

CHEM 3311

Fall 2001

Exam I

Name: _____

Your **Recitation TA's** name: _____

Please write your name on each exam page.

Please check to see that you have all 7 questions. Read the questions very carefully. Note: All questions ARE NOT weighted equally!!!!

Question #	Points Earned
1 (25 points)	_____
2 (12 points)	_____
3 (8 points)	_____
4 (15 points)	_____
5 (15 points)	_____
6 (13 points)	_____
7 (12 points)	_____
Max: 100	Total _____

A. AttachmentsTable of pK_a values

Periodic Table

B. Special Instructions

This is a "Closed Book" exam. You are permitted to use molecular models. Answers should be written in the spaces (boxes) provided. Additional scratch paper will not be graded or collected. You have an hour and thirty minutes to complete the exam.

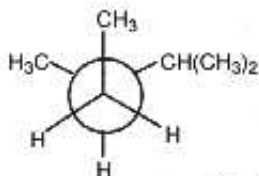
Name: _____

1. (25 points) Multiple Choice: Circle the **best** possible answer.

(i) Identify the compound with the lowest (magnitude of $\Delta H^\circ_{\text{combustion}}$) heat of combustion.

- (A) Heptane
(B) 2,4-Dimethylpentane
(C) 3-Methylhexane
(D) 2,2,3-Trimethylbutane

(ii) What is the IUPAC name of the compound shown in the following Newman projection?



- (A) 1,2,3-Trimethylbutane
(B) 2,3-Dimethylpentane
(C) 2-Isopropylbutane
(D) 2,3,4-Trimethylpentane

(iii) Arrange the following alkanes in order of increasing boiling point.

1. 2,3-Dimethyl pentane
2. Heptane
3. 2,2,3-Trimethylbutane

- (A) 2,2,3-Trimethylbutane < 2,3-Dimethyl pentane < Heptane
(B) 2,3-Dimethyl pentane < Heptane < 2,2,3-Trimethylbutane
(C) 2,3-Dimethyl pentane < 2,2,3-Trimethylbutane < Heptane
(D) 2,2,3-Trimethylbutane < Heptane < 2,3-Dimethyl pentane

(iv) Which one of the following is not a good method to prepare bromocyclopentane?

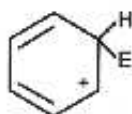
- (A) Cyclopentane is reacted with Br_2 in the presence of light.
(B) Cyclopentanol is heated with HBr .
(C) Cyclopentanol is reacted with PBr_3 .
(D) Cyclopentanol is heated with NaBr .

(v) Which compound produces five different monochlorination products?

- (A) 2,2-Dimethylbutane
(B) 2,3-Dimethylbutane
(C) 2-Methylpentane
(D) 3-Methylpentane

Name: _____

2. (12 points) In the first step of the reaction of electrophilic reagents with benzene, the electrophile accepts an electron pair from the π system of benzene to form the cyclohexadienyl cation shown below (E is the electrophile):

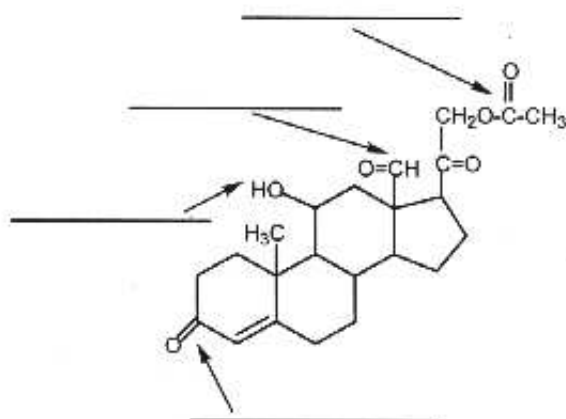


(A) Draw the two most important resonance forms of the cyclohexadienyl cation. You may use a line for each bonding pair of electrons, but show lone pairs and formal charges, as necessary. Show the curved arrow notation for electron delocalization.



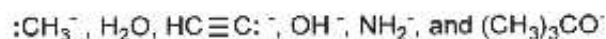
(B) What is the hybridization of carbon at the cationic center?

3. (8 points) Name (in the spaces provided) the functional groups in the molecule shown below:



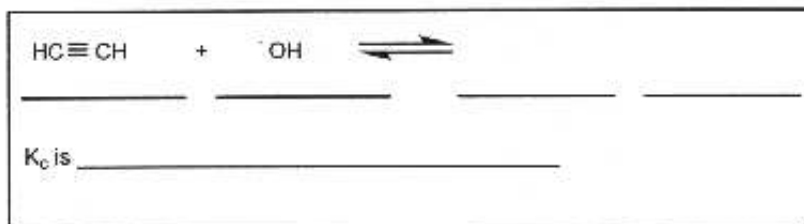
Name: _____

4 (A) (6 points) Arrange the following bases in order of increasing basicity:



_____ < _____ < _____ < _____ < _____ < _____

4 (B) (5 points) Complete the following acid-base reaction, and show lone pairs and formal charges where necessary. Label the stronger acid, weaker acid, stronger base, and weaker base. Indicate whether the equilibrium constant K_c is equal to, less than, or greater than 1.



4 (C) (4 points) The acetylide ion is a useful nucleophile in organic synthesis. It is prepared by the reaction of acetylene (ethyne) with NaNH_2 (sodium amide) in liquid ammonia as the solvent. Why is water not used as the solvent? Write an equation to support your answer, and show VERY CLEARLY the direction in which equilibrium is favored.

Use this space for scratch work. **Only the information in the above boxes will be graded!!!!!!**

Name: _____

5. (15 points) Two stereoisomers of 1-bromo-4-methylcyclohexane are formed when *trans*-4-methylcyclohexanol reacts with HBr. Draw the most stable chair conformation(s) of

(i) *trans*-4-methylcyclohexanol, and

(ii) the two stereoisomers of 1-bromo-4-methylcyclohexane (**label your structure as *cis*- or *trans*-**)

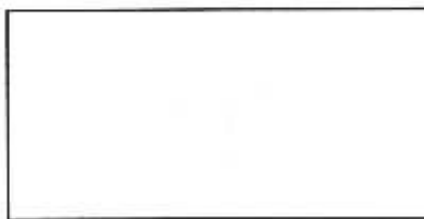
A hydroxyl group is a somewhat "smaller" substituent on a six-membered ring than is a methyl group.

The bromine atom is about the same size as a methyl group.

(i)



(ii)



Briefly (using two or three sentences) explain (in the box provided) why two stereoisomers of 1-bromo-4-methylcyclohexane were formed instead of a single product.



Use this space for scratch work. **Only the information in the above boxes will be graded!!!!!!**

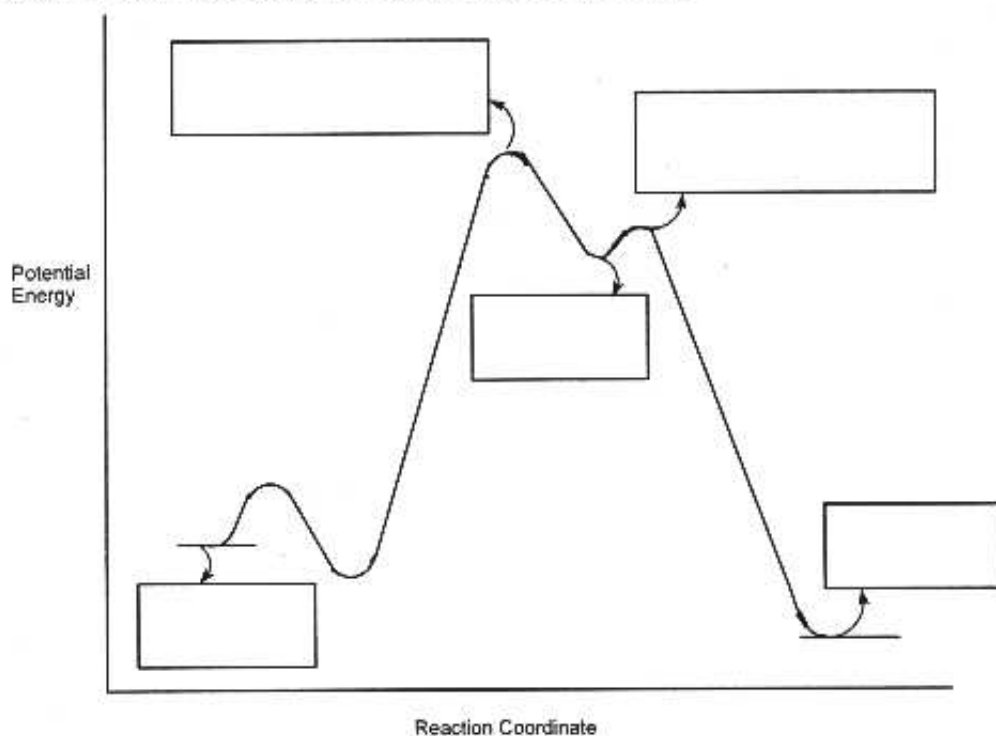
Name: _____

6. (13 points) Cyclopropyl chloride has been prepared by the free-radical chlorination of cyclopropane. Write a stepwise (using a logical sequence) mechanism for this reaction in the boxes provided (only one step per box). Label the step as initiation, propagation, termination, etc. **Show CLEARLY the correct arrow notation.**

Use this space for scratch work. **Only the information in the above boxes will be graded!!!!!!**

Name: _____

7. (12 points) The energy diagram for the reaction of 2-methyl-2-butanol with HCl is shown below. Draw the structures of the reactants, intermediates, transition states, and products in the appropriate boxes. Show all lone pairs, formal charges and partial charges as necessary.




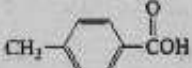


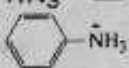


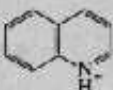
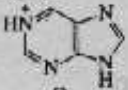


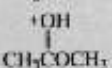


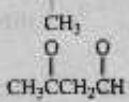





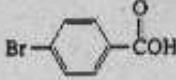
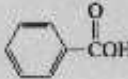

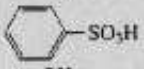

Use this space for scratch work. Only the information in the above boxes will be graded!!!!!!

PERIODIC CHART OF THE ELEMENTS

		I H 1.01																0 2 He 4.00													
IA 3 Li 6.94	IIA 4 Be 9.01											IIIA 5 B 10.8	IVA 6 C 12.0	VA 7 N 14.0	VIA 8 O 16.0	VIIA 9 F 19.0	10 Ne 20.2														
11 Na 23.0	12 Mg 24.3	IIIB 21 Sc 45.0	IVB 22 Ti 47.9	VB 23 V 51.0	VIB 24 Cr 52.0	VIIB 25 Mn 54.9	VIII 26 Fe 55.8, 27 Co 58.9, 28 Ni 58.7			IB 29 Cu 63.5	IIB 30 Zn 65.4	13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9														
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 51.0	24 Cr 52.0	25 Mn 54.9	26 Fe 55.8	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8														
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 96.0	43 Tc (99)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3														
55 Cs 132.9	56 Ba 137.4	57 *La 138.9	72 Hf 178.5	73 Ta 181.0	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)														
87 Fr (223)	88 Ra (226)	89 *Ac (227)	<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="border: 1px solid black; padding: 2px;">58 Ce 140.1</td> <td style="border: 1px solid black; padding: 2px;">59 Pr 140.9</td> <td style="border: 1px solid black; padding: 2px;">60 Nd 144.3</td> <td style="border: 1px solid black; padding: 2px;">61 Pm (147)</td> <td style="border: 1px solid black; padding: 2px;">62 Sm 150.4</td> <td style="border: 1px solid black; padding: 2px;">63 Eu 152.0</td> <td style="border: 1px solid black; padding: 2px;">64 Gd 157.3</td> <td style="border: 1px solid black; padding: 2px;">65 Tb 158.9</td> <td style="border: 1px solid black; padding: 2px;">66 Dy 162.5</td> <td style="border: 1px solid black; padding: 2px;">67 Ho 164.9</td> <td style="border: 1px solid black; padding: 2px;">68 Er 167.3</td> <td style="border: 1px solid black; padding: 2px;">69 Tm 168.9</td> <td style="border: 1px solid black; padding: 2px;">70 Yb 173.0</td> <td style="border: 1px solid black; padding: 2px;">71 Lu 175.0</td> </tr> </table>															58 Ce 140.1	59 Pr 140.9	60 Nd 144.3	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
58 Ce 140.1	59 Pr 140.9	60 Nd 144.3	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0																		
+ Actinide Series			<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="border: 1px solid black; padding: 2px;">90 Th (232)</td> <td style="border: 1px solid black; padding: 2px;">91 Pa (231)</td> <td style="border: 1px solid black; padding: 2px;">92 U 238.1</td> <td style="border: 1px solid black; padding: 2px;">93 Np (237)</td> <td style="border: 1px solid black; padding: 2px;">94 Pu (242)</td> <td style="border: 1px solid black; padding: 2px;">95 Am (243)</td> <td style="border: 1px solid black; padding: 2px;">96 Cm (247)</td> <td style="border: 1px solid black; padding: 2px;">97 Bk (249)</td> <td style="border: 1px solid black; padding: 2px;">98 Cf (251)</td> <td style="border: 1px solid black; padding: 2px;">99 Es (254)</td> <td style="border: 1px solid black; padding: 2px;">100 Fm (253)</td> <td style="border: 1px solid black; padding: 2px;">101 Md (256)</td> <td style="border: 1px solid black; padding: 2px;">102 No (253)</td> <td style="border: 1px solid black; padding: 2px;">103 Lr (257)</td> </tr> </table>															90 Th (232)	91 Pa (231)	92 U 238.1	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (249)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (253)	103 Lr (257)
90 Th (232)	91 Pa (231)	92 U 238.1	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (249)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (253)	103 Lr (257)																		

* Lanthanide Series
 + Actinide Series
 () means mass number of most stable or best known isotope.

Table of pK_a Values

pK_a Values					
Compound	pK_a	Compound	pK_a	Compound	pK_a
$\text{CH}_3\text{C}=\ddot{\text{N}}\text{H}$	-10.1		1.0		4.3
HI	-10		1.0		4.5
HBr	-9	Cl_2CHCOOH	1.3		4.6
	-8	HSO_4^-	2.0	CH_3COOH	4.8
	-7.3	H_3PO_4	2.1		4.9
HCl	-7		2.5		5.1
CH_3SH	-6.8	FCH_2COOH	2.7		5.2
	-6.5	ClCH_2COOH	2.8		5.3
	-6.1	BrCH_2COOH	2.9	$\text{CH}_3\text{C}=\ddot{\text{N}}\text{HCH}_3$	5.5
H_2SO_4	-5	ICH_2COOH	3.2		5.9
	-3.8	HF	3.2	HONH_2	6.0
$\text{CH}_3\text{CH}_2\overset{\text{H}}{\text{O}}\text{CH}_2\text{CH}_3$	-3.6	HNO_2	3.4	H_2CO_3	6.4
$\text{CH}_3\text{CH}_2\overset{\text{H}}{\text{O}}\text{H}$	-2.4		3.4		6.8
$\text{CH}_3\overset{\text{H}}{\text{O}}\text{H}$	-2.5	HCOOH	3.8	H_2S	7.0
H_3O^+	-1.7		3.9		7.1
HNO_3	-1.3		4.0	H_2PO_4^-	7.2
$\text{CH}_3\text{SO}_3\text{H}$	-1.2		4.2		7.8
	-0.60				
CH_2CNH_2	0.0				
F_2CCOH	0.2				
Cl_3CCOH	0.64				
	0.79				

pK_a Values (Continued)

Compound	pK _a	Compound	pK _a	Compound	pK _a
	8.0		10.7		17
H ₂ NNH ₂	8.1	(CH ₃) ₂ NH ₂ ⁺	10.7	(CH ₃) ₂ COH	18
	8.2		11.1		20
CH ₃ CH ₂ NO ₂	8.6		11.0		24.5
	8.9	CH ₃ CH ₂ NH ₂ ⁺	11.3	HC≡CH	25
	8.9		11.3	CH ₃ C≡N	25
HC≡N	9.1	HPO ₄ ²⁻	12.3		30
	9.3	CF ₃ CH ₂ OH	12.4	NH ₃	36
	9.4		13.3		36
NH ₄ ⁺	9.4	HC≡CCH ₂ OH	13.5	CH ₃ NH ₂	40
HOCH ₂ CH ₂ NH ₂ ⁺	9.5		13.7		41
	9.8		13.9		43
	10.0		14.4	CH ₂ =CHCH ₃	43
	10.2	CH ₃ OH	15.5	CH ₂ =CH ₂	44
HCO ₂ ⁻	10.2	H ₂ O	15.7		46
CH ₃ NO ₂	10.2	CH ₃ CH ₂ OH	16.0	CH ₄	50
	10.3		16	CH ₃ CH ₃	50
CH ₃ CH ₂ SH	10.5		16.0		52
(CH ₃) ₂ NH ⁺	10.6		-17		
	10.7				
CH ₃ NH ₂ ⁺	10.7				