

# Relative Stabilities of Alkenes

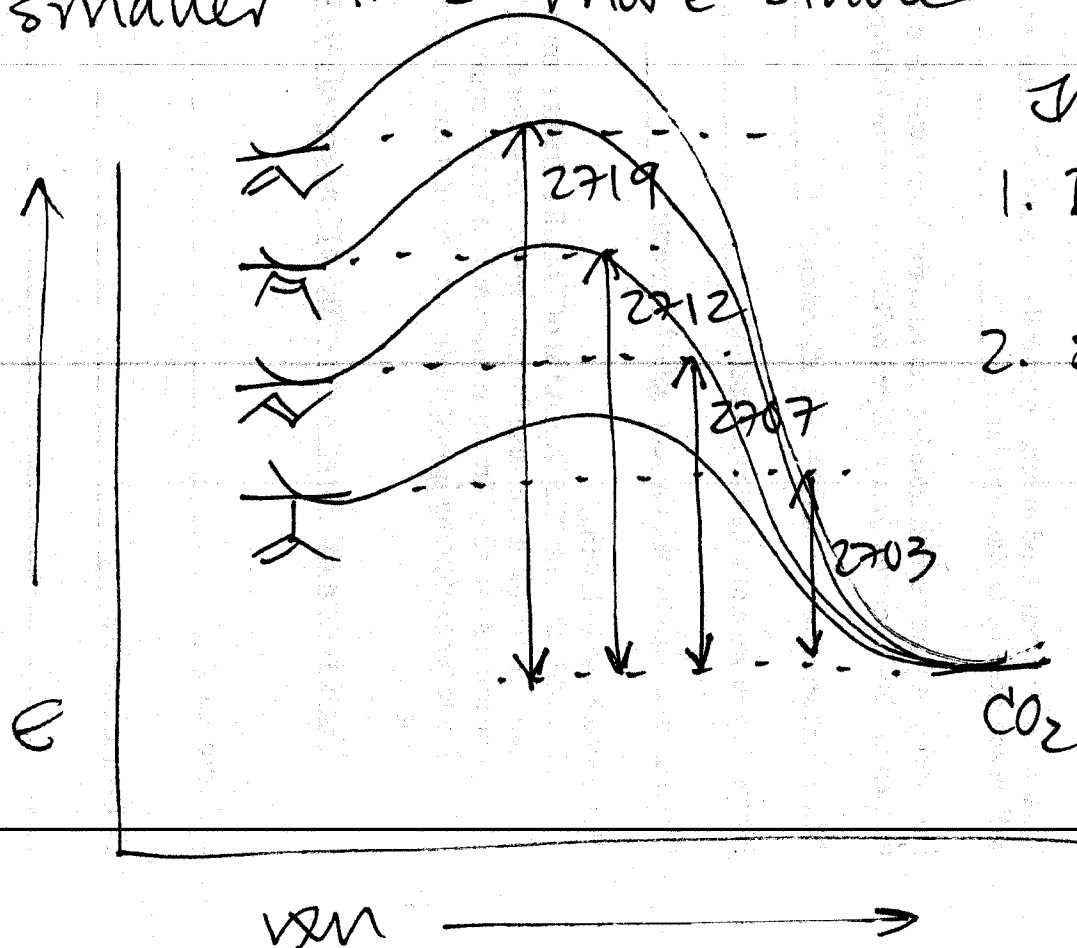
<chem>C=CC</chem>	<chem>C=CC(C)C</chem>	<chem>C=CC(C)C(C)C</chem>	<chem>C=C(C)(C)C</chem>	heat of combustion ( $\Delta H$ )
2719	2712	2707	2703	
kJ/mol				

smaller # = more stable

why?

Important factors:

1. Degree of substitution  
(more subst = more stable)
2. sterics  
(Z is worse than E)  
lower energy  
= more stable



cyclo alkenes - all have  $\geq$  double bonds  
until the ring is  $\geq 8$  C's.

8-11 C's - can have E alkene in the  
ring but Z is more stable (ring strain)

$\geq 12$  C's - no ring strain associated w/  
E alkene; E is now more stable

\* Don't worry about physical properties.

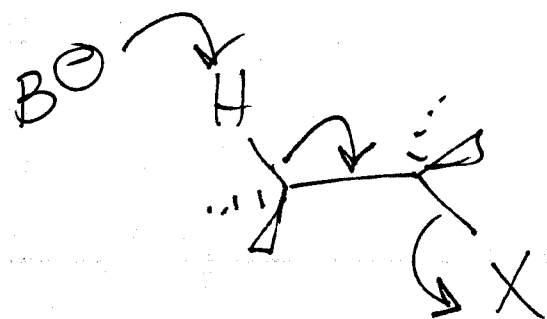
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Preparation of Alkenes - Elimination Rxn.

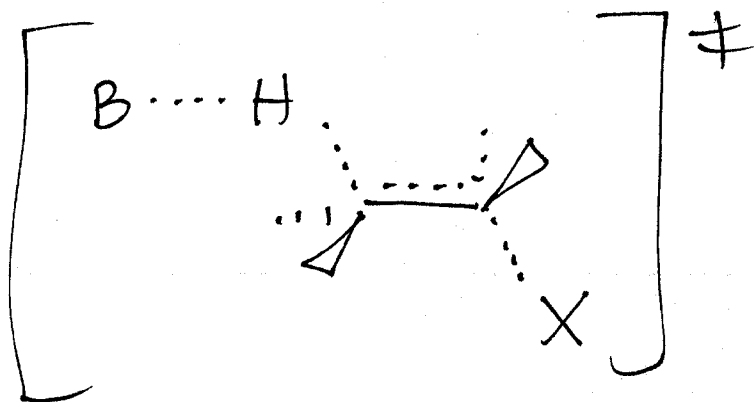
\* often called  $\beta$ -elim

1. Dehydrohalogenation - loss of HX  
works best w/ strong base (E2)  
worry about. mechanism  
regiochem  
stereochem. (E vs. Z)

mechanism of an E2: simultaneous rxn.



T.S.



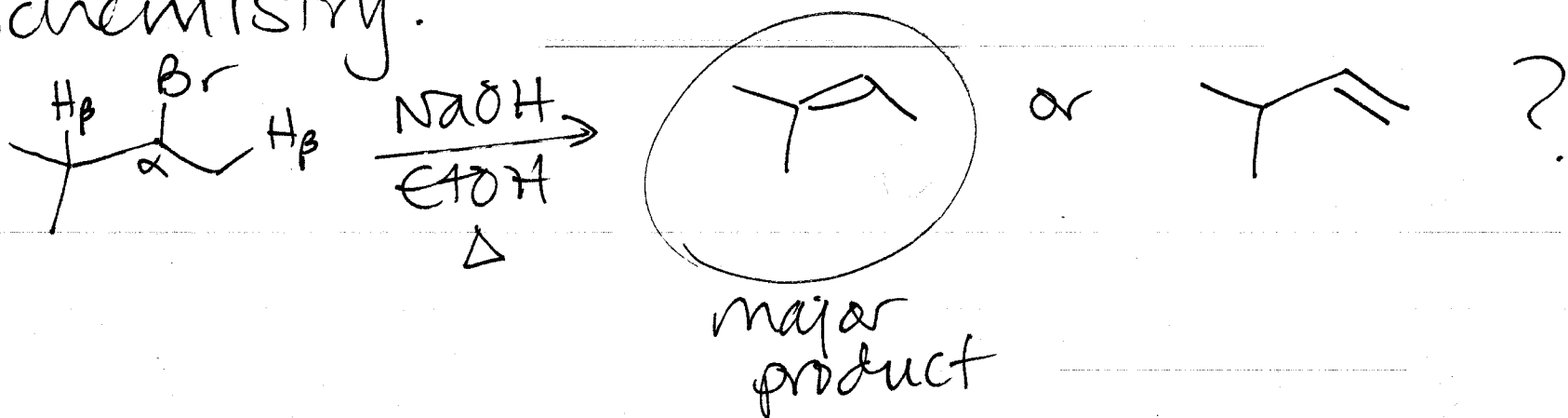
Note: two C's are  
changing from  $sp^3$  to  $sp^2$ .

How to favor E2:

- $2^\circ/3^\circ$  RX (steric hindrance inhibits  $S_N2$ )
- If using  $1^\circ$  RX use a bulky base ( $t\text{-}O^-K^+$ )

- c. use a strong base (hydroxide or alkoxide)  
d. Elevated temp favors elimination.

Regiochemistry:

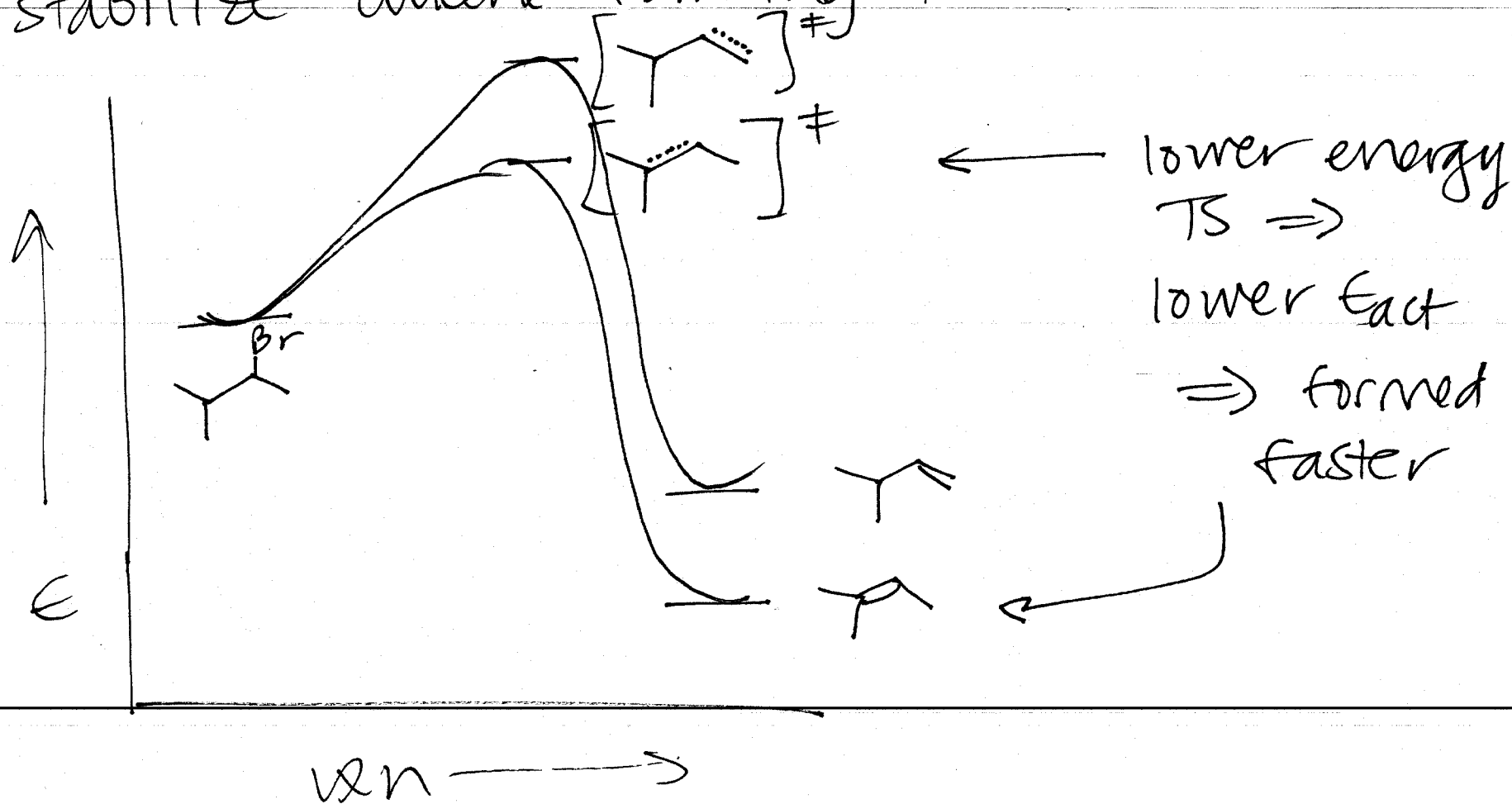


use Zaitsev's Rule: if there is more than one  $\beta$ -H; the one that is lost is the one that will give the more stable product.

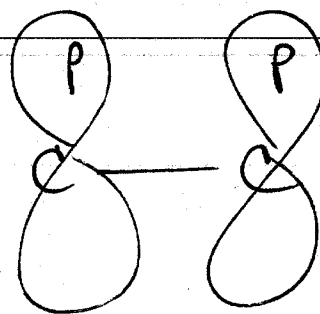
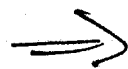
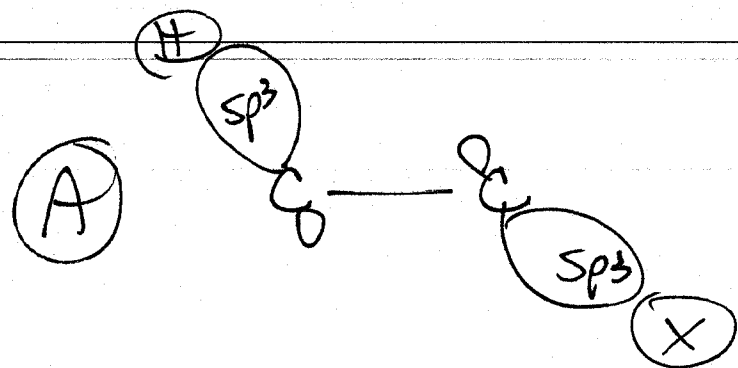
\* exception: if using bulky base ( $\text{t-BuO}^-\text{K}^+$ ) - too sterically hindered to get at  $3^\circ$  H's + has tough time getting at  $2^\circ$  H's - prefers to pull off  $1^\circ$  H's. (Hofmann's Rule - see Ch. 20)

Stereochemistry- E is preferred over Z.

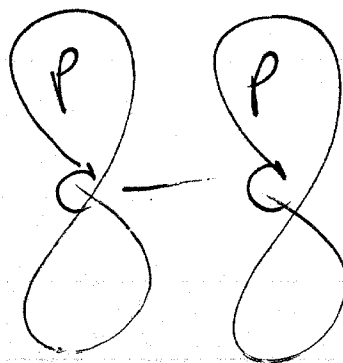
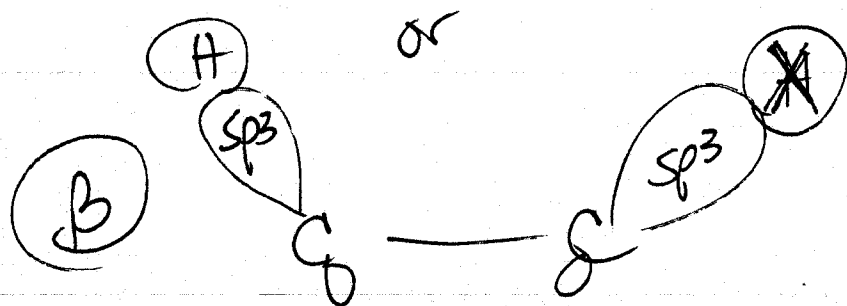
Why does Zaitsev's Rule work? Consider the TS: has partially formed  $\pi$  bond. Alkyl gps. stabilize alkenes;  $\Rightarrow$  also stabilize alkene-forming TS.



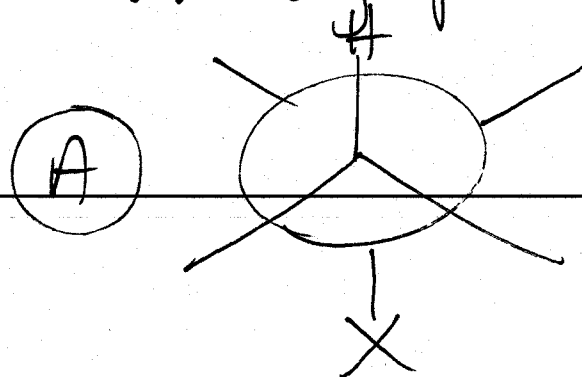
look @ mechanism a little more closely.



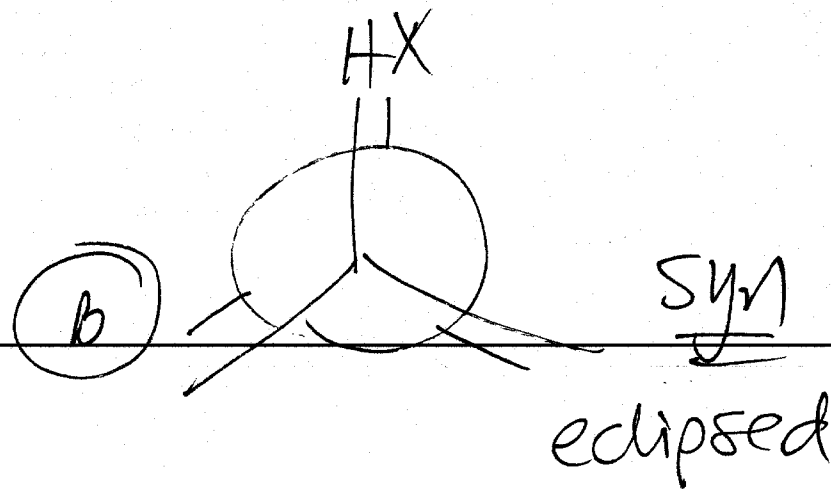
orbitals  
need to  
be ||.



works best when  
the two  $sp^3$ s are  
already parallel.



anti  
staggered



syn  
eclipsed

consider cis + trans 1-bromo-4-*t*-butyl  
cyclohexane

treat w/  $\text{tOK}/\text{tOH}$

think about: products + the relative  
rates.