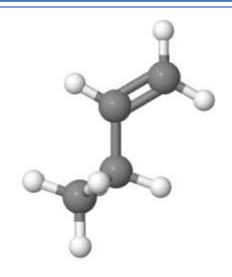
2302263 – Organic Chemistry I – Part III Lecture 2-2

Alkenes – Properties and Preparations



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Recommended Textbook:

Chapter 7 in *Organic Chemistry*, 8th Edition, L. G. Wade, Jr., **2010**, Prentice Hall (Pearson Education)

Alkene energies are often compared by measuring the **heat of hydrogenation**: the heat given off (ΔH°) during catalytic hydrogenation.

$$H_2C = CH - CH_2 - CH_3 + H_2$$

$$\begin{array}{c} H & H \\ | & | \\ CH_2 - CH - CH_2 - CH_3 \\ \text{but-1-ene} \\ \text{(monosubstituted)} \end{array}$$

$$\begin{array}{c} D_1 & H & H \\ | & | \\ CH_2 - CH - CH_2 - CH_3 \\ \text{butane} \end{array}$$

$$\begin{array}{c} D_1 & D_2 \\ D_2 & D_3 \\ D_3 & D_4 \\ D_4 & D_5 \end{array}$$

H H

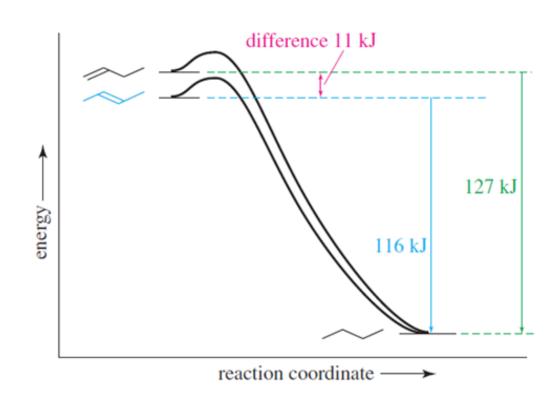
CH₂—CH—CH₂—CH

butane

$$\Delta H^{\circ} = -127 \text{ kJ/mol}$$

$$H_3C$$
 H
 $C=C$
 H
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_4
 CH_3
 CH_4
 CH_5
 CH_5
 CH_5
 CH_5
 CH_6
 CH_7
 CH_7

$$H$$
 H H CH_3 $-CH$ $-CH$ $-CH_3$ butane
$$\Delta H^{\circ} = -116 \text{ kJ/mol}$$



Stability: Disubstituted > Monosubstituted (11 kJ/mol)

$$\begin{array}{c} \text{CH}_{3} \\ \text{CH}_{2} = \text{CH} - \text{CH} - \text{CH}_{3} \\ \text{3-methylbut-1-ene} \\ \text{(monosubstituted)} \end{array} \xrightarrow{\begin{array}{c} \text{H}_{2}, \text{Pt} \\ \text{2-methylbutane} \end{array}} \begin{array}{c} \text{CH}_{3} \\ \text{2-methylbutane} \end{array}$$

$$\begin{array}{c} \text{CH}_{3} \\ \text{2-methylbut-2-ene} \\ \text{(trisubstituted)} \end{array} \xrightarrow{\begin{array}{c} \text{CH}_{3} \\ \text{2-methylbut-2-ene} \\ \text{(trisubstituted)} \end{array}} \xrightarrow{\begin{array}{c} \text{CH}_{3} \\ \text{2-methylbutane} \end{array}} \begin{array}{c} \text{CH}_{3} \\ \text{2-methylbutane} \end{array}$$

Stability: Trisubstituted > Monosubstituted (16 kJ/mol)

		Molar Heat of Hydrogenation (–∆ <i>H</i> °)				
Name	Structure	kJ	kcal	General Structure		
ethene (ethylene)	$H_2C = CH_2$	137	32.8}	unsubstituted		
propene (propylene) but-1-ene pent-1-ene hex-1-ene 3-methylbut-1-ene 3,3-dimethylbut-1-ene	$\begin{array}{l} \text{CH}_{3}\text{CH}\text{=-}\text{CH}_{2} \\ \text{CH}_{3}\text{CH}_{2}\text{CH}\text{CH}_{2} \\ \text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{CH}\text{CH}_{2} \\ \text{CH}_{3}(\text{CH}_{2})_{3}\text{CH}\text{CH}_{2} \\ \text{(CH}_{3})_{2}\text{CH}\text{CH}\text{CH}_{2} \\ \text{(CH}_{3})_{3}\text{C}\text{CH}\text{CH}_{2} \end{array}$	126 127 126 126 127 127	30.1 30.3 30.1 30.1 30.3 30.3	monosubstituted R—CH=CH ₂		
cis-but-2-ene	CH ₃ C=C CH ₃	120	28.6	disubstituted (cis)		
cis-pent-2-ene	CH_3 — CH_2 $C=C$ H	120	28.6	Н Н		
2-methylpropene (isobutylene)	$(CH_3)_2C = CH_2$	117	28.0			
2-methylbut-1-ene	CH ₃ —CH ₂ —C=CH ₂ CH ₃	119	28.5	disubstituted (geminal)		
2,3-dimethylbut-1-ene	$(CH_3)_2CH$ — C — CH_2 CH_3	117	28.0	C = CH_2		
trans-but-2-ene	CH_3 $C=C$ CH_3	116	27.6	disubstituted (trans)		
trans-pent-2-ene	CH_3 — CH_2 $C=C$ CH_3	116	27.6	C=C R		
2-methylbut-2-ene	CH ₃ —C=CH—CH ₃	113	26.9	trisubstituted R ₂ C≔CHR		
2,3-dimethylbut-2-ene	$(CH_3)_2C = C(CH_3)_2$	111	26.6	tetrasubstituted R ₂ C==CR ₂		

More substituted double bonds are usually more stable.

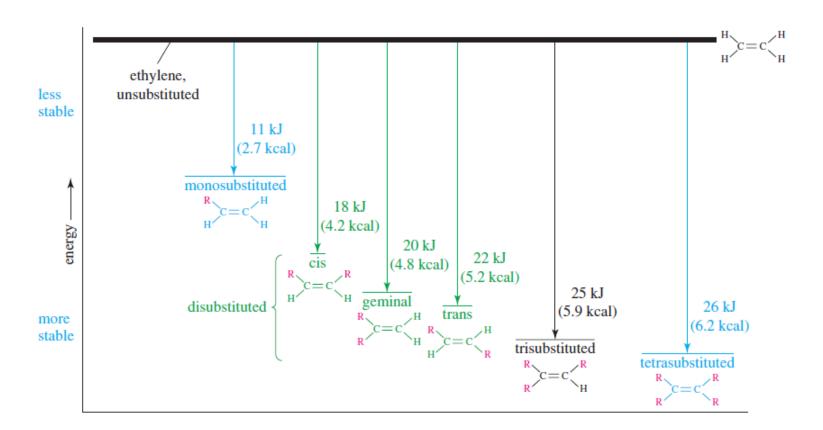
1) Electronic

2) Steric

closer groups

wider separation

trans isomers are generally more stable than the corresponding cis isomers



Stability of Cycloalkenes

Most cycloalkenes react like acyclic (noncyclic) alkenes.

3 and 4-membered rings show evidence of ring strain

HH H H
$$H_2$$
 Pt H_1 H_2 H_3 H_4 H_4 H_4 H_5 H_6 H_7 H_8 H_8

cyclopropene

H

propene

Stability of Cycloalkenes

For acyclic systems, trans alkenes are usually more stable than cis isomers.

For *trans* cycloalkenes:

- 3 6 membered ring = unable to complete the ring systems
- 7 9 membered ring = **less stable** than *cis* isomer

>10 membered ring = nearly as stable as the cis isomer

Example 1 Predict which member of each pair is more stable

(a) 2-methylbut-1-ene

(b) cis, cis-hexa-2,4-diene

or 3-methylbut-1-ene

or trans,trans-hexa-2,4-diene

(c) 1,2-dimethylcyclopropene

(d) trans-1,2-dimethylcyclodecene

or 1,2-dimethylcyclopentene

or trans-1,2-dimethylcycloheptene

Physical Properties of Alkenes

Boiling Points, Densities, and Polarity: similar to those of the corresponding alkanes

Name	Structure	Carbons	Boiling Point (°C)	Density (g/cm ³)
ethene (ethylene)	$CH_2 = CH_2$	2	-104	
propene (propylene)	$CH_3CH = CH_2$	3	-47	0.52
2-methylpropene (isobutylene)	$(CH_3)_2C = CH_2$	4	-7	0.59
but-1-ene	$CH_3CH_2CH = CH_2$	4	-6	0.59
	H ₃ C H			
trans-but-2-ene	C = C	4	1	0.60
irans-bat-2-che	H CH ₃	7	1	0.00
	H ₃ C CH ₃			
cis-but-2-ene	C = C	4	4	0.62
cus out 2 one	"	•	7	0.02
2		5	25	0.65
3-methylbut-1-ene	$(CH_3)_2CH$ — CH = CH_2	5 5	25	0.65
pent-1-ene	$CH_3CH_2CH_2$ — CH = CH_2	3	30	0.64
	H ₃ C H			
trans-pent-2-ene	C=C(5	36	0.65
	H CH ₂ CH ₃			
	H ₃ C CH ₂ CH ₃			
-i		5	37	0.66
cis-pent-2-ene	c=c	5	37	0.66
	Н Н			
2-methylbut-2-ene	$(CH_3)_2C = CH - CH_3$	5	39	0.66
hex-1-ene	$CH_3(CH_2)_3$ — CH = CH_2	6	64	0.68
2,3-dimethylbut-2-ene	$(CH_3)_2C = C(CH_3)_2$	6	73	0.71
hept-1-ene	$CH_3(CH_2)_4$ — CH = CH_2	7	93	0.70
oct-1-ene	$CH_3(CH_2)_5$ — CH = CH_2	8	122	0.72
non-1-ene	$CH_3(CH_2)_6$ — CH = CH_2	9	146	0.73
dec-1-ene	$CH_3(CH_2)_7$ — CH = CH_2	10	171	0.74

Elimination of Alkyl Halides – E2

Use of a Bulky Base: If the substrate is prone to substitution, a bulky base can minimize the amount of substitution.

$$\begin{array}{c|c} H \\ Br \\ H \end{array} \xrightarrow{(i-Pr)_2\ddot{N}H, \text{ heat}} \begin{array}{c} H \\ + [(CH_3)_2CH]_2\ddot{N}H_2 Br^{-1} \end{array}$$

Elimination of Alkyl Halides – E2

Zaitsev vs. Hofmann product:

$$C = C$$
 CH_3
 $C = C$
 CH_3
 CH_3
 CH_3

Zaitsev product

72%

Hofmann product

$$CH_{3} - C - C - CH_{2}$$

$$H Br H$$

$$CH_{3} - C - C - CH_{2}$$

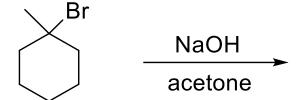
$$H Br H$$

$$CH_{3} - C - C - CH_{2}$$

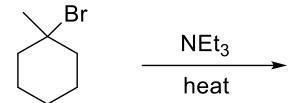
$$CH_{3} - C - C - CH_{3}$$

Example 2 For each reaction, decide whether substitution or elimination (or both) is possible, and predict the products you expect. Label the major products.

(a)



(b)



(c)



(d)

Elimination of Alkyl Halides – E1

Elimination by the E1 mechanism

Accompanied by S_N 1 substitution

Example 3 Propose mechanisms for the following reactions.

Dehydration of alcohol

The mechanism of dehydration resembles the **E1 mechanism**. The **hydroxyl group** of the alcohol is a **poor leaving group (OH-)** but **protonation** by the acidic catalyst converts it to a **good leaving group (H₂O)**

High temperature Industrial Methods



Catalytic Cracking of Alkanes

Catalytic Dehydrogenation of Alkanes