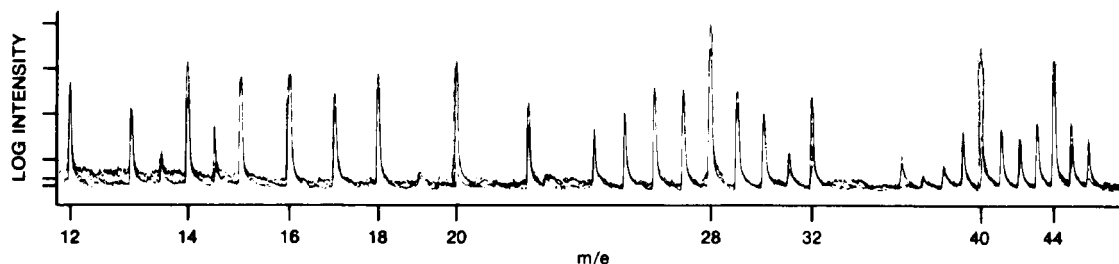# Chemistry 416 "Spectroscopy"
# Winter Semester 1996
# Dr. Rainer Glaser

## Third 1-Hour Examination
## "Mass Spectroscopy"

### Monday, April 8, 1996, 8:40 - 9:30

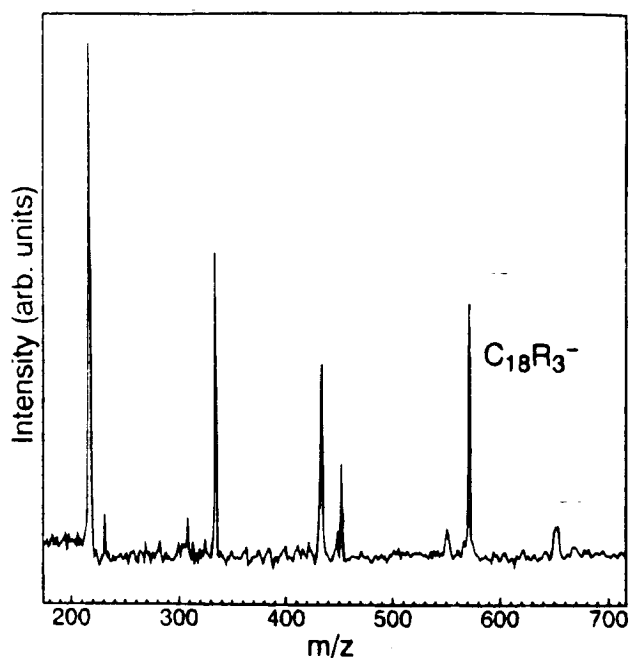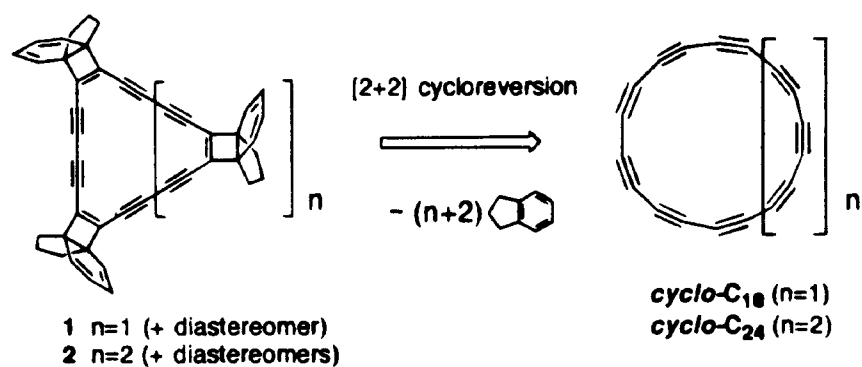Fig. 14.3. First mass spectrum returned from the surface of Mars. (From Rushneck *et al.*, 1978.)



| Name: | | |
|---|---|---|
| | | |

| | | |
|---|---|---|
| Question 1 (Negative Ions) | 34 | |
| Question 2 (Isomers) | 16 | |
| Total | 50 | |
| | * 2 = | |

**Question 1.** Negative Ion LD-TOF MS of "Cyclo($n$)carbons".

"A New Entry into Cyclo($n$)carbons: [2+2] Cycloreversion of Propellane-Annelated Dehydro-annulenes." by Tobe, Y.; Fujii, T.; Matsumoto, H.; Naemura, K.; Achiba, Y.; Wakabayshi, T. *J. Am. Chem. Soc.* **1996**, 18, 2758.

"Cyclocarbons" are the most stable form of carbon in the range between $C_{10}$ and $C_{20}$. The authors have succeeded in the preparation of **1** and **2** and of the photochemical generation of *cyclo*-$C_{18}$ and *cyclo*-$C_{20}$ via [2+2] cycloreversion. LD-TOF MS was employed to characterize the annulenes **1** and **2**. The negative ion LD-TOF mass spectra of **1** is shown below. R denotes the indan fragment.



**1** n=1 (+ diastereomer)
**2** n=2 (+ diastereomers)

[2+2] cycloreversion

– (n+2)

*cyclo*-$C_{18}$ (n=1)
*cyclo*-$C_{24}$ (n=2)



$C_{18}R_3^-$

**(a)** What does "LD" stand for?  Briefly explain the principle and the purpose of the LD method. (4 points)

**(b)** What does "TOF" stand for?  Explain the principle and the purpose of the TOF method.  Be brief.  A schematic drawing might help as well.  (4 points)

**(c)** The positive mode LD-TOF MS of **1** contains only one peak with m/z = 118.179.  What is the molecular formula of this peak?  Suggest a structure for this cation.  (6 points)

**(d)** The negative mode LD-TOF mass spectrum of **1** contains not only the parent ion **1·⁻** but also several strong peaks that provide compelling support, for example, for the intermediates along the multiple [2+2] cycloreversion and for the formation of *cyclo*-$C_{18}$. Explain what molecules cause the following peaks. Give formula and make a suggestion as to the formation of the ion (e.g. loss of __ from ____). (12 points)

| |
|---|
| $\lvert m/z \rvert = 216.1998$ |
| |
| $\lvert m/z \rvert = 334.3791$ |
| |
| $\lvert m/z \rvert = 452.5585$ |
| |
| $\lvert m/z \rvert = 648.5994$ |

**(e)** The spectrum shown is appears not well resolved the way it is displayed (mass range 200 - 700). But, of course, the spectrum was recorded with a much higher resolution and we could examine the intensity of every "M+1 peak" associated with any of the peaks. For each peak, we would expect to find M+1 peaks because of the natural abundance of _____ percent of the carbon isotope _____C. Please, specify what the intensities of these M+1 peaks are. (8 points)

| |
|---|
| $\lvert m/z \rvert = 216.1998$ |
| $M(216.2) : M(217.2) = 100 : $ _____ |
| $\lvert m/z \rvert = 432.3996$ |
| $2.4) : M(433.4) = 100 : $ _____ |

**Question 2.** GC-MS Analysis of the Chlorination of Methylcyclohexane. (16 points)

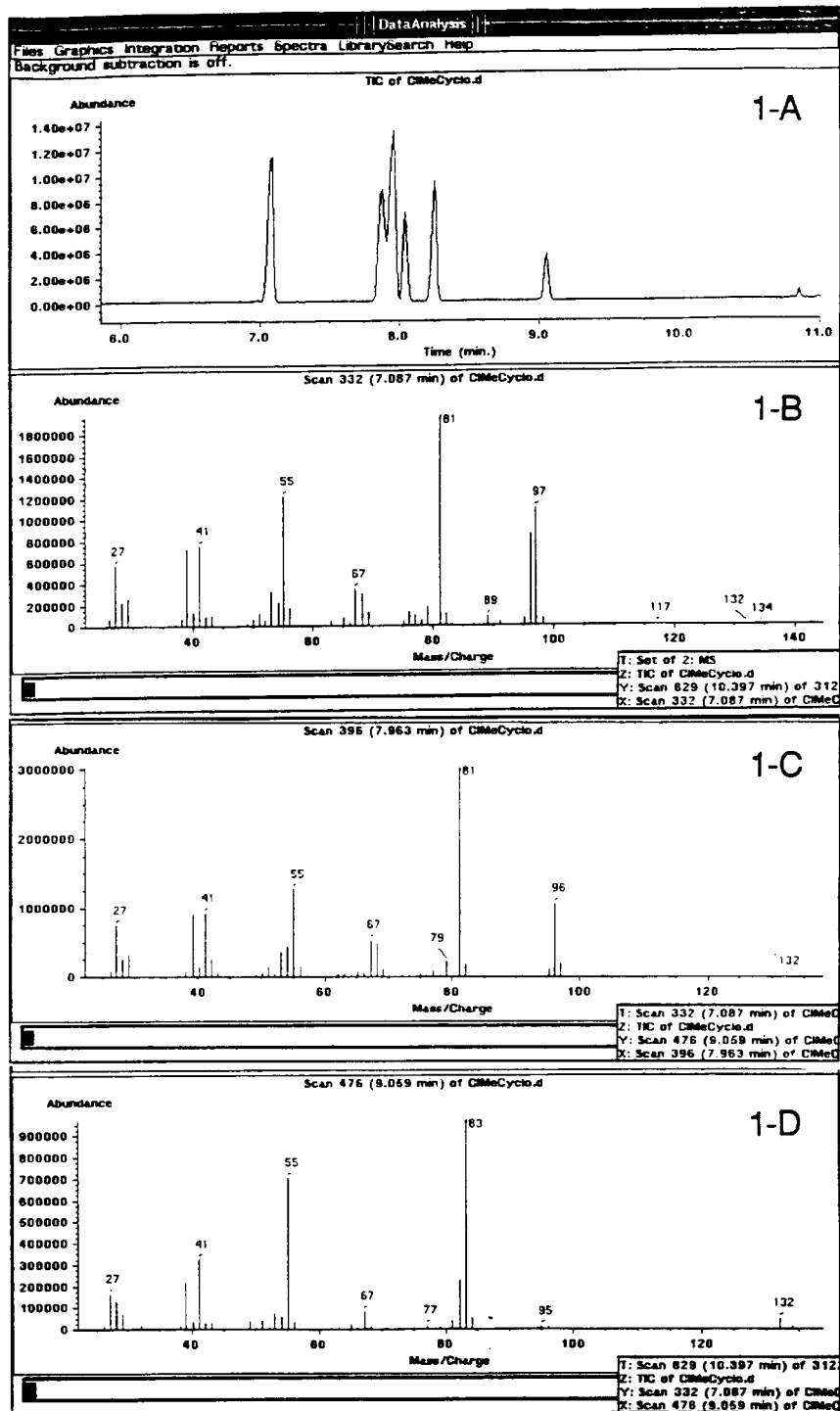Bishop, R. D. *J. Chem. Educ.* **1995**, *72*, 743-745.



Figure 1. A. Segment of the distillate gas chromatogram showing six peaks for the monochloro product isomers. (The remaining two isomer peaks are presumed to be buried beneath the four peaks clustered around the eight-minute mark). B. Mass spectrum for the peak at 7.087 min retention time. C. Mass spectrum for the peak at 7.963 min retention time. D. Mass spectrum for the peak at 9.059 min retention time.

The chlorination of hydrocarbons proceeds via a radical reaction mechanism. As you know, it is one of the fundamental physical organic problems of this reaction to find the relative reactivity ratios of the primary, secondary and tertiary hydrogens toward free-radical substitution by chlorine atoms. The above cited article describes an experiment that allows one to determine just that using GC-MS. The GC spectrum and three mass spectra are shown on the previous page.

**(a)** Write down the structures of (at least) one of the products obtained by reaction of a primary, secondary, or tertiary hydrogen of methylcyclohexane. (3 points)

| **primary** | **secondary** | **tertiary** |
|---|---|---|
|  |  |  |

**(b)** In theory, how many different **structure isomers** can be produced in the chlorination of methylcyclohexane. Consider only monochlorination! Several of the structure isomers allow for stereoisomers. Without counting enantiomers, how many **stereoisomers** can be formed? (2 p.)

# possible structure isomers = _____    # possible stereoisomers = _____

**(c)** Analyze the spectra and suggest structures that fit each spectrum. Explain the significance of the peaks with the specified m/z value as requested. For the secondary system, just give any of the secondary structures. (2 for structure, 1 each m/z; 5+3+3 points = 11 points)

| 1-B | Structure of 1-B |
|---|---|
| m/z = 132 is due to<br><br>m/z = 117 is due to<br><br>m/z = 97 is due to |  |

| 1-C | Structure of 1-C |
|---|---|
| m/z = 55 is due to | |
| 1-D | Structure of 1-D |
| m/z = 83 is due to | |

# The END
of another exciting learning experience