CHEM 3311
Fall 2001
Exam I

Name: Answer Key

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. Attachments

Table 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 $\Delta H^\circ_{combustion}$) heat of combustion.

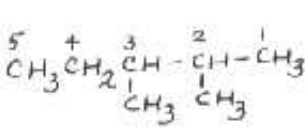
(A) Heptane C_7H_{16} (B) 2,4-Dimethylpentane C_7H_{16}

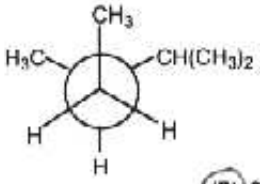
(C) 3-Methylhexane C_7H_{16} (D) 2,2,3-Trimethylbutane C_7H_{16}

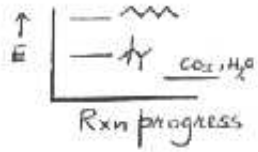
Most highly branched isomer is most stable

Combustion is exothermic.

(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

most polarizable ← least polarizable

(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

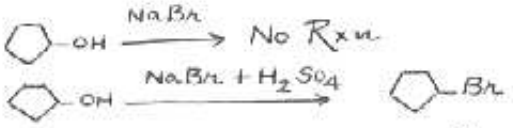
(iv) Which one of the following is not a good method to prepare bromocyclopentane?

(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.

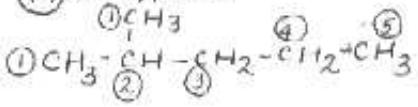
(D) Cyclopentanol is heated with NaBr.



(v) Which compound produces five different monochlorination products? Identify the different types of H atoms on each carbon

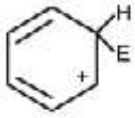
(A) 2,2-Dimethylbutane (B) 2,3-Dimethylbutane

(C) 2-Methylpentane (D) 3-Methylpentane

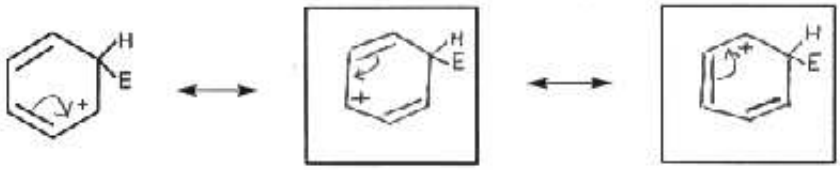


Name: _____

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):

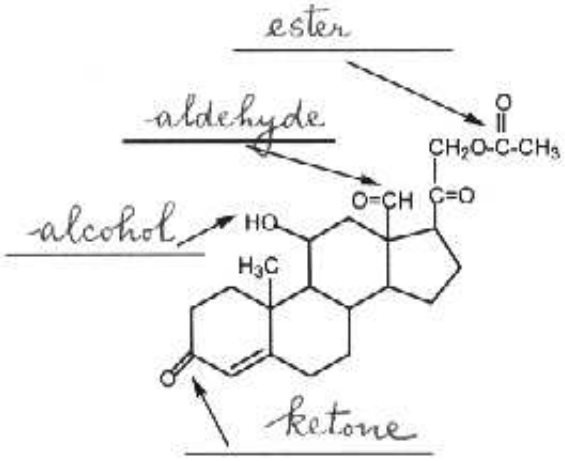


(A) Draw the two most important resonance forms of the cyclohexadienyl cation. You may use a line for each bonding pair of electrons, but show lone pairs and formal charges, as necessary. Show the curved arrow notation for electron delocalization.



(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.



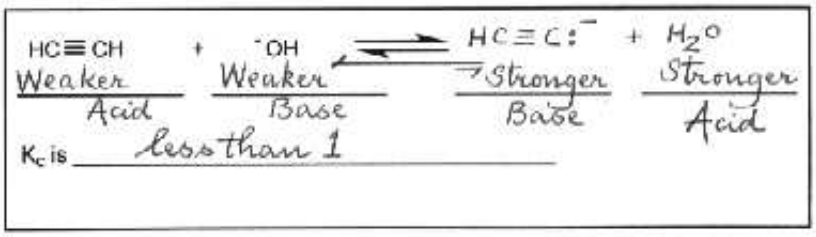
Name: _____

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

$:CH_3^-$, H_2O, $HC\equiv C:^-$, OH^-, NH_2^-, and $(CH_3)_3CO^-$

H_2O < ^-OH < $(CH_3)_3CO^-$ < $HC\equiv C:^-$ < $:NH_2^-$ < $:CH_3^-$

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.



K_c is less 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.

H_2O may react with sodium acetylide ($HC\equiv C:^-Na^+$)

$$HC\equiv C:^- + H_2O \rightleftharpoons HC\equiv CH + OH^-$$

OR H_2O may react with sodium amide ($Na^+ NH_2^-$)

$$H_2O + :NH_2^- \rightleftharpoons NH_3 + OH^-$$

Hydroxide ion is not basic enough to react with $HC\equiv CH$.

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

Name: _____

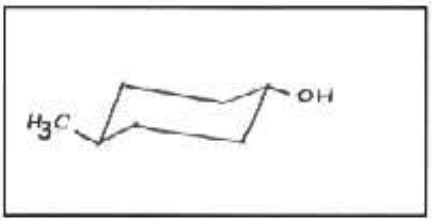
5. (15 points) Two stereoisomers of 1-bromo-4-methylcyclohexane are formed when *trans*-4-methylcyclohexanol reacts with HBr. Draw the most stable chair conformation(s) of

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

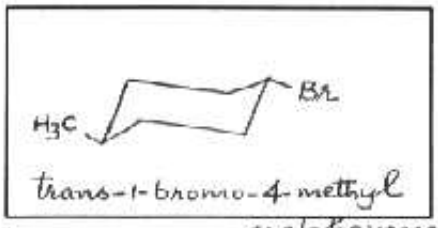
(ii) the two stereoisomers of 1-bromo-4-methylcyclohexane (**label your structure as *cis*- or *trans*-**)

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.

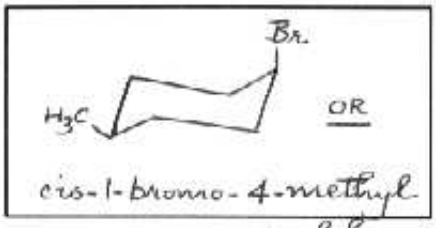
(i)



(ii)



trans-1-bromo-4-methyl cyclohexane



OR

cis-1-bromo-4-methyl cyclohexane

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.

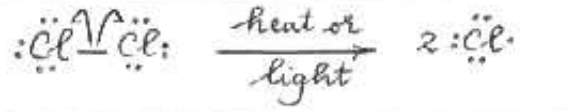
The reaction of the alcohol with HBr produces a carbocation intermediate which is planar. The nucleophile Br^- can approach the carbocation from above or below the plane.

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.**

Initiation



Propagation

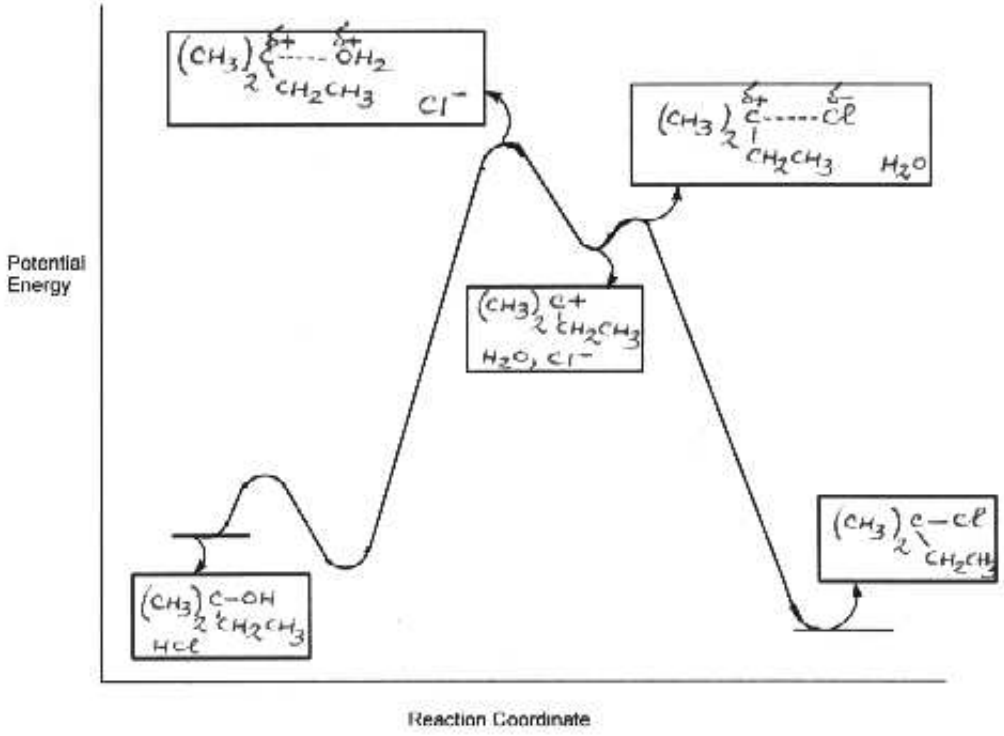
Propagation

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

more cyclopropyl chloride is formed via the propagation step rather than the termination step.

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

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
							1 H 1.01										2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.8	6 C 12.0	7 N 14.0	8 O 16.0	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											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)															

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
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)

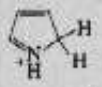
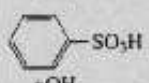
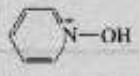
* Lanthanide Series

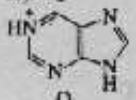
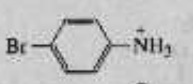
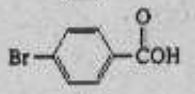
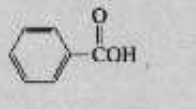
\+ Actinide Series

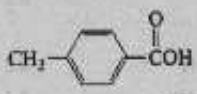
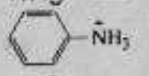
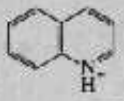
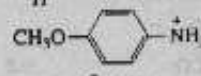
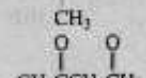
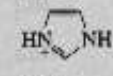
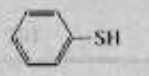
( ) means mass number of most stable or best known isotope.

Table of pK_a Values

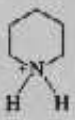
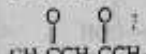
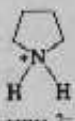
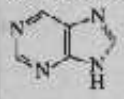
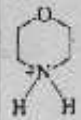
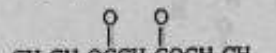
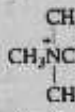
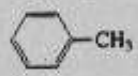
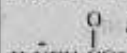
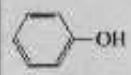
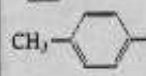
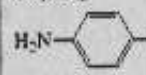
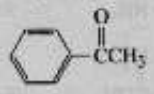
pK_a Values

Compound	pK_a
$CH_3C{=}\overset{+}{N}H$	−10.1
HI	−10
HBr	−9
$CH_3\overset{+OH}{C}H$	−8
$CH_3\overset{+OH}{C}CH_3$	−7.3
HCl	−7
CH_3SH	−6.8
$CH_3\overset{+OH}{C}OCH_3$	−6.5
$CH_3\overset{+OH}{C}OH$	−6.1
H_2SO_4	−5
	−3.8
$CH_3CH_2\overset{H}{\overset{+}{O}}CH_2CH_3$	−3.6
$CH_3CH_2\overset{H}{\overset{+}{O}}H$	−2.4
$CH_3\overset{H}{\overset{+}{O}}H$	−2.5
H_3O^+	−1.7
HNO_3	−1.3
CH_3SO_3H	−1.2
	−0.60
$CH_3\overset{+OH}{C}NH_2$	0.0
F_3CCOH	0.2
Cl_3CCOH	0.64
	0.79

Compound	pK_a
	1.0
	1.0
Cl_2CHCOH	1.3
HSO_4^-	2.0
H_3PO_4	2.1
	2.5
FCH_2COH	2.7
$ClCH_2COH$	2.8
$BrCH_2COH$	2.9
ICH_2COH	3.2
HF	3.2
HNO_2	3.4
	3.4
	3.8
	3.9
	4.0
	4.2

Compound	pK_a
	4.3
	4.5
HN_3	4.5
	4.6
	4.8
	4.9
	5.1
	5.2
	5.3
$CH_3C{=}\overset{+}{N}HCH_3$	5.5
	5.9
$HO\overset{+}{N}H_3$	6.0
H_2CO_3	6.4
	6.8
H_2S	7.0
	7.1
$H_2PO_4^-$	7.2
	7.8

pK_a Values (*Continued*)

Compound	pK_a	Compound	pK_a	Compound	pK_a
	8.0		10.7		17
$H_2\overset{+}{N}H_3$	8.1	$(CH_3)_2\overset{+}{N}H_2$	10.7	$(CH_3)_3COH$	18
	8.2		11.1		20
$CH_3CH_2NO_2$	8.6	$CH_3CH_2\overset{+}{N}H_3$	11.0		24.5
	8.9		11.3	$HC{\equiv}CH$	25
	8.9	HPO_4^{2-}	12.3	$CH_3C{\equiv}N$	25
$HC{\equiv}N$	9.1	CF_3CH_2OH	12.4		30
	9.3		13.3	NH_3	36
	9.4	$HC{\equiv}CCH_2OH$	13.5		36
$\overset{+}{N}H_4$	9.4		13.7	CH_3NH_2	40
$HOCH_2CH_2\overset{+}{N}H_3$	9.5		13.9		41
	9.8		14.4		43
	10.0	CH_3OH	15.5	$CH_2{=}CHCH_3$	43
	10.2	H_2O	15.7	$CH_2{=}CH_2$	44
HCO_3^-	10.2	CH_3CH_2OH	16.0		46
CH_3NO_2	10.2		16	CH_4	50
	10.3		16.0	CH_3CH_3	50
CH_3CH_2SH	10.5		~17		52
$(CH_3)_3\overset{+}{N}H$	10.6				
	10.7				
$CH_3\overset{+}{N}H_3$	10.7				