Course 343 Lecturer Sam Gellman

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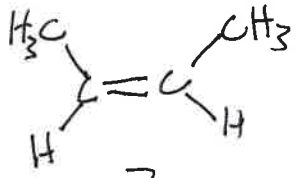
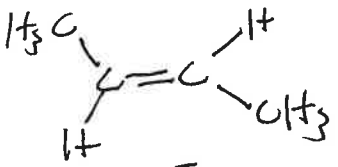
Recall: Designation of Alkene stereoisomers (E and Z)



Z

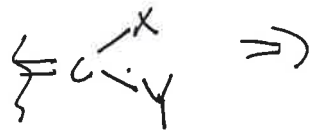
("cis")

vs.

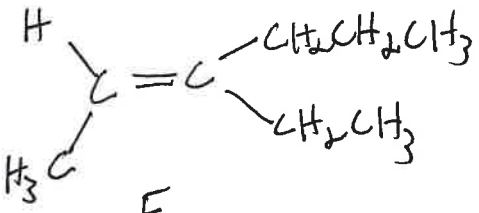


E

("trans")

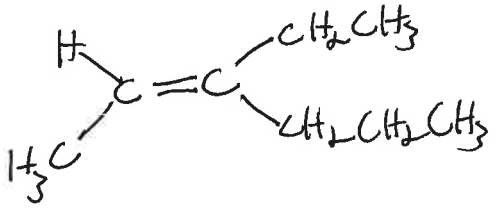


⇒ Assignment of priority



E

vs.



Z

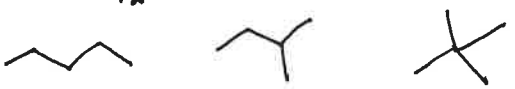
Degree of unsaturation (U)

→ Deduced from a molecular formula

formula – define which structures are and are not possible.

Alkanes w/out rings have molecular formulas of type C_nH_{2n+2}.

C_5H_{12}



} Formula limits the possibilities to these three

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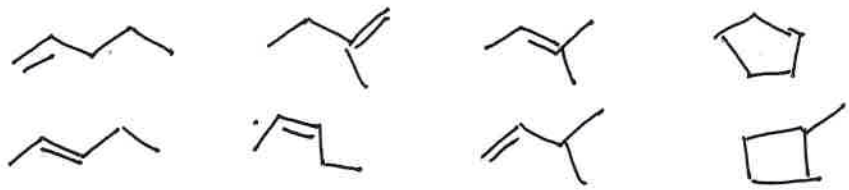
C_5H_{10}



ex.

1 degree of unsaturation ($U = 1$)

- one double bond
- half of a triple bond
- ring

For a hydrocarbon

$$U = \frac{2C + 2 - H}{2}$$

C = # of carbons

H = # of hydrogens

$C_5H_{12} \Rightarrow U = 0$

$C_5H_{10} \Rightarrow U = 1$

$C_5H_8 = U = 2$

C_5H_8

etc.

More generally, for organic molecules containing beyond C and H ~~(hydrocarbons)~~ (halogens, O, N).

$$U = \frac{2C + 2 - H + N}{2}$$

C = # of carbons

H = # of hydrogens + halogens

N = # of nitrogens

(# of oxygens doesn't affect calculating U).

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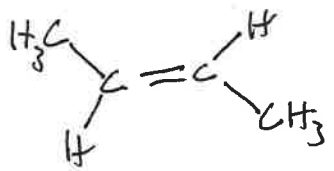
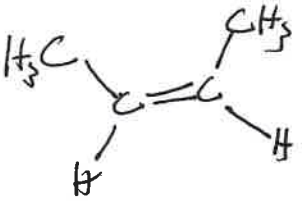
Relationship between alkene structure and their stability.

Ex:  more stable than 

(Comparison useful only w/ isomers).

Relative stability for a pair (or larger set) of isomers is based on the outcome of an appropriate chosen rxn. In particular we compare "heats of reactions"

Exothermic reaction – heat released when reaction occurs ($\Delta H < 0$)

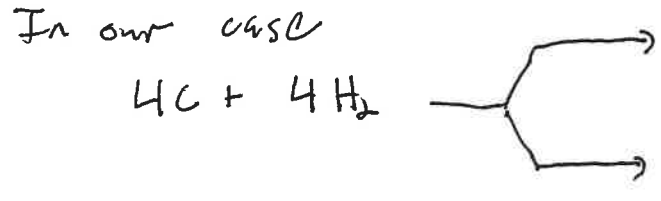
Endothermic reaction – heat absorbed ($\Delta H > 0$)

3 ways to compare stabilities of  and 

1) Heats of formation (ΔH_f°)

[Form molecule from the elements, @ 1 atm, 25°C]

In our case



$\Delta\Delta H_f^\circ$ = 1 kcal/mol ← trans more stable by 1 kcal/mol

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2) Heats of combustion

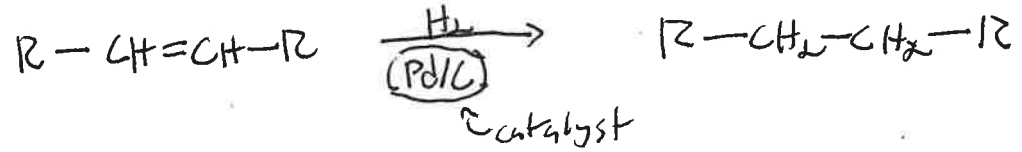
	ΔH (kcal/mol)
 + $6O_2$	−646.8
 + $6O_2$	−647.8

→ $4CO_2 + 4H_2O$

Less stable isomer should release more heat. Trans more stable by 1 kcal/mol than cis.

3. Compare heats of hydrogenation

General:



"Pd/C" ≡ palladium on carbon