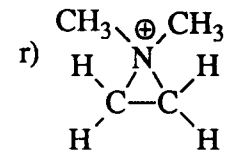
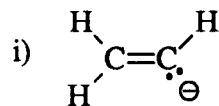
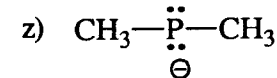
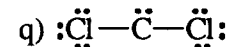
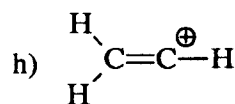
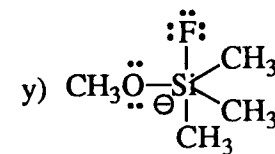
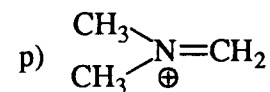
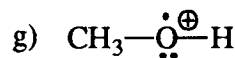
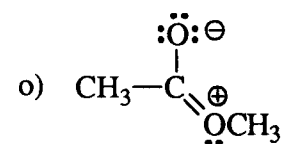
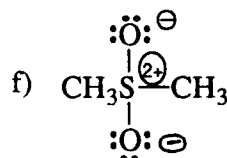
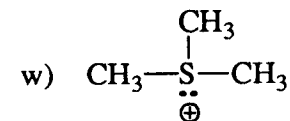
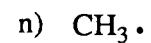
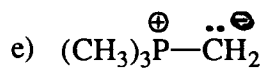
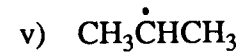
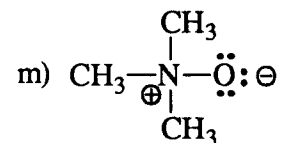
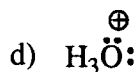
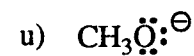
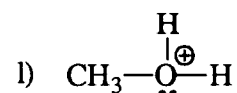
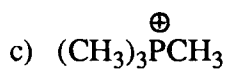
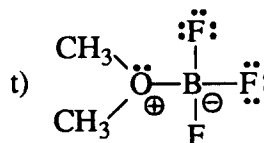
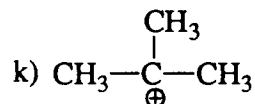
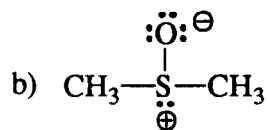
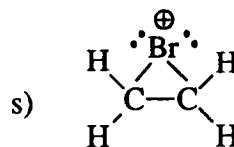
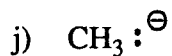
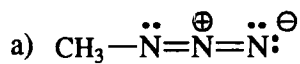


## Answers to Problem 1.



Tetrahedral Geometry: b, c, d, e, f, g, j, l, m, n, r (about n), t, u, w, x, z

note: all CH<sub>3</sub> groups are sp<sup>3</sup> hybridized with bond angles of 109°.

The simple generalizations about hybridization do not readily deal with observed calculated bond angles in r, s, g and v.

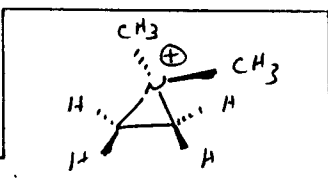
Answers Problem 2. Calculate the formal charge present on any of the atoms in the following molecules.

- a) CH3-N=N=N:
- b) CH3-S(=O)-CH3
- c) (CH3)3PCH3
- d) H3O:
- e) (CH3)3P-CH2:
- f) CH3S(=O)CH3
- g) CH3-O-H
- h) H2C=C+H
- i) H2C=C-
- j) CH3:
- k) CH3-C(CH3)2-CH3
- l) CH3-O-H
- m) CH3-N(CH3)-O-
- n) CH3:   

same as j
- o) CH3-C(=O)OCH3
- p) CH3-C+(N=CH2)-CH3
- q) :Cl-C-Cl:
- r) CH3-N(CH3)-CH2-CH3
- s) CH2=CH-Br
- t) CH3-O-B(F)2
- u) CH3O-
- v) CH3CHCH3   

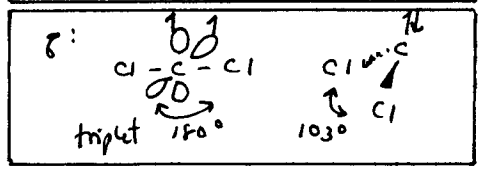
sp<sup>2</sup> or sp<sup>3</sup>?
- w) CH3-S(CH3)2
- x) AlH4
- y) CH3O-S(CH3)3
- z) CH3-P(CH3)2

\* π-bond in b, e, and f involves an empty s-3d and C-2p orbitals.

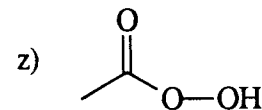
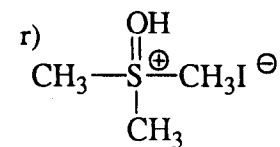
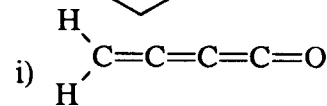
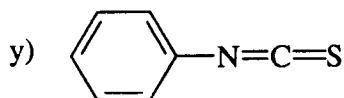
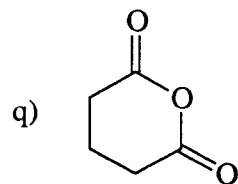
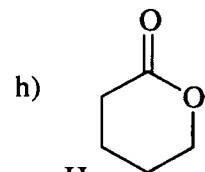
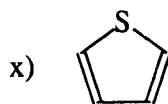
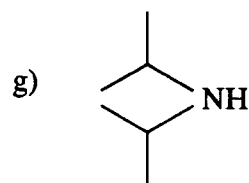
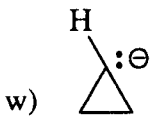
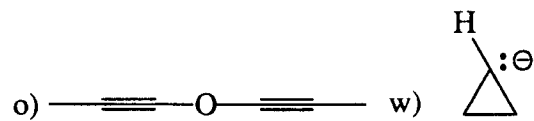
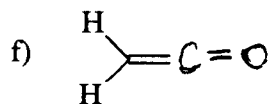
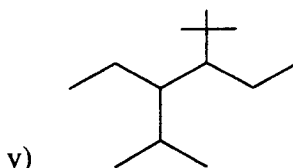
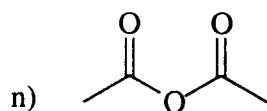
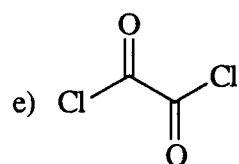
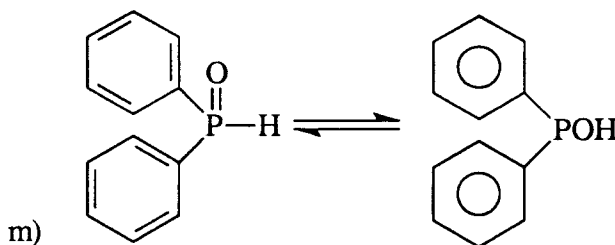
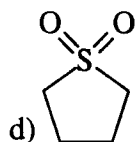
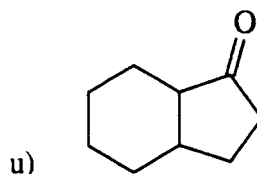
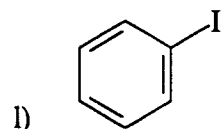
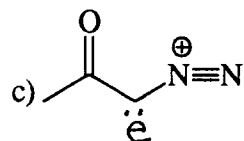
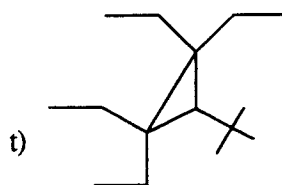
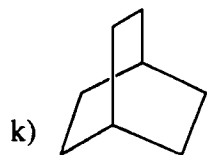
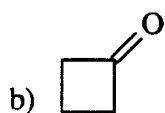
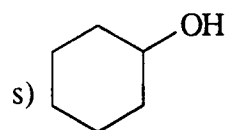
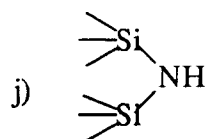
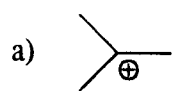


For r and s the three membered rings have bent or banana bonds (i.e. sp<sup>4</sup>-sp<sup>5</sup> hybridization) and the e<sup>-</sup> density of the bonding molecular orbitals (e.g. C-N, C-C, C-Br) does not lie along the internuclear axis. The angles are ≈ 102° between axis of e<sup>-</sup> density

+ v: carbon radicals maybe either sp<sup>2</sup> or sp<sup>3</sup> hybridized.



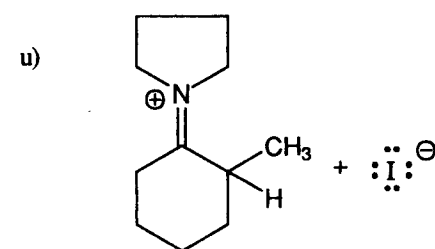
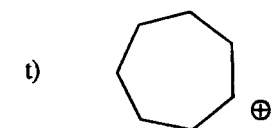
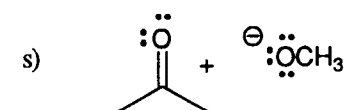
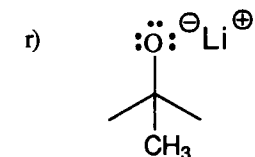
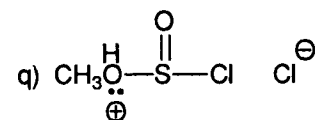
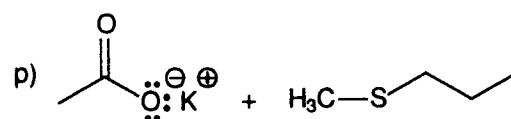
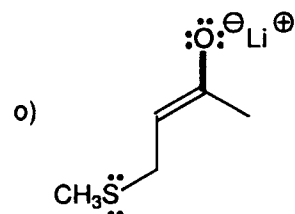
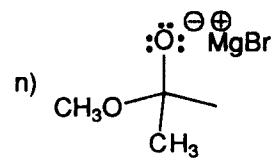
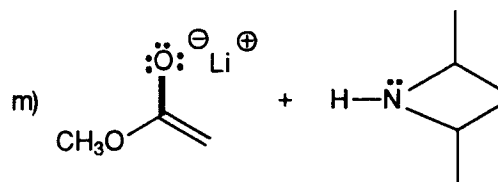
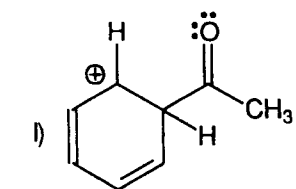
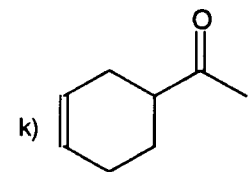
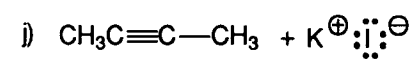
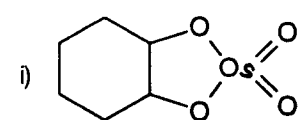
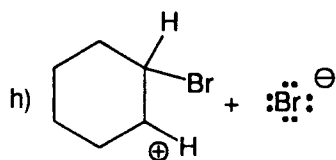
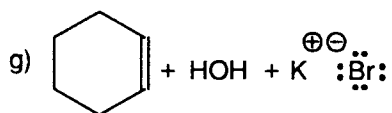
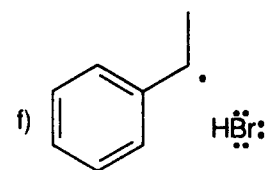
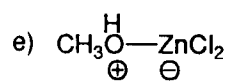
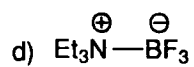
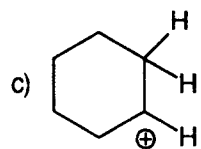
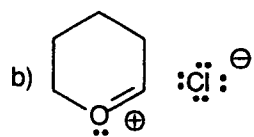
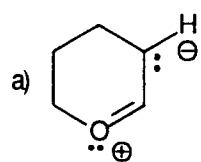
Answers to Problem 3.



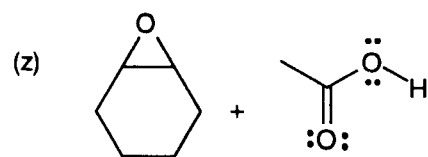
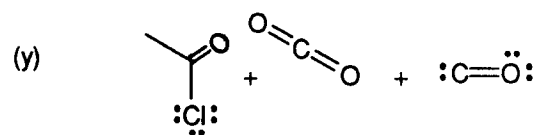
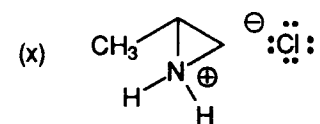
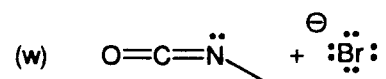
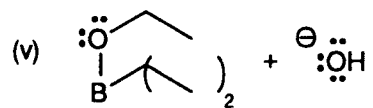
Problem 4. Give the molecular formula for the following bond line notations.

(a) adrenalin	$C_9H_{13}NO_3$
(b) mescaline	$C_{11}H_{17}O_3N$
(c) cocaine	$C_{17}H_{21}O_4N$
(d) valium	$C_{16}H_{13}ClON_2$
(e) pyridoxine	$C_8H_{11}O_3N$
(f) prostaglandin $PGF_2$	$C_{20}H_{34}O_5$
(g) (+)- sucrose	$C_{12}H_{22}O_{11}$
(h) nicotine	$C_{10}H_{14}N_2$
(i) morphine	$C_{17}H_{19}O_3N$
(j) aspirin	$C_9H_8O_4$
(k) aldrin	$C_{12}H_8Cl_6$
(l) perhydrohistrionicotoxin	$C_{19}H_{37}NO$
(m) longifolene	$C_{15}H_{24}$
(n) cedrene	$C_{15}H_{24}$
(o) grasshopper ketone	$C_{13}H_{20}O_3$
(p) cholesterol	$C_{27}H_{46}O$
(q) testosterone	$C_{19}H_{28}O_2$
(r) vitamin D <sub>2</sub>	$C_{28}H_{44}O$
(s) prostaglandin E <sub>2</sub>	$C_{20}H_{32}O_5$
(t) caryophyllene	$C_{15}H_{24}$
(u) vitamin A	$C_{20}H_{30}O$
(v) arachidonic acid	$C_{20}H_{32}O_2$
(w) lysergic acid	$C_{16}H_{16}N_2O_2$
(x) 1-(1-phenylcyclohexyl)piperdine	$C_{17}H_{25}N$
(y) quadrone	$C_{15}H_{20}O_3$
(z) penicillin D	$C_{13}H_{18}O_4N_2S_2$

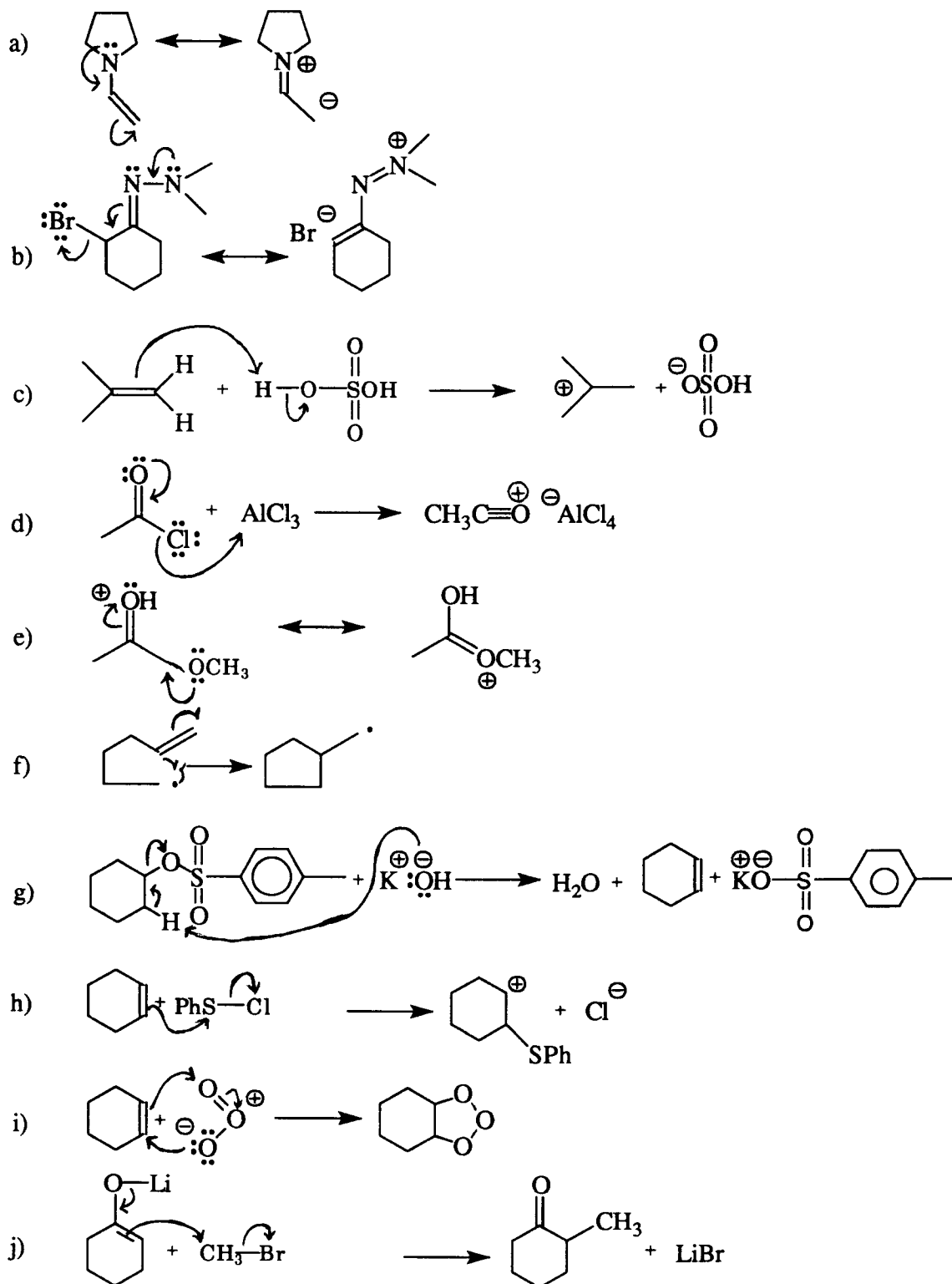
## 5. Answers to Problem 5

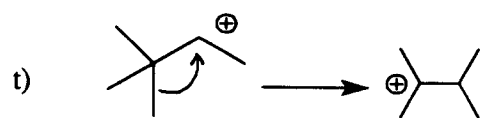
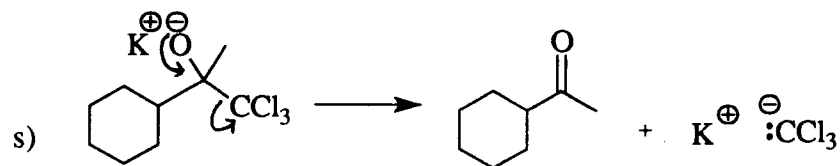
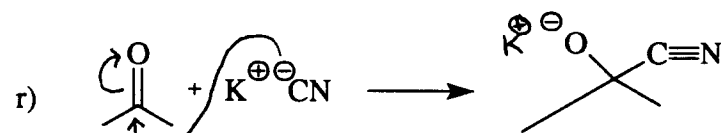
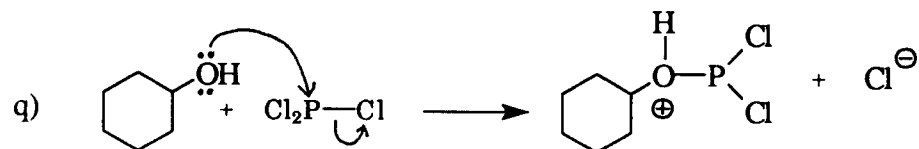
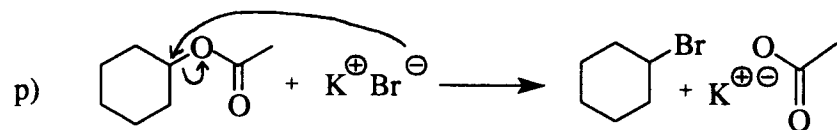
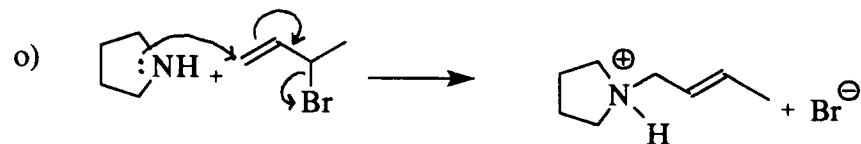
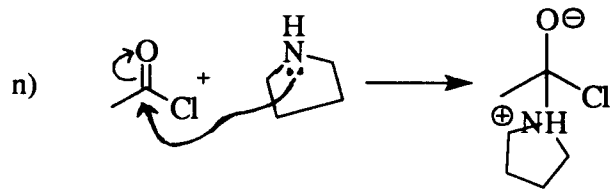
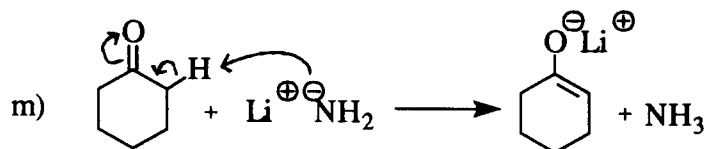
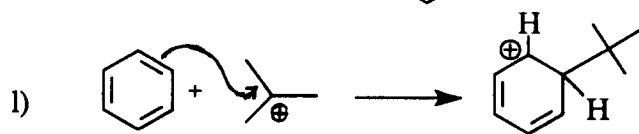
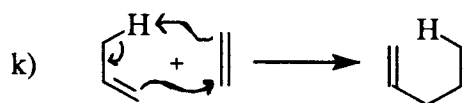


## 5. Answers to Problem 5 (con't)

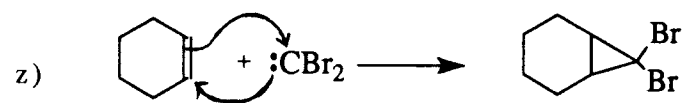
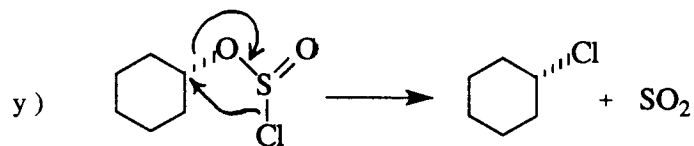
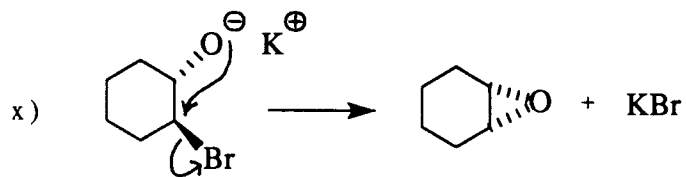
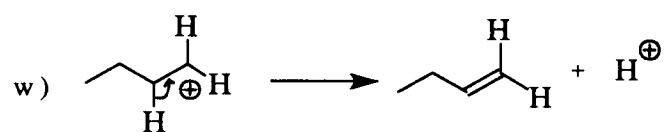
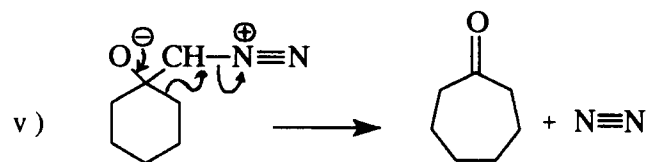
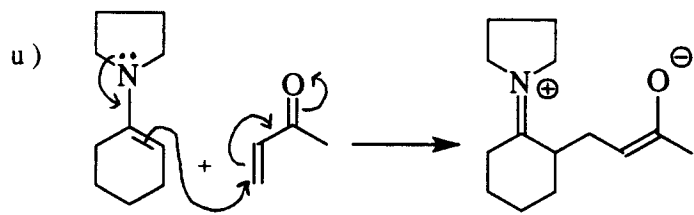


## Answers to Problem 6:





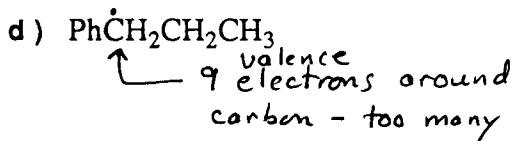
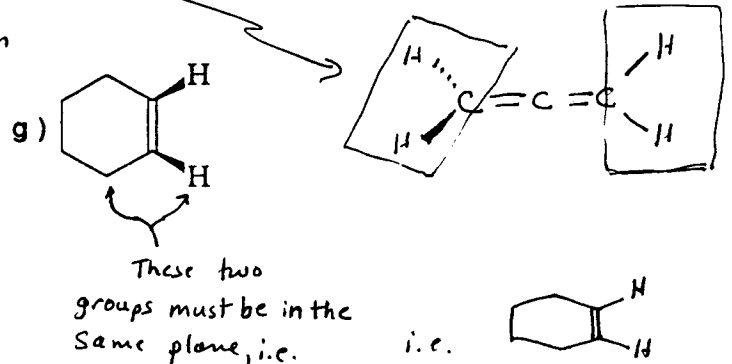
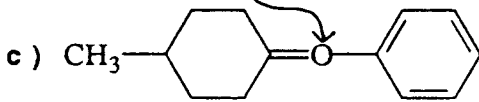
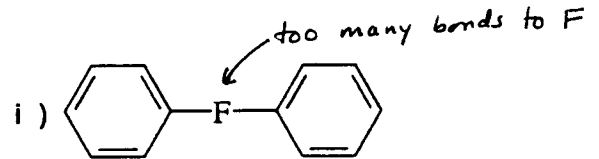
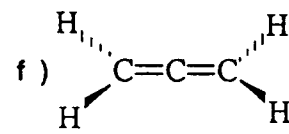
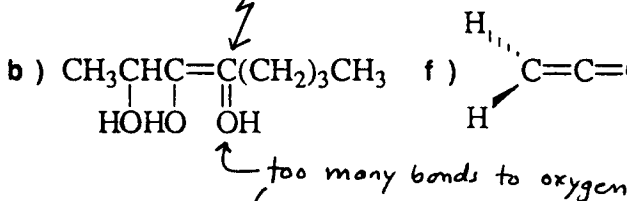
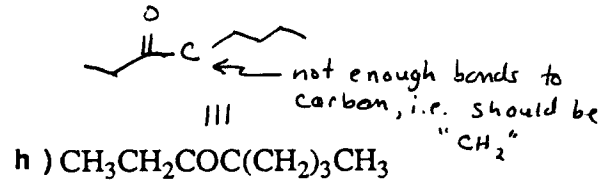
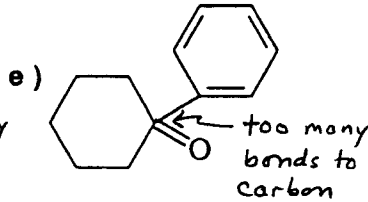
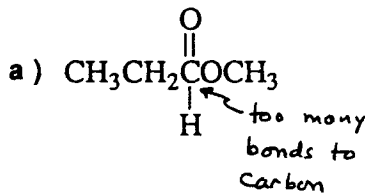




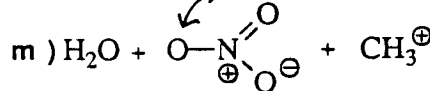
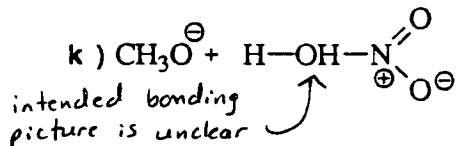
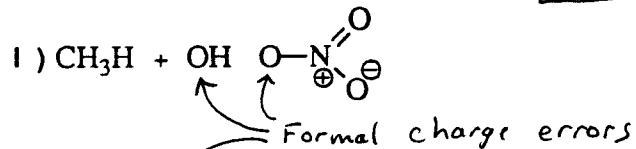
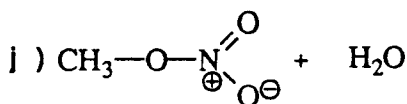
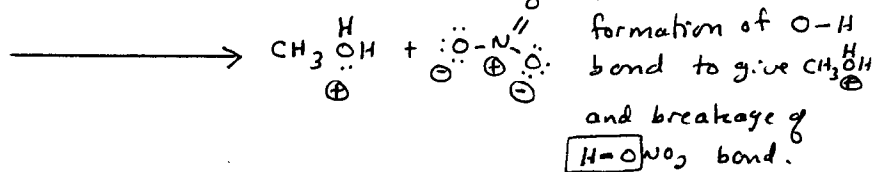
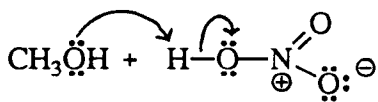
## Answers

Problem 7: The following answers have been provided to examination questions. They contain egregious errors of a type which precludes any chance of understanding the subject matter. For each set, identify the egregious error(s) and where possible, provide a correct answer.

Set A: What is wrong with the following structures?

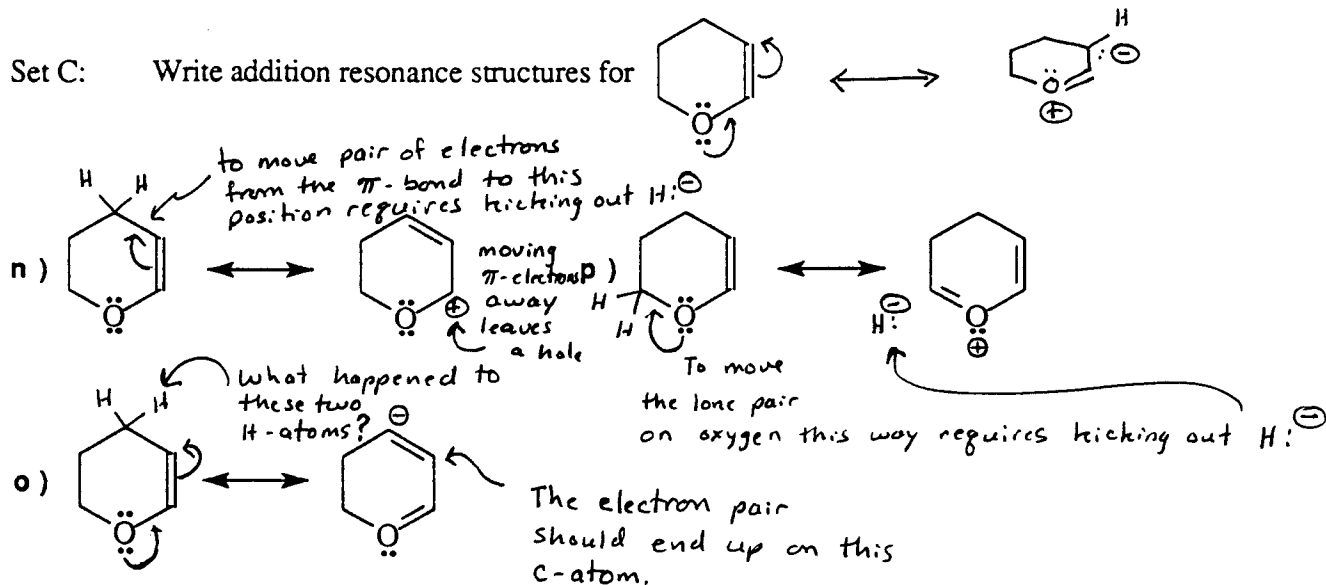


Set B: Draw the products indicated by the arrow formalism. attached to an  $\text{sp}^2$  hybridized C-atom.

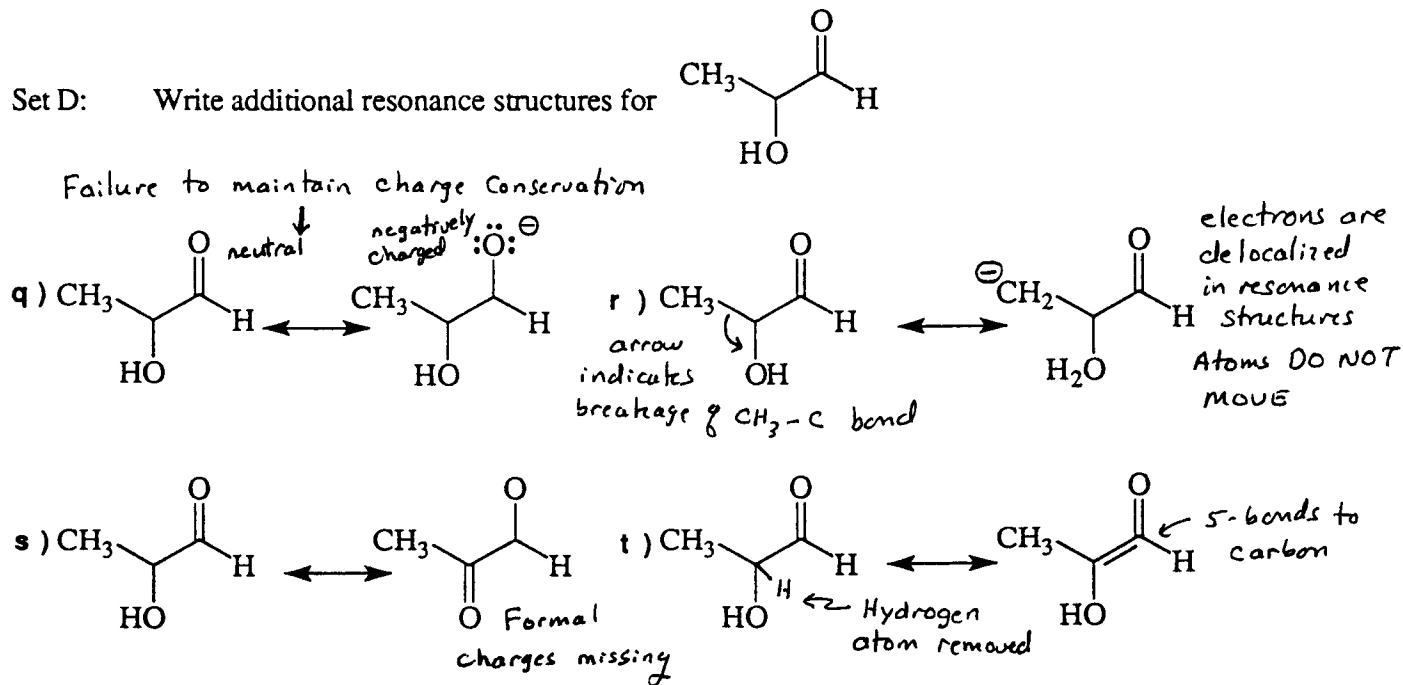


answers given in h-m not only make no sense whatsoever with regard to the arrow formalism of the original problem but also contain serious errors involving valency and formal charges.

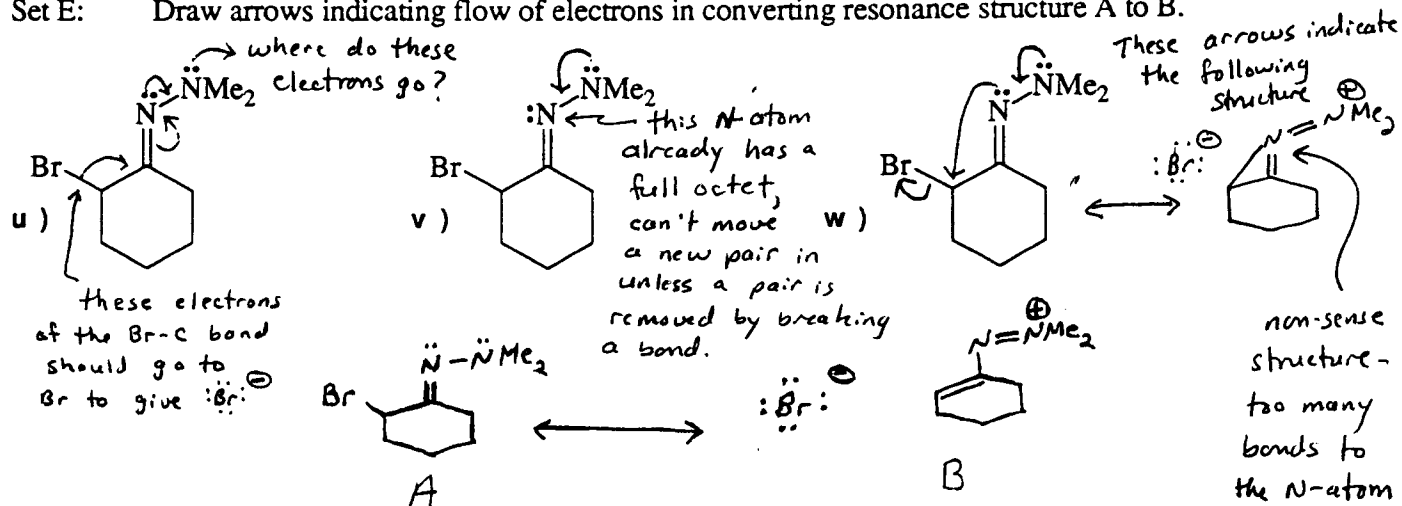
Set C: Write addition resonance structures for



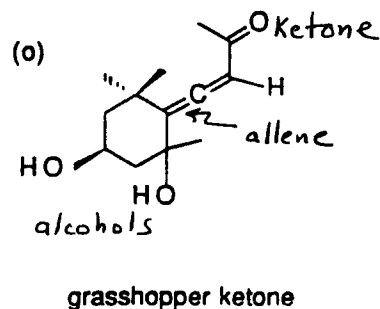
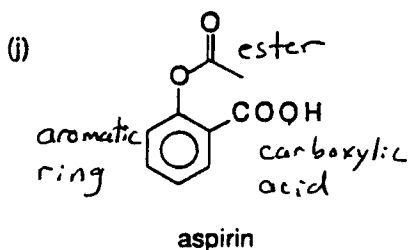
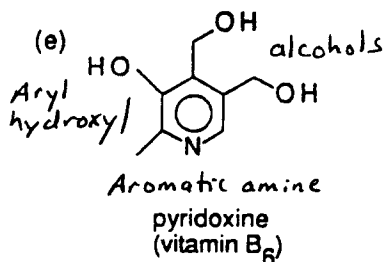
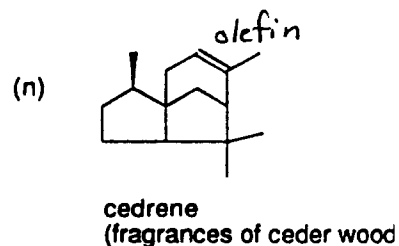
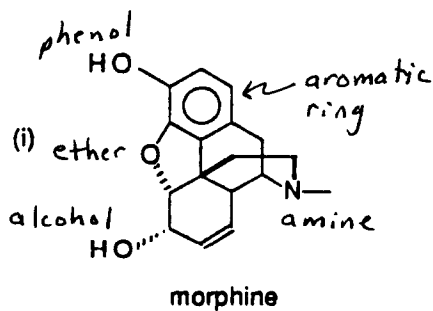
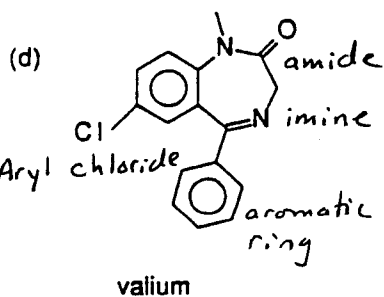
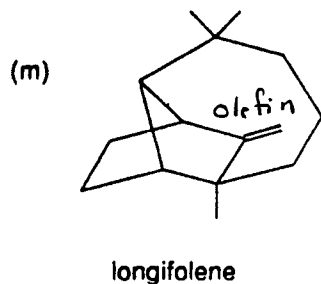
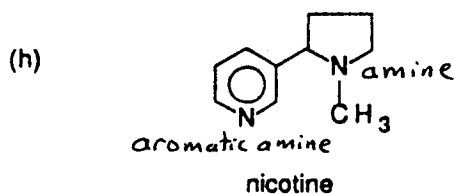
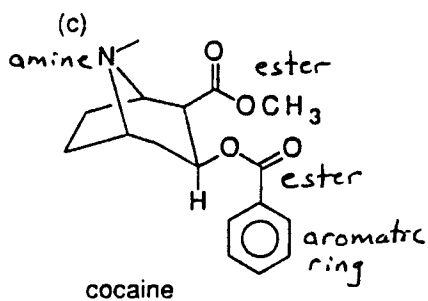
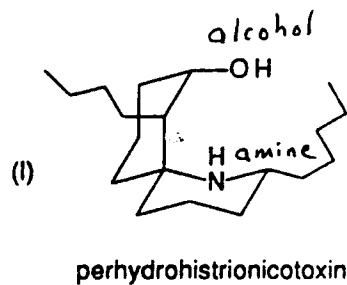
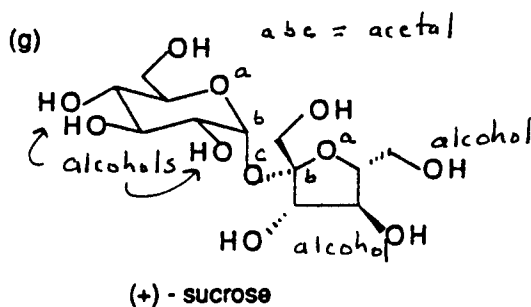
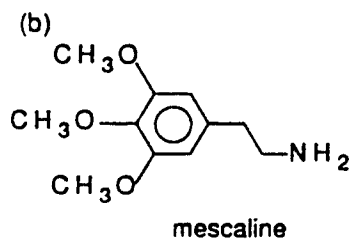
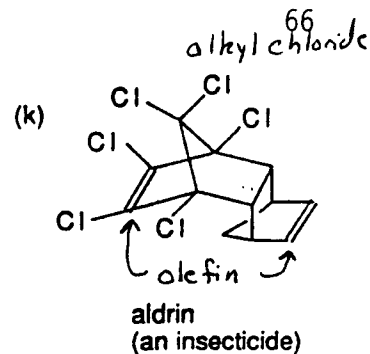
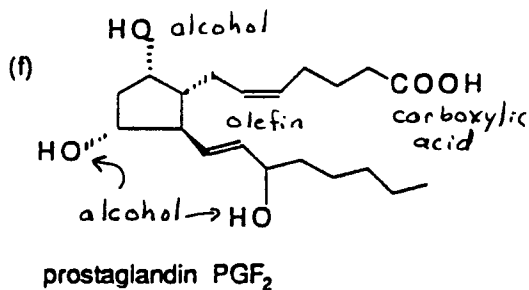
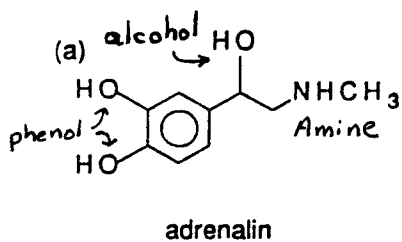
Set D: Write additional resonance structures for

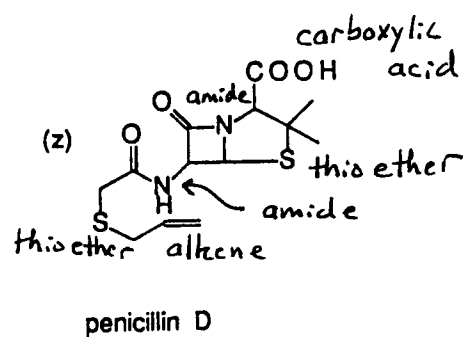
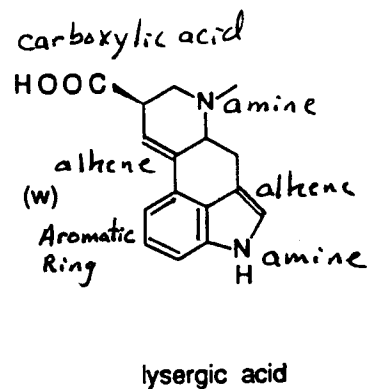
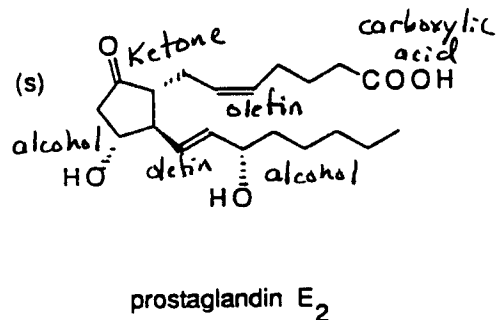
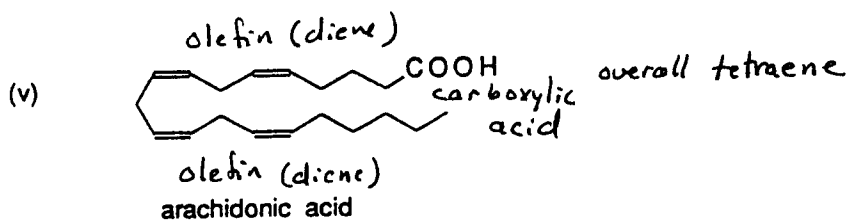
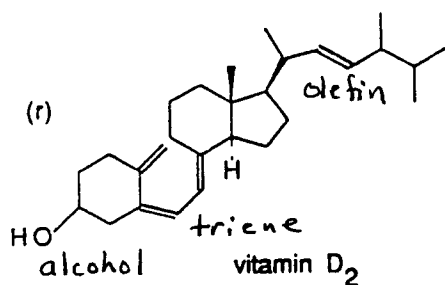
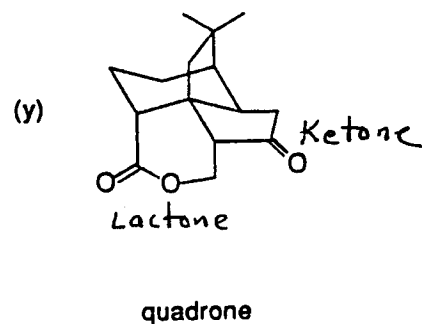
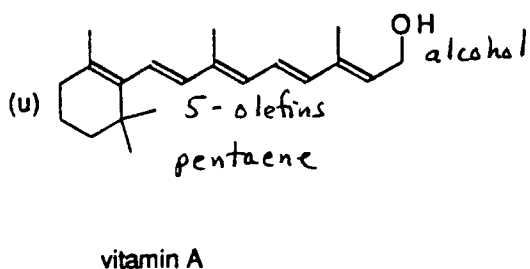
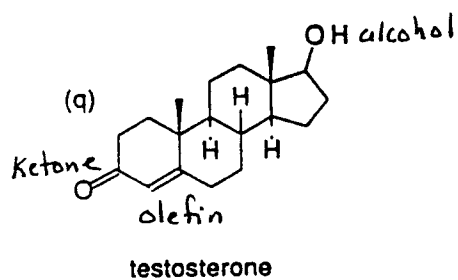
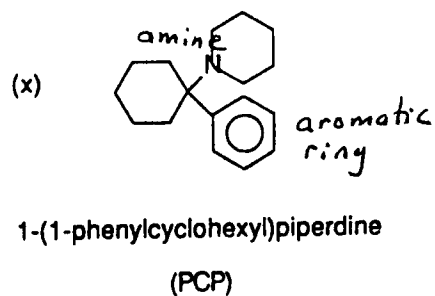
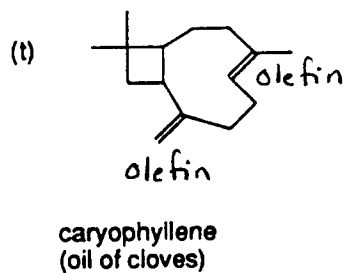
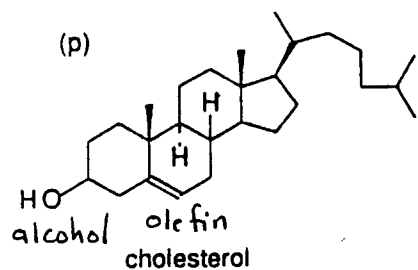


Set E: Draw arrows indicating flow of electrons in converting resonance structure A to B.



Answers to Problem 8.



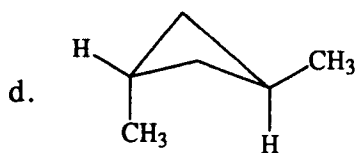
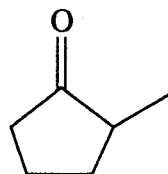
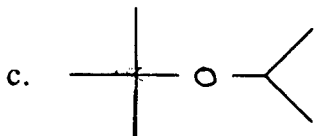
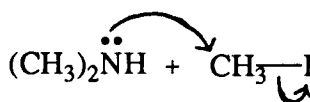
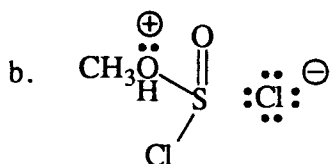


**Exam 1: Answers**

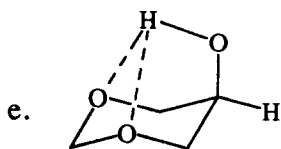
1. a. 3 1 2 F-F Bond is non-polar since both atoms are the same;  $O > N$  in electronegativity  
 b. 1 2 3  $sp > sp^2 > sp^3$  in % of s-character  
 c. 1 3 2 In base strength  $CH_3^\ominus > CH_3NH^\ominus > CH_3O^\ominus$  hence in acidity  $CH_4 < CH_3NH_2 < CH_3OH$   
 d. 2 1 3  $CH_3, \text{ gauche}$ ;  $CH_3, CH_3$ ;  $CH_3, \text{ gauche}$  and  $CH_3, CH_3$  gauche butane interactions respectively.  
 e. 1 3 2 C = 4; O = 2; N = 3 in common valencies.

2. a. (5) D and E      b. (2) B and D      c. (5) All three      d. (3) a place where  $x=0$   
 e. (1)  $CH_3CH_2OH$   
 $K_a = 1 \times 10^{-18}$

3. a. 3-methyl-5-isopropyloctane      Bicyclo[3.1.1]heptane

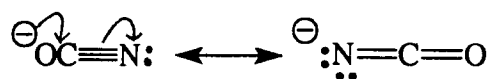


trans-1,3-dimethylcyclobutane



axial -OH can form H-bonds with the ring oxygens.

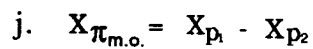
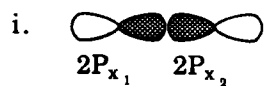
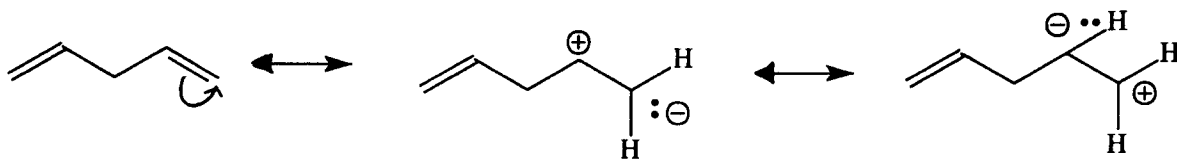
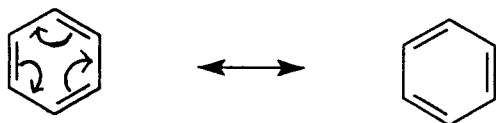
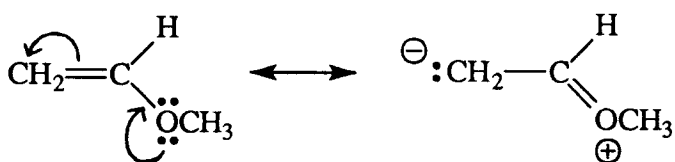
f.  $\text{HOC}\equiv\text{N}$  and  $\text{HN}=\text{C}=\text{O}$  are tautomers - i.e. isomers with a H-atom in different positions or points of attachment.

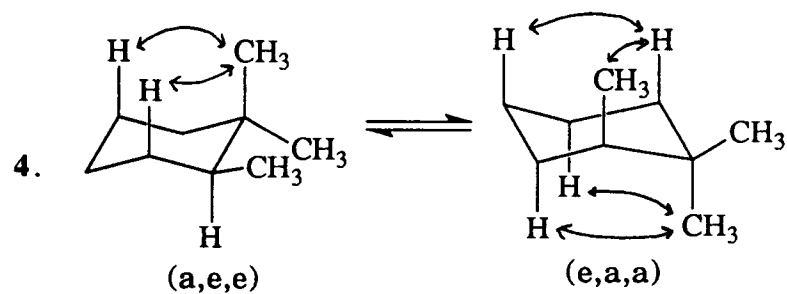


they will afford the same conjugate base  
the two forms being resonance structures



h.





sub-sub gauche  
butane

$$2 \times 0.9 = 1.8$$

$$1 \times 0.9 = 0.9$$

sub-ring carbon

gauche butane

$$2 \times 0.9 = \underline{1.8}$$

$$4 \times 0.9 = \underline{3.6}$$

Total:

$$\underline{3.6}$$

$$\underline{4.5}$$

The (a,e,e) conformation is more stable than the (e,a,a) conformation by 0.9 kcal/mole.



## Exam II: Answers

1. a. 1 3 2 }  
 b. 1 2 3 }

In carbocation stability  $3^\circ > 2^\circ > 1^\circ$

c. 3 2 1

more substituted olefin is generally more stable, trans more stable than cis due to steric effects

d. 3 2 1

$3^\circ > 2^\circ > 1^\circ$  in radical stability

e. 3 2 1

Tri-substituted olefins formed at a faster rate than di-substituted. The more reactive halide leads to the same olefin as 2nd most reactive but has statistically more opportunities to do so at less hindered sites.

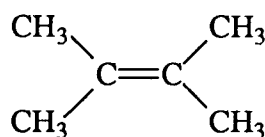
2. a. (4)  $p/sp^3$  C-H  $sp^3/C-P$

b. (5) none

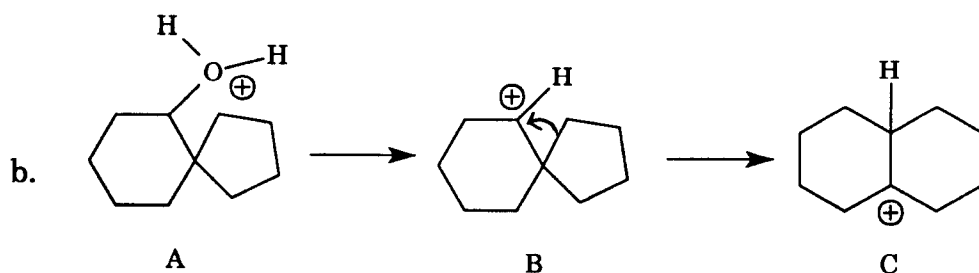
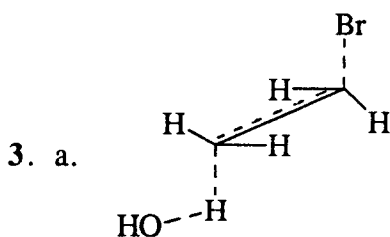
c. (5) both  $S_N1$  and E1 reactions

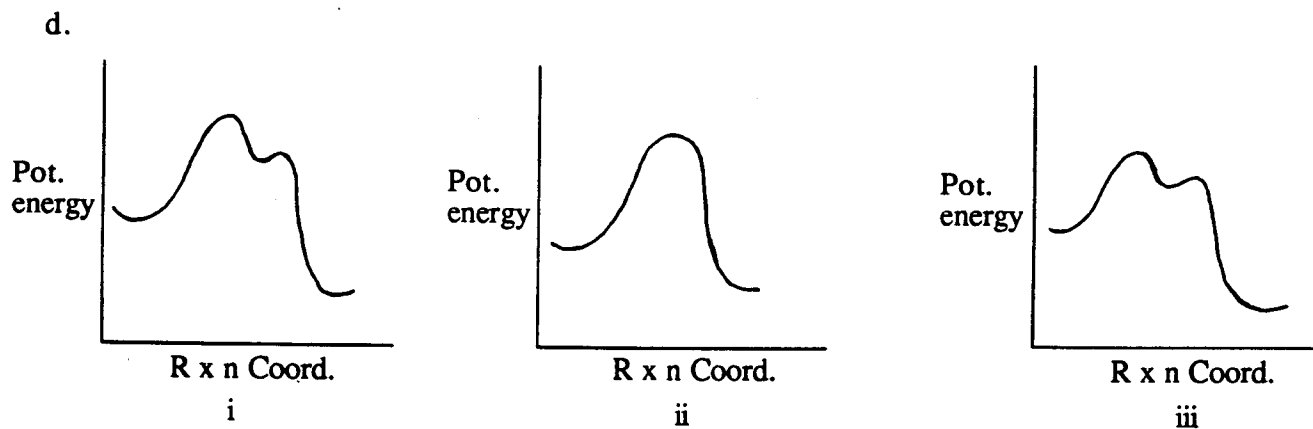
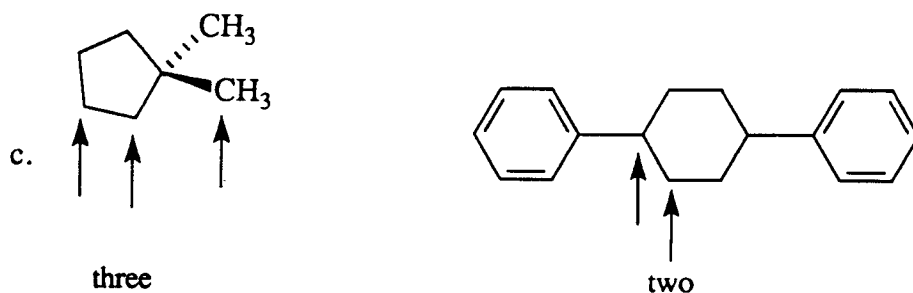
d. (3) B,D

e. (3)

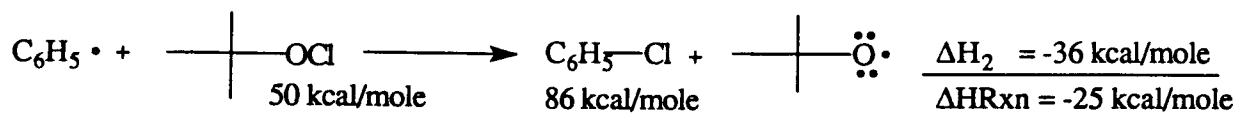
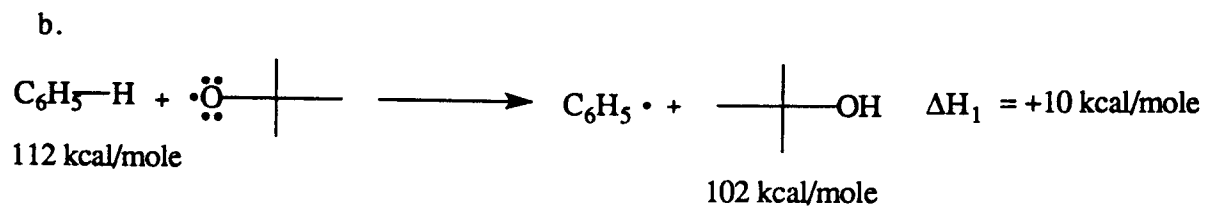
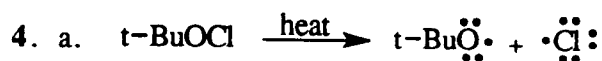


f. (5) all of the above





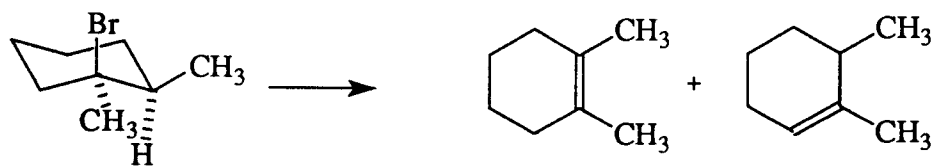
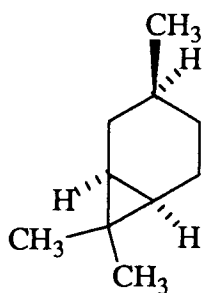
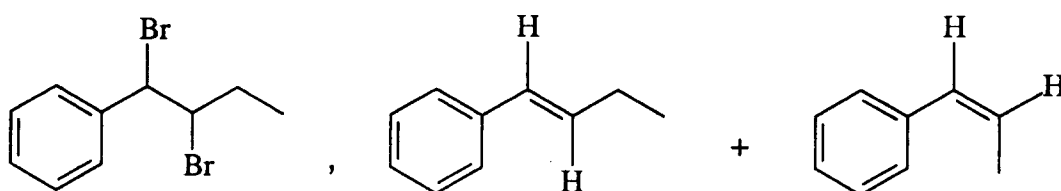
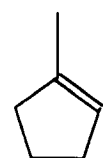
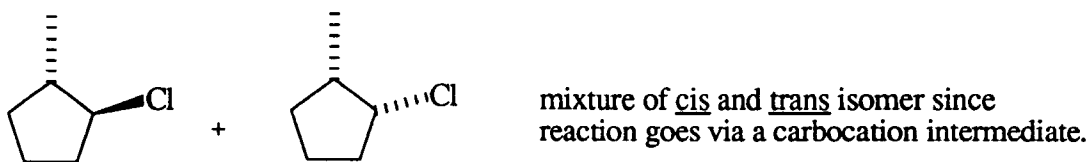
e. valence electrons	O	N	C
	6	5	4
common valency	2	3	4
valency for formal charge of +1	3	4	3



## 4. b. (con't)

Although the reaction is thermodynamically favored ( $\Delta H_{Rxn} = -25$  kcal/mole) it is not a good procedure since the first step ( $\Delta H_1 = +10$  kcal/mole) has a high activation energy and would be very slow.

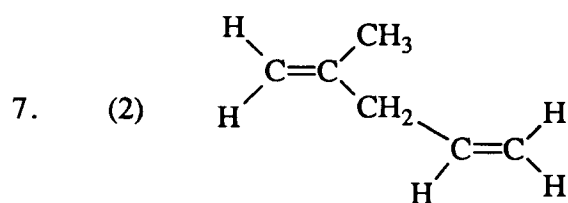
## 5.



## Exam III: Answers

## 1. Part A.

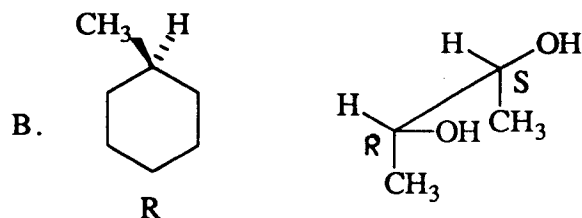
1. 2 1 3 more alkyl substituted double bonds are more nucleophilic  
 2. 1 3 2 E, Z and R, : cis and trans; d, l and meso  
 3. 3 1 2  $1^\circ > 2^\circ > 3^\circ$  in  $S_N2$  substitution  
 4. 1 3 2  $I^\ominus$  is more polarizable;  $RCOO^\ominus$  is charged  
 5. 3 1 2  $3^\circ > 2^\circ > 1^\circ$  in carbocation stability  
 6. (2)  $\oplus HgOAc$

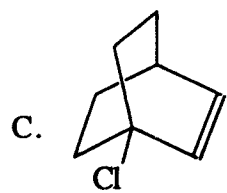


8. (5) answers (1) and (3)  
 9. (5) answers (1), (2) and (3) are true  
 10. (3) have the same specific rotation  
 11. (4) Answers (1) and (3) only are true.

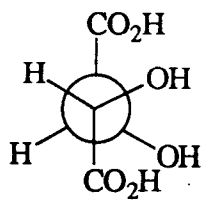
## 2.

- A. i.  $S_N2$ , E2  
 ii.  $S_N2$ , E2  
 iii.  $S_N1$ , E1  
 iv.  $S_N1$ ,  $S_N2$ , E1, E2

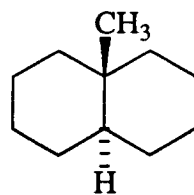




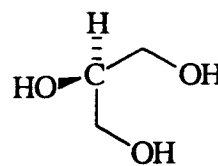
achiral



chiral



achiral



achiral

- D. conformational enantiomers  
 identical  
 conformational diastereomers  
 configurational enantiomers  
 configurational diastereomers

Products:

