Chemistry 210 — WS '97

The Final Learning Experience

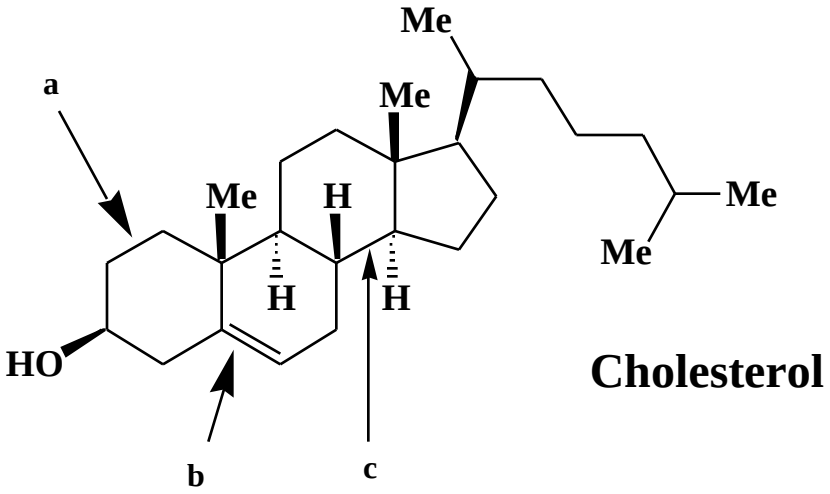
University of Missouri—Columbia, Prof. Rainer Glaser
Monday, May 12, 1997, Ellis Auditorium, 7:40 - 9:40

Your Name:

	Max.	Yours
Question 1 (Prop. & Bonding)	32	
Question 2 (Mechanism Concepts)	24	
Question 3 (Alcohols & Ethers)	58	
Question 4 (Epoxides & Diols)	56	
Question 5 (NMR Spectroscopy)	30	
Total	200	

Do not turn the page until advised to do so.

Question 1. Basic Properties, Bonding and Nomenclature. (32 points)



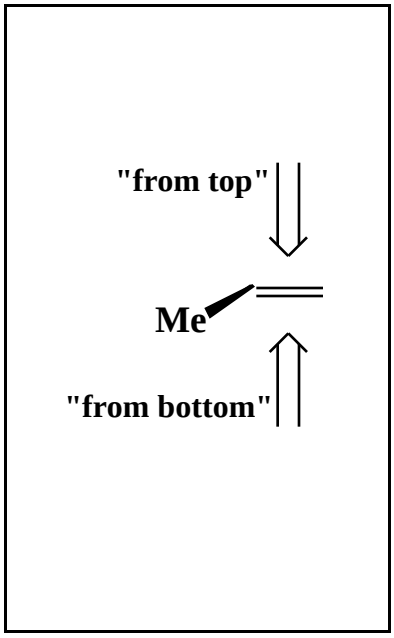
Cholesterol

The molecule shown is **cholesterol**. Cholesterol is a soft, waxy substance found among the lipids (fats) in the bloodstream and in all your body's cells. It's an important part of a healthy body because it's used to form cell membranes, some hormones and other needed tissues. But a high level of cholesterol in the blood — hypercholesterolemia — is a major risk factor for heart attack (coronary heart disease).

Chemistry starts with observation and the skills to recognize and to name what has been recognized. So, please exercise your "**skills to observe, recognize & name**": (a) Cholesterol contains one "iso propyl" group. Find it and circle it. (b) The configuration about the C=C double bond is _____ (*E, Z*) in the Cahn-Ingold-Prelog system. (c) The term "cis" _____ (is, is not) applicable to this C=C double bond. (d) The "double bond equivalent" (DBE), defined as the sum of rings and unsaturations in a molecule, of cholesterol is _____. (e) The chirality of the C-atom carrying the alcohol function is _____ (*R*,*S*). (f) The alcohol is _____ (primary, secondary, tertiary). (g) Cholesterol _____ (contains, does not contain) a "vinylic hydrogen". (h) For the C-O bond, indicate the bond dipole moment by drawing (in the above structure) an arrow from the positively charged end to the negatively charged end. (i) Cholesterol is part of the "lipids" since the nonpolar, _____ (lipophilic, hydrophilic) part of the molecule is much _____ (bigger, smaller) than the polar _____ (lipophobic, hydrophobic) segment of the molecule. (j) The C-C single bond indicated by the arrow "a" is about _____ Å long while the C=C bond indicated by the arrow "b" is about _____ Å long (1 Å = ____ pm). (k) The H-atoms attached to the bond indicated by the arrow "c" are _____ (*cis, trans, gauche*). (l) The C-C single bond is formed by overlap between two _____ (sp, sp^2, sp^3) hybrid orbitals.

Question 2. Electrophilic Addition of Bromine to Propene. (24 pts.)

Let' look at the addition of Br_2 to propene. This reaction involves the electrophilic addition of a Br^+ to the C=C bond of propene and a bridged _____ ion is formed. This intermediate is then attacked by a bromide ion. The Br^- can attack either at the terminal or at the central C-atom but the attack at the _____ (central, terminal) position will be favored since this carbon carries a _____ (smaller, larger) positive charge in the intermediate because it is _____ (more, less) substituted. In the end, a 1,2-dibromopropane is formed that contains one -CH_2Br group and a -CHBr- group. Now we note that the central carbon has become chiral as the result of the bromination. The ratio of *R* and *S* centers is, however, exactly unity and the product is _____. To fully realize this stereochemistry, complete the following chart.



Draw the intermediate formed by attack of Br^+ from "the top"	
	Draw the intermediate formed by attack of Br^+ from "the bottom"
Draw the product formed by *trans* addition of Br^-	R or S:
R or S:	Draw the product formed by *trans* addition of Br^-

Question 3. Alcohols and Ethers. (58 points)

(a) Show the synthesis of the 1° alcohol $H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$, **1**, from bromopropane using a Grignard reaction. Show the structure of the alkoxide intermediate and indicate how it is worked up. Indicate pertinent bond polarities in the Grignard reagent and the other substrate. (10 points)

(b) Now consider the deuterated alcohol **2**, $CH_3CH_2CH_2CHDOH$, which is optically active and has the *R* configuration at the chiral C atom. On treatment with thionylchloride, Cl_2SO, **2** gives 1-chlorobutane, **3**. Give perspective drawings of **2** and **3**. What is the configuration of alkylchloride **3**? Show the mechanism of the reaction. (14 p.)

(c) Suggest a synthesis of racemic alcohol $CH_3CH_2CH_2CHDOH$ from the aldehyde $CH_3CH_2CH_2CHO$. Be clear about what reagent is used to introduce the deuterium and where the hydroxyl hydrogen comes from. (No need to consider resolution at this point.) (6 points)

(**d**) Show how the alcohol (*R*)-**2** can be converted into the ether (*S*)-$CH_3CH_2CH_2CHDOCH_3$, **4**, and into the ether (*R*)-$CH_3CH_2CH_2CHDOCH_3$, **5**. One of the ethers is made *via* the Williamson ether synthesis. Be specific about the reagents used to make the alkoxide in that case. Indicate the mechanisms of the reactions (just the type, no details). (12 points)

Synthesis of **4**:

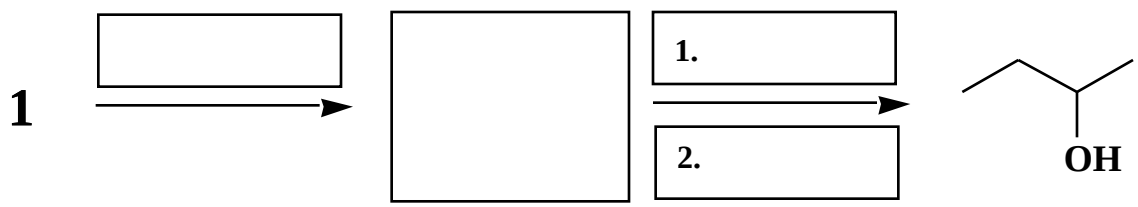
Synthesis of **5**:

(e) Complete the following functional group transformations. (16 points)

Alcohol **1** is oxidized to the corresponding **aldehyde**: (3 points)

Alcohol **1** is oxidized to the corresponding **carboxylic acid**: (3 points)

Alcohol **1** is turned into a secondary alcohol via an **oxymercuration** reaction: (10 points)



Question 4. Preparations and Reactions of Epoxides (aka oxirane) and Some Related Functional Group Chemistry. (56 points)

(a) (2*R*,3*S*)-3-chloro-2-butanol, **1**, is allowed to react with NaOEt in ethanol to give an optically active oxirane, **2**. Draw the structure of **2**, indicate all chiral carbons and give their configurations with the *R*/*S* nomenclature. In **2**, the methyl groups are _____ (*cis* or *trans*). Use a model set! (10 points)

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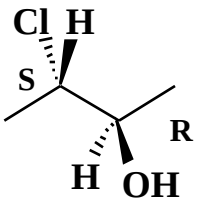
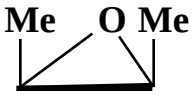


(b) The oxirane **2** is treated with KOH in water to obtain 2,3-butanediol, **3**. Draw the structure of **3** and pay attention to stereochemistry. What can you say about to optical rotation of the product **3**? Remember that the ring opening reaction in alkaline media is an _____ (S_N1, S_N2) process. (10 points)

(c) Suggest a synthesis of **4** from an olefine and a peroxyacid. Draw the appropriate geometrical isomer of the olefine. Give the structural formula and the name of a specific peroxyacid. (8 points)



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(d) There are several other ways to make 1,2-diols from olefines. One of these methods is called the "**Baeyer Test"** and it involves the oxidation of alkenes with cold, aqueous solutions of potassium permanganate. One of the best modern synthetic methods to obtain diols involves a reaction sequence where **osmiumtetroxide** is used in the first step.

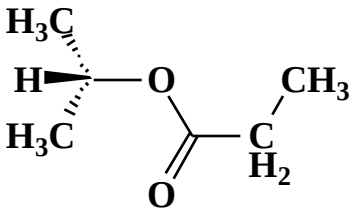
What does the Baeyer Test test for? Explain the principle of the Bayer Test. (8 points)

Show the complete reaction leading to diol formation via OsO_4 oxidation of *cis* pentene-2. (10 points)

(e) Consider the **ozonolysis** of *cis* pentene-2. Draw the structures of the primary ozonide, of the ozonide, and of the products after reductive workup. Specify the reagent used in the workup. (10 points)

Question 5. Basic ^{1}H-NMR Spectroscopy. (30 points)

Consider the NMR spectrum of the ester.



(a) How many **types of protons** are present in the ester and in what **ratio**. (8 points)

(b) Estimate the **chemical shifts** in ppm (reasonable estimates are expected). Write the chemical shifts next to the appropriate H in the above structure. (8 points)

(c) Determine the **splitting pattern** for each signal. Give the multiplicity (singlet, doublet, and so on) and the relative ratios of the lines in each multiplet (e.g. 1:1 for a doublet). (8 points)

(d) Now we are ready to draw the spectrum. Do it. Pay attention to chemical shift, multiplicity, and don't forget to reflect the number of absorbing hydrogens correctly in the intensities. Include the signal for the reference material _____ (abbreviated TMS). (6 points)

The End