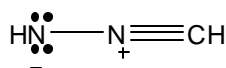
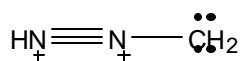
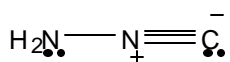
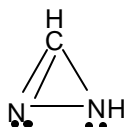
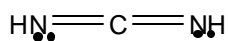
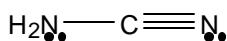
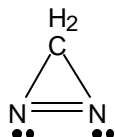
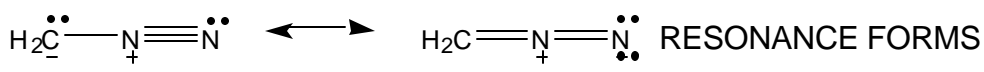


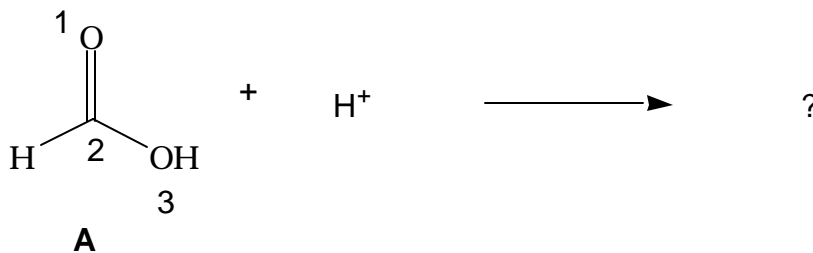
Exam 1 Chem 3045x Friday, October 1, 1999

ANSWER KEY:

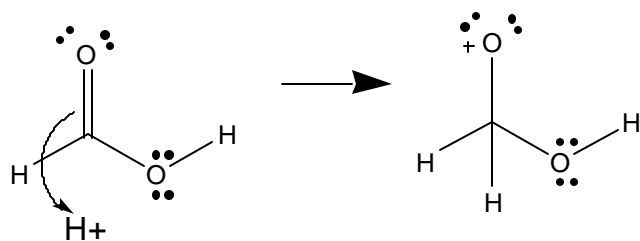
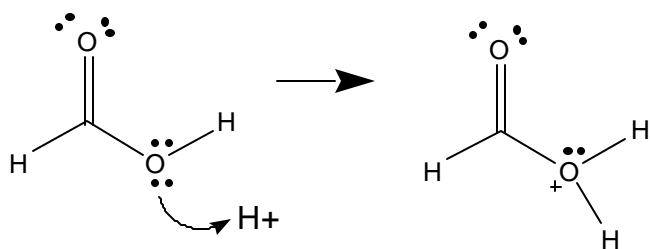
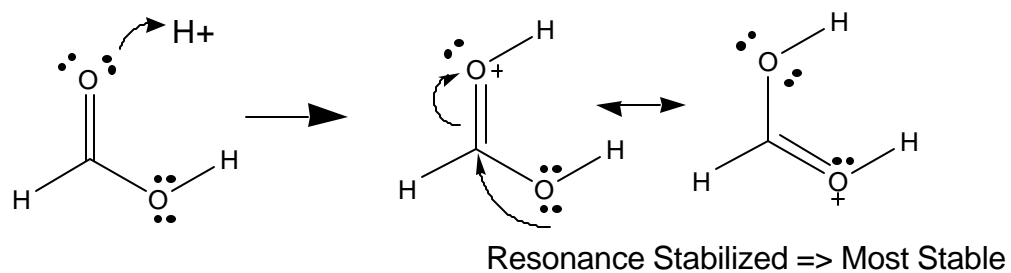
1. (10 Points). Consider the composition CH_2N_2 . Draw the Lewis structures of 5 constitutional isomers which possess this composition. The structures must obey the octet rule and explicitly indicate the formal charges on any of the atoms.



2. (15 Points). Consider the reaction of formic acid (**A**) with a proton. The proton could be imagined to add to either of the oxygen atoms (1 or 3) or to the carbon atom (2).



- (a) Draw the Lewis structures resulting from each possibility and draw a circle around the Lewis structure that you believe would be the most likely (most stable).

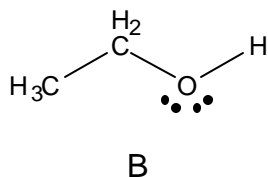
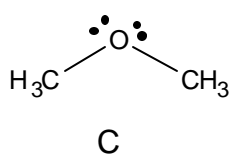


(b) Give your reasoning for selection of the most stable structure.

O1 protonation most stable because it is resonance stabilized.

3. (15 Points). Consider the composition C_2H_6O . There are two constitutional isomers which are consistent with this composition.

(a) Draw the Lewis structures for each these two isomers.

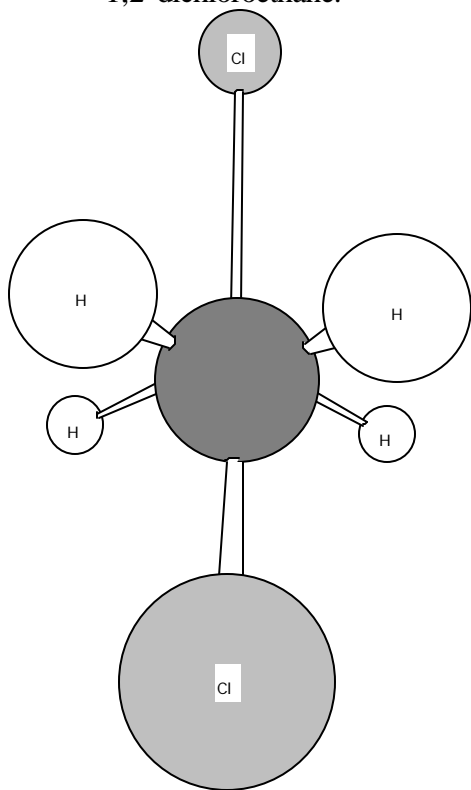


- (b) In fact, two substances and only two substances possessing the composition are known to exist and are quite stable. One of these substances (**B**) boils at 78 °C and the other substance (**C**) is a gas at room temperature (20 °C). Draw a circle around the structure you have written above for the isomer that boils at 78 °C and label it **B**.
- (c) Explain why **B** has a much higher boiling point than **C**.

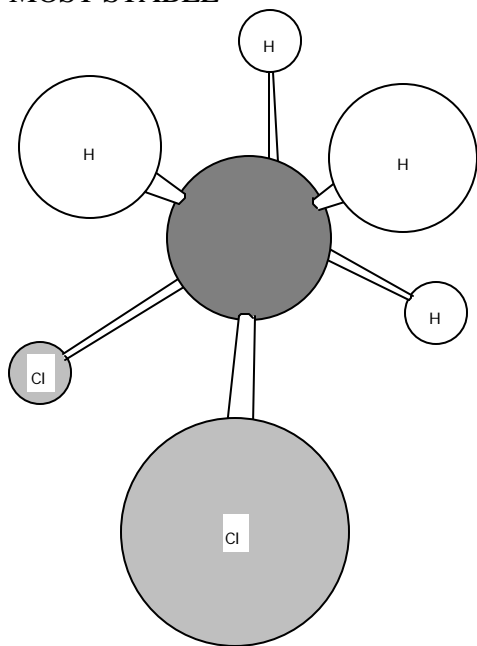
Both molecules have similar shapes and sizes. **C** does not possess hydrogen bonding ability. **B** can hydrogen bond, like water. Intermolecular hydrogen bonding causes strong intermolecular interactions for **B** and a higher boiling point.
(see p. 127 Text)

4. (15 Points). Consider the substance 1,2-dichloroethane.

(a) Draw the Newman projection for the most stable and the next most stable conformer of 1,2-dichloroethane.



MOST STABLE



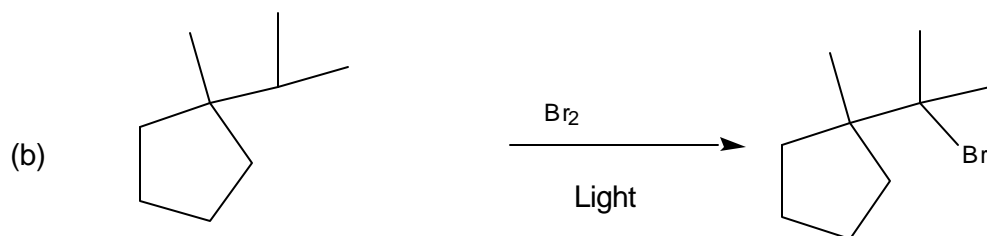
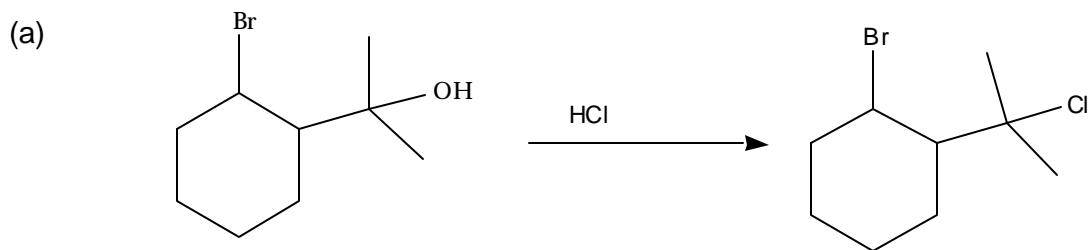
Next Most Stable

- (b) At room temperature 1,2-dichloroethane is reported to possess a dipole moment of approximately 1 Debye. However, at very low temperatures (near -273°C), it is reported that the dipole moment of 1,2-dichloroethane is approximately 0 Debye units. Assuming that both reports are correct, use your knowledge of conformational analysis to explain why the dipole moment of 1,2-dichloroethane is finite (1 Debye) at room temperature and 0 at very low temperature.

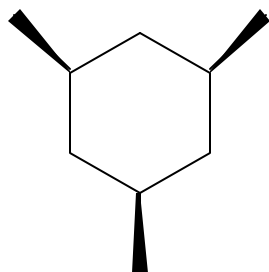
At Room Temperature, a small population of gauche dichloroethane exists (since the thermal energy is high enough to allow some of this higher energy conformation). This form has a dipole moment.

At very low temperature, only the anti-form exists. This form has zero dipole moment.

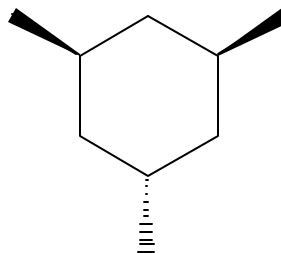
5. (10 Points). Draw the structure of the major product expected from each of the following reactions. You do not need to draw a mechanism, just the Lewis structure of the major product:



6. (10 Points). Consider the two isomeric 1,3,5-trimethyl cyclohexanes (**D** and **E**) whose wedge-dash structures are shown below.

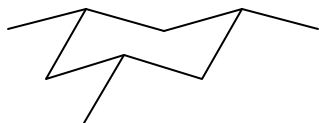


D



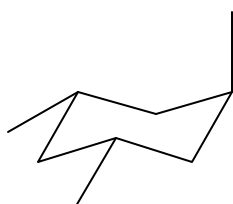
E

- (a) Draw clearly the most stable conformation of **D** and the most stable conformation of **E**. Label the methyl groups as axial or equatorial in each drawing.



All equatorial.

D, most stable conformer



2 eq. 1 axial.

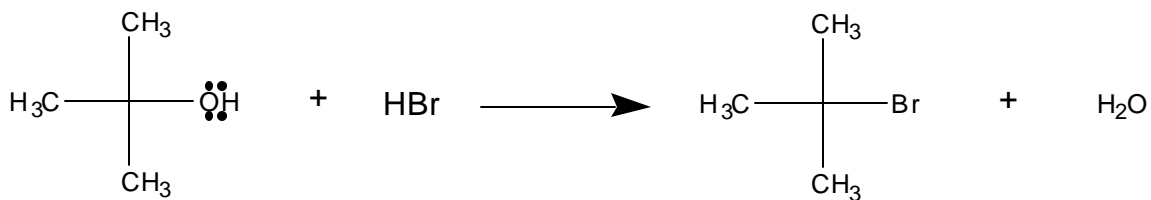
E) most stable conformer

- (b) Which of the two isomers, **D** or **E** is more stable? Explain.

D is more stable since in this conformation all methyl groups are equatorial, compared to **E**, in which 1 methyl group is axial.

7. (20 Points). Consider the reaction of $(\text{CH}_3)_3\text{COH}$ with HBr .

(a) Draw the Lewis structure of the major product expect from reaction.



(b) Draw an energy diagram of the reaction profile for all of the elementary steps leading from reactants to products, indicating clearly energy maxima and minima and their relative energies. Draw the structures of any reactive intermediates and transitions above the appropriate energy positions in the energy diagram.

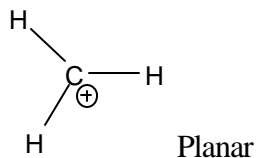
See Text p. 141, Figure 4.11

(c) Would you the addition of NaBr to influence the rate of the reaction? Explain.

This is an $\text{S}_\text{N}1$ reaction. The rate determining step involves breaking the carbon-oxygen bond of the oxonium ion. This step does not involve Br^- , therefore no effect of added NaBr .

8. (10 Points). The most stable structure of a methyl carbonium ion could theoretically be either planar or non-planar.

(a) Draw clearly the most stable structure of the methyl carbonium ion and indicate whether it is planar or non-planar.



(b) Discuss briefly the reason(s) for your selection of the planar or non-planar structure.

- 1) sp^2 bonds stronger than sp^3 , planar conformation has 3 sp^2 bonds.
- 2) planar conformation puts all s-character into bonds which have electrons.
- 3) planar conformation has less steric hindrance between bonds (VSEPR), C-H bond electrons come closer to the nucleus.