Today

Chap 9 Substitution and Elimination

Sections 9.7 & 9.8
E2 and E1 Reactions

Section 9.9
Competition Between E1 and E2

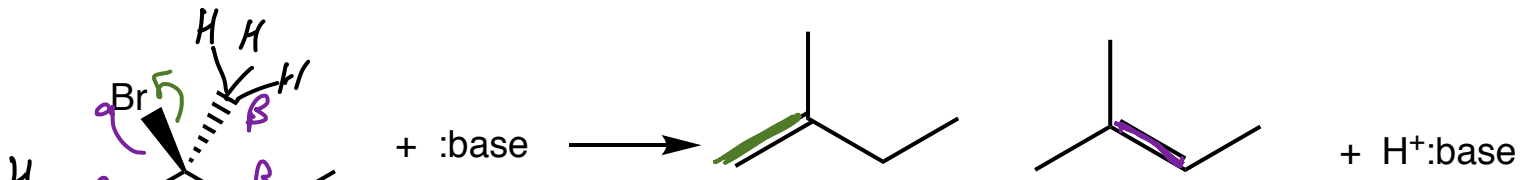
Next Class

Section 9.10
Stereochemistry of Elimination Reactions

Section 9.11
Elimination on cyclohexanes

Section 9.12

E1/S_N1 or E2/S_N2



base: :base

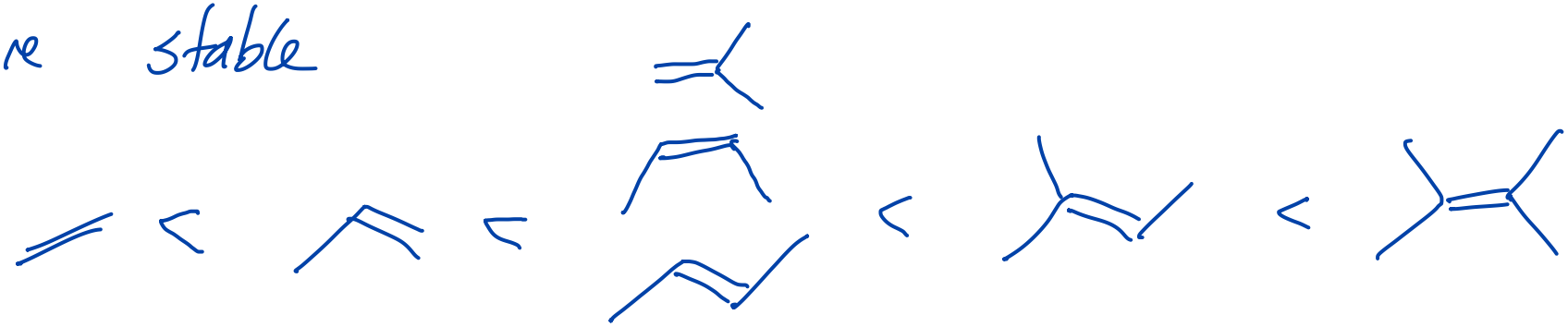
Elimination reactions make a mixture of products when there are more than 1 set of β-H's to react with

α-C is the C with the LG
β-C are the C atoms next to the α-C
β-H are the H atoms attached to the β-C

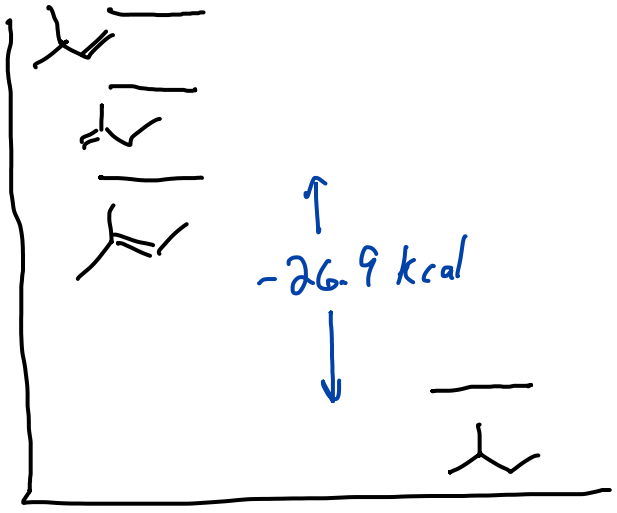
$$-\,d[RX]/dt = k_{E2}[RX][base] + k_{E1}[RX] + k_{SN2}[RX][Nu] + k_{SN1}[RX]$$

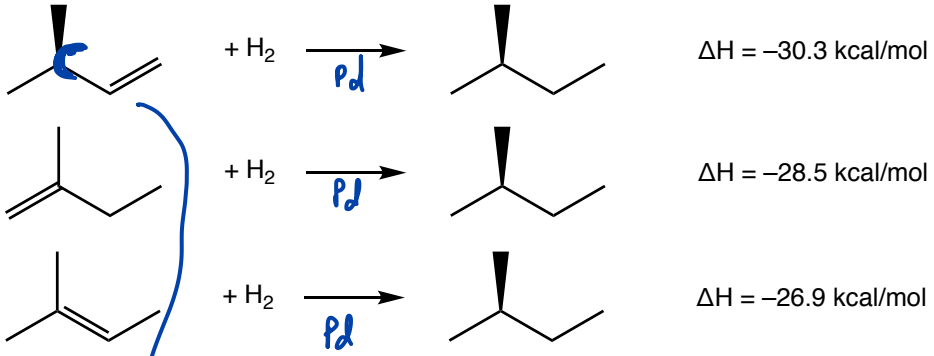
This is just a kinetic expression that says both E1 + E2 can compete to consume the reactant RX

more substitution around a db makes the db more stable



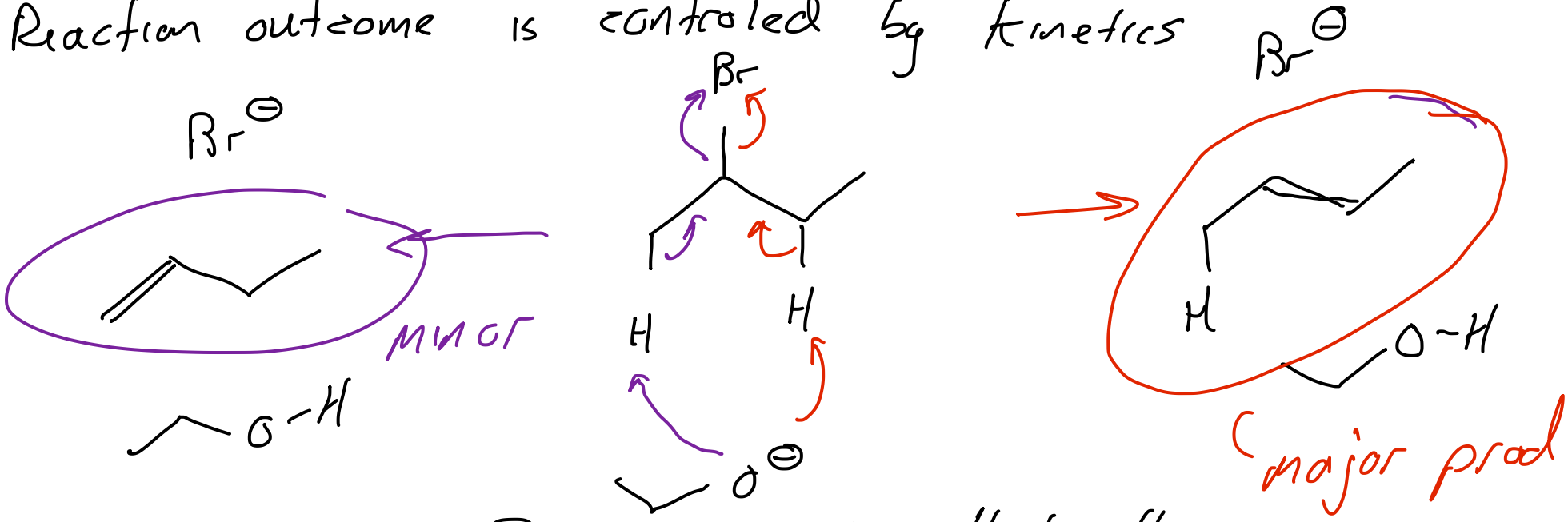
Because the endpoint is the same ( ) & because each reaction uses 1 mole of H_2, the difference in E must be due to the difference in stability of the db



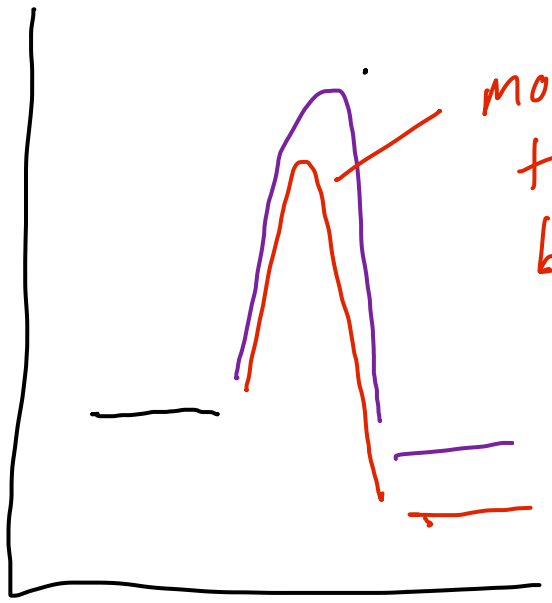


monosubstituted alkene

Reaction outcome is controled by kinetics



which ever one forms fastest will be the major product

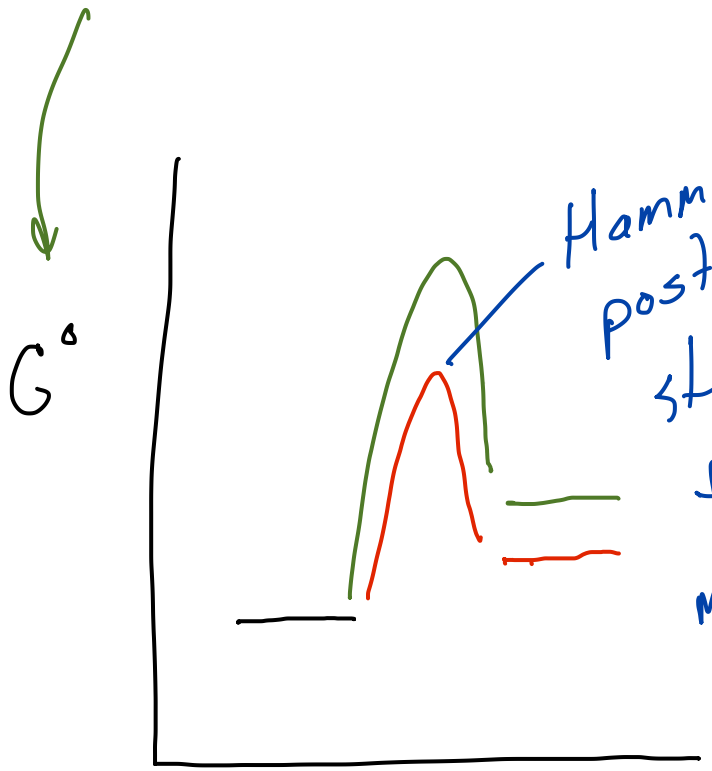


more stable transition state because transition state is part way to alkene + more substituted alkene is more stable, so TS that leads to it is more stable

$\rightleftharpoons$

when there are no kinetic problems stability can stand in for product distribution

standard state conditions

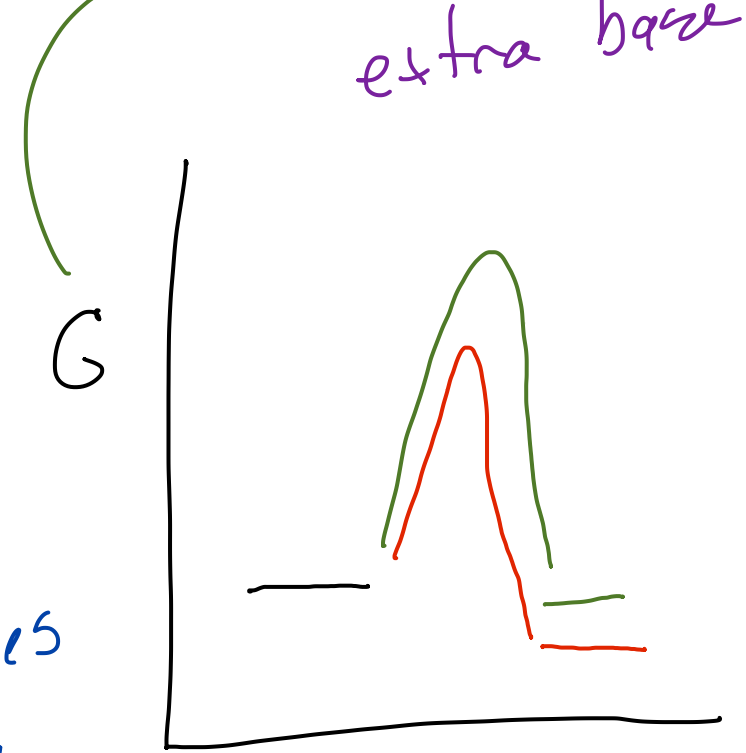


Hammond postulate states that the TS more closely resembles the species that it is closer to in E

equilibrium constant not favorable

actual conditions

extra base

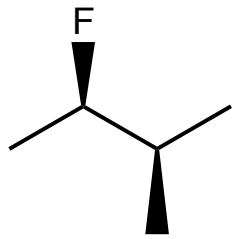


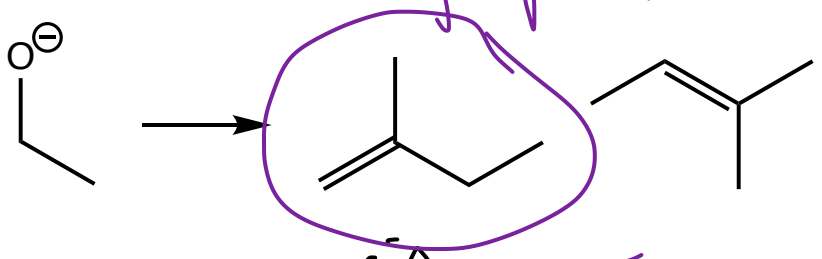
actual reaction conditions favor product formation

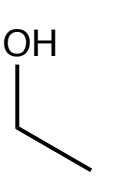
How do we make a reaction with an unfavorable K produce products? ↑ conc of a reactant remove product from the reaction

this is a kinetic problem

NR_3

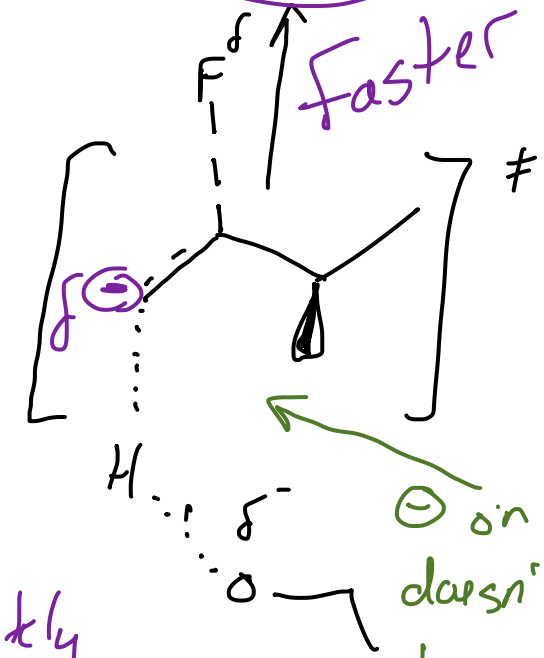




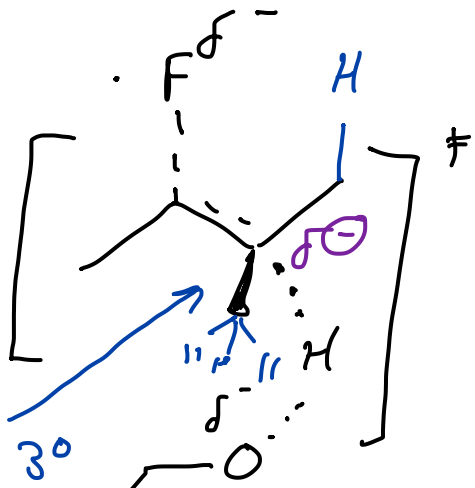


LG carries away ⊖ charge

IF the TS is exactly between the reactants & prods C atoms remain neutral



or



⊖ on 1° doesn't have as many destabilizing neighboring σ-bonds

⊖ on 3° surrounded by e⁻ density from adjacent σ-bonds making ⊖ less stable

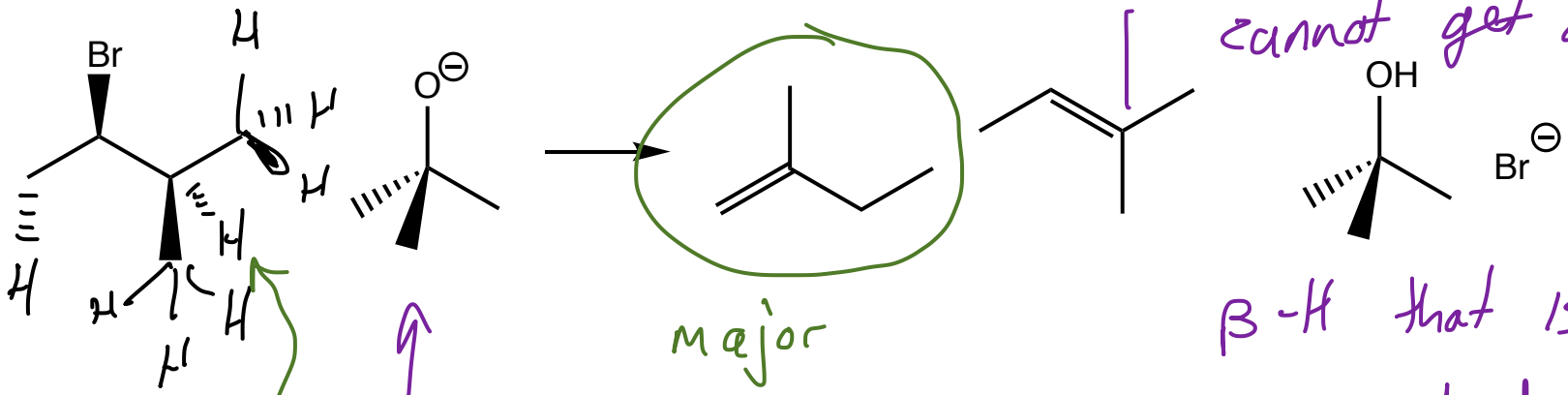
If F doesn't leave quickly enough ⊖ charge builds up on β-C

$H\text{-}Cl \rightarrow H^{\oplus}_{aq} \quad Cl^{\ominus}_{(aq)}$

$H\text{-}F \rightleftharpoons H^{\oplus}_{(aq)} \quad F^{\ominus}_{(aq)}$

Good LG's are extremely weak bases Cl^-, Br^-

large base cannot get at

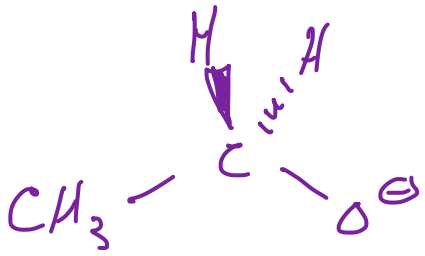


major

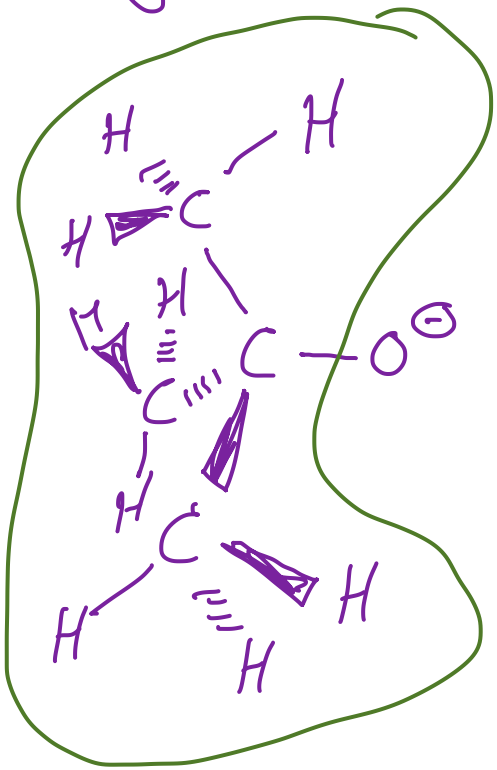
β-H that is surrounded by organic shubbery

hard to get to β-H

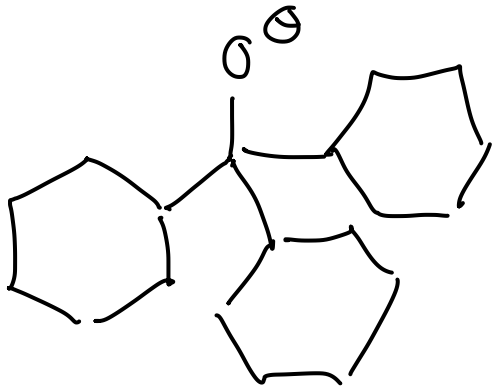
t-butoxide it's big



in lab



organic shrubbery

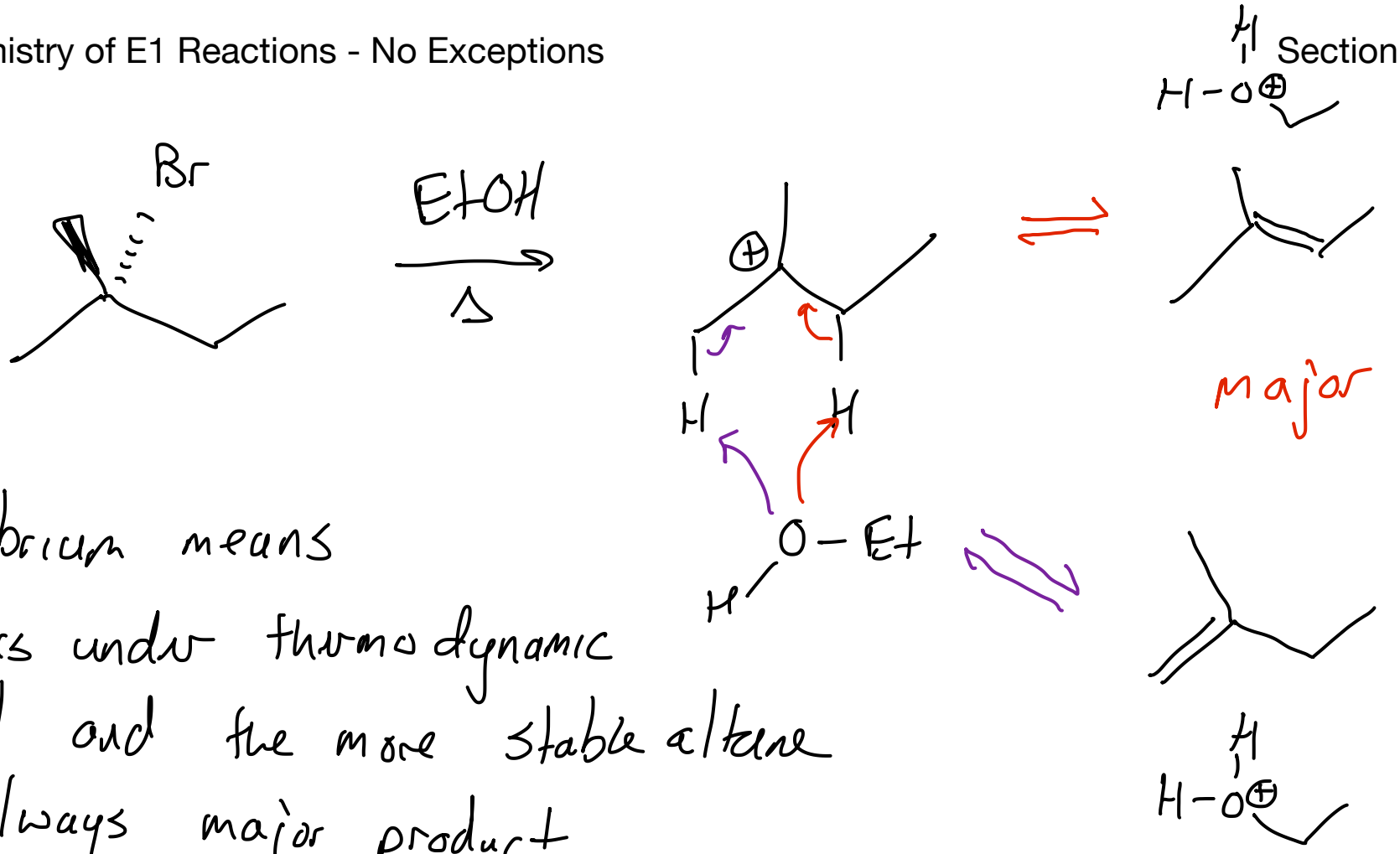


In E2 reactions the major product will be the more stable alkene because it forms faster unless ...

The LG is a poor LG like F and then the less substituted alkene is major product (⊖ builds up on less substituted β-C)

OR

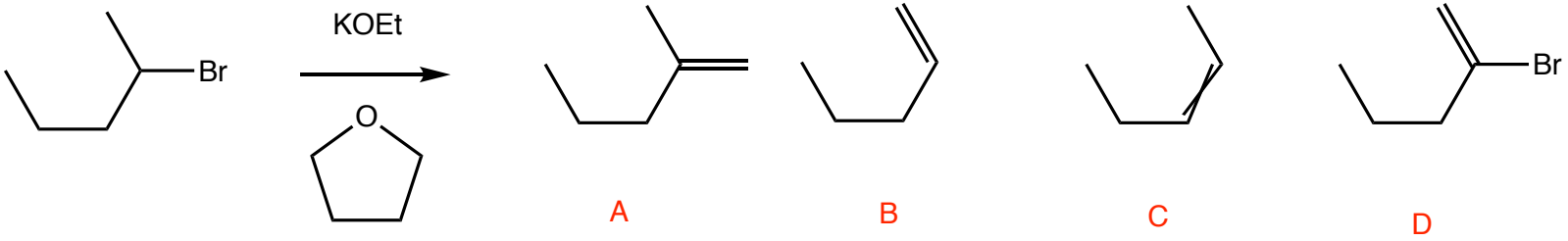
The base is big & cannot get to the β-H on the more substituted β-C so less substituted is major product

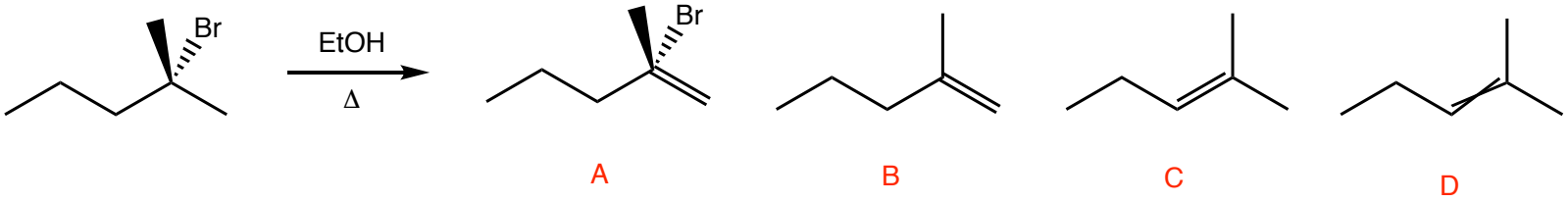


Equilibrium means rxn is under thermodynamic control and the more stable alkene is always major product

Big bases won't be a problem because of the thermodynamic control

Reactions: Predict the Major Elimination Products





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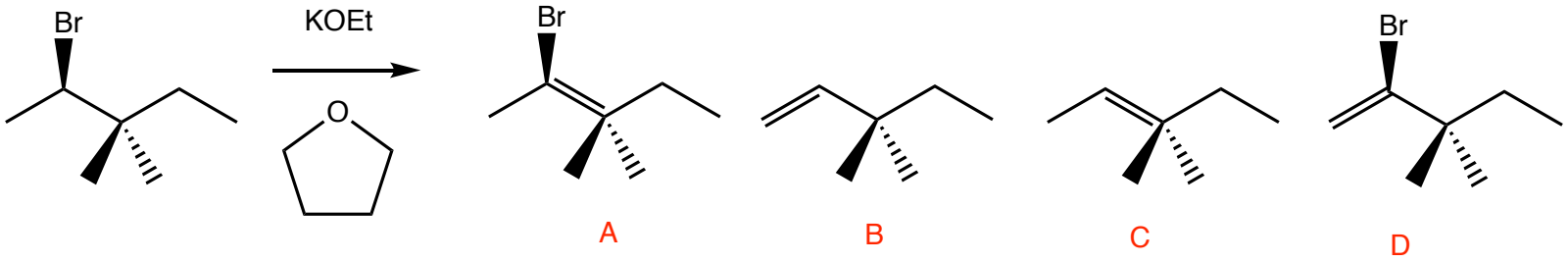

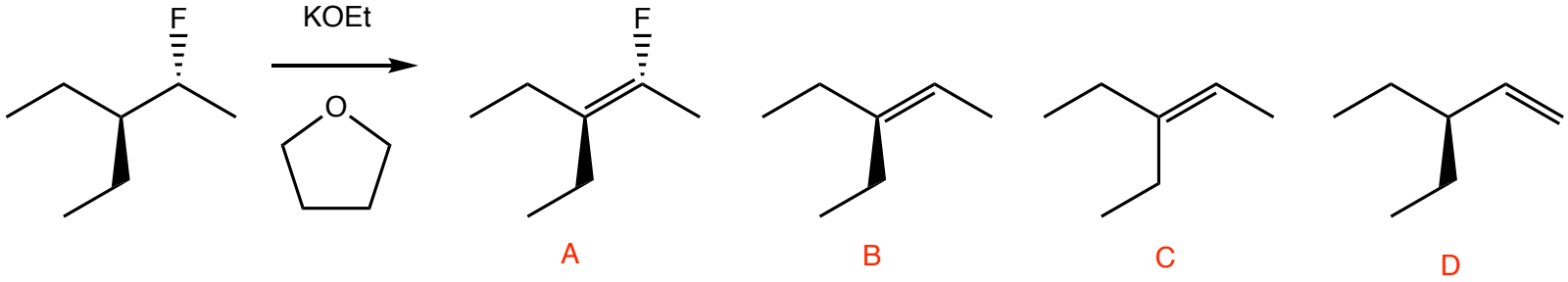

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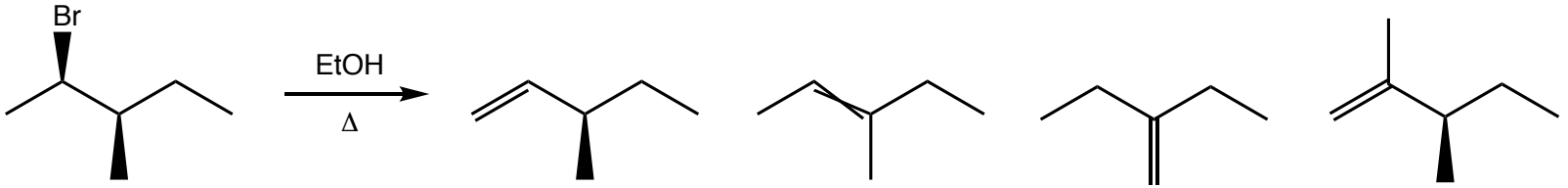
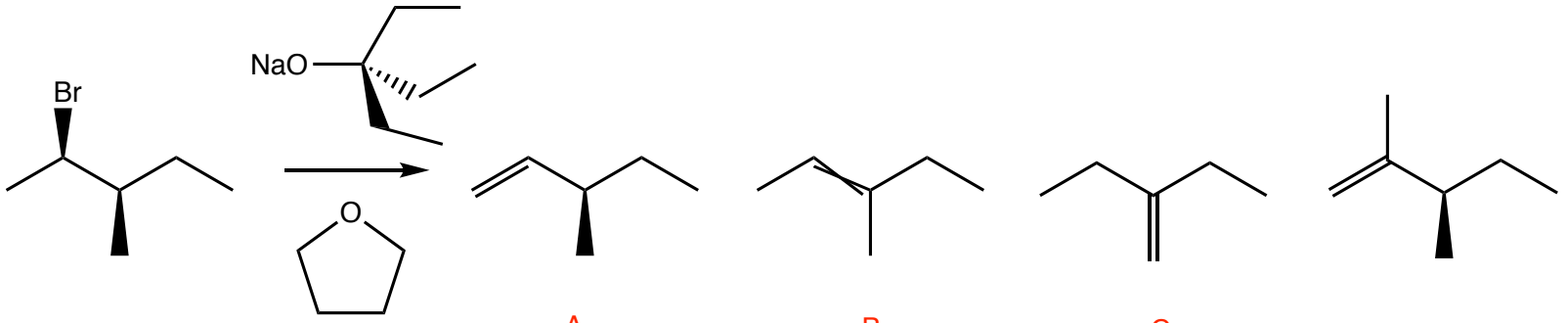


A B C D



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