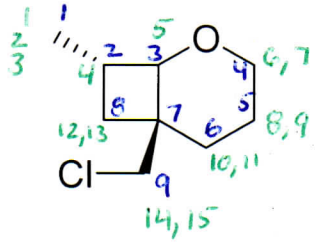
Section I. Multiple choice/Fill in the blank *(1.25 points each)*
(If there are no answers given below, you must write in the correct answer)



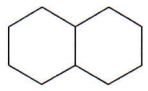
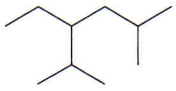
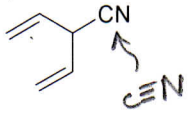
1. The molecular formula of the compound on the right is $C_9H_{15}ClO$.

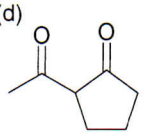
2. A compound has the molecular formula of $C_6H_9Br_2ON$. It has 4 degrees of unsaturation.
(For partial credit, show your work)
(a) 0 (b) 1 (c) 2 (d) 3 (e) 4 (f) 5
(g) none of the above is correct

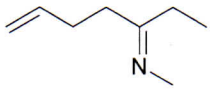
w/N subtract 1H per N

$$u = \frac{(2\times \#C + 2) - (\#H + X)}{2} = \frac{(2\times 6+2) - (9+2-1)}{2} = 2$$

3. The compound below with the most degrees of unsaturation is compound (c) .

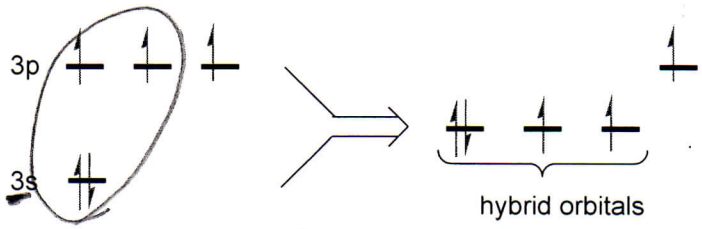
(a) u=2 
(b) u=0 
(c) u=4 

(4 π)
(d) u=3 

(2 π, 1 ring)
(e) u=2 

u = ring or π bond

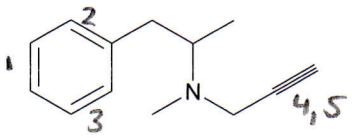
4. The diagram on the right indicates a C .
(a) sp^4 hybridized atom
(b) sp^3 hybridized atom
(c) sp^2 hybridized atom
(d) sp hybridized atom
(e) a nonhybridized atom
(f) it's going to be a long test..



mixed 2p's, 1 p left unmixed

5. The diagram in Question 2 would be for a(n) P atom with 1 π bonds.
(The first blank should be an atom, preferably one that occurs on the periodic table)
p orbitals only thing that make π bonds
5 val e- in 3rd shell => P

6. The compound on the right has f π bonds.
(a) 0 (b) 1 (c) 2 (d) 3
(e) 4 (f) 5 (g) more than 5
(h) apple – yummy!!!!



selegiline
(a MAO-B inhibitor,
used as an anti-Parkinsonian)

overall bond strength of multiple bonds greater than that of single bond

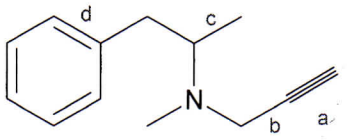
better overlap of orbitals = stronger bonds

7. The weakest covalent bond of those below is c .

(a) C-C (b) C-Si (c) C-As (d) C=C

2nd period 4th period (big difference in size)

8. The correct order of bond lengths, from shortest to longest, is d .

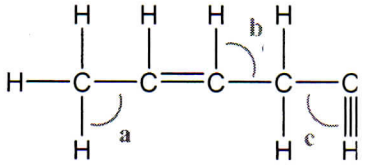


(a) b > c > d > a (b) a > d > c > b
(c) c > b > d > a (d) a > d > b > c
(e) none of the above (f) extra mayo and no onions

single > double > triple (since p orbitals need to get closer to make effective bond)

(b vs c, one C is sp^3, one is sp^3 or sp
sp orbitals shorter than sp^3 (less p character))

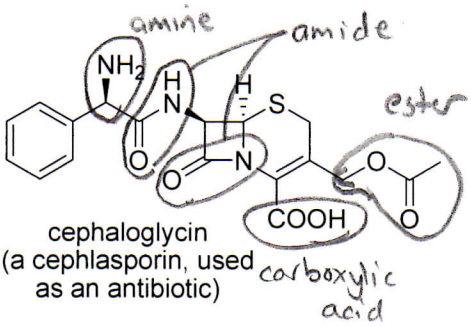
9. Bond angle b in the structure that would be approximately 120°.
(Note the structure on the right was drawn by a 3rd grader and hence the bond angles you see in the structure might not be chemically correct)



(a) a (b) b (c) c
(d) none of the above

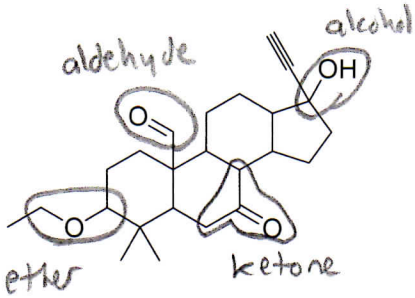
sp^3 109.5°
sp^2 120°
sp 180°

10. The compound to the right contains a c, d, e, f.
(Note there is more than one correct answer for this question, but I only want one. For partial credit, circle the group in the structure.)



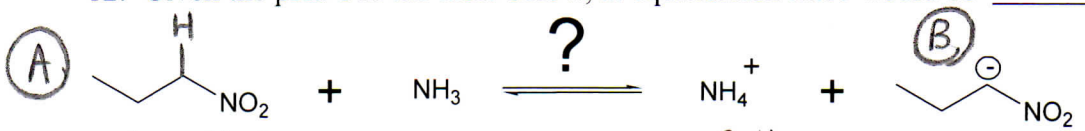
~~(a) alcohol~~ ~~(b) aldehyde~~ (c) amide
(d) amine (e) carboxylic acid (f) ester
~~(g) ether~~ ~~(h) ketone~~

11. The compound to the right contains a a b g k .
(Note there is more than one correct answer for this question, but I only want one. For partial credit, circle the group in the structure.)
YOU MUST CHOOSE A DIFFERENT FUNCTIONAL GROUP THAN YOU CHOSE IN QUESTION 10.



(a) alcohol (b) aldehyde ~~(c) amide~~
~~(d) amide~~ ~~(e) carboxylic acid~~ ~~(f) ester~~
(g) ether (h) ketone

12. Given the pKa's in the table below, at equilibrium there would be ___f___ .



pkA 10.4 pkA 8.4

acid	pK_a
$CH_3CH_2NO_2$	10.4
$CH_3CHNO_2^{1-}$	-12
NH_3	38
NH_4	8.4

(a) about 1:1 ratio of A to B
(b) about a 2:1 ratio of A to B (c) about a 1:2 ratio of A to B
larger pkA = weaker acid (d) about a 10:1 ratio of A to B (e) about a 1:10 ratio of A to B
(f) greater than a 10:1 ratio of A to B (g) greater than 1:10 ratio of A to B

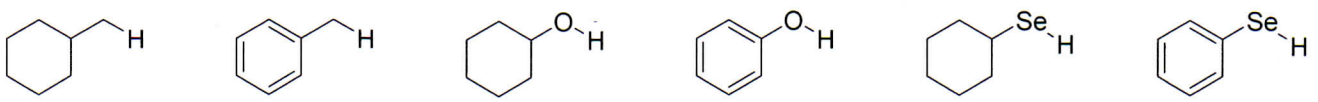
rxn goes to weaker acid

diff in pkA is 2 units but pkA base 10 unit so $10^2 = 100$

13. The strongest ACID of those listed below would be ___f___ .

$H\text{-}A \rightleftharpoons H^+ + A^-$

(a) (b) (c) (d) (e) (f)



(g) you cannot determine this

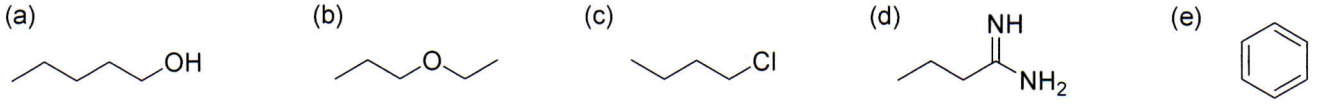
H off heteroatoms usually more acidic than H off C (c,d,e,f > a,b)
weaker HA bond = stronger acid (e,f > c,d) (overlap)
more stable A^-, stronger acid (f vs e, resonance)

14. The strongest BASE would be made by deprotonating compound ___a___ in the question 13 above.

strongest base comes from weakest acid
a vs b resonance

For questions 15 – 17, use the structures below

(a) (b) (c) (d) (e)



15. Compound (c) would have ___e___ in terms of intermolecular forces with itself.

(a) dipole-dipole attractions (b) hydrogen bonds (c) London forces
(d) a and b (e) a and c (f) b and c
(g) a, b, c

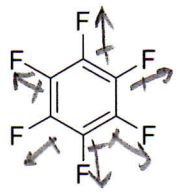
16. The compound that would be MOST soluble in water would be ___d___ .

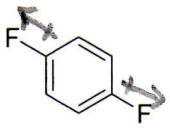
most H-bonding

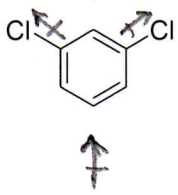
17. The compound that would be LEAST soluble in water would be ___e___ .

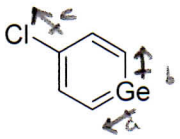
least H-bonding
most nonpolar

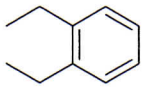
18. The MOST polar compound of those below would be d .

(a) 
dipoles all cancel

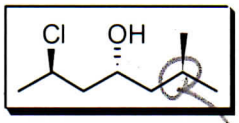
(b) 
dipoles cancel

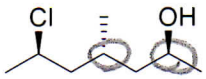
(c) 

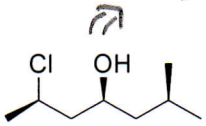
(d) 
sum a, b gives reinforces c

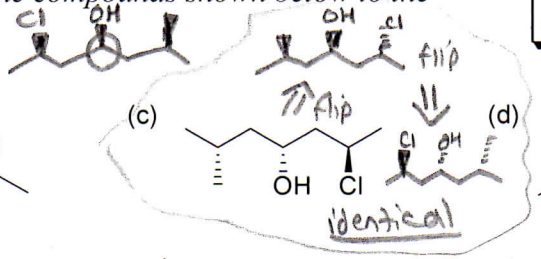
(e) 
no dipoles

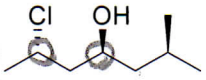
Questions 19-20 refer to the relationship of the compounds shown below to the compound shown in the box on the right.



(a) 
const. isomer groups in diff spot

(b) 

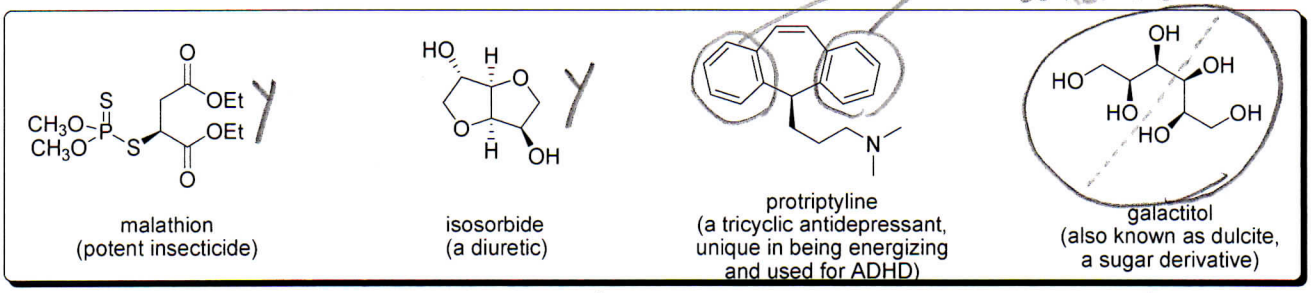
(c) 

(d) 
not a stereocenter

19. The enantiomer of the compound in the box is d . all stereo switched

20. An diastereomer of the compound in the box is b . some but not all changed

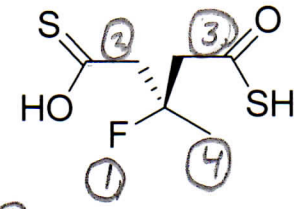
Questions 21 - 22 refer to the wily compounds caged up in the box below. these 2 groups equal so not a stereocenter



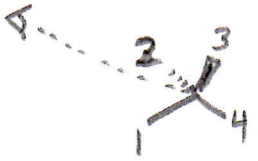
21. There are 1 meso compounds in the box. has internal mirror plane (reflects upon itself) molecule has to have symmetry
(For partial credit circle those that are meso)

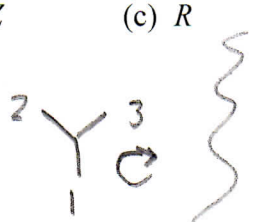
22. There are 2 chiral compounds the box.
(For partial credit put a "Y" through those that are chiral))

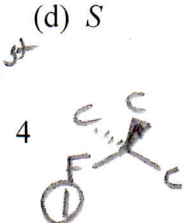
23. The absolute stereochemistry in the compound shown on the right is c .
(For partial credit, show your rankings)

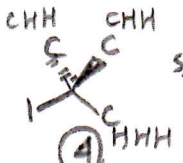


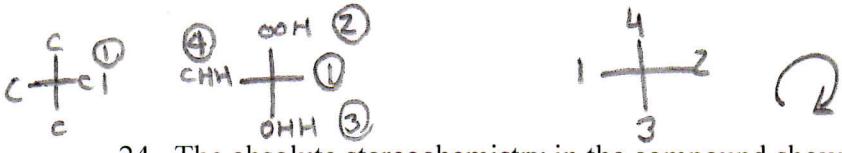
(a) *E* (b) *Z* (c) *R* (d) *S* (e) there is none

2nd 

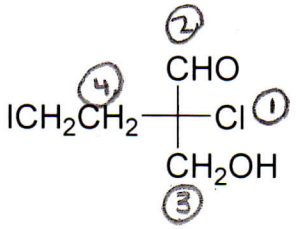


1st 





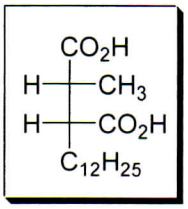
24. The absolute stereochemistry in the compound shown on the right is ___c___ .
(For partial credit, show your rankings)



(a) *E* (b) *Z* (c) *R* (d) *S* (e) there is none

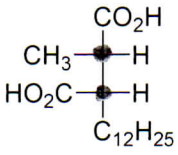
Fischer 4 needs to be vertical

25. A compound below that is IDENTICAL to the compound on the right is ___b and c___.



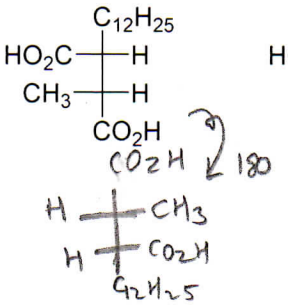
rocccellic acid (compound made by lichens to promote/inhibit plant growth)

(a)

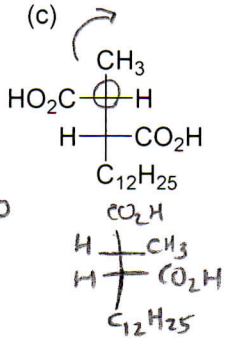


enant

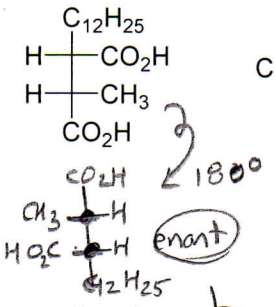
(b)



(c)



(d)



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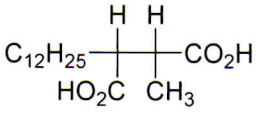
(e)



looks same but CANNOT turn Fischer 90°

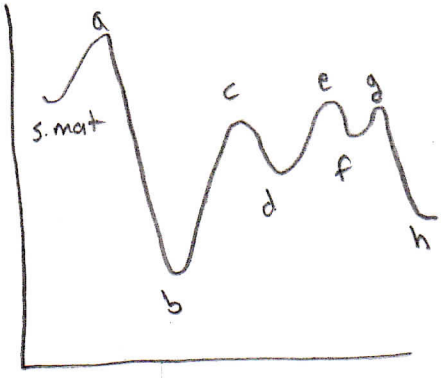
26. When discussing reactions, the ΔH can be thought of as measuring the ___b___, while the ΔS can be thought of as measuring the ___c___ .
(please use one letter below for each blank)

(a) spontaneity of the reaction $-\Delta G$
(b) bond strength
(c) freedom of motion of the molecules
(d) speed of the reaction — this kinetics
k

27. As the ΔG of a reactant becomes more similar in value to the ΔG of a product, the reaction will ___c___ .

(a) go more towards the product
(b) go more towards the reactant
(c) become an equilibrium reaction
(d) you cannot predict with only this info

28. According to the reaction coordinate diagram on the un-left, this reaction occurs in ___4___ steps and the rate-limiting step would be going from ___b___ to ___d___ .

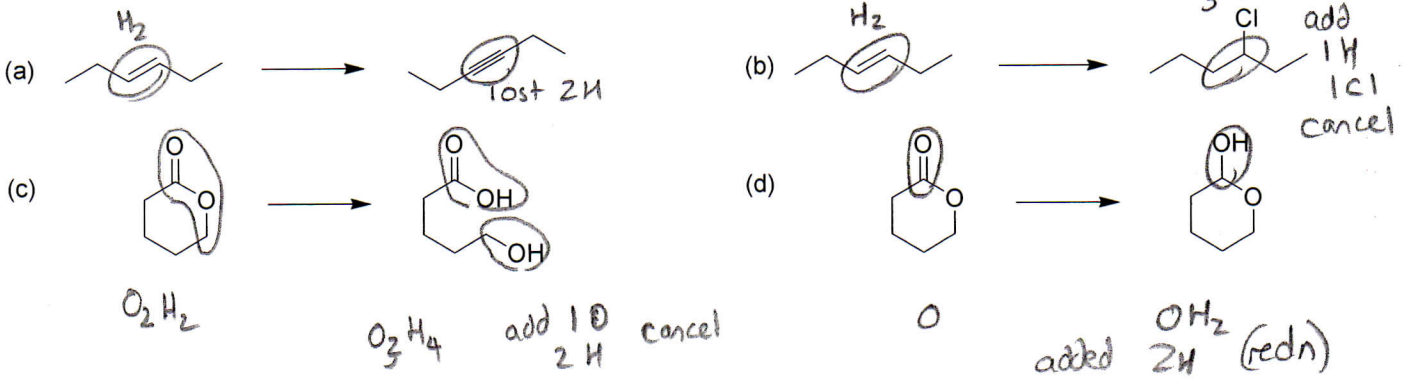


s.mat → b
b → d
d → e
e → h
4 steps

one that requires most energy between 2 structures

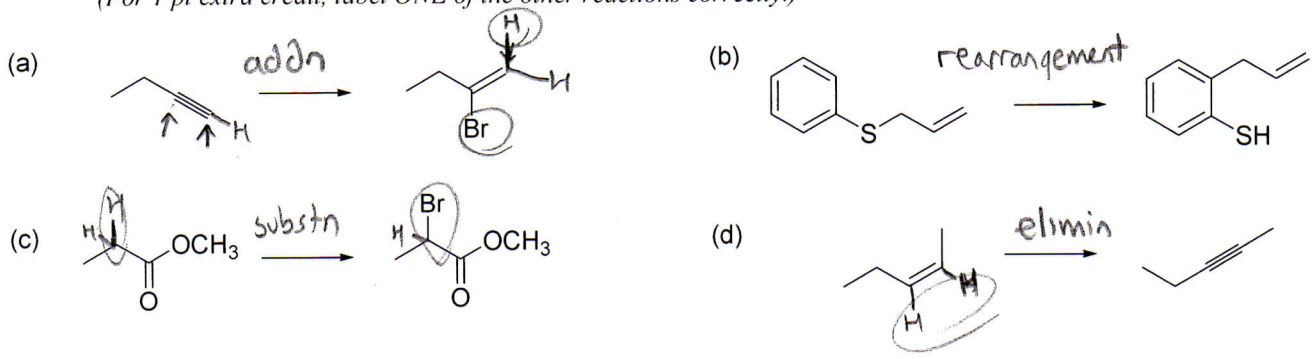
29. Reaction a below would be classified as an oxidation reaction.

(electroneg) net add O or net lose H



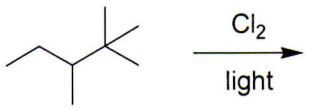
30. A good example of a substitution reaction would be reaction C .

(For 1 pt extra credit, label ONE of the other reactions correctly.)

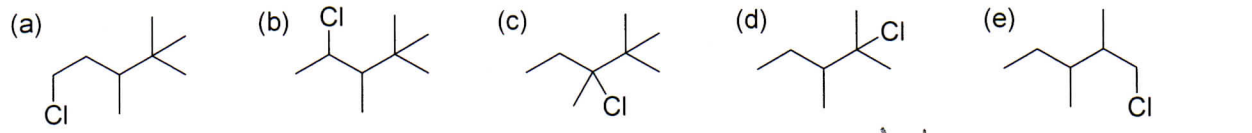


31. The MAJOR free radical halogenation product of the reaction below would be C .

occurs via most stable radical = most sub radical



pulls H off C to make C• then Cl• attacks here



least made

cannot be made since lost C

least made

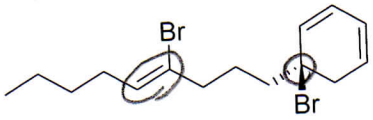
32. The best part of this class is _____ . *(Note: no answer will be marked wrong on this one)*

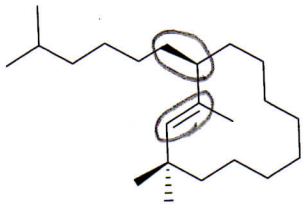
(a) dodging the chalk that somehow seems to be flying around in the room
(b) the really short and easy exams that don't cut into your social life at all
(c) the stares you get when you play with the models in the library
(d) the fact that it is over for 4 months

Section II. Nomenclature.

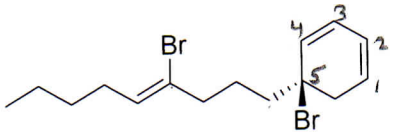
33. (*12 points*) For ONE of the compounds below..

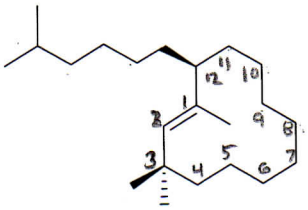
(a) Circle all the stereocenters (both sp^3 and sp^2 in the compound)

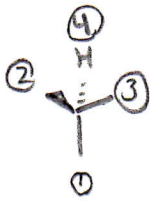




(b) Now provide an acceptable name for this compound, including any depicted stereochemistry. (Note that these are the same compounds as above, just redrawn fresh for this part of the question).





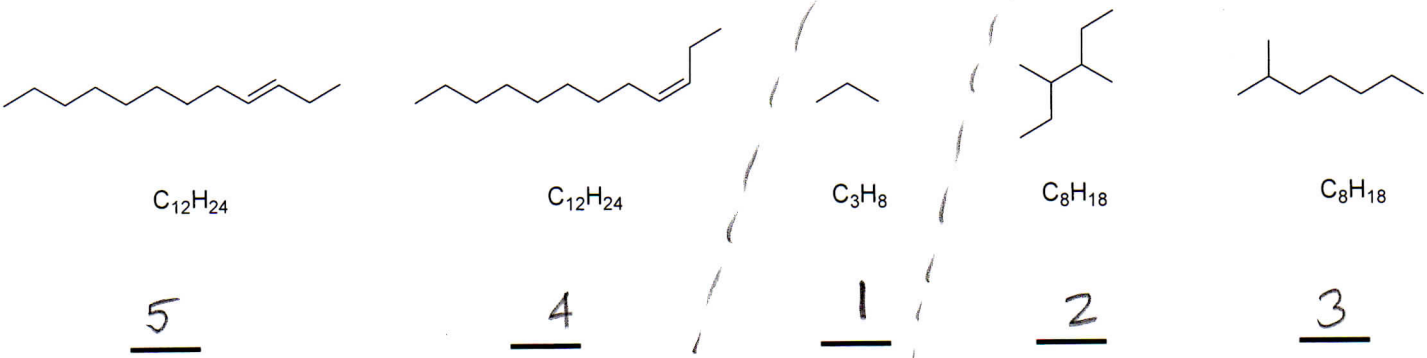


R, Z – 5-bromo-5-(4-bromo-4-nonenyl)-1,3-cyclohexadiene

R, Z – 12-sec-heptyl-1,3,4-trimethyl-1-cyclododecene

Section III. Short answer.

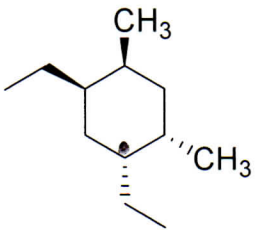
34. (*7 points*) Rank the following compounds based on increasing boiling point, with 1 being the lowest boiling point compound and 5 being the highest boiling point compound.

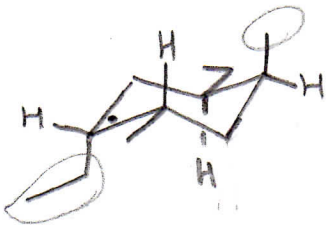


(1) smaller mass = lower bp
(2) more H bonds = higher bp

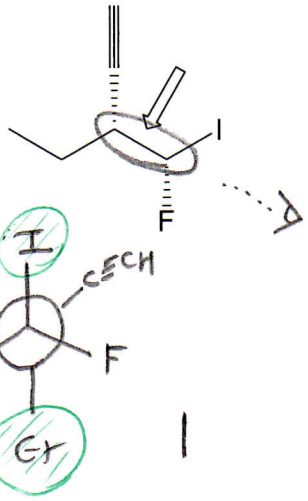
34. (*9 points*) Note that you should only do parts (b) and (c) for ONE of the compounds below.

(a) Draw ONE Newman projection underneath the compound on the right, and ONE chair form underneath the compound on the left.



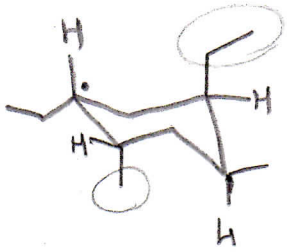


2 axial



1

(b) Now EITHER draw 3 more Newman projections, or the other chair conformer, AND rank them according to their relative energy, with 1 being the lowest energy conformer.

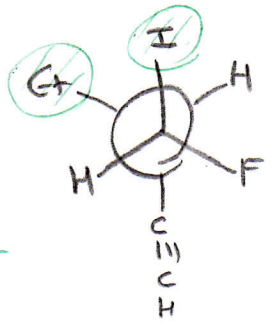


2 axial

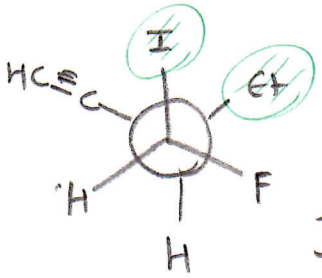
biggest group front C = I

biggest group back C = Et (not linear)

hold front steady rotate clockwise ↑ back



2



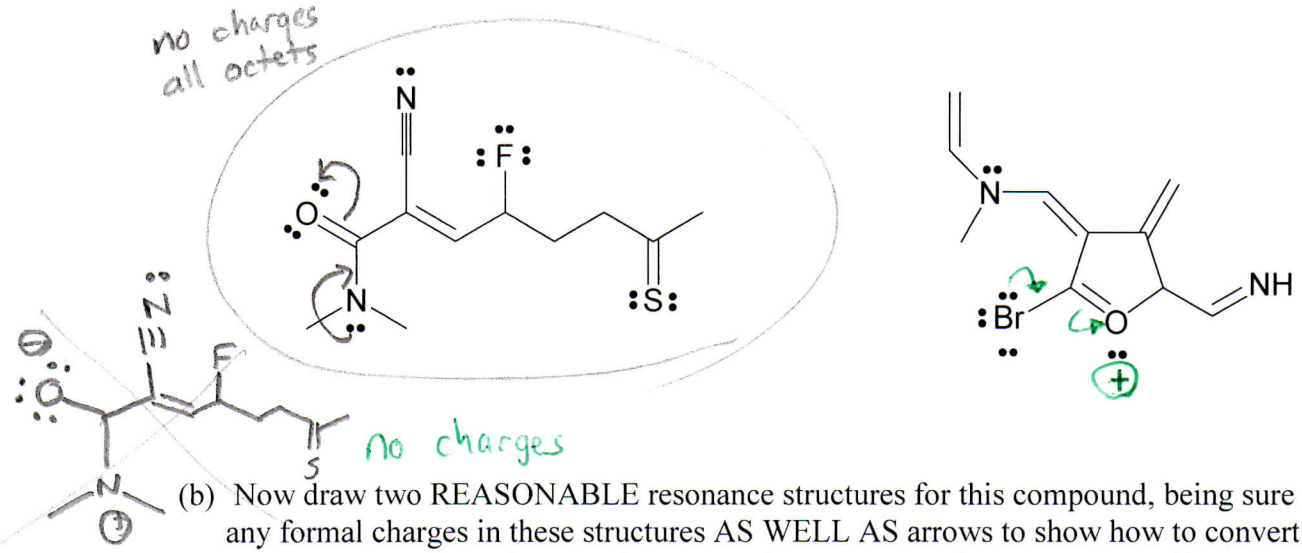
3

same axials between 2 equal energy

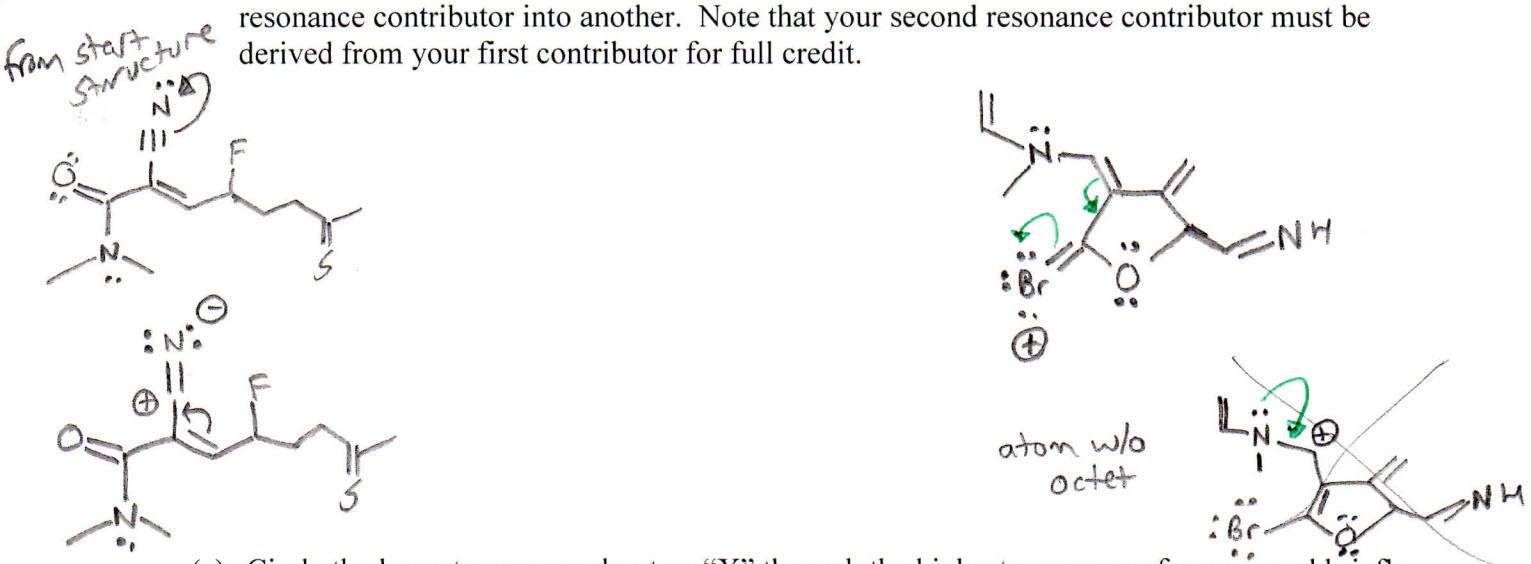
(Did you remember to rank them?)

38. (*14 points*) Resonance

(a) Draw in any and all formal charges in ONE of the compounds below.

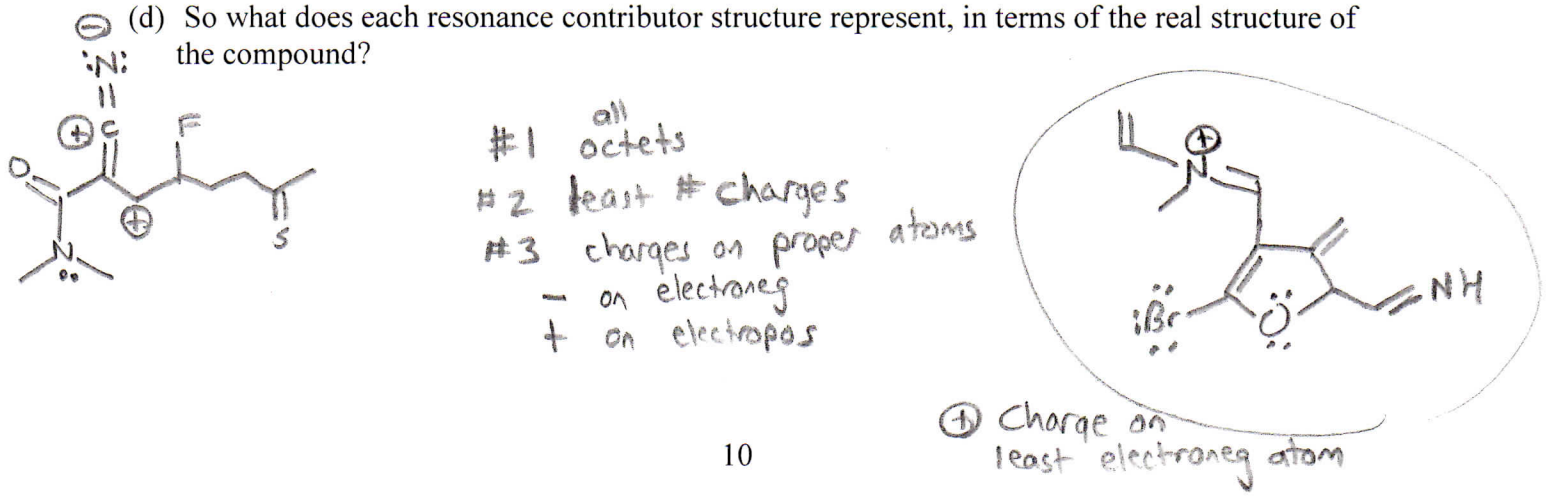


(b) Now draw two REASONABLE resonance structures for this compound, being sure to show any formal charges in these structures AS WELL AS arrows to show how to convert one resonance contributor into another. Note that your second resonance contributor must be derived from your first contributor for full credit.

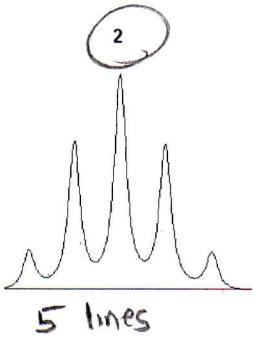


(c) Circle the lowest energy and put an "X" through the highest energy conformers, and briefly explain your answer.

(d) So what does each resonance contributor structure represent, in terms of the real structure of the compound?



39. (*11 points*) Spectroscopy



(a) Consider the ^{1}H NMR signal shown on the right. Is this signal from a CH, a CH_2, a CH_3, 2 CH_2's, 2CH_3's, or none of the above?

integration of 2 H
(could be 2 CH's but this not option)

(b) Draw TWO different but possible 3-carbon fragments of a structure that would give this signal, considering both the integration and the splitting.

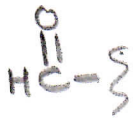
n+1 = 5
n = 4 neighbors

Extra credit question (1 point)
Why would it NOT make chemical sense if this signal was found at 4.1 ppm?

the shift suggests the H's on a C connected to heteroatom. can only then have 3 H adj at most

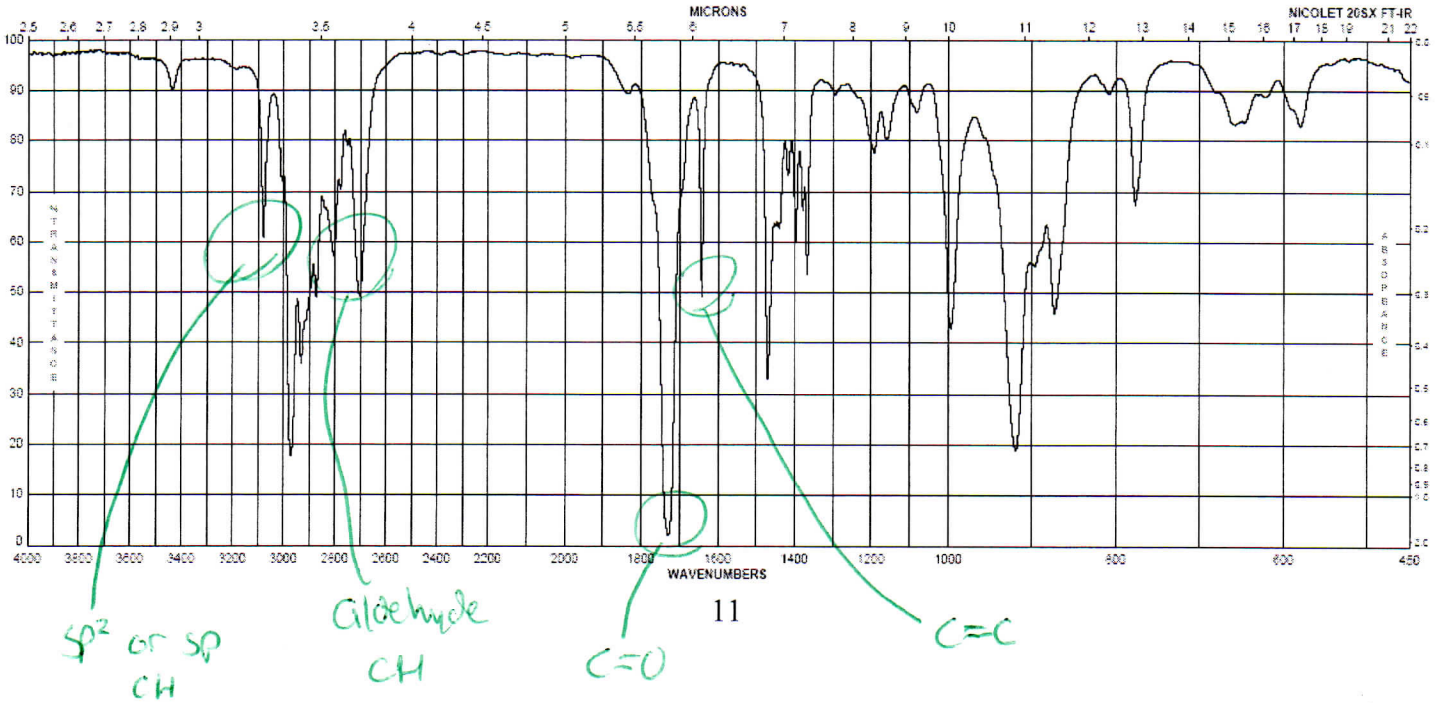
O–CH_2–CH_3 O–CH_2–CH_3 (CH)

(c) The compound also had the signal on the right. What does this suggest?



aldehyde on C w/ no adj H

(d) Now circle AND LABEL all the identifiable peaks in the IR spectrum below.

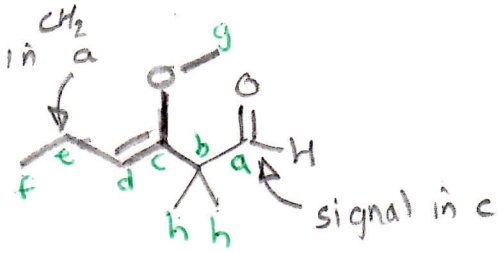


$$\frac{(9\times2+2)-(16)}{2} = 2$$

(e) So draw a structure for a compound of a compound with the formula $C_9H_{16}O_2$ that would give all the above fragments in the spectrum.

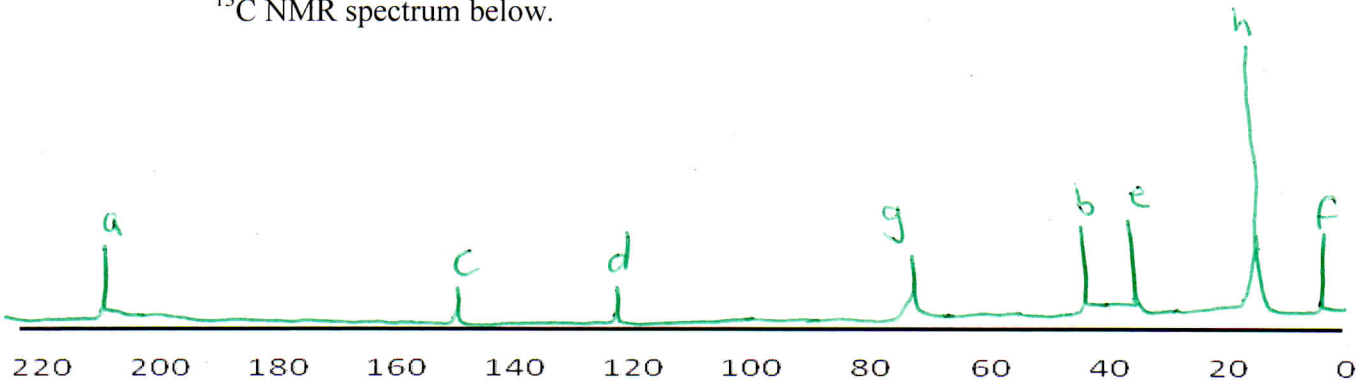
1 C=O

1 C=C



are other possible answers

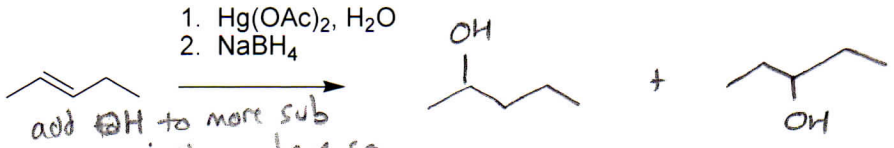
(f) Now label each carbon in your structure, and indicate where it would appear in the ^{13}C NMR spectrum below.



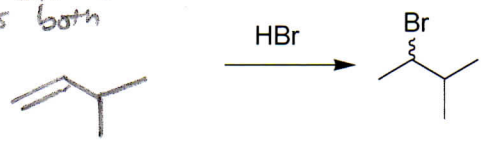
Section IV. Reactions

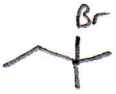
41. (*17.5 points*) Alkenes

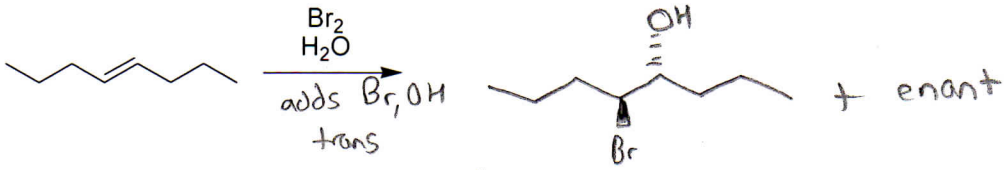
Draw the MAJOR product(s) / MISSING starting material for **FIVE** of the reactions shown below, being sure to carefully consider issues of regio- and stereo-selectivity. At LEAST ONE reaction must be from the next page (rxns j-m).

(a) 

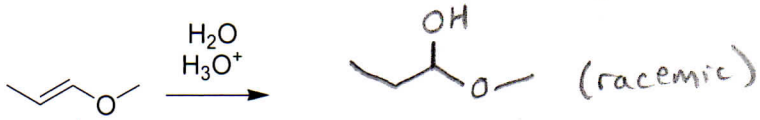
add OH to more sub C. isn't one here so adds both

(b) 

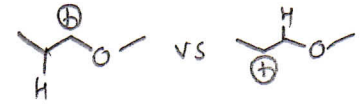
adds Br to more sub C
if had  would give 

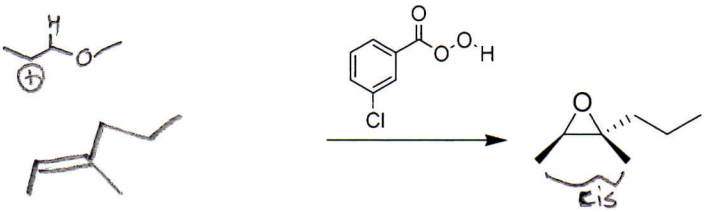
(c) 

adds Br, OH trans
+ enant

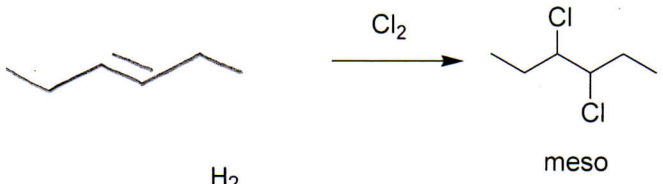
(d) 

1st forms C+

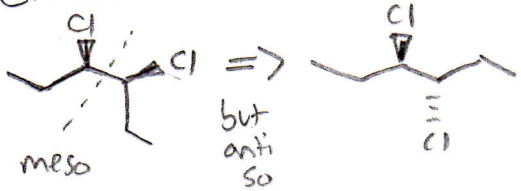


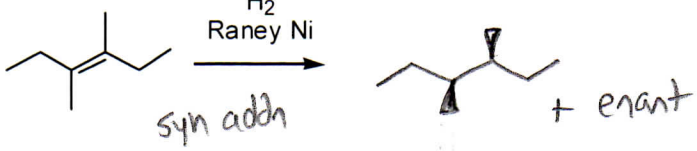
(e) 

adds epoxide w/o altering stereochem around C=C

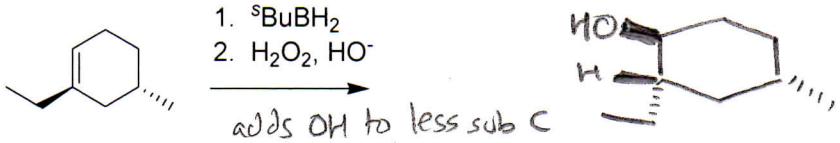
(f) 

Cl's add anti



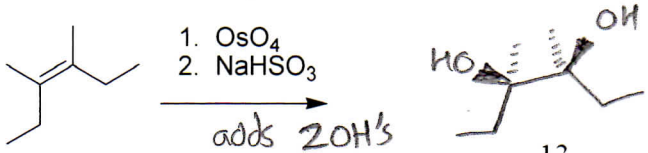
(g) 

syn addn
+ enant

(h) 

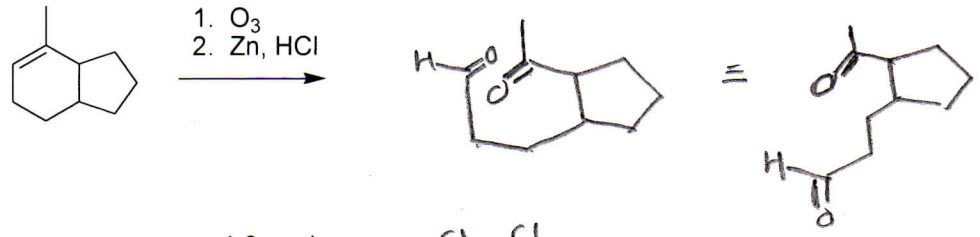
adds OH to less sub C
syn addn

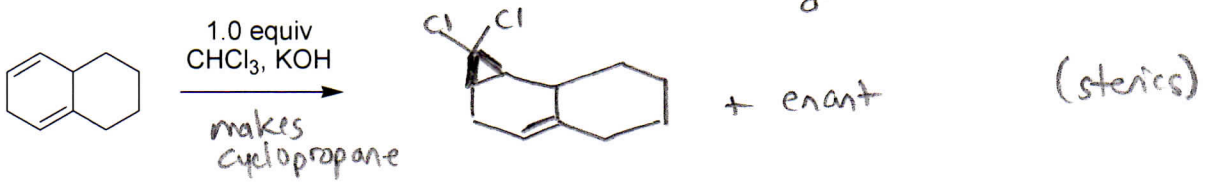

blocks bottom face

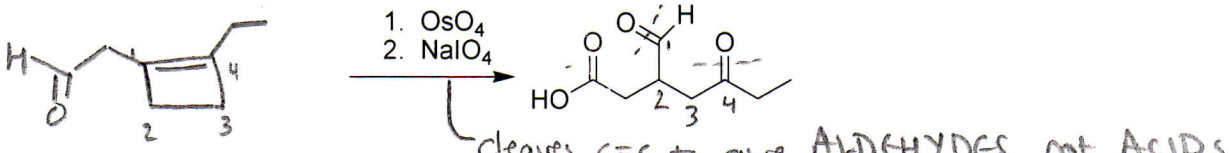
(i) 

adds 2 OH's syn

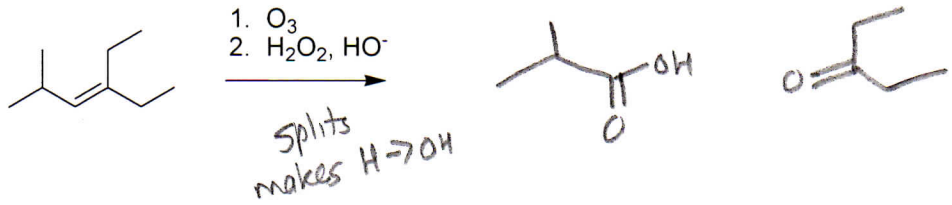
(meso)

(j) 

(k) 

(l) 

(note: the starting material contains a carbonyl group in it already)

(m) 

3° SN1/E1 or E2 — E2 strong base — SN2 strong Nu — bulky => elimin

1° SN2 or E2

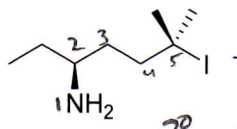
40. (*14 points*) Alkyl halides.

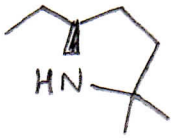
For **FOUR** of the reactions shown below, fill in the oval with the correct reaction type(s) (S_N1, S_N2, E1, or E2), and draw the major product(s) for the reaction.

SN2 - inversion

SN1 - racemization

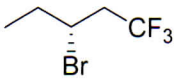
(a) SN1 (E1)

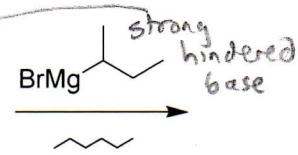




3°, weak Nu/base

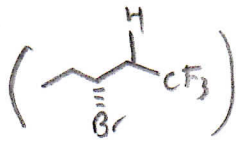
(b) E2



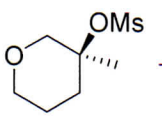


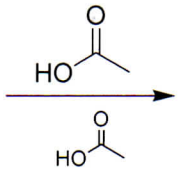
2° any possible

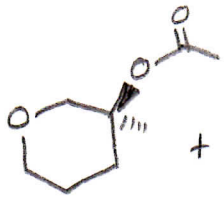
most acidic H since CF_3 is ewg



(c) SN1 E1



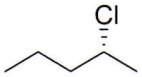




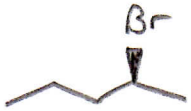
+ enant +

3°
SN1 or E1

(d) SN2

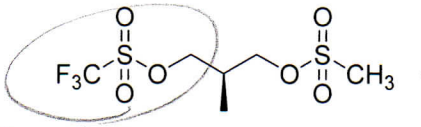


strong Nu
LiBr
aprotic solvent
not a base



2°

(e) SN2



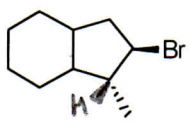
1.0 equiv NaCN

good Nu
poor base

CF_3 makes this better LG

10

(f) E2

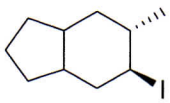


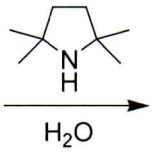
strong, hindered base
KO^tBu

2° RX

E2 requires anti H to X

(g) E1





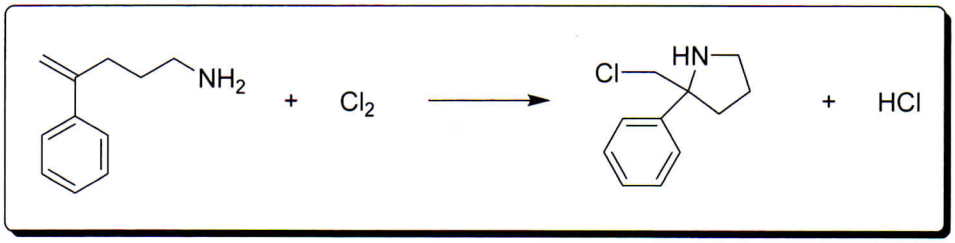
2°

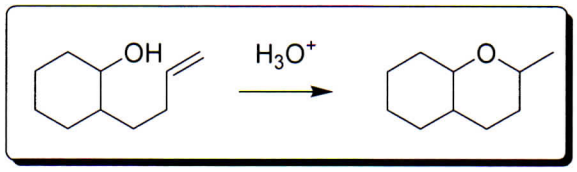
bulky weak base

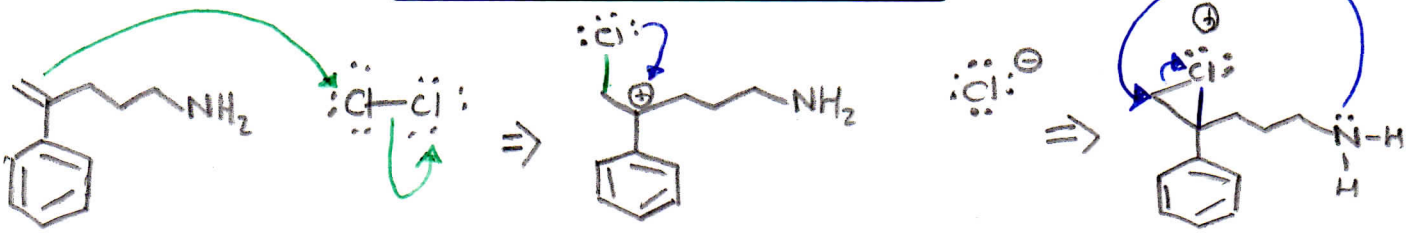
E1 has no stereochem requirement

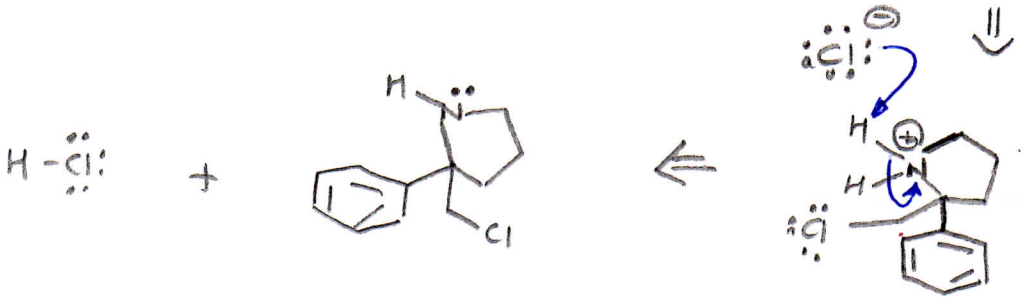
Section V. Mechanisms.

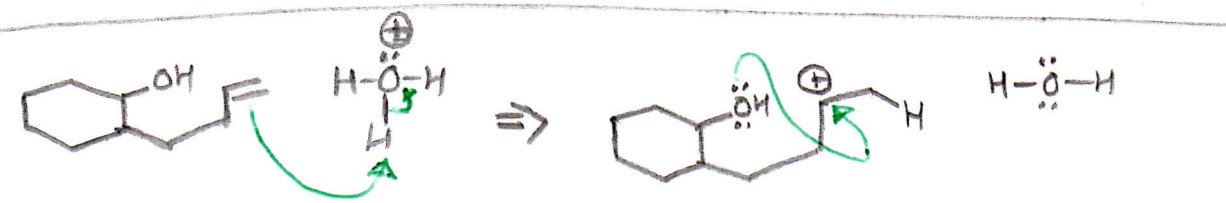
42. (*11 points*) Using curved arrow formulism, provide a reasonable mechanism for ONE of the reactions shown below.

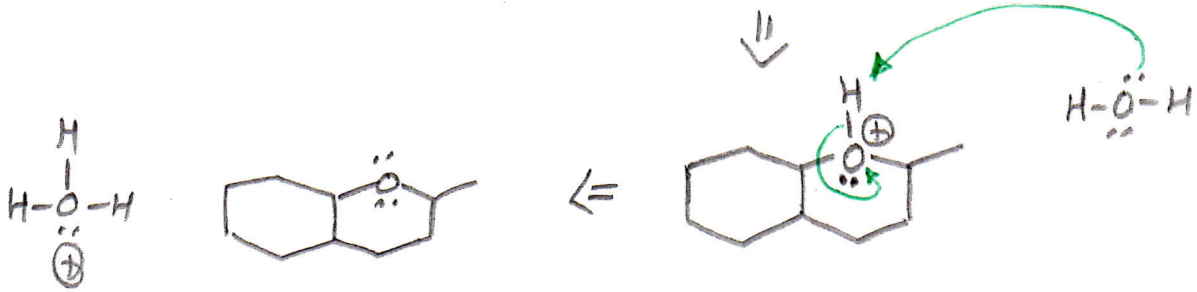






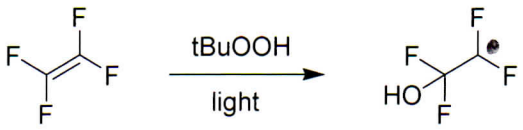






43. (*5 points*) Polymerization reactions..

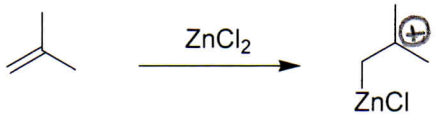
(a) Choose ONE polymerization initiation step below, and write in the box if it occurs by an anionic, cationic, or free radical mechanism



teflon

free radical

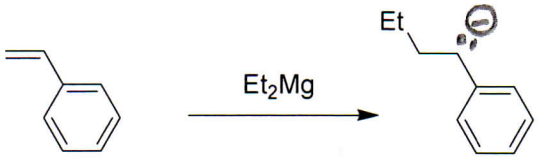
peroxide, light as reagent



polyisobutylene
(used in basketball, roofing, and gas masks)

cationic

$ZnCl_2$ is Lewis acid



polystyrene
(used in styrofoam, as well as many other things)

anionic

Et_2Mg = $Et^{\ominus}$

(b) Now for the reaction you chose, complete the structure of the intermediate shown above (to make it an anion, a cation, or a free radical)

(c) Finally, use curved arrows to show the mechanism of how two more monomer units would add to this intermediate to give a 3-unit polymer.