Professor Pete Marsden July 27, 2012

Chemistry 3A – Midterm #2

Student Name: _____

SID Number: _____

TA or Section: _____

Point Breakdown

Problem 1	_____	/ 11
	_____	/ 13
Problem 2	_____	/ 18
	_____	/ 10
	_____	/ 17
Problem 3	_____	/ 24
Problem 4	_____	/ 27
	_____	/ 15
	_____	/ 15
Total	_____	/ 150

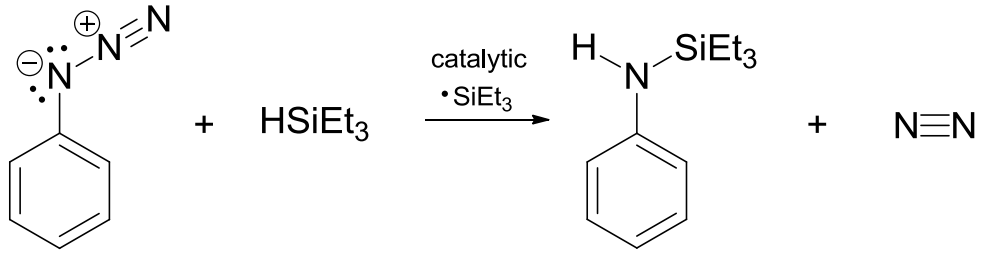
Check that you have 11 pages.

You will have 120 minutes for this exam.

Remember: Homolytic and Heterolytic reactions require different electron-pushing arrows and stereochemistry is very important.

1. RADICAL CHEMISTRY SECTION!!! In class, we have focused on radical halogenation. Another radical reaction is the hydrosilation of azides. (24 points)

1. A. Using the data on the last page, calculate the overall energy of the reaction shown below. Be sure to show your work and place the answer in the box labeled "$\Delta H_{overall}$". (5 points)

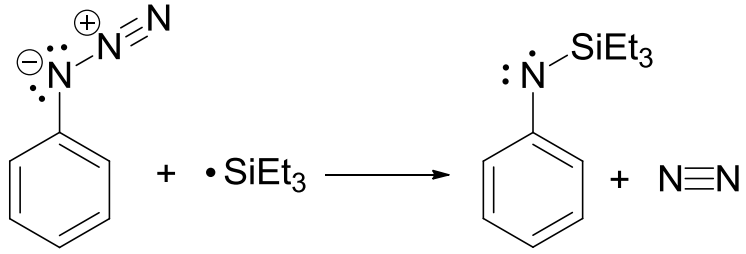


phenyl azide | triethylsilane | hydrosilation product | dinitrogen gas

Show work

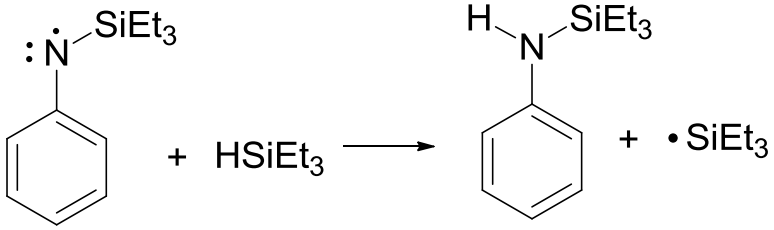
$\Delta H_{overall}$ = kcal/mol

1. B. Below are the propogation steps for this reaction. Calculate the ΔH for each step and place the number in the box to the right of the reaction. (6 points)



Show work

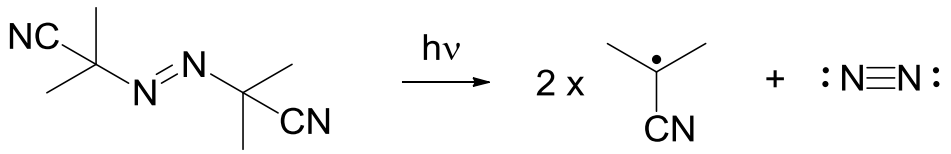
ΔH = kcal/mol

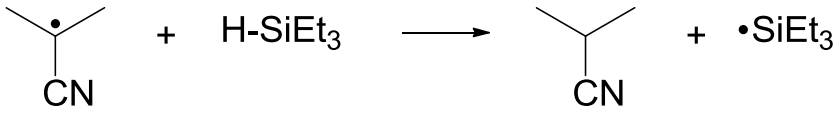


Show work

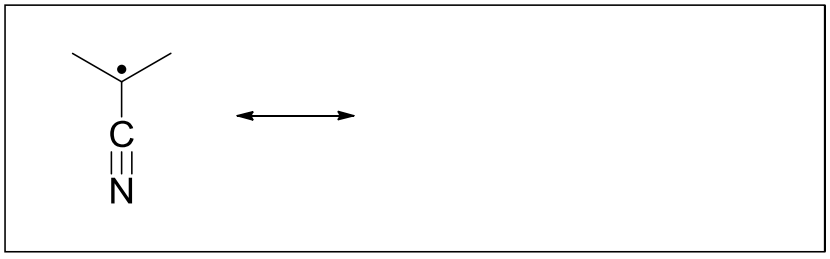
ΔH = kcal/mol

1. C. The catalytic amount of •$SiEt_3$ is actually formed via the reaction of a radical species with $HSiEt_3$. Provide a rational arrow pushing mechanism for the two following reactions. Be sure to show how all products are formed. (10 points)

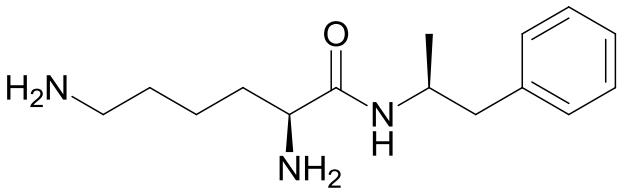




1. D. Provide one more resonance structure for the radical species shown below. (3 points)



2. Vyvanse® (lisdexamfetamine) is a new drug that treats ADHD. We will explore the chemistry of this fascinating drug. (45 points)



Vyvanse® [α] = +20º

2. A. Based on what you know about resonance contributors, clearly circle the nitrogen atom on the structure above that is the LEAST NUCLEOPHILIC. (2 points).

2. B. On the structure above, clearly mark the stereocenters with an asterisk (*). (2 points)

2. C. Label all of the stereocenters on Vyvanse as "R" or "S". (4 points)

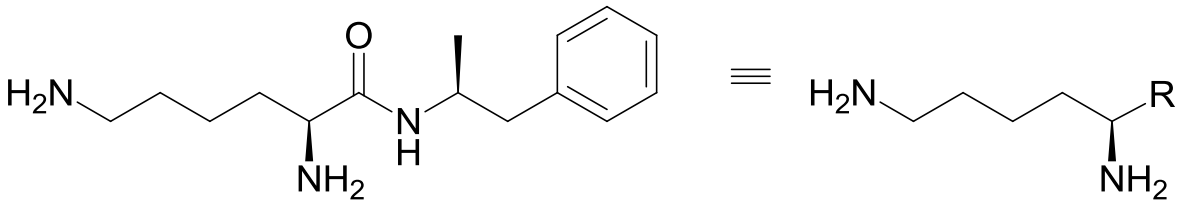
2. D. In the space provided below, draw the enantiomer of Vyvanse. (3 points)

Vyvanse® enantiomer	[α] =

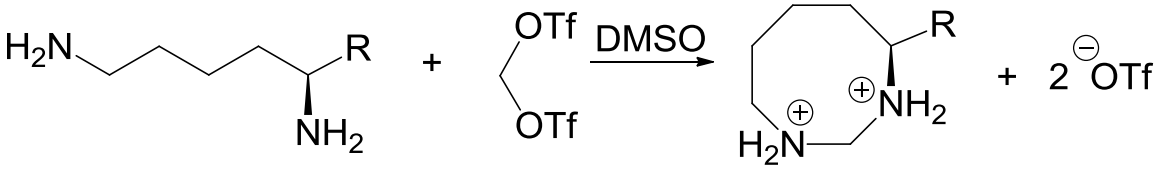
2. E. What is the optical rotation you would expect for this enantiomer? Place the value in the appropriately labeled box above. (2 points)

2. F. A mixture of Vyvanse and its enantiomer gave an optical rotation of -2º. What percentage of the mixture is the MINOR enantiomer? You must show your work to receive any credit. (5 points)

Show work:	
	% minor enantiomer =

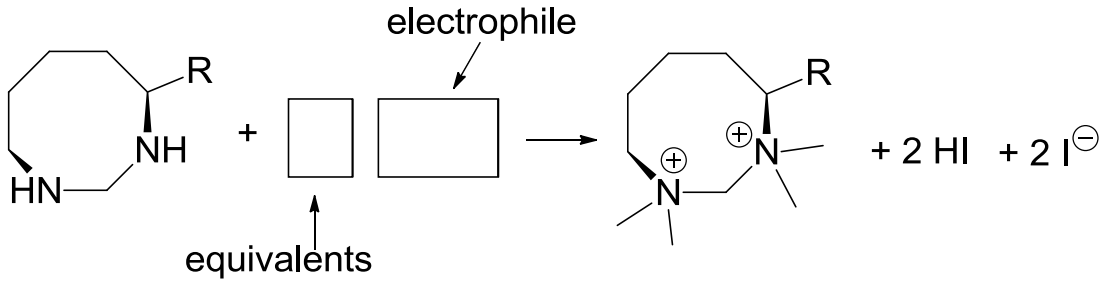


2. G. Provide a rational arrow-pushing mechanism for the following reaction. Be sure to show the formation of all products. (10 points)

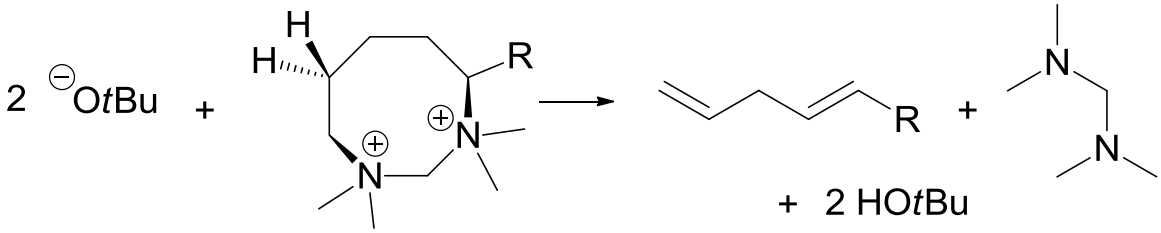


You won't need all of this space.

2. H. Fill in the number of equivalents as well as the identity of the electrophile for the following reaction. (4 points)



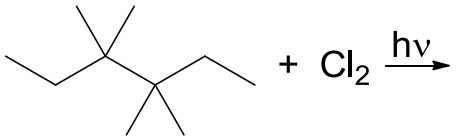
2. I. Provide a rational arrow-pushing mechanism for the reaction shown below. To receive full credit, you must clearly show the proper stereochemical relationship for any elimination reactions. (8 points)



Hint: For your first mechanistic step, remove one of the hydrogens shown

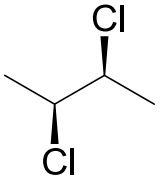
2. J. For the reaction shown in 2.I., would it be possible to form another stereo-isomer of the alkene product? Please say "yes" or "no" and explain your answer with one or more Newman Projections. (5 points)

3. Predict the products of the following reactions. Pay careful attention to the reaction conditions as well as any instructions in the answer boxes. Be wary of stereochemistry. Repeat answers will cancel out correct answers. (24 points)



+ HCl

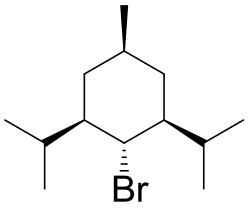
All possible mono-chlorinated products, including stereoisomers.



+ 1 equiv $\ominus$OH DMF

All possible organic molecules resulting from concerted reaction mechanisms.

4. A. Predict the products of the following reaction. Place your answers in the appropriate boxes. (12 points)



*i*PrSH

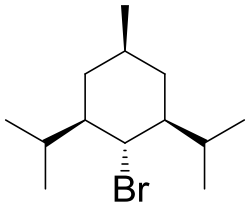
warm

Major Substitution Product	Minor Substitution Product
Elimination Product **1**	Elimination Product **2**

4. B. Label the stereocenters on the starting electrophile as "R" or "S". (4 pts)

4. C. Is the starting material chiral? (3 points) Yes or No

4. D. Provide a rational arrow-pushing mechanism for the reaction leading to the MINOR substitution product. To receive full credit, you must clearly show the high-energy interactions between the nucleophile and the active electrophile. (8 points)



*i*PrSH

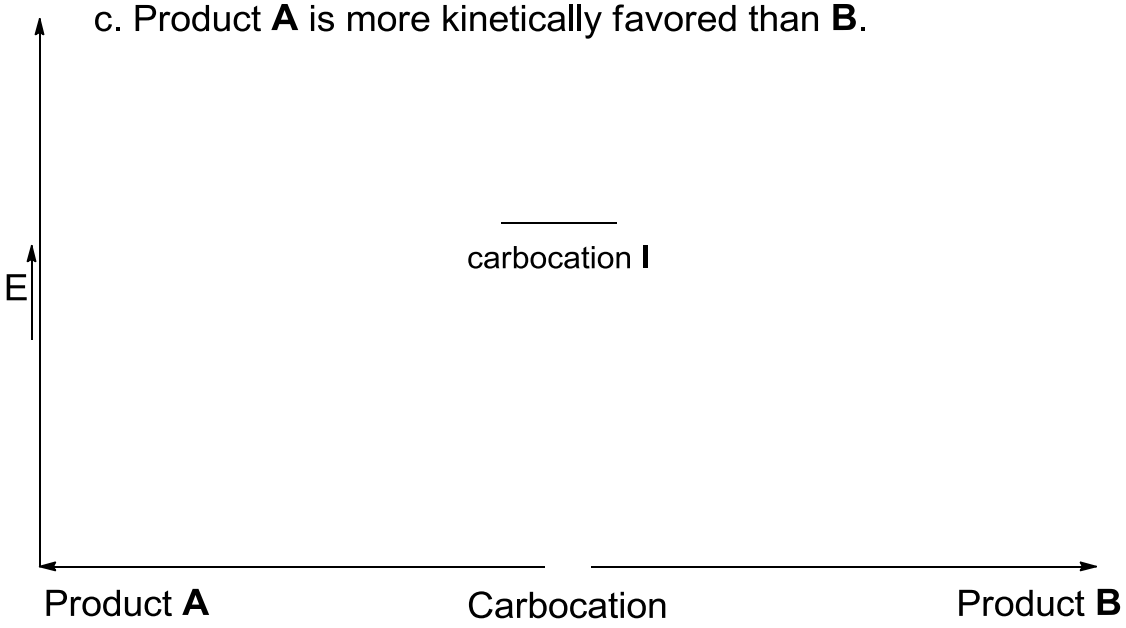
warm

MINOR substitution product

+ HBr

4. E. Using the information below, draw an appropriate energy diagram. You do NOT NEED to write in any structures on the diagram. (8 points)

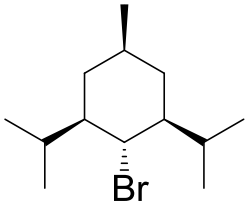
a. Both substitution products **A** and **B** are lower in energy than carbocation **I**
b. Product **B** is more thermodynamically stable than **A**.
c. Product **A** is more kinetically favored than **B**.



4. F. Which product on the above diagram corresponds to the MAJOR product from 4.A.? (3 points)

Product **A** or Product **B**

4. G. The addition of a strong base (NaS*i*Pr) to the reaction from 4.A. HAS NO effect on the distribution of the elimination products. Clearly explain why this is the case using words and pictures. (4 points)

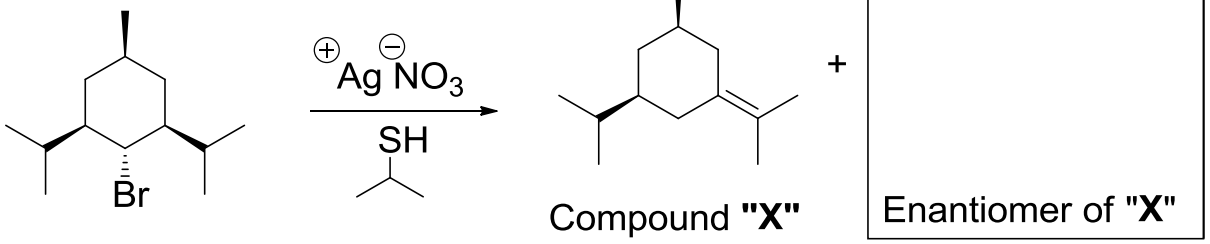


+ *i*PrS$^{\ominus}$ $\oplus$Na $\xrightarrow[\text{warm}]{i\text{PrSH}}$ Same elimination products and distribution as those seen in 4.A.

Addition of a strong base does not change the distribution of elimination products because:

4. H. For the reaction below, draw the enantiomer of compound "**X**" in the appropriately labeled box. (3 points)

4. I. Provide a rational arrow-pushing mechanism for the reaction below. Be sure to show how each product is formed. To receive full credit, you must clearly state at which mechanistic step the stereochemical differentiation occurs. (12 points)



+ AgBr + HNO_3

Mechanism:

SUCCESS! THIS MIDTERM IS DONE! ENJOY SOME FUN IN THE SUN

Feel free to remove this page from the exam

Important Bond Dissociation Energies in kcal/mol

Bond	Energy	Bond	Energy
$PhN-N_2$	10	Et_3Si-H	75
R_2N-Si	110	R_2N-H	100

Abbreviated Periodic Table

Valence e^-	3	4	5	6	7
	B	C	N	O	F
		Si	P	S	Cl
		Sn			Br