Lecture # 1B

► Qualitative organic chemistry has been in use since long before the advent of modem spectroscopy. Modem spectroscopic techniques have assisted the chemist by providing spectra that can be interpreted to give more detail of the interaction between atoms and functional groups.

► Some students have difficulty identifying structures using exclusively nuclear magnetic resonance (NMR) spectra, infrared spectra, and mass spectra.

► The information obtained through chemical tests allows the student to narrow down the possible functional groups.

► Additionally, by taking a course in qualitative organic chemistry, a student is given the freedom of selecting, for himself or herself, the particular chemical tests that are needed to identify a compound.

► In roughly two dozen chapters of a standard organic text, the student encounters many chemical reactions. Literally millions of different organic compounds have been synthesized.

► Chemical companies sell thousands of compounds, and industrial-scale production generates thousands of different compounds on various scales. Characterization of organic compounds can be done by a handful of physical and chemical observations if it is done in a systematic manner.

► The list of more common and more readily available chemicals is much smaller than the millions that are possible.

► In this text we have focused our attention on an even smaller list of compounds that can be used as "unknowns." The melting point-boiling point tables give a very accurate idea of the focus of this book.

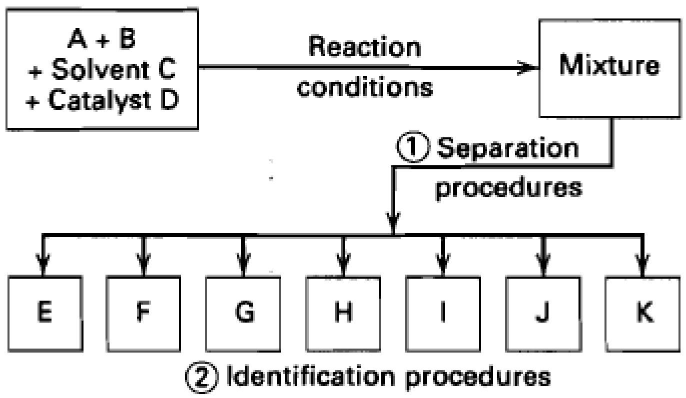
► Instructors using this book may very well use other references (CRC reference volumes, the Aldrich Company catalog, etc.) for a more extensive list of possibilities for "unknown" compounds.

Organic chemists are often confronted with either of the following extreme situations:

1. Determination of the identity of a compound that has no prior history. This is often the case for a natural-products chemist who must study a very small amount of sample isolated from a plant or animal. A similar situation applies to the forensic chemist who analyzes very small samples related to a lawsuit or crime.
2. The industrial chemist or college laboratory chemist who must analyze a sample that contains a major expected product and minor products, all of which could be expected from a given set of reagents and conditions. It is entirely possible that such a sample with a well-documented history will allow one to have a properly preconceived notion as to how the analysis should be conducted.

► The theory and technique for identifying organic compounds constitute an essential introduction to research in organic chemistry. This study organizes the accumulated knowledge concerning physical properties, structures, and reactions of thousands of carbon compounds into a systematic, logical identification scheme. Although its initial aim is the characterization of previously known compounds, the scheme of attack constitutes the first stage in the elucidation of structure of newly prepared organic compounds.

► As an example:



► Immediately two questions arise:

1. What procedure should be chosen to separate the mixture into its components?
2. How are the individual compounds (E through K) to be definitely characterized? Which ones are unchanged reactants? Which compounds have been described previously by other chemists? Finally, which products are new?

► These two problems are intimately related. Separations of organic mixtures use both chemical and physical processes and are dependent on the structures ofthe constituents.

► The present course of study focuses on the systematic identification of individual compounds first. The specific steps are given in Chapter 2.

► Physical properties are described in Chapter 3.

► The use of these principles for devising efficient procedures for the separation of mixtures is outlined in Chapter 4.

► Solubility techniques are described in Chapter 5.

► Spectroscopy methods are discussed in Chapters 6 through 8.

► The practical laboratory methods are given in Chapters 9 and 10.

► In recent years the question of scale has become an issue. Scale has always been a focal point for qualitative analysis. The issue has been recognized at an even earlier point in the chemistry curriculum, and a very large number of colleges now incorporate some sort of microscale approach into their sophomore organic courses.

► Here we loosely define microscale chemistry as the use of tens of milligrams of organic compound in a procedure, while macroscale reactions employ tens of grams.) Organic qualitative analysis has always been a test-tube subject and thus should philosophically be in tune with the microscale revolution.

► We anticipate that scaling down to 1/2, 1/5, or 1/10 of the cited amount should be very straightforward in most cases, and thus scale is the option of the course coordinator. The only warning is that certain reactions (for example, conversion of acarboxylic acid to an amide or of an alcohol to a 3,5-dinitrobenzoate) are notoriously sensitive to the purity of the reagents. Thus a larger-scale reaction is likely desirable here.

Cleanup and Waste Disposal

►A related, and in some ways bigger, issue is that of waste disposal.

► Most instructors are not qualified to dispose of waste and thus they can only provide cleanup guidelines.

► It is usually the job of the instructor to provide containers for waste disposal (it is now very rare that a chemical can be washed down the sink). Waste disposal vessels are usually labeled as to their use, such as solids vs. liquids and inorganic vs. organic compounds. In some cases a special vessel is provided for especially toxic wastes such as halogenated organic compounds.

► Moreover, there are usually special containers for glass (especially broken glass) objects. There may be places to recycle paper, and finally there are Simple trash cans for garbage.

SUGGESTIONS TO STUDENTS AND INSTRUCTORS

► Laboratory Work-Unknowns:by use of spectroscopic data and chemical reactions it is possible for students to work out six to eight single compounds and two mixtures (containing two or three components each) in a I5-week semester.

► To get a rapid start and illustrate the systematic scheme, it may be useful to give a titratable acid to each student for a first unknown. The student is told that the substance is titratable and that he or she is to get the elemental analysis, melting orboiling point, and neutralization equivalent and to calculate the possible molecular weights.

► If the unknown contains halogen or nitrogen, the student is to select and try three or four (but no more) classification tests. Next, a list of possible compounds with derivatives is prepared by consulting the table of acids (Appendix 11). One derivative is made and turned in with the report (see pp. 17-21). This first unknown should be completed in two 3-h laboratory periods.

► The other unknowns should be selected so as to provide experience with compounds containing a wide variety of functional groups.

► It is often desirable to check the student's progress after the preliminary tests, solubility classification, and elemental analyses have been completed. This checking procedure is highly recommended for the first one or two unknowns for each student.

► Purity of Unknowns: Although every effort is made to provide samples of compounds with a high degree of purity, students and instructors should recognize that many organic compounds decompose or react with oxygen, moisture, or carbon dioxide when stored for a considerable time. Such samples will have wide melting or boiling point ranges, frequently lower than the literature values. Hence, for each unknown the student should make a preliminary report of the observed value for melting or boiling point. The instructor should verify these data and if necessary tell the student to purify the sample by recrystallization or distillation and to repeat the determination of the physical constant in question. This avoids waste of time and frustration from conflicting data.

► **Amounts of Unknowns:** As a general guide, the following amounts are suggested:

► **Unknown**,

No.1, a titratable acid, 4 g of a solid or 10 mL of a liquid Unknown

No.2, 3 g of a solid or 8 mL of a liquid Unknown

No.3, 2 g of a solid or 5 mL of a liquid Unknown

No.4, 1 g of a solid or 5 mL of a liquid mixtures should contain 4-5 g of each component.

Note: If repurification of a sample is required, an additional amount should be furnished to the student.

► **Timesaving Hints**

► It is important to plan laboratory work in advance. This can be done by getting the elemental analyses, physical constants, solubility behavior, and infrared and NMR spectra on several unknowns during one laboratory period. This information should be carefully recorded in the notebook and then reviewed (along with the discussion in each of these steps) the evening before the next laboratory period.

► A list of a few selected classification tests to be tried is made and carried out in the laboratory the next day. In some cases a preliminary list of possible compounds and desirable derivatives can be made. It is important to note that few of the 47 classification tests should be run on a given compound. It should not be necessary to make more than two derivatives; usually one derivative will prove to be unique.

► The object is to utilize the sequence of systematic steps outlined in Chapter 2 in the most efficient manner possible.

LABORATORY SAFETY

► *At all times, the instructor and students should observe safety rules. They should always wear safety glasses in the laboratory and should become familiar with emergency treatment.*

► Laboratories are places of great responsibility. Careful practice and mature behavior can prevent most mishaps. The following are all very important. Treating the lab with respect makes it far less dangerous.

► **Eye Protection** Goggles or safety glasses must be worn at all times. Eyeglasses, with shatterproof glass, are inadequate without goggles or safety glasses. Side shields are required for all protective eyewear.

► **Shoes** Shoes that completely cover the feet are required in the laboratory.

► **Protective Clothing** Aprotective apron or lab coat is recommended in the laboratory. If any chemical is spilled on your skin or clothing, it must be washed off immediately.

► **Food and Drink** Food and beverage are strictly prohibited in the laboratory. Do not taste or smell any che'mical. No Unauthorized Experiments Do not perform any unauthorized experiments. Chemicals, supplies, or equipment must not be removed from the laboratory. All experiments must be approved by the instructor.

► **Smoking** Smoking is prohibited in the laboratory.

► **Personal Item** No bookbags, coats, books (except the lab book), or laptop computers should be brought into the laboratory. Ask your instructor where these items can be stored while you are in the laboratory. Bring in only the items that are needed during the laboratory period. These items can be damaged by the chemicals in the laboratory.

► **Use of Equipment** Do not use any equipment until the instructor has shown you how to use it.

► **Glassware** Do not use any broken, chipped, or cracked glassware. Get replacement glassware from your instructor.

► **Bench Cleanup** At the end of the laboratory period, put away all equipment, clean the laboratory bench, and wash your hands.

► **Use of Chemicals** Take only the amount that is needed. Leave all bottles in their proper places. Place the lids on the bottles after use. Clean up all spilled chemicals immediately.

► **Careful Reading of Labels** A Material Safety Data Sheet is available for each chemical in the laboratory. Ask your instructor where the paper copies are located. Material Safety Data Sheets are also available on the web. Many chemical companies have posted this information. Use web search engines to locate this information. Students are encouraged to obtain this information prior to using the chemical in the laboratory. The safety, health, and fire precautions are the most important information to locate. Special instructions for the handling of certain reagents may be posted by the instructor.

► **Waste Disposal** In recent years, the rules regarding waste disposal have become more rigidly defined. Reagents are never poured down the sink. Containers for chemical wastes are provided in the laboratory. Different containers are needed for different types of waste chemicals, such as chlorinated hydrocarbons, hazardous materials, and metals. All reagents in the waste container are listed on the container.

► **Fume Hoods** Most laboratories provide fume hood areas or bench-top fume hoods. Always use these. If you think the hoods are not turned on, bring this to the attention of your instructor. Often students are provided with simple methods of testing hood efficiency, and these should be used periodically. Safety regulations usually prohibit storage of toxic substances in hoods, and fume cupboards for such compounds are normally available.

► **Gloves** Most laboratories provide boxes of gloves. Modem gloves are quite manageable and allow for handling of equipment with some agility. Gloves have their place and can certainly protect your hands from obnoxious odors or chemicals that can cause allergic responses. But they are not a license for sloppy technique. Moreover, they often are easily penetrated by some compounds. Due care is still required.

► **Compressed Gas Cylinders** Compressed gas cylinders, especially those that are nearly as tall as an adult, can be dangerous if not clamped to the bench top. Gas cylinders containing inert gases such as nitrogen or helium may well be around the lab. Cylinders containing chlorine or more toxic reagents should be stored in a fume cupboard.

► **Safety Equipment** The location of safety equipment should be made known to you. Moreover, you should know if and when you should use these.

Most of the following items should be readily available in the chemistry laboratory; items on this list or their description may vary due to local safety regulations:

Fire blanket

Fire extinguisher

Eye-wash

fountain Shower

First aid kit

Washes for acid or base (alkali) bums

► **Accident Reporting** All accidents should be reported. The manner in which they should be reported will be provided by the instructor. It is also important that someone accompany an injured person who is sent out of the laboratory for special care; if the injured person should faint, the injury could easily become compounded.

Medical treatment, except in the Simplest of cases, is usually not the responsibility of the instructor. Very simple, superficial wounds can be cleaned and bandaged by the instructor. But any reasonably serious treatment is the job of a medical professional. The student should be sent to the college medical center accompanied by someone from the chemistry department. In all labs, the instructor should provide the students with instructions that are consistent with local regulations.

► Explosion Hazards of Common Ethers

► A number of violent explosions due to accidental detonation of peroxides, which can build up in common ether solvents, have been reported. These ethers include diethyl ether, diisopropyl ether, dioxane, and tetrahydrofuran. Apparently, the greatest hazard exists when ethers have been exposed to air, especially for extended periods of time.

► Each ether container should be labeled with the date that it is opened. Check with your instructor if this date is several months old.