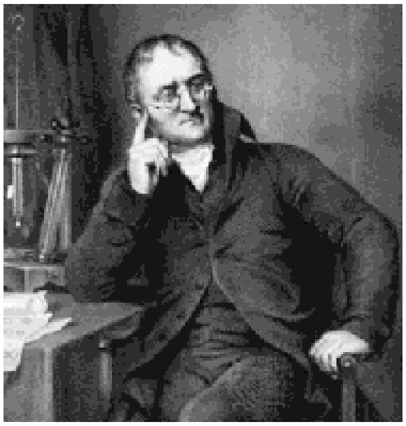
Chem 225b - Comprehensive Organic Chemistry

Problem Set 1

Chapters 1 and 2

Due: Monday, January 23, 2006



John Dalton

(1766-1844)

John Dalton's formulation of an Atomic Theory in the first decade of the 19th century provided a theoretical basis for understanding chemical behavior. In addition to defining the Law of Multiple Proportions, he also formulated the Rule of Greatest Simplicity, which held that water was a binary compound, OH. (Note: Dalton did not use our modern symbols, which came to us from Berzelius, but rather circles that were distinguishable from one another.) Dalton established the combining masses of H to O in water as ~1:6. This ratio was later refined to 1:8. The Rule of Greatest Simplicity, which was at odds with Gay-Lussac's Law of Combining Volumes of Gases, did not lead to a correct formulation for the atomic composition of water. Moreover, although there was agreement regarding the combining masses of atoms in the first half of the nineteenth century, there was disagreement as to the unit mass of the common atoms encountered in organic chemistry: hydrogen (1), carbon (2x6 or 1x12), oxygen (2x8 or 1x16). Since hydrogen was the lightest of the elements, it was assigned a mass of one, a notion that is unrelated to today's mass of hydrogen owing to the presence of a single proton in the hydrogen nucleus. Berzelius's proposal of a mass scale based upon O = 100 would have worked as well.

For a Brief History of Organic Chemistry (PowerPoint), click here.

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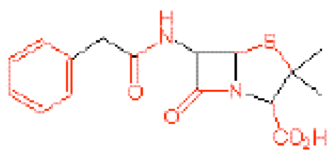
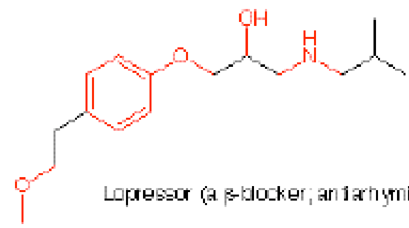
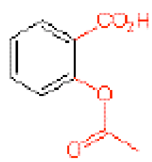
1. Circle and name the functional groups (in red) in each of the following compounds. Pages 66 and 351 will be of help.



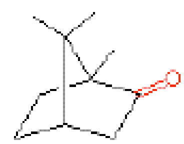
Penicillin G (antibiotic)



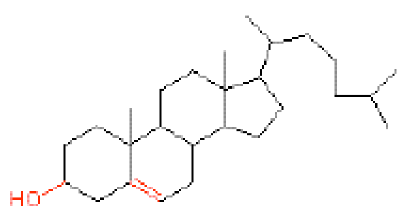
Lopressor (a β-blocker; antiarrhymia)



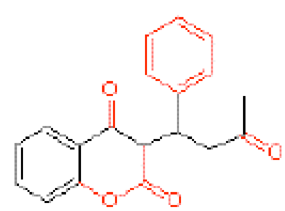
Aspirin (acetylsalicylic acid)
(antiinflammatory, antipyretic, analgesic)



camphor (a terpene)



Cholesterol (a steroid)



Coumadin (warfarin, anticoagulant)

2. In the structure of cholesterol (problem #1), how many primary sp^3 carbons (methyl groups) are present? How many secondary sp^3 carbons (methylene groups)? How many tertiary sp^3 carbons (one hydrogen attached)? How many quaternary sp^3 carbons (no hydrogens attached)? How many sp^2 hybridized carbons? What is the molecular formula of cholesterol? Calculate the percentage of C, H, and O in cholesterol.

3. For each of the following acids or bases, identify the corresponding conjugate base or acid, whichever is appropriate.

a) $NaNH_2$ (sodamide)

b) acetic acid

c) NaOH

d) CH_3OH

e) CH_3Li

4. Arrange the acids and conjugate acids in problem #3 in order of decreasing acidity (increasing pKa).

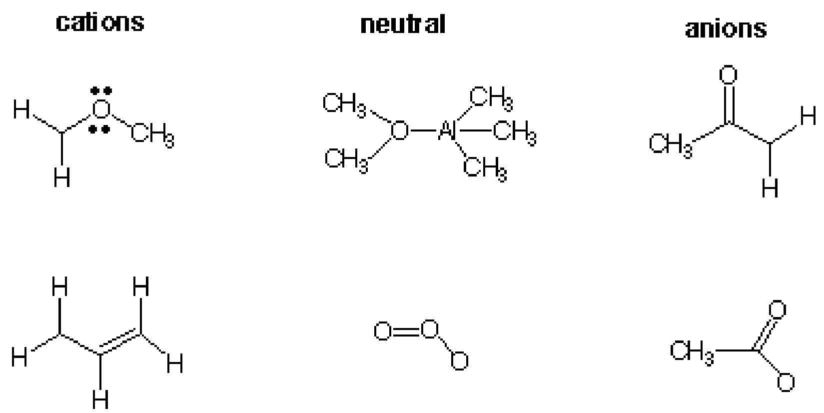
5. Combustion analysis was, and still is, an effective method for determining the composition of organic compounds. Qualitative tests were run to determine the elements present in the sample. Historically, an organic compound was oxidized to CO_2 (absorbed by KOH) and H_2O (absorbed by a dessicant). The classical studies of Williamson's on the structure of ether from 1850-1852 employed this technique. Williamson prepared unsymmetrical ethers such as $C_5H_{11}OC_2H_5$ (n-amyl ethyl ether; N.B.: amyl is a common name for a 5-carbon chain). Data from Williamson's paper [*Journal of the Chemical Society*, **1852**, *4*, 229] is shown on the bottom of page 233 in this paper. [Note: Carbonic acid is treated as CO_2.]

a)Using Williamson's calculated values for the percentage of carbon, hydrogen and oxygen in the ether, determine the atomic masses of C, H, and O that he employed. Assume H =1.00)

b) Using the atomic masses from a), the mass of the sample, CO_2, and H_2O, calculate the empirical formula of the ether. Comment.

c) Use the ideal gas law to show that d=PM/RT, where d = vapor density and M = molecular weight. Use the experimental vapor density [How many times heavier a given volume of vapor is compared with air.] of the ether and the density of air (you should know the composition of air from general chemistry) to show that the molecular and empirical formulas are the same. All measurements are at the same temperature and pressure.

6. Place charges in the following structures in the proper locations. For those structures that are resonance stabilized, draw the two canonical resonance structures. For the anions, which one is the stronger base? Explain briefly.



7. Given that a regular tetrahedron (methane) may be inscribed in a cube, use trigonometry to calculate the bond angle in methane. [Hint: Consider a cube whose center is at the coordinates x=1, y=1 and z=1.]