

Chem 314
Final Exam
Spring, 2006
Beauchamp

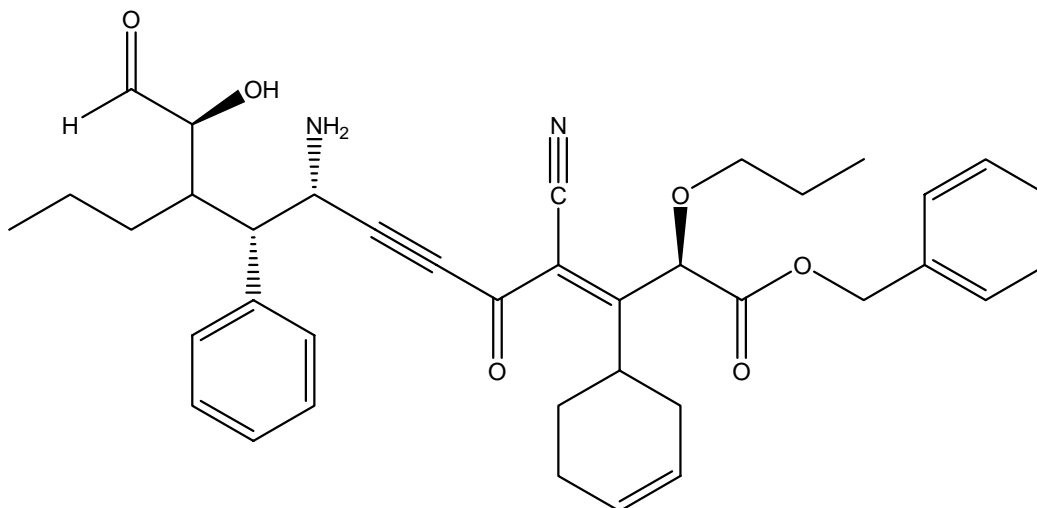
Name _____

Problem	Points	Credit
1. Nomenclature (one structure)	25	
2. 2D Lewis structure (large structure with possible formal charge)	20	
3. 3D Structures, Formal Charge, Resonance, Curved Arrows, Hybridization	30	
4. Thermodynamics, Conformations, Configurations, Stereoisomers, Energy Diagram, Newman Projections	35	
5. Stereochemistry Questions	27	
6. Acid/Base Chemistry (arrow pushing, explanation)	28	
7. S_N and E mechanisms, including stereochemical details	46	
8. RX compounds in S_N and E reactions, including stereochemistry details,	33	
9. Free Radicals, Predict products provide mechanism	27	
10. Synthesis using reactions learned this quarter	24	
Total	277	

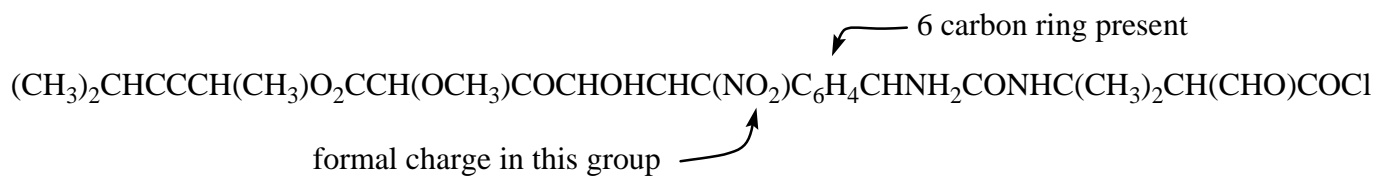
This is a long exam. It has been designed so that no one question will make or break you. You are not expected to completely finish the exam. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement. Do your best to show me what you know in the time available.

Nobody made a greater mistake than he who did nothing because he could only do a little. Edmund Burke

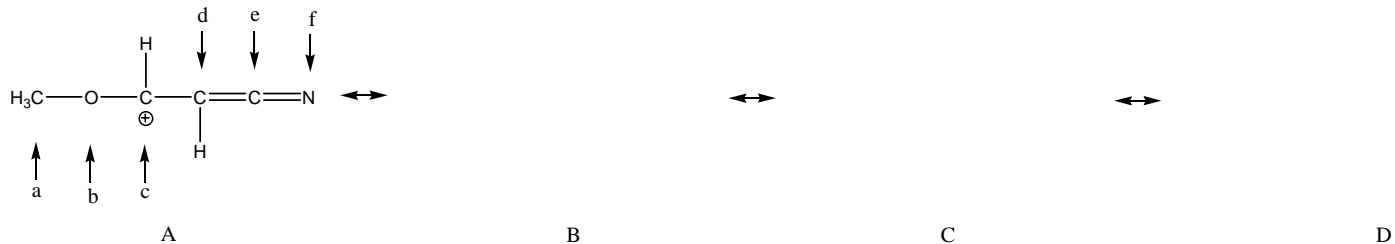
1. Provide an acceptable name for the following structure. Indicate the absolute configuration of any chiral centers shown in three dimensional form (R/S) and any E/Z stereogenic centers. (25 pts)



2. Draw an acceptable 2D Lewis structure for the following formula. Indicate any formal charges present. (20 pts)



3. First, draw three other 2D resonance structures to quench any formal charge present. Include proper curved arrow conventions, including lone pairs and formal charge. Rank your structures from best (= 1) to poorest. Draw a three-dimensional Lewis structure of "A" and the best other resonance structure. Show σ bonds as lines, wedges and dashes and the p orbitals in π bonds as well as any orbitals holding lone pairs. Draw 2 dots for lone pair and π bond electrons. Use structure A to fill in the table at the bottom. **Assume that all nonhydrogens atoms have full octets, unless a carbocation is written.** (30 pts)



3D (A)

3D (best other)

Use structure A to fill in the following table.

	Hybridization	Angles	Shape	# σ bonds	# π bonds	# lone pairs
a						
b						
c						
d						
e						
f						

4. a. Draw both chair conformations of trans-1-ethyl-2-isopropylcyclohexane and cis-1-ethyl-2-isopropylcyclohexane. Indicate which conformation is more stable in each pair. Which conformation, overall, is most and least stable? What is the absolute configuration of all stereogenic atoms in chair 1? (16 pts)



most stable (1 or 2) = _____

most stable (1 or 2) = _____

most stable overall (1,2,3,4) = _____

least stable overall (1,2,3,4) = _____

stereochemical relationship of 1 with 2? enantiomer, diastereomer, meso, none

stereochemical relationship of 1 with 3? enantiomer, diastereomer, meso, none

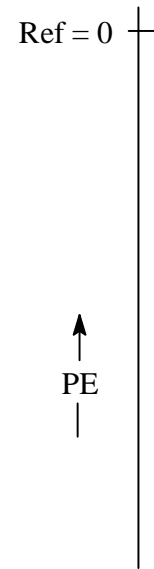
stereochemical relationship of 1 with 4? enantiomer, diastereomer, meso, none

stereochemical relationship of 3 with 4? enantiomer, diastereomer, meso, none

- b. Write a balanced combustion equation for any isomer of 1-ethyl-2-isopropylcyclohexane. (2 pts)

c. The heats of combustion of carbon graphite (per mole) and hydrogen (H_2) are -94.0 and -57.8 kcal/mole, respectively. Given that the heats of combustion of cis-1-ethyl-2-isopropylcyclohexane and trans-1-ethyl-2-isopropylcyclohexane are -1612.1 and -1610.3, respectively, calculate the heat of formation, ΔH°_f , for each of these isomers. Show all work and analysis clearly. Sketch a very simple diagram showing the zero reference point, heat of formation and heat of combustion for one of the isomers. Indicate what structures would be drawn at each of those energy points. (10 pts)

show work:

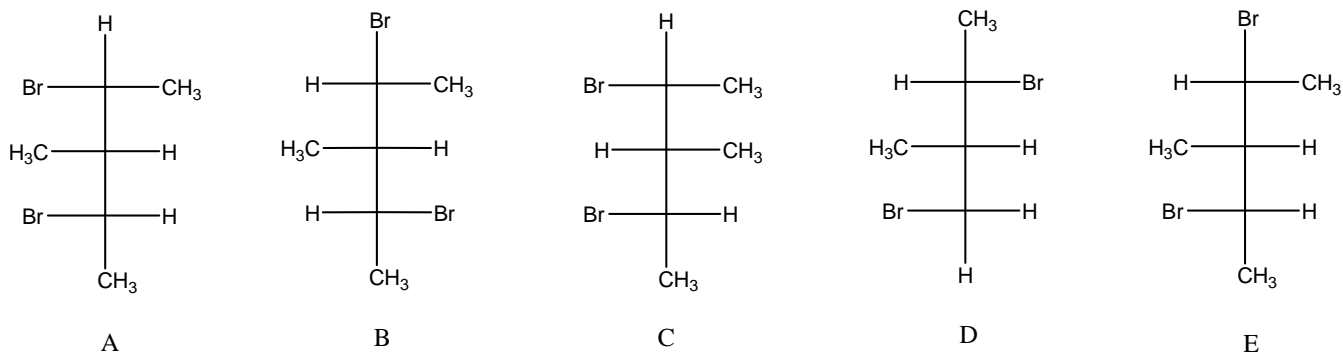


d. Use the thermodynamic data from part c and the most stable conformation of the cis and trans isomers to estimate the energy of an axial ethyl in a cyclohexane ring. Briefly, show your reasoning for the value provided. (3 pts)

e. Use the third most stable conformation from part a and draw a Newman projection using bonds $C_1 \rightarrow C_2$ and $C_5 \rightarrow C_4$ for your structure. Point out any gauche relationships in the branches and/or the ring. (4 pts)

Newman projection of the third most stable conformation from part a

5. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections having the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration. (15 pts)

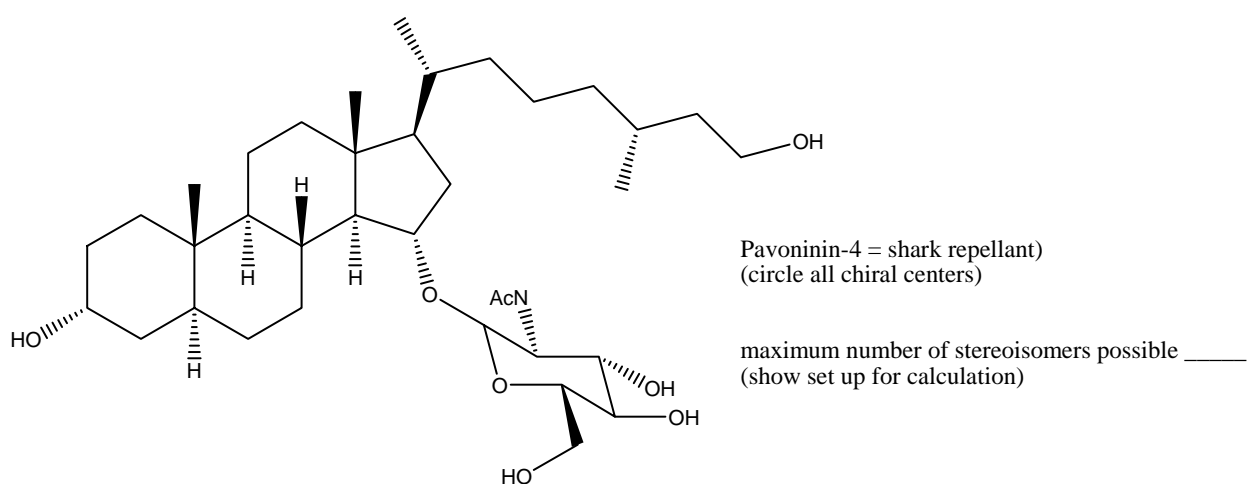


- | | | | | | | | | | | |
|--|----|----|----|----|----|----|----|----|----|----|
| a. Which are meso? | A | B | C | D | E | | | | | |
| b. Which is not an isomer with the others? | A | B | C | D | E | | | | | |
| c. Which pairs are enantiomers? | AB | AC | AD | AE | BC | BD | BE | CD | CE | DE |
| d. Which pairs are identical? | AB | AC | AD | AE | BC | BD | BE | CD | CE | DE |
| e. Which pairs are diastereomers? | AB | AC | AD | AE | BC | BD | BE | CD | CE | DE |
| f. Which would not rotate plane polarized light when mixed as a 50/50 racemic mixture? | AB | AC | AD | AE | BC | BD | BE | CD | CE | DE |

g. Draw a Fischer projection of any stereoisomers which are not shown above. If there are none, indicate this. (4 pts)

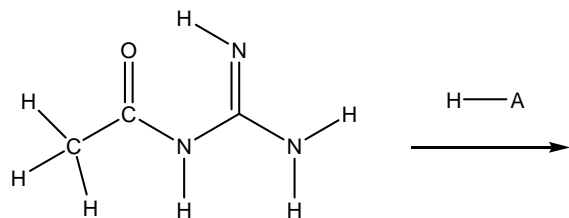
h. Briefly, what would happen in the above structures if the top Br was switched with a Cl? You don't have to redo the problem, but do show at least one example where the problem would change. (4 pts)

i. The synthesis of a complicated steroid structure used as a shark repellent was recently published (Org. Lett. p.2253, 2006). Circle all chiral centers and calculate the maximum number of stereoisomers possible. (4 pts)

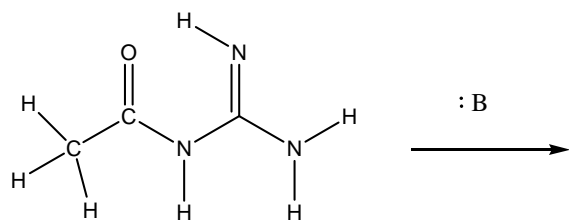


6. The following molecule can act as either an acid or a base (it's amphiprotic). Use a general acid, HA, and show the molecule acting as a base at its most basic site. Use a general base, B:, and show the molecule reacting as an acid at its most acidic site. Use curved arrows to show the flow of electrons and include formal charge and lone pairs. Draw all resonance structures important to the conjugate acid or base. Provide an explanation for why your answers are the "best" choices. (28 pts)

a. reaction in acid, HA

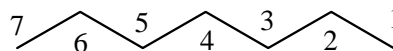


b. reaction in base, B:



7. Use 4R-bromo-3S-methylheptane to provide a simple, arrow-pushing mechanism for each of the following reaction conditions (show curved arrows, lone pairs & formal charge). Fill in the necessary details to clearly indicate any stereochemical features and/or conformational requirements. If reactants are not drawn in the proper orientation to show how the reaction must proceed, then redraw them in a more informative way that shows this. If rearrangement to a more stable carbocation is possible, assume this occurs and then show any SN/E products from that carbocation. (46 pts)

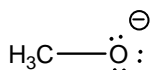
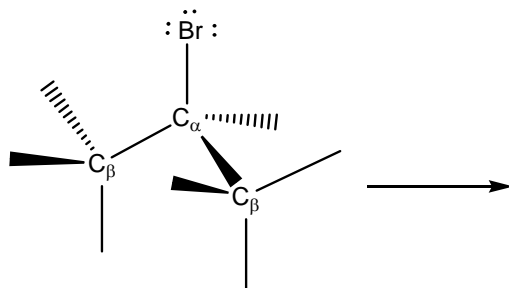
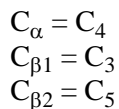
a. Draw a 2D structure and then a 3D structure of the reacting molecule. A 3D structure will be provided for the cost of the points of this part. (3 pts)



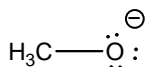
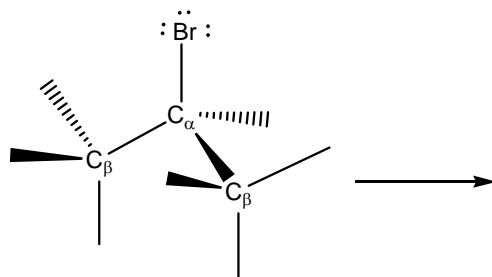
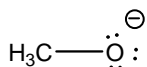
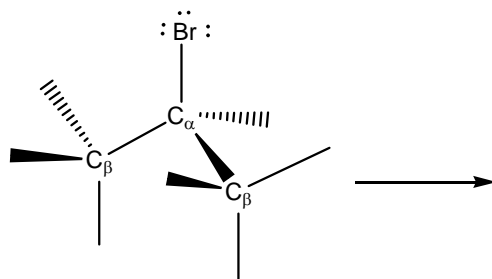
2D structure

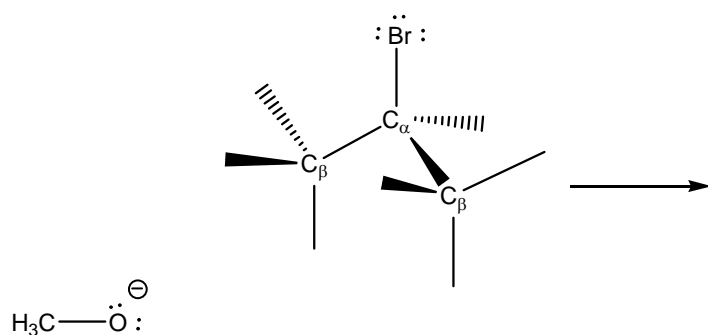
3D structure of 4R-bromo-3S-methylheptane

b. Show the S_N reaction (what kind?), indicate absolute configuration of all chiral centers. (4 pts)

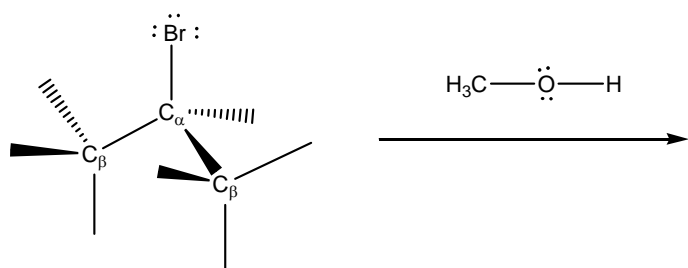


c. Show all possible E reaction products (what kind?). Indicate if E, Z or neither. (15 pts)



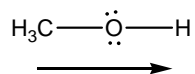


d. Show the S_{N} reaction (what kind?). Indicate absolute configuration of all chiral centers. (8 pts)

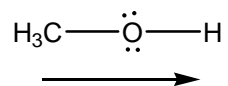


e. Show all possible E reaction products. Indicate if E, Z or neither. If multiple products are formed between two atoms, you can show a single mechanism and just draw the additional possible products. (16 pts)

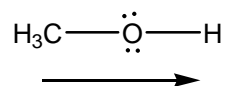
Redraw the intermediate used in 8d above.



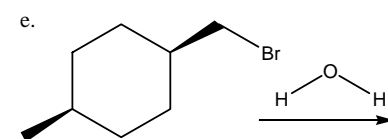
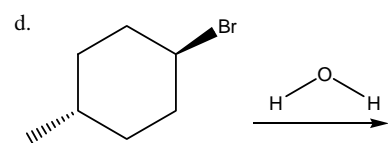
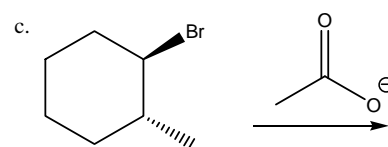
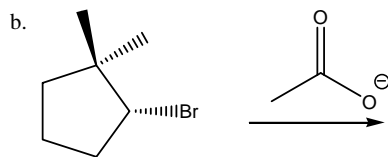
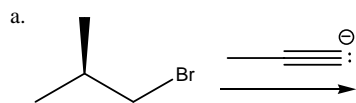
Redraw the intermediate used in 8d above.



Redraw the intermediate used in 8d above.



8. Predict all possible S_{N} product(s). Only predict the major E product. State whether S_{N} or E is major, minor or they are about the same. Finally, state by what mechanism(s) each product was formed. (15 pts)



9. a. How many different types of hydrogen atoms are present in 2-methylbutane? Show all possible products when 2-methyl butane is monobrominated with $\text{Br}_2/h\nu$? If any chiral centers are present in the starting material or the products, draw them clearly with a 3D representation and specify the absolute configuration of each one. If stereoisomers form, specify what type of isomerism is present (enantiomers, diastereomers, meso compounds, achiral, etc.). Indicate the approximate relative amounts of each product formed if the relative rates of reaction of a bromine atom with an sp^3 C-H bond are: primary = 1, secondary = 80 and tertiary = 1600. (15 pts)

b. Provide a complete arrow pushing mechanism to explain formation of the major product from the above reaction (show proper curved arrow conventions, lone pairs as two dots and single electrons as one dot). Clearly label each distinct part of the reaction mechanism. Calculate an overall ΔH for each step of your mechanism using the given bond energies. (12 pts)

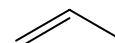
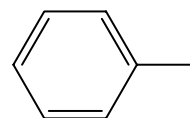
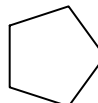
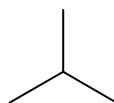
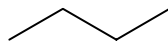
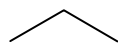
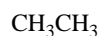
	ΔH (kcal/mol)
Br—Br	46
H—Br	87

$\text{Me}^{\circ}\text{C—H}$	105
1°C—H	98
2°C—H	95
3°C—H	92

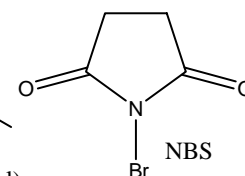
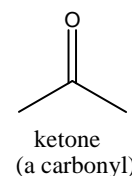
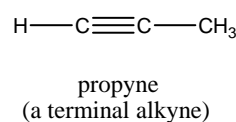
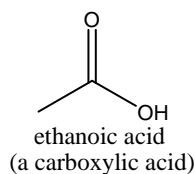
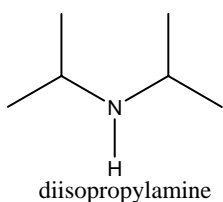
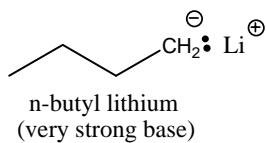
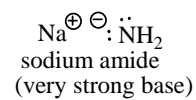
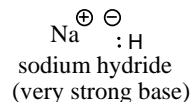
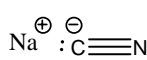
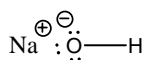
$\text{Me}^{\circ}\text{C—Br}$	70
1°C—Br	68
2°C—Br	68
3°C—Br	65

10. Propose a reasonable synthetic approach for four of the following six molecules (a-f) starting from an alkane. You may use any of the reagents available below. A molecule made in one part can be reused in another part without making it again. Just refer back to the part where it was made previously. Circle the letters of the four you want me to grade. If no letters are circled, I will grade a-d. (24 pts)

Starting hydrocarbons with sp^3 C-H

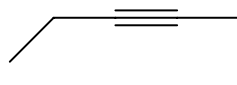


Miscellaneous Reagents

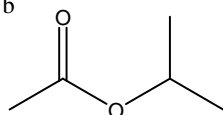


Synthetic targets

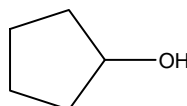
a



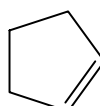
b



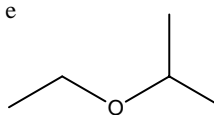
c



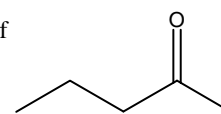
d



e

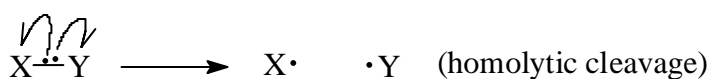


f



Typical Bond Energies for Common Substitution Patterns Found in Organic Chemistry (X-Y)

X =	Y = H-	Me-	(1°) Et-	(2°) i-Pr-	(3°) t-Bu-	(phenyl) Ph-	F-	Cl-	Br-	I-	HO-	H ₂ N-	N≡C-
CH ₃ - methyl (Me-)	105	90	86	86	84	102	110	85	71	57	93	85	122
CH ₃ CH ₂ - primary (Et-)	98	86	82	81	79	98	108	80	68	53	92	82	118
CH ₃ CH ₂ CH ₂ - primary (Pr-)	98	86	82	80	79	98	107	81	68	53	92	82	117
(CH ₃) ₂ CH- secondary (i-Pr-)	95	86	81	79	76	96	106	80	68	54	93	82	116
(CH ₃) ₃ C- tertiary (t-Bu-)	93	84	79	76	71	93	110	80	67	52	93	82	-
C ₆ H ₅ - phenyl (Ph-)	111	102	97	96	93	115	126	96	80	65	111	102	131
C ₆ H ₅ CH ₂ - benzyl (Bn-)	88	76	72	71	70	90	-	72	58	48	81	71	-
CH ₂ =CHCH ₂ - allyl (al-)	86	74	70	70	67	-	-	68	54	41	78	-	-
CH ₃ CO- acyl (Ac-)	86	81	76	74	72	94	119	81	66	49	107	-	-
CH ₃ CH ₂ O- alkoxy	104	83	82	-	-	101	-	-	-	-	44	-	-
CH ₂ =CH- vinyl	110	100	96	95	90	103	-	90	78	-	-	-	130
H- hydrogen-	104	105	98	95	93	111	136	103	88	71	119	107	125

**Average Bond Energies (kcal/mole)**

	H	C	Si	N	O	S	F	Cl	Br	I		
H	104	98	76	92	109	83	135	103	87	71	Bond Energy for multiple bonds	
C		81	72	66	79	65	116	79	66	52		
Si			-	-	108	-	135	91	74	56		C=C 146
N				39	39	-	65	46	-	-		C=N 147
O					34	-	45	52	48	56		C=O 176
S						60	-	61	52	-		C≡C 200
F							37	-	-	-		C≡N 213
Cl								58	-	-		
Br									46	-		
I										36		

We study in youth, we understand with age.

Okaa-san (Mom in Japanese)

Problems considered but not used on this exam.

	A $\text{O}^{\ominus}-\text{H}$ Na^{\oplus}	B $\text{O}^{\ominus}-\text{CH}_2\text{CH}_3$ Na^{\oplus}	C $\text{H}_3\text{C}-\text{C}(=\text{O})-\text{O}^{\ominus}$ Na^{\oplus}	D $\text{O}^{\ominus}-\text{C}(\text{CH}_3)_2$ K^{\oplus}	E $\text{C}\equiv\text{N}^{\ominus}$ Na^{\oplus}	F $\text{CH}_3-\text{C}\equiv\text{C}^{\ominus}$ Na^{\oplus}	G H_2O	H $\text{CH}_3\text{CH}_2\text{OH}$	I $\text{H}_3\text{C}-\text{C}(=\text{O})-\text{OH}$
1	<chem>H3C-Br</chem>								
2	<chem>CCCCBr</chem>								
3	<chem>CC[C@H](C)COTs</chem>								
4	<chem>C1CCCCC1C[C@H](C)Cl</chem>								
5	<chem>C1CCCCC1[C@H](C)Br</chem>								
6	<chem>CC(C)C(C)Br</chem>								
7	<chem>CC(C)C(C)Cl</chem>								
8	<chem>CC(C)C(C)I</chem>								
9	<chem>CC(C)C(C)Cl</chem>								
10	<chem>C1CCCCC1COTs</chem>								
11	<chem>C1CCCCC1[C@H](C)Br</chem>								
12	<chem>C1CCCCC1[C@H](C)I</chem>								
13	<chem>CC(C)C(C)Cl</chem>								
14	<chem>CC(C)C(C)I</chem>								
15	<chem>C1CCCCC1[C@H](C)Cl</chem>								
16	<chem>C1CCCCC1[C@H](C)I</chem>								
17	<chem>CC(C)C(C)Cl</chem>								
18	<chem>CC(C)=CCl</chem>								
19	<chem>CC(C)=CCOTs</chem>								
20	<chem>C1=CC=CC=C1[C@H](C)COTs</chem>								
21	<chem>C1=CC=CC=C1[C@H](C)Br</chem>								
22	<chem>CC=C(Cl)C</chem>								
23	<chem>c1ccc(Br)cc1</chem>								

Questions

1. Predict all possible S_N products and state by what mechanism they formed.

2. Predict all possible E products and state by what mechanism they formed. Predict the most stable E product, if there is one.

3. Indicate whether ($S_N > E$) or ($E > S_N$) or similar amounts of both are formed. Consider: a. basicity of the base/nucleophile and b. steric hindrance in the base.

4. If carbocations are possible, show any rearrangement to a more stable carbocation. Do not show similar energy carbocation rearrangements.

5. Show any important stereochemical features of the reactions.

Alcohol / acid conditions

	J H-Cl	K H-Br	L H-I	M $\text{H}_2\text{SO}_4/\Delta$
24	<chem>CH3OH</chem>			
25	<chem>CCCCO</chem>			
26	<chem>C1CCCC1O</chem>			
27	<chem>C1=CC=CC=C1[C@H](C)C1CCCC1O</chem>			

Using the given formula, $C_9H_{17}Br$, draw an isomer which satisfies the given statement. Do not use any given isomer more than one time. If stereochemistry is important make sure you draw your structure so that its three dimensional nature is clearly indicated. Point out the feature of your structure that makes it consistent with the given statement. How many degrees of unsaturation are there? (30 pts)

degrees of unsaturation = _____

a. Undergoes fast S_N2 reaction with CH_3O^-/CH_3OH

b. Undergoes fast S_N1 reaction in CH_3OH

c. Write the expected product from part a.

d. Write a possible S_N1 product from part b.

e. Gives only one alkene in E2 reaction with CH_3O^-/CH_3OH

f. Reacts very slowly whether in CH_3O^-/CH_3OH or CH_3OH

g. Write the expected product from part e.

h. Write a possible E1 product from part b.

i. Undergoes E2 reaction but not S_N2 reaction in CH_3O^-/CH_3OH

j. Can reasonably react by all four mechanisms (S_N2 , E2, S_N1 , E1)

k. A reactive allylic structure in S_N2 reactions

l. Can exist as an enantiomer (also draw the enantiomer)

m. Can exist as a diastereomer (show a diastereomer)

n. Is a meso structure (show a stereoisomer)