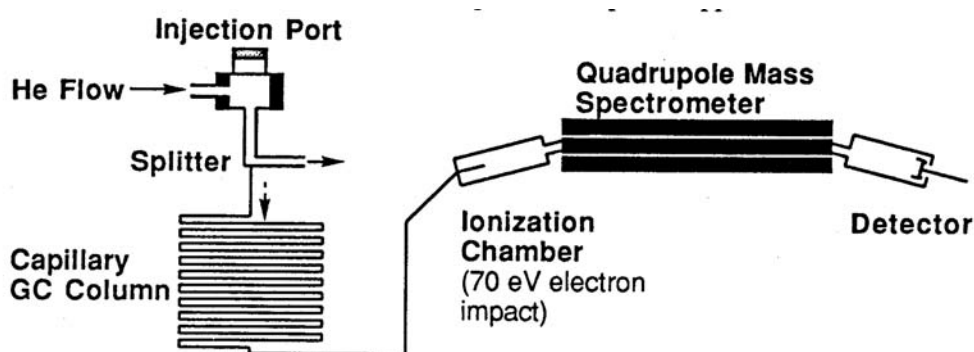


## 9.5 Hewlett Packard GC/Mass Spectrometer and Varian Saturn 2200 GC/MS/MS Operational Guide and Technique Manual

### *The Use of Mass Spectrometry as a Laboratory Tool for Confirming the Molecular Mass and Structure of a Reaction Product*

The GC-Mass Spectrometer has become one of the most sensitive and powerful instruments for the identification of organic compounds. Analysis of trace quantities of organic compounds has advanced to a stage greater than 1 part in  $10^{15}$ . Many impurities and contaminants found in food and water can now be identified unambiguously in trace amounts. To make the process easier many thousands of spectra including insecticides and industrial pollutants have been compiled into databases and are now readily available as packages that can be purchased and downloaded to computers hooked directly to GC/MS systems.

The liquid organic products from our distillations will be injected neat into the heated injector port of the GC/MS using a special custom-designed 0.01 microliter syringe. The volatilized compound is carried in the helium flow to a splitter with a split out ratio set at 1:300 whereby only 0.33% of the sample is diverted to the GC column (the rest is vaporized and exits the system). The GC column used in this instrument is a capillary column, which is 10-30 meters long and only 0.4 mm in diameter. The conditions above insure that no more than  $10^{-9}$  gram of the sample is applied to this column.



### **Schematic Diagram of HP GC/MS Quadrupole Mass Spectrometer**

In the Hewlett Packard GC/MS as the organic compounds elute from the GC, they are introduced immediately into a Quadrupole Mass Spectrometer and a series of mass spectra are repeatedly recorded for each two-second interval. In the ionization chamber, electrons traveling across a 70 eV potential bombard the molecules. When a molecule is struck by one of these high-energy electrons, it loses one of its own electrons

and becomes a radical cation  $M^+$ . Many of the molecular ions will be formed with enough excess energy to undergo subsequent reactions in the ionization chamber. From the ionization chamber, the positively charged ions are attracted through the magnetic field of a quadrupole ion chamber maintained under high vacuum. For a given strength of the magnetic field, only those ions having the correct charge/mass ratio ( $m/e$ ) will be deflected through the magnetic field and reach the detector. The instrument varies the magnetic field continuously to produce a spectrum of  $m/e$  peaks.



**Photo of Varian Saturn 2000 GC/MS**

The Varian Saturn 2000 GC/MS analyzes the gas-phase ions formed from a sample in terms of their mass-to-charge ( $m/z$ ) ratios and their relative abundances in the resulting spectra. The Saturn GC/MS creates the mass spectrum with an ion-trap analyzer. This type of device differs from the beam transport analyzer in the HP Quadrupole GC/MS where the ions to be separated pass through a series of fixed electromagnetic fields. Instead, the ion trap confines the ions within a single region where they experience time-dependent electromagnetic fields. The sample is first introduced into the ion trap analyzer through the directly coupled capillary column. The sample is ionized in the mass spectrometer by causing an electron to be removed from somewhere in the molecule. Depending on the compounds original structure and the excess energy present internally in the structure from the destabilizing process, the molecular ion or ionized compound undergoes further fragmentation and breaks apart. The process forms fragment ions and neutral fragments. The molecular and fragment ions, which are

formed, are stored inside the ion-trap cavity, where they travel around in defined orbits. Helium gas is also present inside the ion trap. It acts as a buffer and helps to focus the ions into more compact orbits, which then produce sharper mass peaks as they are scanned out. Helium is used because it does not ionize as readily as the analyte molecules. Helium ions end up being the most dominant ions inside the trap, but are immediately pumped away as soon as they are formed. Ion analysis takes place by applying a radio frequency (rf) (1.1 MHz) voltage to the ring electrode that encircles the trap cavity. As the voltage increases on the ring electrode, ions are sequentially sucked out and ejected from the trap according to their mass-to-charge ratio.

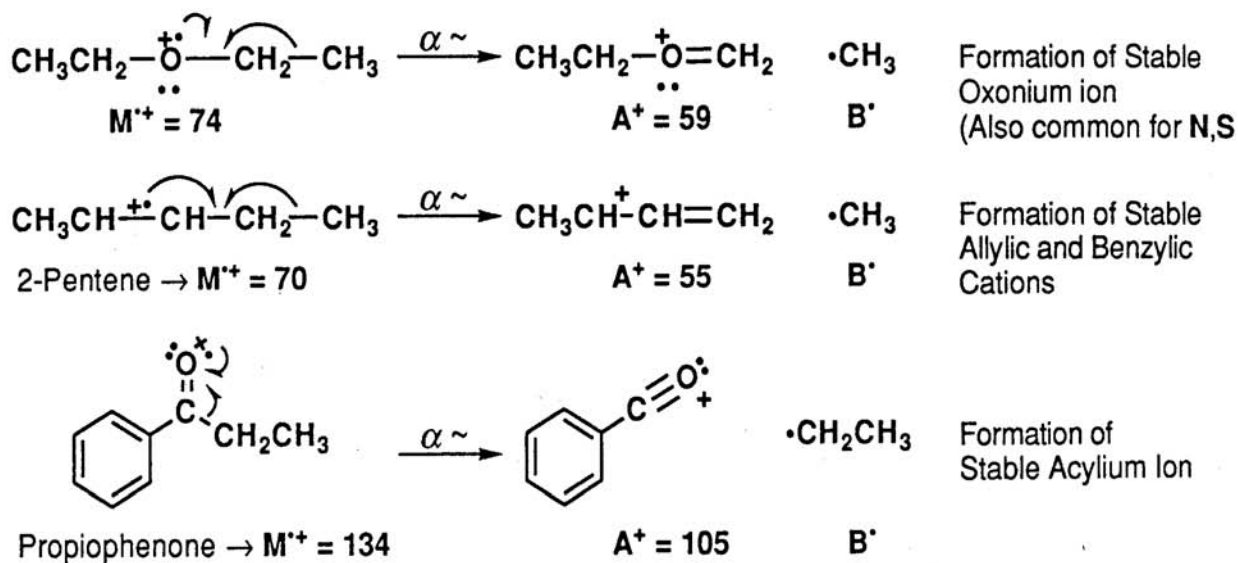
In the next section are detailed mechanisms for common fragmentation and ionization reactions. It is much more difficult to solve the structure of an organic compound from the mass spectrum alone than it is to match the spectrum with that of the known compound. With the help of NMR and IR spectroscopy, mass spectrometry can play an important role in structure determination.

## Reactions Observed in Mass Spectroscopy

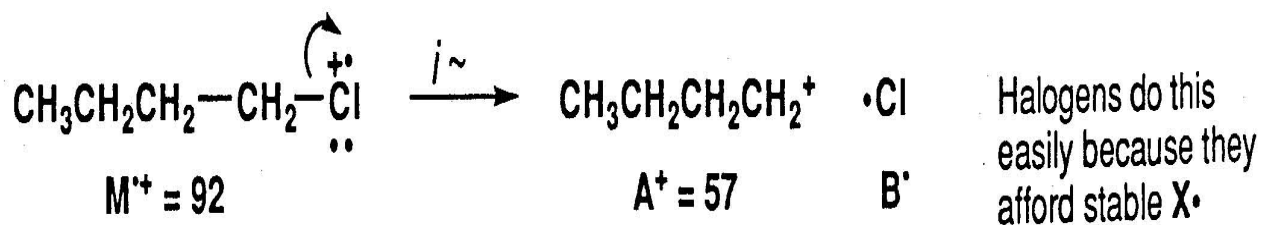
**A Fragmentation Reaction** involves the cleavage of one bond of the radical cation  $\mathbf{M}^{\bullet+}$  to form a cation  $\mathbf{A}^+$  and a radical  $\mathbf{B}^{\bullet}$ . The reaction is especially facilitated by substituents, which stabilize the cation  $\mathbf{A}^+$ .



**$\alpha$ -Cleavage Reaction.** The  $\alpha$ -cleavage reaction is driven by the formation of a stable carbocation as shown in the examples listed below. In the first case, ethers readily undergo the  $\alpha$ -cleavage reaction forming a stable oxonium ion (also common for similar N,S compounds). In the second example, alkenes undergo  $\alpha$ -cleavage reaction to form a stable allylic cation (also common for aryl compounds and alkynes). In the third example, ketones readily undergo  $\alpha$ -cleavage to produce stable acylium ions.



**Inductive Cleavage Reaction.** Alkyl halides often undergo the inductive cleavage reaction in which the halogen atom (e.g. Cl) simply breaks off the initial radical cation. This is most prevalent for bromides and iodides and for compounds, which can produce a stable carbocation.

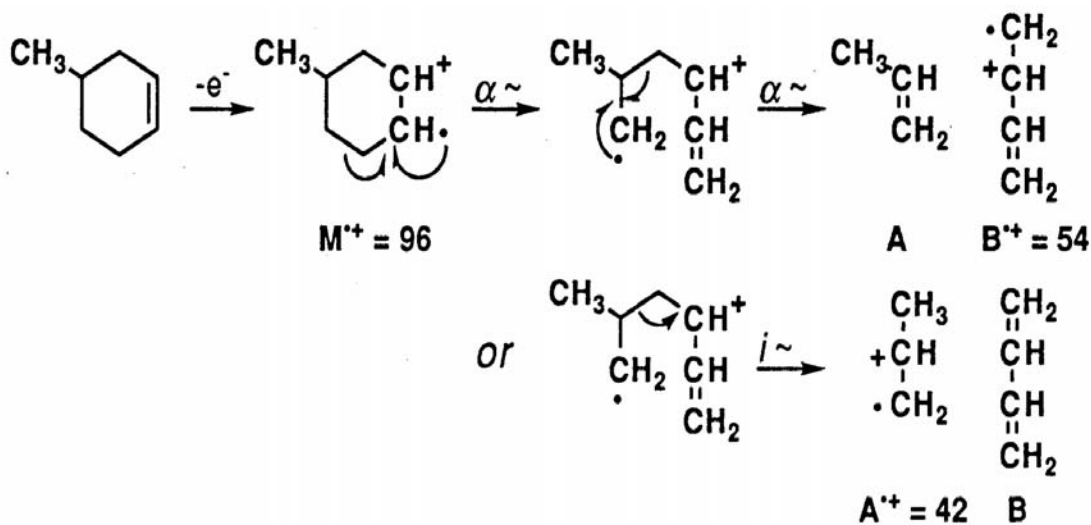


In each case, fragmentation reactions above produce both a radical and a cation from the initial radical cation  $M^+$ . Also, as a consequence of the nitrogen rule: For molecules that do not contain nitrogen, fragmentation reactions of the even-massed radical cations will produce odd-massed  $A^+$  ions. This can be a useful method for finding which ions are produced by one of the above reactions.

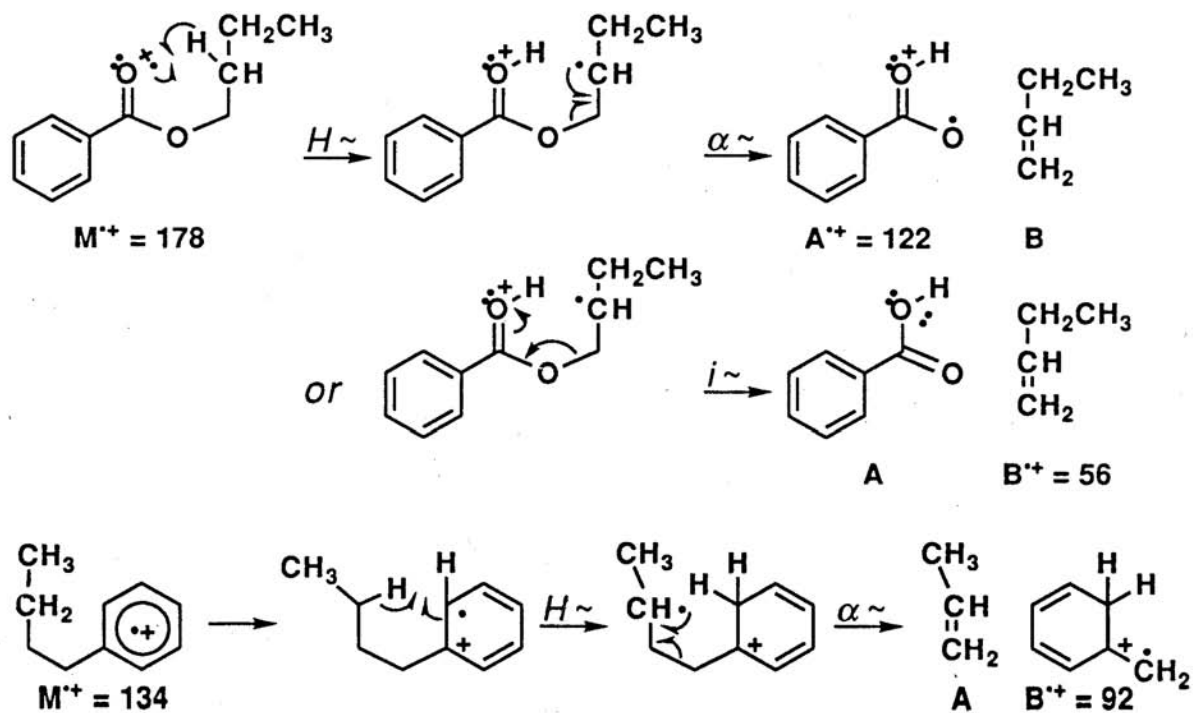
**A Rearrangement Reaction** involves the cleavage of more than one bond of the radical cation  $M^+$  to ultimately form a new radical cation  $A^+$  and a neutral compound **B**. Often, rearrangement reactions may proceed by complementary pathways so that the mass numbers for both parts of the molecule can be found in the mass spectrum.



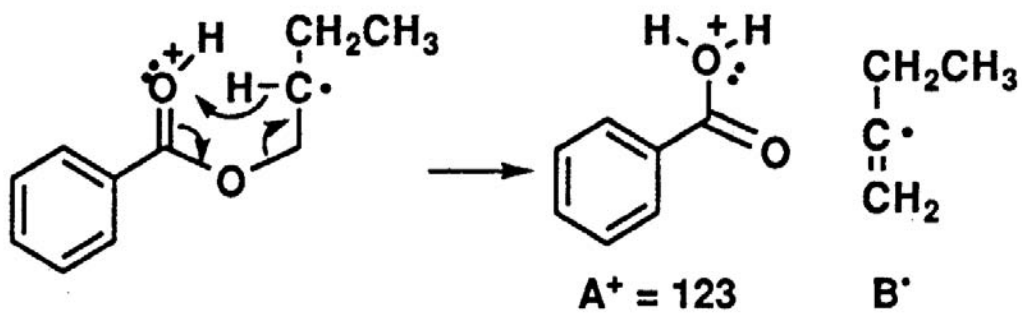
**Rearrangement of Cyclic Structures.** When a cyclohexene derivative is ionized in the mass spectrum, a particularly facile cleavage of the ring is reminiscent of a retro-Diels-Alder reaction.



**Radical Site Rearrangements (McLafferty Rearrangement).** Carbonyl derivatives readily undergo a rearrangement reaction in which the  $M^{+\bullet}$  undergoes intramolecular H atom transfer to the carbonyl oxygen atom. The best geometry involves a six-membered transition state and subsequent  $\alpha$ -cleavage or inductive cleavage leads to the fragment ions of each piece.



For each example of rearrangement reactions, the observed ions are radical cations. For a molecule which does not contain nitrogen, the McLafferty rearrangement of the even-massed  $M^+$  ion produces an even mass  $A^+$  ion and so are easily distinguished from the odd-massed ions from a simple fragmentation reaction. Also, many molecules display a peak in the mass spectrum arising from a McLafferty +1 rearrangement. For the ester above, the mechanism involves a second H atom transfer.



## APPENDIX I<sup>1</sup>

### Procedure for Operating the Hewlett Packard GC-MS

1. Turn on the computer (Pump and GC should already be on) if its already on go to step 6 skip steps 1-5.
2. Strike F1 key when prompted on computer screen
3. When program manager appears left mousclick on chemstation then restore or maximize
4. Left click to highlight MS Top then go to file and select open
5. Top Default screen should now be open
6. Go to methods and Load and Run Methods Select Chem532m and OK
7. Fill in your last name followed by (.D) for the file name, operator, sample unknown #, and any notes, then click on Run Method
8. Now take a 0.01 micro liter syringe and fill with your sample (neat) with one swift movement inject the sample into the GC and quickly press start on the GC until the solid green light appears on GC console. The spectrum appears on the computer and will be blank for the first 2.00 minutes as the solvent delay keeps the MS from turning on when the bulk of the sample hits the source. After 2.00 minutes you should see the tail end of your sample appear on the GC trace.
9. A message appears Override Solvent Delay 2.00 minutes Select "NO" and enter to get rid of the message
10. Once spectrum finishes running it disappears into the data file and you are returned to TOP Chem 532.m
11. Click on the link data analysis and select main panel from drop down menu
12. From file choose load data file click on your file name and open
13. Move you cursor to a point under your peak (2.20 minutes) and right click twice and your mass spectrum appears under your GC trace, you can move it to another location on the GC trace and right double click until you get the cleanest looking mass spectrum that you want to print from
14. Go to file and select Print Trace + Spectrum click only once and wait after a minute you will see message in lower left of computer Printout

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<sup>1</sup> Written by John J. Dolhun



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sent to background spooler be patient it takes a few minutes and then prints

15. Go to the link Spectra then select tabulate spectra then Print and then click Done
16. Go to Integrate select Generate % report respond generate report then Done this may have nothing on it depending on your spectrum
17. You should leave the machine with the MS Top screen open for the next student

## APPENDIX II<sup>2</sup>

### Procedure for Operating the Saturn 2000 GC/MS

1. Open computer and click upper left icon which reads System Control/Automation
2. Allow box to load and you should see System Control-Varian Saturn 2200-Not Ready
3. In lower left corner of computer open the box 2000.40 by clicking in the white box to expand page. This is your system control panel.
4. Click on the folder to the right- Activate a Method (this opens activate a system control method file). Find folder SaturnWS then Service then CHEM532\_CI&EI then click on EI\_JDquick this loads the method you will use to run your GC/MS
5. Click on the Acquisition tab upper right corner and wait until both green lights appear Ready and No Faults. The “Red” Not Ready light will continue to flash at the top of the screen.
6. When both green lights appear click on the word ENDTIME on left side of screen and set the minutes to 10.00 minutes then click OK.
7. Prepare your sample for injection. Make sure the syringe has been cleaned and baked out in the syringe heating block allow time for it to cool completely before drawing your sample. Draw up 0.01 microliters into your syringe. Note the three-pronged injector on the top of the instrument. Insert the syringe and with one quick sequence inject the sample and simultaneously push down on the three-pronged injector switch. The “Red” Not Ready light changes to “Running” and the GC Green run light comes on and the chromatogram begins to record.
8. Once the Chromatogram completes after 10.00 minutes click on the last colored icon box in the middle of the screen above the spectrum, which opens up the GC spectrum in a window called MultiChro1. Click anywhere in the spectrum

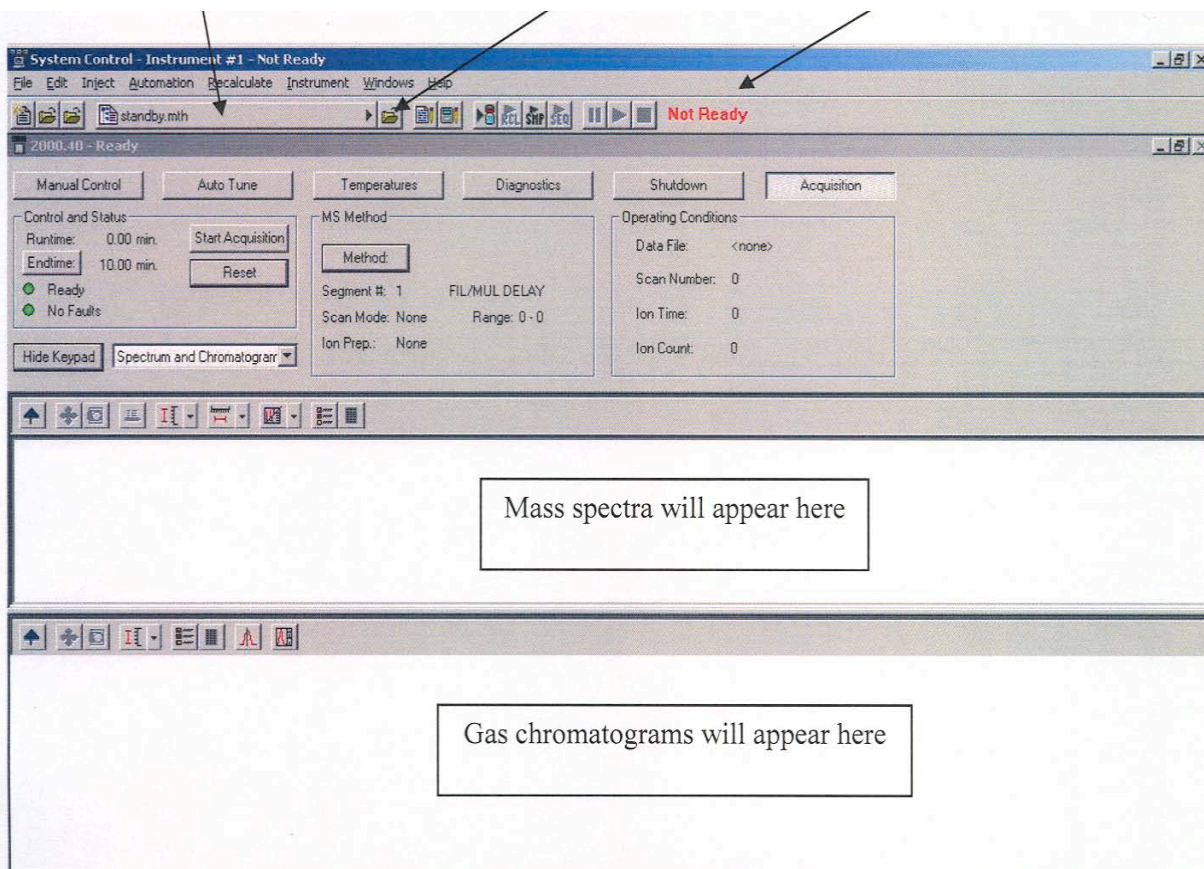
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<sup>2</sup> Written by John J. Dolhun

- and the screen divides in half GC on the left and MS on the right.
9. Click on the GC Spectrum at a point where you want to see a corresponding mass spectrum.
  10. Go to file and select print chromatogram and you will get a printout of the Mass Spectrum above and the gas chromatogram below.
  11. Select Search from the menu bar and click on Library Search then at bottom left click Saturn Search. Type in parameters molecular weight range and Target ion range then hit search and print out sheet of your possible hits. A list of probable compounds prints.
  12. Click on Spectra and Edit Spectrum to get a list of Mass Ions and their intensities. Click on Print button lower left on screen. You should be able to import data to a computer diskette.

## System Control Varian Saturn 2200

Method: EI\_JDquick      File Folder: Allows selection of Method      Injection Status: Changes to Running after Injection



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