Last Name	ANSWER	First Name	KEY	MI

Student ID Number:	Total Score
Circle the name of your TA: MIKE ROB	115
Discussion Section – Day: Time:	/ 100

Chem 30A Winter 2005

MIDTERM #2

(50 Min)

Weds March 2nd

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

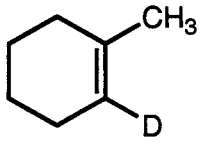
****DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO****

Q1	30 / 30	Q4	20 / 20
Q2	20 / 20	Q5	15 / 15
Q3	15 / 15	Q6 & Q7 *BONUS*	15 / 15
		Total	115 / 100

"People must understand that science is inherently neither a potential for good nor for evil. It is a potential to be harnessed by man to do his bidding"
- Glenn T Seaborg

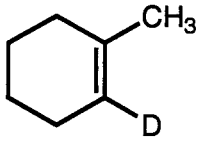
Q1. Each of the reactions drawn below produces ONE MAJOR PRODUCT (in some cases as a racemic mixture). In each case, draw this product (including relative stereochemistry where appropriate) in the box provided (3 points each). Notes: (i) for two-step reactions, just give the final product, DO NOT draw intermediates, (ii) ether is an inert solvent and just serves as a reaction medium in the cases where it is listed below, (iii) deuterium (D) is just a heavier isotope of hydrogen (H) and behaves in exactly the same manner (albeit a little slower, which is of no consequence in these questions) – be sure to carefully consider the position and orientation of the D atoms in your products, and (iv) in the reactions where the major product is formed as a pair of enantiomers, you only need draw one of them.

(a)



H_2 / Pt

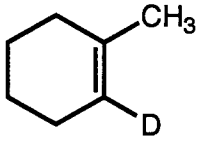
(b)



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

(ii) $NaBH_4$

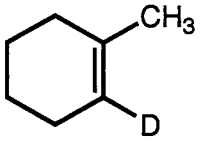
(c)



(i) BH_3·THF

(ii) NaOH / H_2O_2

(d)

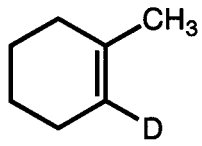


(i) O_3

(ii) Me_2S

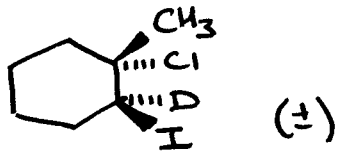
Question 1 is continued on the next page...

(e)

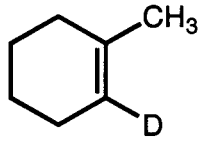


I–Cl

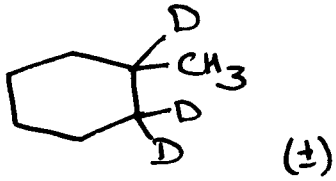
ether



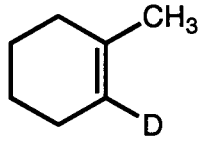
(f)



D_2 / Pd

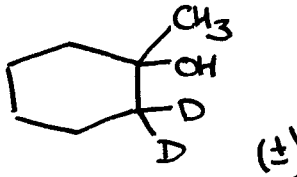


(g)

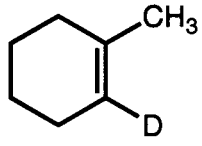


(i) $Hg(OAc)_2$ / H_2O

(ii) $NaBD_4$

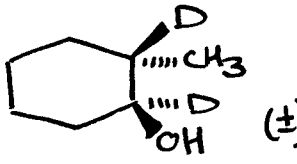


(h)

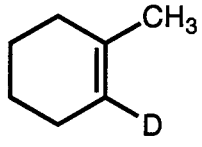


(i) BD_3·THF

(ii) NaOH / H_2O_2

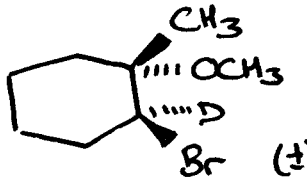


(i)

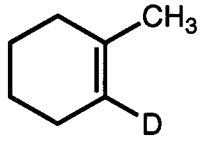


Br_2

CH_3OD

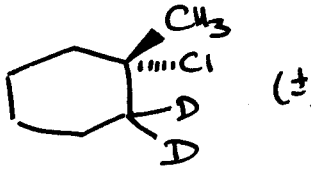


(j)



DCl

ether



Q2. There are 18 alkene isomers with the molecular formula C_6H_{12}, and they are all drawn (**A–R**) in the box at the bottom of this page. You are presented with five flasks (**1–5**), each one containing a single pure sample of one of these alkenes. In a very long and excruciating lab class one afternoon, you run two separate reactions on each sample, (i) ozonolysis (O_3 followed by Me_2S), and (ii) bromination (Br_2/CCl_4). For the ozonolysis reactions, you analyze whether ONE or TWO unique products are formed in each case. For the bromination reactions, you analyze what kind of stereoisomers (if any) are formed in each reaction. The results of the two reactions for each flask are summarized below that flask. Using your knowledge of alkene reactions, identify each sample (**1–5**) as ONE of the alkenes drawn below (**A–R**) by writing that letter in the small box below each flask. (4 points each)

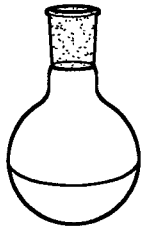
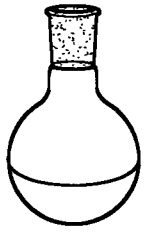
Key:

Racemic Mixture (**Rac**)

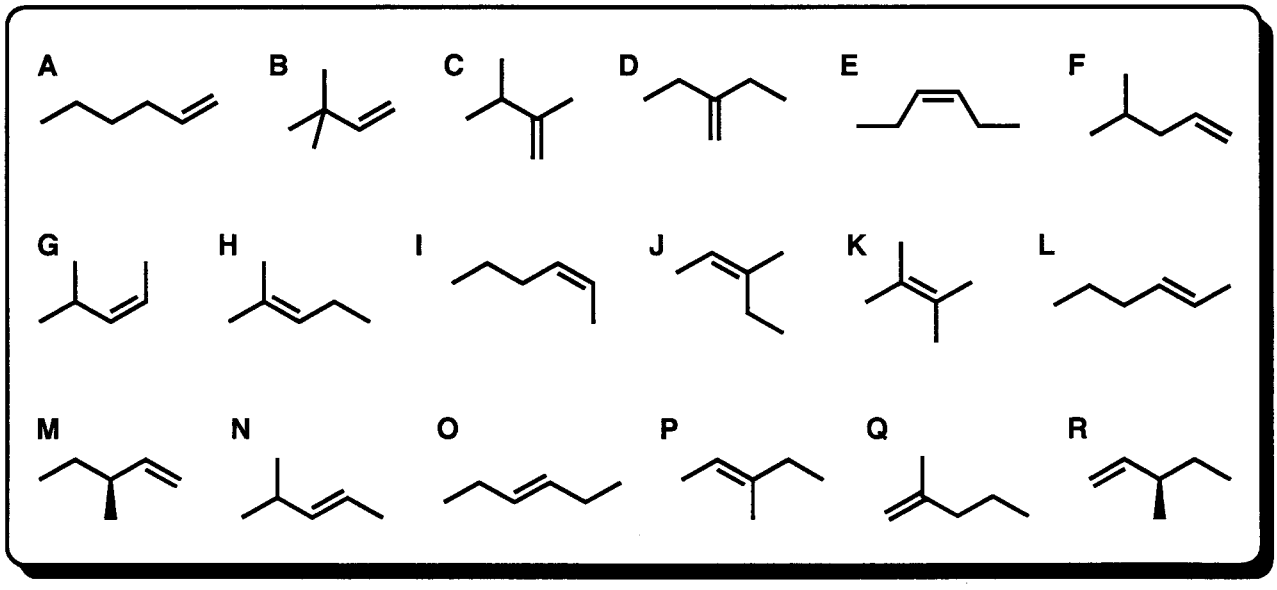
Diastereoisomers (**Dia**)

Achiral meso compound (**Meso**)

Achiral, non-meso, compound (**Ach**)

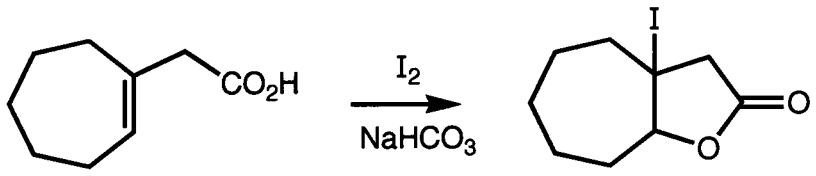
	1	2	3	4	5
					
(i) Number of Unique Ozonolysis (O_3) Products	**One**	**One**	**One**	**Two**	**Two**
(ii) Reaction with Br_2 in CCl_4 gives...	**Ach**	**Rac**	**Meso**	**Ach**	**Dia**
IDENTITY of SAMPLE ⇨	K	E	O	D	M|R

Note: for one of the samples, there are two correct answers, but you only need to indicate one of them



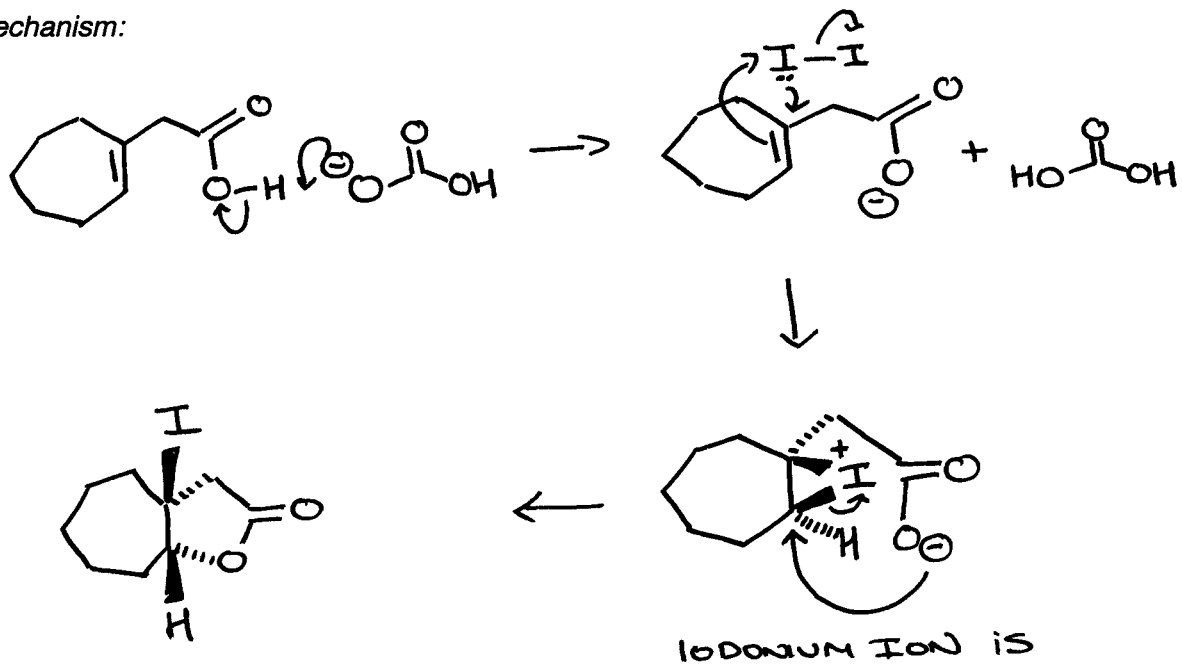
This page is otherwise left blank for you to work through question 2...

Q3. The carboxylic acid compound shown below reacts with iodine (I_2) in the presence of a weak base such as sodium hydrogen carbonate ($NaHCO_3$) to give the fused 7,5-bicyclic compound. The reaction proceeds both regioselectively and stereospecifically – the relative stereochemistry of the product has been deliberately omitted.



In the box below, propose a mechanism for this reaction (show all intermediates, all appropriate lone pairs, formal charges, and curly arrows). Pay particular attention to the stereospecific nature of the final step, and, as such, indicate the relative stereochemistry observed in the 7,5-bicyclic product – i.e., the final step of your mechanism should end with you redrawing the above 7,5-ring system with the appropriate stereochemical relationships. Finally, in no more than two sentences, account for the observed regioselectivity of the final step of the mechanism. (15 points)

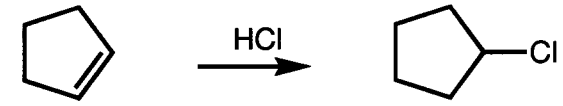
Mechanism:

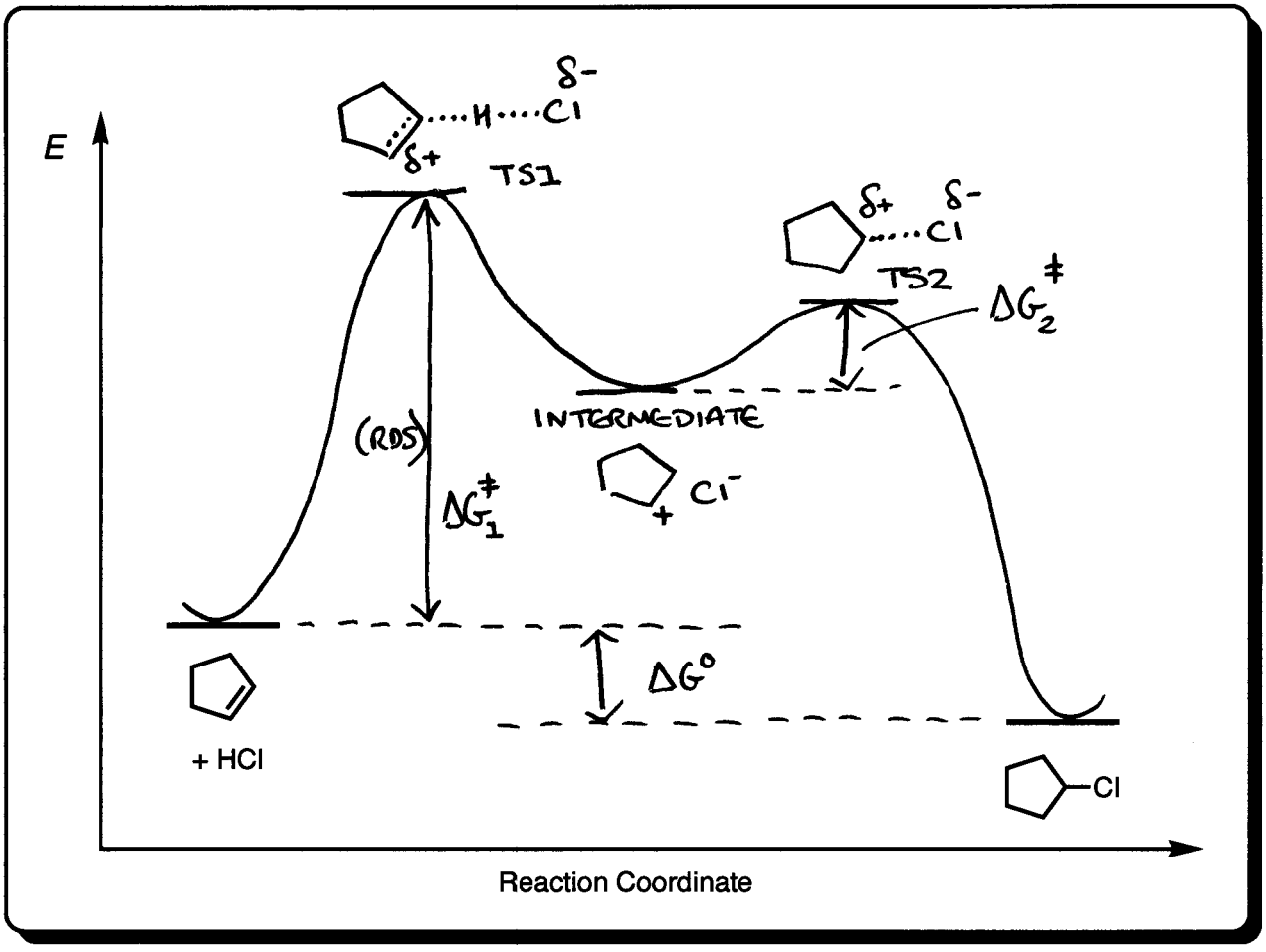


Comments about regioselectivity:

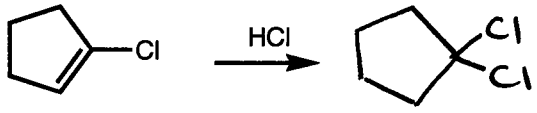
O⁻ ATTACKS AT THE POSITION WHERE LEAST STABLE C⁺ WOULD BE FORMED, RESULTING IN A FIVE-MEMBERED RING, BECAUSE ATTACK AT THE POSITION WHERE MOST STABLE C⁺ WOULD BE FORMED WOULD GIVE A STRAINED 4-MEMBERED RING.

Q4. (a) Cyclopentene reacts with hydrogen chloride (HCl) to form chlorocyclopentane as shown below. In the box below, draw the energy profile for this reaction, and label the following items as necessary: transition states (**TS**), and their proposed structures, reaction intermediates (**INT**), and their structures, activation barriers where applicable ($\Delta G^{\ddagger}$), the Gibbs free energy change associated with the reaction ($\Delta G°$), and the rate determining step (**RDS**). (15 points)





(b) 1-Chlorocyclopentene also reacts with hydrogen chloride (HCl) in an analogous fashion. In the boxes below, indicate what the product of the reaction is, indicate whether this reaction is faster, slower, or proceeds at the same rate as the one above, and give reasons why. (5 points)

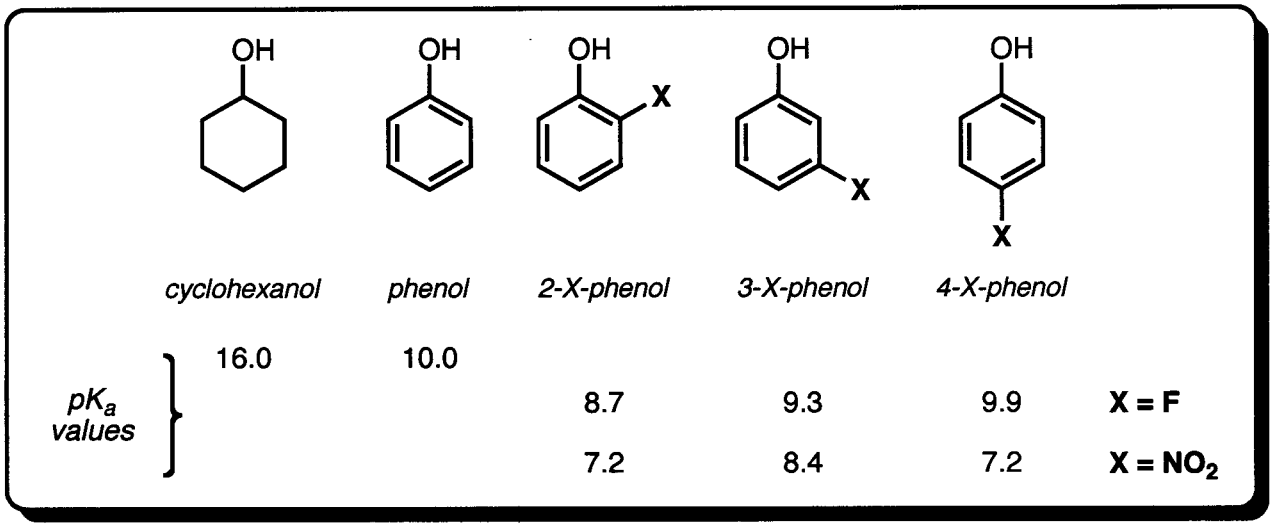


Faster, slower, the same? and why?

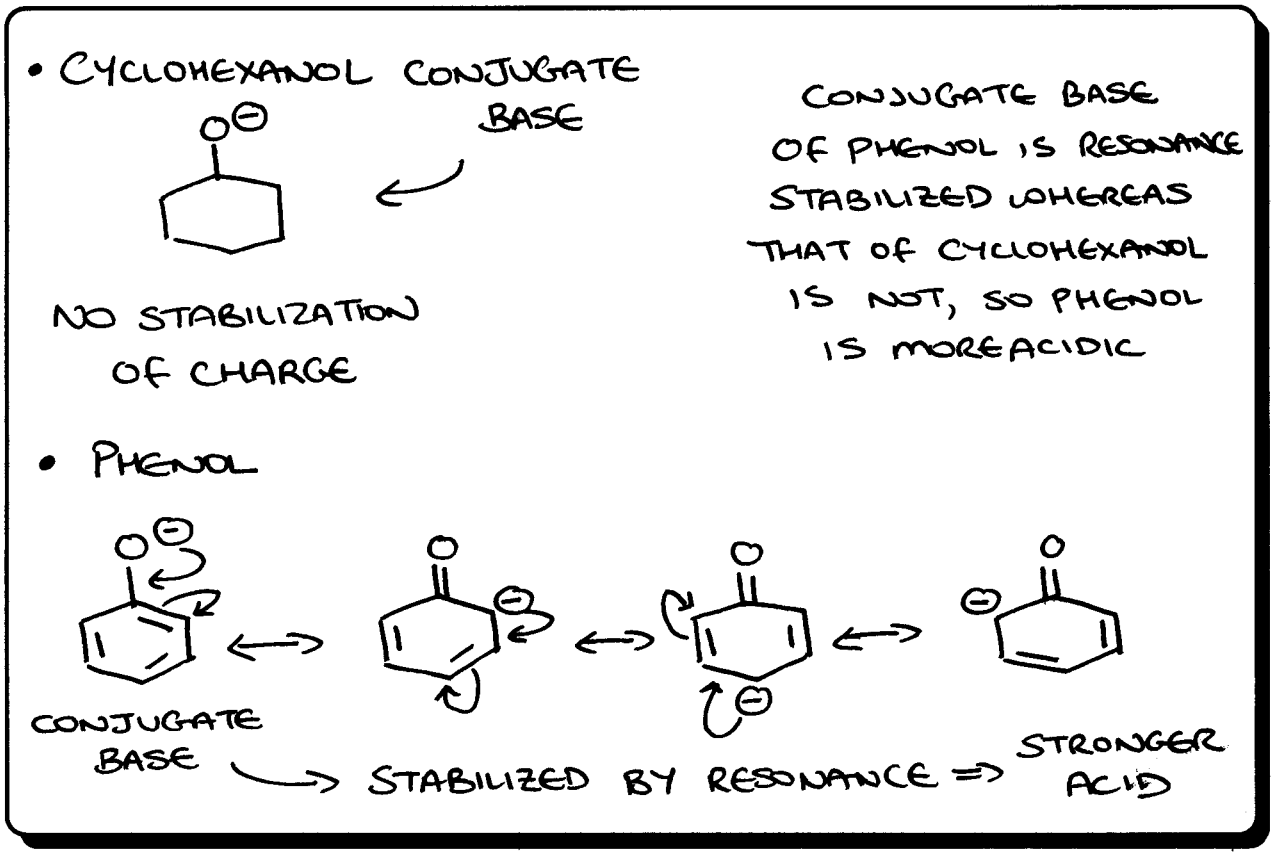
Reaction is faster as it goes through a more stable C+, hence lowering $\Delta G^{\ddagger}_1$

RESONANCE STABILIZED C+

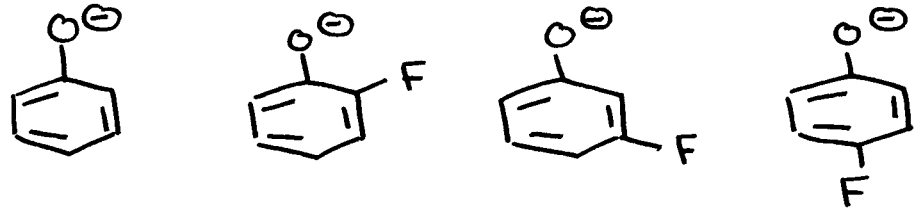
Q5. In the box below, you are given the pK_a values for a series of compounds, the least acidic is cyclohexanol (pK_a = 16.0). The pK_a value for phenol is 10.0, and two series of substituted phenols are given: 2-fluorophenol, 3-fluorophenol, and 4-fluorophenol have pK_a values of 8.7, 9.3, and 9.9, respectively; 2-nitrophenol, 3-nitrophenol, and 4-nitrophenol have pK_a values of 7.2, 8.4, and 7.2, respectively. Note: both –F and $-NO_2$ are strong electron withdrawing groups.



(a) Briefly explain (using words AND illustrations) why phenol is (literally and actually!) a million times more acidic than cyclohexanol (5 points).



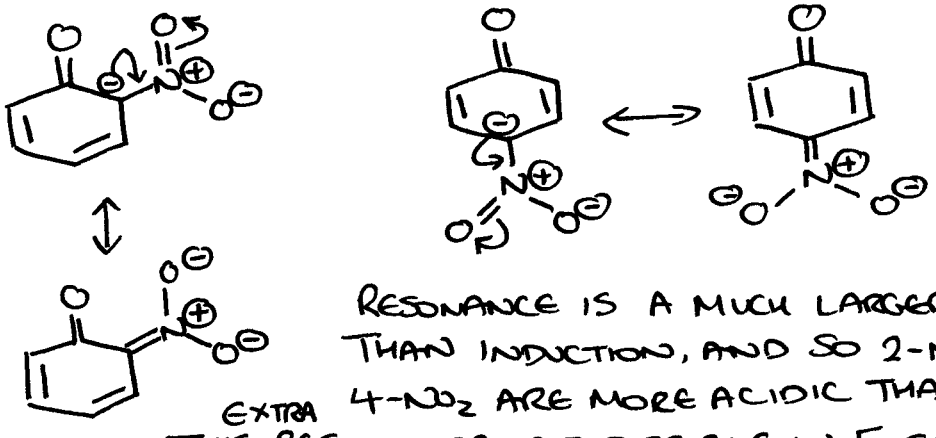
(b) Briefly explain (using words and illustrations as you feel necessary) the trend observed in the acidity of 2-, 3-, and 4-fluorophenol (5 points).



EACH STRUCTURE IS STABILIZED BY RESONANCE, AND THERE IS AN INDUCTIVE EFFECT (THAT ALSO STABILIZES THE ANION) THAT RESULTS FROM THE ELECTRONEGATIVE F ATOMS. THE CLOSER THE F TO THE O^-, THE BIGGER THE INDUCTIVE EFFECT, SO 2-F IS MORE ACIDIC THAN 3-F, WHICH IS MORE ACIDIC THAN 4F

(c) Briefly explain and illustrate why the trend observed in the acidity of 2-, 3-, and 4-nitrophenol is different to that observed for the analogous series of phenolic compounds containing fluorine (5 points).

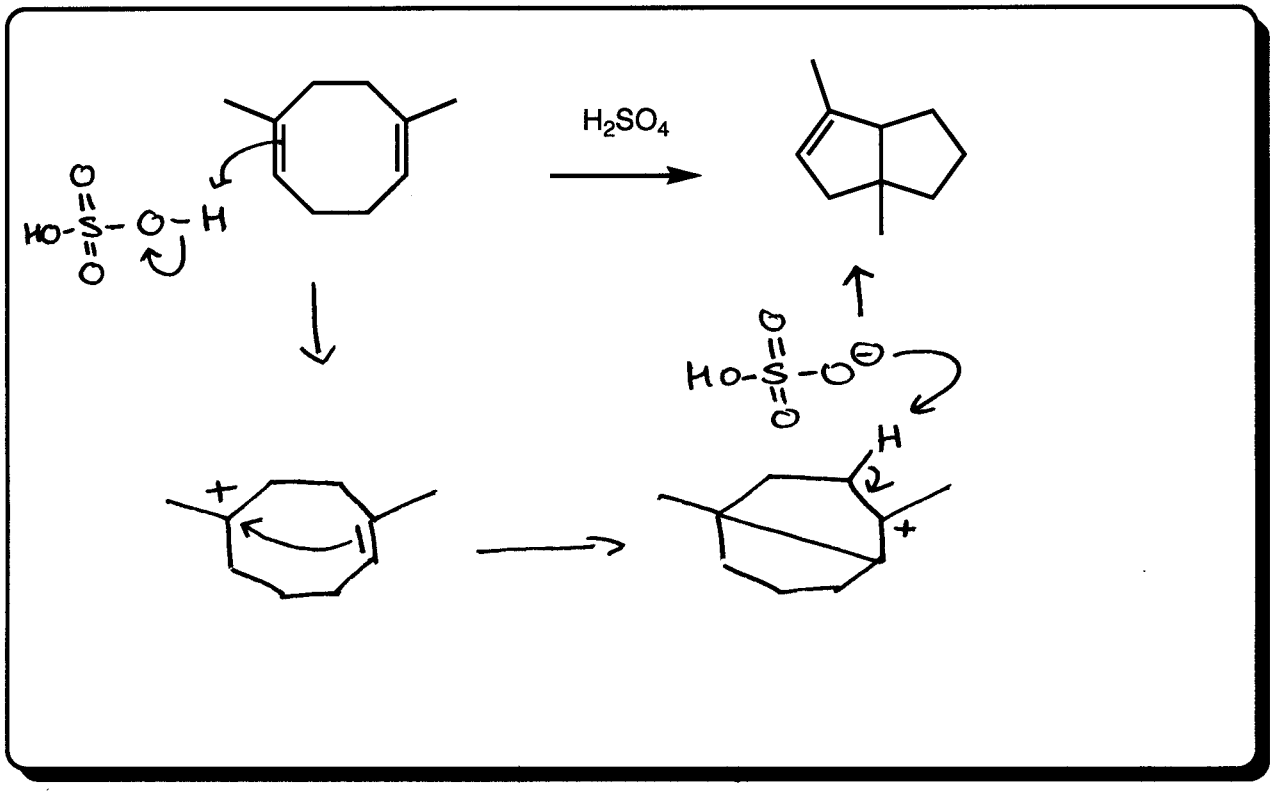
WITH THE NO_2 GROUP IN THE 2- AND 4- POSITIONS, EXTRA RESONANCE STABILIZATION IS POSSIBLE, AND THIS DOES NOT HAPPEN IN THE 3- POSITION



RESONANCE IS A MUCH LARGER EFFECT THAN INDUCTION, AND SO 2-NO_2 and 4-NO_2 ARE MORE ACIDIC THAN 3-NO_2

EXTRA RESONANCE NOT POSSIBLE IN F SERIES

Q6 (BONUS) Propose a mechanism for the rearrangement reaction shown in the box below (show all intermediates, all appropriate lone pairs, formal charges, and curly arrows). Note: there is NO water present in this reaction, just a catalytic amount of concentrated sulfuric acid. (9 points)



Q7 (BONUS) Propose a short sequence of reactions (you can't do it in one-step!) that converts acetylene (C_2H_2) into mono-deuterated formaldehyde (CDHO) as depicted below. Show all intermediate compounds, and the reagents necessary for each transformation. DO NOT SHOW MECHANISMS! (6 points)