Key
Sp 11

# ChemActivity 15

## Part A: Alkene Potential Energy

(What are the relative potential energies of substituted and unsubstituted double bonds?)

### Model 1: Heats of Hydrogenation ($\Delta H_{hydrogenation}$)

$\Delta H_{hydrogenation}$ = heat released when two H atoms are added to a double bond. You do not need to know the mechanism of this reaction (called **catalytic hydrogenation**). Know only that the metal, usually platinum (Pt) or palladium (Pd) delivers two H atoms simultaneously to the **same side** of the double bond, as in Figure 1a (this is called "**syn addition**").

**Figure 1a: Catalytic Hydrogenation of 1,2-dimethylcyclopentene**

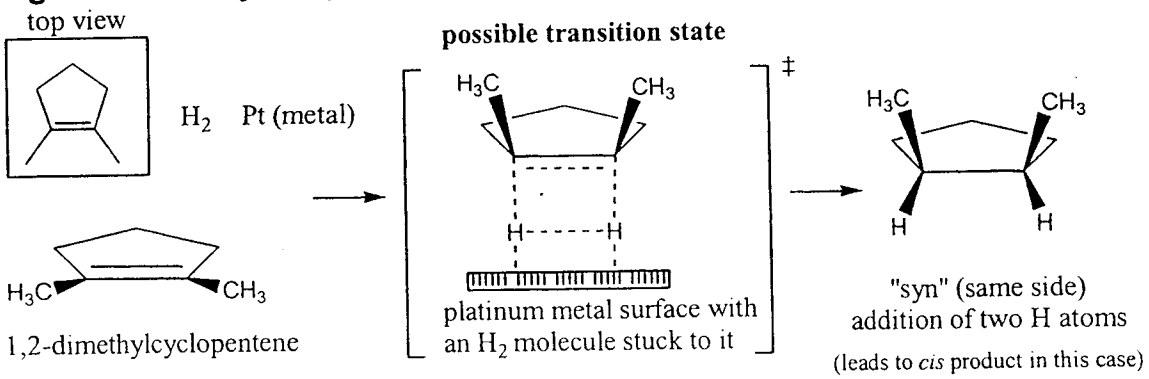
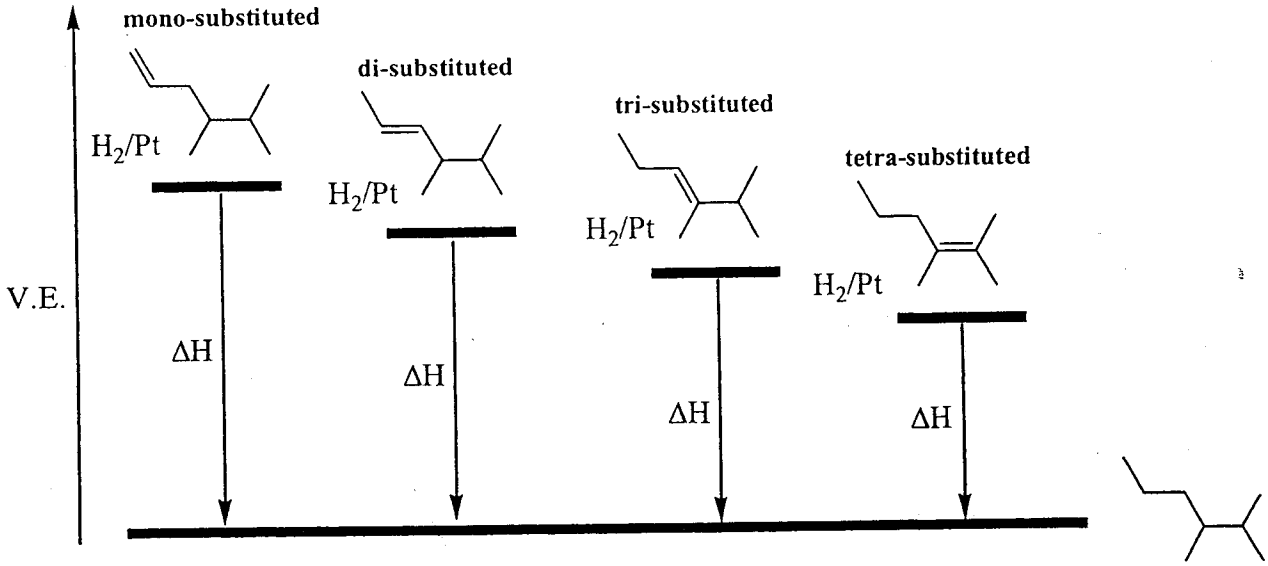


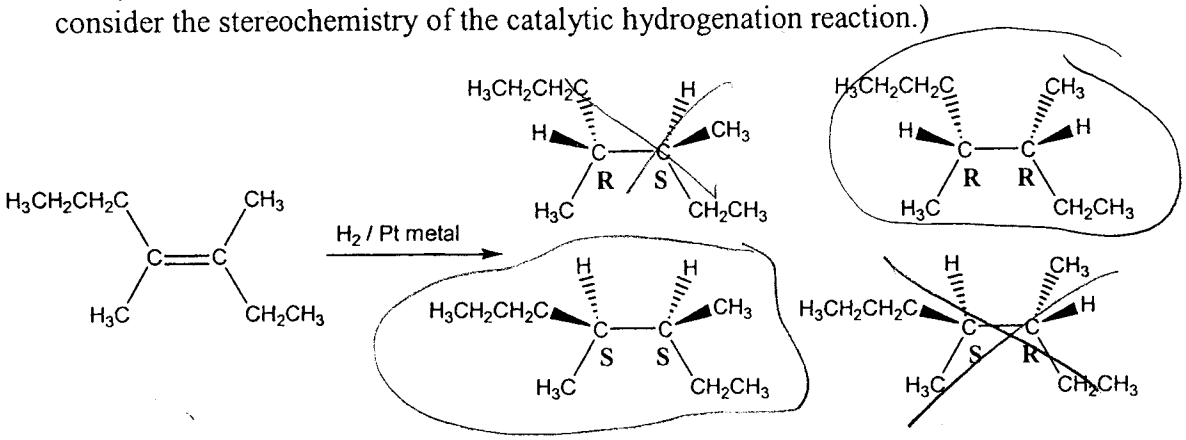

**Figure 1b: Catalytic Hydrogenation of Various $C_8H_{16}$ Constitutional Isomers**




### Critical Thinking Questions

1. Is catalytic hydrogenation an **exothermic** or an **endothermic** [circle one] reaction?

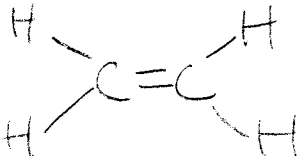
2. For the following catalytic hydrogenation reaction, circle the two products that do form, cross out the two that do not form, and explain your reasoning. (Hint: consider the stereochemistry of the catalytic hydrogenation reaction.)




3. What do the labels **mono-substituted, di-substituted, tri-substituted and tetra-substituted** in Figure 1b refer to? The # of R grps bonded to the 2 carbons forming the double bond.

4. An **un-substituted** alkene has a molecular formula of $C_2H_4$. Draw the structure of this molecule and explain why it is called **un-substituted**. (This is the only "unsubstituted" alkene.)

There are no R grps bonded to either carbon.

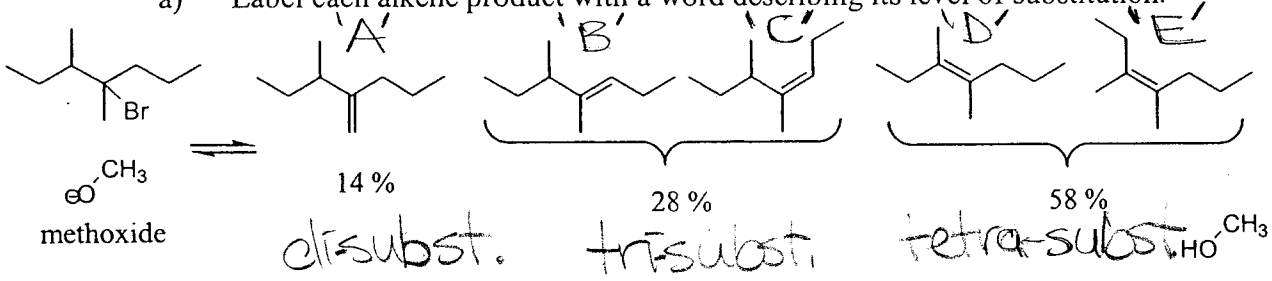


5. According to the information in Figure 1b, what is the relationship between the level of substitution of a double bond and the potential energy of the alkene?

The PE of the alkene ↓ as the level of substitution ↑.

6. Consider the following elimination reaction:

a) Label each alkene product with a word describing its level of substitution.




b) Is your conclusion in CTQ 5 consistent with the product distribution shown above? Explain. yes, the more stable products are synthesized in greater percentages

c) Explain why the words ***cis*** and ***trans*** are not adequate to describe the difference between the two tri-substituted products above.

Because we do not have enough information to determine the structure of the tri-substituted alkene.

## Model 2: E vs. Z (more general than *cis* vs. *trans*)

As you saw on the previous page, some molecules are too complex to be called simply *cis* or *trans*. For these molecules, the E vs. Z system was invented.

- For the two groups attached to each $sp^2$ carbon, assign one as larger and the other as smaller using the same rules you learned for assigning R and S.
- If the two larger groups are on the same side of the double bond (*cis*-like), the structure is called **Z**, for the German word *zusammen* meaning "**together**."
- If the two larger groups are on opposite sides of the double bond (*trans*-like), the structure is called **E**, for the German word *entgegen* meaning "**opposite**."

There are several good ways to remember the definitions of E and Z:

- Think Z for "*zis*-like."
- Think Z for "zee zame zide" (say it in a German accent).
- Think consonant with consonant, vowel with vowel: **Z**/Together **E**/Opposite

## Critical Thinking Questions

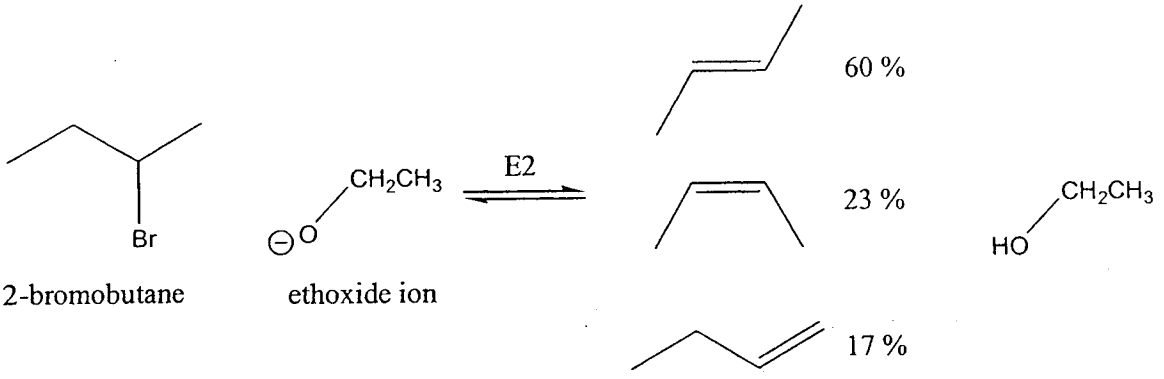
7. E vs. Z applies to four of the products in CTQ 6. Assign these structures E or Z.
8. E vs. Z does not apply to one of the alkene products in CTQ 6. Explain why.

'A' = no E/Z b/c both substitutions are on the same carbon (NO cis/trans either)

'B' = E 'C' = Z 'D' = E 'E' = Z

## Model 3: A Closer Look at E2 Reaction Product Distributions

- Based simply on alkene potential energies you would predict that the mono-substituted alkene is the minor product of the E2 reaction below.
- And, in general, *trans* or E molecules are lower in potential energy than *cis* or Z molecules, but this difference is not enough to explain the large preference for *trans* in this case. Indeed, something else is going on!




2-bromobutane ethoxide ion

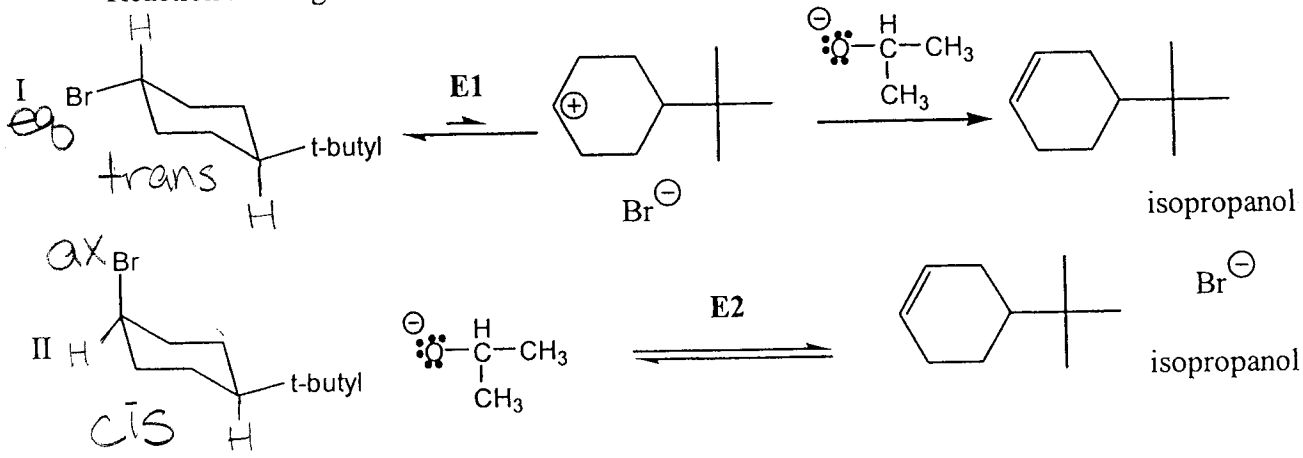
## Critical Thinking Questions

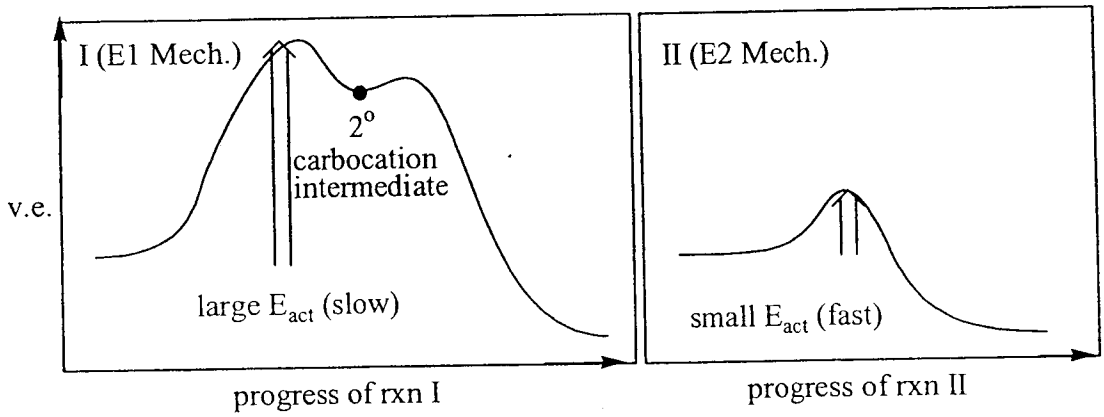
9. Why are *trans* or E molecules usually lower in potential energy than *cis* or Z molecules. The transition state & products are lower in E b/c there is less steric hindrance*
10. According to Model 3, is the energy difference between *trans*-2-butene and *cis*-2-butene large enough to account for the product distribution shown above? yes

* between the substituents 1/

## Model 4: Leaving Group Position in an E2 Reaction

- Both reactions are run in a mildly polar solvent that does not support ions well.
- Reaction I, below, can ONLY go via a carbocation intermediate (E1 reaction).
- Reaction II can go via an E2 mechanism and is much faster in this solvent.




## Critical Thinking Questions

11. Why is an E1 mechanism much slower than an E2 mechanism in a mildly polar solvent? It takes more energy to form the C⊕ creating a larger Ea (slower rate).

12. Label one of the starting materials above *trans* and the other *cis*. (It may help to draw in the H's on $C_1$ and $C_4$ of the ring. see above

    a) Label each leaving group (Br) as being axial or equatorial in each . (Recall that the very large t-butyl group "demands" the more roomy equatorial position.) see above

    b) According to Model 4, an E2 mechanism is possible on a substituted cyclohexane ring when the leaving group is in an **axial position** or **equatorial position** [circle one].

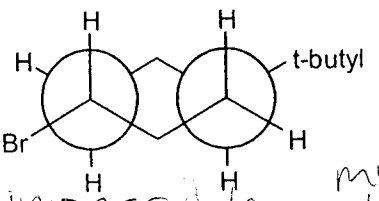
E2 requires anti-coplanar geometry of β-H & LG.

# Part B: Stereochemistry of E2 Reactions

(What conformation favors one-step elimination (E2)?)

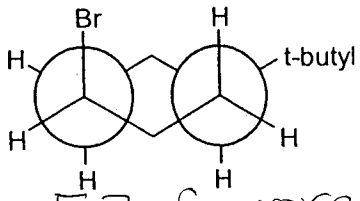
## Model 5: Newman Projections of Molecules from Model 4

*(note that the t-butyl group takes an equatorial position in each case)*




E2 impossible- must go by E1

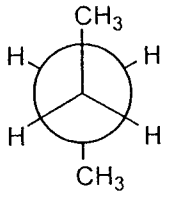
*trans*-1-bromo-4-*tert*-butylcyclohexane



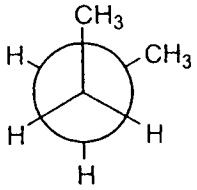

E2 favorable

*cis*-1-bromo-4-*tert*-butylcyclohexane

### Review of Newman Projection Terminology




the two methyl groups are said to be **anti to one another**



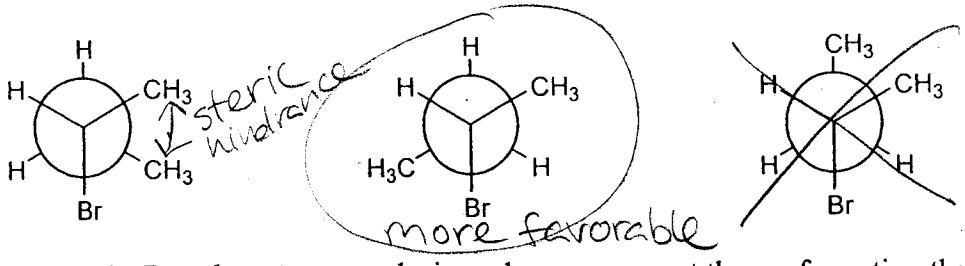

the two methyl groups are said to be **gauche to one another**

## Critical Thinking Questions

13. Based on the information on the previous page, write the words "**E2 favorable**" under one structure in Model 5 and "**E2 impossible-must go by E1**" under the other. see above

14. Circle the statement that is consistent with your conclusions above.
    I. For an E2 reaction to occur there must be an H **gauche** to the leaving group. F
    II. For an E2 reaction to occur there must be an H **anti** to the leaving group. T

15. The three possible staggered conformations of (S)-2-bromobutane are shown below.

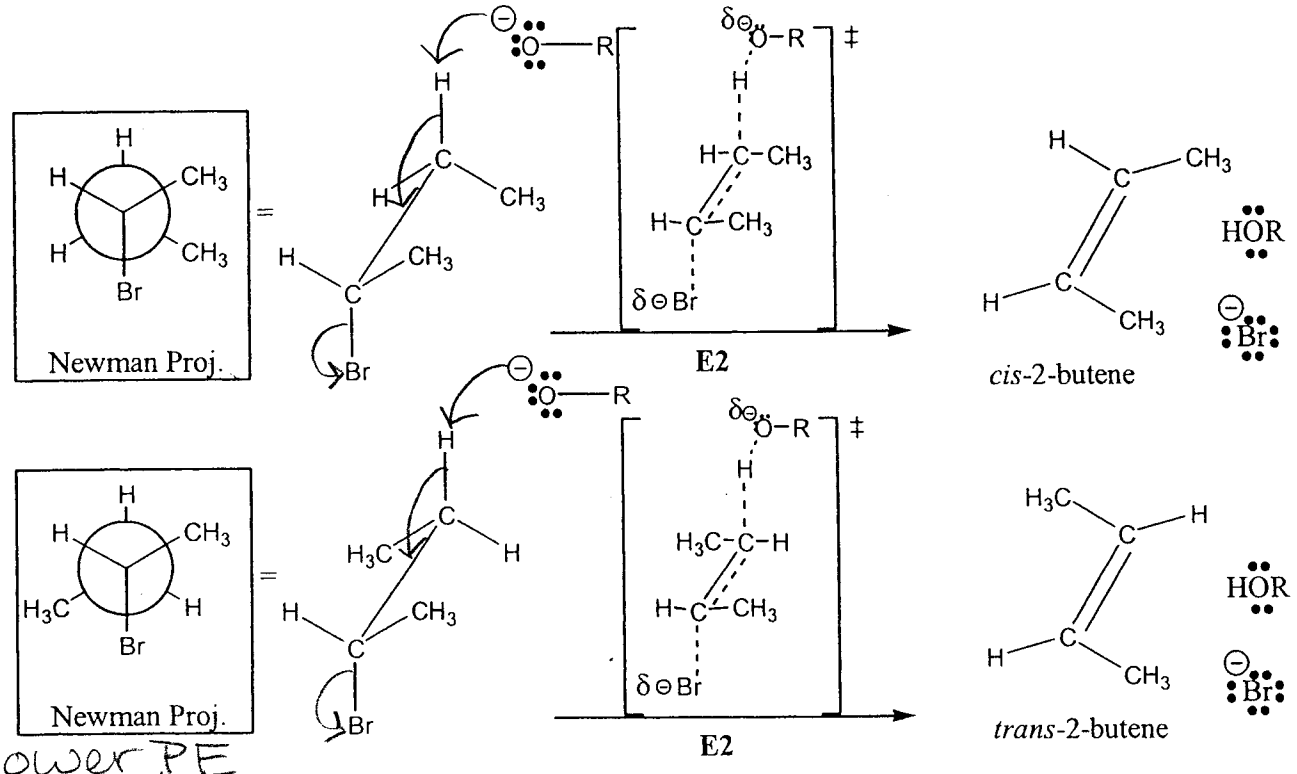



a) Based on your conclusions above, cross out the conformation that **cannot** lead to an E2 reaction.

b) Which of the remaining two conformations is more favorable, in terms of potential energy? Explain your reasoning.

Less steric hindrance between the methyl grps

16. Below are Newman and "sawhorse" representations of the two conformations of (S)-2-bromobutane that can lead to E2 reactions, along with the products of these E2 reactions.




lower PE will spend more time in this conform.

a) On the sawhorse representations of the reactants above, use curved arrows to show the flow of electrons during each E2 reaction. see above

b) Are your curved arrows consistent with the electron changes depicted in the transitions state for each reaction (shown in brackets above each reaction arrow)? yes

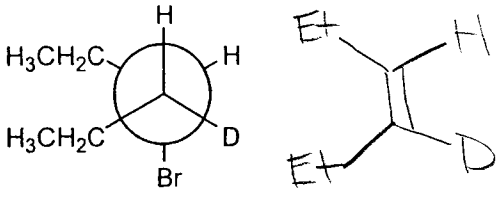
c) Relate the following statement to the example above: "The reactions above are E2 reactions so the changes happen all at once in one step. This **'traps'** the methyl groups: either **on the same side** of the newly forming double bond (*see* transition state leading to *cis* product), or **on opposite sides** of the newly forming double bond (*see* transition state leading to *trans* product)."

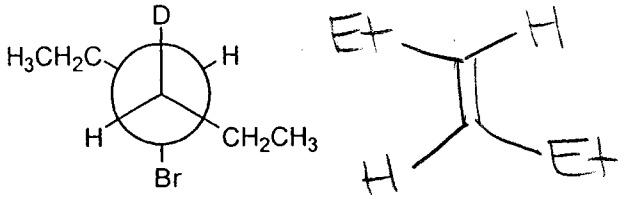
d) Label one of the Newman Projections above with the words "**lower P.E. – will spend more time in this conformation.**"

e) Based on the fact that each conformation gives exclusively the product shown, predict which will be more prevalent in the product mixture: ***trans*-2-butene** or ***cis*-2-butene** [circle one] and explain your reasoning. lower E transition state has lower Ea & faster rxn rate & more prod.

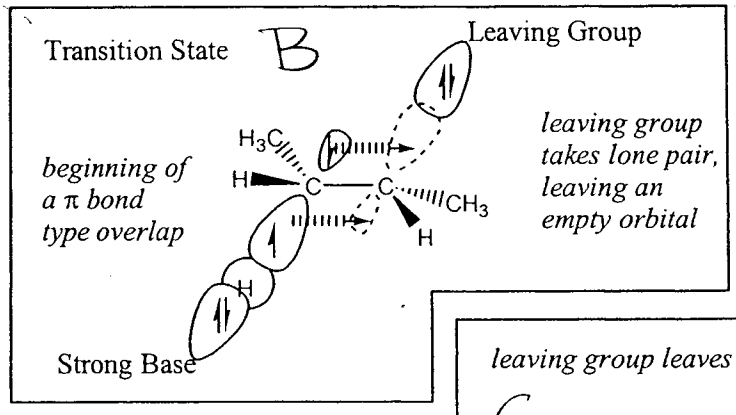
f) Is your answer above consistent with the product distribution in Model 3? yes

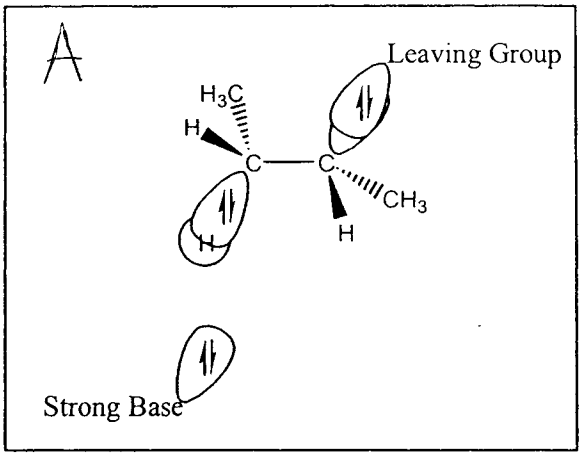
17. For each conformation of the deuterated 3-bromohexane stereoisomer below, draw the alkene product that will form if the conformation shown undergoes an E2 reaction. (**Deuterated** means that one or more of the H atoms has been replaced with a "heavy" hydrogen called a deuterium atom (D). Assume D and H have the same chemical reactivity. (e.g. $D_2O$ has the same chemistry as $H_2O$)

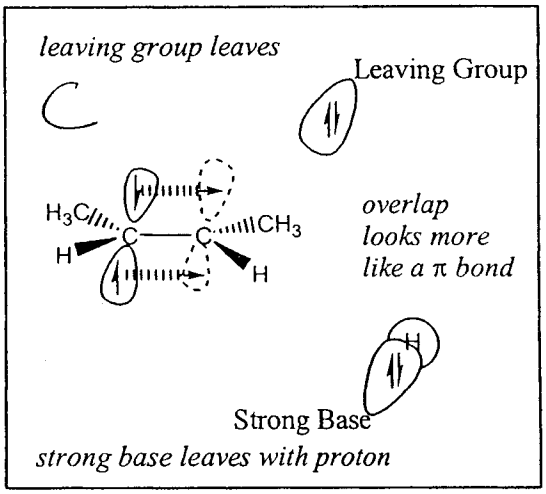


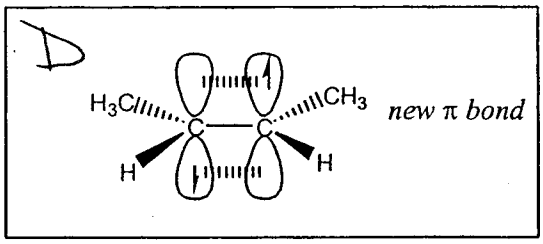




## Model 6: Orbital Explanation for "Anti-Only" E2 Reaction



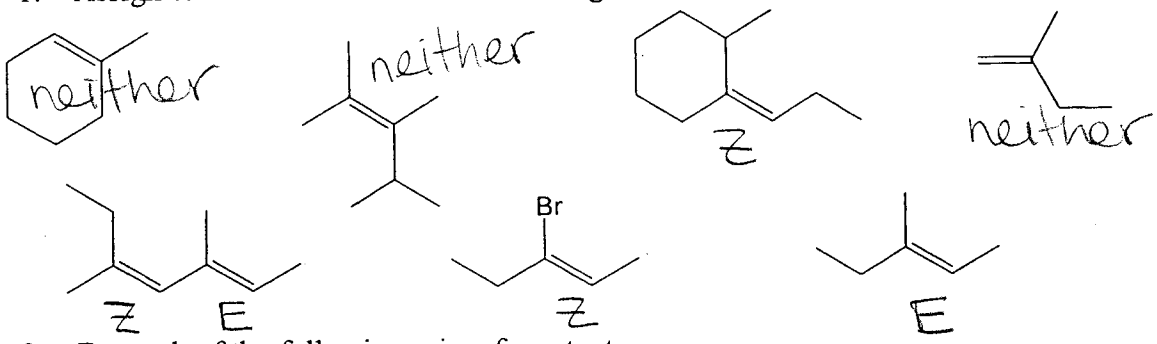

## Critical Thinking Questions

18. Label the boxes above A-D according to the order in which they occur in an E2 rxn.

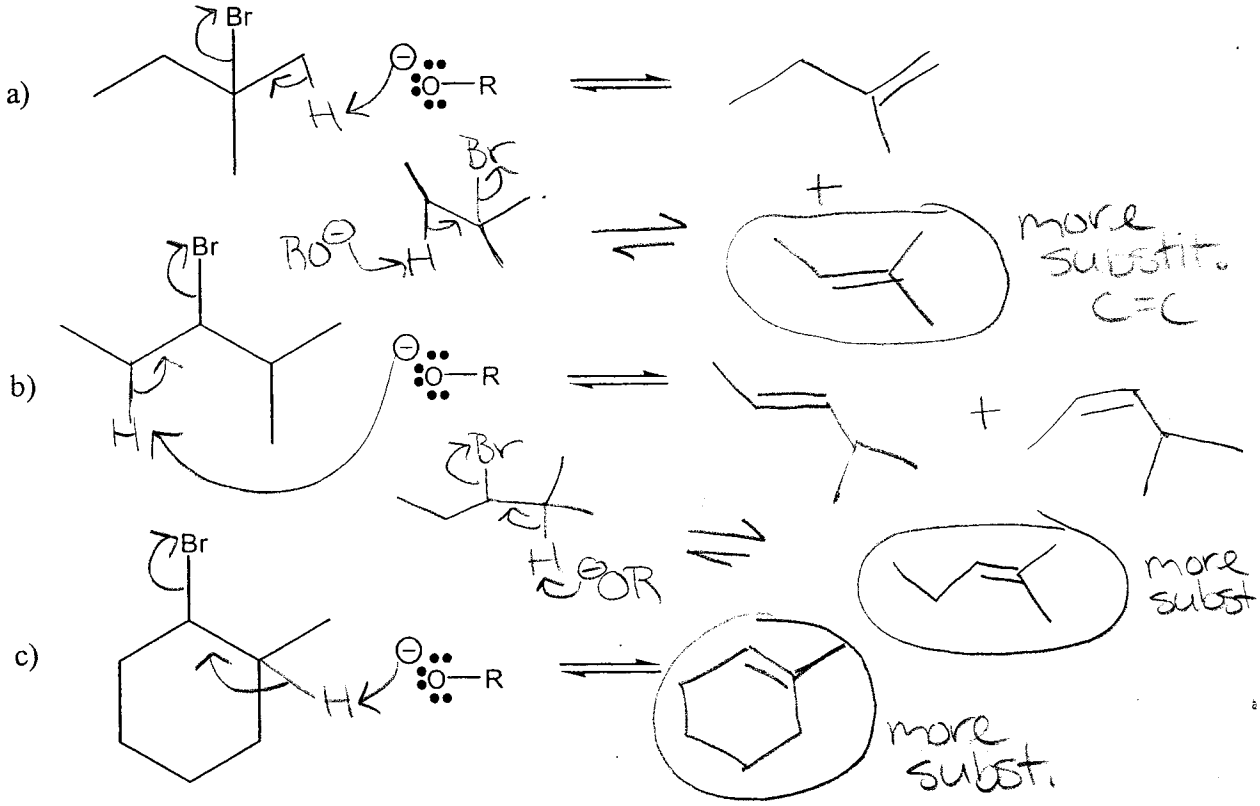
See above

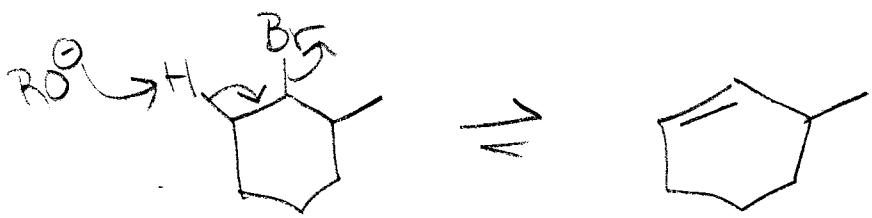
## Exercises for Part A

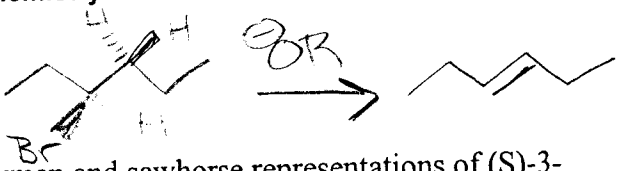
1. Assign each double bond in the following molecules as E, Z, or *neither*.




2. For each of the following pairs of reactants
   a) Draw all possible E2 products.
   b) Use curved arrows to show the formation of each different product. Redraw the reactants for each new product so as to clearly show each set of arrows.
   c) Circle the lowest potential energy product in each case.

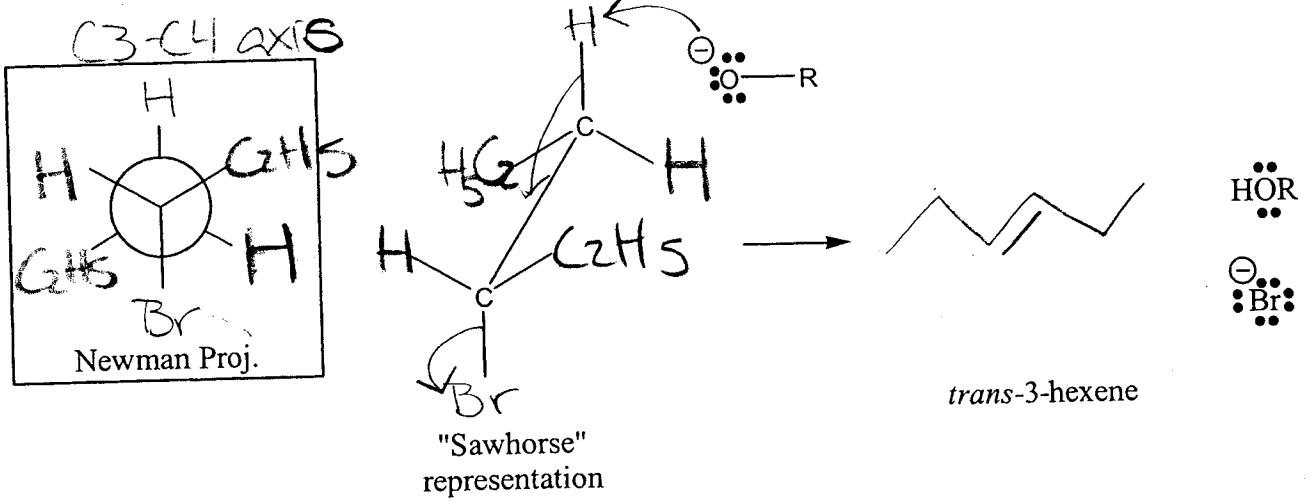


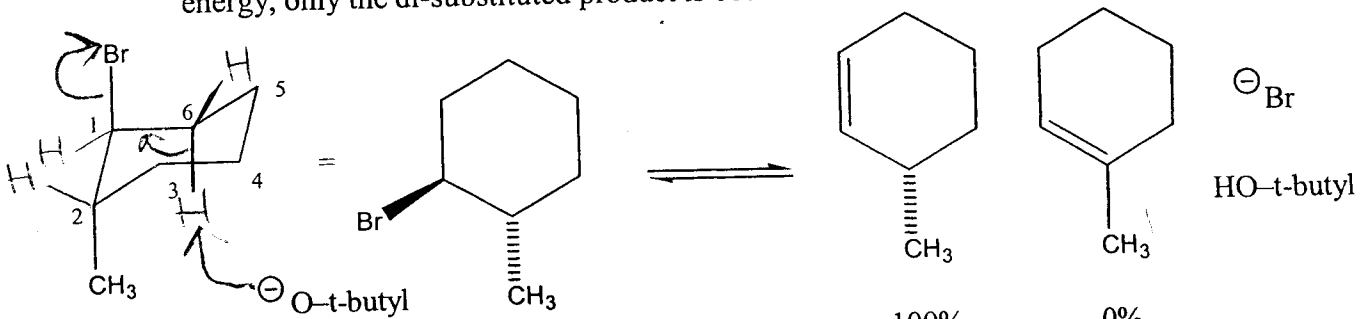


## Exercises for Part B

4. Complete the following Newman and sawhorse representations of (S)-3-bromohexane showing a conformation that would give rise to ***trans*-3-hexene**. Also draw *trans*-3-hexene and show the mechanism of formation using curved arrows.




5. Even though the tri-substituted alkene product on the right is lower in potential energy, only the di-substituted product is observed.




a) Draw in the β-H's and show the mechanism on the reaction above.

b) Explain why the tri-substituted product does NOT form.

The tri-substituted product does NOT form b/c the β-H can NOT be anti-coplanar to the bromine atom.

6. Mark TRUE each of the following statements that helps explain the product distribution in Model 3. (More than one may be true.)

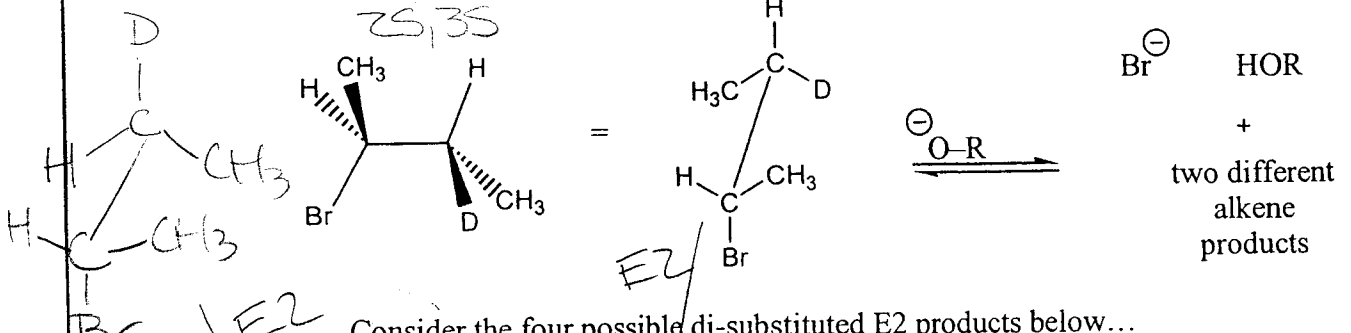
True I. The conformation leading to the *cis* product is less favorable than the conformation leading to the *trans* product.

True II. The methyl groups of the *trans* product are farther apart than in the *cis* product. This leads to less steric hindrance and therefore lower P.E. for the *trans* product.

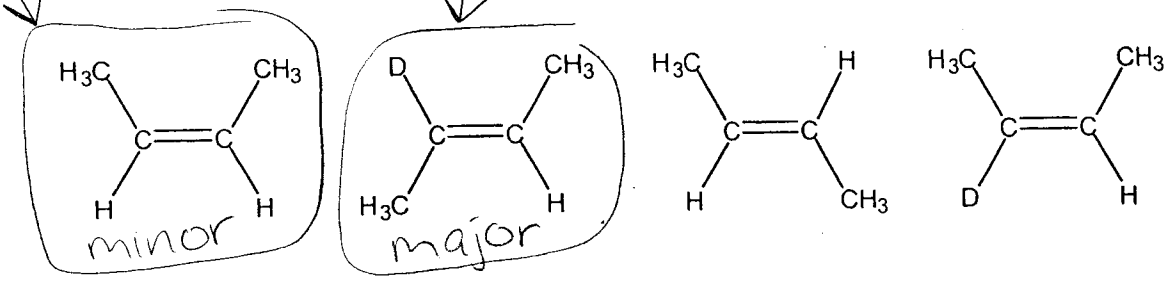
True III. A terminal double bond (one at the end of a chain) is higher in potential energy then an internal double bond (one in the middle of a chain).

7. Deuterium (D) has nearly identical reactivity as hydrogen (H). Consequently, the one-step elimination of Br from (S,S)-2-bromo-3-deuterobutane (shown below) yields two different alkene products.

**(Note: D is given a higher priority than H when assigning absolute configuration.)**

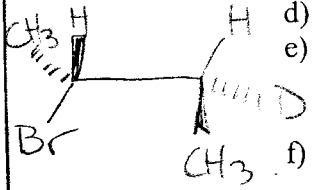



Consider the four possible di-substituted E2 products below...




d)

2R,3R-2-bromo-3-deutero butane



a) Circle the two that could be produced by E2 reaction of the (S,S) stereoisomer. see above

b) Mark one as the "major product" and one as the "minor product." see above

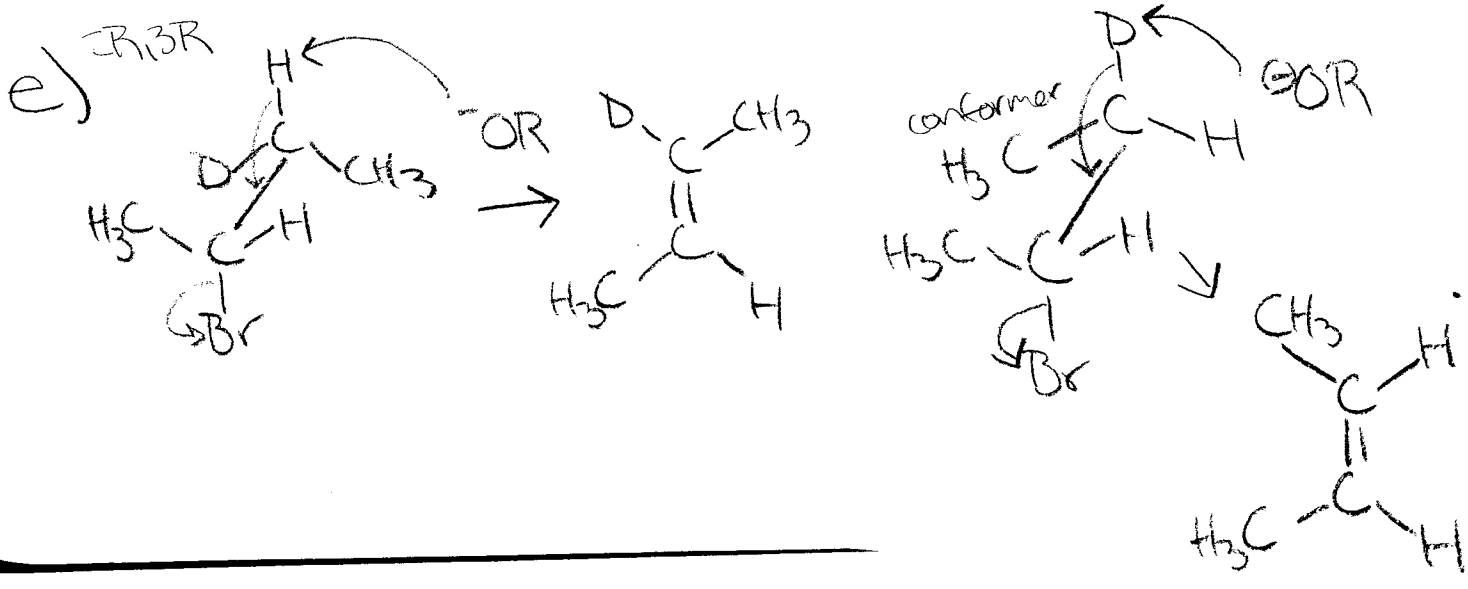
c) Draw a sawhorse representation of the conformation that would give rise to each of these two products. see above

d) Draw and name the enantiomer of (S,S)-2-bromo-3-deuterobutane. look left

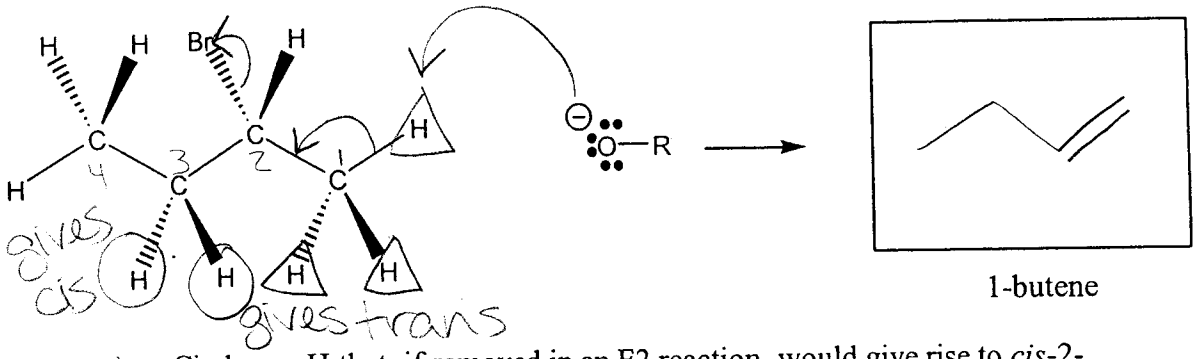
e) Could E2 reaction with this stereoisomer give rise to either of the two uncircled alkene products? Show the sawhorse representation of the conformation giving rise to each product. NO - see below

f) Draw AND NAME a diastereomer of 2-bromo-3-deuterobutane: either (S,R) or (R,S)-2-bromo-3-deuterobutane. see next page

g) Can this stereoisomer give rise to the other two products? If so, show the sawhorse representation of the conformation giving rise to each product.



8. On the following drawing of (R)-2-bromobutane…




a) Circle any H that, if removed in an E2 reaction, would give rise to *cis*-2-butene, and label it "**gives *cis***."
b) Circle any H that, if removed in an E2 reaction, would give rise to *trans*-2-butene, and label it "**gives *trans***."
c) Draw 1-butene in the box provided.
d) Put a triangle around any H that, if removed, would give rise to 1-butene.
e) Use curved arrows to show the mechanism of an E2 reaction leading to 1-butene.
f) A student predicts that the ratio of *trans*-2-butene to 1-butene should be 1:3 in the final product mixture. Explain how she came up with the ratio 1:3, and explain the **flaw** in her reasoning.

The student only looked at the probability based on the number of H's available. The flaw was to ignore the relative energies of the rxn pathways.

7. f) Yes, the 2R,3S or 2S,3R stereoisomers give rise to the other 2 products from previous page (2-bromo-3-deutero butane)