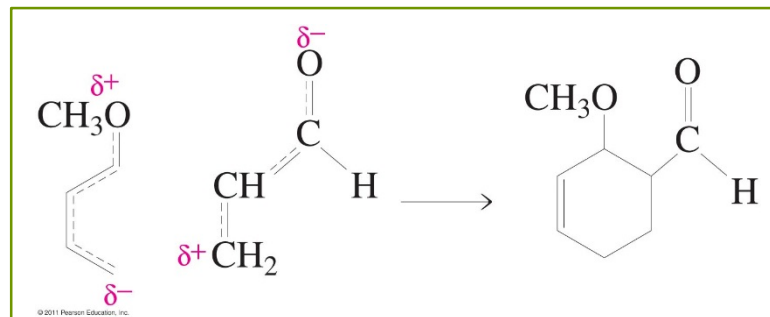
Ch 7 #48



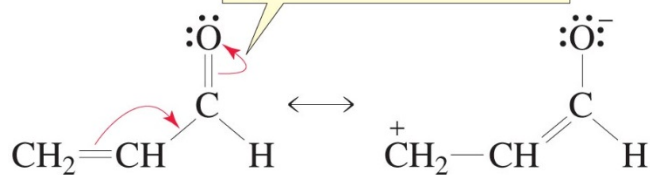
donating electrons by resonance



resonance contributors of the diene

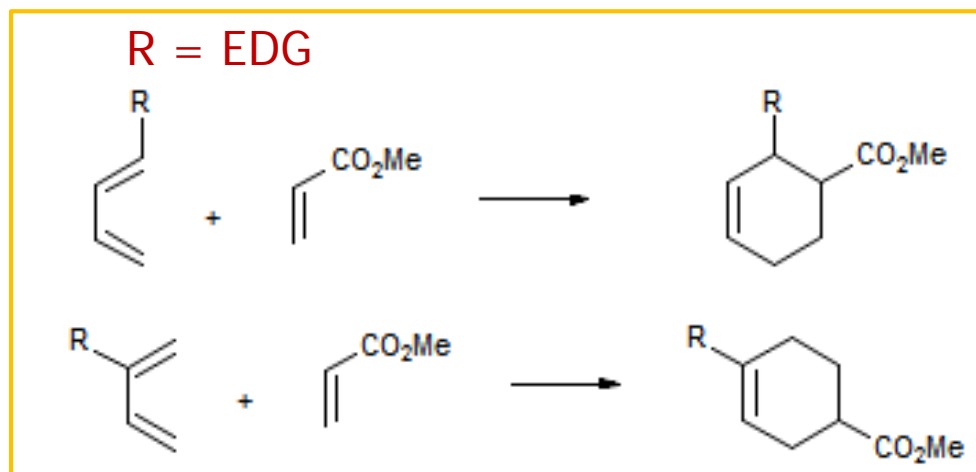


withdrawing electrons by resonance



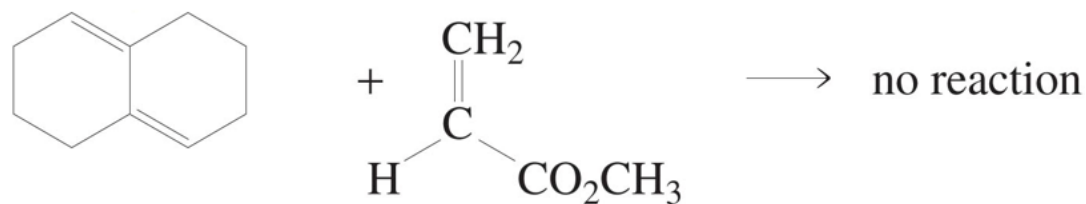
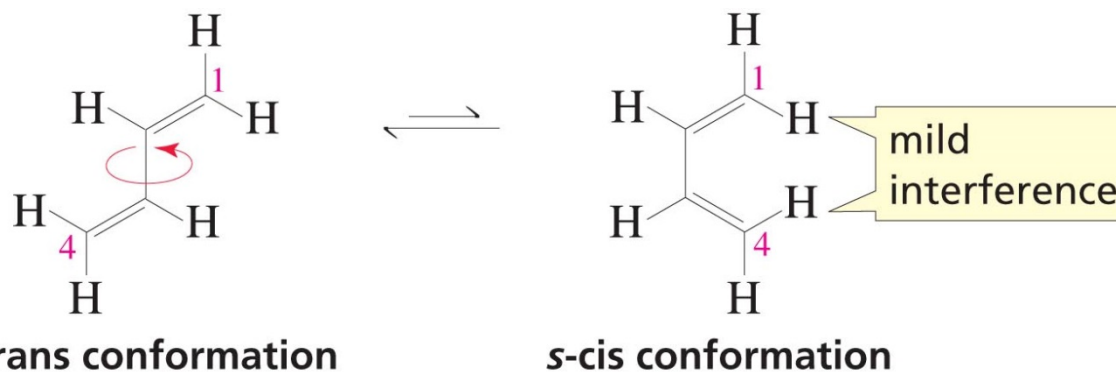
resonance contributors of the dienophile

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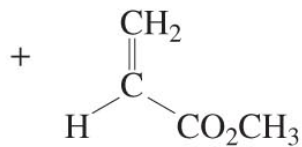


D-A reaction: conformation of diene

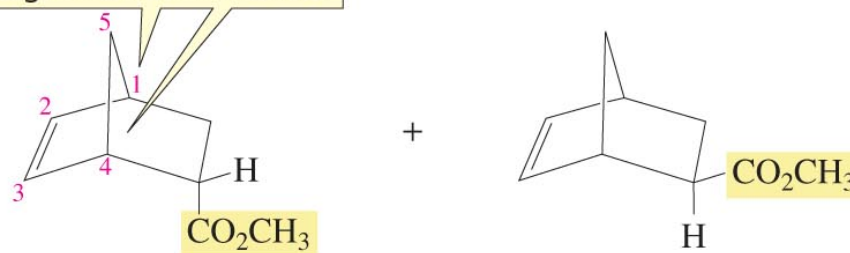
Ch 7 #49



locked in an s-cis conformation



both rings share these carbons

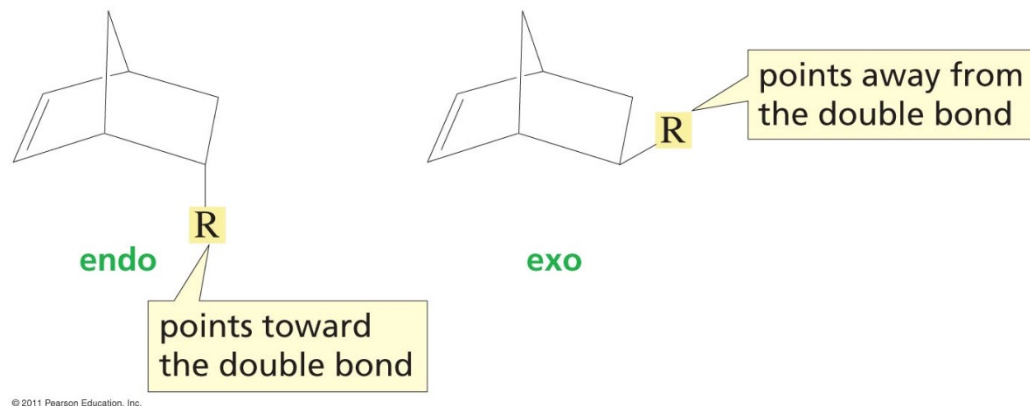


bridged bicyclic compounds

D-A reaction: stereochemistry

Ch 7 #50

□ endo rule (by Alder)



endo sterically hindered,
but some (secondary π orbital)
interaction \rightarrow favored

