Chem 220 - Organic Chemistry

Solution Set

Problem Set 1

Chapters 1 and 2, Structure, Bonding, Reactivity

Due: Monday, September 13, 2010

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. Dalton postulated that in a molecules comprised of two different atoms, the simplest one in the series would be binary. While this rule applied to CO and CO_2, it did not apply to the pair, water and hydrogen peroxide. Thus, water, according to Dalton, was OH. The Rule of Greatest Simplicity, which was at odds with Gay-Lussac's Law of Combining Volumes of Gases that demonstrated the volume of hydrogen produced upon electrolysis of water was twice that of oxygen, was dismissed by Dalton as a faulty result. 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 (Prout's Hypothesis), 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.

1. The chemical structures shown below all occur in nature. They have also been made (synthesized) by chemical means from simpler organic compounds in this department over the past 40 years. [See the background on the website homepage.] You will learn about Classes of Compounds one class at a time. They will be for the most part mono-functional compounds. All of

the compounds shown below are multi-functional compounds.

a) Identify the Class of Compound of the functionality present with in each of the circles. Print this page and use it to designate answers. [See the inside front cover of your textbook for Classes of Compounds, Functional Groups and Abbreviations.] *See answers in the diagram below (red italics). The compounds that end in -one contain ketones while the compounds ending in -ol contain alcohols. This is a common way of naming compounds but not necessarily.*

b) You should have identified two alcohols [ROH, where R = alkyl (aliphatic), **not** aryl (aromatic)]. Of these two alcohols, one is said to be primary, the other tertiary. Why? Is there another primary alcohol in the structures? Another tertiary alcohol? Are there any secondary alcohols? *Cyclophellitol has a primary alcohol circled. The carbon to which the hydroxyl group is attached has one (primary) carbon attached to it while the circled alcohol in steviol has a carbon bearing one hydroxyl group and three (tertiary) carbons. [The definition need not be only attached carbons. The compound CH_3OCH_2Cl, is a primary chloride even though there are no carbons attached to the carbon to which the chlorine is attached.] The hydroxyl group in the center of forskolin is tertiary. There are five secondary alcohols: three in cyclophellitol and two in forskolin. The symbol Ac in forskolin stands for acetyl (see the Tables on the inside cover of your text). Acetic acid may be written in shorthand as AcOH.*
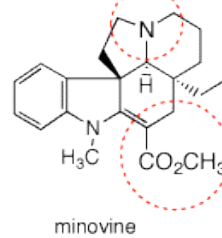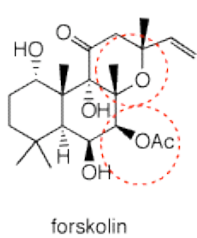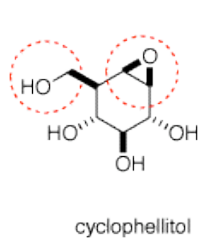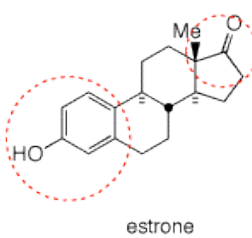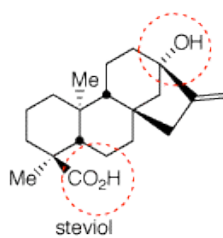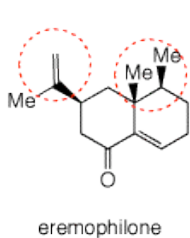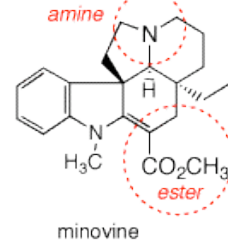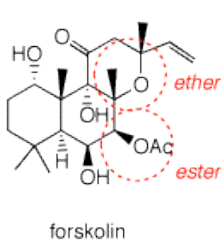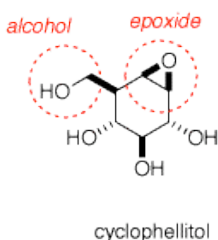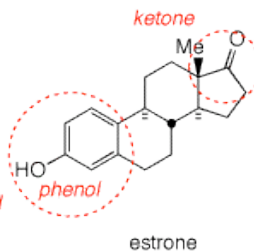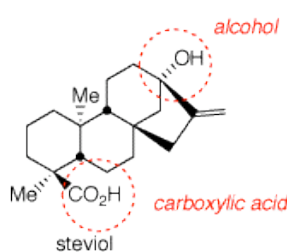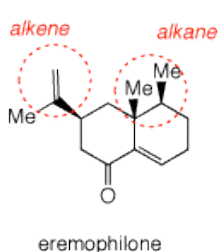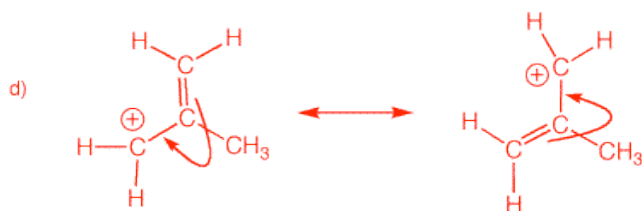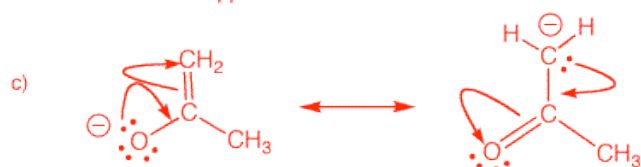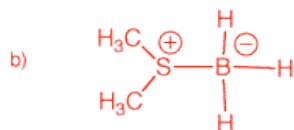

2. Draw resonance structures (if they exist) for the following compounds. Include all formal charges.

a) CH_2N_2 b) $(CH_3)_2SBH_3$ c)   d)
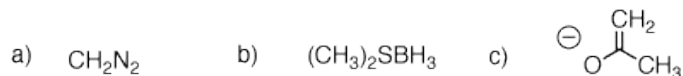
(C-N-N atom connectivity,   (borane dimethylsulfide)
diazomethane)

a)

b)

c)

d)
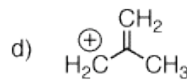
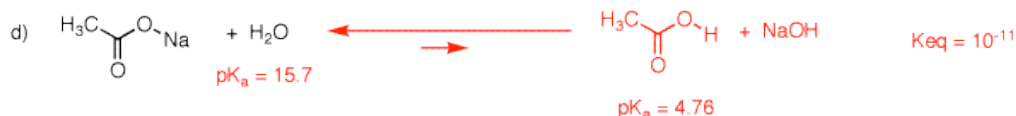*a) Diazomethane is a resonance stabilized, neutral molecule.*

b) No resonance. This is a "salt" formed from the the reaction of the base dimethyl sulfide (pair of electrons on sulfur) and the acid BH_3 (boron is electron deficient). none of the hydrogen atoms is acting as an acid.

c) The negatively charged species is the resonance stabilized, conjugate base of acetone.

d) This species is the resonance stabilized structure of an allyl cation.

3. For each of the following acid/base reactions, provide appropriate equilibrium arrows reflecting the position of the equilibrium. For the right side of the equilibrium, provide the conjugate acids and bases. Estimate the equilibrium constant for each reaction. The pKa table will be of help.

a) $CH_3CH_2CH_2CH_2Li$ + C_2H_5OH $CH_3CH_2CH_2CH_3$ + C_2H_5OLi $Keq = 10^{34}$
                    $pK_a = 15.9$ $pK_a = \sim 50$

b) NH_3 + $NaC\equiv CH$ NH_2Na + $HC\equiv CH$ $Keq = 10^{-10}$
 $pK_a = 35$ $pK_a = 25$

c) CH_3ONa + CH_3OH + $Keq = 10^{5.5}$
                         $pK_a = 10$ $pK_a = 15.5$

d)   + H_2O + $NaOH$ $Keq = 10^{-11}$
 $pK_a = 15.7$ $pK_a = 4.76$

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

Follow the pKa values. n-Butane (pK_a = 50) the least acidic; acetic acid the most acidic (pK_a = 4.76).

5. Draw an orbital picture for the alkyne, 2-butyne (CH_3CCCH_3). Identify σ- and π-bonds and hybridization.

All H orbitals are 1s. The terminal carbons are sp^3 hybridized. They are each bonded to three hydrogens and one carbon, which is sp-hybridized. The two central carbons are sp-hybridized, bonded linearly to the two terminal sp^3-hybridized carbons. All bonds are thus far σ-bonds. The remaining p-orbitals of the central carbons form two π-bonds designated p_y and p_z. The positive phase of the p-orbital is arbitrarily darkened.
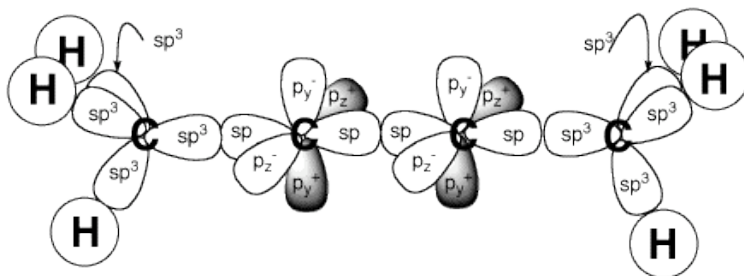
6. A normal alkane, C_nH_{2n+2}, is found to have a vapor density of 2.52 mg/mL at 250°C and 720 mm pressure. Using the ideal gas law, determine the structure of the alkane. (In the early 19th century, the vapor density of an unknown liquid was compared to the vapor density of air to determine the liquids molecular weight.)

Recall from general chemistry the ideal gas law: PV = nRT, where n = g/M; P (atmospheres), V (liters), n (moles), g (grams), M = MW = (grams/mole), T (temperature in ^oK) and R = (gas constant, 0.0821 l-atm/moles-^oK). Since density (d) = mass/volume; d = g/V. Since PV = nRT or PV = gRT/M, then d = g/V =PM/RT. Transposing, M = dRT/P. At a given temperature and pressure, d is proportional to M by a factor of R. P = 720 mm Hg/760 mm Hg = 0.947 atm.; T = 250° + 273° = 523^oK. M = dRT/P = (2.52) x (0.0821) x (573)/0.947 = 114.2. M.W. = 114. Based upon the formula, the alkane is a completely saturated, acyclic alkane. There are n carbons at mass 12 and 2n +2 hydrogens at mass 1 in the compound. Therefore, (12)n + [(1)(2n +2)] = 114 or 14n = 112; n = 8. The alkane is C_8H_{18}. Since it is a normal alkane, it is unbranched. Ans: n-octane. See below. Click here for a dynamic version.