Chem 314
Final Exam   Name _____
Spring, 2007
Beauchamp

Problem	Points	Credit
1. Nomenclature (one structure)	30	
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	36	
5. Stereochemisty Questions	42	
6. Acid/Base Chemistry (arrow pushing, explanation)	30	
7. S_N and E mechanisms, including stereochemical details	48	
8. RX compounds in S_N and E reactions, including stereochemistry details,	24	
9. Free Radicals, Predict products provide mechanism	30	
Total	290	

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.
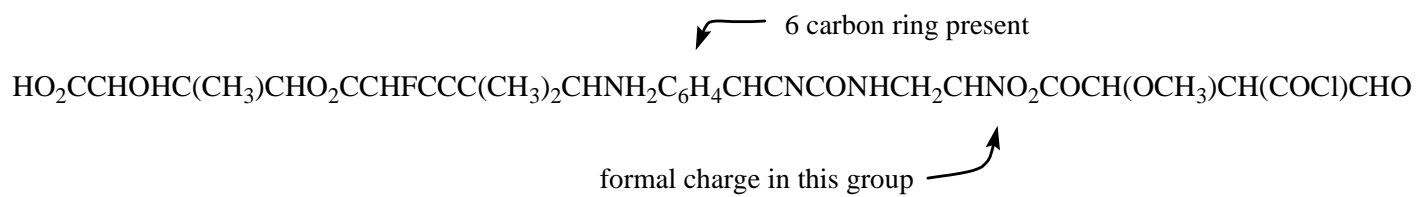
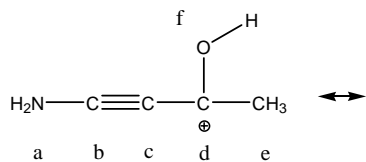You cannot teach people anything. You can only help them discover it within themselves.   Galileo

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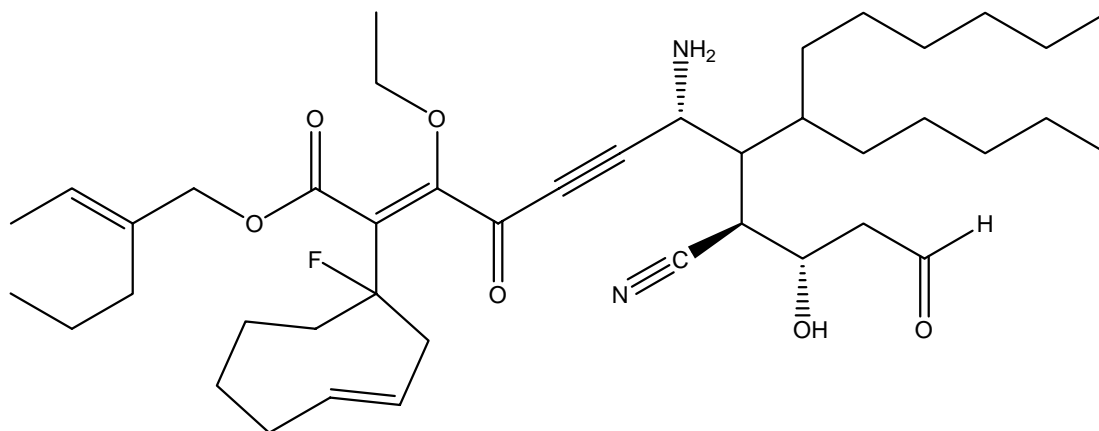
2. Draw an acceptable 2D Lewis structure for the following formula. Indicate any formal charges present. (20 pts)

6 carbon ring present

$HO_2CCHOHC(CH_3)CHO_2CCHFCCC(CH_3)_2CHNH_2C_6H_4CHCNCONHCH_2CHNO_2COCH(OCH_3)CH(COCl)CHO$

formal charge in this group

3. First, draw three other 2D resonance structures to delocalize 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)

$$H_2N-C\equiv C-\overset{\overset{\overset{f}{O}\overset{H}{\diagup}}{|}}{\underset{\oplus}{C}}-CH_3 \quad \longleftrightarrow \qquad \longleftrightarrow \qquad \longleftrightarrow$$

a   b   c   d   e

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

trans

cis

chair 1   chair 2   chair 3   chair 4
(absolute congifigurations)
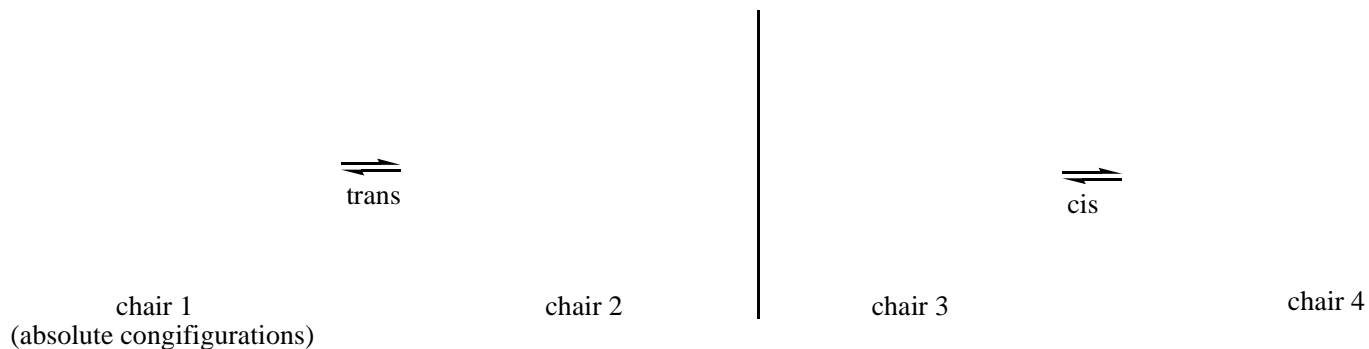
most stable (1 or 2) = _____   most stable (3 or 4) = _____

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

sterochemical relationship of 1 with 2? enantiomer, diastereomer, meso, identical, none

sterochemical relationship of 1 with 3? enantiomer, diastereomer, meso, identical, none

sterochemical relationship of 1 with 4? enantiomer, diastereomer, meso, identical, none

sterochemical relationship of 3 with 4? enantiomer, diastereomer, meso, identical, none

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

c. Use the second 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 (indicate which chair you are using from part a: 1,2,3,4 and number it appropriately in part a). Point out any gauche relationships in the branches and/or the ring. (4 pts)

Newman projection of the second most stable conformation from part a

d. 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-diisopropylcyclohexane and trans-1,2-diisopropylcyclohexane are -1756.3 and -1754.1 , 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. (10 pts)

show work:

$$\text{Ref.} = 0 \quad +$$

PE
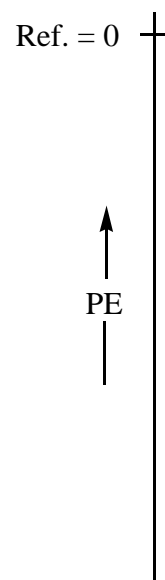
e. Use the thermodynamic data from part d, and the most stable conformation of both the cis and trans isomers to estimate the energy of an axial isopropyl in a cylclohexane ring. Briefly, show your reasoning for the value indicated using sketches of these conformations. (4 pts)

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

```
              H
              |
      Br——————————CH3
              |
     H3C——————————H
              |
      H——————————CH2CH3
              |
              Br
```

B

```
              Br
              |
    H3C——————————H
              |
    H3C——————————H
              |
     Br——————————CH3
              |
              H
```

C

```
              Br
              |
    H3C——————————H
              |
      H——————————CH3
              |
      H——————————Br
              |
            CH2CH3
```

D

```
             CH3
              |
      H——————————Br
              |
      H——————————CH3
              |
      H——————————Br
              |
            CH2CH3
```

E

```
           CH2CH3
              |
     Br——————————H
              |
    H3C——————————H
              |
      H——————————Br
              |
             CH3
```

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 probably rotate plane polarized light?

              A   B   C   D   E

g. Draw a Fischer projection of any stereoisomers of "A" which are not shown above. If there are none, indicate this. (7 pts)

h. Using isomers of dimethylcyclobutane, draw a pair of enantiomers, a pair of diastereomers where at least one of the stereoisomers is chiral, a pair of achiral diastereomers, a meso compound and an achiral compound that is does not have any stereoisomer. (16 pts)

a pair of enantiomers

a pair of diastereomers where at least one of the stereoisomers is chiral

a meso compound

an achiral compound that is does not have any stereoisomer

a pair of achiral diastereomers

i. The synthesis of a compound with selective anticancer activity against ovarian cancer was recently published (Org. Lett. p.2071, 2007). Circle all chiral centers and calculate the maximum number of stereoisomers possible. (4 pts)
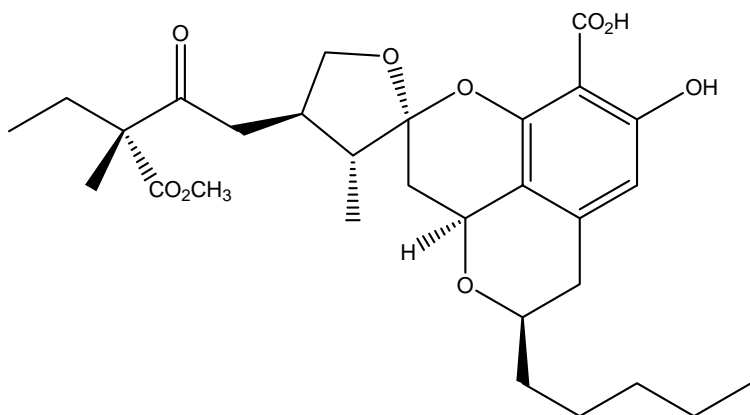
berkelic acid - selective anticancer compound for ovarian cancer, from an acid mine waste fungal extremophile

Circle all chiral centers.

Calculate the maximum number of stereoisomers possible, show your set up and answer.

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. (30 pts)

a. reaction in acid, HA

H—A
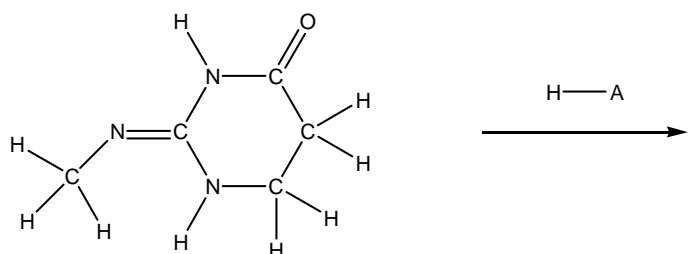
b. reaction in base, B:

B:
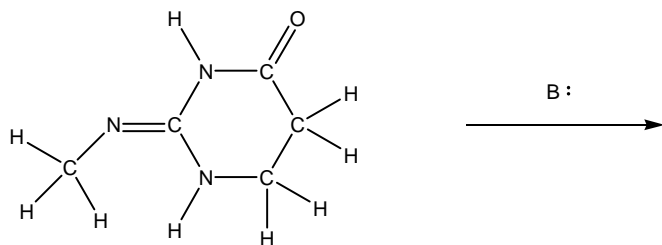
7. Use 2S-deuterio-3S-bromo-4S-methylhexane to provide a simple, arrow-pushing mechanism for each of the following reaction conditions (show curved arrows, lone pairs & formal charge). Fill in the necessary details to clearly indicate any stereochemical features and/or conformational requirements. If 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. Do not consider carbocation rearrangement possibilities, since we did not cover them. (48 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)
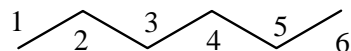
2D structure

3D structure of 2S-deuterio-3S-bromo-4S-methylhexane

b. Show the S_N reaction (what kind?), indicate the absolute configuration(s) of the C_α center in the product. (6 pts)
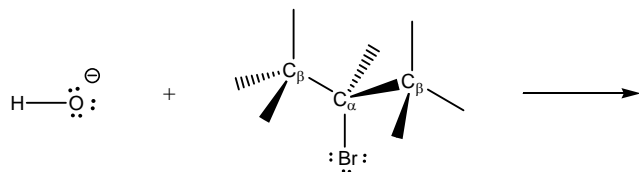
mechanism

C_α
configuration

c. Show all possible E reaction products (what kind?). Indicate if E, Z or neither. (16 pts)

mechanism

E or Z

H—$\overset{\ominus}{\underset{..}{\overset{..}{O}}}$:   [structure with C_β, C_α, C_β and :Br:]   ⟶   □
                                                                                          E or Z

- -
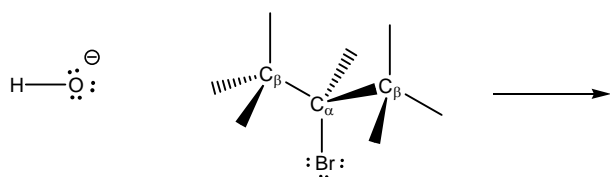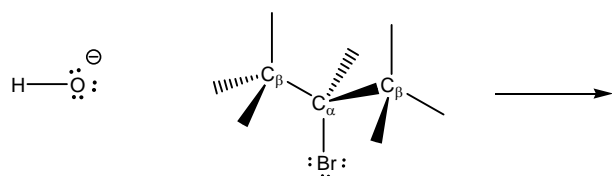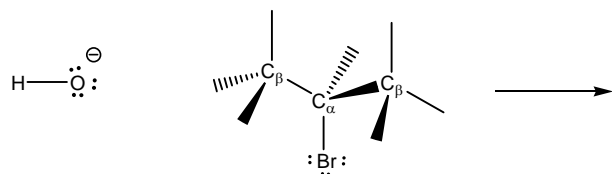
H—$\overset{\ominus}{\underset{..}{\overset{..}{O}}}$:   [structure with C_β, C_α, C_β and :Br:]   ⟶   □
                                                                                          E or Z

- -

d. Show the S_N reaction (what kind?). Indicate absolute configuration(s) of the C_α center in the product. (10 pts)

[structure with C_β, C_α, C_β and :Br:]   H—$\underset{..}{\overset{..}{O}}$—H   ⟶

□
mechanism
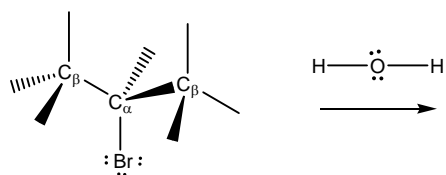
□
C_α
configuration(s)

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 (4 possible products).

□
E or Z

H—$\underset{..}{\overset{..}{O}}$—H   ⟶
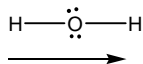
Redraw the intermediate used in 8d above (2 possible products).

$$H-\overset{..}{\underset{..}{O}}-H$$

☐ E or Z
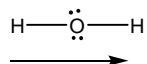
8. Predict all possible S_N product(s); if none are expected, indicate so. Only predict the major E product. State whether S_N or E is major, minor or they are about the same. What functional group is obtained in the final product? Finally, state by what mechanism(s) each product was formed. (20 pts)

a.

Na⊕ ⊖:H
sodium hydride
(very strong base)

---

b.

Na⊕
⊖:C≡N:

---

c.

---

d.

H—O—H

---

e.

Na⊕
⊖:NH₂
sodium amide
(very strong base)

---

f.

Na⊕
⊖:ÖH
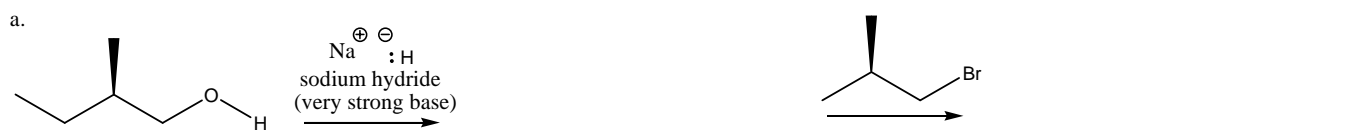
9.   a. How many different types of sp³ hydrogen atoms are present in 2R-phenylbutane? Show all possible products when 2R-phenylbutane is monobrominated with $Br_2/h\nu$? If any chiral centers are present in the starting material or the products, draw them clearly with a 3D representation and specify 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 sp³ C-H bond are: primary = 1, secondary = 80 and phenyl substituted carbon = 2000. (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. (15 pts)

Br——Br	46
H——Br	87
Me C-H	105
1° C-H	98
2° C-H	95
3° C-H	92
benzylic C-H	82
Me C-Br	70
1° C-Br	68
2° C-Br	68
3° C-Br	67
benzylic C-Br	61

Two people look out through the same bars; one sees mud, and one the stars.   Frederick Langbridge

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

Y =	H-	Me-	(1°) Et-	(2°) i-Pr-	(3°) t-Bu-	(phenyl) Ph-	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——Y ⟶ X· ·Y   (homolytic cleavage)
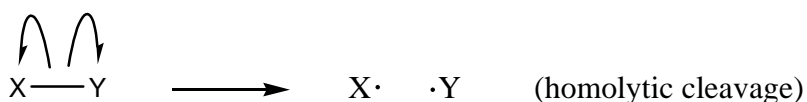
Average Bond Energies (kcal/mole)

	H	C	Si	N	O	S	F	Cl	Br	I
H	104	98	76	93	111	83	135	103	87	71
C		83	72	82	92	65	110	81	68	52
Si			-	-	108	-	135	91	74	56
N				39	53	-	65	46	-	-
O					47	-	45	52	48	56
S						60	-	61	52	-
F							37	-	-	-
Cl								58	-	-
Br									46	-
I										36

C=C	146
C≡C	200
C=N	147
C≡N	213
C=O aldehyde	176
C=O ketone	179

Two people look out through the same bars; one sees mud, and one sees the stars.   Frederick Langbridge

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

CH_4 CH_3CH_3
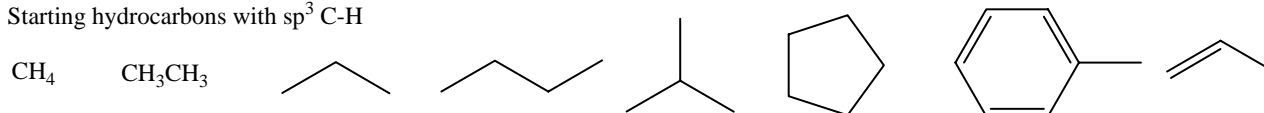
Miscellaneous Reagents
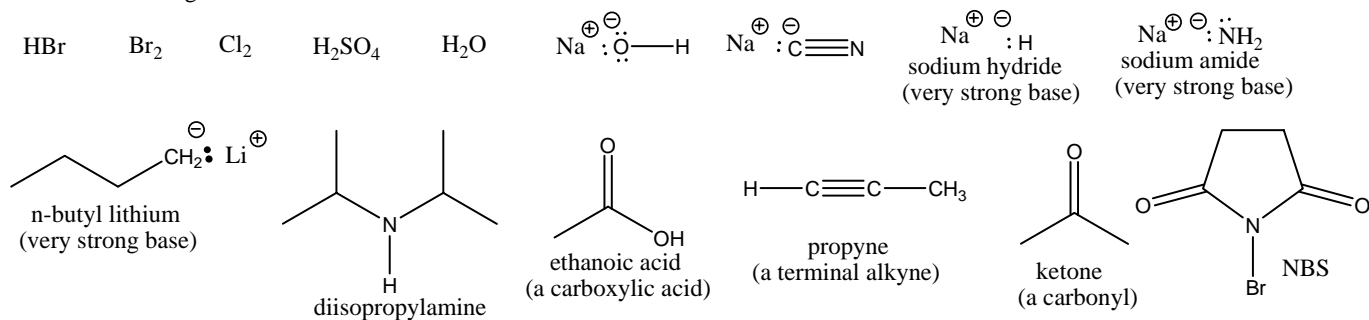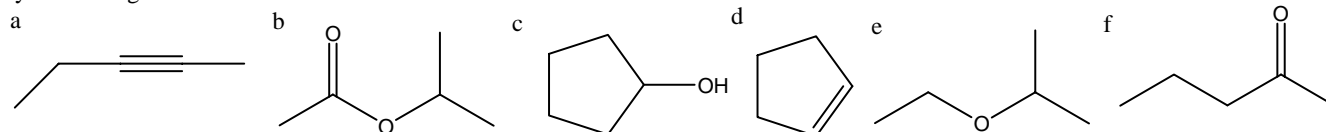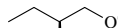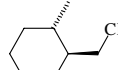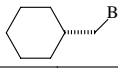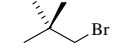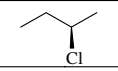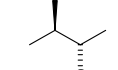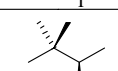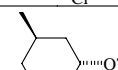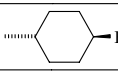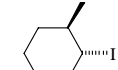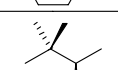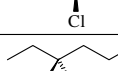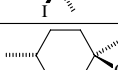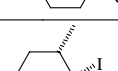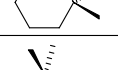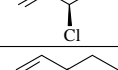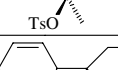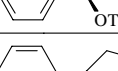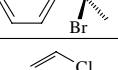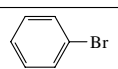
HBr Br_2 Cl_2 H_2SO_4 H_2O $Na^{\oplus} :\overset{\ominus}{\underset{..}{O}}$—H $Na^{\oplus} :\overset{\ominus}{C}{\equiv}N$ $Na^{\oplus} \overset{\ominus}{:}H$
sodium hydride
(very strong base)

$Na^{\oplus} \overset{\ominus}{:}\overset{..}{N}H_2$
sodium amide
(very strong base)

$CH_2^{\ominus} :Li^{\oplus}$
n-butyl lithium
(very strong base)

diisopropylamine

ethanoic acid
(a carboxylic acid)

H—$C{\equiv}C$—CH_3
propyne
(a terminal alkyne)

ketone
(a carbonyl)

NBS

Synthetic targets

a

b

c   OH

d

e

f

Problems considered but not used on this exam.

Reagent columns across top:

A	B	C	D	E	F	G	H	I
$\ominus\ddot{O}-H$ $Na^{\oplus}$	$\ominus\ddot{O}$ $Na^{\oplus}$	$H_3C-C(\ddot{O})(\ddot{O}^\ominus)$ $Na^{\oplus}$	$\ominus\ddot{O}-C(CH_3)(CH_3)(CH_3)$ $K^{\oplus}$	$\ominus:C\equiv N:$ $Na^{\oplus}$	$CH_3-C\equiv C:^\ominus$ $Na^{\oplus}$	H_2O	$\diagup\diagdown OH$	$H_3C-C(O)(OH)$

Substrates (rows 1–23):

1. H_3C-Br
2. Br (butyl)
3. OTs (2-methylbutyl, stereo)
4. Cl (cyclohexane, CH2Cl)
5. Br (cyclohexane)
6. Br
7. Cl
8. I
9. Cl
10. OTs (cyclohexane)
11. Br (cyclohexane)
12. I (cyclohexane)
13. Cl
14. I
15. Cl (cyclohexane)
16. I (cyclohexane)
17. Cl
18. Cl (allylic)
19. TsO (allylic)
20. OTs (benzylic)
21. Br (benzylic)
22. Cl (vinyl)
23. Br (aryl)

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 H$_2$SO$_4$/Δ
24 CH$_3$OH				
25 ⌒OH				
26 (cyclopentanol) OH				
27 (phenylcyclopentanol) 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)