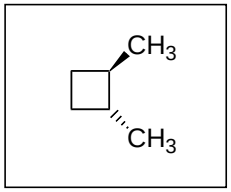
CHEMISTRY 313-01
MIDTERM # 1 – answer key
September 29, 2005

Statistics:

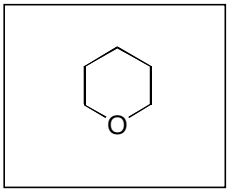
- Average: **75 pts (75%)**;
- Highest: **99 pts (99%)**; Lowest: **31 pts (31%)**
- Number of students performing at or above average: **28 (57%)**
- Number of students performing at or below 55%: **7 (14%)**

1. (12 pts) Mark as true (**T**) or false (**F**) the following statements. Do not explain!
   - (**T**) σ–bonds are stronger than π-bonds;
   - (**T**) Single bonds are always σ-bonds;
   - (**F**) The *gauche* conformation of butane is a global minimum;
   - (**F**) The chair conformation of cyclohexane is a local minimum;
   - (**T**) Cyclopropane has the largest amount of angle strain;
   - (**F**) Molecules with polar bonds always have non-zero dipole moments;
   - (**T**) Stronger acids have lower pK_a values;
   - (**F**) Lewis acids are proton donors;
   - (**T**) Increasing oxidation number indicates an oxidation process;
   - (**F**) Concerted reactions have no more than two elementary steps;
   - (**T**) The *Hammond* postulate relates the energies and structures of two neighboring species on the potential energy profile;
   - (**T**) S_N2 processes are always bimolecular;

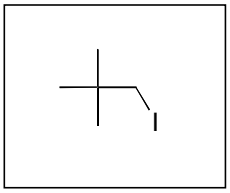
2. (5 pts) Provide the structural formula for each of the following molecules.



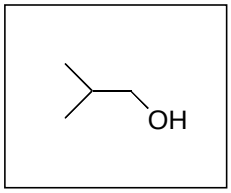
***trans*-1,2-dimethyllcyclobutane**



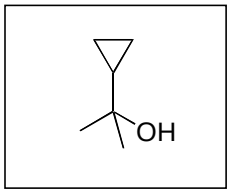
tetrahydropyran



neopentyl iodide



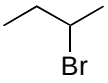
isobutyl alcohol



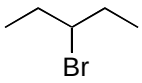
2-cyclopropyl-2-propanol

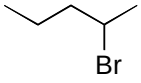
3. (2 pts) While the name *sec*-butyl bromide defines a specific structure, the name *sec*-pentyl bromide is ambiguous. Explain.

***Sec*-butyl bromide defines the following structure:**



The name *sec*-pentyl bromide could be used to define either of the structures below and it is, therefore, ambiguous.

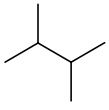




4. (2 pts) Provide a structure for each of the following compounds:
   a. Bicyclo[2,2,2]octane.

   b. Spiro[2,2]pentane.

5. (2 pts) Write the structure of the hexane isomer that has only primary and tertiary carbon atoms.



2,3-dimethylbutane

6. (3 pts) Without referring to tables, decide which member of each of the following pairs would have the higher boiling point. Do not explain!

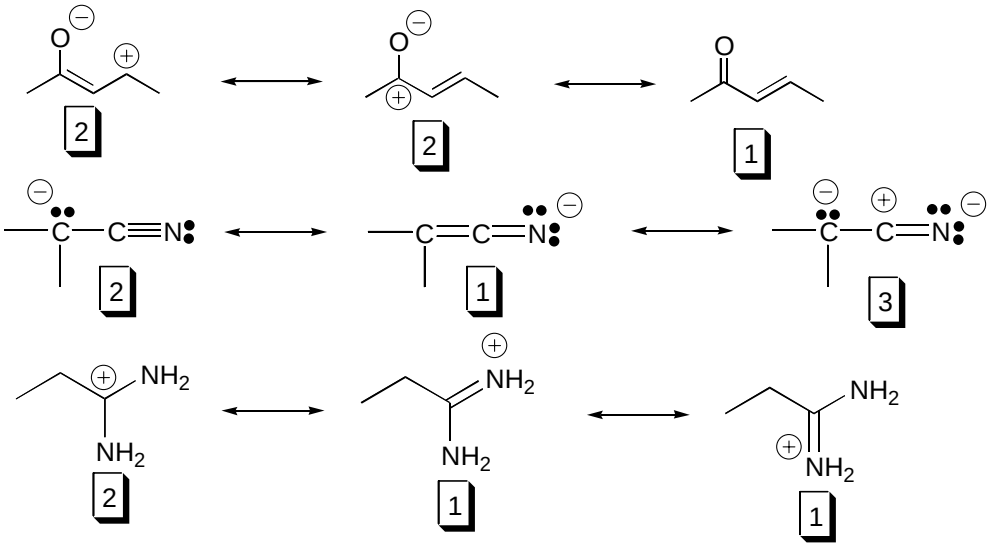
a. Pentane or 2-methylbutane;

b. Heptane or pentane;

c. Propane or 2-chloropropane;

d. 2-Chlorobutane or 2-butanol;

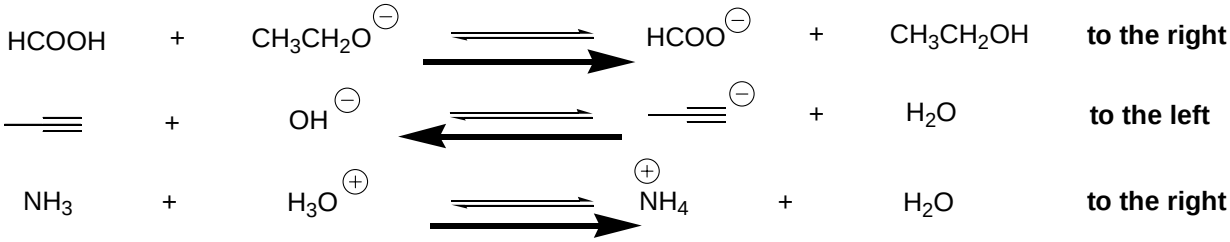
7. (6 pts) Several sets of resonance forms are given below. In each case draw one additional resonance form, then rank the resonance forms (Some may have equal ranking!).



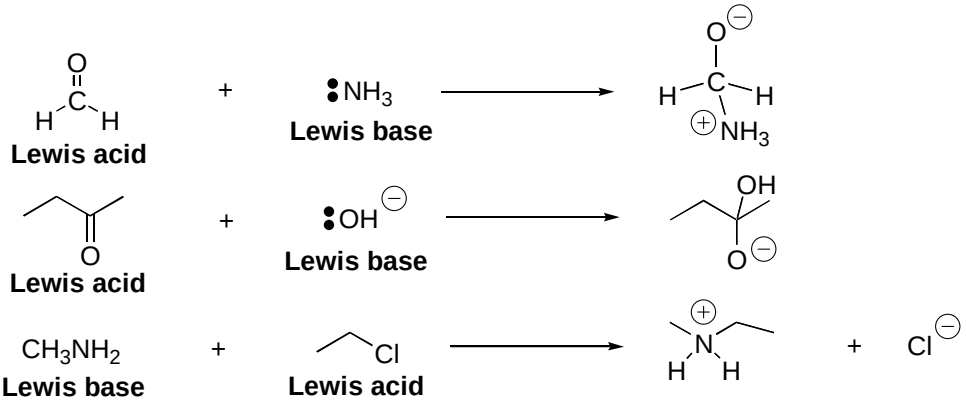
8. (4 pts) Rank the following species in order of increasing basicity. Do not explain!

CH_3O^-	CH_3COO^-	$CH_3CH_2S^-$	NH_2^-	H_2O	HSO_4^-
5	**3**	**4**	**6**	**2**	**1** least basic

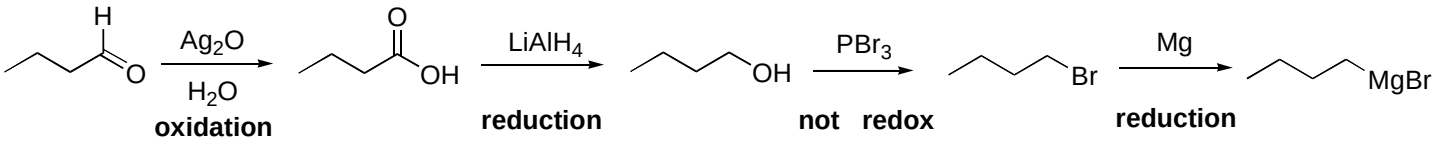
9. (6 pts) Predict the shift of equilibrium (to the left or right) for the following acid – base reactions.



10. (6 pts) Label the reactants in the following acid – base reactions as *Lewis* acids (electrophiles) or *Lewis* bases (nucleophiles).



11. (6 pts) The following is a multistep transformation. Label each step as a **reduction**, **oxidation** or **not redox** with respect to the organic compound.



oxidation **reduction** **not redox** **reduction**

12. (4 pts) Provide formulas for the following functional groups:

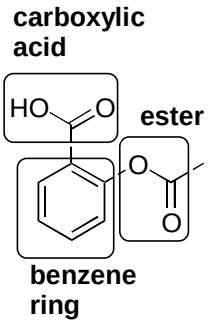
a. Thiol;
-SH

b. Nitrile;
—C≡N

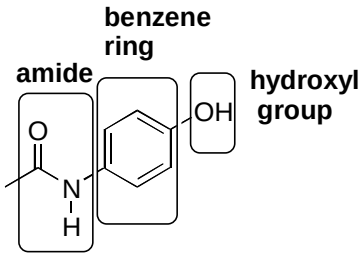
c. Aldehyde;


d. Alkyne;
—C≡CH

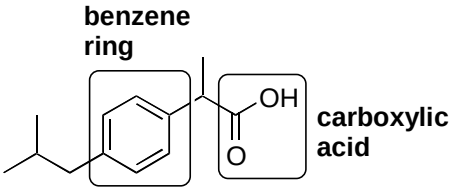
13. (6 pts) Circle and name all functional groups in the following structures.



aspirin



acetaminophen (*Tylenol*)

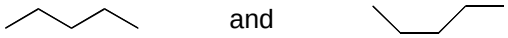


ibuprofen (*Advil*)

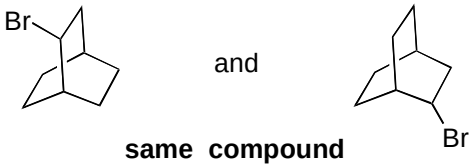
14. (4 pts) Give the relationship between the following pairs of structures. There are four (4) possible relationships: **same compound**, **constitutional isomers**, ***cis-trans* isomers**, **not isomers** (i.e. different molecular formula).

a. $CH_3CH_2CH_2CH_3$ and $(CH_3)_3CH$

constitutional isomers

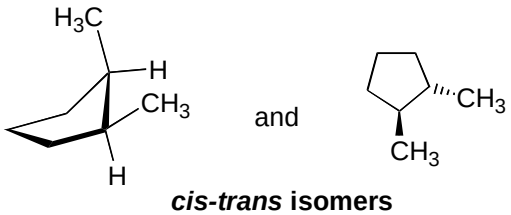
b.  and

same compound

c. 

and

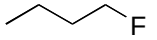
same compound

d. 

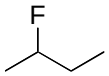
and

***cis-trans* isomers**

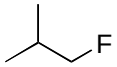
15. (4 pts) There are several isomeric fluorides with formula C_4H_9F. Draw the bond – line formulas of all isomers, provide appropriate names and label the structures as primary, secondary or tertiary fluorides.



1-fluorobutane
or
butyl fluoride
(primary)



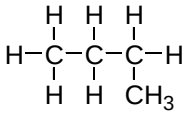
2-fluorobutane
or
***sec*-butyl fluoride**
(secondary)

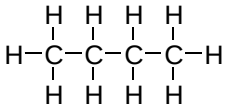


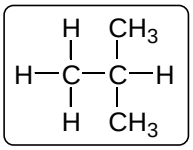
1-fluoro-2-methylpropane
or
isobutyl fluoride
(primary)

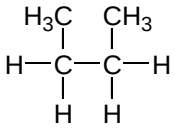
2-fluoro-2-methylpropane
or
***t*-butyl fluoride**
(tertiary)

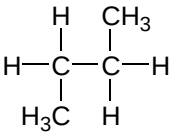
16. (4 pts) In each of the following sets indicate the (one) structure that represents a different compound.

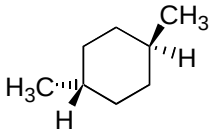


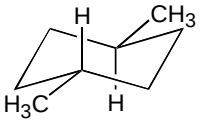


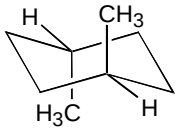


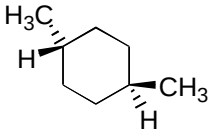


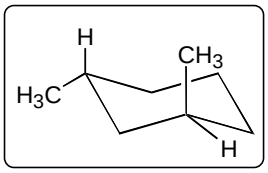




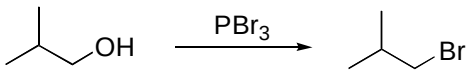


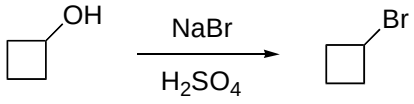


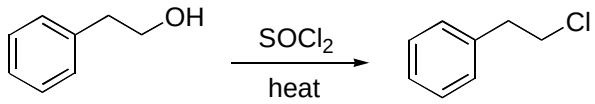




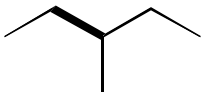
17. (6 pts) Draw the structure of the principle organic product of each of the following reactions.

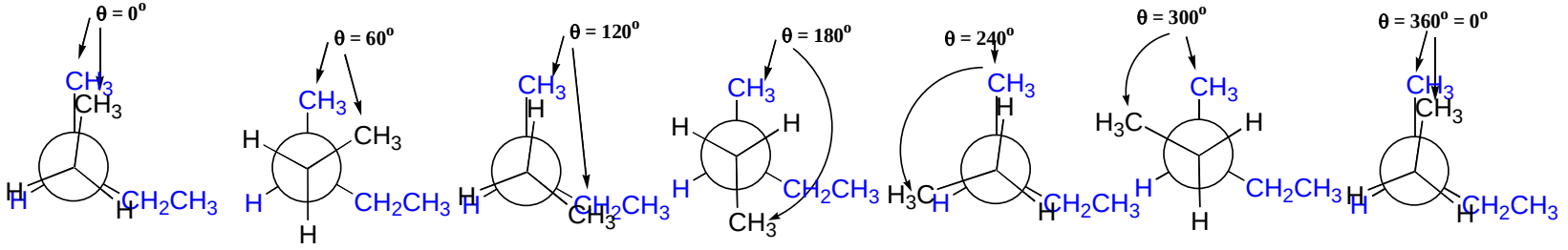






18. (6 pts) Using *Newman* projections, draw the conformations arising upon a full 360° turn (in 60° steps) around the C2 – C3 bond of 3-methylpentane. Represent the energy changes on a qualitative potential energy/dihedral angle diagram. Assign the proper term (i.e. minimum, transition state, etc.) to each conformation.





eclipsed, <u>one</u> CH_3 --- CH_3 *van der Waals* interaction

staggered, <u>one</u> CH_3 --- CH_3 and one CH_3 --- CH_2CH_3 *gauche* interaction

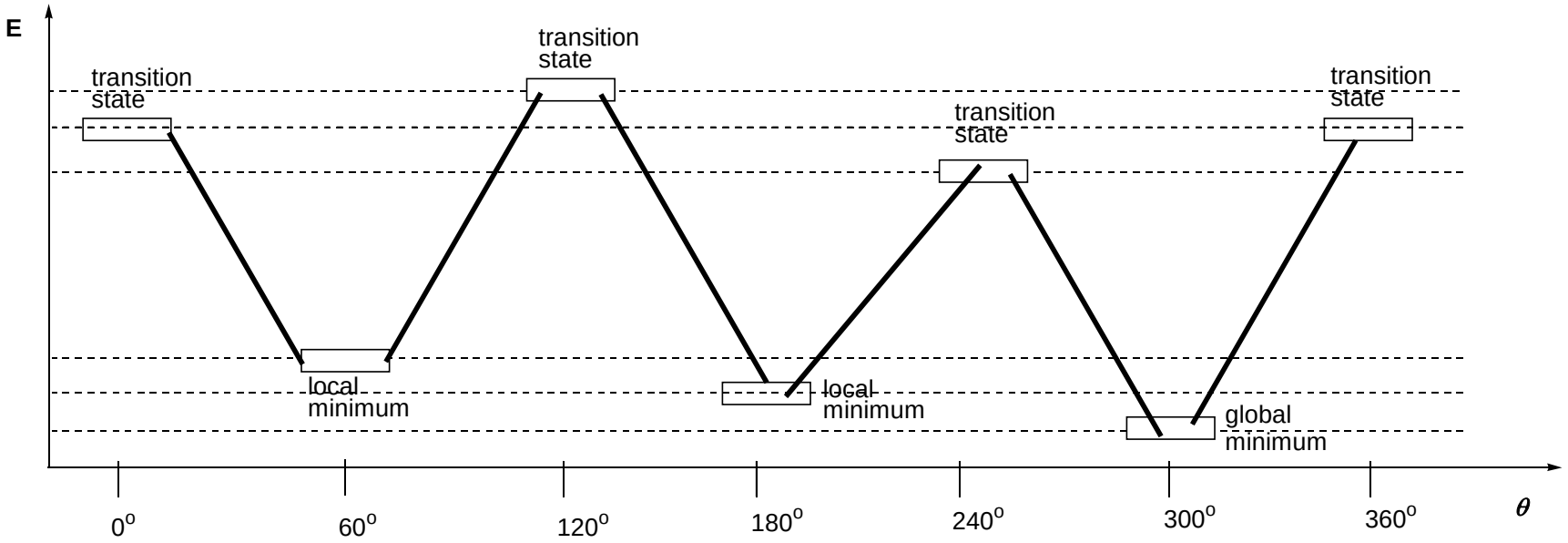
eclipsed, <u>one</u> CH_3 --- CH_2CH_3 *van der Waals* interaction

staggered, <u>one</u> CH_3 --- CH_2CH_3 *gauche* interaction

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

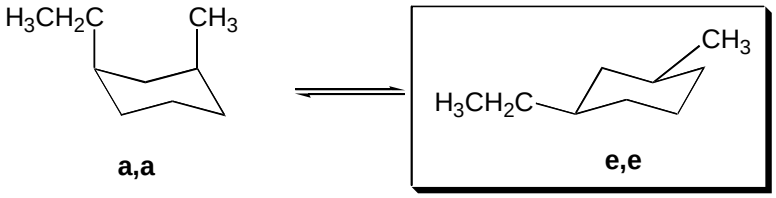
staggered, <u>one</u> CH_3 --- CH_3 *gauche* interaction

eclipsed, <u>one</u> CH_3 --- CH_3 *van der Waals* interaction



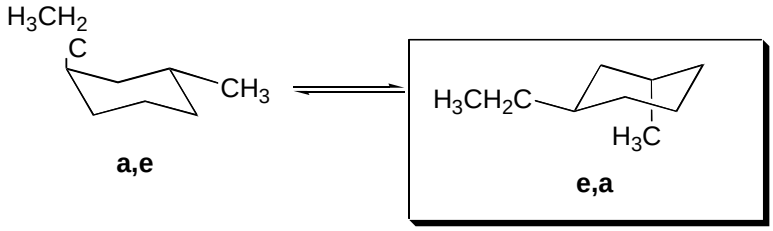
19. (6 pts) Determine whether the *cis*- or *trans*-isomer of 1-ethyl-3-methylcyclohexane is the more stable isomer by providing explicit structural analysis.

Cis-isomer:



more stable conformation

Trans-isomer:



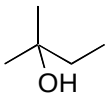
more stable conformation

The more stable conformation of the *trans*-isomer still has on axial methyl group, whereas the more stable conformation of the *cis*-isomer has no axial substituents. Therefore the *cis*-isomer is the more stable isomer.

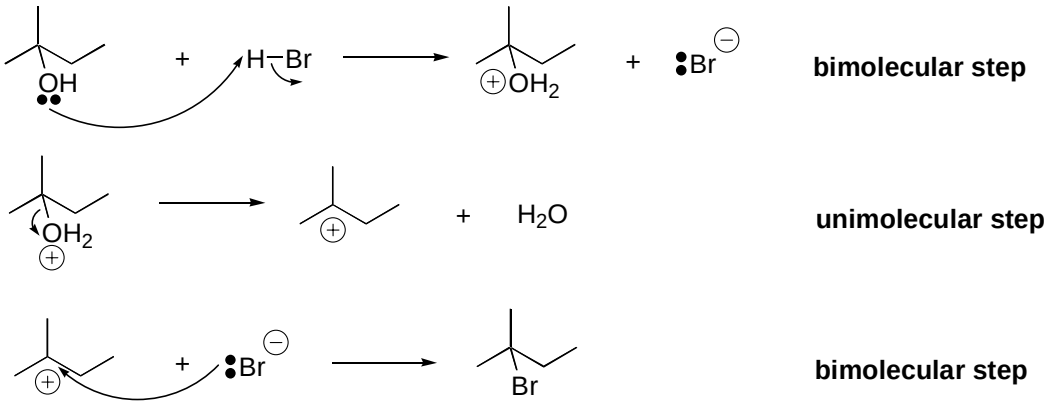
20. (6 pts) Consider isomeric pentanols ($C_5H_{10}O$).
    a. Indicate the alcohol that is most likely to undergo a reaction with HBr according to the S_N1 mechanism (*Hint:* What type of alcohols react fastest in S_N1 reactions?).
    b. Write the individual elementary steps.
    c. Provide a potential energy profile and label appropriately all minima and maxima on the profile.
    d. Classify each elementary step according to molecularity.
    e. Classify each transition state as reactant- or product-like.
    f. Indicate the rate-determining step.

Solution:

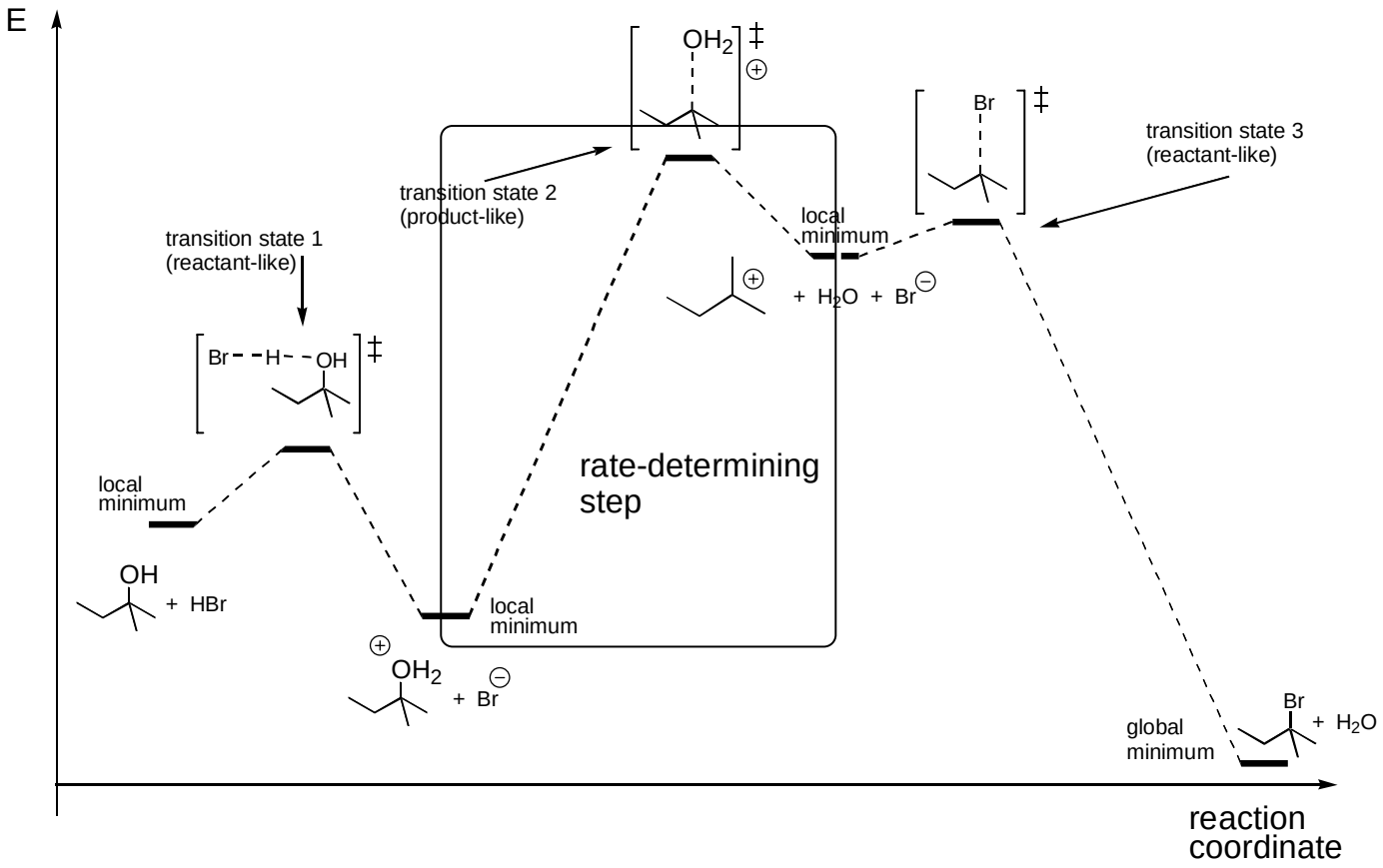
a. Of all possible pentanol isomers, there is only one tertiary alcohol: **2-methyl-2-butanol.** Since it is a tertiary alcohol, then it is the one most likely to undergo an S_N1 process, because it forms the most stable carbocation.



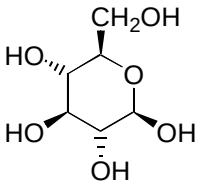
b, d. As any reaction of alcohol with HX, occurring by an S_N1 mechanism, it will have three elementary steps.



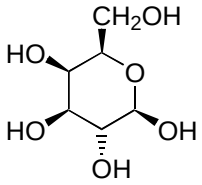
c, e, f. The profile can be presented in the following manner



21. **(3 pts) BONUS PROBLEM (In order to receive credit for this problem, it has to be solved entirely!!).** The structural formulas below belong to two naturally occurring, isomeric carbohydrates: glucose and galactose. Determine which of the two isomers is the more stable one. Support your decision by appropriate structural representations.

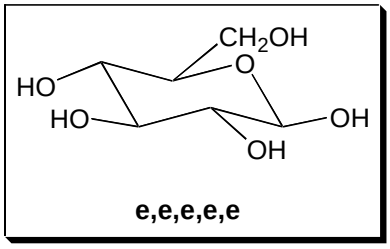


β-D-glucose

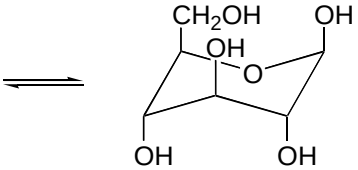


β-D-galactose

For β-D-glucose:



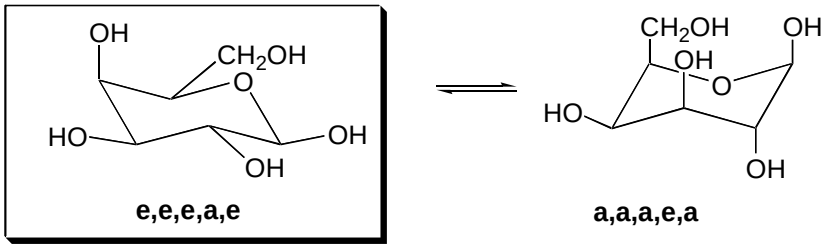
e,e,e,e,e



a,a,a,a,a

more stable conformation

For β-D-galactose:



more stable conformation

The more stable chair conformation of β-D-glucose has all substituents equatorial. In the more stable conformation of β-D-galactose one OH-group is axial. Hence β-D-glucose has lower energy (is more stable) than β-D-galactose.