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

Chem 30A Fall 2005

MIDTERM #2

(50 Min)

Mon Nov 21st

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	20 / 20	Q3	20 / 20
Q2	36 / 36	Q4	39 / 39
		Total	115 / 100

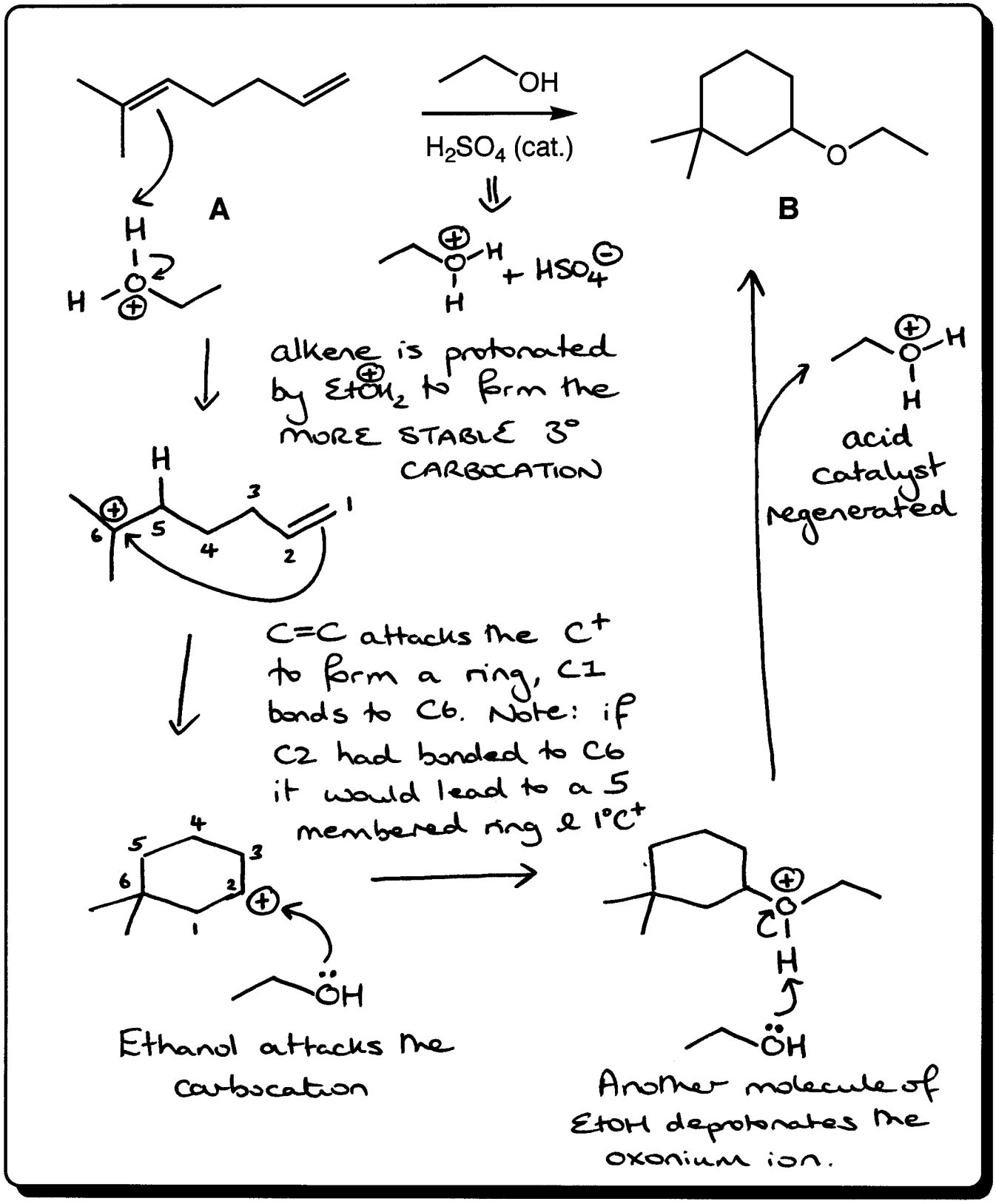
"We didn't lose the game; we just ran out of time."

- Vince Lombardi

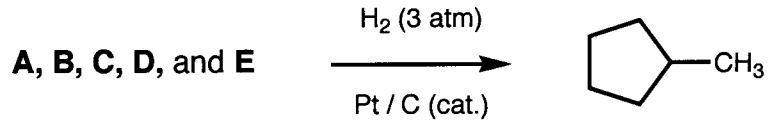
"All truth passes through three stages. First, it is ridiculed. Second, it is violently opposed. Third, it is accepted as being self-evident."

- Arthur Schopenhauer

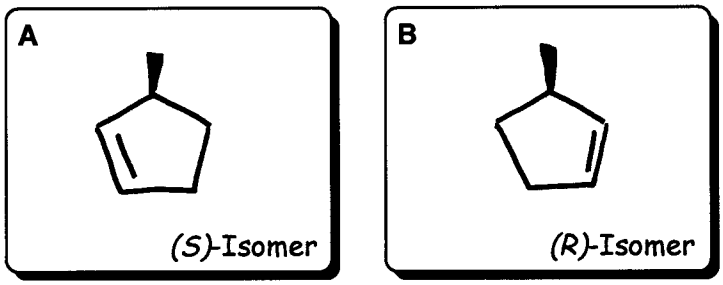
Q1. Propose a reasonable mechanism that accounts for the transformation of compound **A** into compound **B** shown below – (show all intermediates, all appropriate lone pairs, formal charges, significant resonance forms, and curly arrows). Explain each step with a few words. (20 pt)



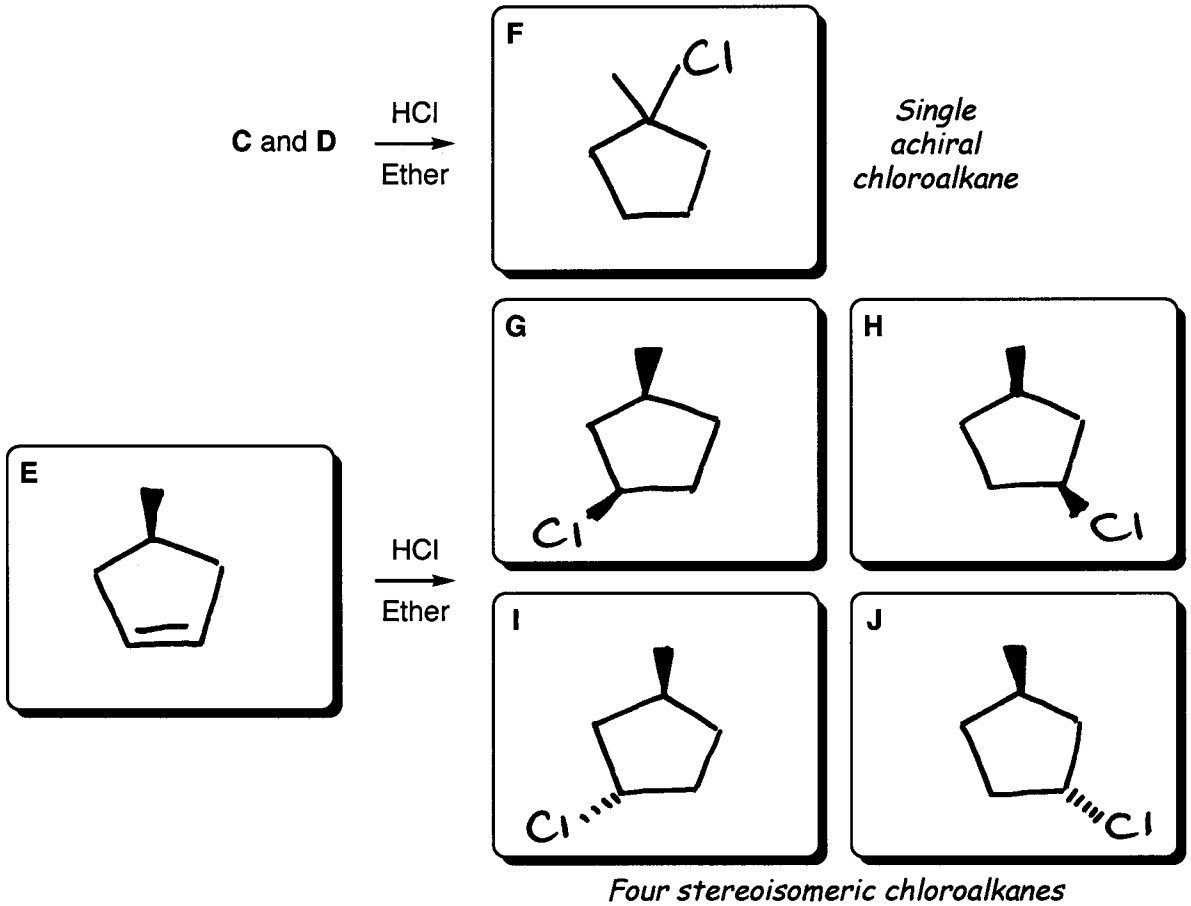
Q2. Five different cycloalkenes (**A–E**), each with the molecular formula C_6H_{10}, will yield methylcyclopentane when subjected to catalytic hydrogenation (H_2/Pt catalyst) – as shown below.



(**a**) Two of these cycloalkenes constitute a pair of enantiomers; the absolute configuration of the stereogenic center in compound **A** is (*S*) and in **B** it is (*R*). Draw these compounds below. (6 pt)



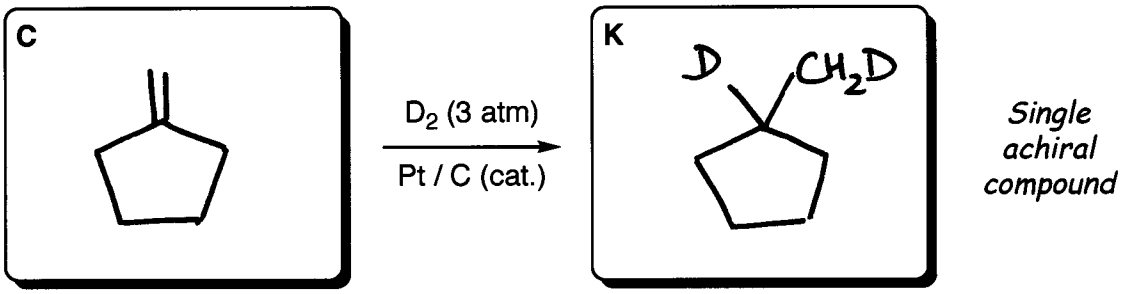
(**b**) The other three cycloalkenes (**C, D, & E**) are achiral. When reacted with HCl in ether (an inert solvent), cycloalkenes **C & D** give only the achiral chloroalkane (**F**), whereas cycloalkene **E** gives four stereoisomeric products (**G, H, I, & J**). Fill in the structures of **E, F, G, H, I, & J** in the boxes below – note, the labels **G–J** are arbitrary, i.e., any stereoisomer can go in any box (12 pt)



Question 2 is continued on the next page...

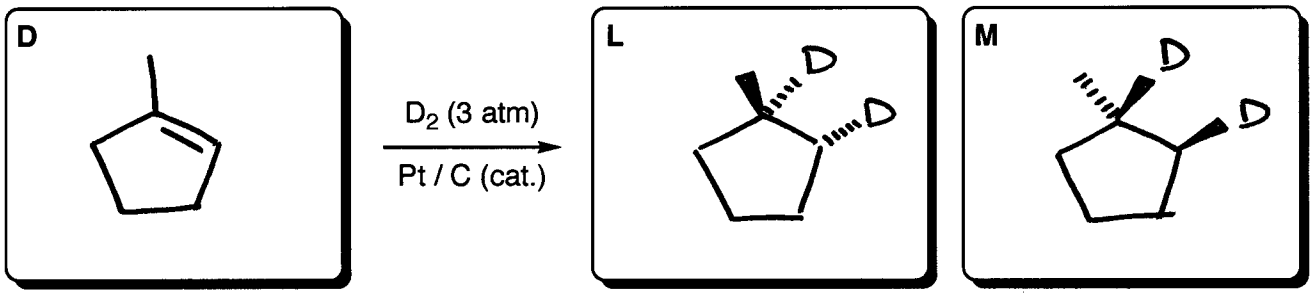
(c) When cycloalkenes **C** & **D** are reacted with deuterium gas (D_2) instead of hydrogen gas (H_2), different results are observed.

(i) Cycloalkene **C** reacts to form a single achiral product (**K**) – draw these compounds in the appropriate boxes below: (4 pt)



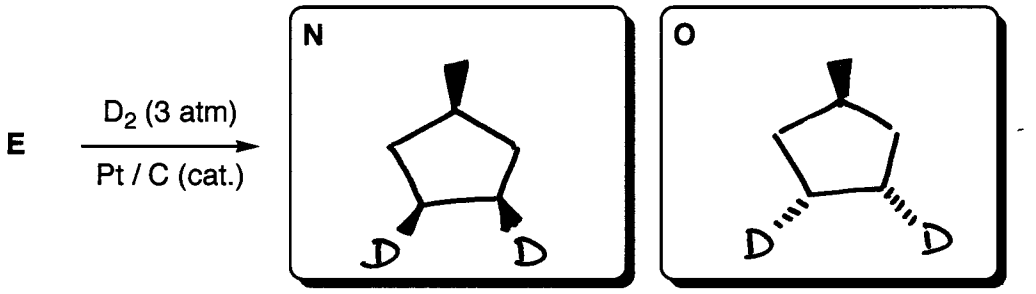
Single achiral compound

(ii) Cycloalkene **D** reacts to form a pair of enantiomers (**L** & **M**) – draw these compounds in the appropriate boxes below (note – the labels **L** & **M** are arbitrary): (6 pt)



Pair of Enantiomers

(d) Cycloalkene **E** reacts with deuterium gas (D_2) to form two different ACHIRAL products (**N** & **O**) – draw these compounds in the appropriate boxes below (note – the labels **N** & **O** are arbitrary): (6 pt)



Two different ACHIRAL compounds

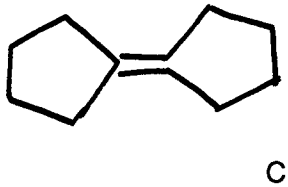
(e) Circle ONE of the following words/phrases that best describes the relationship between compounds **N** & **O**: (2 pt)

CONSTITUTIONAL ISOMERS | THE SAME | CONFORMATIONAL ISOMERS

ENANTIOMERS | DIASTEREOISOMERS

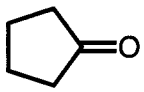
Q3. Compounds **A**, **B**, **C**, **D**, and **E** are all alkenes, and their molecular formulae are shown in the appropriate boxes below. Each alkene undergoes an ozonolysis reaction (O_3 followed by Me_2S) to give ONLY the compounds shown to the right of the reaction arrow in each case (as well as the $Me_2S{=}O$ byproduct). In the reactions that form more than one unique product (**D** & **E**), the products are NOT necessarily formed in equal amounts. Determine the structures of the alkenes **A**–**E** and draw their structures in the appropriate boxes. Hint: for each compound, it may be advantageous to calculate the hydrogen deficiency index (number of double bond equivalents) based upon the given formula. (20 pt)

A

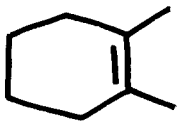


$C_{10}H_{16}$

(i) O_3
(ii) Me_2S

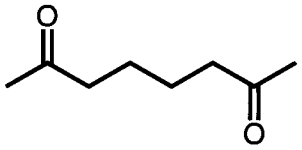


B

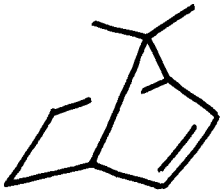


C_8H_{14}

(i) O_3
(ii) Me_2S

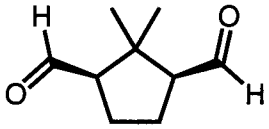


C

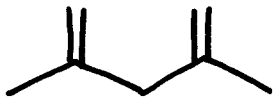


C_9H_{14}

(i) O_3
(ii) Me_2S

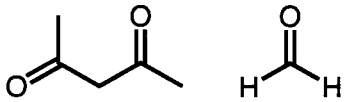


D

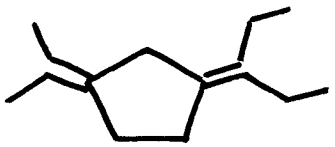


C_7H_{12}

(i) O_3
(ii) Me_2S

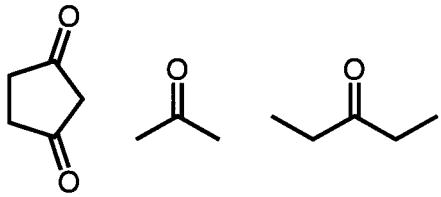


E



$C_{13}H_{22}$

(i) O_3
(ii) Me_2S



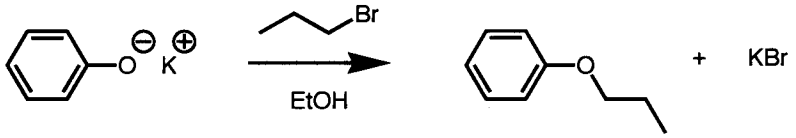
Q4. Phenol and potassium hydroxide undergo an acid-base reaction as shown below:

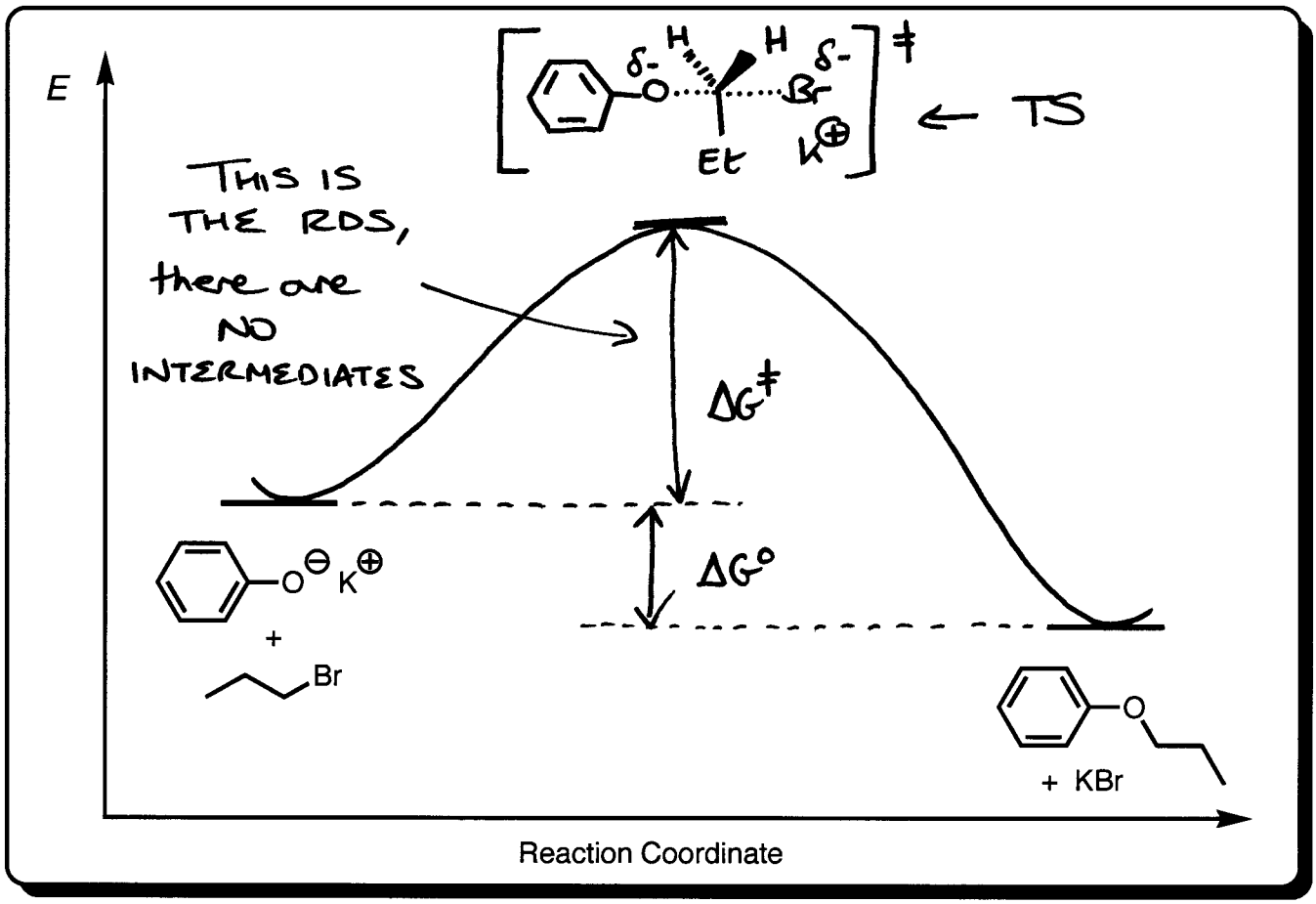
$pK_a = 10$ $pK_a = 16$

(a) What is the equilibrium constant for the acid-base reaction shown above? (3 pt)

10^6 or 1000000

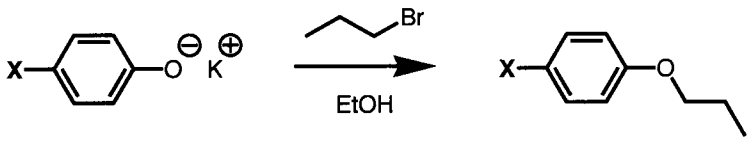
(b) Phenoxide anions react with 1-bromopropane to form ethers as shown below. In the box below, draw the energy profile for this reaction. Draw the STRUCTURES of any proposed transition states or intermediates and label them as **TS** or **INT** as appropriate. Also indicate activation barriers where applicable (**ΔG‡**), the Gibbs free energy change associated with the reaction (**ΔG°**), and the rate determining step (**RDS**). (12 points)





Question 4 is continued on the next page...

(c) The unsubstituted phenoxide anion (**X** = H, below) reacts with 1-bromopropane FIVE times faster than 4-nitrophenoxide (**X** = NO_2, below) to form the corresponding ethers as shown below. In the box below, using words AND pictures, explain the difference in the observed rates of reaction. (8 points)

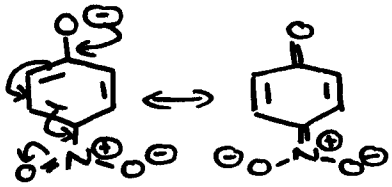


Relative rate of reaction

X = H, $k = 5$

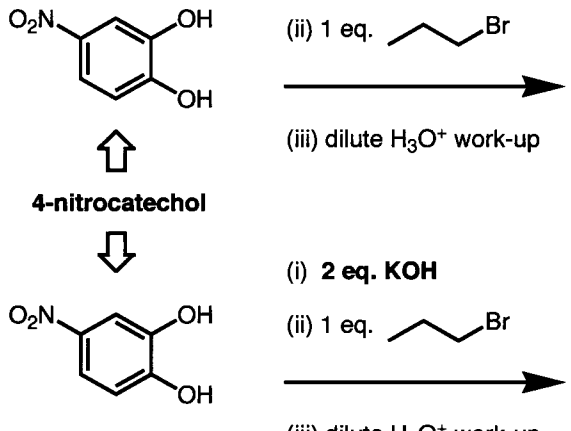
X = NO_2, $k = 1$

THE CONJUGATE BASE OF 4-NITROPHENOL IS MORE STABLE THAN THE C-B OF PHENOL, BECAUSE OF EXTRA DELOCALISATION BECAUSE OF A RESONANCE FORM INVOLVING THE NO_2 GROUP, i.e.,

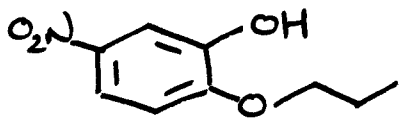


SO, THE $O^{\ominus}$ IS NOT AS NEGATIVE IN THE NITRO COMPOUND AS IT IS IN PHENOL, SO IS LESS NUCLEOPHILIC AND HENCE THE SN2 REACTION PROCEEDS MORE SLOWLY.

(d) The reaction of 4-nitrocatechol with **ONE** equivalent of 1-bromopropane gives a DIFFERENT product depending upon how many equivalents of potassium hydroxide (KOH) are used in the reaction. In each case, however, the product has the formula $C_9H_{11}NO_4$. Predict the products (**A** & **B**) of the reaction sequences shown below, and then explain your answers in the box underneath. (16 pt)

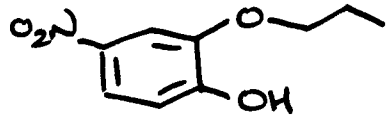


A



$C_9H_{11}NO_4$

B

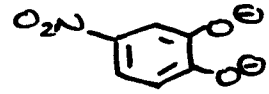


$C_9H_{11}NO_4$

Explanation THE REACTIVE SPECIES FOR THE TOP REACTION IS

AS ONLY 1 EQUIVALENT OF BASE IS USED, AND SO THE MOST ACIDIC H IS REMOVED (RESONANCE)

IN THE SECOND REACTION, THE REACTIVE SPECIES IS THIS ONE:



← THIS $O^{\ominus}$ MORE NUCLEOPHILIC (NO RESONANCE STABILISATION)

← THIS $O^{\ominus}$ LESS NUCLEOPHILIC BECAUSE OF RESONANCE STABILISATION INTO NO_2 GROUP