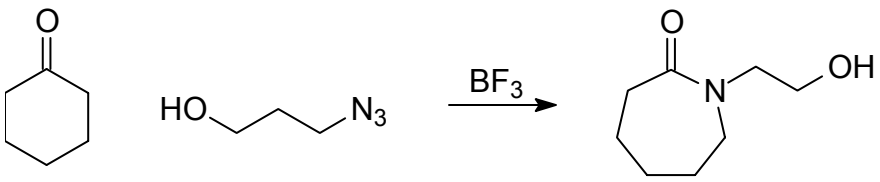
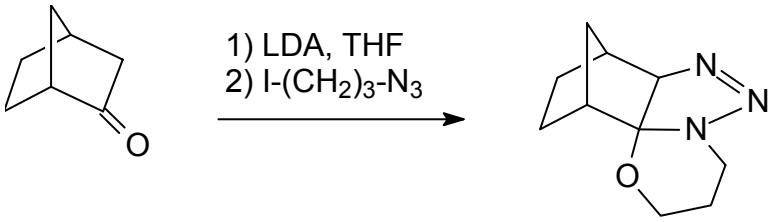
Organic Cumulative Examination. October 7, 2004

1. Provide a detailed mechanism for the following multi-step conversion. Your mechanism should show all intermediates formed in the reaction. Show electron flow with arrows.



2. When 2-methoxycyclohexanone is used as a substrate in the above reaction, two products are formed in a 10:1 ratio.
2A. Draw the two products expected from reaction of 2-methoxycyclohexanone under the conditions of the reaction shown in problem 1.
2B. Indicate which of your two predicted products is the major product, and explain why it is the major product.

3. Treatment of norbornanone with LDA followed by addition of 1-azido-3-iodopropane gives the product shown below.

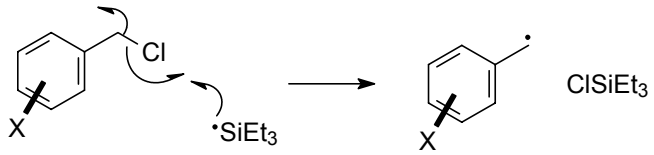


3A. The product shown above can be formed by different reaction pathways. Show two different reaction pathways for formation of the product. Draw out all intermediates in the reactions, and show electron flow with arrows.

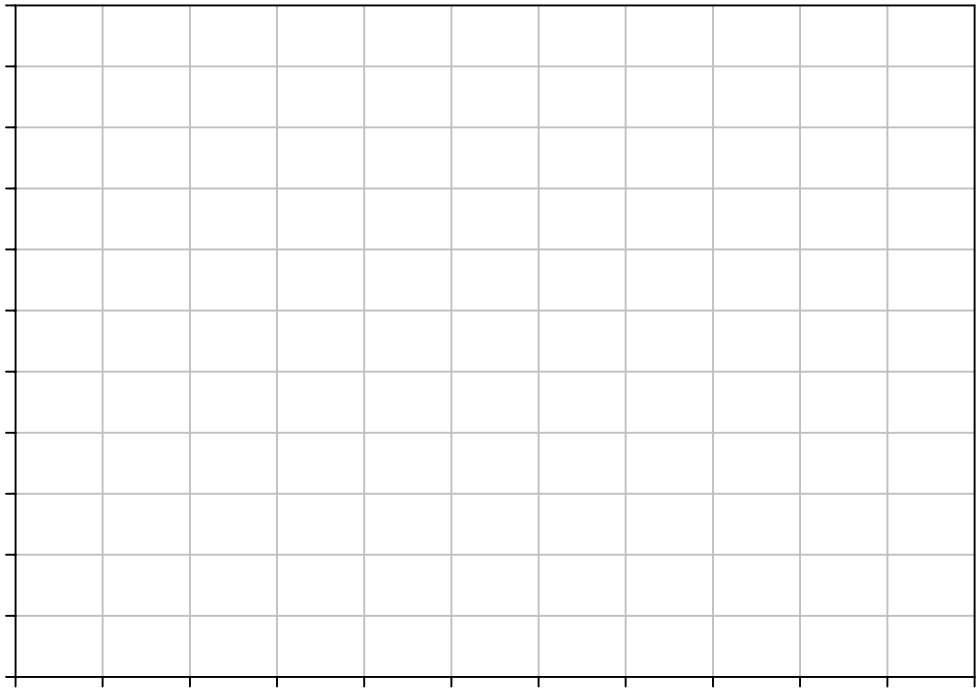
3B. Describe experimental tests that might be conducted to determine which of your reaction pathways is correct.

Remove the last two pages of this exam, and return them with your answer book.

4. Construct a Hammett plot using the following kinetic data for the radical abstraction reaction shown below.



substituent X	sigma value	$10^{-7} \times k$ (M^{-1} s^{-1})
H	0	1.9
m-MeO	0.10	3.1
p-F	0.15	3.3
m-Cl	0.37	3.7
m-F	0.34	4.2
m-CF_3	0.46	4.5
p-CN	0.70	8.3



B. Determine the approximate rho value in your plot. ρ = _____

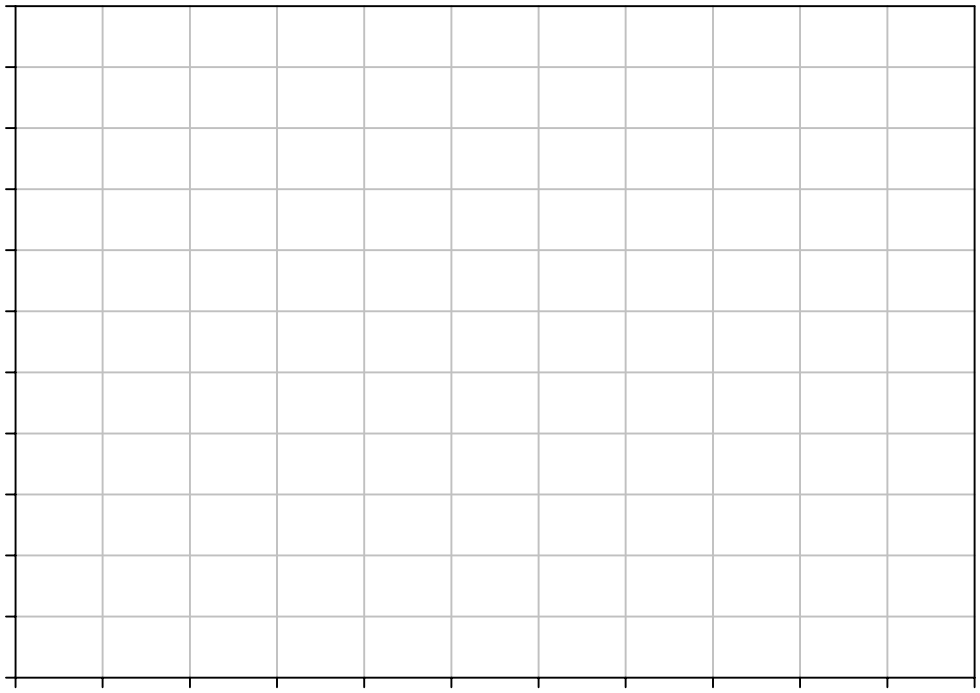
C. Explain the degree of charge development in the transition state for the chlorine abstraction reaction. Your **short** discussion should include a rationalization for the type of charge development (that is, + or -) and the amount of charge.

5. The following kinetic data was obtained for a first-order reaction. What are the activation parameters for the reaction (log A and E_a in kcal/mol)? (Use a value for the gas constant R of 2 cal/mol-°K)

Temp (°C)	k (s^{-1})
2.85	4.81E+05
12.4	7.36E+05
19	1.08E+06
24.6	1.37E+06
30.1	1.71E+06
35.1	2.13E+06
41.4	2.67E+06

log A = _____

E_a = _____ kcal/mol



B. Is entropy increased or decreased in the transition state of this reaction? Explain your answer.