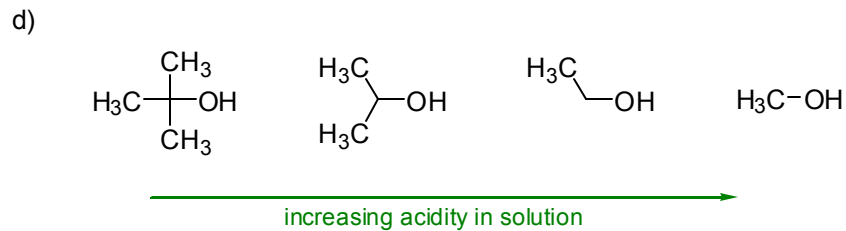
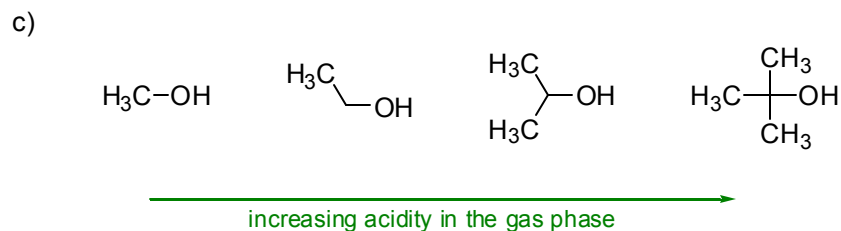
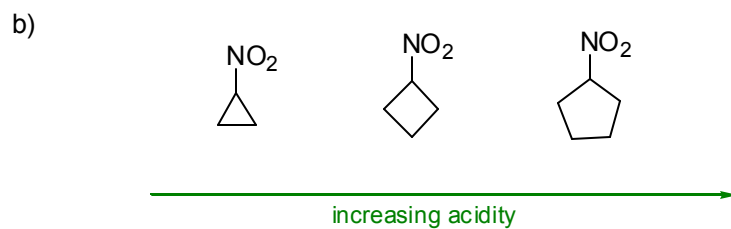
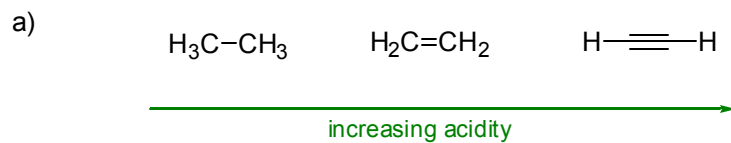


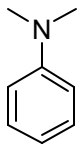
Exam I Review Problem Set

Problem 1 (refer to the Evans pK_a table and *Solvents and Solvent Effects in Organic Chemistry* by C. Reichardt). Explain the trend in relative acidity for each of the following series of compounds.



Problem 2 Answer the following set of ostensibly unrelated questions.

- a) Compounds **A** and **B** both contain sp^2 hybridized nitrogens. Which compound do you expect to be more basic? Explain.

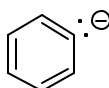


A



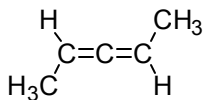
B

- b) Draw all resonance structures for **C**

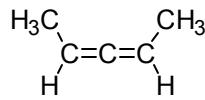


C

- c) Which compound below is more reactive/less stable? Do you expect their difference in energy to be greater or less than that of *E*- vs. *Z*-2-butene?



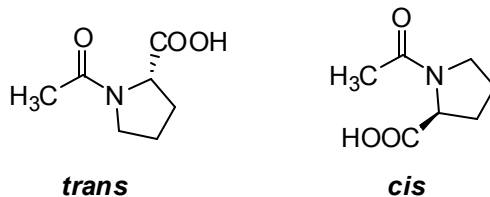
D



E

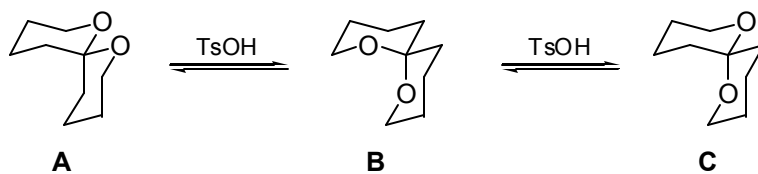
Problem 3 (based on K.R. Williams. *J. Chem. Educ.* **2002**, 79, 372). The study of conformational analysis is especially important in protein chemistry.

- a) N-acetyl-L-proline exists as two stereoisomers that interconvert at room temperature and can be distinguished by NMR. Explain how a *cis-trans* relationship can exist about a single bond:

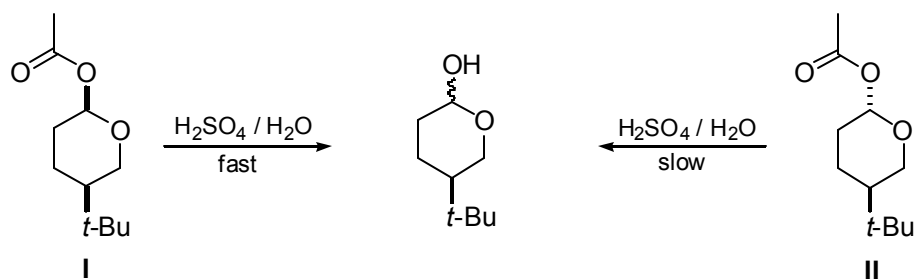


- b) The equilibrium constant, K , for *cis-to-trans* interconversion can be determined by NMR. In a deuterated benzene-methylene chloride ($C_6D_6-CDCl_2$) solvent system, $K = 8.7$ (favoring the *trans* isomer). In heavy water (D_2O) buffered at pH = 7, $K = 0.81$. Explain why the *trans* stereoisomer is favored in organic solvent and why this predominance is reversed in the latter case.

Problem 4 (taken from Chem 30, Exam I, Fall 2000). The spiroketal compound below isomerizes in the presence of acid. Of the three isomers shown (**A–C**), which structure would you expect to be the most stable? Which structure would you expect to be the least stable? Explain your selections.



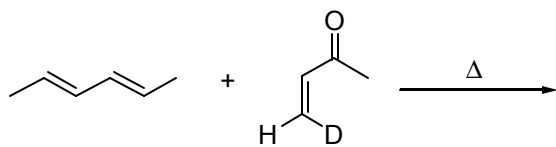
Problem 5 (taken from Chem 30, Exam I, Fall 2000). The rate of hydrolysis of acetals **I** and **II** is observed to depend on the concentration of acid in solution.



a) Using either isomer, propose an arrow formalism mechanism for this transformation that is consistent with the observation that the rate depends on $[\text{H}^+]$.

b) Explain why isomer **I** hydrolyzes faster than isomer **II**

Problem 6. Answer the following question about the reaction below.

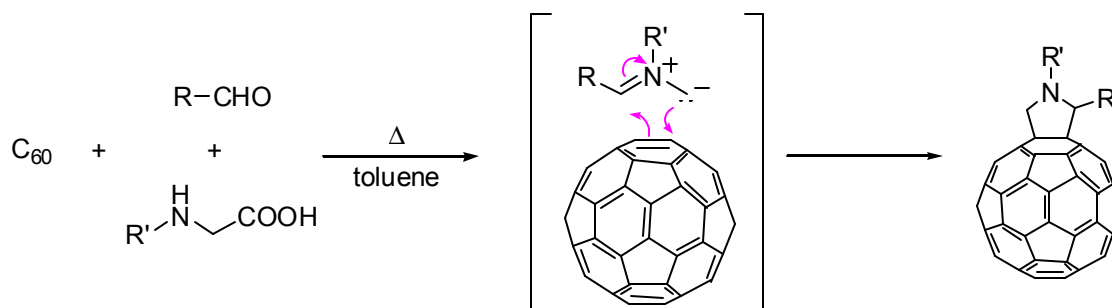


a) Predict the major product of this reaction. Indicate the relative stereochemistry of the substituents.

b) Build all of the π molecular orbitals for the diene and dienophile. Classify the reaction as [m+n].

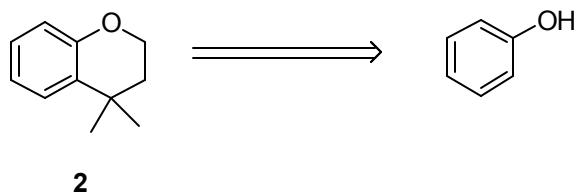
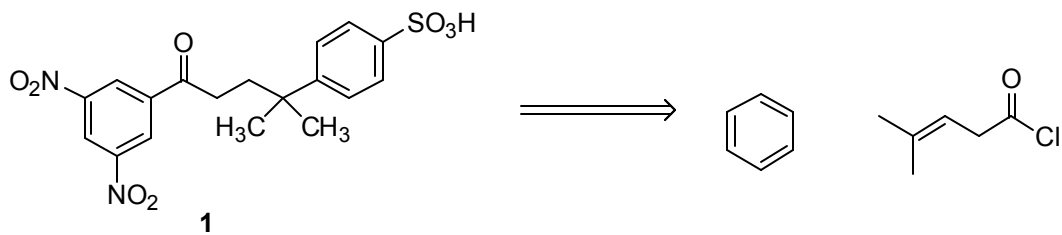
c) The reaction is accelerated when AlCl_3 is added. Provide an explanation that accounts for this result.

Problem 7 (taken from Chem 30, Problem Set 9, 2003). The [6,6] double bonds in C_{60} show similar reactivity to electron deficient olefins. The addition of azomethine ylides to C_{60} is known to fullerene chemists as the Prato Reaction. It is the most popular method to functionalize “buckyballs,” allotropes of carbon with cage-like structures.

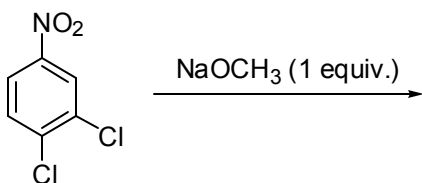
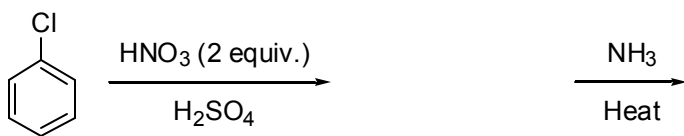


- Classify the cycloaddition in the last step shown above as $[m+n]$
- Build all of the π molecular orbitals for both the ylide and the olefin.
- Assign the HOMO–LUMO interaction for this reaction. Explain why it is allowed to proceed as a concerted process with heat.

Problem 8. Provide syntheses of the following compounds from the indicated starting materials. You may also use any reagents containing five or fewer carbon atoms as a source of carbon in your product.



Problem 9. Predict the products of the reactions shown below. Justify the substitution patterns.



Problem 10. The compound below has an unusually high dipole moment for a hydrocarbon. Provide an explanation for this observation.

