Course 343 Lecturer Hackenberger

Day Monday Date 9/23/13

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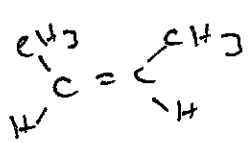
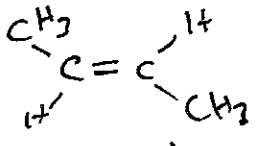
Review Session (Group office hour) Tomorrow, 5:00 pm B371 Gelleman office Rm 7132

Recall: Alkene structure & stereoisomers



vs.



trans

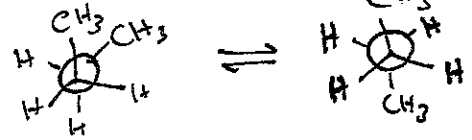
Stable

~60 kcal/mol for inter-conversion

('cis' – CH_3 groups on same sides)

See fig 4.7 in text – must break a π-bond temporarily to cis ⇌ trans

Contrast:



gauche ⇌ anti

~3 kcal/mol

happens @ room temp.

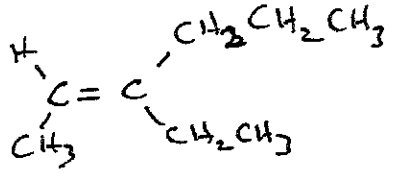
Rapid

Specification of alkene stereoisomers

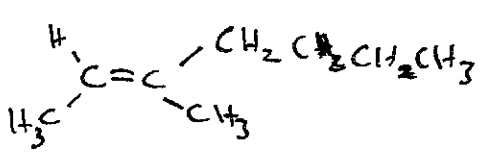
E vs. Z designation (Entgegen) vs. (Zusammen)

"opposite" "same"

Consider isomer pairs



vs.



"Constitutional isomers" → different bonding pattern

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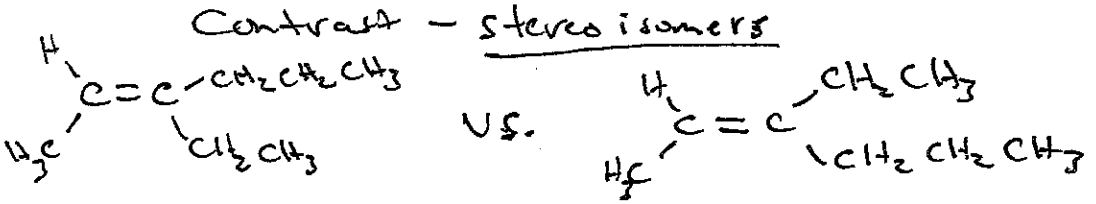
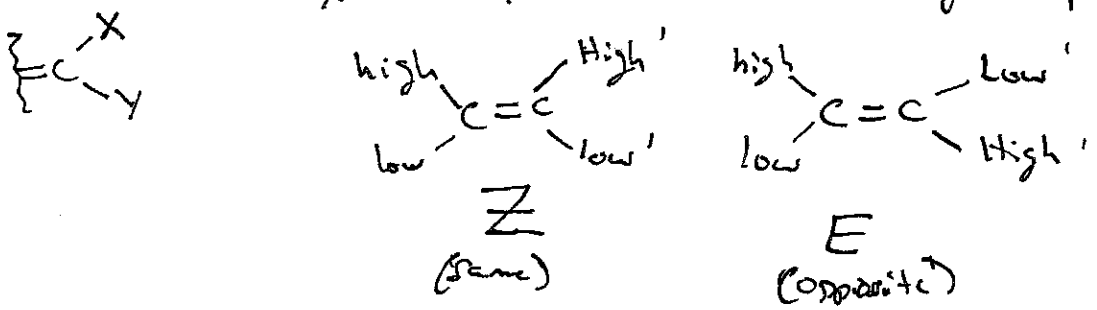
Contrast – stereoisomers



Differ only in spatial arrangement of atoms (same bonding relationship)

To assign E vs Z, we must assign Priorities to alkene substituents:

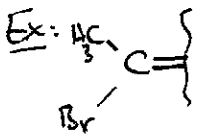
X vs. Y – which has higher priority?

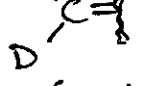


Z (same) E (opposite)

Priority assignment protocol:

1) Atoms directly attached to Alkene C → higher atomic number = higher priority

Ex:  C vs. Br → Br is "high"

 D vs H → D is 'high'

(D = deuterium)

↳ isotope of H w/ 1 neutron heavier nucleus

2) IF atoms directly attached to alkene C are the same, move out to the next set of bonding partners looking for the 1st point of distinction. Then, higher atomic # ⇒ higher priority

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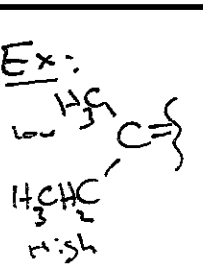
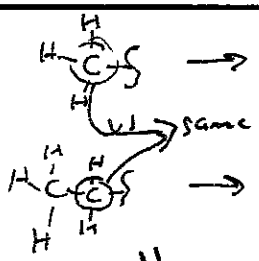
Ex:

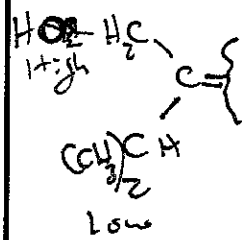


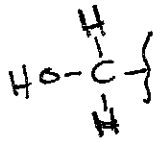


→ surrounded by 2 H's

→ surrounded by 2 H's + 1 C

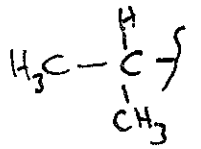
↳ makes the ethyl group higher priority





2 × H + (O) → Larger atomic # so this is the higher priority

vs

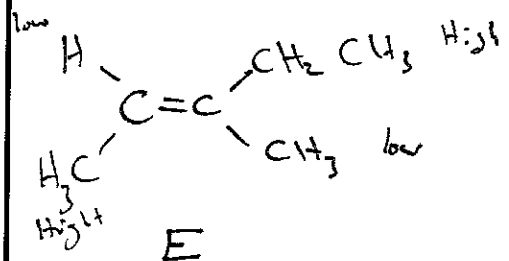


1 H + 2 × C

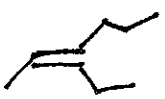
Note: See text → on handling of double + triple bonds in substituents in terms of priority assignment

Finally, "reconnect" alkene C's to decide E vs Z.

Ex



E



E

New topic – how to extract structural insight from a molecular formula.

Degree of Unsaturation (U)

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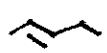
Alkanes w/out rings, have molecular formulas: $C_n H_{(2n+2)}$

C_5H_{12} or or (Branched or linear)

If ring or double bond => 2 fewer H's

Thus: C_5H_{10}   or 

 etc

Each degree of unsaturation corresponds to one ring or one π bond

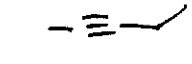
For hydrocarbons:

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

(where C = # of carbons, H = # of hydrogens)

C_5H_{12}, $u = 0$ (fully saturated)

C_5H_{10}, $u = 1$

C_5H_8, $u = 2$ →  or  or

 or  or . . .

More general

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

(N: # of nitrogens; H: # hydrogens + halogens)