

Chemistry 212 — Fall Semester 1996 Examination #1

University of Missouri—Columbia
Prof. Rainer Glaser
Wednesday, September 18, 1996
103 Schlundt Hall, 8:40 - 9:30

featuring
Benzene, Aromaticity, and Electrophilic Aromatic Substitution
Chemistry of Aldehydes and Ketones (A's & K's)

Your Name:

Herr Rainer Glaser

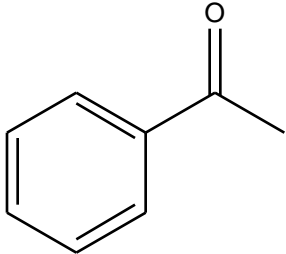
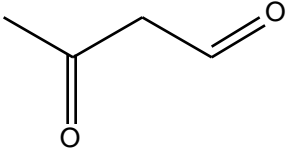
	Max.	Yours
Question 1	20	
Question 2	20	
Question 3	20	
Question 4	20	
Question 5	20	
Total	100	



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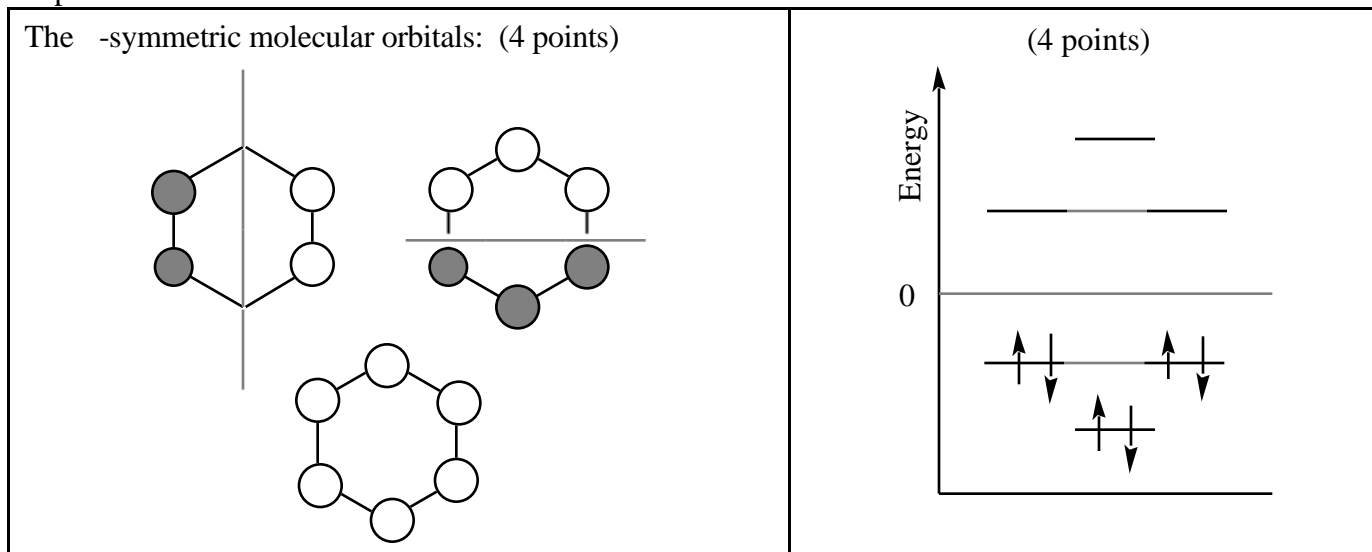


Question 1. Things to Know: Nomenclature, Special Reagents, and Numbers. (20 points)

 Trivialname: Acetophenone (1 point)	<p style="text-align: center;">Styrene Draw structure & provide IUPAC name</p> <p style="text-align: center;">Ph-CH=CH₂ Ethenylbenzene (1 point, 0.5 str., 0.5 name)</p>	<p style="text-align: center;">Mesitylene Draw structure</p> <p style="text-align: center;">draw 1,3,5-trimethylbenzene (1 point)</p>
<p style="text-align: center;">para-Chlorobenzaldehyde Draw structure</p> <p>0.5 points for constitution 0.5 points for getting para OK (1 point)</p>	 IUPAC Name: 3-oxobutanal (1 point)	<p style="text-align: center;">Acetaldehyde Draw structure and name using the -al nomenclature</p> <p style="text-align: center;">Draw Me-CHO Ethanal (1 point)</p>
The CC bond length in benzene: 1.40±0.02 Å (1 for number, 0.5 for unit)	Wavenumber of (CO) of A's & K's: 1700±100 1/cm (1 for number, 0.5 for unit)	
The chemical shift of the hydrogen in the -CHO group occurs at about <u>10</u> ppm because the H is attached to a highly <u>electron-deficient</u> carbon. (deshielded OK) (1+0.5 points)	The chemical shifts of aromatic hydrogens fall in the range <u>7.5 - 8.5</u> ppm. These high chemical shifts are due to a ring current that causes the aromatic hydrogens to be <u>more</u> (more/less) deshielded. (1+0.5 points)	
A reagent to oxidize allylic alcohols to , - unsaturated aldehydes and ketones without touching any other alcohol functions present in the molecule: <p style="text-align: center;">MnO₂ (1 point)</p>	A reagent to oxidize primary alcohols to aldehydes without overoxidation to the respective carboxylic acid (do not just write down the three letter abbreviation, write down what the reagent contains): <p style="text-align: center;">PCC = CrO₃, pyridine, HCl (3 points)</p>	
A reagent to oxidize aniline to nitrobenzene: <p style="text-align: center;">F₃CCO₃H (2 points)</p>	A reagent to reduce nitrobenzene to aniline. <p style="text-align: center;">Zn / HCl or Fe / HCl (2 points)</p>	

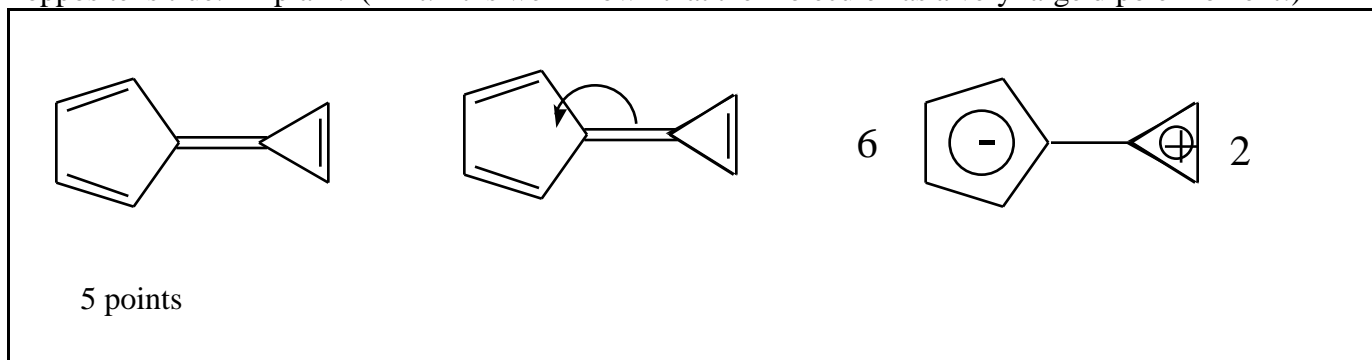
Question 2. Things to Understand: Benzene & Aromaticity. (20 points)

(a) Draw the occupied molecular orbitals of benzene using the “top view” style frequently used in the lecture. Indicate nodes clearly. To the right, draw a schematic energy level diagram for all of the benzene -MOs. Clearly indicate whether any of the MOs are degenerate. Indicate occupancy of the MOs with “up” and “down” arrows in the usual fashion.



(b) The Hückel rule states that cyclic, planar, conjugated systems with $4N+2$ electrons are particularly stable, where “N” is an integer and $N=0$ is the lowest possible number. What matters is the number of electrons in the π -system while the ring size is not so important. For example, benzene contains 6 π -electrons distributed over an equal number of atoms. However, in tropylium ion (1,3,5-cycloheptatrienyl cation) 6 π -electrons are distributed over 7 atoms and in cyclopentadienyl anion six π -electrons are distributed over 5 atoms and both of these systems clearly are aromatic. ($2+1+1+1+1+2$ p.)

(c) The molecule shown is “kind of weird”. Counting electrons in the π -system, we’d say that this molecule obviously is not (is, is not) aromatic. Yet, a closer inspection reveals that in fact the opposite is true. Explain. (Hint: It is well known that the molecule has a very large dipole moment!)

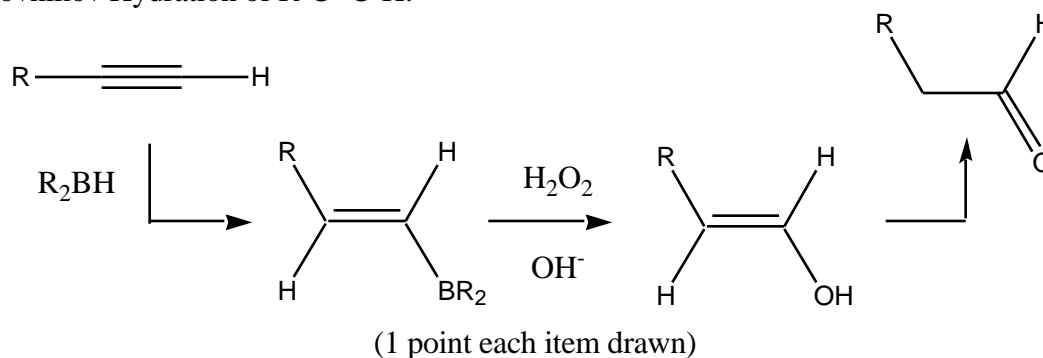


Question 3. Things to Control: Regiochemistry. (20 points)

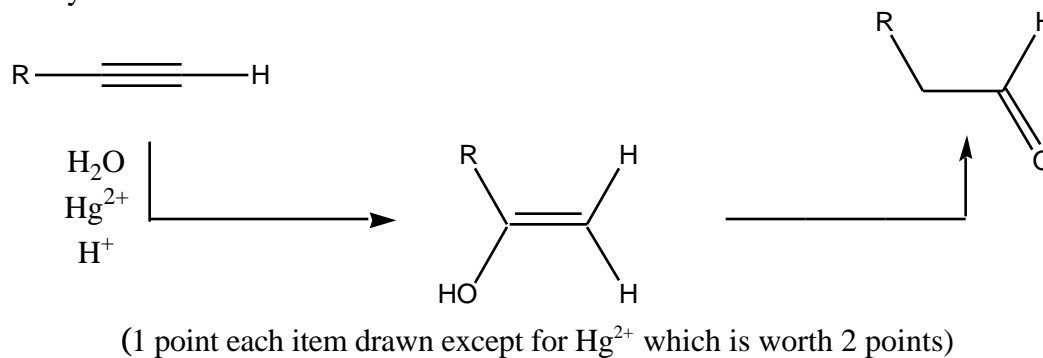
Whenever a reaction has the potential to result in different constitution isomers, then we need to pay attention to regiochemical issues. Whenever a reaction has the potential to result in cis/trans isomers or in chiral products, then we need to pay attention to stereochemical issues. Knowing a reaction that affords the making and breaking of certain bonds will get us only so far. To get there with the right regiochemistry and the right stereochemistry is the real task and solving the regio- and stereochemical issues can be just as hard as finding a new reaction in the first place. Let's review two regiochemical issues that we have studied in the past few weeks.

(a) The hydration of a terminal alkyne R-C≡C-H poses a regiochemical issue in that the new C-O bond can be formed with the C-atom that carries the H-atom or with the C-atom that carries the R-group. Fortunately, the problem has been solved and reactions are now at our disposal that can afford either outcome in a selective fashion. Show these reactions in the appropriate boxes. Show relevant intermediates and clearly show the reagents, catalysts and so on.

Anti-Markovnikov Hydration of R-C≡C-H:

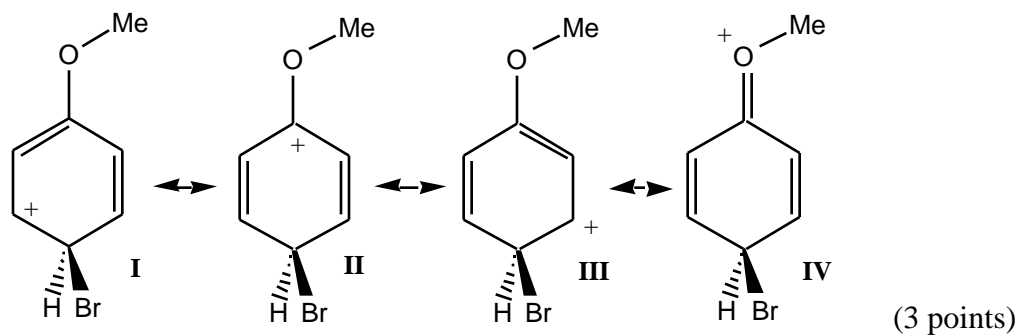


Markovnikov Hydration of R-C≡C-H:

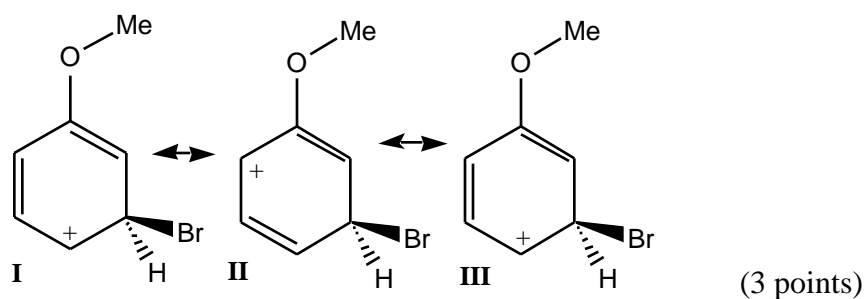


(b) Studying the “directing effects” of substituents on a subsequent electrophilic aromatic substitution is one of **the** classical regiochemical issues. Briefly explain why anisole (aka methoxybenzene) is more likely to be brominated in the *para*-position than in the *meta*-position. Draw relevant resonance forms of the two σ -complexes and explain the preference. (Don’t say anything about the *ortho*-substitution. We all know by now that it is pretty much the same as with the *para*-substitution.)

The σ -complex leading to the *para*-substituted product:



The σ -complex leading to the *meta*-substituted product:



Explain why the formation of the *para*-product is preferred over the formation of the *meta*-product:

para case allows for Rfs where the + charge is close to O.

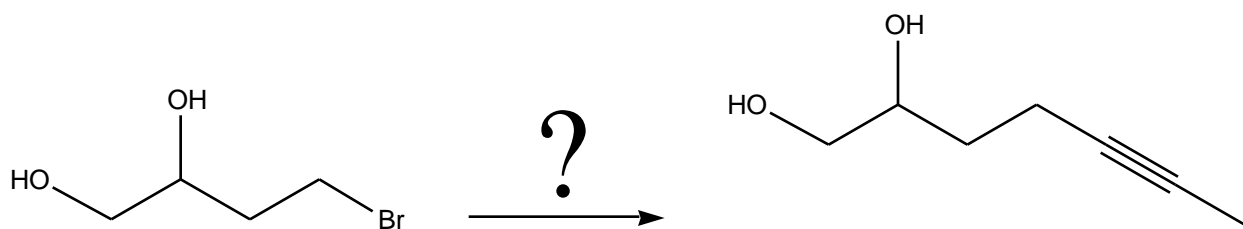
O effectively stabilizes the + charge (RF IV above).

One more RF for the para-case.

Question 4. Things to Cover-Up: Protecting Groups. (20 points)

Interference of a certain reagent used for a transformation of one functional group with other functional groups in the molecule often is a big problem. We have seen several cases in the lecture and it was shown that the solution to the problem often involves the use of “protecting groups”. You may recall, for example, that we protected an aniline as an acetanilide in the synthesis of *ortho*-nitroaniline. To do so, the aniline was reacted with Me-COCl (give the formula of the reagent used for the protection) to form the acetanilide. After the sulfonation, nitration, desulfonation sequence was done, the protecting group was removed easily by reaction with OH⁻, H₂O (give the formula of the reagent used for the deprotection). (2 points each blank)

(a) Now let's use some of our knowledge of protecting groups in the synthesis of the alkyne from the precursor diol shown. Suggest a synthesis and give the reagents for every step of the synthesis.



We did this in lecture with a system that differed only in that it had one less CH₂ group.

make acetal (3 p. for structure) with R₂C=O (1 p.), H⁺ (1 p.), -H₂O (1 p.)

Do nucl. subst. using Me-C≡C⁻ M⁺ / - M⁺ Br⁻

M⁺ = Li⁺ or ⁺MgBr

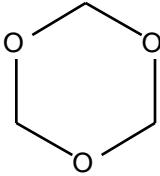
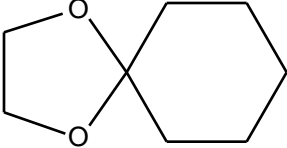
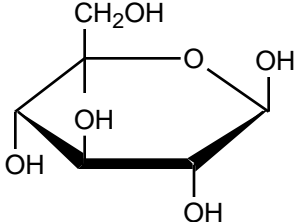
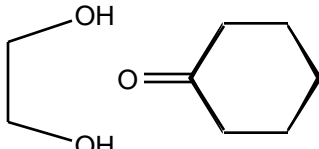
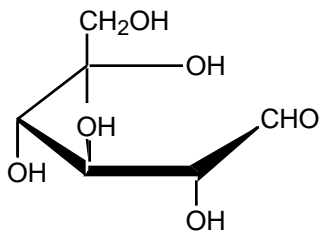
(4 points)

Show the acetal with the Me-C≡C group

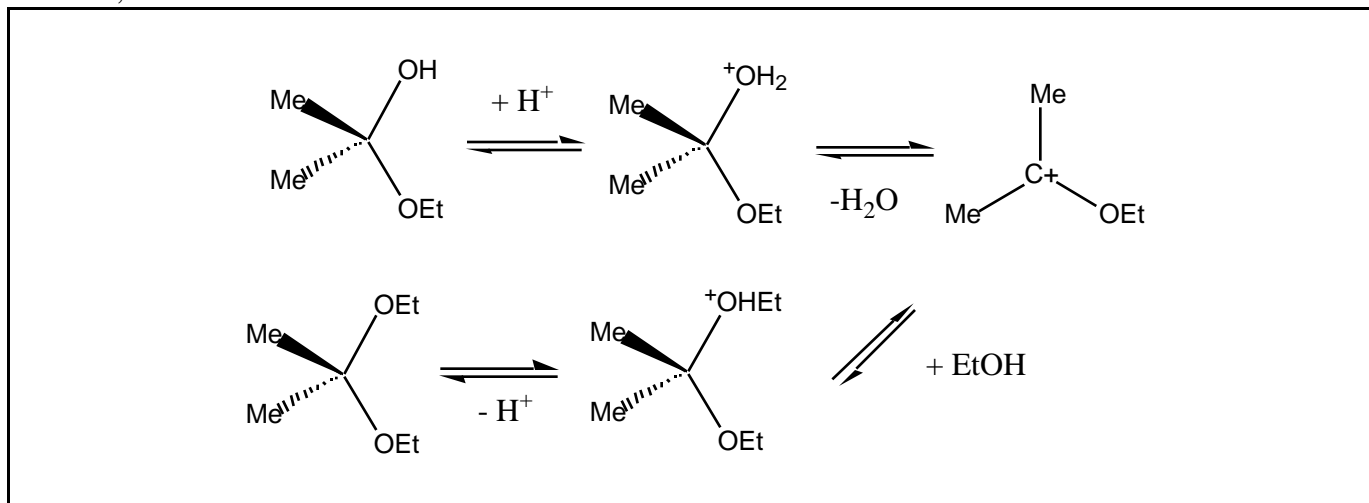
Do deprotection with H⁺ (1.5 p.), H₂O excess (1.5 p.)

Question 5. Things to Recognize: Hydrates, Hemiacetal and Acetal formation. (20 points)

(a) Classify the following three structures as hydrate, hemiacetal or acetal. If the structure does not belong to any of these classes, then write “neither”.

<p>Compound I:</p>  <p>Classify: <u>Acetal</u></p>	<p>Compound II:</p>  <p>Classify: <u>Acetal</u></p>	<p>Compound III:</p>  <p>Classify: <u>Hemiacetal</u></p>
<p>(b) For II and III, show to the right the product(s) of hydrolysis (just below the boxes containing II and III).</p>	 <p>(1 p. each)</p>	 <p>(2 points)</p>

(c) Explain why acid catalysis is necessary for acetal formation. Using acetone as carbonyl and ethanol as alcohol, show the detailed mechanism for the formation of the acetal from the hemiacetal.




The End
