Chemistry 3A – Exam #2

Student Name: _____

Student ID Number: _____

Point Breakdown

Problem 1	_____	/ 20
	_____	/ 23
	_____	/ 8
Problem 2	_____	/ 12
	_____	/ 10
Problem 3	_____	/ 10
	_____	/ 14
Problem 4	_____	/ 15
Problem 5	_____	/ 11
	_____	/ 12
	_____	/ 15

Total _____ / 150

Abbreviated Periodic Table

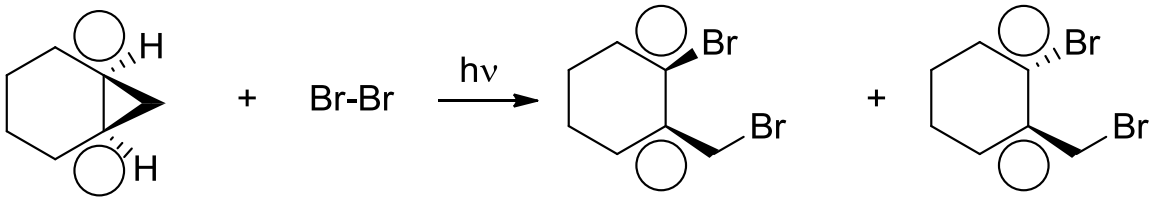
3	4	5	6	7
B	C	N	O	F
		P	S	Cl
				Br

Check that your exam has 12 total pages.

You will have 120 minutes for this exam.

REMEMBER: Electronegativity helps figure out acid/base equilibria, there is a logical progression to mechanisms, resonance is still a thing, and READ THE QUESTIONS.

1. The following reaction is different than your average radical bromination.



"A" **"B"** **"C"**

1. A. Assign each of the 6 stereocenters in the molecules above as R or S. Place the label in the circles near each stereocenter. (6 points)

1. B. Which compound is meso, **"A"**, **"B"**, or **"C"**? (2 points)

1. C. Draw the enantiomers of compounds **"B"** and **"C"** in the appropriate boxes below. (4 points)

Enantiomer of **"B"**	Enantiomer of **"C"**

1. D. Using the following approximate data, calculate the OVERALL reaction energy leading to compound **"B"**. (5 points)

Approximate BDEs

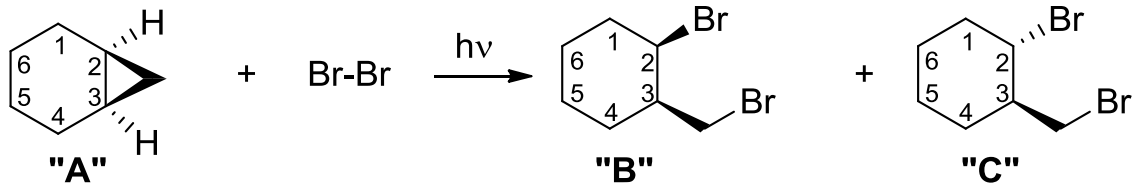
Bond	BDE (kcal/mol)
Br-Br	50
sigma C-C	90
sigma C-Br	60
cyclopropane ring strain	30

Show work:

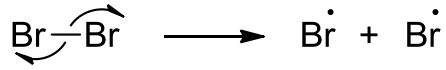
Overall Reaction Energy:

1. E. Radical bromination is usually selective for reaction at tertiary C-H bonds. Why is that not possible in the reaction shown above? (3 points)

Use 10 words or fewer



1. F. Propose a reaction mechanism leading to both products shown. The initiation has been drawn for you. DO NOT SHOW any termination steps. **Indicate any stereodetermining steps**. (10 points)

Initiation: 

Propagation 1: (remember, you are not making H-Br)

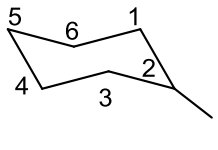
ΔH =

Propagation 2: (remember to show formation of **"B"** and **"C"**)

ΔH =

1. G. Calculate the reaction energy for each of your mechanistic steps using the BDE data on the previous page. (5 pts)

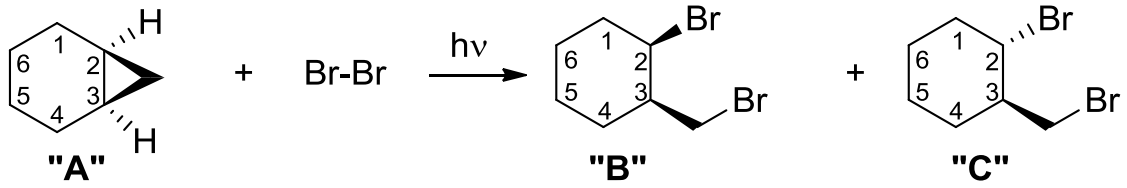
1. H. In the box below, complete the 3D drawing of the radical intermediate formed at the end of the first propagation step. (4 pts)



Radical Intermediate

1. I. Which compound will be kinetically favored, **"B"** or **"C"**? Circle your choice and explain in 15 words or fewer. (4 pts)

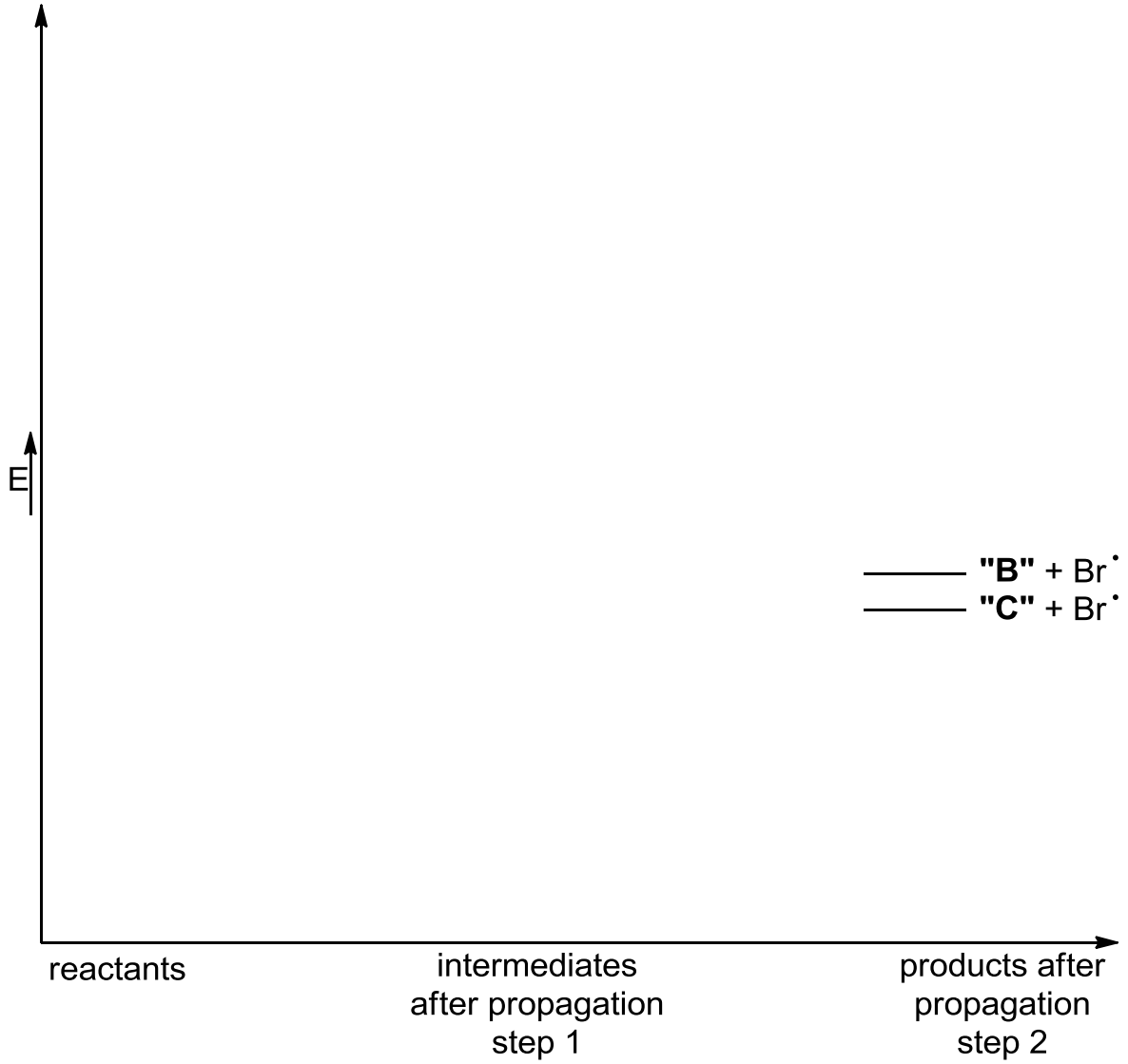
"B" / **"C"** is kinetically favored because:



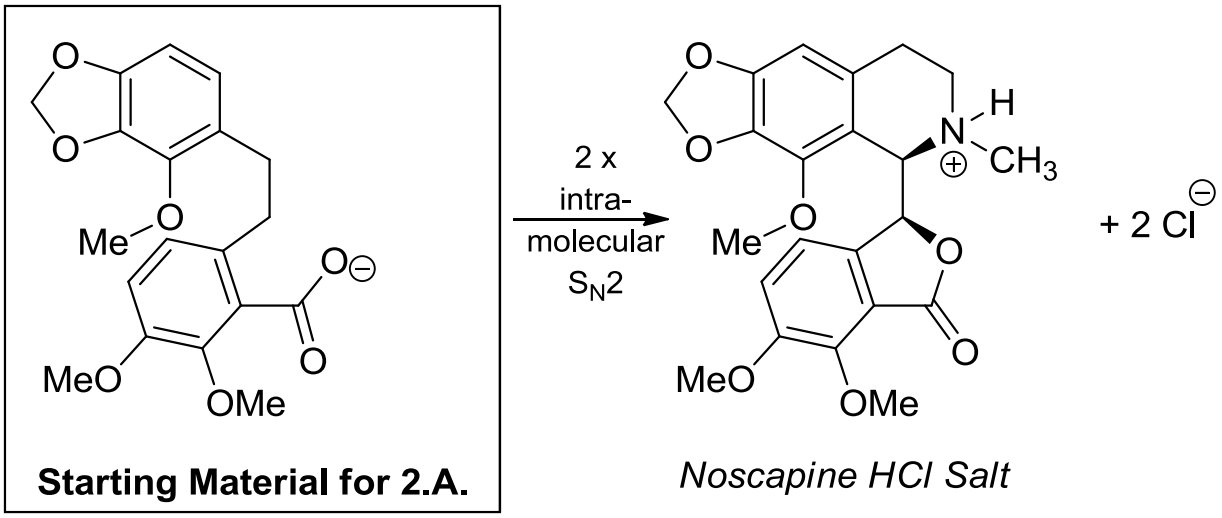
1. J. Complete the reaction coordinate energy diagram for this reaction. Add appropriate energy levels for the reactants relative to the products as well as the intermediates relative to both the products and the reactants. Assume the First Propagation step is the Rate Determining Step. (8 pts)

To help you draw the diagram, and to help us grade it, please re-write the answers to the following questions in the boxes below.

1.G. ΔH of Prop 1:	1.G. ΔH of Prop 2:	1.D. ΔH of overall rxn:



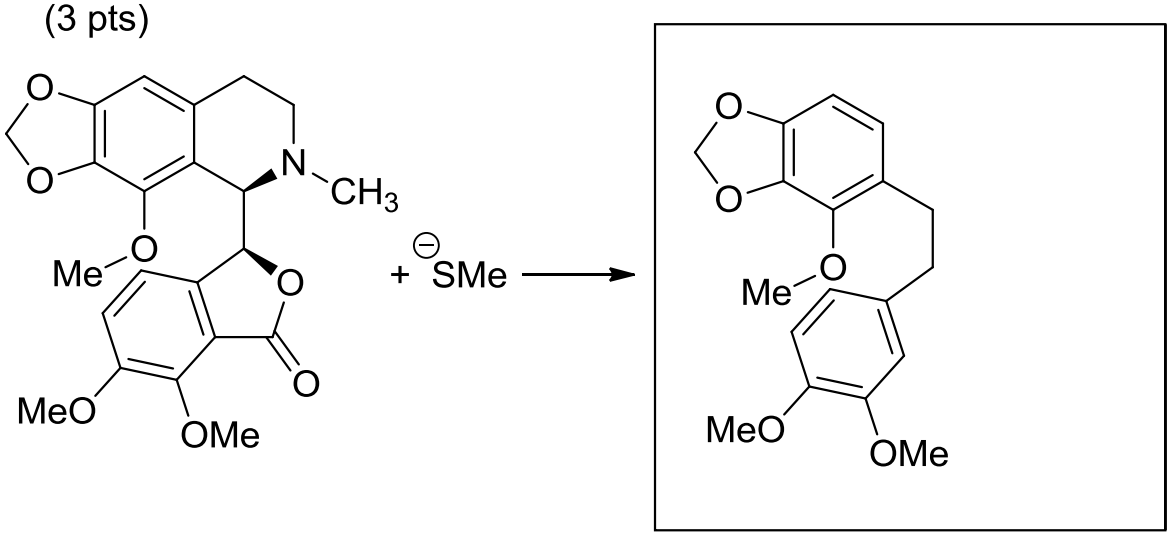
2. Noscapine is a cough-suppressant with some pretty terrible side effects.



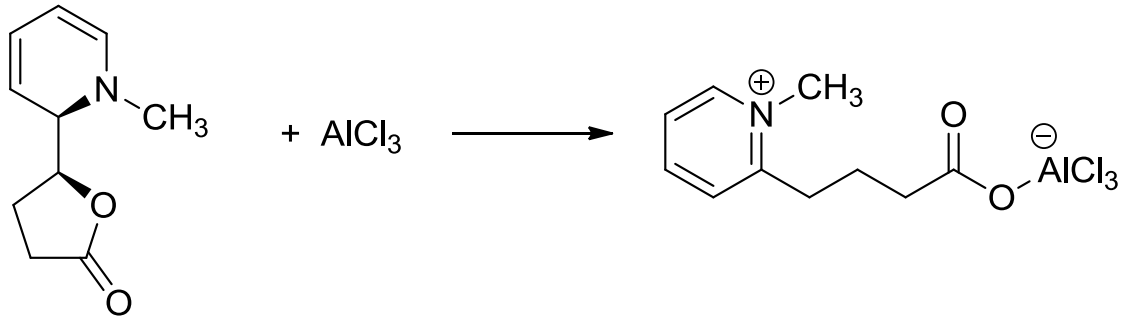
2. A. Finish drawing the starting material on the left that leads to Noscapine product on the right. Your starting material should be able to undergo two intra-molecular S_N2 reactions to yield the desired product. (5 pts)

2. B. Add electron-pushing arrows to your starting material in 2.A. that are consistent with two S_N2 attacks leading to the product shown. (4 pts)

2. C. Carboxylates, the conjugate bases of carboxylic acids, are also good leaving groups. Show the product(s) of the following S_N2 reaction. (3 pts)



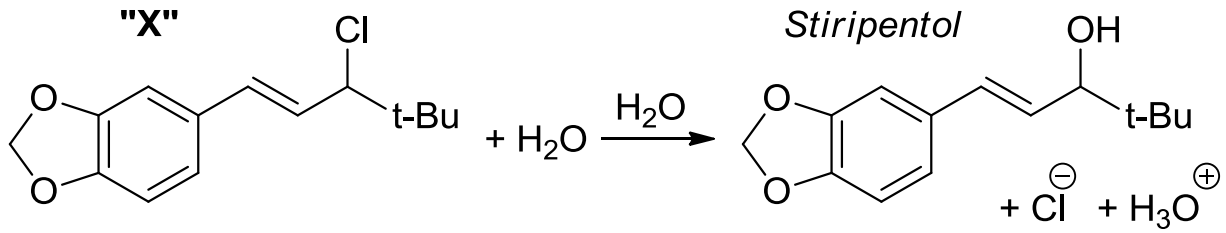
2. D. Provide a rational arrow-pushing mechanism for the following reaction. Hint: the first step is a Lewis Acid / Lewis Base step. Hint: there will need to be some resonance. (10 pts)



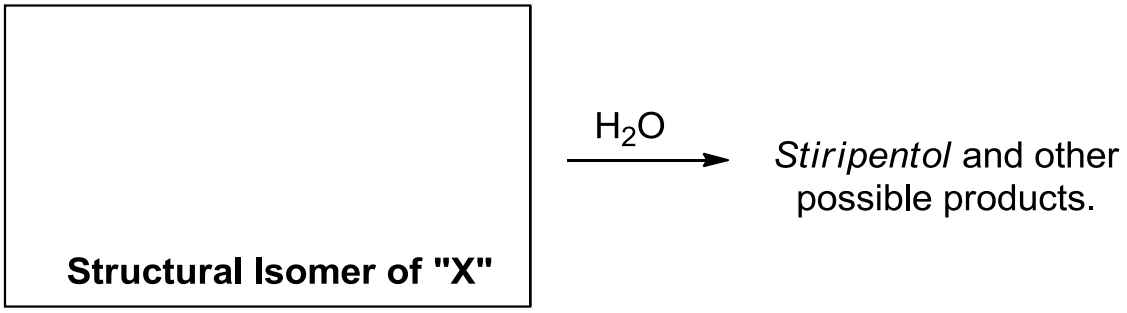
You will not need all of this space.

3. Epilepsy drugs tend to increase production of GABA in the body. GABA is responsible for reducing neuron over-stimulation in mammals. Two epilepsy drugs that we will investigate are Stiripentol and Gabapentin.

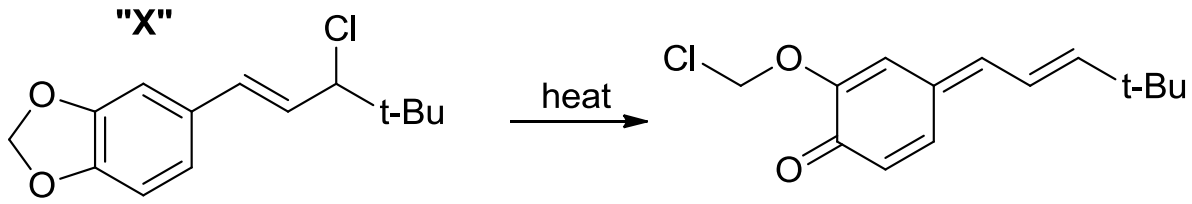
3. A. Draw the S_N1 mechanism for the transformation of "X" into the products below. Remember to show formation of all products and use accurate equilibrium arrows for any acid/base steps. (5 pts)



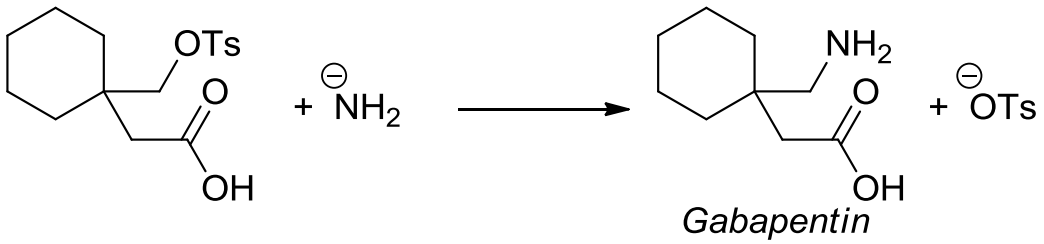
3. B. Draw a structural isomer of **"X"** that can also yield Stiripentol under these same S_N1 conditions. (5 pts) (note: it will also yield other pdts)



3. C. A possible decomposition product of compound "X" is shown below. Draw the mechanism. (5 pts)



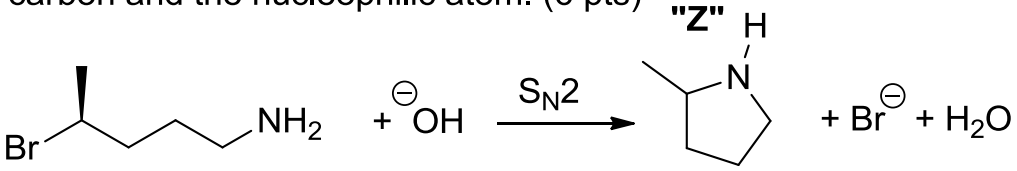
3. D. A student proposes the following synthesis of Gabapentin. It will not yield Gabapentin as desired. Indicate TWO problems with the reaction and show the actual products you would expect. (9 pts)



Problem 1:	Problem 2:	Actual Products:

4. ***QUIZ REDEMPTION!***

4. A. Draw a logical arrow-pushing mechanism for the following reaction. Show an accurate equilibrium arrow for any acid-base reactions. In the mechanism, CLEARLY DRAW ORBITAL OVERLAP of the alpha carbon and the nucleophilic atom. (6 pts)



4. B. Add stereochemistry (wedge or dash) to the methyl group of the above product "Z" so it is consistent with your mechanism. (2 pts)

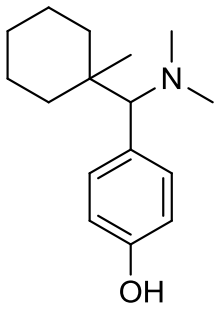
4. C. Draw a transition state for the first mechanistic step from question 4.A. Do not worry about relative bond-lengths in the transition state. (3 pts)

Transition state for first mechanistic step of 4.A.

4. D. The rate expression for any reaction is expressed as k[stuff] where "stuff" is what is reacting in the rate determining step. What is the rate expression for the reaction of 4.A.? (4 pts)

rate =

5. Desvenlafaxine (Pristiq) is a flea medication for domestic animals. Let's investigate its synthesis.



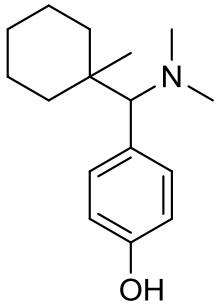
Desvenlafaxine (Pristiq)

5. A. On the structure to the left, place a star (*) next to the stereocenter. (1 pts)

5. B. Circle the hydrogen atom that is most acidic on Desvenlafaxine. (1 pts)

5. C. Draw a BOX around the atom that is most basic on Desvenlafaxine. (1 pts)

5. D. Desvenlafaxine can exist as a zwitterion (neutral overall compound, but there are two opposite formal charges). This happens when the most basic atom deprotonates the most acidic proton in the same molecule. Draw the zwitterion of Desvenlafaxine below. (4 pts)

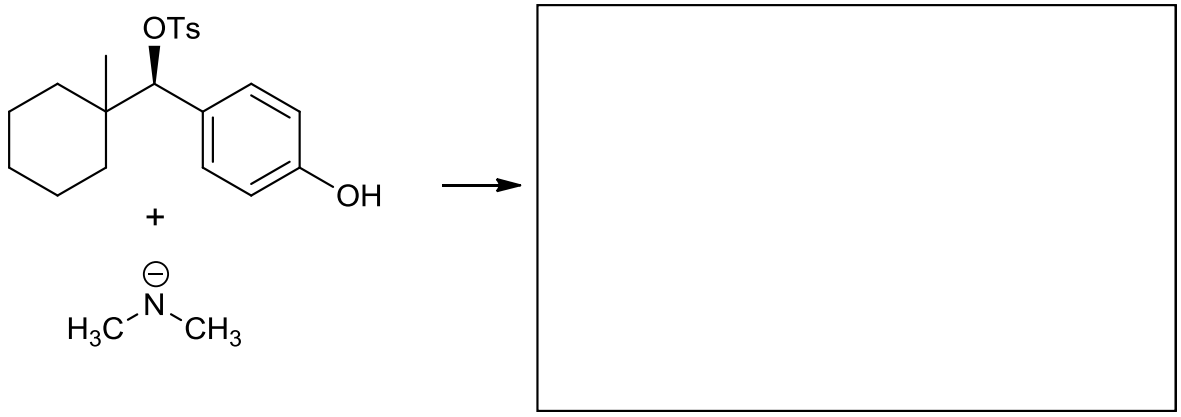


Zwitterion of Desvenlafaxine

5. E. The equilibrium constant, K_{eq}, between Desvenlafaxine and its zwitterion is 1. What does that tell you about the relative pKas of the two compounds? (2 pts)

5. F. The equilibrium constant, K_{eq}, between Desvenlafaxine and its zwitterion is 1. What does that tell you about the relative thermodynamic stabilities of the two compounds? (2 pts)

5. G. Predict the products of the first mechanistic step, an acid-base reaction, between the following reactants. (3 pts)



5. H. The neutral starting material in question 5.G. can't act as an electrophile in an S_N2 reaction. Explain in 10 words or fewer. (3 points)

The compound cannot act as an S_N2 electrophile because:

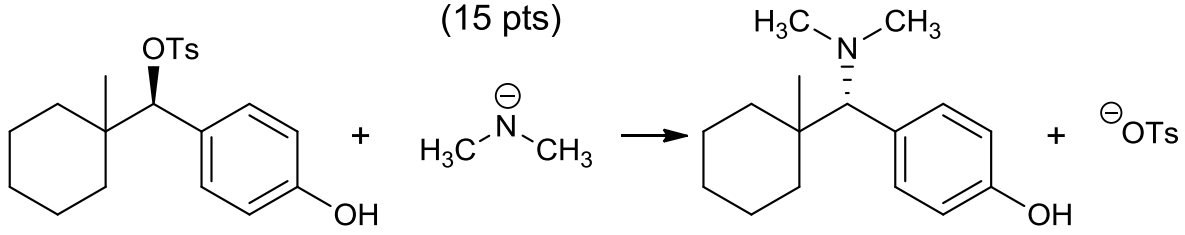
5. I. Can the neutral starting material in question 5.G. act as an electrophile in an S_N1 reaction? Circle your answer and explain in 10 words or fewer. (3 points)

The compound can / cannot act as an S_N1 electrophile because:

5. J. Unrelated to this compound, draw the structure of a tosylate anion ($\ominus$OTs). (3 pts)

Structure of tosylate anion ($\ominus$OTs)

5. K. Using the information you've learned in the earlier parts of this question, (see 5.G., 5.H., and 5.D) draw a logical arrow-pushing mechanism for this reaction. Add appropriate equilibrium arrows for all acid-base steps. (15 pts)



Extra Credit: This reaction's rate expression is actually bimolecular. Propose a 15 word explanation for this strange result. (4 pts)