Last Name KEY	First Name ANSWER	MI
Student ID Number:		Total Score 115 / 100
Circle the name of your TA: CARI / PHIL / ADAM / HEATHER		
Discussion Section – Day: Time:		

Chem 30A Fall 2004

MIDTERM #2

(50 Min)

Mon November 22nd

INTERPRETATION OF THE QUESTIONS IS PART OF THE EXAM – DO NOT ASK FOR THE QUESTIONS TO BE EXPLAINED TO YOU

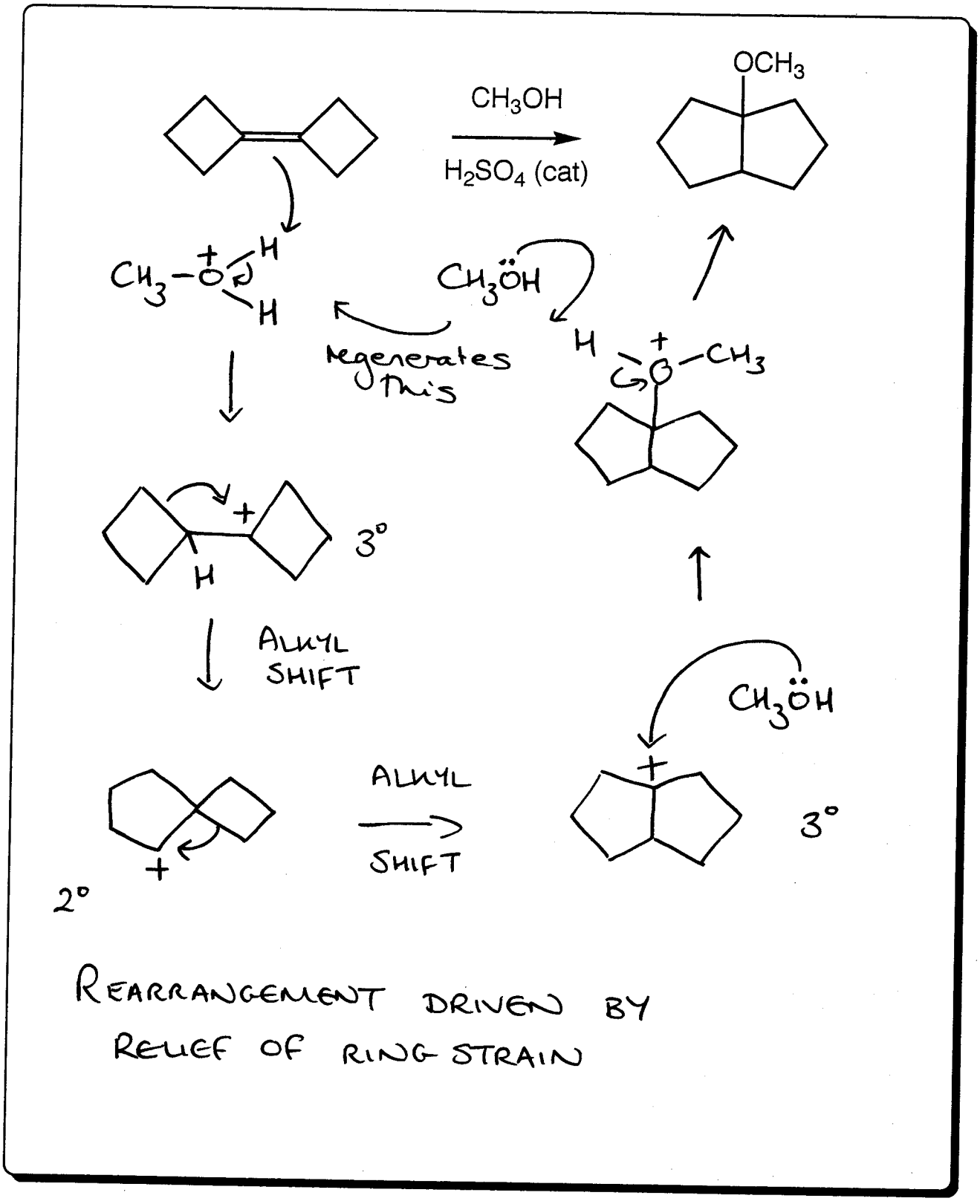
ONLY ANSWERS WRITTEN IN THE BOXES PROVIDED WILL BE GRADED

****DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO****

Q1	15 / 15	Q4	20 / 20
Q2	35 / 35	Q5	15 / 15
Q3	15 / 15	Extra Credit	15 / 15
		Total	115 / 100

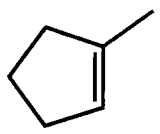
Human beings, who are almost unique in having the ability to learn from the experience of others, are also remarkable for their apparent disinclination to do so.
- Douglas Adams

Q1. What is the mechanism of the reaction shown below? (15 points) (Show all intermediates, all appropriate lone pairs, formal charges, and curly arrows).

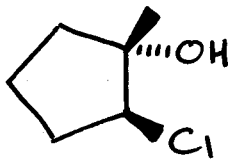


Q2. Each of the reactions drawn below produces ONE MAJOR PRODUCT. In each case, draw this product (including relative stereochemistry where appropriate) in the large box provided (3 points each). Note: for two-step reactions, just give the final product, DO NOT draw intermediates. If a reaction produces a racemic mixture (i.e., a pair of enantiomers), write an '**E**' in the small box next to it – be sure of your answer, +1 point for each correct '**E**' and –1 point for each incorrect '**E**'.

(a)

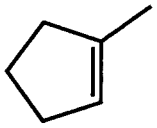


Cl_2 / H_2O



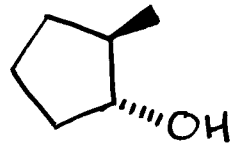
E

(b)



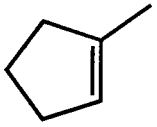
(i) BH_3·THF

(ii) NaOH / H_2O_2

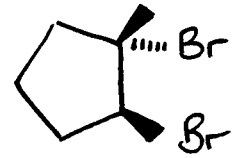


E

(c)

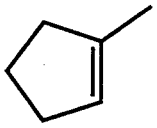


Br_2 / CCl_4



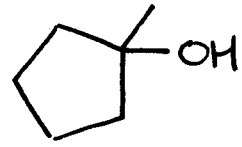
E

(d)

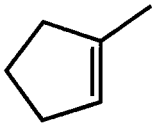


(i) $Hg(OAc)_2$ / H_2O

(ii) $NaBH_4$

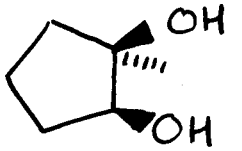


(e)



(i) OsO_4

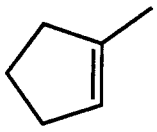
(ii) $NaHSO_3$ / H_2O



E

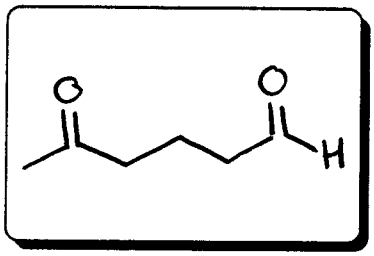
Question 2 continues on the next page...

(f)

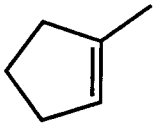


(i) O_3

(ii) Me_2S

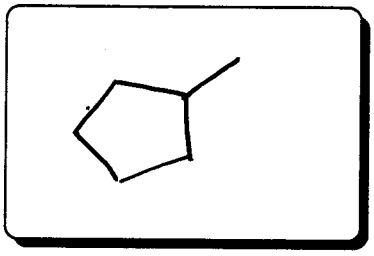


(g)

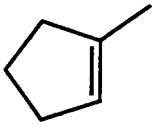


H_2

Pt

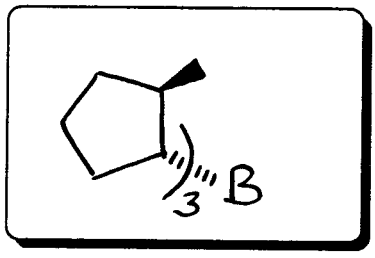


(h)



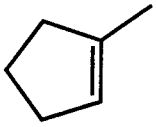
1/3 equiv of

BH_3·THF



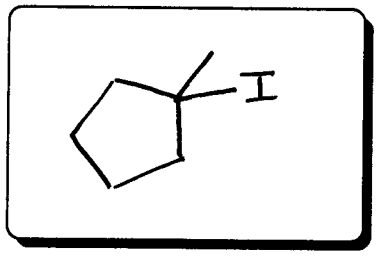
E

(i)

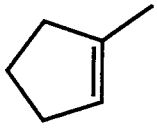


HI

ether

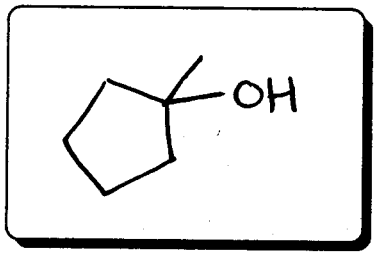


(j)



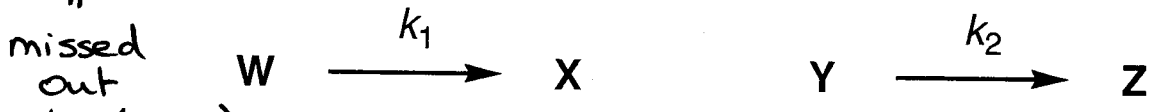
H_2O

H_2SO_4 (cat)



Q3. Consider the two reactions shown below. At a temperature of 500 K, the reaction of **Y** to give **Z** is 100 times faster than the reaction of **W** to give **X** (i.e., $k_2/k_1 = 100$). Both of the reactions have a pre-exponential factor (A) of 10^{12} s^{-1}. The Arrhenius equation, linking the rate constant (k) of a reaction to the Gibbs free energy of activation ($\Delta G^{\ddagger}$), is shown below. You may find it useful to know that R = 2 cal/mol, and that the natural logarithm of a number N (lnN) is equal to 2.3 × $\log_{10}$N.

⇑ missed out k (sorry)



$R = 2\ cal\ K^{-1}\ mol^{-1}$

$$k = A \cdot e^{q} \quad \text{where } q = \left(\frac{-\Delta G^{\ddagger}}{RT}\right)$$

(a) Which reaction has the highest activation barrier ($\Delta G^{\ddagger}$)? (3 points)

W → X

(b) What is the numerical difference (**in kcal/mol**) between the activation barriers ($\Delta G^{\ddagger}$) for these two reactions? (12 points)

$k_1 = Ae^{q_1}$
$k_2 = Ae^{q_2}$ so, if $k_2/k_1 = 100$ $\quad \frac{Ae^{q_2}}{Ae^{q_1}} = 100$

So, $\frac{e^{q_2}}{e^{q_1}} = 100$, $\ln\left(\frac{e^{q_2}}{e^{q_1}}\right) = \ln 100$

$= 2.3 \log_{10} 100$

$= 2.3 \times 2$

$= 4.6$

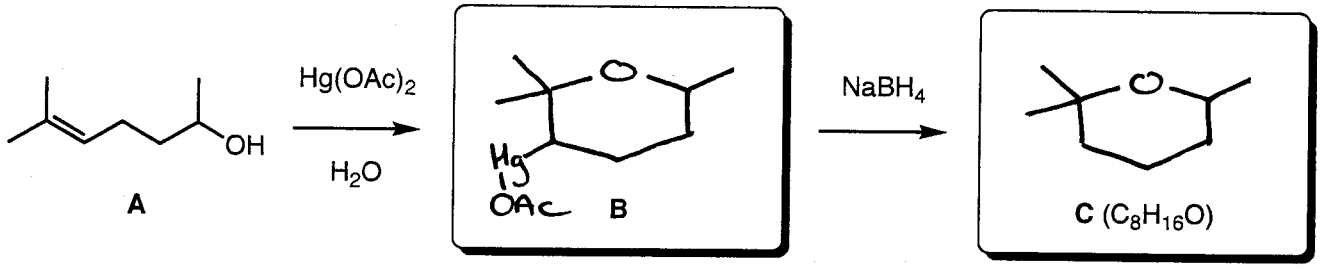
THIS EQUALS 1 ⇓

$\ln\left(\frac{e^{q_2}}{e^{q_1}}\right) = \ln e^{q_2} - \ln e^{q_1} = q_2 - q_1 = 4.6$

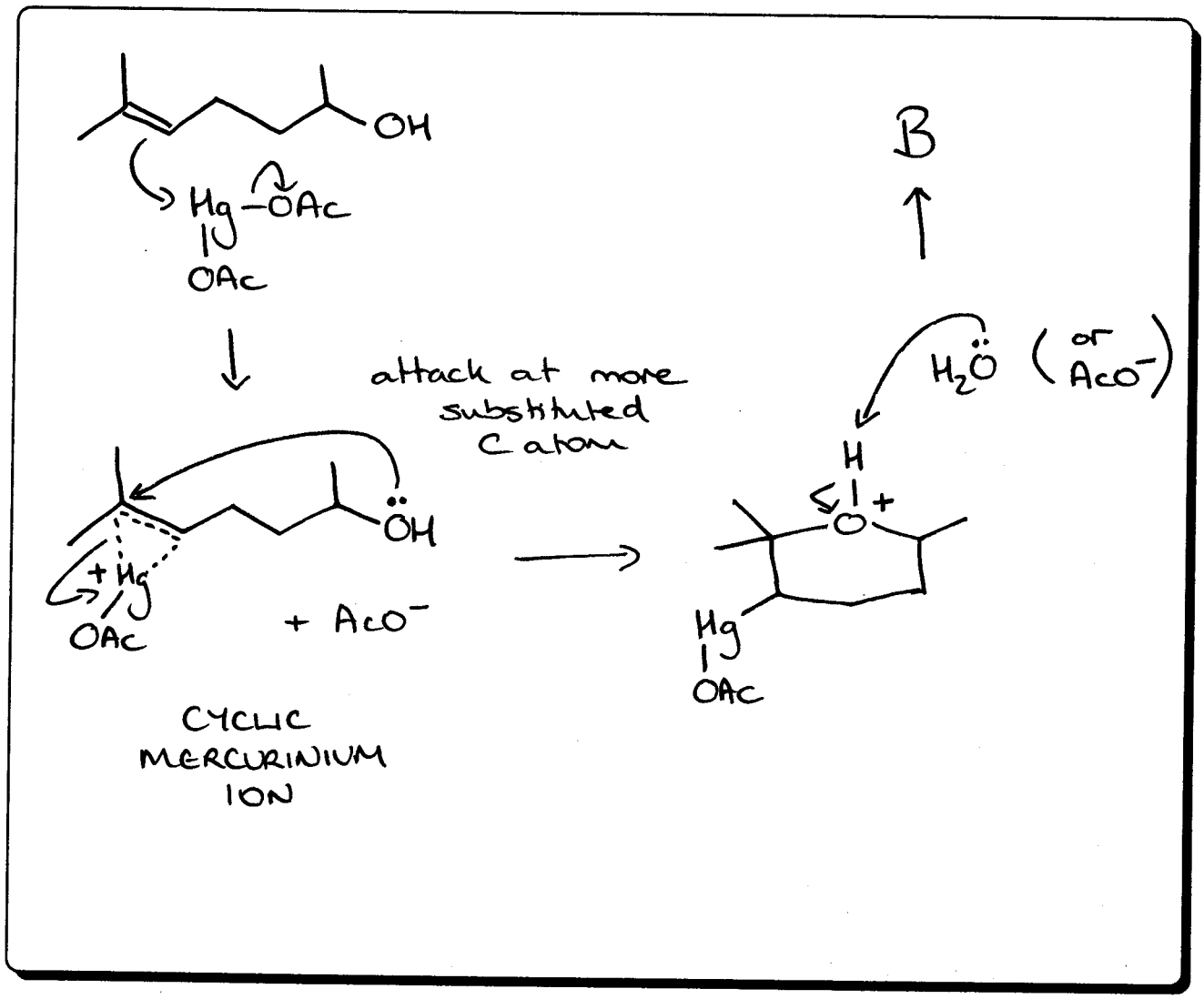
so $-\frac{\Delta G_2^{\ddagger}}{RT} - \left(-\frac{\Delta G_1^{\ddagger}}{RT}\right) = 4.6$, so $\Delta G_1^{\ddagger} - \Delta G_2^{\ddagger} = 4.6\ RT$

$= 4.6\ kcal\ mol^{-1}$

Q4. (a) When 6-methyl-hept-5-en-2-ol (**A**) is reacted with mercury acetate in water, compound **B** is obtained, which is converted to compound **C** (molecular formula $C_8H_{16}O$) upon reaction with sodium borohydride. What are the structures of **B** and **C**? (4 points each)

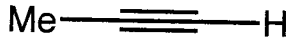


(b) In the box below, draw the mechanism of the reaction that converts **A** into **B**. (12 points) (Show all intermediates, all appropriate lone pairs, formal charges, and curly arrows).



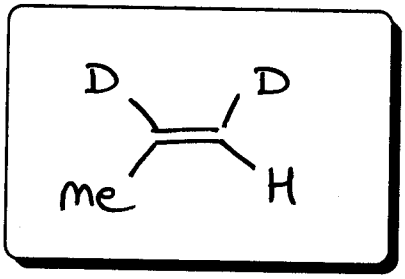
Q5. Each of the reactions drawn below produces ONE MAJOR PRODUCT. In each case, draw this product in the box provided, CAREFULLY INDICATING the position of any D atoms it may contain. (3 points each). Note: for two-step reactions, just give the final product, DO NOT draw intermediates, and... deuterium (D) is just a heavier isotope of hydrogen (H) – it reacts just as H would.

(a)

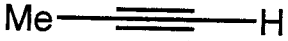


(i) $(sia)_2BD$

(ii) CH_3CO_2D

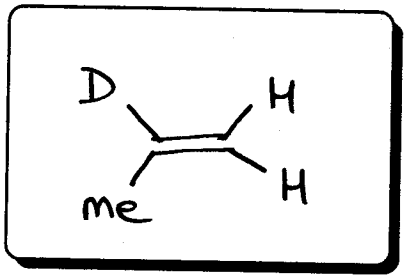


(b)

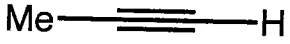


(i) $(sia)_2BD$

(ii) CH_3CO_2H

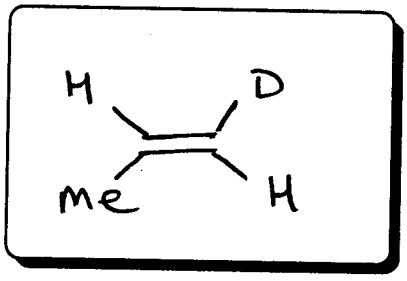


(c)

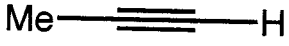


(i) $(sia)_2BH$

(ii) CH_3CO_2D

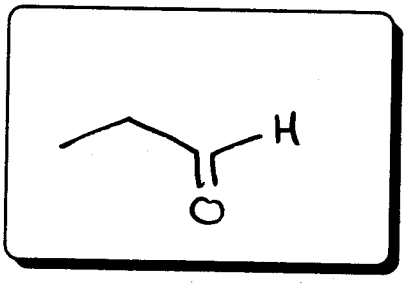


(d)

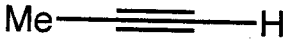


(i) $(sia)_2BH$

(ii) $NaOH / H_2O_2$

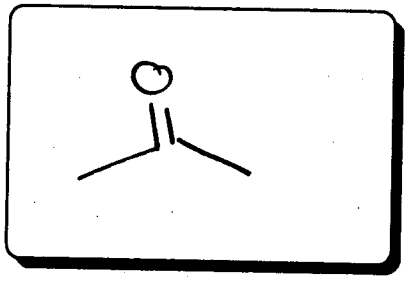


(e)

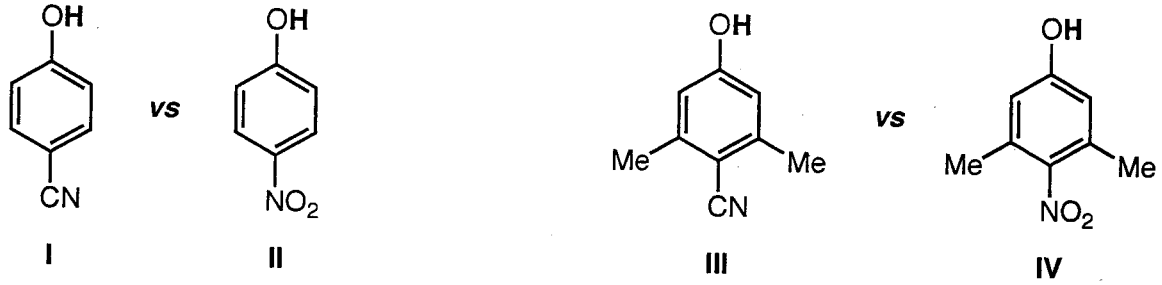


$Hg(OAc)_2$

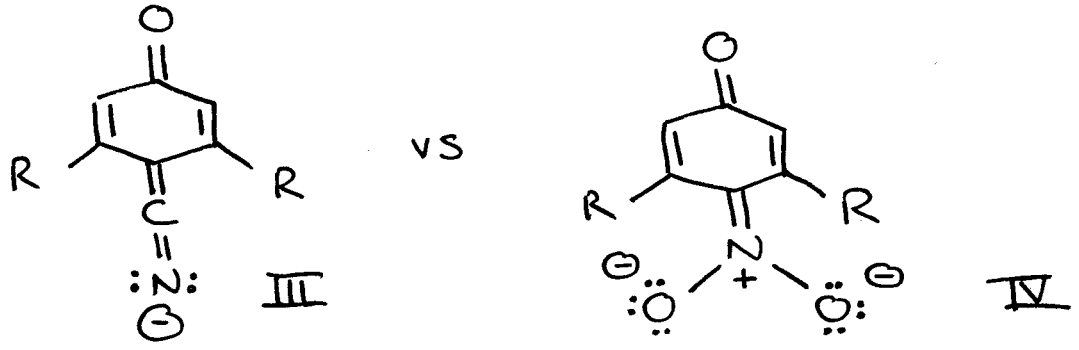
H_2SO_4 / H_2O



EXTRA CREDIT. The pK_a values for 4-cyanophenol (**I**) and 4-nitrophenol (**II**) are approximately the same, i.e., the phenolic protons (**bold**) in each of these compounds are equally acidic. In contrast, however, the dimethyl-substituted compounds differ significantly in their acidity; the dimethyl-cyano compound (**III**) is much more acidic than the dimethyl-nitro compound (**IV**). Explain (using both words and drawings as you feel appropriate) this observation in the box below. (15 points) Hint: think resonance...



ALL OTHER RESONANCE CONTRIBUTORS BEING APPROXIMATELY EQUAL, CONSIDER THE FOLLOWING:



WHEN R = H, BOTH CONTRIBUTORS ARE OK, BUT WHEN R = Me, STERIC INTERACTIONS BETWEEN THE Me GROUPS AND THE OXYGEN ATOMS IN IV DISFAVOR THIS RESONANCE CONTRIBUTER. THE CN GROUP DOES NOT SUFFER FROM THIS PROBLEM AS IT IS LINEAR (NO_2 IS TRIANGULAR) AND SO III IS MORE ACIDIC THAN IV