Chem 314
Final Exam   Name _____
Spring, 2005
Beauchamp

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	37	
5. Stereochemisty Questions	27	
6. Physical Properties or Bond Energies and Common Names	15	
7. Acid/Base Chemistry (arrow pushing, explanation)	28	
8. S_N and E mechanisms, including stereochemical details	46	
9. RX compounds in S_N and E reactions, including stereochemistry details,	33	
Total	261	

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 <u>show all of your work</u>. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement. Do you best to show me what you know in the time available.

Forgiveness does not change the past, but it does enlarge the future."   Paul Boese
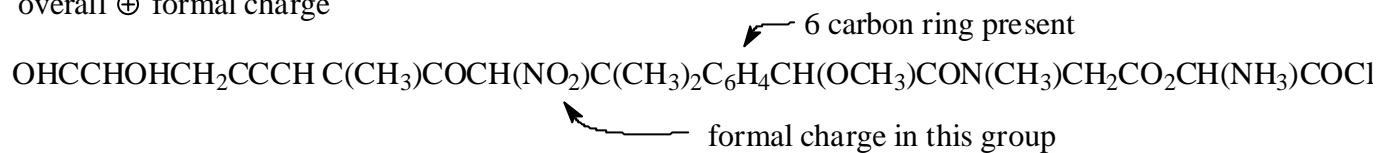
1. Provide an acceptable name for the following structure. Indicate the absolute configuration of any chiral centers shown in three dimensional form (R/S) and any E/Z stereogenic centers. (25 pts)
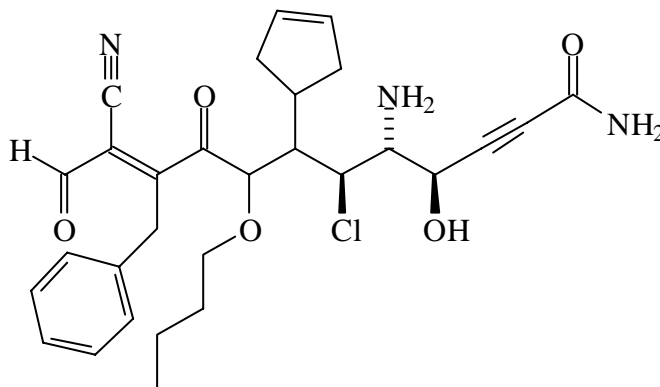

2. Draw an acceptable 2D Lewis structure for the following formula. Indicate any formal charges present. (20 pts)

overall ⊕ formal charge

6 carbon ring present

$OHCCHOHCH_2CCCH C(CH_3)COCH(NO_2)C(CH_3)_2C_6H_4CH(OCH_3)CON(CH_3)CH_2CO_2CH(NH_3)COCl$

formal charge in this group

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)
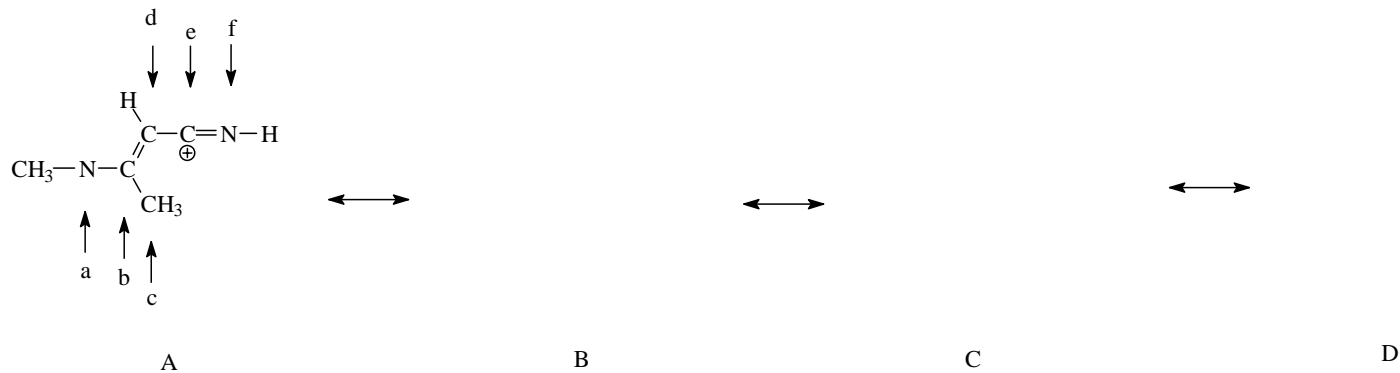
A   B   C   D

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 cis-1,2-diethylcyclohexane and trans-1,2-diethylcyclohexane. 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)

$\rightleftharpoons$
cis

$\rightleftharpoons$
trans

chair 1

chair 2

chair 3

chair 4

most stable (1 or 2) = _____

most stable (3 or 4) = _____

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

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

sterochemical relationship of 1 with 2? _____ (enantiomer, diastereomer, meso, none)

sterochemical relationship of 1 with 3? _____ (enantiomer, diastereomer, meso, none)

sterochemical relationship of 1 with 4? _____ (enantiomer, diastereomer, meso, none)

sterochemical relationship of 3 with 4? _____ (enantiomer, diastereomer, meso, none)

b. Write a balanced combustion equation for any isomer of 1,2-diethylcyclohexane. (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-1,2-diethylcyclohexane and trans-1,2-diethylcyclohexane are -1467.1 and -1465.2 , respectively, calculate the heat of formation, ΔH°_f , for each of these isomers. Show all work and analysis clearly, so that I can understand your logic in solving this problem. 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)
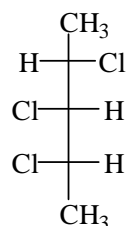
show work:

Ref = 0

PE
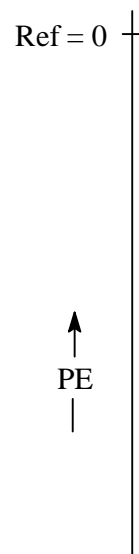
d. Use the thermodynamic data from part c and the most stable conformation of the cis and trans isomers to estimate the energy of an axial ethyl in a cylclohexane ring. Briefly, show your reasoning for the value provided. (3 pts)
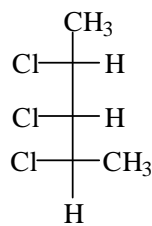
e. Use the second most stable conformation from part a and draw a Newman projection using bonds $C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$ for your structure (or...$C_1 \rightarrow C_2$ and $C_5 \rightarrow C_4$). Point out any gauche relationships in the branches and/or the ring. (6 pts)

Newman projection of the second 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	B	C	D	E
CH_3	CH_3	Cl	CH_3	CH_3
H—Cl	Cl—H	CH_3—H	H—Cl	H—Cl
Cl—H	Cl—H	H—Cl	Cl—H	H—Cl
Cl—H	Cl—CH_3	H—CH_3	Cl—H	CH_3—H
CH_3	H	Cl	H	Cl
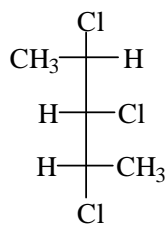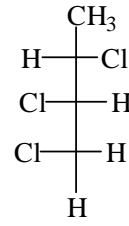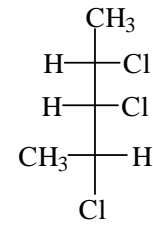
a. Which are meso?   A   B   C   D   E

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 in a 50/50 ratio?

                                              AB   AC   AD   AE   BC   BD   BE   CD   CE   DE

g. Draw a Fischer projection of any stereoisomers of 2,3,4-trichloropentane 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 Cl was switched with a Br? You don't have to redo the problem, but do show at least one example where the problem would change. (4 pts)

i. A sesterterpene (25 carbons) was discovered from a small tree in the Himalayas of Nepal (Org. Lett. p.4139, 2004). It is used as an insecticidal agent. Circle all chiral centers and calculate the maximum number of stereoisomers possible. (4 pts)
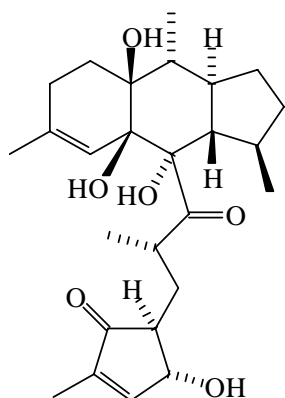
leucosesterterpenone - naturally occuring sesterpenoid
(circle all chiral centers)

maximum number of stereoisomers possible? _____
(show set-up for calculation)

6. Indicate the bond energy between the two atoms indicated. Use the specific bond energy table provided on the last page. Write the common nomenclature term of each carbon group about the bond energy requested. Draw an arrow to any part of any structure to indicate where a methyl, methylene, methine, primary, secondary, tertiary and quaternary carbon is located. A table of bond energies is provided on the last page (12 pts)
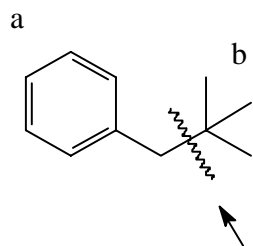
indicated bond energy = _____

fragment a = _____
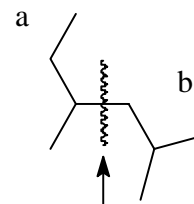
fragment b = _____

indicated bond energy = _____

fragment a = _____

fragment b = _____

b. Estimate the pi bond energy in an alkyne pi bond. (3 pts)

7. 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
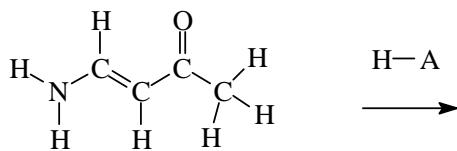
b. reaction in base, B:
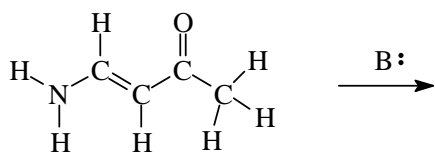
8. Use 3S-bromo-4R-methylhexane to provide a simple, arrow-pushing mechanism for each of the following reaction conditions (show curved arrows, lone pairs & formal charge). Fill in the necessary details to clearly indicate any stereochemical features and/or conformational requirements. If reactants are not drawn in the proper orientation to show how the reaction must proceed, then redraw them in a more informative way that shows this. (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)
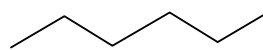
2D structure   3D structure of 3S-bromo-4R-methylhexane

b. Show the S$_N$ reaction (what kind?), indicate absolute configuration of all chiral centers. (6 pts)
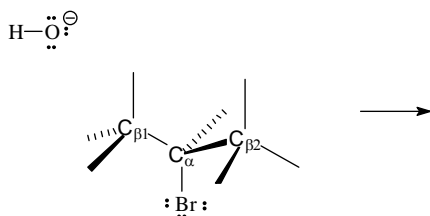
$C_{\beta1} = C_2$, $C_\alpha = C_3$, $C_{\beta2} = C_4$

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

_____

_____
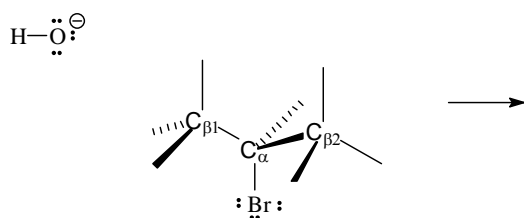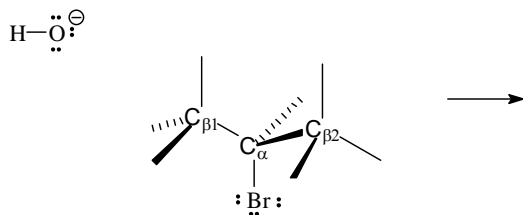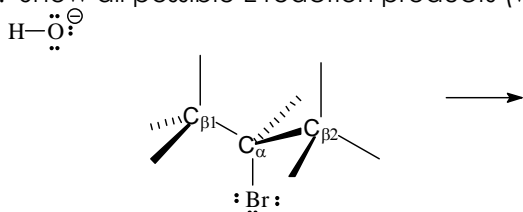
d. Show the S$_N$ reaction (what kind?), indicate absolute configuration of all chiral centers. (6 pts)
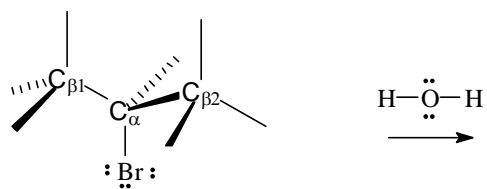
e. Show all possible E reaction products. Indicate if E, Z or neither. If multiple products are formed between two atoms, you can show a single mechanism and just draw the additional possible products. (16 pts)
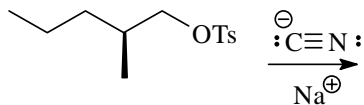
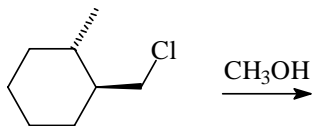redraw intermediate from 8d (above)
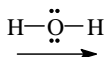
redraw intermediate from 8d (above)
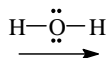
9. Predict all possible S_N product(s). Only predict the major E product. State whether S_N or E is major, minor or they are about the same. Finally, state by what mechanism(s) each product was formed. (33 pts)

a.

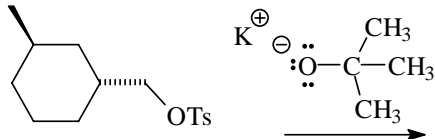$:C≡N:^\ominus$ $Na^\oplus$ (OTs substrate)

b.

CH_3OH

d.

H_3C-C (with $:O:$ double bond and $:O:^\ominus$) $Na^\oplus$

e.

$CH_3-C≡C:^\ominus$ $Na^\oplus$

f.

OH (ethanol)

g.

$K^\oplus$ $:O:^\ominus-C(CH_3)(CH_3)-CH_3$

h.

HBr

i.

H_2SO_4 / Δ

j.

$:O:^\ominus$ (ethoxide) $Na^\oplus$

k.

$-OH$

l.

$:O:^\ominus$ (ethoxide) $Na^\oplus$
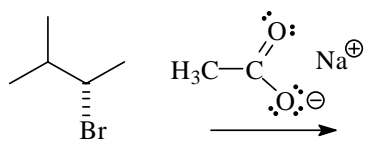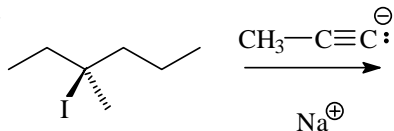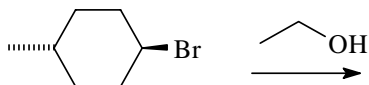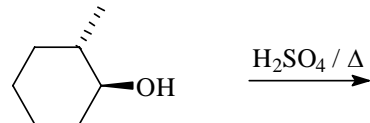
Typical Bond Energies for Common Substitution Patterns Found in Organic Chemistry (X-Y)

Y =	H-	Me-	Et- (1°)	i-Pr- (2°)	t-Bu- (3°)	Ph- (phenyl)	F-	Cl-	Br-	I-	HO-	H$_2$N-	N≡C-
X =													
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

$$X \overset{\cdot\cdot}{-} Y \longrightarrow X\cdot \quad \cdot Y \quad \text{(homolytic cleavage)}$$
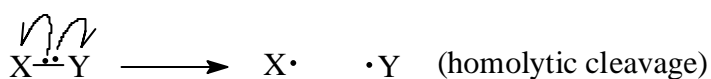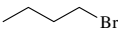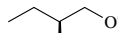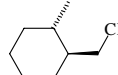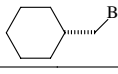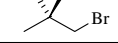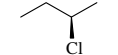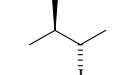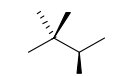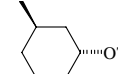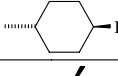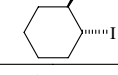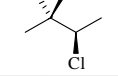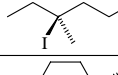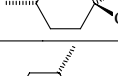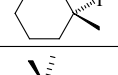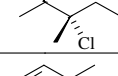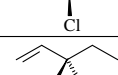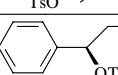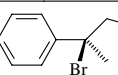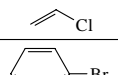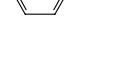
Average Bond Energies (kcal/mole)

	H	C	Si	N	O	S	F	Cl	Br	I
H	104	98	76	92	109	83	135	103	87	71
C		81	72	66	79	65	116	79	66	52
Si			-	-	108	-	135	91	74	56
N				39	39	-	65	46	-	-
O					34	-	45	52	48	56
S						60	-	61	52	-
F							37	-	-	-
Cl								58	-	-
Br									46	-
I										36

Bond Energy for multiple bonds

C=C	146
C=N	147
C=O	176
C≡C	200
C≡N	213

We study in youth, we understand with age.   Okaa-san(Mom in Japanese)

Problems considered but not used on this exam.

Reagent columns (A–I):

- **A**: $:\overset{\ominus}{\underset{\ddots}{O}}-H$ / $Na^{\oplus}$
- **B**: $\overset{\ominus}{:\overset{\ddots}{O}}\diagup$ / $Na^{\oplus}$
- **C**: $H_3C-\overset{:O:}{\underset{:\overset{\ominus}{O}:}{C}}$ $Na^{\oplus}$
- **D**: $\overset{\ominus}{:\overset{\ddots}{O}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$ $K^{\oplus}$
- **E**: $\overset{\ominus}{:C\equiv N:}$ / $Na^{\oplus}$
- **F**: $CH_3-C\equiv\overset{\ominus}{C:}$ / $Na^{\oplus}$
- **G**: H_2O
- **H**: $\diagup\diagdown OH$
- **I**: $H_3C-\overset{O}{\underset{OH}{C}}$

Substrates (1–23):

1. H_3C-Br
2. propyl/butyl—Br
3. (structure)—OTs
4. (cyclohexane)—Cl
5. (cyclohexane)—Br
6. (structure)—Br
7. (structure)—Cl
8. (structure)—I
9. (structure)—Cl
10. (cyclohexane)—OTs
11. (cyclohexane)—Br
12. (cyclohexane)—I
13. (structure)—Cl
14. (structure)—I
15. (cyclohexane)—Cl
16. (cyclohexane)—I
17. (structure)—Cl
18. (structure)—Cl
19. (structure)—TsO
20. (benzene structure)—OTs
21. (benzene structure)—Br
22. (structure)—Cl
23. (benzene)—Br

Questions

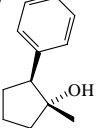1. Predict all possible S_N products and state by what mechanism they formed.

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 H₂SO₄/Δ
24 CH₃OH				
25 (structure)—OH				
26 (cyclopentane)—OH				
27 (phenyl cyclopentane)—OH				

Using the given formula, **C₉H₁₇Br**, 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 $CH_3O^{\ominus}/CH_3OH$	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 $CH_3O^{\ominus}/CH_3OH$	f. Reacts very slowly whether in $CH_3O^{\ominus}/CH_3OH$ 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 $CH_3O^{\ominus}/CH_3OH$	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)