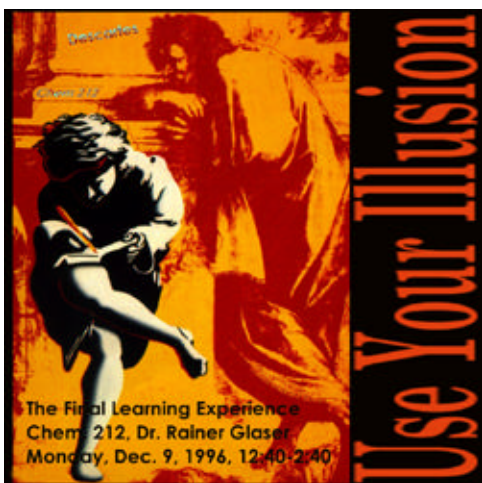


Chemistry 212 — Fall Semester 1996



The Final Learning Experience

**University of Missouri—Columbia, Prof. Rainer Glaser
Monday, December 9, 1996, 103 Schlundt Hall, 12:40 - 2:30**

Your Name:

	Max.	Yours
Question 1 (Sugars)	55	
Question 2 (Alkenes)	70	
Question 3 (Carbenes)	25	
Question 4 (Benzenes)	50	
Total	200	

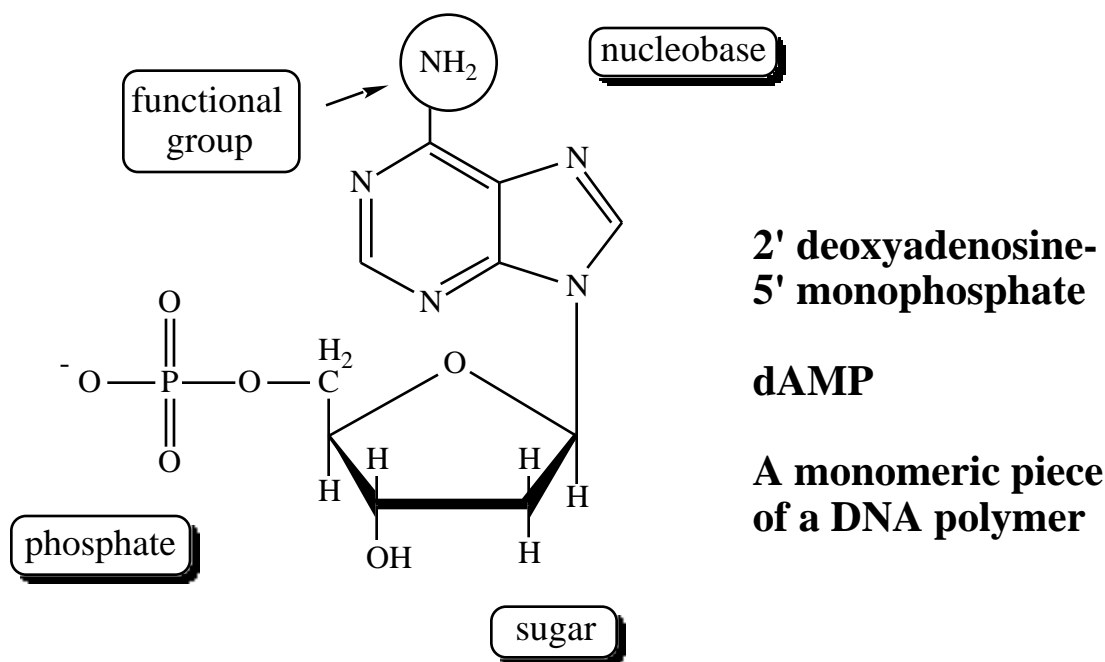


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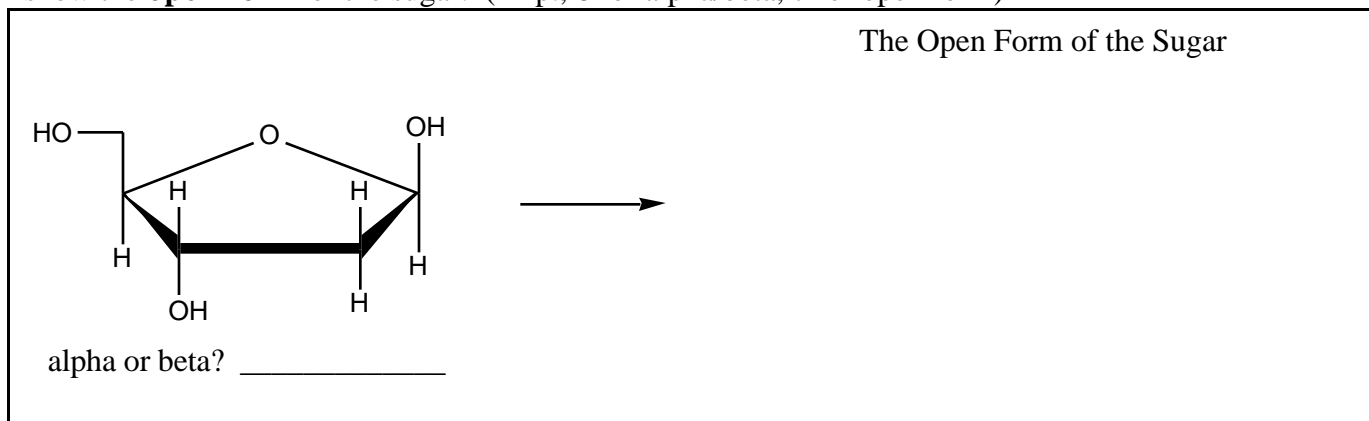
Question 1. Sugar Structure and Stereochemistry. (55 points)

(Recognition, Stereochemistry, Functional Group Chemistry, Evaluation)



(a) In the syllabus, the above picture was shown. With what we have learned in the last few months, we can now understand much more about this piece of DNA. Let's begin with a look at the sugar moiety contained in dAMP. The sugar in dAMP is a _____ (tetrose, pentose, hexose, heptose). The sugar in dAMP is a _____ (furanose, pyranose). (8 points)

(b) Below, the Haworth formula is shown of the sugar in dAMP after removal of the nucleobase and of the phosphate. Indicate the C-atom that gives rise to epimers during the hemiacetal formation and indicate whether the epimer shown is the **alpha or beta epimer**. Furthermore, disconnect the hemiacetal and show the **open form** of the sugar. (11 p., 6 for alpha/beta, 7 for open form)



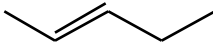
(c) Draw the **Fischer Projection** of the open form of the sugar shown in (b). Indicate whether this stereoisomer of the sugar is **D** or **L**. (12 points)

(d) Draw the **Fischer projection of ribose**. Just in case you forgot the Fischer projection of ribose, the correct IUPAC name of ribose is (2R,3R,4R)-2,3,4,5-tetrahydroxypentanal. State the structural difference between ribose and the sugar dealt with above. Does the name **2-deoxyribose** fit for the sugar in dAMP? (12 points)

(e) **Epimerism** constitutes a special case of _____ in that epimers are stereoisomers that differ only in the configuration of one chiral carbon. State whether the **optical activities of epimers** are the same or whether they are different. Make a statement about the magnitude (same or different) and the sign (same or different). Define the term “mutarotation”. (10 points)

Question 2. Wittig Reaction and Hofmann Elimination. (70 points)
(Geometrical Isomerism, Synthesis, Mechanisms, Electronic Structures)

(a) Let's look at making structural isomers of pentene. There are two of them: 1-Pentene and 2-pentene. Draw the structure of 1-pentene. 2-Pentene can form two geometrical isomers and one of these is shown. Draw the structure of the other geometrical isomer as well and label the geometrical isomers both with the *cis/trans* and with the *E/Z* nomenclatures. (14 points; 3 per structure, 2 per label)

1-pentene	isomer 1 of 2-pentene	isomer 2 of 2-pentene
		
<i>cis</i> or <i>trans</i> :		
<i>E</i> or <i>Z</i> :		

(b) Suppose you are given **2-bromopentane**. Which of the isomeric pentenes can you synthesize from this starting material by way of a simple base-catalyzed elimination? Suggest a base to use. Clearly state what products are formed and which ones are major and minor, respectively. Finally, explain why the major product is formed preferentially. (16 points: 2 for base, 6 points for products, 4 points for deciding minor/major, 4 points for explanation of major.)

(c) Suppose you are given **2-aminopentane** and you subject this amine to **Hofmann elimination**. First write down the overall reaction (include the intermediate quaternary ammonium salt in the overall reaction) clearly showing all reagents and all products. Second, show the mechanism for the formation of the quaternary ammonium ion. Third, specify what type of elimination mechanism is operative in the Hofmann elimination (E1, E1cb, E2) and explain the preferential formation of the _____ (more, less) substituted alkene. (20 points for this part)

Overall reaction (8 points):

Mechanism of quaternary ammonium ion formation (6 points):

Explanation (4 points):

(d) Suggest a synthesis of 1-pentene via the Wittig reaction. In principle, there are two ways to disconnect the 1-pentene. Of these possibilities, consider only that possibility that employs butanal as one of the reagents in the Wittig reaction. First, describe the formation of the ylide (structures and reagents) and draw all relevant resonance structures for the ylide. Second, show the reaction between the ylide and the carbonyl compound. (20 points)

Ylide formation:

Resonance forms for Ylide:

Wittig reaction:

Question 3. Carbenes. (25 points)

(Cyclopropane Synthesis, Amine Nitrosation, Carbene Synthesis and Reactivity)

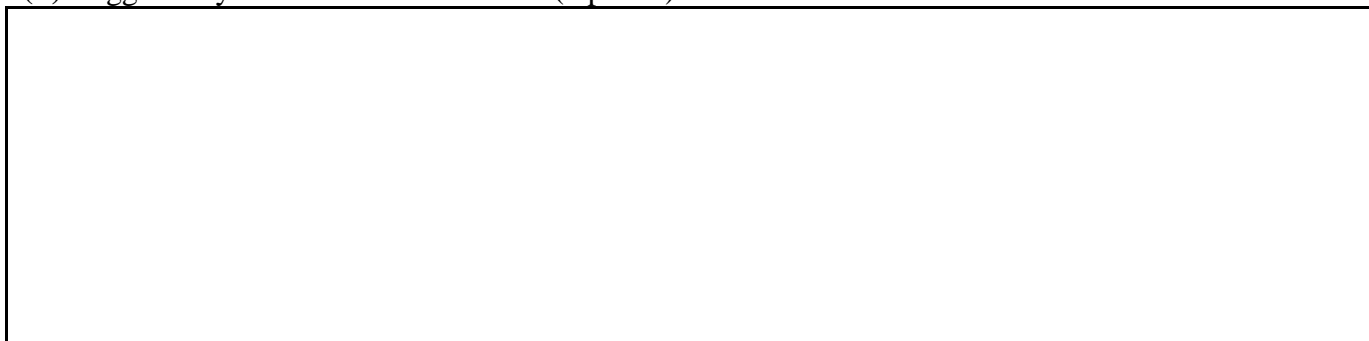
(a) The reaction of chloroform and *trans* 2-pentene in the presence of *tert.*-BuOK in the solvent *tert.*-BuOH yields a **racemate of enantiomeric cyclopropane derivatives**. Draw the structures of both of these enantiomers formed and specify the absolute configuration of all asymmetric C-atoms present in **one** of these enantiomers. (14 points; 4 each structure, 6 for R/S labels)



(b) The reaction of chloroform and 1-pentene in the presence of *tert.*-BuOK in the solvent *tert.*-BuOH also yields a cyclopropane derivative. Draw the structure of this cyclopropane. Is this structure chiral or is it not chiral? (7 points)



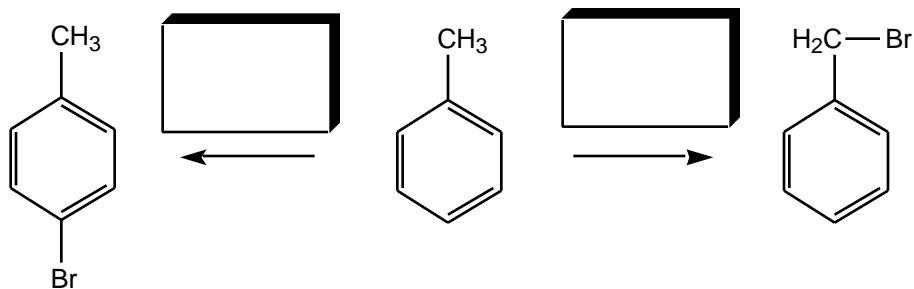
(c) Suggest a synthesis of diazomethane. (4 points)



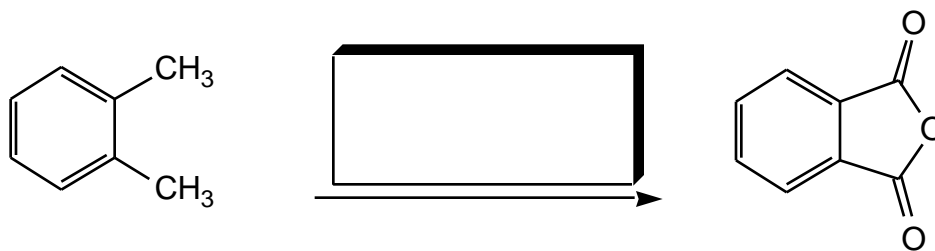
Question 4. Aromatic Substitutions and Chemistry of Benzenes. (50 points)

Provide structures of starting materials, products and reagents as needed. Answer the additional question. (10 points each item)

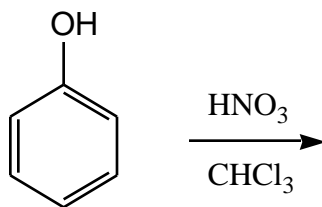
(a) Provide reagents and specify the mechanisms operating in each case.



(b) Provide the trivial name of the starting material. Name the functional group in the product.

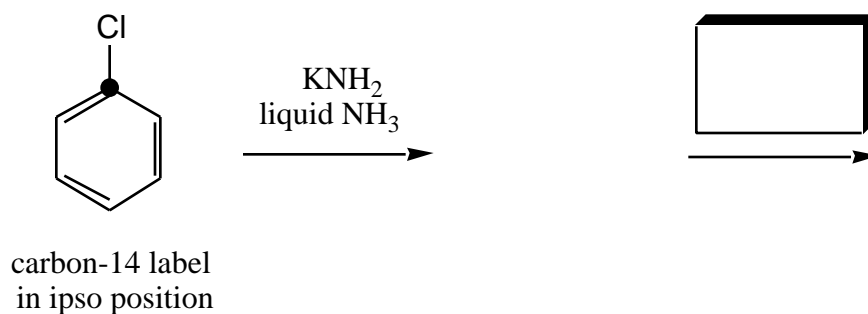


(c) Show all products and circle the major product.



(d) *Para*-nitrochlorobenzene undergoes nucleophilic aromatic substitution faster than *meta*-nitrochlorobenzene. Show all resonance forms for the intermediate of the faster reaction. Then explain.

(e) Show the structures of the intermediate and of the products.



"I have also benefited from teaching: as I try to explain my views to students with critical and open minds, I find myself continually challenged to go back and rethink ideas. I now see teaching and research as complementary, mutually reinforcing activities."

Mario J. Molina in his Nobel Lecture

Angew. Chem. Int. Ed. Engl. **1996**, 35, 1779-1785.



The End

