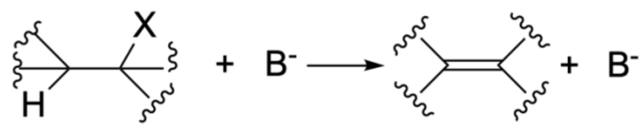
Problem Set 10

Organic Chemistry 1 (Greenberg)

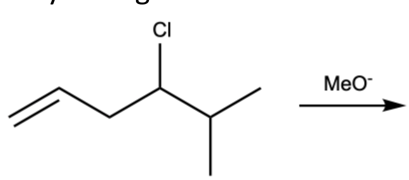
Fall 2025

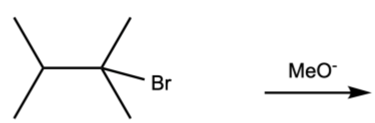
1. Elimination. Ray is thinking of taking orgo. However, he doesn't want to be eliminated by the curve. He comes to PILOT to learn about elimination. Help him out!
   a. Let's start with E1 and E2 reactions. What do they stand for?

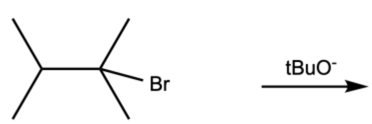
   b. Draw the mechanism for an E1 and E2 reaction using the following reaction. For each reaction, include the transition state/intermediate.



   c. Regioselectivity. Draw the product for the following reactions. Think about stability and kinetics. Hint: Methoxide is a small strong base, tert-butoxide is a bulky strong base.

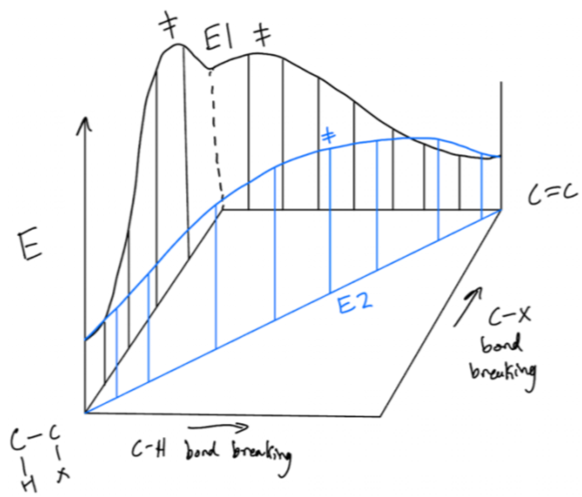


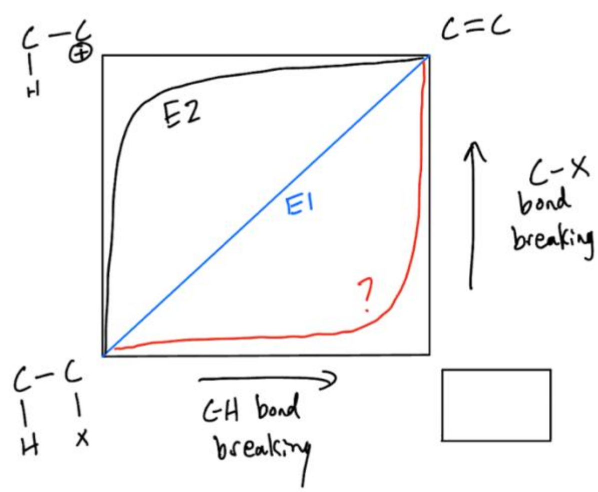




d. Draw the reaction coordinate for a generic E1 and E2 reaction.

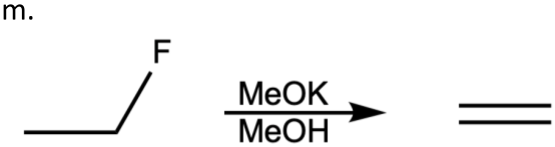
e. It is strange to draw the bond breaking and forming on the same reaction coordinate. We have a 3-dimensional reaction coordinate. Look at the following reaction coordinate diagram on the left. The black line describes the E1 mechanism with two separate transition states. The blue line has only one transition state and is a one-step E2 reaction directly from the start to the end. The diagram on the right shows a 2D projection when viewing the reaction coordinate from above. Fill in the red intermediate in the box given.





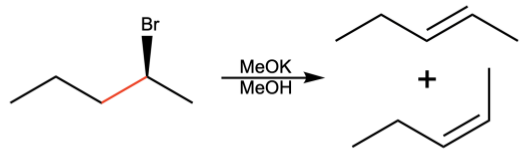
Note: This is only to help you understand the differences between E1 and E1cb. Do not get hung up on the details or math. If you are interested to learn more, check the answer key.

f. The red path above is called the E1cb: Elimination Unimolecular Conjugate Base. This reaction involves formation of the carbanion intermediate. Draw the E1cb mechanism, then give three reasons why the following reaction undergoes the E1cb mechanism.

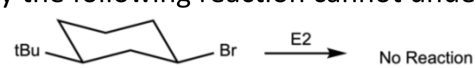


g. For an E2 elimination mechanism, which orbital on the carbon bearing the leaving group must be populated to allow the C–X bond to break? Illustrate the geometry of this orbital in relation to the C–H σ bond that is being broken. This geometry is required for E2 reactions, and is called antiperiplanar.

h. Using the above diagram and a Newman projection along the red bond as a hint, determine whether this E2 reaction prefers E/Z stereochemistry (MeO^- is a small strong base).



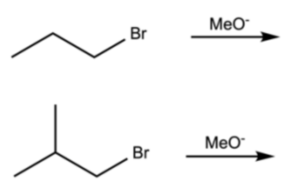
i. Rationalize why the following reaction cannot undergo an E2 mechanism.



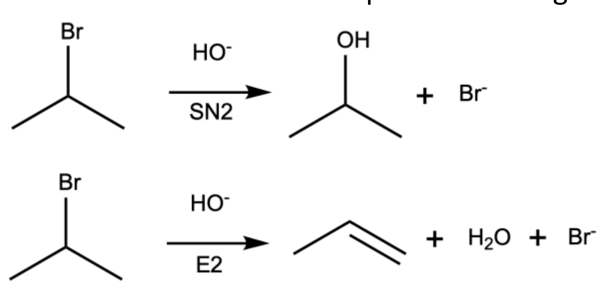
2. Summary. We have done a lot of thinking about elimination and substitution reactions. Summarize your findings in the table below.

	SN1	SN2	E1	E2	E1cb
Intermediate					
Preferred Carbon E+					
Preferred Nuc Strength					
Preferred Base Strength					
Leaving Group					
Solvent					

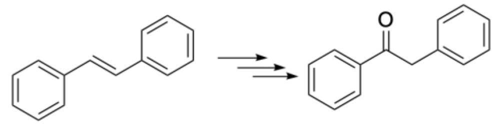
3. Generally, substitution/elimination pathways will prefer one reaction type. For example, it is rare to see 50-50 SN1 and SN2. However, conditions which favor SN1 can also favor E1! Let's consider a couple last things.
   a. Sterics. Predict the major product and reaction mechanism for the following reactions.



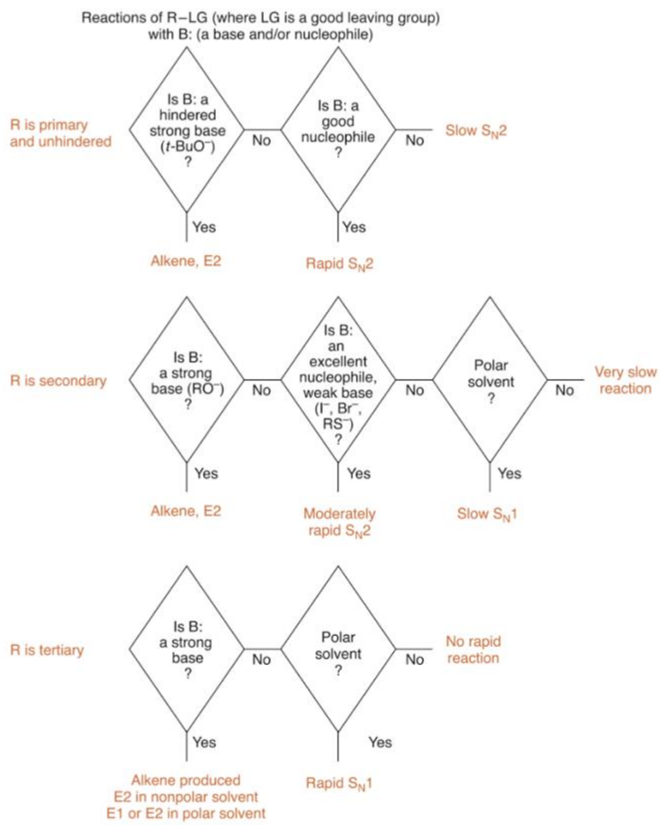
   b. Entropy. First determine whether ΔΔS is positive or negative for the following two reactions, use the following equation: ΔS(E2) – ΔS(SN2). Then determine whether Elimination or Substitution is preferred at high temperatures.



4. A quick synthesis question.



5. No question here. Just a couple diagrams for your reference and a disclaimer. Secondary carbon substrates **can** undergo both E1 and SN1 reactions. The textbook is wrong about this. Make sure you understand the expectations for this class.
   https://pubs.acs.org/doi/10.1021/ed400908g This article also has a helpful figure for you to look at.
   Anslyn and Dougherty.



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