Experiment #1: Identification of Unknown Compounds via Chemical Reactions and Spectroscopic Data
(Tuesday, Feb. 2st – Thursday, Feb. 4th)

PART A: Determination of Free-Radical Bromination Relative Reaction Rates
PART B: Elucidation of Unknown Compounds via NMR spectroscopy and GCMS Data

Part A is in part derived from Gilbert, J. C., Martin, S. F., Experimental Organic Chemistry, A Miniscale and Microscale Approach, 5th ed, p. 327.

In Part A of the laboratory session several unknown compounds will be subjected to free-radical bromiation conditions. In Part B free-radical reaction outcomes, as well as ^1H and ^{13}C-NMR spectroscopy data for starting material and products of analogous reactions will be provided. The structure of the starting materials and products will be determined using all available data. A justification for the observed free-radical bromination reaction rates will be determined.

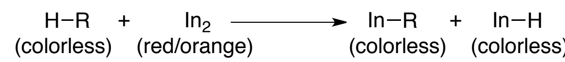
Reading
G&M Sections 9.1-9.3 (Radical Reactions)
Jones 5th ed. Sections 12.1-12.8 (Radical Reactions)
G&M Sections 8.3 and 8.5 (NMR spectroscopy and GCMS – *review from last term*)
Jones 5th ed. Sections 9.2, 9.3, 9.6-9.10 (NMR spectroscopy and GCMS – *review from last term*)

Some Key Terms
Free radical, initiation, propagation, termination, (1°, 2°, 3°) aliphatic, vinylic, aromatic, acetylenic, (1°, 2°, 3°) allylic, (1°, 2°, 3°) benzylic
Review terms: Nuclear Magnetic Resonance (NMR), splitting pattern, n+1 rule, coupling constant, chemical shift, equivalent protons, enantiotopic protons, diasteriotopic protons, gas chromatography (GC), mass spectrometry (MS), molecular ion, parent ion, isotopes, molecular weight, exact mass, mass spectrometer (MS), degree of unsaturation

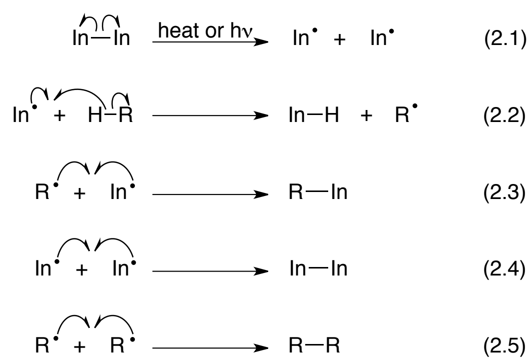
Video Instruction
See the video links related to NMR spectroscopy and GCMS in the "Pre-Term Laboratory Proficiency Requirements" document posted on NYU Classes.

Other Prelab Information
- Prepare your notebook according to the 'Notebook Guidelines' posted on NYU Classes under the Resources tab, in the Course Documents folder. Also, **create at table in your notebook to keep track of your observations in PART A of the experiment**.
- Always read the Material Safety Data Sheets (MSDS) posted on NYU Classes under the Resources tab, in the Experiment #1 subfolder.
- In preparation for all experiments you should be able to explain/answer the following questions:
  - What will you be doing in the lab (carefully think through each steps/reagents/etc.)?
  - Why will you do it (i.e. what is the theory that justifies each action/reagent/etc.)?
  - What outcome do you expect to result from each action and what theory supports your hypotheses?

Monitoring Reaction Progress
Bromine (Br_2) is red/orange in color. All reaction products and HBr are colorless. Therefore the rate of the reaction can be monitored visually as it is indicated by the disappearance of the red/orange Br_2.



Scheme 1. General overall reaction scheme. "In" = Initiator = Br_2 for this experiment



Scheme 2. Initiation, propagation, and termination steps of a radical reaction. Note that arrows with a single headed barb indicate the movement of *one* electron.

Rate of Hydrogen Atom Abstraction
Hydrogen atom abstraction (Scheme 2.2) is the rate-determining step of the free-radical bromination process. The rate of this step depends on two factors: a statistical factor and an energy factor. The statistical factor refers to the number of equivalent hydrogen atoms that can be abstracted through the radical mechanism. The energy factor is determined by the strength of the C-H bond. See Figure 1 and the assigned reading for a review of the classifications of hydrogen atom.

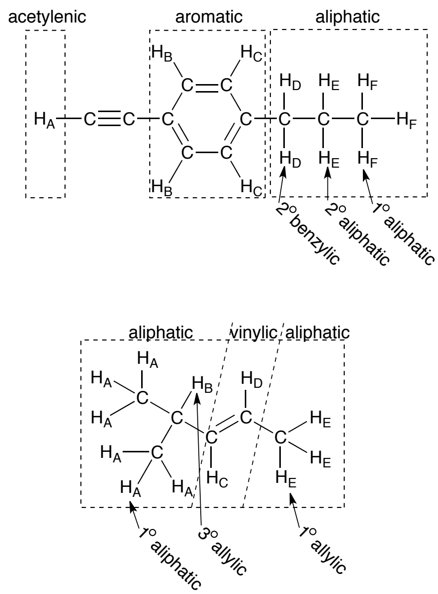


Figure 1. Examples of aliphatic, vinylic, aromatic, acetylenic, allylic, benzylic hydrogen atoms. Identical hydrogen atom subscripts within the same molecule signify equivalent hydrogen atoms.

The energy required to remove a hydrogen atom and generate the open shell, high energy species (R•) through free-radical bromination depends on the type of hydrogen atom being removed. The formation of this high-energy species (R•) is more favorable if adjacent orbitals can contribute to stabilization of the radical, e.g. through resonance. Therefore, when predicting the rate of reaction between two molecules, the molecule that forms the more stable radical will be the molecule with the lower energy transition state and thus the molecule that will proceed with the faster relative reaction rate.

When predicting relative reaction rates, the following are some general guidelines. Vinylic and aromatic hydrogen atoms do not react with radicals. An unpaired electron in an isolated sp^2 orbital is high in energy and difficult to form. Further, the vinylic and aromatic sp^2 orbitals are orthogonal to the π-system and therefore are not stabilized by resonance. Allylic benzylic and hydrogen atoms involve sp^3 orbitals that are stabilized by resonance with the alkene and aromatic ring, respectively (Figure 2). Note that the relative rate of reaction generally follows: 3° allylic/benzyllic > 2° allylic/benzyllic > > 1° allylic/benzyllic >>> R_3CH > R_2CH_2 > RCH_3 > CH_4.

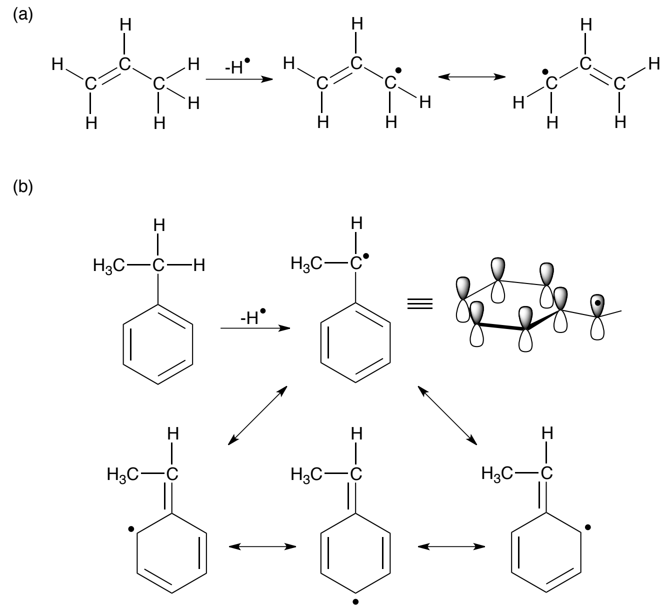


Figure 2. Resonance stabilization of (a) allylic and (b) benzyllic radical species.

Before your laboratory session you should practice drawing the arrows that show electron movement between resonance structures. Remember, to show the movement of only one electron use a curved arrow with clearly only one barb.

Experimental Details
CAUTION:

- Acetone and bromine should NEVER be mixed, even in waste containers. Acetone and bromine will react to form bromoacetone which is a lachrymator (tear gas).
- Always keep your hood sash at half-height and cover containers containing chemicals while transporting.
- Bromine may cause serious chemical burns if it comes in contact with your skin. If bromine contacts your skin, immediately wash the area with soap and water, and alert an instructor. If the bromine solution contacts your gloves, discard them immediately and wash your hands thoroughly. This means that you should bring at least 5 pairs of gloves to the laboratory session.

PART A

Label six 13x100mm test tubes "1A," "2A,"…."6A."
Label six 13x100mm test tubes "1B," "2B,"…."6B."
Label one 13x100mm test tubes "Control A" and another "Control B"
In all test tubes dispense 2.5 mL of dichloromethane and cover each with aluminum foil. Keep the test tubes covered except when adding reagents. Then, to each

numbered test tube add 10 drops of the corresponding unknown compound (e.g. dispense Unknown #1 into test tubes 1A *and* 1B, dispense Unknown #2 into test tubes 2A *and* 2B). Dispense 10 drops of dichloromethane into each of the Control test tubes only. Carefully obtain 4 mL of the provided 1 M bromine (in dichloromethane) solution in your graduated cylinder. In rapid succession add 0.5 mL of the 1 M bromine solution to each of the test tubes labeled "1A…6A" and "Control A." After addition of the Br_2 solution, cover the test tube and swirl to create a homogeneous solution. Record your observations (time, color) with regards to the discharge of color in each solution as compared to the control. Terminate the experiment after 1 hour.

Carry out the same procedure for the test tubes labeled "1B…6B" and "Control B," except after adding bromine, place the test tubes about 6 inches from the provided lamp. Record your observations (time, color). Both series may be run concurrently, but offset the start times by about 10 minutes.

IMPORTANT Clean-up protocol

There is a special waste container for all solutions that contain bromine. Also, ALL glassware AND test tubes that came in contact with bromine must be rinsed with ~1 mL of 0.6 M sodium thiosulfate before discarding or further washing. AFTER RINSING, test tubes should be discarded into the blue barrels.

PART B

In Part B free-radical reaction outcomes, as well as ^{1}H and ^{13}C-NMR data for starting material and products of analogous reactions will be provided. The structure of the starting materials and products will be determined using all available data. A justification for the observed free-radical bromination reaction rates will be determined. This data interpretation will be useful practice for the postlab assignment.

Post-lab Assignment

For this experiment you will *not* write a report. Instead you will complete a postlab assignment that will be distributed via NYU Classes (in the experiment folder) after your laboratory session. Although you will not write a report, your data and observations from the experiment will be required to complete the postlab assignment.