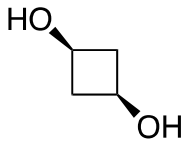
NTNU

Faculty of Natural Sciences and Technology

Exam in:	**TKJ 4180 – Physical Organic chemistry**
Date:	**15. December 2012**
Time for exam:	**9:00-13:00**

Contact person during exam: Mohamed Amedjkouh
Phone no: 904 12 166
12 pages.

Problem 1. (10 points)
The next question refers to the set of diols that are drawn below. Circle the diols that are chiral. Next, put a (*) near any structure that is meso. Then, state the relationship of the alcohol groups (homotopic, enantiotopic, diastereotopic) on the line below each diol.



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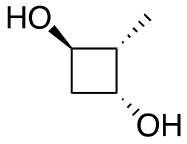

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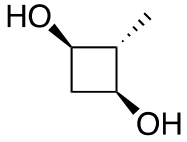

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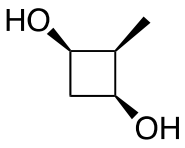

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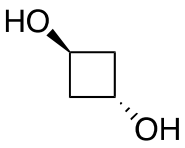

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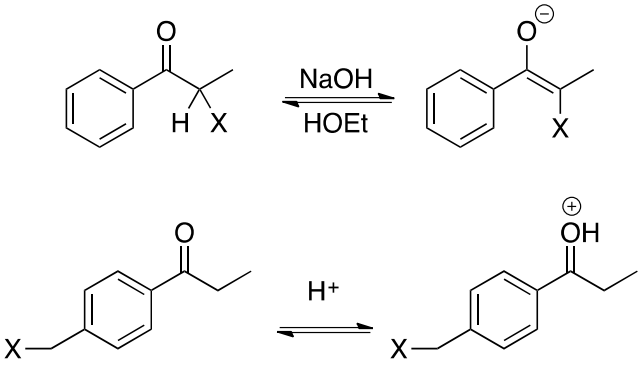
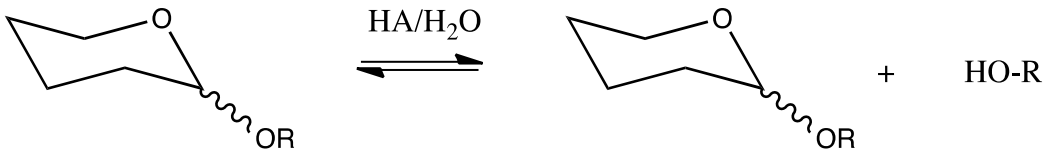
Problem 2. (10 points)

In the following reactions substituent X was varied between electron donating and electron withdrawing. If you use the usual σ values, do you expect a positive or a negative ρ value for each equilibrium? Should each reaction be more sensitive to the X substituent than benzoic acid? Explain

your reasoning for each answer.



Problem 3. (10 points)
For the general cleavage of pyranyl ethers shown below:

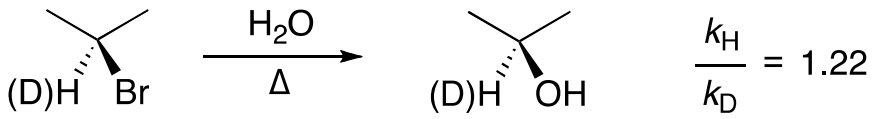


a) Write a specific-acid-catalyzed mechanism for this reaction. Show all arrow pushing.

b) Write a general-acid-catalyzed mechanism for this reaction. Show all arrow pushing.

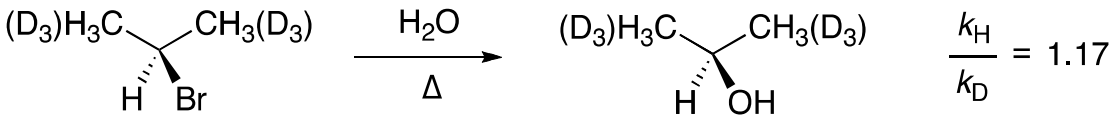
c) In the general-acid-catalyzed mechanism, is the reverse mechanism also general-acid catalyzed or some kinetic equivalent? Briefly explain your answer.

Problem 4. (8 points)
During the S_N1 solvolysis of isopropyl bromide in water, we see the following isotope effect:



a) Explain the origin of this isotope effect by explaining what vibrational mode is changing in the rate determining step of this reaction.

We also observe the following isotope effect:

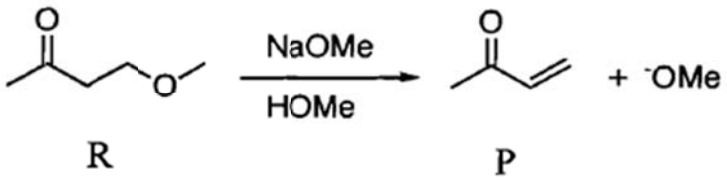


b) During the S_N1 rate-determining step, explain how the methyl groups are involved in facilitating the reaction?

c) Explain the origin of this isotope effect by explaining what vibrational mode is changing.

Problem 5. (12 points)

a) Draw the ElcB mechanism for the following reaction. Show all arrow pushing.



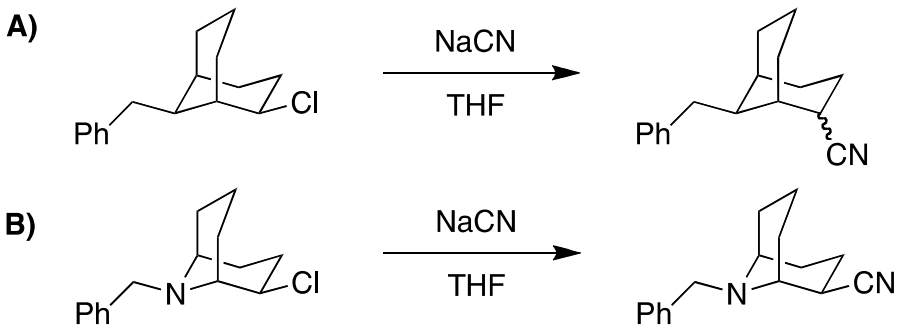
b) Derive the rate law for this reaction using the steady state approximation for the intermediate you drew in part (a), as seen in class and the text. Show all work.

c) If methoxide/methanol is used as a buffer in large excess of R, how does the kinetic expression change? Show your work.

d) Briefly explain why this mechanism is called ElcB.

e) What kind of base catalysis is involved in the ElcB mechanism?

Problem 6. (12 points)
This question refers to cyanide substitution of two different bicyclo[3.3.1]nonane compounds. The reactions are shown below.



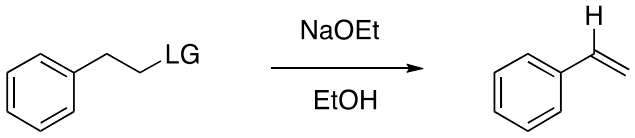
a. When the substitution noted in A) is carried out, we see no dependence of the rate on the concentration of the nucleophile. Additionally, we see that the stereochemistry of the addition is scrambled. Draw a mechanism that is consistent with these experimental observations.

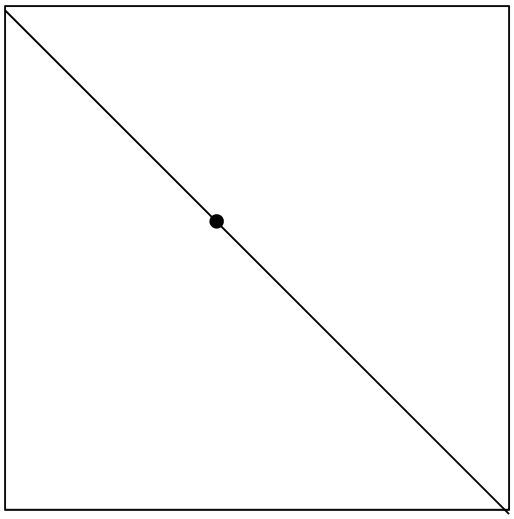
b. When the substitution noted in B) is carried out, we also see no dependence of the rate on the concentration of the nucleophile. In this case we see that substitution leads to a retention of stereochemistry. Draw the intermediate you would expect for this reaction.

c. This question refers to the intermediate that you have drawn for the mechanisms in parts a and b. Considering the structure of these intermediates, how can you rationalize the stereochemical outcome of these reactions?

d. One of these reactions proceeds significantly faster than the other. Which reaction goes faster? Why?

Problem 7. (20 points)
For the following elimination reaction, fill in the corners on the More-O'Ferrall-Jencks plot.





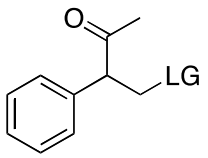
a. Show what happens to the E2 transition state when the leaving group is changed from I to F, label this point as “T.S.1”.

b. How does this affect leaving group departure?

c. How does this affect the extent of deprotonation?

d. As the leaving group is changed from I to F, the ρ value in the corresponding Hammett plot changes from 2.07 to 3.12. Explain this result, by relating back to your results obtained with the More-O’Ferrall-Jencks plot.

e. If the reactant is changed to put an acetyl group at the benzyl position, (pictured at the right) show on the above plot what happens to E2 transition state and label this point as “T.S.2”.



f. How does this affect leaving group departure?

g. How does this affect extent of deprotonation?

h. With the acetyl group, the mechanism might change to $E1_{CB}$. If the mechanism were to convert to $E1_{CB}$, write a rate law for this elimination mechanism. Use the steady state approximation if you like.

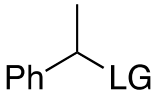
$$\frac{dP}{dt} =$$

i. What experimental parameter actually controls the reaction rate as concluded by your rate law in part h, if the second step is rate determining?

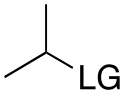
Problem 8. (8 points)

Choose between the following options to maximize the probability of an S_N2 mechanism and to minimize the probability of an S_N1 mechanism. Briefly explain each of your choices. (For part c, ε=dielectric constant).

a. Reactant:



or



b. Nucleophile:

Me_3N or $N_3^{\ominus}$

c. Solvent:

CF_3CH_2OH or CH_3OH

(ε= 39) (ε= 33)

d. Concentration of Nucleophile: High or Low

Problem 9. (10 points)

Consider the following pericyc1ic reaction:

To help you, we have labeled one bond bold that is NOT changing in the reaction.

Methyl group points over the ring

Methyl group points out and away from the ring

(a) Draw arrow pushing that is appropriate for this reaction.

(b) What is the pericyc1ic reaction name for this reaction?

(c) Using the generalized orbital symmetry rule and the terms antarafacial and suprafacial, explain if the reaction is allowed with the stereochemistry given.