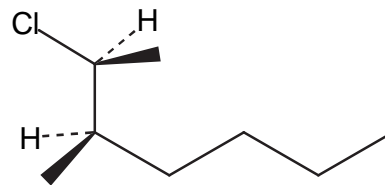


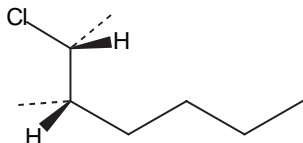
# Chemistry 125 Third Examination Answers November 14, 2003

1. (6 minutes) A. Give the **complete** systematic name of this compound :

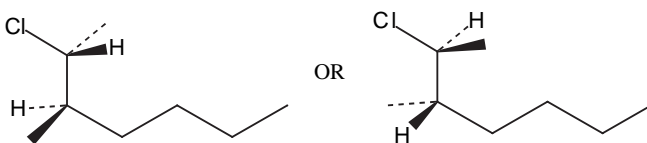
(2S,3R)-2-chloro-3-methylheptane



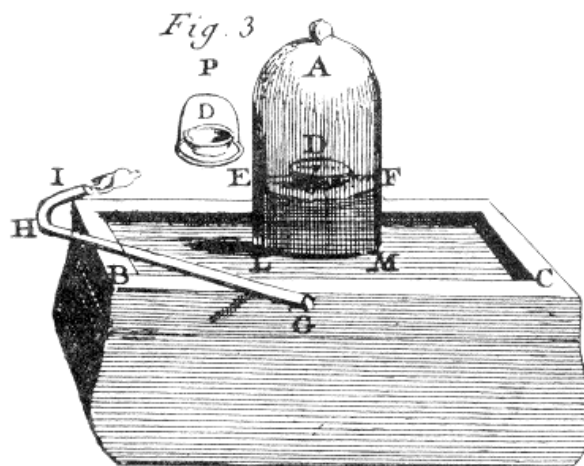
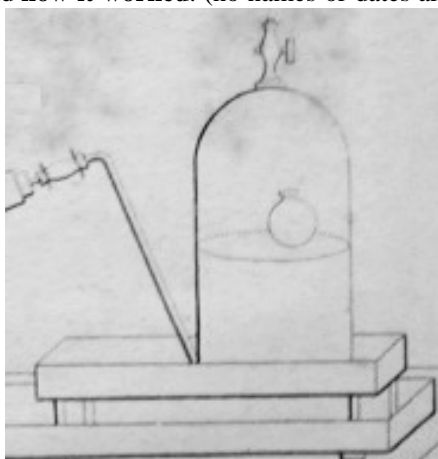
B. Draw the compound's **enantiomer**



C. Draw the compound's **diastereoisomer**



2. (6 min) Choose one (**ONE ONLY**) of the following two pieces of apparatus and explain briefly **what it was used for** and **how it worked**. (no names or dates are necessary)



The first apparatus measures the  $\text{CO}_2$  generated by combustion of an organic sample. The mixture of  $\text{O}_2$  and  $\text{CO}_2$  from combustion bubbles into the bell jar displacing mercury. The bulb floating on the mercury contains solid  $\text{KOH}$  which absorbs the  $\text{CO}_2$ . The opening of the bulb is closed with glove leather to allow gases, but not mercury to enter. As the  $\text{CO}_2$  is absorbed, the pressure falls and mercury rises in the jar. One waits 12 hours after the mercury has stopped rising to be certain all of the  $\text{CO}_2$  has been absorbed. Then one retrieves the bulb with a wire tied to its bottom, carefully removes all mercury adhering to the bulb, and weighs to determine the increase in weight due to  $\text{CO}_2$ . (The apparatus was used by Berzelius.)

[ <http://classes.yale.edu/chem125a/125/LectureSlides/Lecture102903.ppt> ]

The second apparatus measures the amount of oxygen consumed during combustion of a fixed weight of a material such as phosphorous. The bell jar was filled with oxygen. Then the sample was introduced in the dish "D" and some of the oxygen was removed by sucking (!) on the tube GHI (which had a twist of paper to keep from filling with mercury). The phosphorous was then lit with a curved, red hot rod (or a magnifying glass) and, after combustion was complete, the change in height of mercury was used to measure the volume of oxygen consumed in combustion. (The apparatus was used by Lavoisier.)

[ <http://classes.yale.edu/chem125a/125/history99/2Pre1800/Lavoisier/Quantitation/carbonoxidn.htm> ]

3. (12.5 min) For over two centuries tartaric acid,  $\text{HOOCCH(OH)-CH(OH)COOH}$ , and its relatives have repeatedly played important roles in the development of **experiment, theory, and nomenclature** in organic chemistry.

Briefly describe 5 (**FIVE ONLY**) of these developments. Mentioning specific experiments/theories/notation is most important - modest additional credit will be given for dates and chemist's names,

[HINT: some relevant dates are 1769, 1789, 1830, 1848, 1874, 1891, 1949]

In 1769 Carl Wilhelm SCHEELE prepared pure samples of a number of organic acids, including tartaric acid, using salts with lead or another heavy metal. Pure samples were necessary to make the Law of Definite Proportions applicable serving as a bridge from analysis to structure.

In 1789 Antoine Laurent LAVOISIER published his theory of oxidation in "*Traité Élémentaire de Chimie*." This theory held that acids were formed by combination of oxygen with an elemental base or a compound radical, containing several elements. The radical of Scheele's tartaric acid was one of the compound radicals included in Lavoisier's table.

In 1830 Jöns Jakob BERZELIUS coined the word "isomers" to describe compounds which gave the same analysis, and had the same molecular weight, but possessed different properties. This was a key step in the discovery that compounds were more than just a collection of atoms, and it led nearly 30 years later to the concept of structure. The word *isomers* was first used to describe the relationship between tartaric and racemic acids, whose analysis Berzelius reported in this paper.

In 1848 Louis PASTEUR, attempting to repeat careful crystallographic studies on salts of tartaric acid, noticed that crystals of the sodium ammonium salt of racemic acid existed in two mirror image forms, one of which was identical to the corresponding salt of tartaric acid. From the mirror image crystals he was able to prepare the levorotatory enantiomer of dextrorotatory tartaric acid. This showed a new kind of isomerism, which was initially called "optical isomerism", between substances that were identical except for the way they influenced polarized light. (*Note that Pasteur was not the individual who first prepared mesotartaric acid. He was just responsible for optical isomerism, which we now call chirality.*)

In 1874 Jacobus Henricus VAN'T HOFF explained the known existence of optical isomers, such as the tartaric acids and the lactic acids, (as well as *cis-trans* isomers and meso compounds) on the basis tetrahedral carbon. This was the first definitive, correct discussion of stereochemistry and the importance of the arrangement of atoms in space. The number of isomers of tartaric acid (*d*-, *l*-, and *meso*-tartaric acids) was a key feature of his argument.

In 1891 Emil FISCHER used the isomers of tartaric acid to illustrate his new convention (the Fischer Projection) for drawing the configuration of chiral carbons in a chain, the four bond from a carbon being drawn as a cross in a plane with the understanding that vertical bonds are receding from the carbon while horizontal bonds project toward the viewer. Fischer used his projection to show the relationship between molecules and the corresponding enantiomers of glyceraldehyde from which they could be prepared, showing that *l*-tartaric acid was related to *d*-glyceraldehyde and thus could be referred to as D-tartaric acid.

In 1949 Johannes Martin BIJVOET uses the x-ray phenomenon of anomalous scattering to determine the absolute arrangement of substituents on the chiral carbons in the sodium rubidium salt of *d*-tartaric acid. This was the first case in which absolute configuration was determined and provided an experimental basis for replacing Fischer's relative names with Cahn-Ingold-Prelog absolute names for chiral compounds.

4. (6 minutes) Halogen substitution of Arppe's nitroaniline,  $C_6H_4(NH_2)(NO_2)$ , a "relative" of "hydroxybenzoic acid", played a key role in Koerner's proof of the equivalence of the positions of hydrogen atoms in benzene,

- A. Explain schematically how the halogen substitution experiments contributed to the logic of Koerner's proof.  
(Don't worry about the nitty-gritty mechanism of the actual reactions in HOMO/LUMO terms)

Koerner had already shown the three isomers of hydroxybenzoic acid did not differ in the absolute position of their hydroxyl groups, nor in the position of their carboxyl groups, but only in the relative position of these groups. Thus if the position of OH in these compounds was called  $\omega$ , the COOH positions could be called x, y, and z, differing only in their relationship to the position  $\omega$ . Replacing the  $NH_2$  group of Arppe's nitroaniline with one halogen and then its  $NO_2$  group with a different halogen gave the same compound no matter which of the two halogens was used in the first substitution. This showed that the positions of these two groups in Arppe's nitroaniline are equivalent. This added a fourth position to the set of three equivalent positions, *i.e.*  $\omega = x = y = z$ .

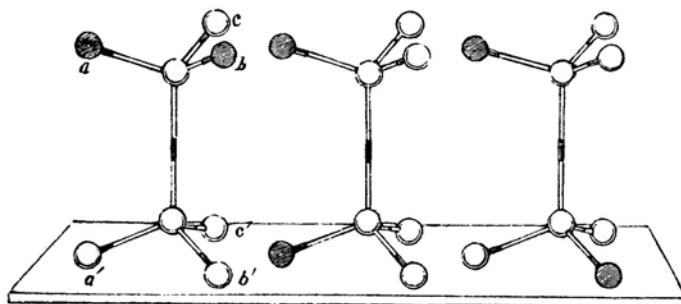
- B. Why was it important that Arppe's nitroaniline was shown to be a relative of hydroxybenzoic acid?

Otherwise the  $NH_2$  and  $NO_2$  positions might both have been from the set x, y, z, which had already been shown to be equivalent. It was necessary to show that the fourth equivalent position was not one of the first three, a condition that must be satisfied the position,  $\omega$ , of the hydroxyl group in hydroxybenzoic acid.

5. (4.5 min) In 1869 Paternó published this figure.

- A. What experimental observation(s) was Paternó trying to explain?

The supposed existence of three isomers of dichloroethane.



- B. Lieben then cautioned Paternó that "Shooting off into space one risks losing the ground under his feet" He specifically mentioned a supposed conflict between Paternó's model and the facts about dichloromethane. Explain.

He warned that if one attempted to apply geometric thinking to chemical formulas, one would predict the existence of two isomers of a disubstituted methane (*e.g.* dichloromethane or chloroethane). Lieben's problem was that he was thinking of a square planar two-dimensional model, which would indeed have isomers with the substituents adjacent or opposite to one another (also called *cis* and *trans*). Lieben failed to see that by using a three-dimensional tetrahedron Paternó had sidestepped this particular objection, since in the tetrahedron all pairs of vertices are equivalently related. Lieben's advice shows just how far spatial thinking was from the minds of most chemists in the 1860s and early 1870s.

