Chemistry 112B: Midterm 1, Thursday February 24, 2011

Name: KEY

UCSID: _____ *GSI:* _____

Question 1 _____ (35 points)

Question 2 _____ (15 points)

Question 3 _____ (15 points)

Question 4 _____ (10 points)

Question 5 _____ (15 points)

Question 6 _____ (10 points)

Question 7 _____ (20 points)

Question 8 _____ (25 points)

Question 9 _____ (30 points)

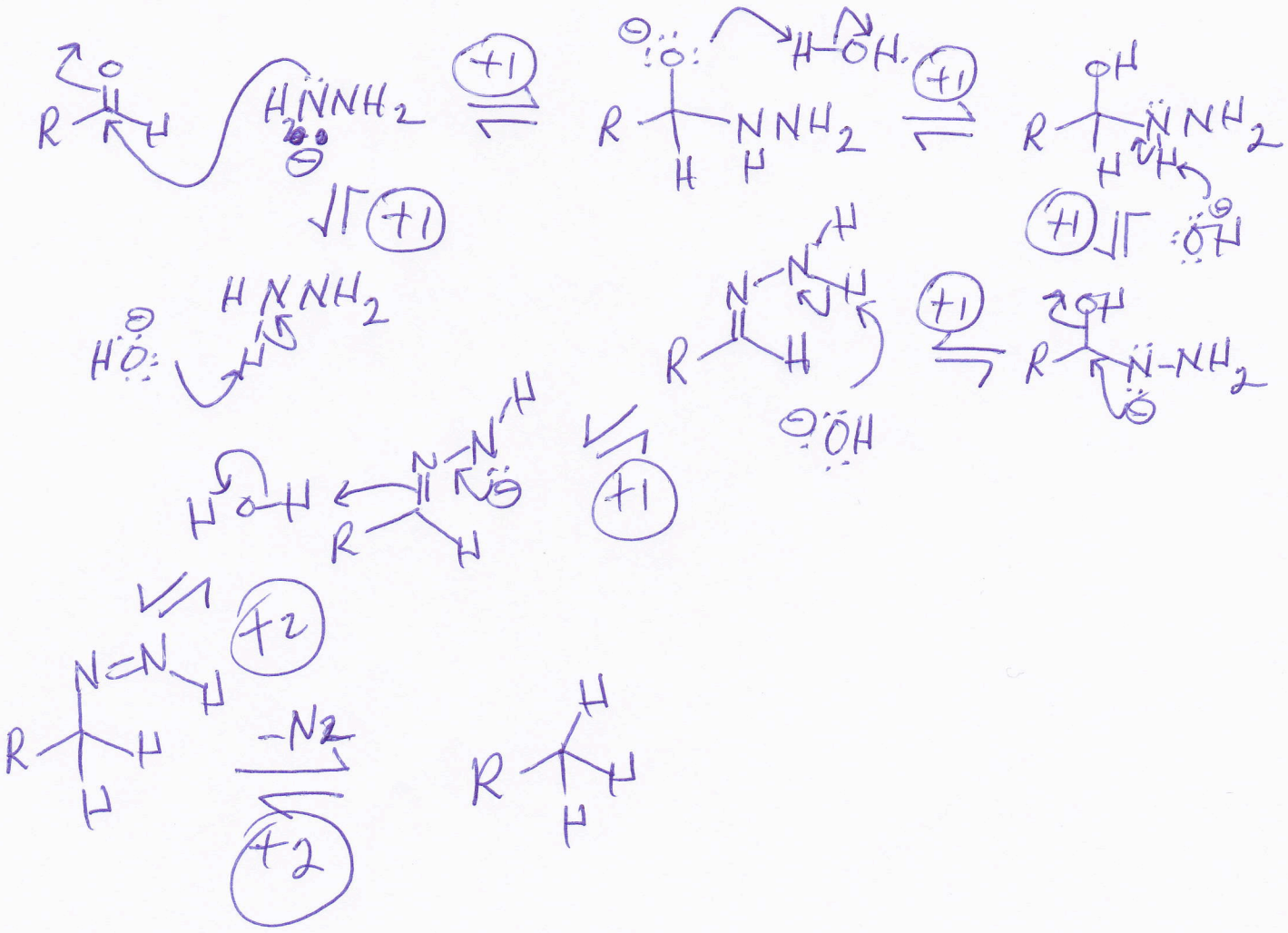
Total ———————————/175 points

Question 1

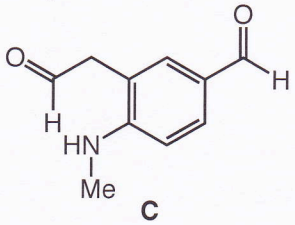
(a) Propose reagents for the following transformation of **A** to **B** and a name for this type of reaction. (10 points; 5 points each)

Name: Wolff Kishner 5 pts

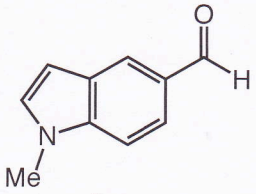
(b) Propose a mechanism for the transformation of **A** to **B** shown above (10 points)



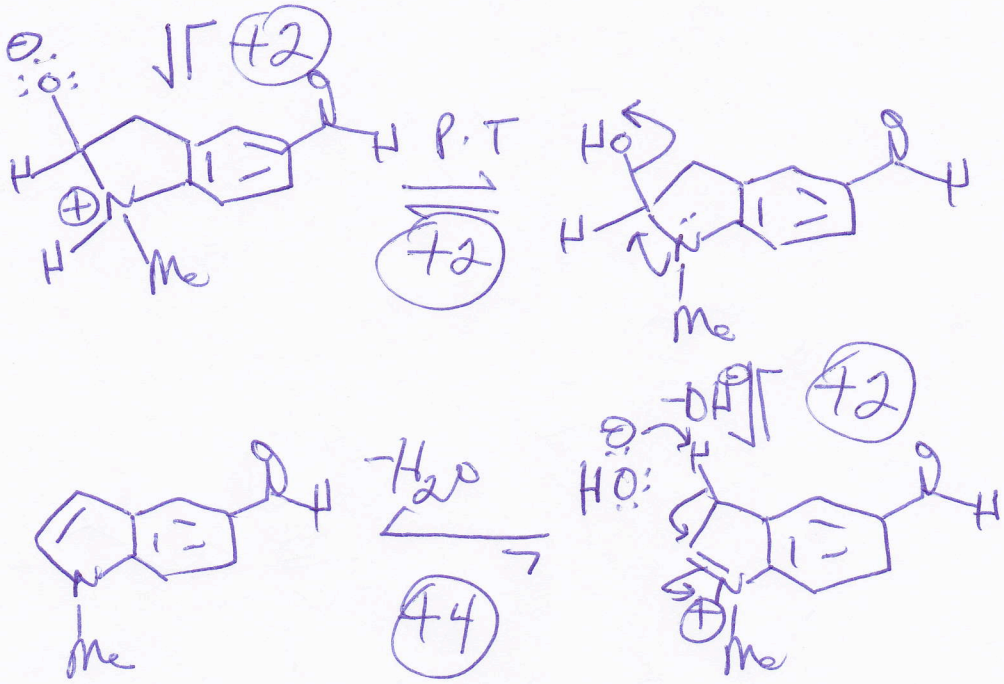
(c) Propose a mechanism for the conversion of **C** to **A**. (10 points)



C



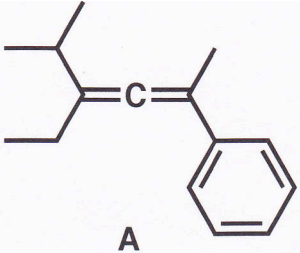
A



They may also propose an acid or base-catalyzed mechanism: In those cases, avoid -ve charges in acid and positive charges in base unless we are referring to the conjugate base or acid respectively.

(d) On the basis of your mechanism above, how would you favor the formation of **A** from **C** (One sentence)? (5 points)

By removing water

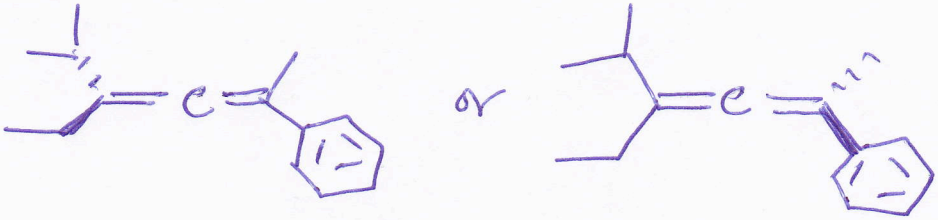


A

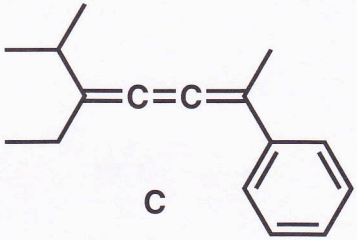
(a) What general name is given to compounds of type A? (2 points)

cumulene or allene

(b) Redraw structure **A** in the space below paying careful attention to stereochemistry. (5 points)



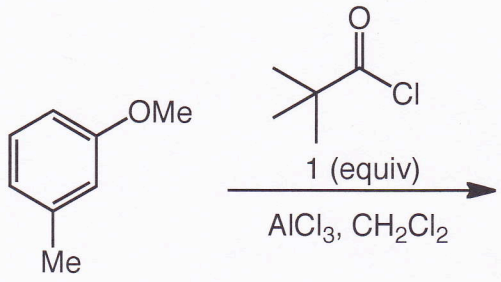
(c) Explain why the structure of **C** is as shown by drawing the relevant orbital interactions. (8 points)



C

Question 3

(a) Predict 2 possible products of the following reaction after workup. 1 equivalent of acid chloride is used. (6 points).



(b) Do you need catalytic or stoichiometric $AlCl_3$?: Stoichiometric (2 points)

(c) Provide a mechanism for the formation of *one* of the products from Part (a). (7 points)

also possible but less likely... (2 pts)

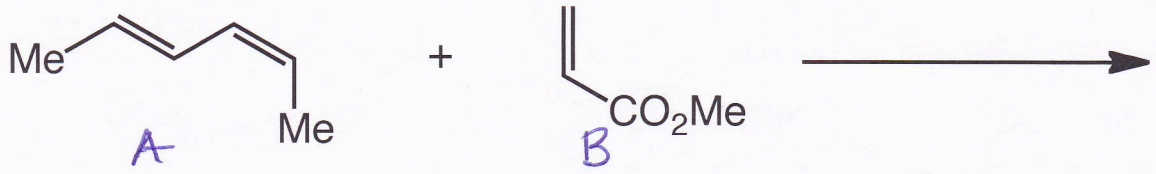
must show this resonance form

must show this

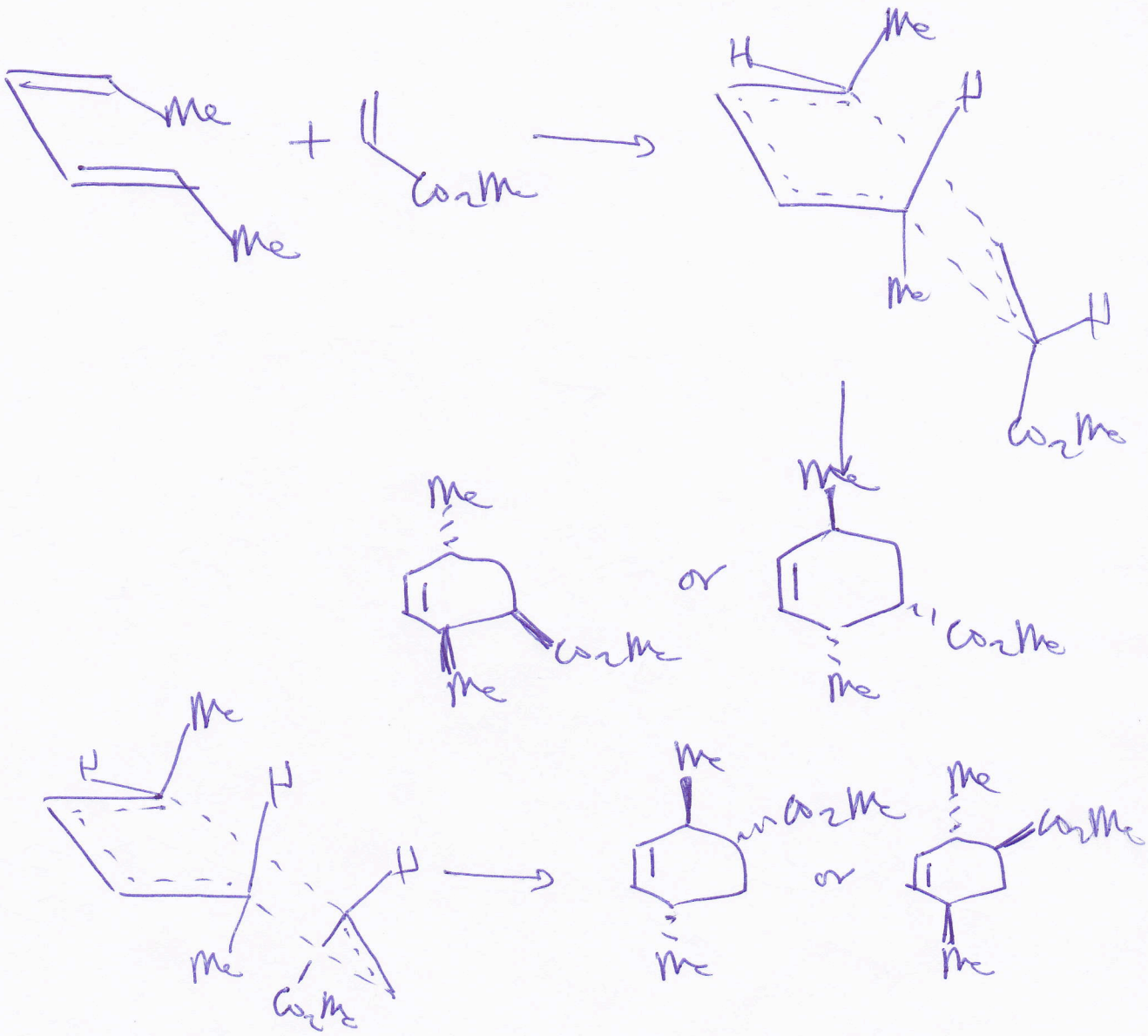
W/up

Question 4

(a) Predict the expected **major** product (with stereochemistry) of the following Diels-Alder reaction between **A** and **B** (Show only one enantiomer). (5 points)

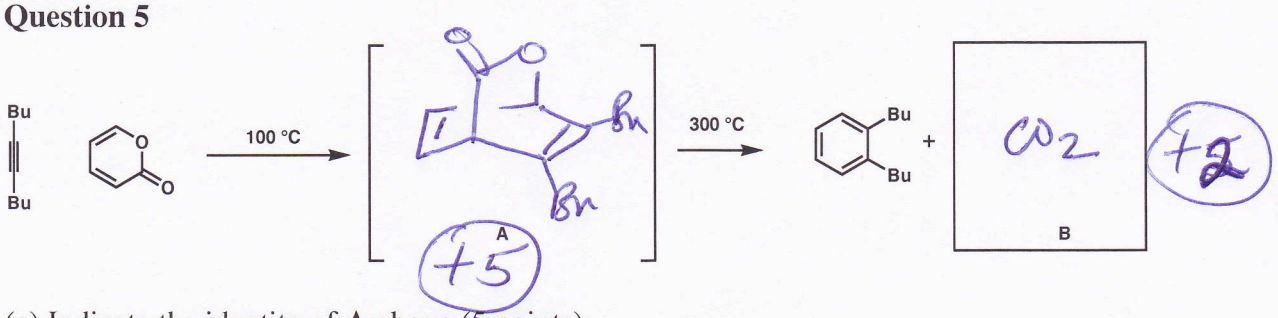


(b) Propose a transition state for the product you drew in Part (a). Be sure to include stereochemical detail in the transition state to rationalize the product. (5 points)



They must show the rationalization for the product in Part (a) to get credit for it.

Question 5



+5 +2

(a) Indicate the identity of **A** above (5 points)
(b) Indicate the identity of **B** above (2 points)
(c) Using the relationship $\Delta G = \Delta H - T\Delta S$, give *two* reasons why heating **A** leads to **B** and 1,2-dibutylbenzene (4 points each; 8 points total)

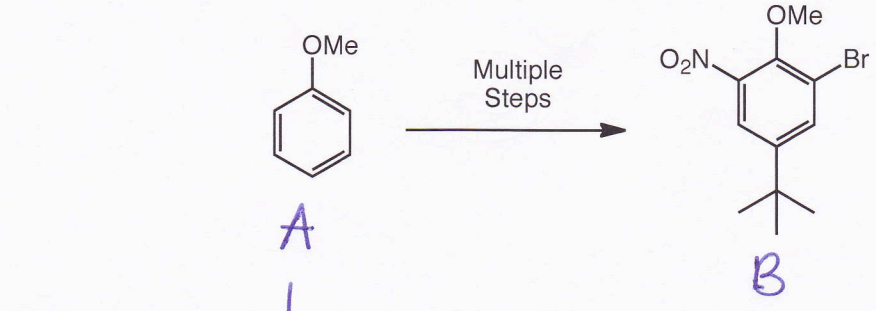
Reason 1: Form a benzene (aromatic) ring
ΔH is very -ve because of resonance stabilization

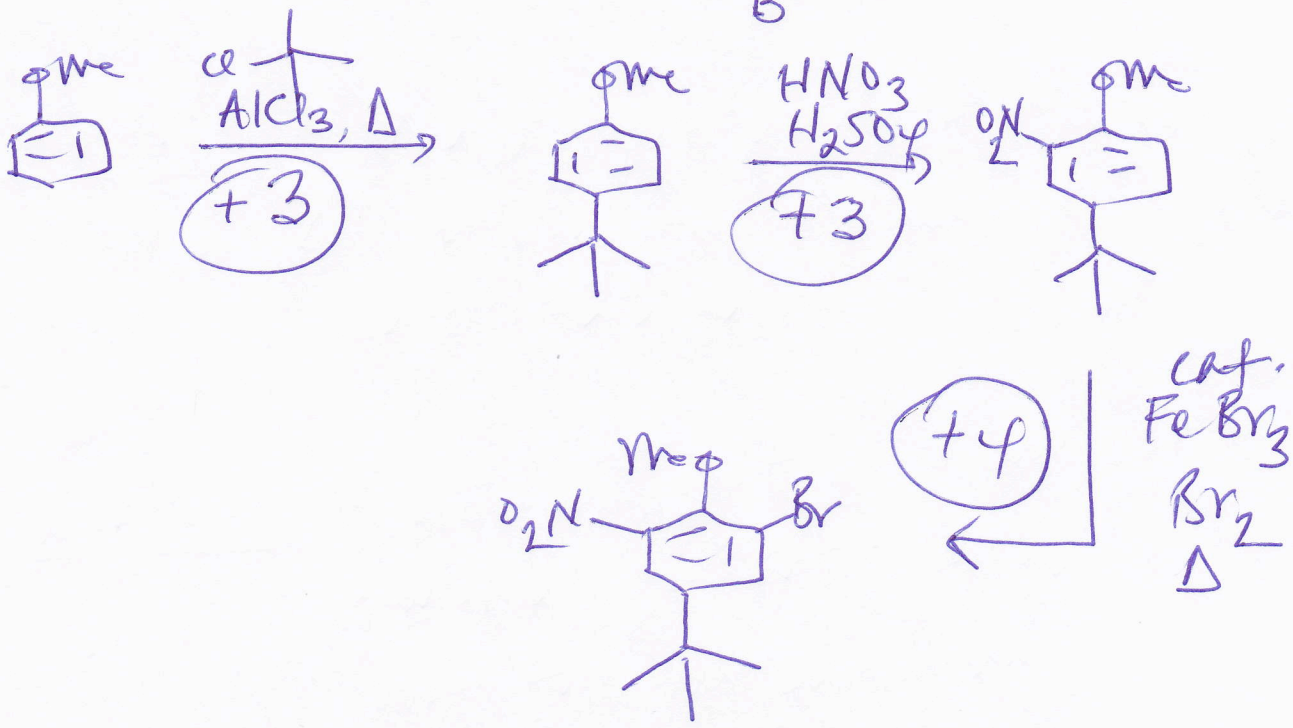
Reason 2: ΔS is positive because of increase in entropy (gas is formed and two molecules from 1)

$\therefore$ $-T\Delta S$ becomes more -ve term and ΔG becomes more negative

Question 6

Propose a synthesis that gives **B** as the major product starting from **A** (Don't show mechanisms, just reagents). (10 points)

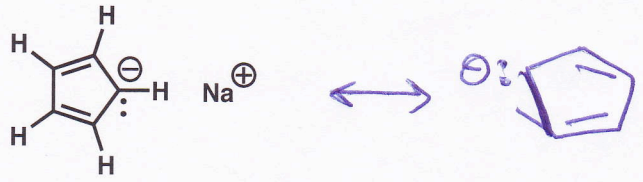




If Br is introduced before nitro (-I) because directing ability is opposed in that case.

Question 7

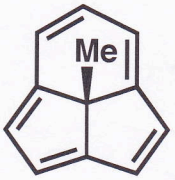
(a) The NMR spectrum of the sodium salt of cyclopentadiene (**A**) consists of a singlet, why? Provide structures to illustrate your answer. (10 points)



A

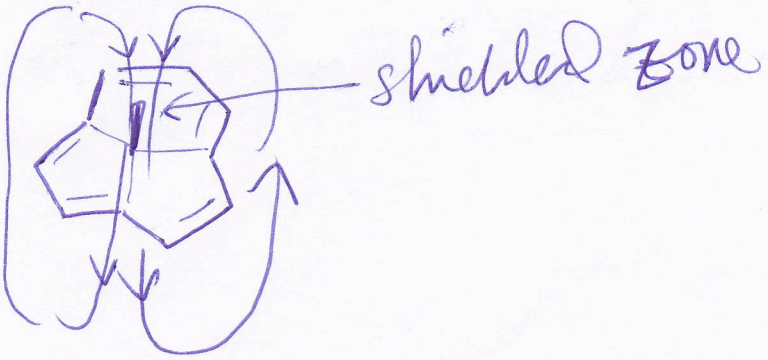
Must show resonance forms and talk about all H's being identical as a result.

(b) The methyl group in the following compound (**B**) has an unusual chemical shift of δ (-1.67), about 4 ppm lower than the chemical shift of a typical allylic methyl group, why? (10 points).



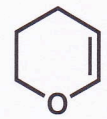
B

Me sits in the shielding zone of this aromatic system

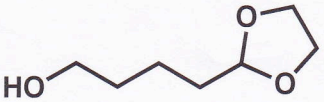


Question 8

Propose a mechanism for the conversion of **A** to **B** using **C** and acid. (25 points)

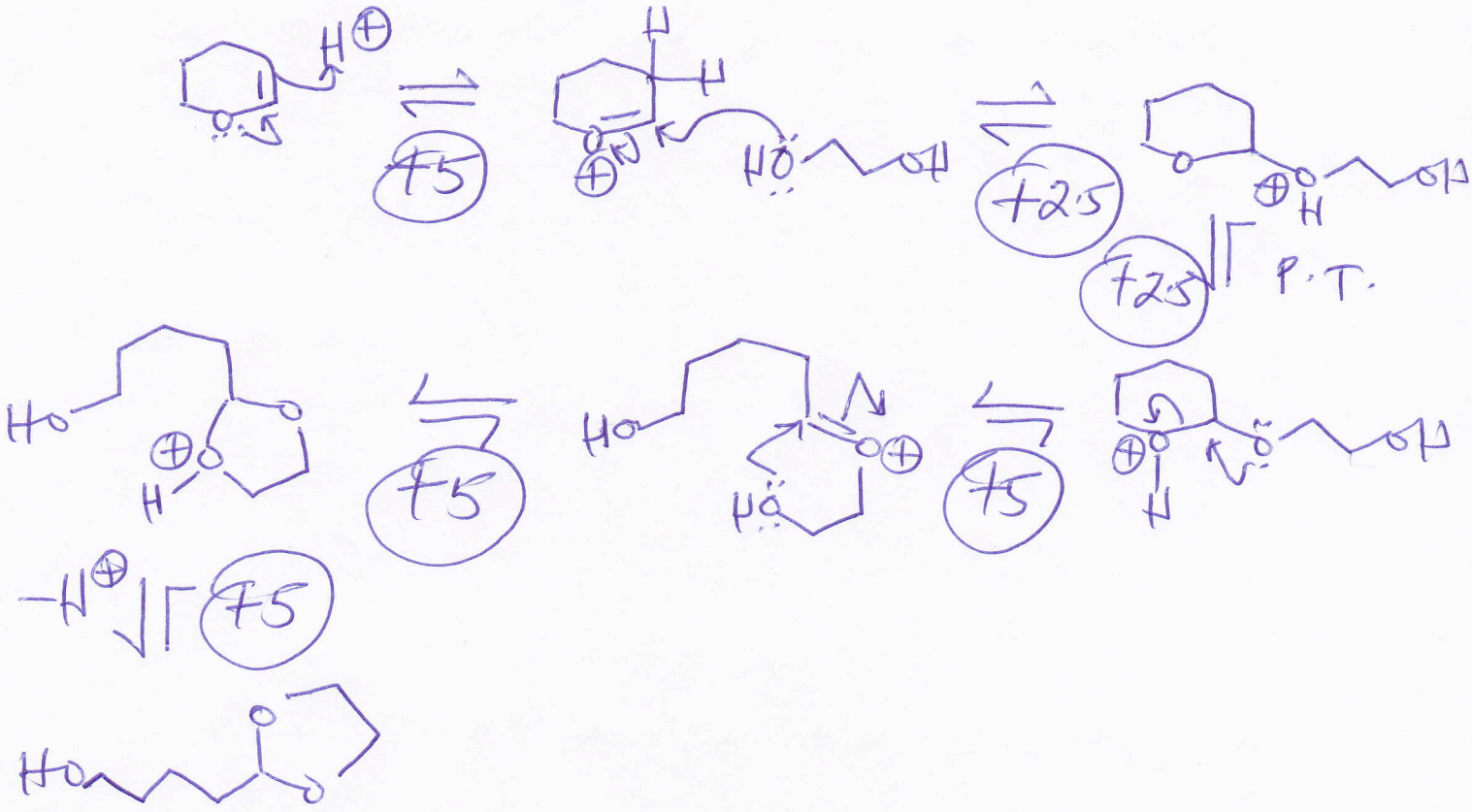


A



B

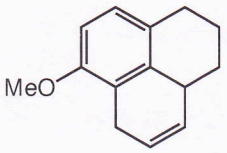
C



* Must show all steps as reversible. If not, −5 for each step not shown as such.

Question 9

Propose a synthesis of **A** from the starting materials indicated in the box. (Hint: The following reactions will be important in your synthesis: Friedel-Crafts acylation, electrophilic aromatic substitution, Wolff-Kishner reaction, Wittig reaction, Diels-Alder reaction). Additional reagents may be used. There is no need to show mechanisms. Simply show reagents for each step. (30 points)



A