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MASS SPECTROMETRY IN STRUCTURAL AND STEREOCHEMICAL PROBLEMS
CLII*. ELECTRON IMPACT PROMOTED FRAGMENTATION OF SOME SUBSTITUTED GERMACYCLOPENTANES AND GERMACYCLOPENTENES

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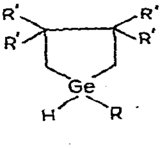
SUMMARY

The mass spectra of substituted germacyclopentanes and germacyclopentenes have been measured. Deuterium labeling, supported by low voltage measurements, has enabled plausible mechanistic rationalizations to be presented for the origin of the principal ions in these spectra. The nearly ubiquitous loss of ethylene in germacyclopentanes was found to involve only C-2 and C-3.

INTRODUCTION

The mass spectra of several organogermanes have been reported in the literature[2] and the fragmentation of germacyclopentane has been discussed in a study[3] describing the effect that different heteroatoms have on the fragmentation of five-membered heterocycles. The details of a computer technique previously used[3] to unravel the complex series of peaks obtained in the mass spectra of germanium compounds (due to five isotopes) into monoisotopic form when two or more adjacent peaks (M, $M-1$ and $M-2$) are present has been published[4]. Our interest in the mass spectrometry of germacycloalkanes was initiated by the use of this technique, in conjunction with NMR spectroscopy, in the structure identification of the compounds obtained by the reaction of germanium diiodide with conjugated dienes[5,6].

A. 1-SUBSTITUTED GERMACYCLOPENTANES



(I): $R=R'=H$
(II): $R=n\text{-}C_3H_7, R'=H$
(III): $R=n\text{-}C_4H_9, R'=D$
(IV): $R=C_6H_5, R'=D$
(V): $R=Cl, R'=H$

All the compounds investigated in this section showed easily identifiable molecular ions[7] in their mass spectra (Figs. 1–5) and in each instance loss of 28-mass

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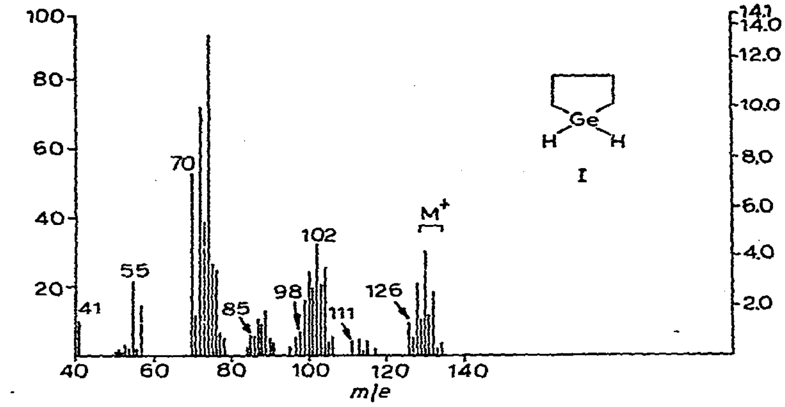
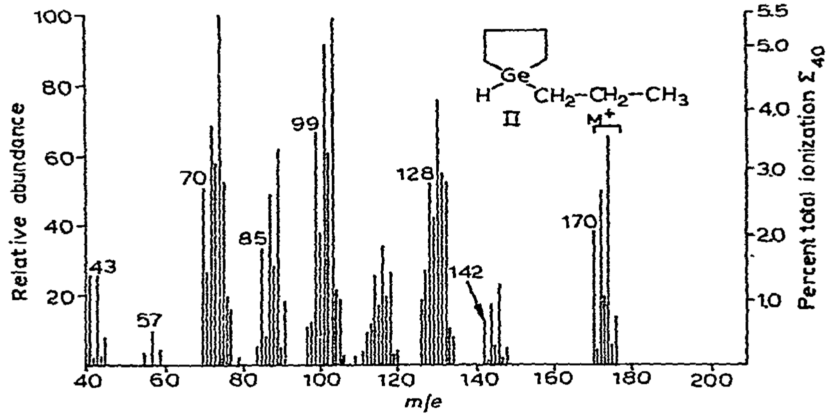
* For Part CLI see ref. 1.





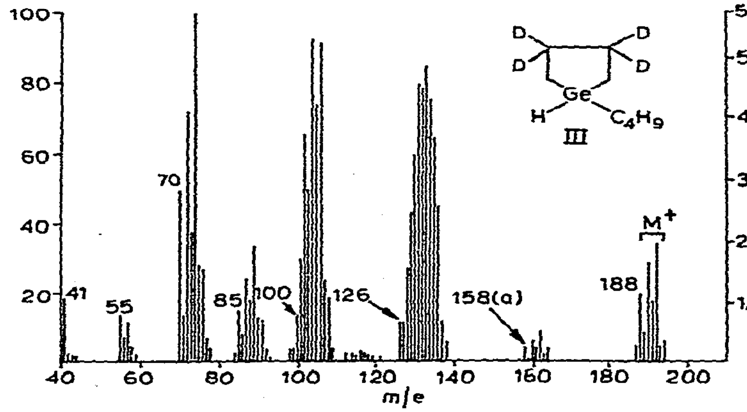
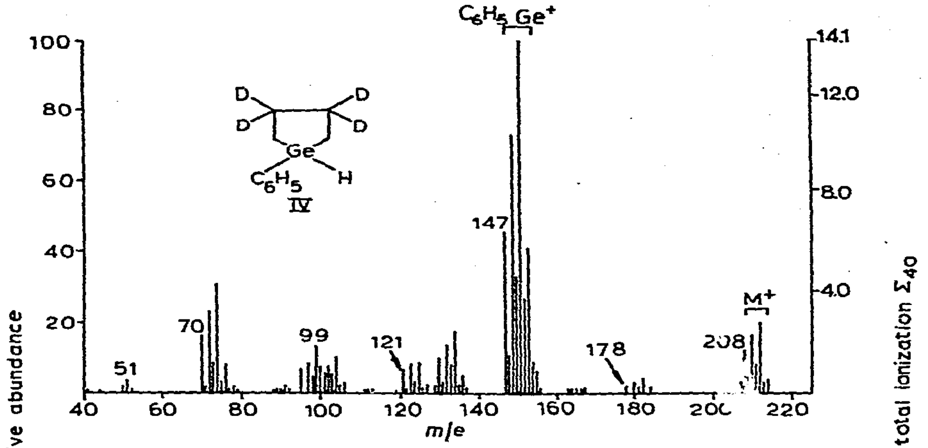


Fig. 1. Mass spectrum of germacyclopentane.
Fig. 2. Mass spectrum of 1-n-propylgermacyclopentane.
Fig. 3. Mass spectrum of 1-n-butylgermacyclopentane-3,3,4,4-d_4.

units (ethylene) yields the fragment ion of highest mass. Compounds (III) and (IV), labeled with deuterium in the 3,3,4,4-positions, expell $CH_2{=}CD_2$ (Figs. 3 and 4) demonstrating that the ethylene originates from C-2 and C-3 [(III) → (A), *m/e* 158].



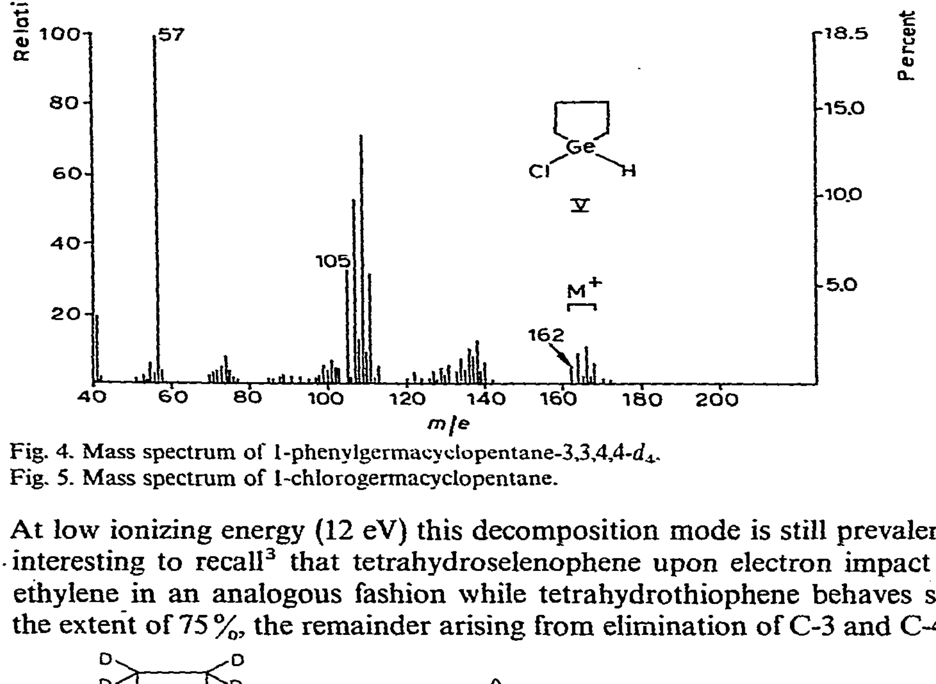
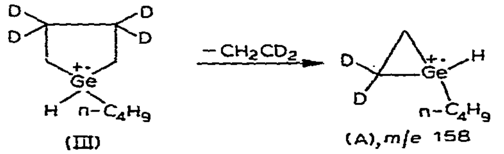


Fig. 4. Mass spectrum of 1-phenylgermacyclopentane-3,3,4,4-d_4.
Fig. 5. Mass spectrum of 1-chlorogermacyclopentane.

At low ionizing energy (12 eV) this decomposition mode is still prevalent and it is interesting to recall[3] that tetrahydroselenophene upon electron impact eliminates ethylene in an analogous fashion while tetrahydrothiophene behaves similarly to the extent of 75%, the remainder arising from elimination of C-3 and C-4.



The most intense ions in the mass spectra (Figs. 1, 2 and 3) of germacyclopentane (I), its 1-n-propyl (II) and 1-n-butyl (III) analogs is the germanium ion radical (*m/e* 70)[7][*]. Upon the introduction of a 1-phenyl substituent (IV), this ion is greatly

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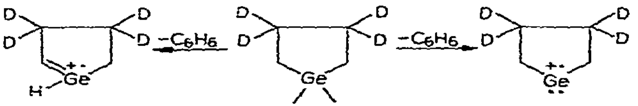
[*] Germanium contains five stable isotopes: ^{70}Ge (20.5%), ^{72}Ge (27.4%), ^{73}Ge (7.8%), ^{74}Ge (36.5%) and ^{76}Ge (7.8%). Throughout this paper peaks will be identified by ^{70}Ge and metastable ion positions were calculated using this isotope.

reduced (Fig. 4; 16% relative abundance) and is almost completely suppressed (Fig. 5) in the 1-chloro compound. The high ion current transported by the germanium ion radical in (I)–(III) is in contrast to the usual preference of germanium compounds for the elimination of one or three substituents rather than two or four ligands[8].

An interesting feature of the mass spectrum (Fig. 1) of germacyclopentane (I) is the occurrence of appreciable $M-1$ and $M-2$ ions: the latter was shown[3] to arise in part (33%) from the loss of both hydrogen atoms attached to germanium. At low electron energy (10 eV) the $M-2$ ion is energetically more favored than the $M-1$ species which is entirely suppressed at this ionizing voltage.

The propensity towards the loss of both groups attached to germanium in the electron impact-promoted fragmentation of germacyclopentanes is manifested in the spectra (Figs. 2–4) of compounds (II)–(IV). Thus at 70 eV strong peaks in the spectra of these compounds are due to the loss of the 1-substituent together with an additional hydrogen atom. The low voltage spectrum (10 eV) of the 3,3,4,4-d_4 analog of 1-phenylgermacyclopentane (IV) demonstrated that no deuterium was lost in this process. In view of the behavior of 1,1-disubstituted germacyclopentanes (see below) in which both groups attached to germanium are readily expelled, we prefer to postulate in the present instance abstraction of the itinerant hydrogen atom from germanium [(IV) → (B), *m/e* 130]*, although the evidence at hand does not eliminate the possibility that participation of an α-hydrogen atom from the five-membered ring may occur in this process [(IV) → (B′)].

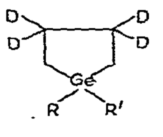


(B′), *m/e* 130 IV (B), *m/e* 130

By contrast, the mass spectrum (Fig. 5) of 1-chlorogermacyclopentane (V) contains a peak due to the loss of chlorine and only a negligible peak (1% relative abundance) due to the expulsion of hydrogen chloride. The spectrum of this compound is dominated by the C_4H_9 and GeCl ions and at low ionizing voltage (10 eV) it is the hydrocarbon moiety which is present to the greater extent.

The most abundant ion in the 70-eV spectrum (Fig. 4) of 1-phenylgermacyclopentane-3,3,4,4-d_4 (IV) corresponds to $Ge^+C_6H_5$ while at low voltage (12 eV) the abundance of this fragment is surpassed by that of the ion (B) (*m/e* 130).

B. 1,1-DISUBSTITUTED GERMACYCLOPENTANES



(VI): $R = n\text{-}C_4H_9, R' = Br$
(VII): $R = n\text{-}C_4H_9, R' = C_6H_5$
(VIII): $R = R' = C_6H_5$
(IX): $R = n\text{-}C_4H_9, R' = C{\equiv}CH, D = H$

All four 1,1-disubstituted germacyclopentanes (VI)–(IX) examined yielded easily identifiable molecular ions. A mechanistic rationalization for the formation of the principal ions in the mass spectrum (Fig. 8) of the diphenyl derivative (VIII) is presented in scheme 1.

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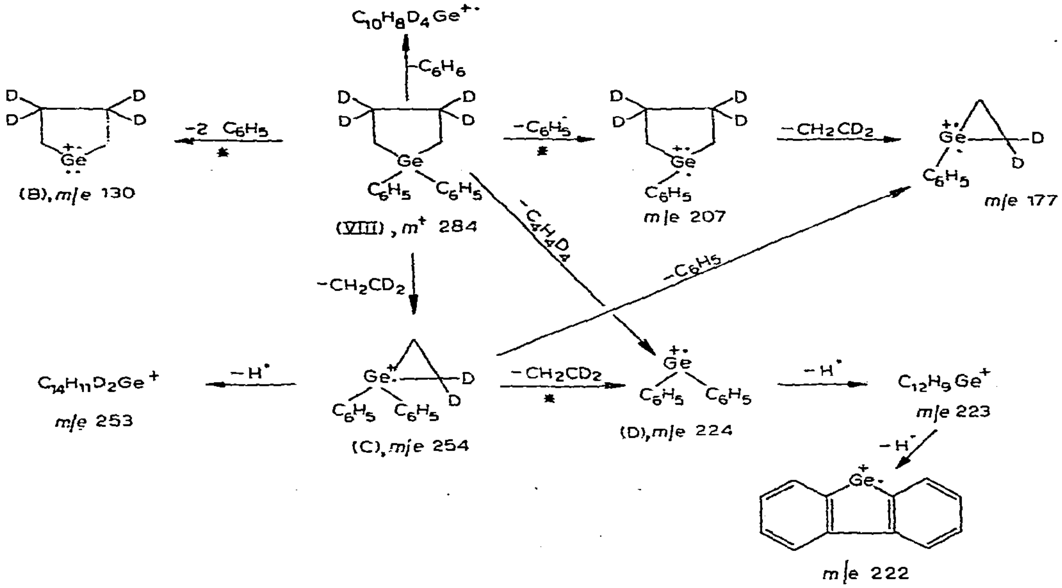
* Ions such as (B) may exist as either an open chain form or alternatively as some cyclic form in which an α-hydrogen atom is transferred to germanium, for instance (B′).

SCHEME 1

RATIONALIZATION OF THE ELECTRON IMPACT-PROMOTED FRAGMENTATION OF 1,1-DIPHENYLGERMACYCLOPENTANE-3,3,4,4-d_4 (metastable ions are denoted by an asterisk).

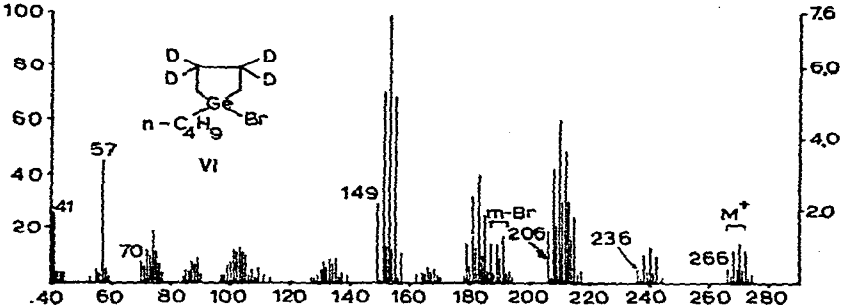


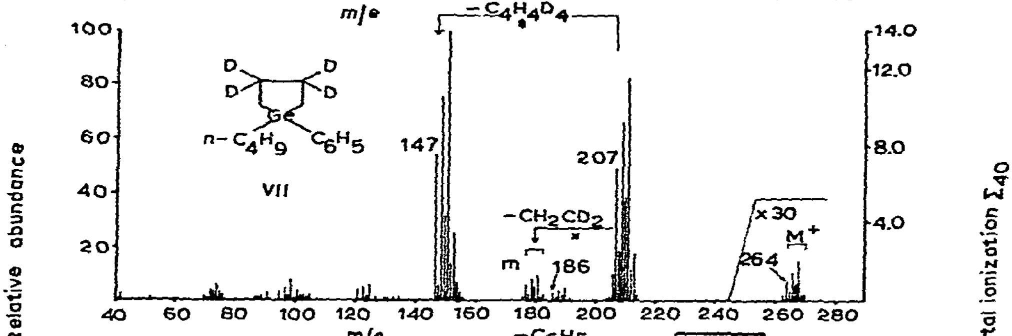
The mass spectrum (Fig. 8) of 1,1-diphenylgermacyclopentane-3,3,4,4-d_4 (VIII) contains several interesting features. As previously observed with 1-substituted germacyclopentanes loss of ethylene (elimination of 28-mass units in the unlabeled derivative) from (VIII) is always associated with the expulsion of C-2 and C-3 with their attached hydrogen and deuterium atoms. This result was also observed for the two remaining tetradeuterated 1,1-disubstituted germacyclopentanes (VI) and (VII) investigated.

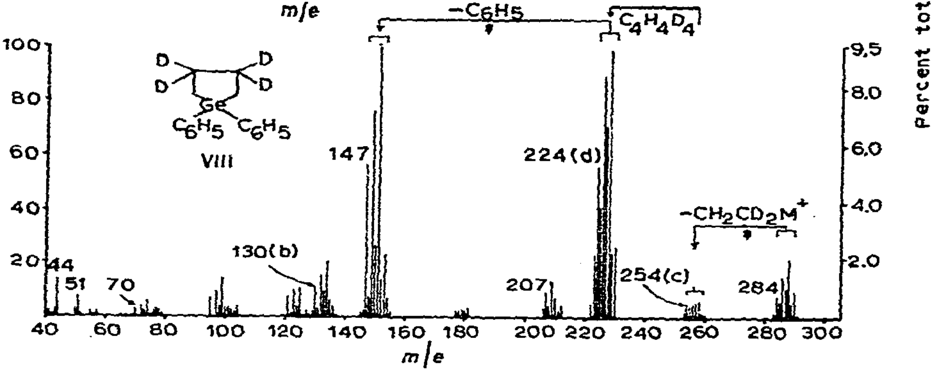
A metastable ion corresponding to the loss of both phenyl substituents from the molecular ion of (VIII) indicated that the ion (B), *m/e* 130, was formed in a single step. Confirmatory evidence was obtained from the low voltage spectrum (12 eV) of compound (VIII) in which the ion of mass 130 now corresponded to the base (100% relative abundance) peak.

Although a metastable ion was observed in the mass spectrum (Fig. 8) of (VIII) corresponding to the process (C) (*m/e* 254) → (D) (*m/e* 224), the latter species must also be formed by direct decomposition of the molecular ion since in the low voltage (12 eV) spectrum of (VIII) it was the second most abundant ion present.

Two groups of adjacent peaks at *m/e* 206 and 207 (Fig. 8) correspond to the respective losses of C_6H_6 and C_6H_5 from the molecular ion of (VIII). Both peak groups remain in the 12-eV spectrum of this compound and at this ionizing energy the abundance of the ion due to the loss of benzene has increased relative to that due to the elimination of a phenyl radical. This must be interpreted as the ion of mass 206 having its origin from ejection of a benzene molecule directly from the molecular ion of (VIII) rather than the alternative loss of a hydrogen atom from the ion of mass 207 due to the elimination of a phenyl radical.







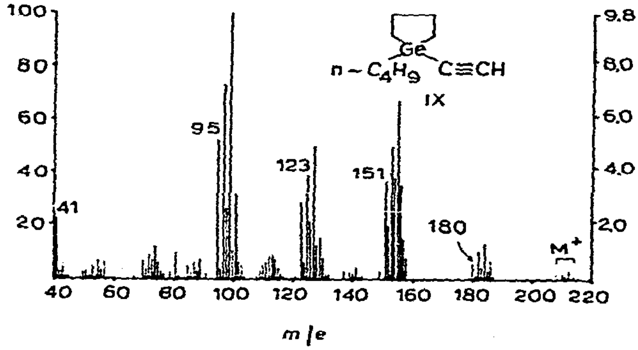
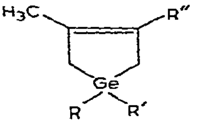


Fig. 6. Mass spectrum of 1-n-butyl-1-bromogermacyclopentane-3,3,4,4-d_4.
Fig. 7. Mass spectrum of 1-n-butyl-1-phenylgermacyclopentane-3,3,4,4-d_4.
Fig. 8. Mass spectrum of 1,1-diphenylgermacyclopentane-3,3,4,4-d_4.
Fig. 9. Mass spectrum of 1-n-butyl-1-ethynylgermacyclopentane.

The mass spectrum (Fig. 7) of 1-n-butyl-1-phenylgermacyclopentane-3,3,4,4-d_4 (VII) is unique among the 1,1-disubstituted germacyclopentanes investigated in that it lacks an ion due to the loss of ethylene-1,1-d_2 from the molecular ion. The fragment ions of highest mass in this instance correspond to $M-C_4H_9$ and $M-C_4H_{10}$. Thus at low ionizing voltage (12 eV) both of these ions retained the same relative ratio to one another and hence eliminated the possibility that loss of a hydrogen atom from the $M-C_4H_9$ species yielded the ion corresponding to expulsion of butane from the molecular ion. Metastable ions testify to the subsequent loss of $CH_2{=}CD_2$ and $C_4H_4D_4$ from the $M-57$ species while a direct elimination of a benzene molecule from the molecular ion of (VII) is responsible for the ion of mass 186 and this fragment remains prominent at low voltage (12 eV).

The mass spectrum (Fig. 9) of the acetylene derivative (IX) is noteworthy for the retention of the acetylenic unit in all the abundant fragments. Apart from this, its decomposition modes parallel those documented in Scheme 1 for 1,1-diphenylgermacyclopentane-3,3,4,4-d_4 (VIII). Similarly 1-bromo-1-n-butyl-germacyclopentane (VI) fragments subsequent to electron impact in an analogous fashion to its diphenyl counterpart (VIII). One exception is the retention of the butyl cation (*m/e* 57) in the low voltage (12 eV) spectrum of (VI).

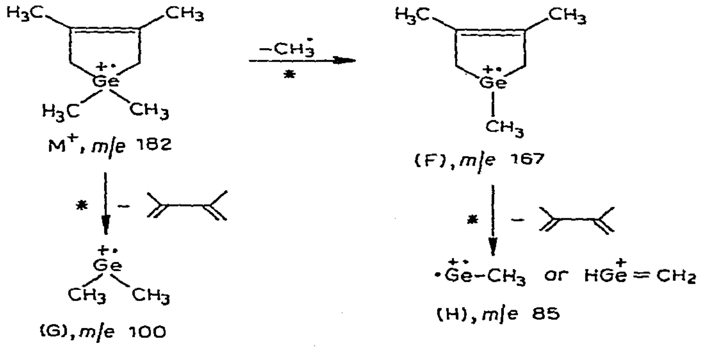
C. 1,1-DIALKYLGERMA-3-CYCLOPENTENES



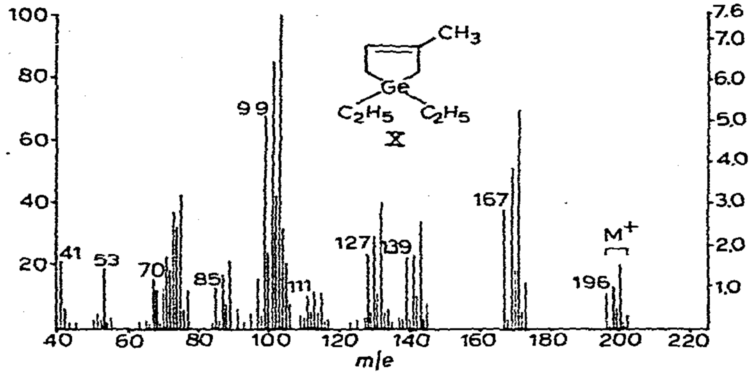
(X): $R=R'=C_2H_5, R''=H$
(XI): $R=R'=R''=CH_3$
(XII): $R=R'=C_2H_5, R''=CH_3$

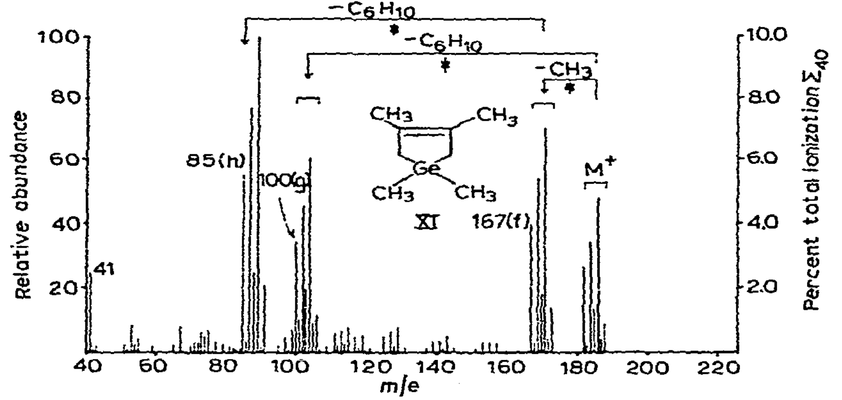
As anticipated the unsaturation within the five-membered ring of compounds (X), (XI) and (XII) alters the mass spectral fragmentation of these compounds relative to that of the fully saturated ring system previously discussed. Thus the double bond in the five-membered ring precludes the loss of ethylene via the expulsion of C-2 and C-3 [(III) → (A)], a process which was particularly prevalent in the majority of the mass spectra of the substituted germacyclopentanes examined.

The mass spectrum (Fig. 11) of the dimethyl analog (XI) contains abundant peaks corresponding to the loss of a methyl radical [(F), *m/e* 167] and of the carbon atoms of the five-membered ring [(G), *m/e* 100] from the molecular ion and metastable ions are present to verify these processes. The base (100% relative abundance)



peak in the spectrum (Fig. 11) of the dimethyl derivative (XI) occurs at *m/e* 85 and this fragment arises from the loss of the carbon atoms of the five-membered ring from the ion (F) such that the charged entity corresponds to (H), *m/e* 85. The transition (F) → (H) was supported by a metastable ion.





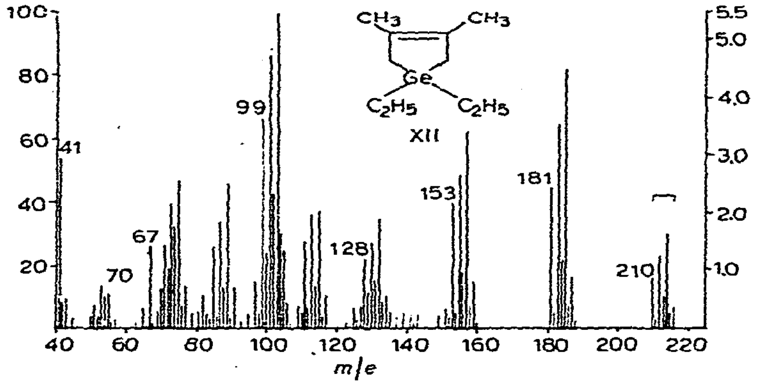
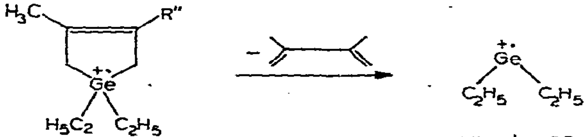


Fig. 10. Mass spectrum of 1,1-diethyl-3-methylgerma-3-cyclopentene.
Fig. 11. Mass spectrum of 1,1,3,4-tetramethylgerma-3-cyclopentene.
Fig. 12. Mass spectrum of 1,1-diethyl-3,4-dimethylgerma-3-cyclopentene.

The two 1,1-diethyl derivatives (X) and (XII) fragment upon electron impact by the loss of an ethyl radical followed by expulsion of ethylene. In the absence of metastable ions the low voltage spectra (12 eV) of both compounds are consistent with this series of events since the relative abundance of the ions due to elimination of an ethyl radical far exceeds that due to the consecutive loss of an ethyl radical plus ethylene. The $M-29$ species in both (X) and (XII) may expel the six carbon atoms of the substituted five-membered heterocycle to yield the most intense ions at mass 99 in the spectra (Figs. 10 and 12) of the compounds. This ion of mass 99 is thus analogous to the species (H), *m/e* 85 (when CH_3 is substituted by C_2H_5). An alternative genesis for the ions of mass 99 in the spectra (Figs. 10 and 12) of compounds (X) and (XII) may be visualized through an initial loss of the carbon atoms of the ring system [formation of (J), *m/e* 128] followed by ejection of an ethyl radical from this species. However, in the absence of metastable ions no decision can be reached between these two possibilities.



(X) ; R''=H
(XII); R''= CH_3

(J), *m/e* 128

In summary the mass spectra of the germacyclopentane and germa-3-cyclopentene derivatives studied are remarkable for the presence of abundant ions which result from fission of one, two, three or occasionally four bonds to the germanium atom with charge retention on the metal-containing species in each instance. Loss of ethylene in the germacyclopentane derivatives always is accomplished by elimination of C-2 and C-3. Expulsion of the carbon atoms of the heterocyclic ring system is frequently observed in the mass spectra of both germacyclopentane and the germa-3-cyclopentene derivatives studied.

EXPERIMENTAL

Mass spectra were determined with an Atlas CH-4 mass spectrometer using the TO-4 ion source equipped with a gas cartridge except for compounds (X) and (XII) which were run on a CEC 103C instrument (ion source temperature 250°) using an all glass inlet system maintained at 200°.

The compounds used in the present study have been described previously[6,9]. The deuterated analogs were prepared from 1,4-dibromobutane-2,2,3,3-d_4 which was synthesized by the following procedure. Acetylene dicarboxylic acid dimethyl ester (20 g) in ethyl acetate (150 ml) was reduced during 5 h in a deuterium atmosphere over a 5% palladium on carbon catalyst to dimethyl succinate-2,2,3,3-d_4 (19 g). Lithium aluminum hydride reduction yielded 1,4-butanediol-2,2,3,3-d_4 (16 g) which on bromination afforded the desired 1,4-dibromobutane-2,2,3,3-d_4 (14 g, 90% d_4, 10% d_3 species) which was converted to the labeled germanium compounds studied by standard methods.

ACKNOWLEDGEMENT

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REFERENCES

1 G. JONES AND C. DJERASSI, *Steroids*, 10 (1967) 653.
2 A. CARRICK AND F. GLOCKLING, *J. Chem. Soc., A*, (1966) 623; D. B. CHAMBERS, F. GLOCKLING, J. R. C. LIGHT AND M. WESTON, *Chem. Commun.*, (1966) 281; J. J. DE RIDDER AND G. DIJKSTRA, *Rec. Trav. Chim. Pays-Bas*, 86 (1967) 737.
3 A. M. DUFFIELD, H. BUDZIKIEWICZ AND C. DJERASSI, *J. Amer. Chem.Soc.*, 87 (1965) 2920.
4 J. I. BRAUMAN, *Anal. Chem.*, 38 (1966) 607.
5 A. M. DUFFIELD, L. J. DURHAM, C. DJERASSI, M. LESBRE, P. MAZEROLLES AND G. MANUEL, *Bull. Soc. Chim. Fr.*, in preparation.
6 P. MAZEROLLES AND G. MANUEL, *Bull. Soc. Chim. Fr.*, (1966) 327.
7 *Handbook of Chemistry and Physics*, The Chemical Rubber Publishing Co., Cleveland, Ohio, 47th Ed., 1966, pp. 13–19.
8 H. BUDZIKIEWICZ, C. DJERASSI AND D. H. WILLIAMS, *Mass Spectrometry of Organic Compounds*, Holden-Day Inc., San Francisco, 1967, p. 654.
9 P. MAZEROLLES AND J. DUBAC, *C. R. Acad. Sci., Paris*, 257 (1963) 1103; P. MAZEROLLES, *Bull. Soc. Chim. Fr.*, (1962) 1907; P. MAZEROLLES, J. DUBAC AND M. LESBRE, *J. Organometal. Chem.*, 5 (1966) 35.