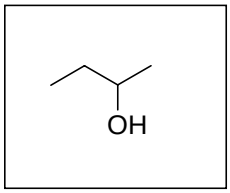
CHEMISTRY 313-02
MIDTERM # 1 – answer key
October 06, 2009

Statistics:

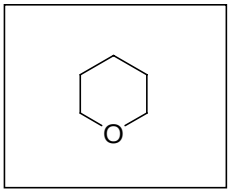
- Average: **75 pts (75%)**;
- Highest: **97 pts (97%)**; Lowest: **35 pts (35%)**
- Number of students performing at or above average: **21 (58%)**
- Number of students performing at or below 55%: **4 (11%)**
- Number of students performing at or above 90%: **5 (14%)**

1. (12 pts) Mark as true (**T**) or false (**F**) the following statements. Do not explain!
   - (**T**) Single bonds are always σ-bonds;
   - (**F**) Constitutional isomers have different molecular formulas;
   - (**F**) The conformations of a particular substance are stereoisomers;
   - (**T**) The chair conformation of cyclohexane is a global minimum;
   - (**F**) Cyclopropane suffers from *van der Waals* strain;
   - (**F**) Molecules with polar bonds are always polar;
   - (**T**) All *Brønsted* bases are also *Lewis* bases;
   - (**T**) Nucleophiles are *Lewis* bases;
   - (**T**) Increasing oxidation number indicates an oxidation process;
   - (**T**) Intermediates are not formed in concerted reactions;
   - (**T**) The *Hammond* postulate relates the energies and structures of two species on the energy diagram;
   - (**T**) Carbocations are electron-deficient species;

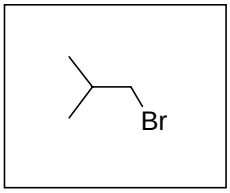
2. (4 pts) Provide the structural formula for each of the following molecules.



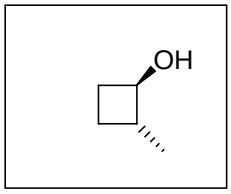
***sec*-butyl alcohol**



tetrahydropyran

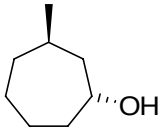


isobutyl bromide

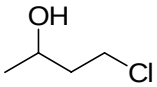


***trans*-2-methylcyclobutanol**

3. (3 pts) Provide an acceptable name for each of the following:



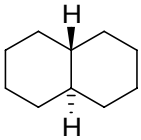
***trans*-3-methylcycloheptanol**



4-chloro-2-butanol

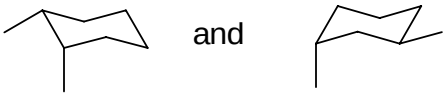
tetrahydrofuran

4. (2 pts) Provide a structure for each of the following compounds:
   a. *Trans*-decalin.

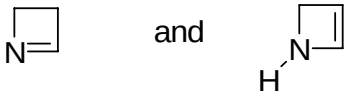


   b. Bicyclo[1,1,1]pentane.

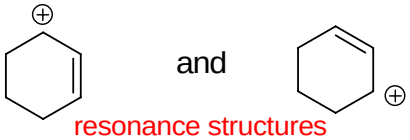
5. (4 pts) What is the relationship of the molecules or ions in each of the following pairs? Classify them as resonance structures, constitutional isomers, or neither.



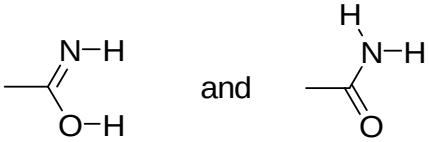
constitutional isomers



constitutional isomers

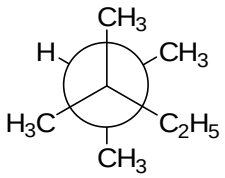


resonance structures

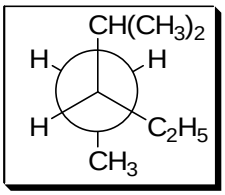


constitutional isomers

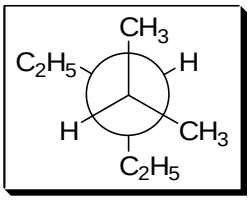
6. (2 pts) Within the set below, which two *Newman* projections represent the same compound?



A

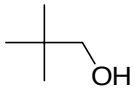


B

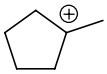


C

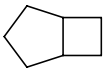
7. (3 pts) Provide examples of the following:
   a. A compound with one quaternary C;



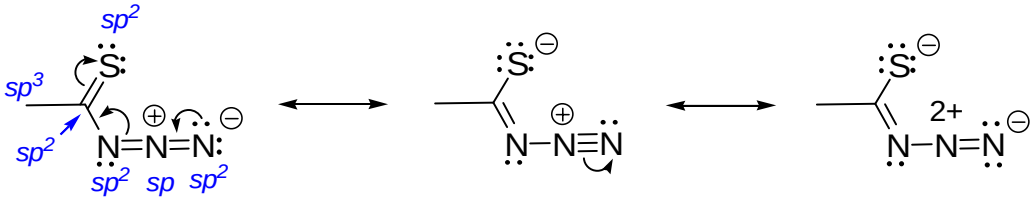
   b. A tertiary carbocation;



   c. A fused bicyclic compound;



8. (7 pts) Consider the species below.
   a. Complete the Lewis structure
   b. Provide two additional valid resonance structures and use the curved arrow formalism to show the flow of electrons.
   c. Rank the resultant resonance structures.
   d. Assign hybridization to each non-hydrogen atom in the structure below.

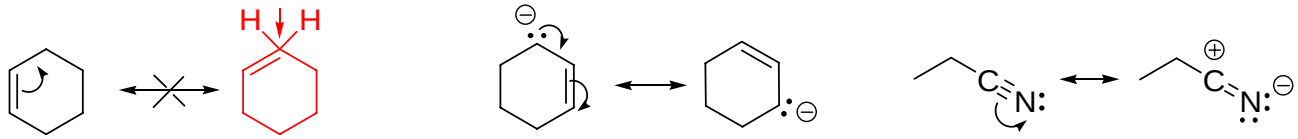


Rank: **1**
Negative charge on N

Rank: **2**
Negative charge on S

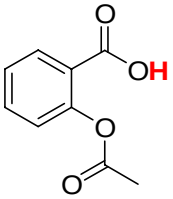
Rank: **3**
Fewer bonds,
greater charge separation

9. (3 pts) Consider the compounds and ions drawn below. When the curved arrows give a second valid resonance structure, draw that resonance structure. When the curved arrows generate an invalid resonance structure, explain why the structure is unacceptable

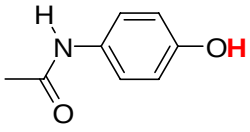


invalid resonance structure!!! C atom indicated with an arrowhas 5 bonds: One double to C, one single to C, and two to H(not shown typically in the bond-line formula, but shown above for clarity)

10. (2 pts) Indicate the most acidic hydrogen in the structure of each of the following drugs.



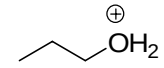
Acetylsalicylic acid (Aspirin)



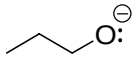
Acetaminophen (Tylenol)

11. (4 pts) For each of the molecules below, draw both the conjugate acid and the conjugate base:

a. 1-Propanol;

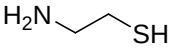


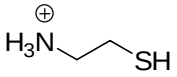
conjugate acid



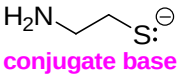
conjugate base

b.



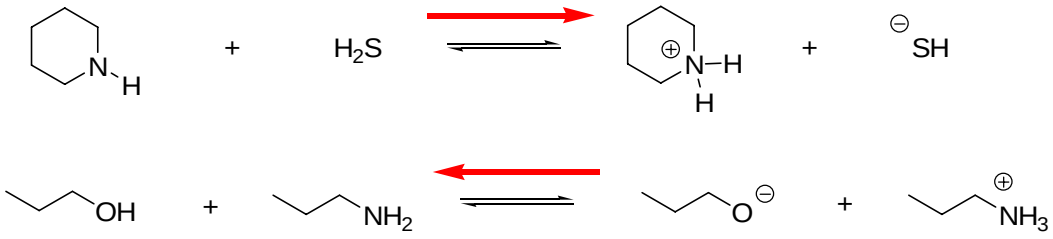


conjugate acid

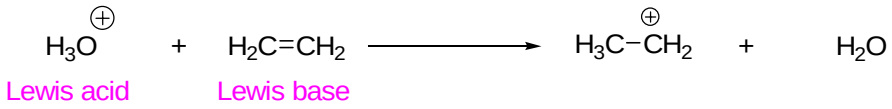


conjugate base

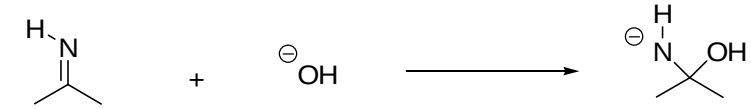
12. (4 pts) Predict the shift of equilibrium (<u>to the left or right</u>) for the following acid – base reactions.



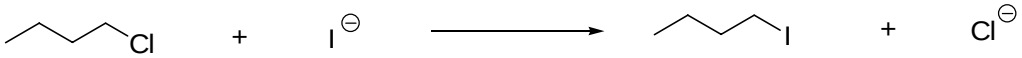
13. (6 pts) Label the reactants in the following reactions as *Lewis* acids or *Lewis* bases.



Lewis acid Lewis base

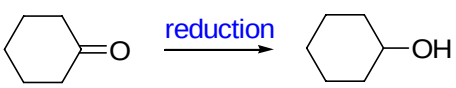


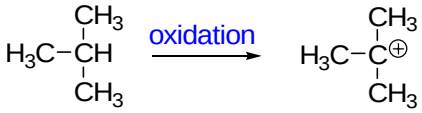
Lewis acid Lewis base

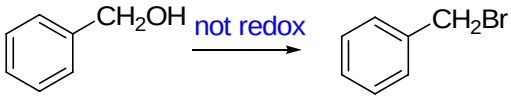


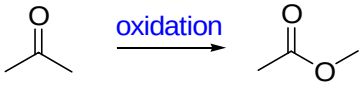
Lewis acid Lewis base

14. (4 pts) Classify each of the following transformations as a **reduction**, **oxidation** or **not redox**.

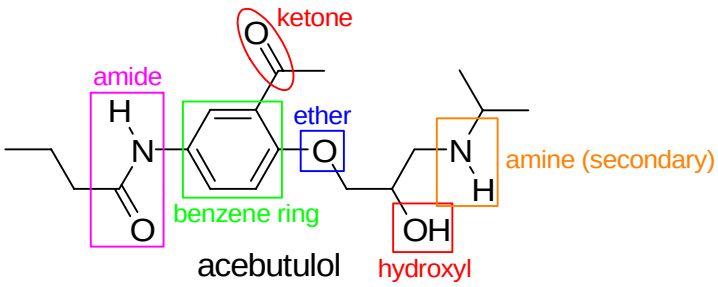




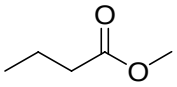
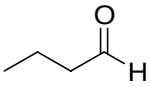
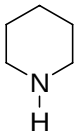
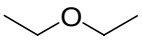
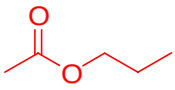
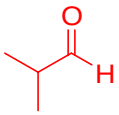


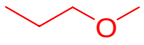


15. (5 pts) Identify and name the functional groups present in acebutulol, a drug that blocks certain part of the nervous system.

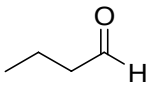


16. (4 pts) For each of the following compounds, draw an isomer that has the same functional group.

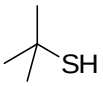









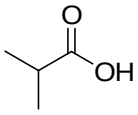
17. (4 pts) Propose structures for the following:
    a. An aldehyde with molecular formula C_4H_8O;



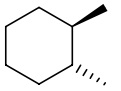
    b. A thiol with molecular formula $C_4H_{10}S$;



    c. A carboxylic acid with molecular formula $C_4H_8O_2$;



18. (6 pts) Give the relationship between the following pairs of structures. There are four (4) possible relationships: **same compound**, **constitutional isomers**, ***cis-trans* isomers**, **not isomers** (i.e. different molecular formula).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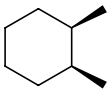
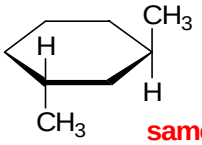


cis - trans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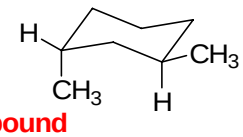
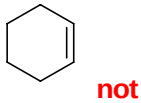


same compound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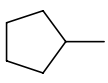
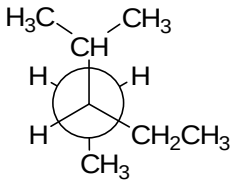


not isomers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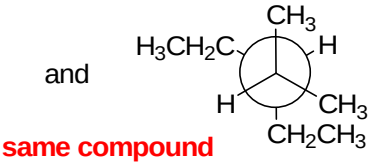
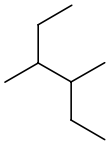
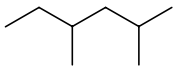
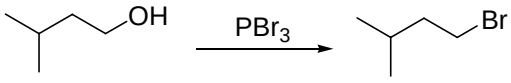


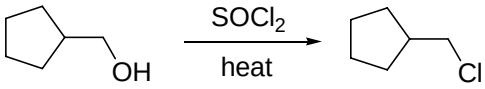
same compound


and


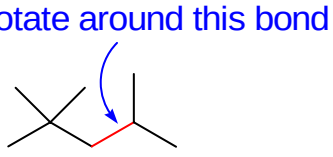
constitutional isomers

19. (4 pts) Draw the structure of the principle organic product of each of the following reactions.

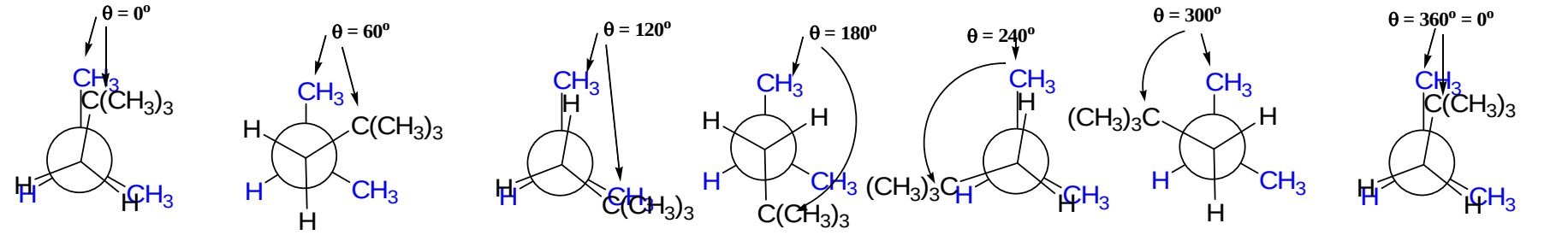




20. (6 pts) Using *Newman* projections, draw the conformations arising upon a full 360° turn (in 60° steps) around the **C3 – C4** bond in 2,2,4-trimethylpentane. Represent the energy changes on a qualitative energy/dihedral angle diagram. Assign the proper term (i.e. minimum, transition state, etc.) to each conformation.



2,2,4-trimethylpentane



eclipsed,
<u>one</u> CH_3 --- $C(CH_3)_3$
***van der Waals* interaction**

staggered,
<u>two</u> CH_3 --- $C(CH_3)_3$
***gauche* interactions**

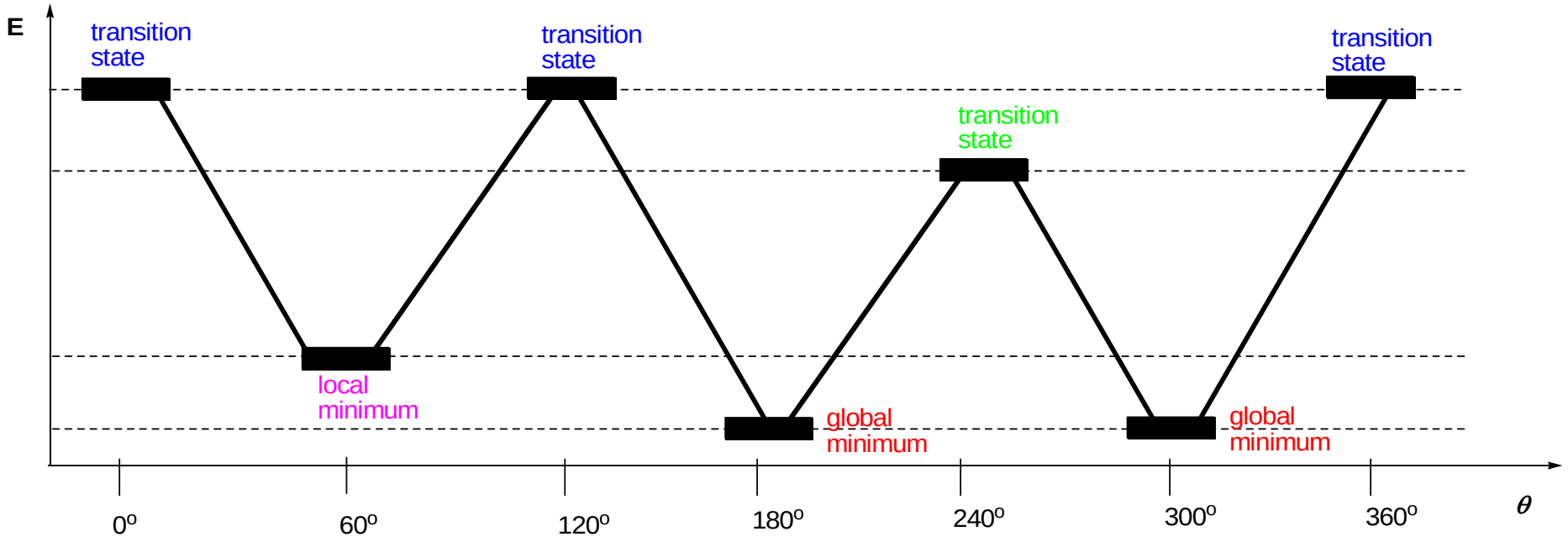
eclipsed,
<u>one</u> CH_3 --- $C(CH_3)_3$
***van der Waals* interaction**

staggered,
<u>one</u> CH_3 --- $C(CH_3)_3$
***gauche* interaction**

eclipsed,
<u>zero</u> *van der Waals* interactions

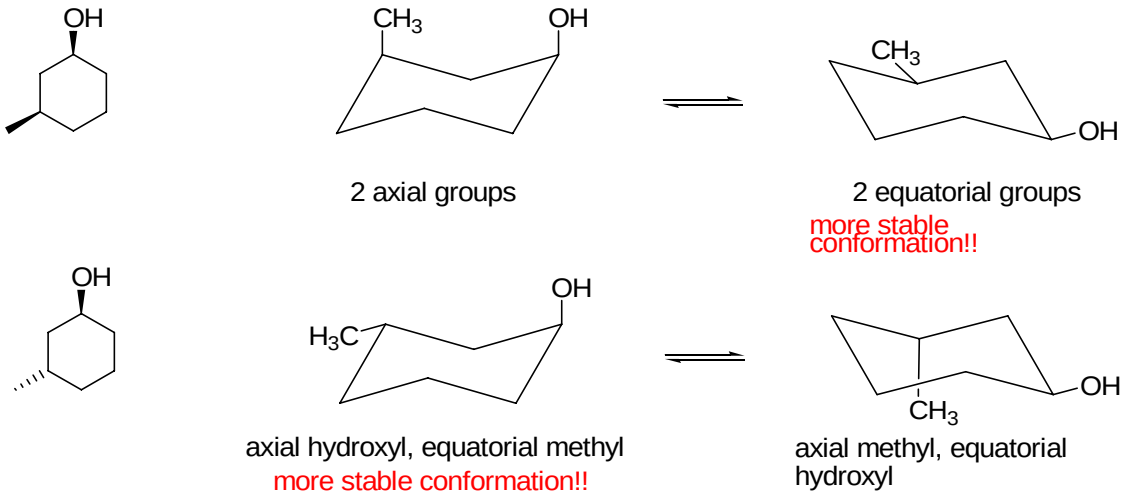
staggered,
<u>one</u> CH_3 --- $C(CH_3)_3$
***gauche* interaction**

eclipsed,
<u>one</u> CH_3 --- $C(CH_3)_3$
***van der Waals* interaction**



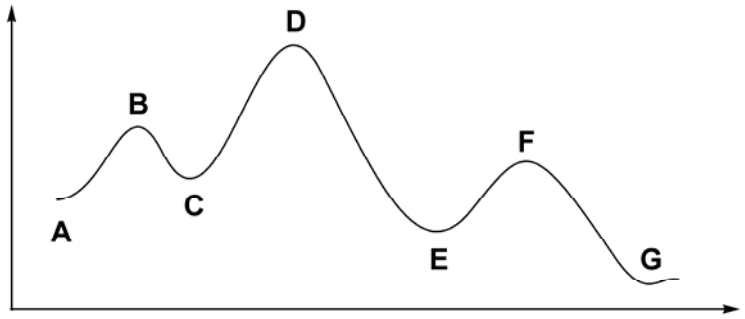
21. (4 pts) Using detailed chair conformation analysis, find out if *cis*-3-methylcyclohexanol or *trans*-3-methylcyclohexanol is the more stable stereoisomer.

Solution: First, analyze each isomer individually, and find out the more stable conformation:



Next, compare the most stable conformations of the two stereoisomers. In the case of the trans isomer we have inevitably one of the substituents axial, while in the cis isomer they are both equatorial and there are no unfavorable interactions. **Conclusion:** Cis-3-methylcyclohexanol is the more stable stereoisomer.

22. (4 pts) Consider the energy diagram shown below and answer the following questions:



a. Does the diagram represent a concerted or a stepwise process? If stepwise, how many steps does it have?

Stepwise, 3 steps

b. What is the rate-determining step?

C ⟶ **E**

c. Which transition states are reactant-like?

D, F

d. Which transition states are product-like?

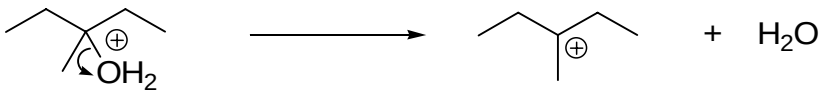
B

e. Which elementary steps are exothermic?

C ⟶ **E** and **E** ⟶ **G**

23. (3 pts) Write the rate-determining step in the reaction of 3-methyl-3-pentanol with HBr.

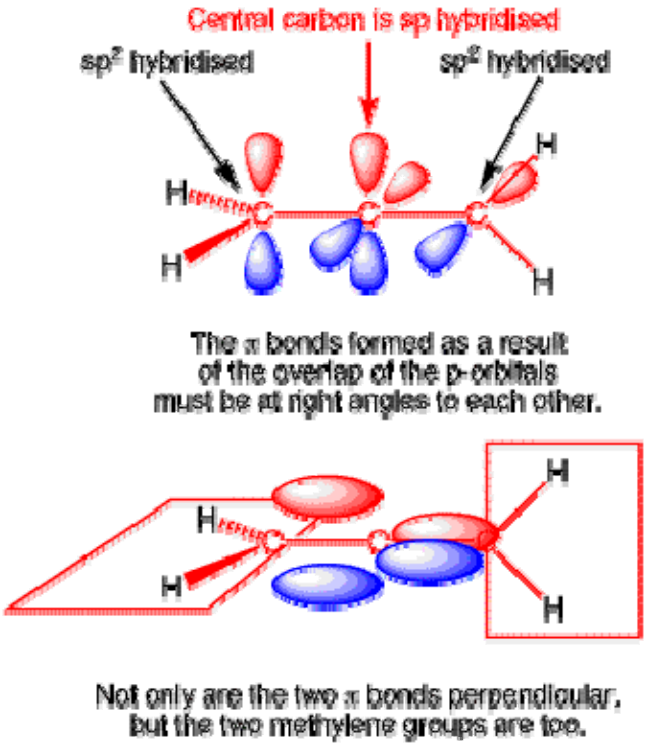
Solution: 3-Methyl-3-pentanol is a tertiary alcohol. When tertiary alcohols react with hydrohalic acids, then the S_N1 mechanism is followed. Therefore the rate-determining step is the formation of the carbocation *via* heterolytic cleavage of the corresponding alkyloxonium ion.



24. (2 pts) **BONUS PROBLEM (In order to receive credit for this problem, it has to be solved entirely!!).** In class, as part of our discussion in Chapter 2, we considered the bonding models of the various carbon – carbon bonds, i.e. single, double and triple. Using the same approach, construct a bonding model for allene (see below). Indicate hybridization for all C – atoms and show how bonds are formed using hybrid or unhybridized orbitals as necessary. Predict the geometry of the molecule.

$H_2C=C=CH_2$

allene



In the molecule of allene the two terminal methylene groups are at a 90° angle with respect to one another: