

MASS SPECTROMETRY OF ORGANOGERMANIUM COMPOUNDS.
FRAGMENTATION PROCESS OF 1-GERMACYCLOHEXANE AND THEIR METHYL DERIVATIVES.

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Abstract—The mass spectrometric fragmentation caused by electron impact of germacyclohexane, 3-methyl- and 4-methyl derivatives and their deuterated species were analyzed. Initially the cleavage of Ge-C bond took place, followed by loss of hydrocarbon moieties. The whole fragmentation processes can be explained by the combination of elimination of hydrocarbon moiety (neutral and radical) and hydrogen transfer (McLafferty rearrangement). The base peaks were at m/z 74 (germanium cation radical) in contrast to that of 1,1-dimethyl-1-germacyclohexanes at m/z 89.

There have not been known many kinds of heterocyclic compounds with a germanium atom (or atoms) as the ring constituent. Hence, mass spectrometric studies on the relation between the structure of these heterocyclic organogermanium compounds and their fragmentation pattern are rather scarce. So far, studies on mass spectrometric fragmentation patterns have been reported only for 1,1-dimethyl-1-germacyclobutanes¹, germacyclopentanes² and 1-germacyclopentenes.³ We have previously analyzed the mass spectra of 1,1-dimethyl-1-germacyclohexanes and reported the fragmentation patterns which was proved much more complicated as depicted in the previous reports.⁴ In this paper we describe the process of fragmentation of germacyclohexanes. Thus, we prepared some germacyclohexanes together with their 1,1-deuterated species, and determined the ionic species generated by electron impact by a combination of the shift technique based on the comparison with the results of deuterated and/or methylated species.

EXPERIMENTAL

The preparation of germacyclohexane(GC) was described by Mazerolles.⁵ 3-Methyl-(3MGC) and 4-methyl-(4MGC) 1-germacyclohexanes were prepared in an essentially identical manner.⁶ Their deuterated species, 1,1-deuteriogermacyclohexane(GC-d₂), and its 3-methyl-(3MGC-d₂) and 4-methyl-(4MGC-d₂) derivatives were prepared by treating the precursors of GC, 3MGC and 4MGC, 1,1-dichloro-1-germacyclohexane, its 3-methyl- and 4-methyl- derivatives with lithium aluminum deuteride.

The crude products were distilled by means of a K6geirrohr (B6uchi GKR-50) and purified by a preparative gas chromatograph (Shimadzu GC-3BT). The structures were confirmed by spectroscopic means including ¹H nmr(Varian EM-390), ¹³C nmr (JEOL FX-90Q) and ir(JASCO 200A) spectra.

Mass spectra(GC/MS) were determined with a Hewlett-Packard 9550A QP type mass spectrometer. The condition of gas chromatography is as follows: carrier gas, He; flow rate, 1.2 ml/min; temperature, 100 °C to 200 °C, 4 °C/min(ascending temperature method); column, cross-linked methylsilicone (0.2φ x 25m); ionizing energy, 70 eV; mass accuracy, ±0.1 mass unit.

RESULTS AND DISCUSSION

The mass spectrum of the parent compound GC is given in Figure 1. In the spectrum a group of peaks associated with the five stable isotopes of germanium were observed. The intensity of each of five peaks corresponds to the population of stable isotopes. The intensity of molecular ions(M⁺) is substantial; to the contrary, relative intensities of ions originated from hydrocarbons are very weak. The molecular ions(M⁺) may initiate cleavage of either Ge-H or Ge-C bonds. Since the bond energy is 68 kcal mol⁻¹ for the former and 59 kcal mol⁻¹ for the latter bond, the cleavage of Ge-C bond is more favorable. In Table 1, the mass spectrometric characteristics of compounds investigated are summarized. Relative intensities of ions generated from GC and GC-d₂ were compared to obtain insights in the cleavage processes. Deuterated ions show an increase of relevant mass number. There seems, however, no isotope effect upon the relative intensities.

This is also the case with methyl-substituted species, e.g., 3MGC, as compared with GC. Taking all these observations into consideration, we like to propose the fragmentation processes as depicted in Figure 2.

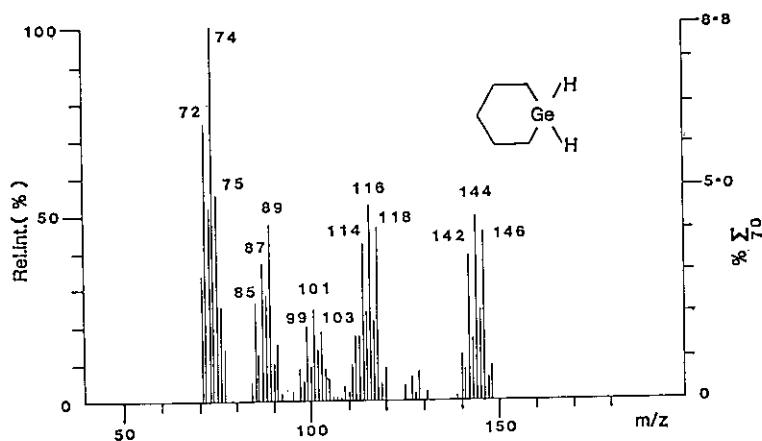


Figure 1. Mass Spectrum of Germacyclohexane(GC).

Table 1. Intensity of Base Peak and Molecular Ions Relative to Total Ionization.

| Compound | base peak | | molecular ion | |
|---------------------|-----------|---------------|---------------|---------------|
| | m/z | % \sum_{70} | m/z | % \sum_{70} |
| GC | 74 | 8.8 | 146 | 3.8 |
| GC-d ₂ | 74 | 11.6 | 148 | 2.1 |
| 3MGC | 89 | 5.9 | 160 | 1.7 |
| | (74) | (5.6) | | |
| 3MGC-d ₂ | 74 | 6.8 | 162 | 1.3 |
| 4MGC | 130 | 8.2 | 160 | 2.3 |
| | (74) | (7.3) | | |
| 4MGC-d ₂ | 74 | 8.8 | 162 | 1.3 |

m/z based on ⁷⁴Ge

In Figure 2, base peak at m/z 74 corresponds to the peak due to ⁷⁴Ge cation. As is shown in Figure 2, the main pathway of fragmentation initiates with

+ ⁷⁰Ge, 20.56%; ⁷²Ge, 27.42%; ⁷³Ge, 7.79%; ⁷⁴Ge, 36.46%; ⁷⁶Ge, 7.76%.

the cleavage of Ge-C bond, followed by elimination of neutral species to yield the base peak ion. All fragment ions with strong relative intensities contain germanium.

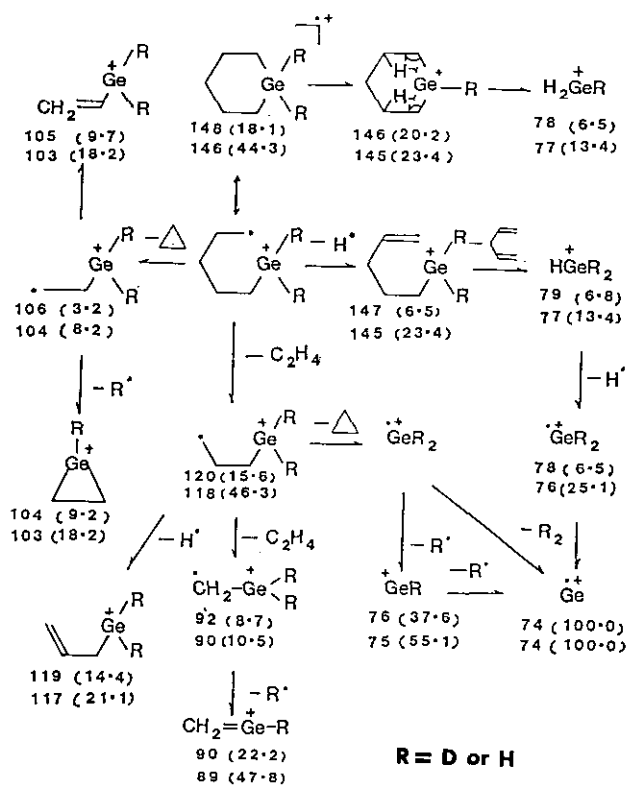


Figure 2 Fragmentation Process of Germacyclohexane.

Fragmentations other than shown in Figure 2 are also possible. One such process is a McLafferty rearrangement⁷ in which a hydrogen atom rearranges via a five- or six-membered cyclic transition states (Figure 3). A possibility of a direct elimination of cycloalkane moieties cannot be denied (Figure 4). Ionic species generated in the processes depicted in Figures 3 and 4 are identical with those generated in the processes depicted in Figure 2. Hence the ions observed may be originated from more than one processes. The quantitative determination of each contribution is, however, impossible from the present data alone.

In order to prove the existence of processes depicted in Figure 2, fragmentation patterns of 3MGC to 4MGC- d_2 were determined and the substituent shift effects

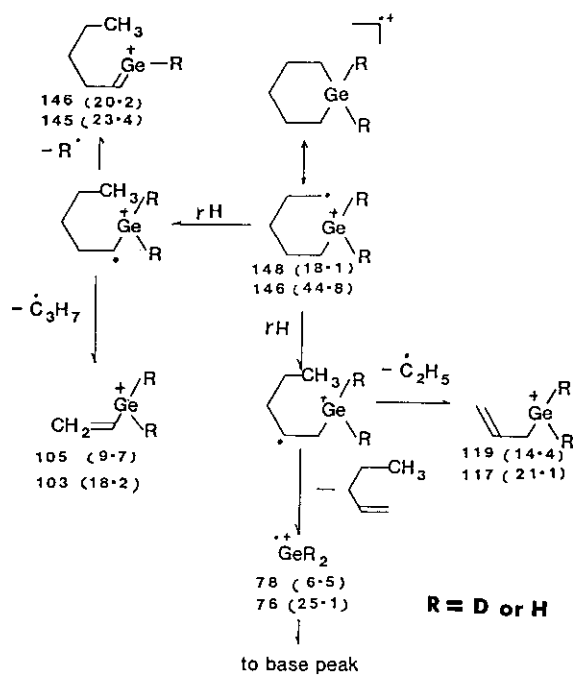


Figure 3. McLafferty Rearrangement via Five- and Six-Membered Cyclic Transition States.

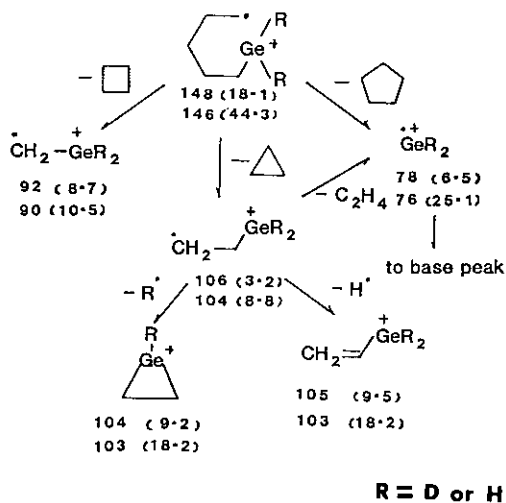
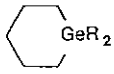
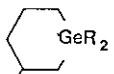
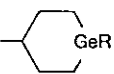

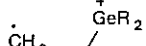
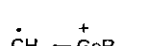
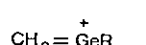
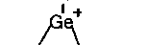
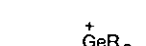




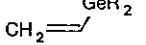


Figure 4. Fragment Ions Formed by Elimination of Cycloalkane Moieties.

were analyzed. The results are summarized in Table 2. Evidently, the relative intensities of ions containing the methyl moiety is larger than these of other ions, which are essentially identical with these in GC, to indicate a considerable stabilizing effect of a methyl group. These results seem to support the processes depicted in Figure 2.

As is given in Table 2, 3MGC and 4MGC exhibit base peak other than that with m/z 74. 1,1-Dimethyl-1-germacyclohexanes discussed in the previous report⁴ exhibited the base peak at m/z 89 (CH_3Ge^+), to indicate that GC, GC-d₂, 3MGC-d₂ and 4MGC-d₂ are more metallic in the sense that all the organic moieties are removed during the fragmentation. In the case of 3MGC, the base peak has m/z 89, and at the same time the relative intensity of m/z 74 peak is 94%, which indicated that, as is shown in Figure 5, the characteristic base peak ion at m/z 89 was formed by the competitive cleavage (via route A or route B) of the ion with

Table 2. Ion Structures and Relative Intensities(%) for GC and Derivatives.

| R = D or H |  |  |  |
|---|---|---|---|
| M^+ | 148 (18.1) | 162 (19.0) | 162 (14.9) |
|  | 146 (44.3) | 160 (28.8) | 160 (27.9) |
|  | 120 (15.6) | 134 (10.4) | 134 (58.3) |
|  | 118 (46.3) | 132 (18.8) | 132 (98.5) |
|  | 106 (3.2) | 120 (16.1) | 106 (8.3) |
|  | 104 (8.2) | 118 (38.7) | 104 (14.5) |
|  | 92 (8.7) | 92 (20.2) | 92 (8.2) |
|  | 90 (10.5) | 90 (14.2) | 90 (8.9) |
| $\text{CH}_2=\text{GeR}^+$ | 90 (22.2) | 90 (47.6) | 90 (18.6) |
|  | 89 (47.8) | 89 (100.0) | 89 (40.7) |
|  | 104 (9.5) | 118 (37.1) | 104 (17.2) |
|  | 103 (18.2) | 117 (45.6) | 103 (23.6) |
| $\text{CH}_2=\text{GeR}_2^+$ | 105 (9.7) | 119 (34.9) | 105 (12.9) |
|  | 103 (18.2) | 117 (45.6) | 103 (23.6) |

m/z 132. This is an interesting example of isotope effect in which the Ge-H and Ge-D bonds suffer from McLafferty rearrangement in a considerably different extent. Since there is only a small isotope effect in route A, the relative intensities of peak at m/z 74 are similar for 3MGC and 3MGC-d₂.

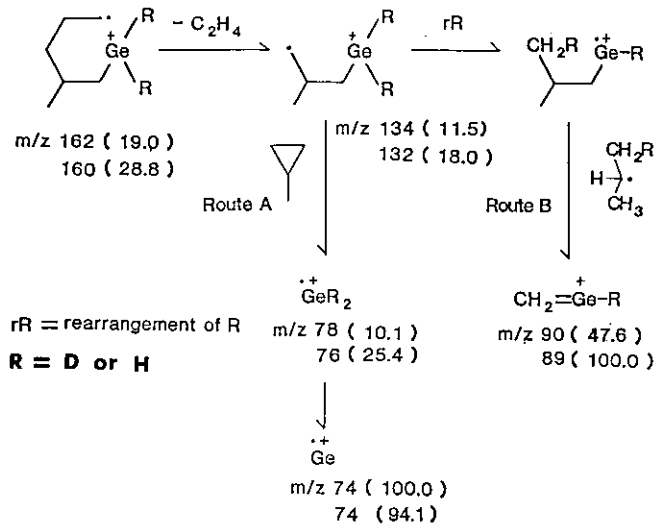


Figure 5 Competitive Fragmentation of m/z 134 and m/z 132 Ions.

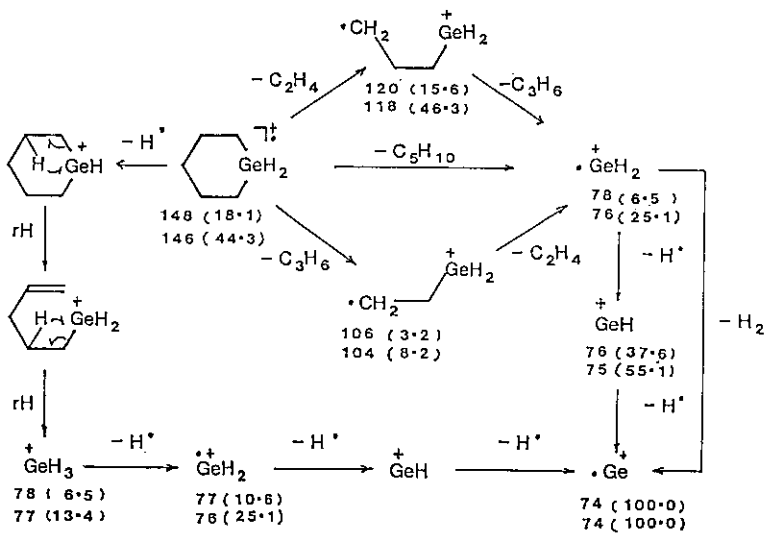


Figure 6 Fragmentation Process of GC and GC-d₂ Leading to Base Peak.

Numerical figures given below ion structures represent m/z and numerical figures in parentheses denote relative intensity (Upper, D and lower, H compounds).

Furthermore, due to the enhanced stability of the branched hydrocarbon moiety, elimination of hydrocarbon residue is facilitated in 3MGC, where the two pathways are equally effective. The base peak for 4MGC is m/z 130, but the pathway from $M^{+\bullet}$ to the species of m/z 130 is not straightforward. On the other hand, an ion at m/z 132 stabilized by a methyl group attached to position 4 have a high relative intensity of 98.5 percent.

On the other hand, 4MGC- d_2 cleaves, following the standard pathway to yield the base peak at m/z 74. In Figure 6 the most reasonable cleavage pathway to the base peak is summarized based on the discussion above.

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