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MASS SPECTROSCOPY OF ORGANOMETALLIC COMPOUNDS

by

William F. Bryant

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In Charge of Major Work

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Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Ames, Iowa

1970

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PART I: MASS SPECTROSCOPY OF ORGANOMERCURY COMPOUNDS

INTRODUCTION: ORGANOMERCURY COMPOUNDS

Organometallic compounds are currently an active area of interest in mass spectrometry (1). Organomercurials, and indeed the group II-B organometallic compounds in general, have largely been ignored. The studies that do appear in the literature deal mainly with determinations of appearance potentials, ionization potentials, or of carbon-mercury bond dissociation energies (2, 3, 4). The only organomercury compounds previously subjected to fragmentation studies are dimethyl, diethyl, and di-n-butylmercury (5; 6, p. 654). Few other group II-B organometallic compounds have been examined; however, the reported behavior of dimethyl- (7) and di-*n*-butylzinc (8) is quite different from that observed for the corresponding mercury compounds.

In general, when organometallic compounds[1] fragment in the mass spectrometer, the most abundant ions produced are those containing the metal atom. This is reasonable for the cationic charge may be localized on an atom less electronegative than carbon. Organomercurials would appear to be anomalous in this respect. Mercury-containing fragment ions are apparent but the base peak and the more abundant ions

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[1] For example, compounds of Ge (6, p. 654), Si (9), Sn (6, p. 655), Pb (6, p. 655), Fe (6, p. 657), Al (7, 10), and Sb (7) have been studied.

usually do not contain mercury. This behavior is not consistent even within the group II-B family. For example, the base peak in the spectrum of di-n-butylzinc is the butylzinc cation (8) but the most abundant ion in the spectrum of di-n-butylmercury (6) is the butyl cation. Because this behavior is quite unusual,[1] an investigation of a wider variety of organomercurials was initiated in order to determine the generality of these observations.

Also, we were interested in demonstrating the potential of mass spectrometry as a structural elucidation method for a variety of synthetically important organomercurials.[2] Determination of olefin stereochemistry via mass spectrometry of diastereomeric olefin-mercury salt adducts was also an initial goal. We have, therefore, investigated the mass spectrometric behavior of a variety of diaryl- and dialkylmercurials, aromatic and aliphatic mercuric chlorides and acetates, hydroxyalkyl- and methoxyalkylmercury chlorides, and mercury containing methylene transfer agents.

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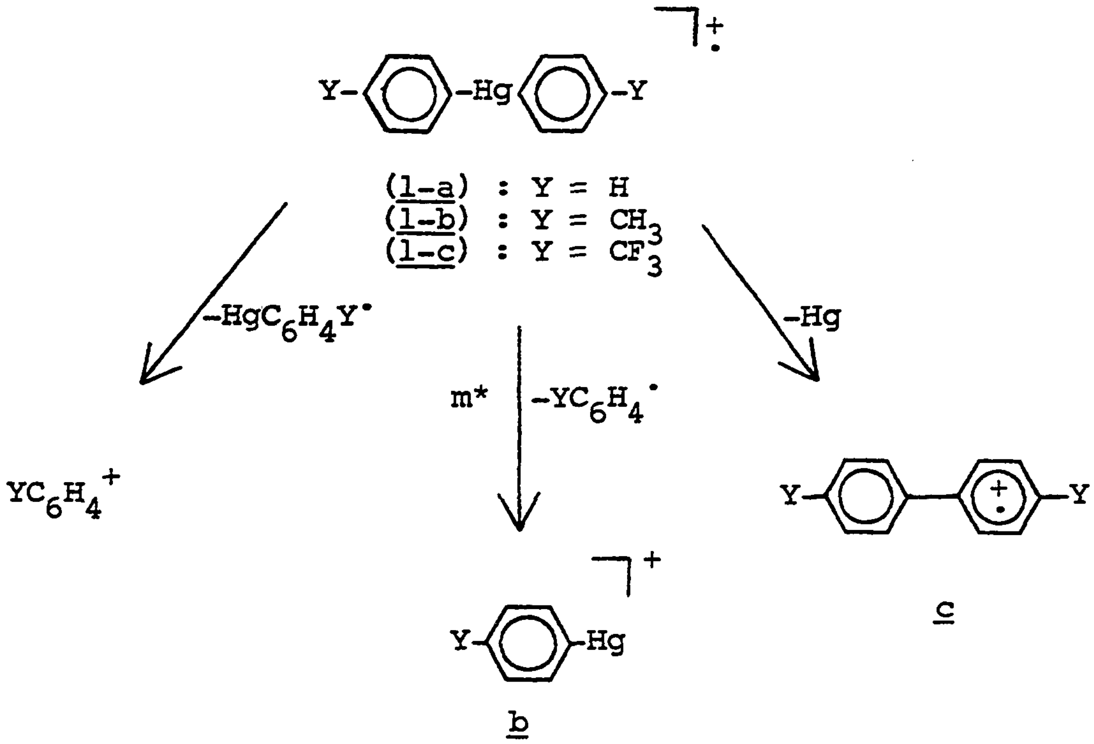
[1] In a recent publication (11) the portion of the total ion current carried by tin containing ions from tetraphenyl tin was found to be 90%. In contrast, only 30% of the total ion current is carried by mercury containing ions from diphenylmercury.

[2] Examples of the use of organomercury compounds in the preparation of ketones (12, 13), aldehydes (14), ethers (14, 15), amines (16), perfluoro-polymers (17), oxiranes (18), and as a convenient source for dihalomethylenes (18, 19, 20, 21) have appeared recently in the literature.

RESULTS AND DISCUSSION

Diaryl Mercury Compounds

Scheme 1 summarizes the electron impact induced modes of fragmentation common to diphenyl- (1-a), di-*p*-tolyl- (1-b), and di-*p*-trifluoromethylphenylmercury (1-c). In each case the most abundant ion, a, is formed by cleavage of the carbon-mercury bond with charge retention on carbon. The parent ions of 1-a, 1-b, and 1-c are present in the respective spectra but



Scheme 1. Fragmentation pattern of 1-a, 1-b, and 1-c

there is considerable variation in their abundances.[1] The molecule ion 1-b has a relative abundance of 92.4%. Note, however, that the abundance of the parent ion of 1-c is rather small [9.18%] and that the parent ion of 1-a is of intermediate intensity [44.7%]. The ions b are formed from the molecule ions 1-a, 1-b, and 1-c through a metastable process. When Y = CF_3, ion b is least abundant [11.1%] and the analogous ions with Y = H [21.2%] and Y = CH_3 [18.3%] are approximately of equal intensity.

Ion c is formed through an elimination-recombination rearrangement in which the mercury atom is expelled from the molecule ion. The appropriate metastable for the transition has not been observed under the conditions used, including low electron energy impact which would not be expected to lead to complete rupture of the carbon-mercury bond (22).

The structure of ion c is proposed to be a di-p-substituted biphenyl on the basis of comparisons of the mass

---

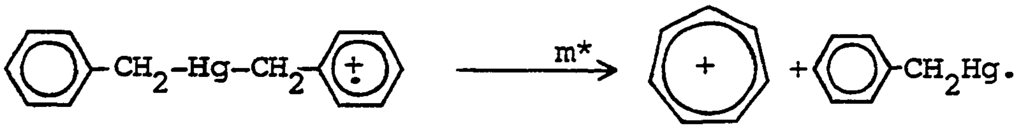
[1] Since mercury has seven isotopes the molecular weights have arbitrarily been based on the ^{202}Hg isotope. In determining the relative abundances of the ions in the spectra, the summation[2] of the abundances of all mercury isotopes was utilized so that the reported data would not be distorted to exaggerate the charge retention on carbon.

[2] In reality the abundance of the ^{202}Hg isotope was multiplied by the factor 100/29.8. The calculated values and the experimental summations are in good agreement: 1-a (m/e 356-cal. 44.7, exp. 45.8); 1-b (m/e 293-cal. 18.3, exp. 18.6); 1-c (m/e 345-cal. 11.1, exp. 11.6).

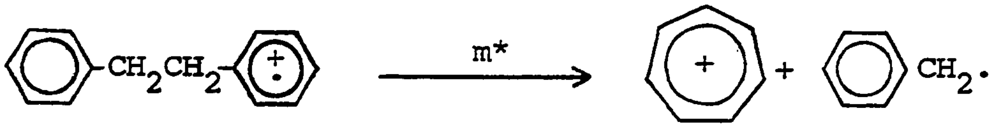
spectra of 4,4'-bitolyl and 1-b. The m/e 182 ion from 1-b and the 4,4'-bitolyl parent ion undergo the same fragmentations. Both spectra contain the same metastable peaks with the same shape and intensity. In the mass spectrum of 1-b, there is an ion at m/e 92 [19.8%] (toluene parent ion?) but no analogous ions are present in the spectra of 1-a and 1-c. No metastable was found to correlate with its formation.[1]

Dialkyl Mercury Compounds

Dibenzylmercury (2) is an isomer of 1-b. In the 70 eV spectrum the base peak is ion m/e 91 formed by cleavage of a carbon-mercury bond (Reaction 1) and from ion m/e 182 (Reaction 2). Both transitions show the appropriate metastable



(1)



(2)

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[1] For the sake of completeness the ion m/e values and abundances for each compound are recorded in the experimental section.

peaks. The m/e 182 ions found in the spectra of 2 and 1-b are definitely different. In the spectrum of 2 loss of benzene is observed from ion m/e 182 to form m/e 104, probably the molecule ion of styrene. Ion m/e 182 from 1-b does not undergo this fragmentation. Examination of the mass spectrum of dibenzyl reveals that the dibenzyl parent ion behaves like the m/e 182 ion from 2.

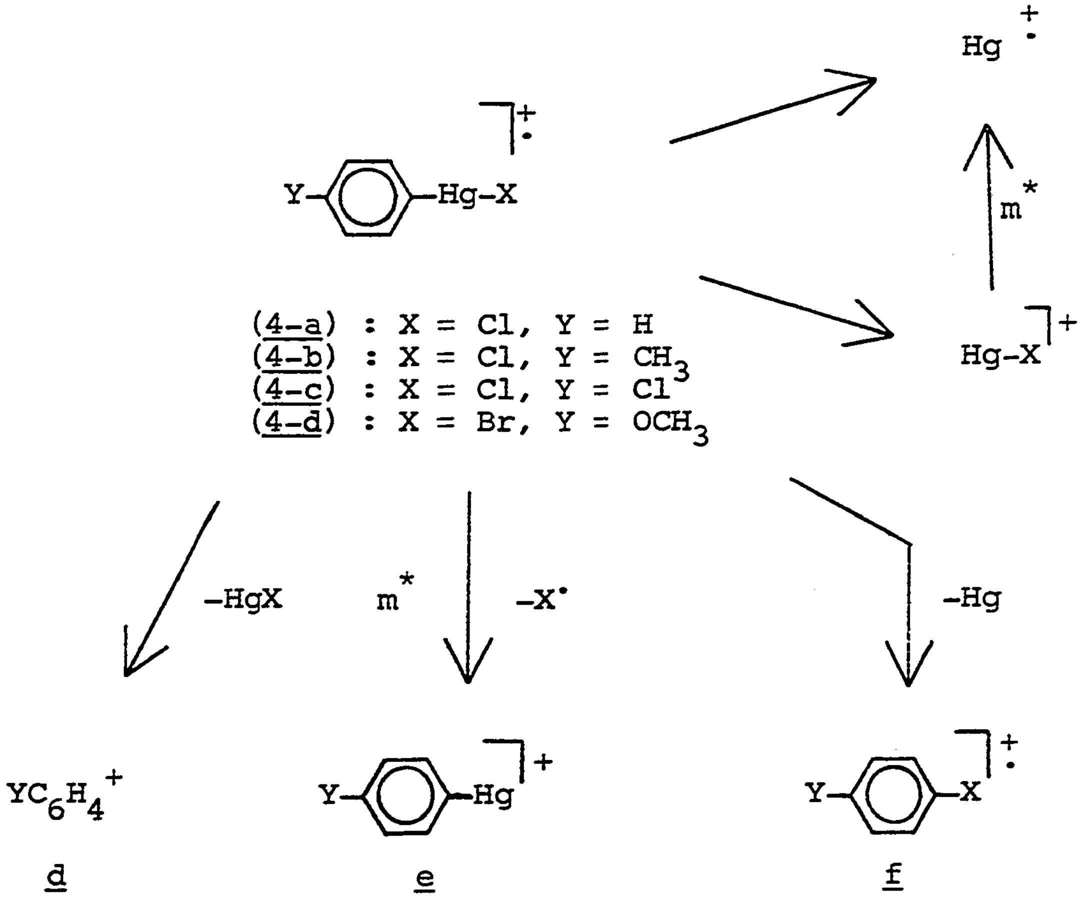
At 16 eV the parent ion of 2 is the base peak in the spectrum. The rearrangement ion m/e 182 is still very intense but m/e 91 has decreased in intensity relative to ion m/e 182. The increased relative abundance of m/e 182 at low energy is in agreement with an elimination-recombination rearrangement with a low frequency factor. The fragmentation of the m/e 182 ion from 2 to form m/e 104 is still pronounced and the appropriate metastable is observed.

The mass spectrum of di-n-butylmercury (3) was rerun and is discussed here because of certain differences from the previously reported spectrum (5). Furthermore, some of the organomercury ions have interesting compositions. At 70 eV the base peak is the butyl cation, m/e 57. The molecular ion is observed and is of moderate abundance. The highest molecular weight fragment ion is m/e 287 ($M-C_2H_5$). No loss of methyl radical from the parent ion is observed. The other organomercury ions present are m/e 230 (C_2H_4Hg) and m/e 216 (CH_2Hg). The spectra we obtained gave no indication that elimination of mercury from the molecular ion with recombination of the alkyl moieties occurs as the earlier investigation reported (5). The mercuric cation was found to be of low abundance (1.1% relative to the butyl cation) though Dibeler and Mobler reported an abundance of 16.2% (also relative to the butyl cation). The previous investigators were also able to observe a mercuric hydride, HgH^+, which we did not observe.

These discrepancies may well be a result of the quite different instrumental conditions utilized. Our inability to detect mercuric hydride ions is doubtlessly the result of their low abundance and concomitant difficulties in separating their contributions from the unavoidable mercury background in the spectrometer (from mercury vacuum pumps).

Aryl Mercuric Halides

Another group of compounds investigated were arylmercuric halides. Scheme 2 summarizes the fragmentation behavior observed for phenylmercuric chloride (4-a), p-tolylmercuric chloride (4-b), p-chlorophenylmercuric chloride (4-c), and p-methoxyphenylmercuric bromide (4-d) at 70 eV. All four compounds give intense peaks in the parent ion region. Indeed, in the spectrum of 4-c and of 4-d the parent ion is the most abundant ion observed. For 4-a and 4-b, however, ion d forms the base peak. In every



Scheme 2. Fragmentation pattern of 4-a, 4-b, 4-c, and 4-d

case formation of d is favored over cleavage of the mercury-halogen bond which produces ion e. Note also that the loss of halogen from the parent ion is often the only metastable process observed. Elimination of mercury from the molecule ion with concomitant rearrangement of halogen to the aromatic ring is observed. The resulting ion f is usually of low abundance.

Again cleavage of the carbon-mercury bond predominately results in more favorable charge retention on carbon. As a result $[HgX]^+$ ions are found in only low to moderate abundance in these spectra.

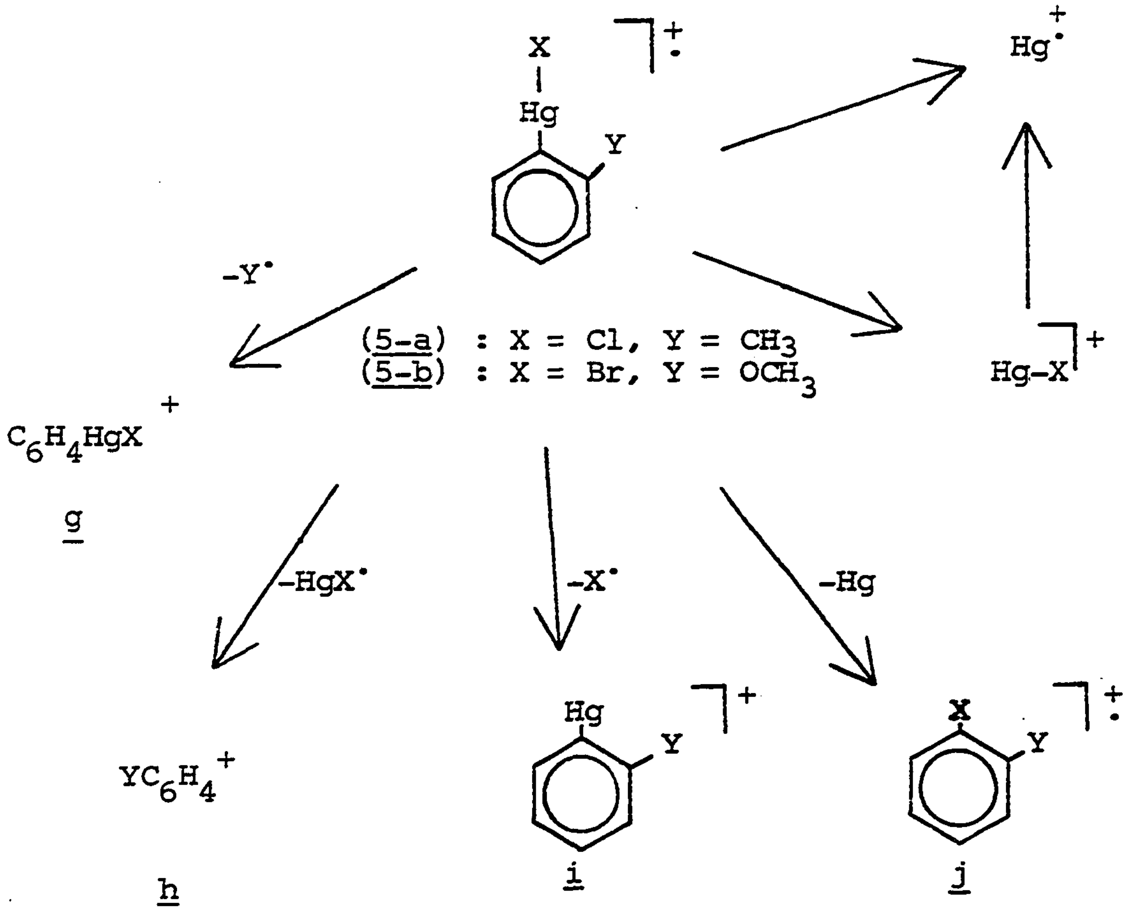
Only in the spectrum of 4-c is the following transition

$$[Hg\text{-}X]^+ \longrightarrow Hg^{+\cdot} + X^\cdot$$

substantiated by the appropriate metastable ion. The $Hg^{+\cdot}$ ion might also be formed directly from the parent ion.

At low energies (16-18 eV), the parent ion is the most abundant ion in each spectrum. The rearrangement-elimination reaction in which mercury is ejected from the molecule ion is still observed.

Several ortho-substituted phenylmercuric halides were investigated for the purpose of detecting possible "ortho-effects". Included were the ortho-methylphenyl (5-a), ortho-methoxyphenyl (5-b) and ortho-hydroxyphenyl (6) groups. Scheme 3 summarizes the fragmentations of 5-a and 5-b, none of which are due to normal ortho-interactions. The base peak of 5-a is formed by cleavage of the carbon-mercury bond to give ion h, while the base peak of 5-b is the molecular ion, The elimination-rearrangement loss of mercury produces ion j in each case. A somewhat unique fragmentation of 5-a is the loss of the ortho-methyl substituent to produce ion g. This process did not occur in the isomeric para-compound. At reduced electron energies (20 eV) the ion j is no longer



Scheme 3. Fragmentation pattern of 5-a and 5-b

observed, but ion g is still present.

Ortho-chloromercuriphenol (6) exhibits behavior quite different from that of 5-a and 5-b. This is illustrated in Scheme 4. The molecular ion, which is also the base peak of the spectrum, loses both Cl• and HCl[1] in metastable

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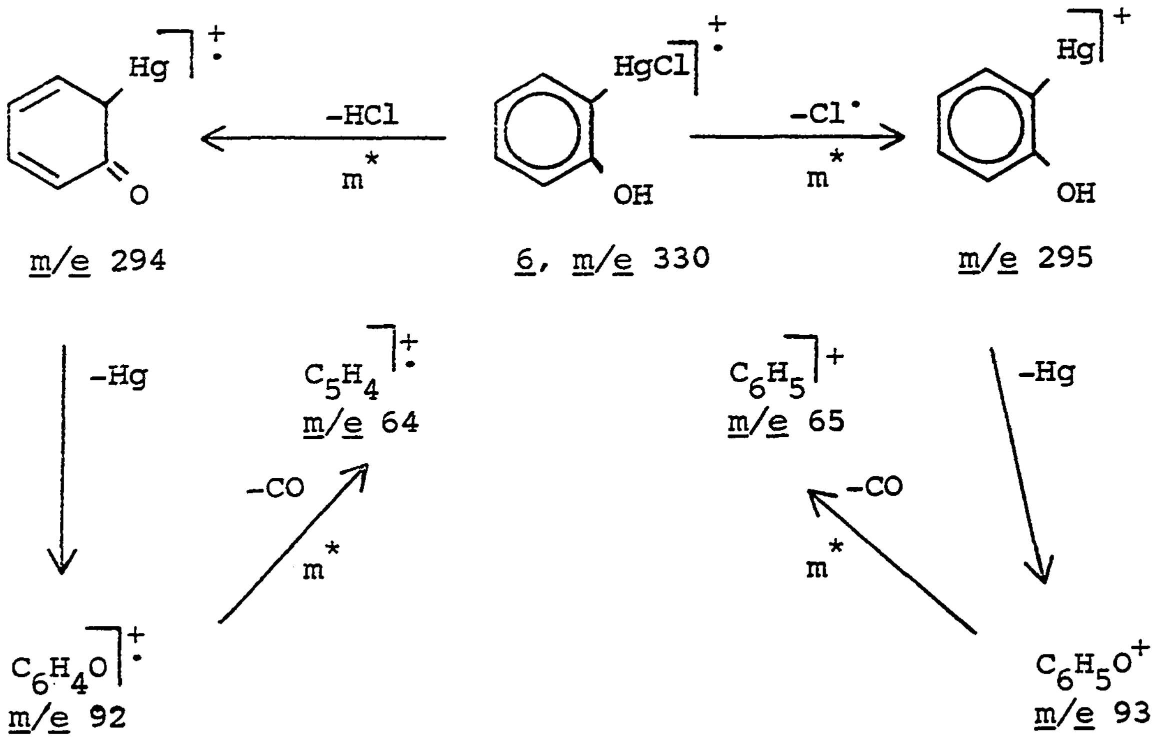
[1] The loss of HCl probably occurs as the simultaneous loss, or rapid sequential loss, of a hydrogen and a chlorine radical, because the interatomic distance between the phenolic hydrogen and the chlorine is quite large.

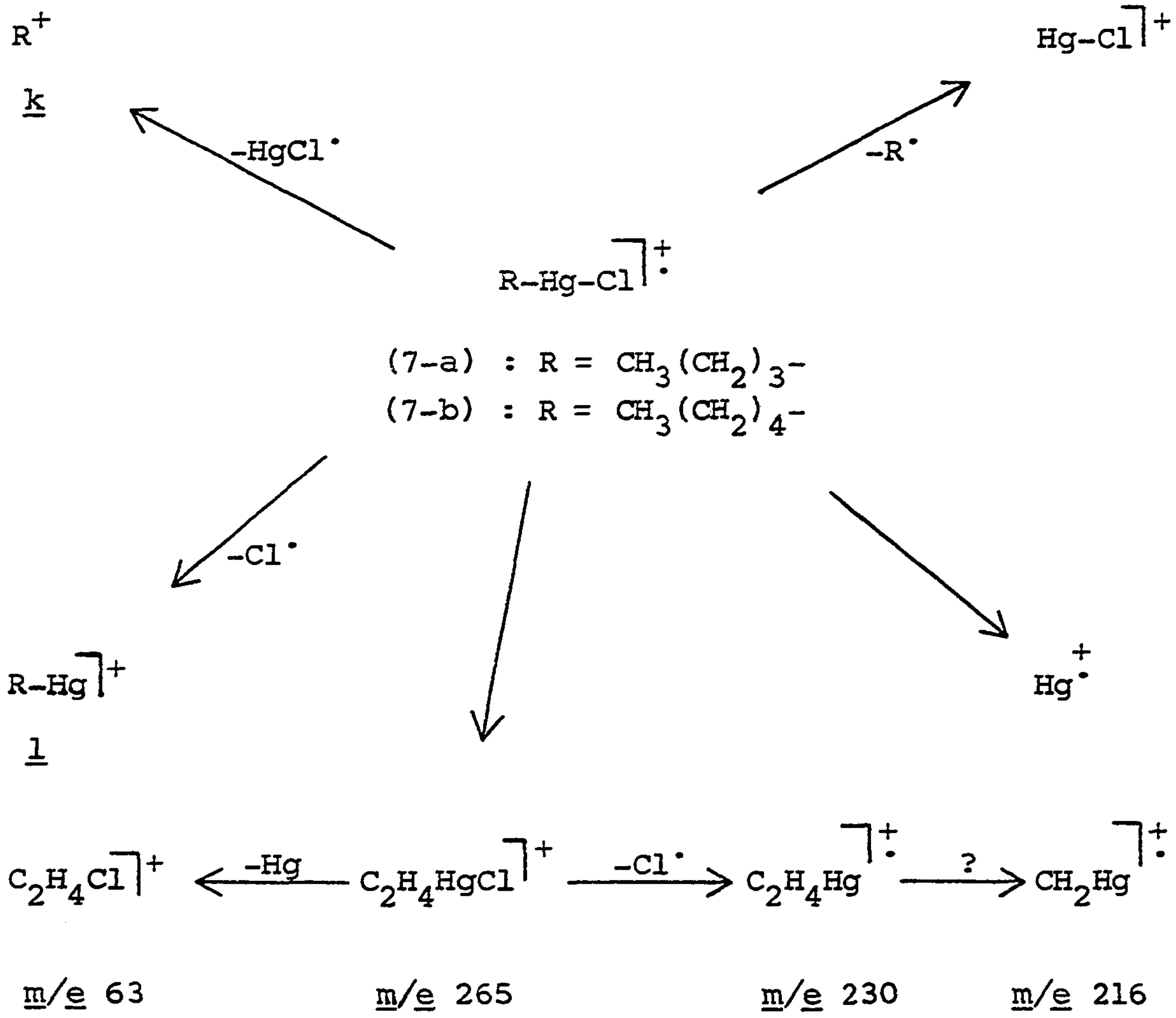


Scheme 4. Fragmentation pattern of 6

processes to generate the *m/e* 294 and *m/e* 295 ions, each of which lose their mercury atom to give the *m/e* 92 and *m/e* 93 ions. The intensities of the *m/e* 294 and *m/e* 295 ions are abnormally large, possibly due to some stabilizing interaction with the *ortho*-substituent. Another difference noted was the absence of an elimination-rearrangement loss of mercury from the molecular ion.

Alkyl Mercuric Chlorides

Scheme 5 summarizes the fragmentation behavior of two primary alkylmercuric chlorides: *n*-butylmercuric chloride (7-a) and *n*-amylmercuric chloride (7-b). At 70 eV both



Scheme 5. Fragmentation pattern of 7-a and 7-b

compounds give parent ions of moderate intensity with base peaks due to the alkyl carbonium ions k.

A variety of mercury-containing organic ions are observed. The alkylmercury ion l is observed but the intensity is quite low. The m/e 265 ion arises by cleavage *beta* to the mercury atom. *Beta* cleavage predominates quite noticeably over *alpha* or *gamma* cleavage (59.8% and 17.7% abundances of *m/e* 265 from *7-a* and *7-b*, respectively). No methyl loss occurs from the molecular ion of *7-a* and methyl or ethyl loss from the molecular ion of *7-b* is insignificant.

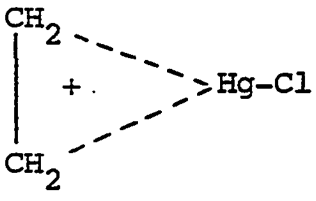
The *m/e* 230 and *m/e* 216 ions, which were observed in the spectrum of di-*n*-butylmercury, are also present in the spectra of *7-a* and *7-b* and along with the *m/e* 265 ion offer several interesting structural possibilities. They may be open chain species such as *m* and *n*. But structures such as *o* and *p* might also account for the predominance of *beta* cleavage. The importance of analogous bromonium ion participation is mass spectral ions has been the subject of several recent reports (23).

$CH_2CH_2HgCl^{+}$

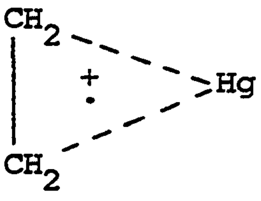
m

$CH_2CH_2Hg^{+\cdot}$

n



o



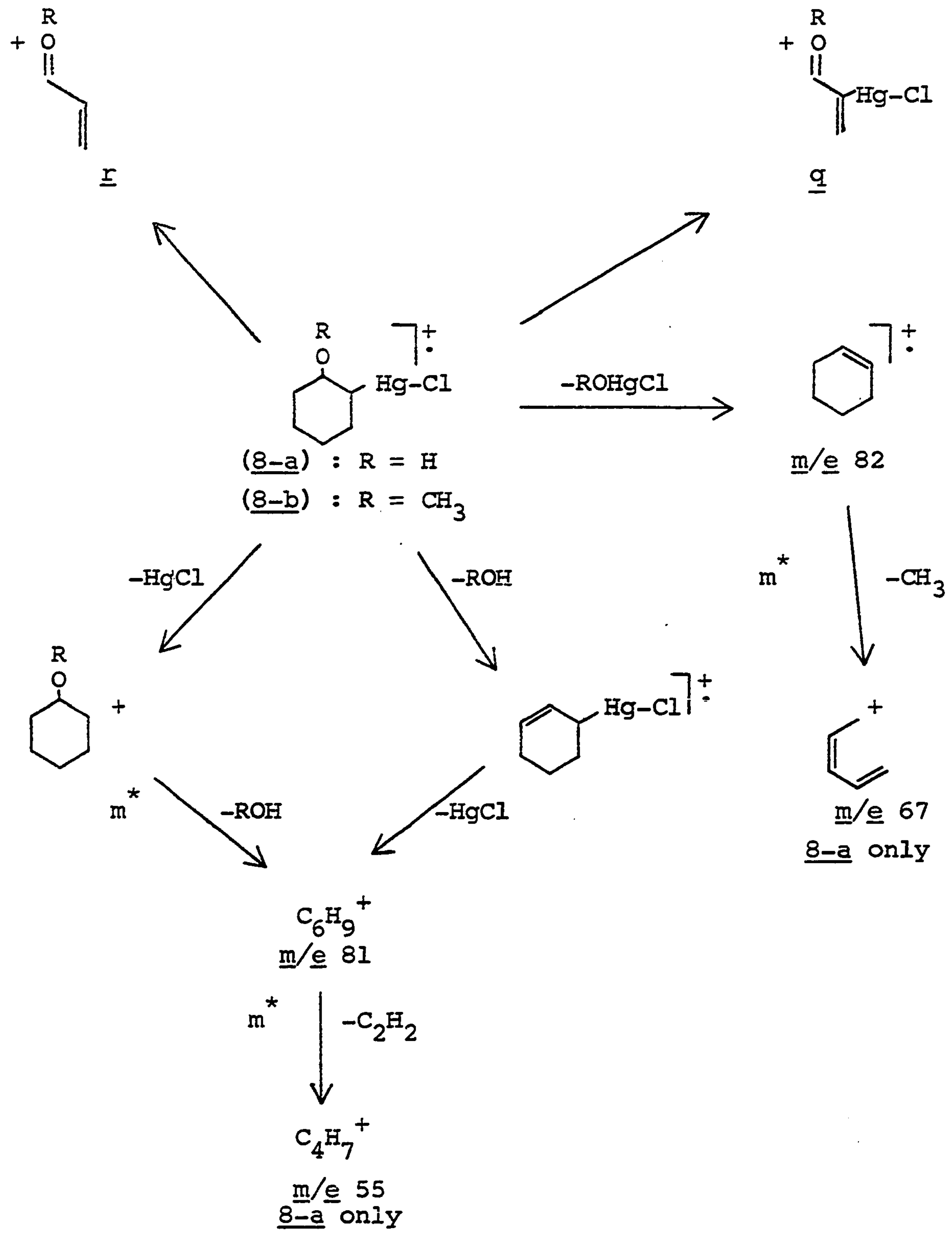
p

The alkyl ions *k* from *7-a* and *7-b* exhibit an interesting fragmentation. In the spectrum of *7-a* there is a metastable for the transition from *m/e* 57 to *m/e* 41 and in the spectrum of *7-b*, there appears a metastable for the analogous fragmentation of m/e 71 to m/e 55. This loss of methane is not a common or abundant ion in the spectra of supposedly similar alkyl ions derived from other precursors such as alkyl bromides (6, p. 429). The reasons for their abundance in the spectra of 7-a and 7-b are not clear, but might be associated with a greatly modified energy content (probably lower) and energy distribution due to the very large mercury atom which was lost as a neutral moiety.

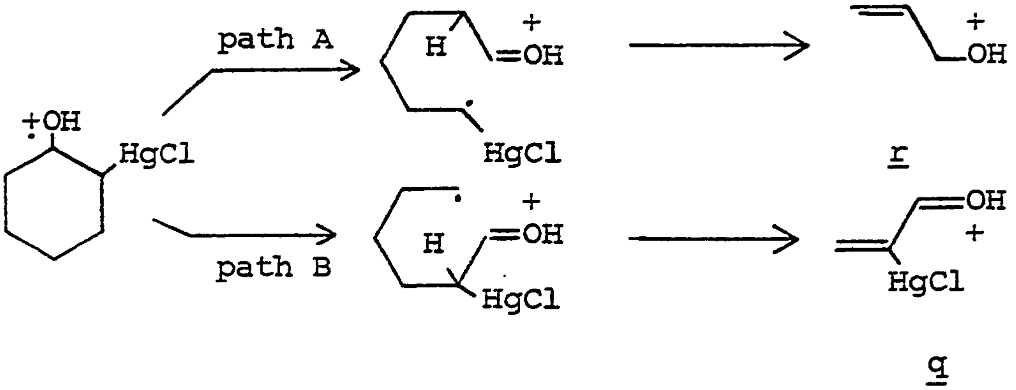
2-hydroxyalkyl- and 2-methoxyalkyl- mercuric chlorides

In Scheme 6 is outlined the 70 eV fragmentation behavior of 2-hydroxycyclohexylmercuric chloride (8-a) and 2-methoxycyclohexyl-mercuric chloride (8-b). In each spectrum only weak parent ions are observed. The base peak m/e 81 ion is formed through sequential loss of HgCl and ROH, in both orders. Formal reversal of the oxymercuration process occurs to produce the m/e 82 ion which decomposes further in a manner exactly analogous to cyclohexene (6, p. 26).

The ions q and r are formed *via* fragmentations controlled by the oxygen-containing substituent. The base peak in the spectrum of cyclohexanol is m/e 57 ($CH_2=CH-CH=\overset{+}{O}-H$) which is formed by initial cleavage *alpha* to the hydroxyl group. Analogous fragmentation mechanisms lead to ions q and r. Pathway A is favored resulting in very low abundances of ion q (0.8% and a trace from 8-a and 8-b respectively).



Scheme 6. Fragmentation pattern of 8-a and 8-b



When the mercury-containing ions of 2-hydroxycyclooctylmercuric chloride (9) (Scheme 7) are compared to the mercury-containing ions from 8-a, certain distinct differences are noted. The elimination of $:CH_2$ from the molecular ion to produce *m/e* 350[1] is one of the rare examples (24) of methylene elimination. The most often cited example of such a fragmentation, i.e. loss of $:CH_2$ from thioxanthene (25), has recently been shown to be non-repeatable (26).

Hydrogen rearrangements must accompany the losses of ethanol or the butyl radical which result in the *m/e* 318 and 307 ions, respectively, but no specific mechanism has been established for these processes.

The base peak in the spectrum of 9 is the hydrocarbon

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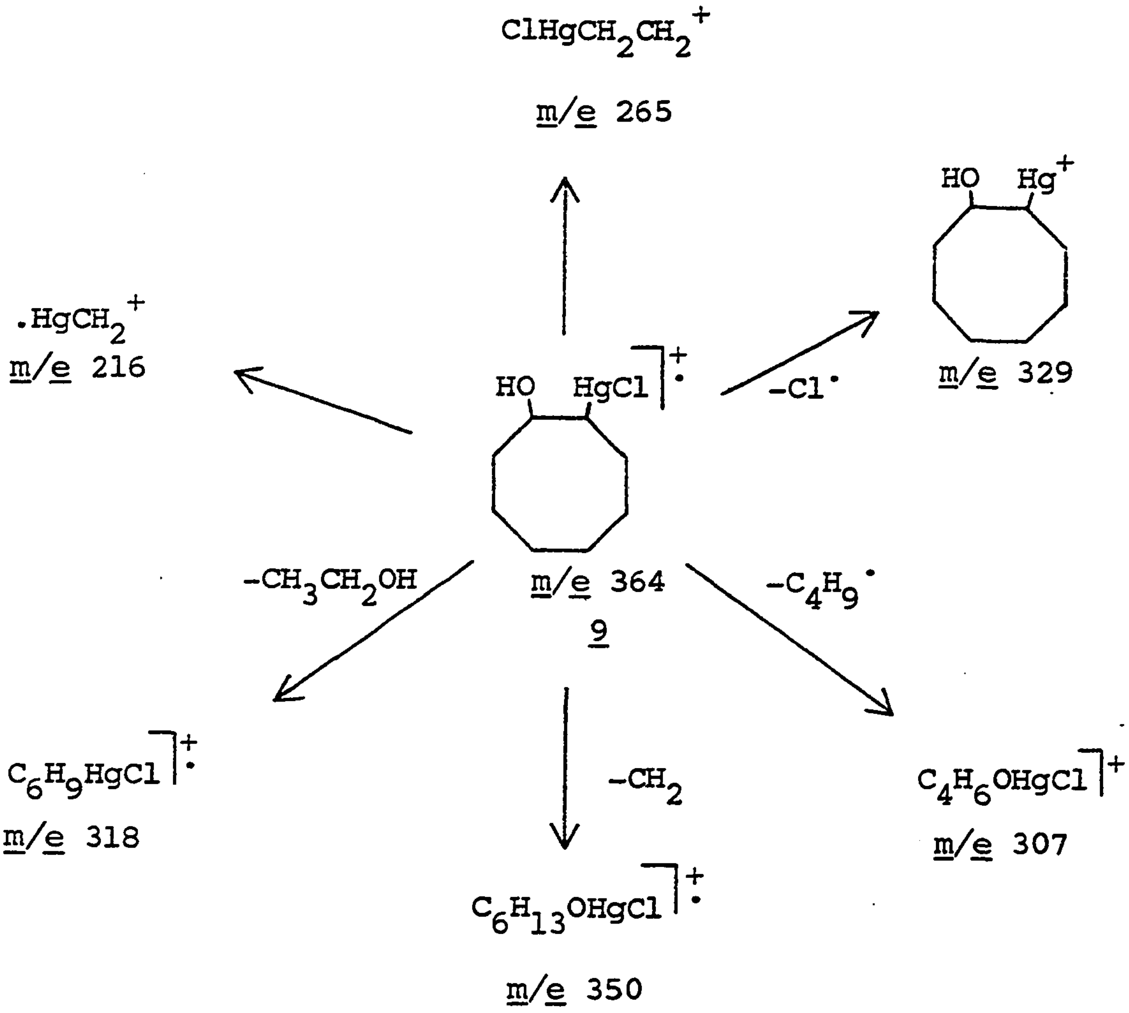
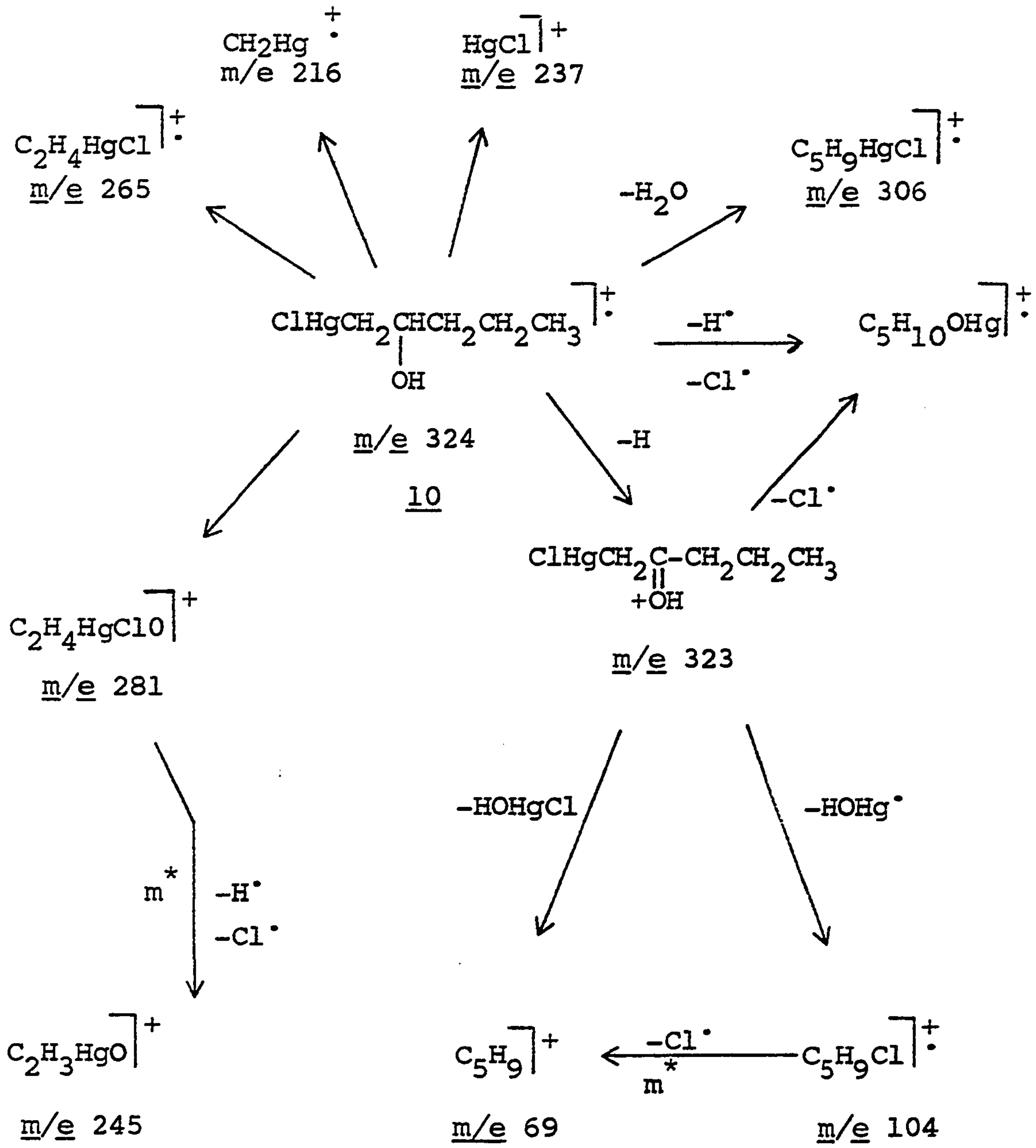
[1] This observation raises the interesting possibility that 9 might be a useful source of $:CH_2$ under thermal reaction conditions, a possibility we have not yet investigated. The electron impact induced behavior of two well known carbene percursors is discussed later in this paper.



Scheme 7. Fragmentation pattern of 9

m/e 81 ion, formed at least in part by the metastable loss of methanol from a structurally undefined m/e 113 rearrangement ion. The reversal of the oxymercuration process is not observed, undoubtedly because of the high rates of competing reactions which fragment the less stable 8-membered ring.

The fragmentation of the hydroxymercuration product of of an open chain olefin, that of 1-pentene (10), is shown



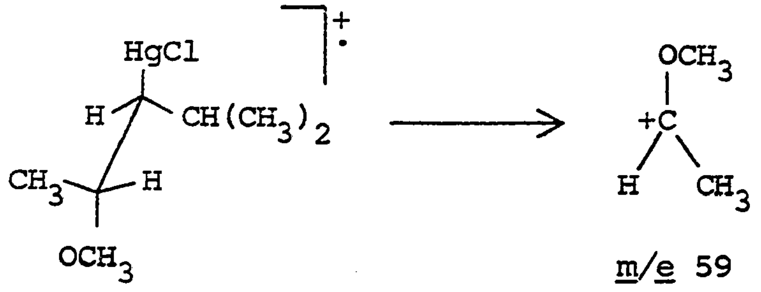
Scheme 8. Fragmentation pattern of <u>10</u>

in Scheme 8. The low intensity parent ion is cleaved very preferentially between carbons two and three to produce the base peak at *m/e* 281. In this process the usual cleavage *beta* to mercury is reinforced by the tendency for cleavage *alpha* to a hydroxyl group. Subsequent metastable loss of HCl produces the abundant *m/e* 245 ion.

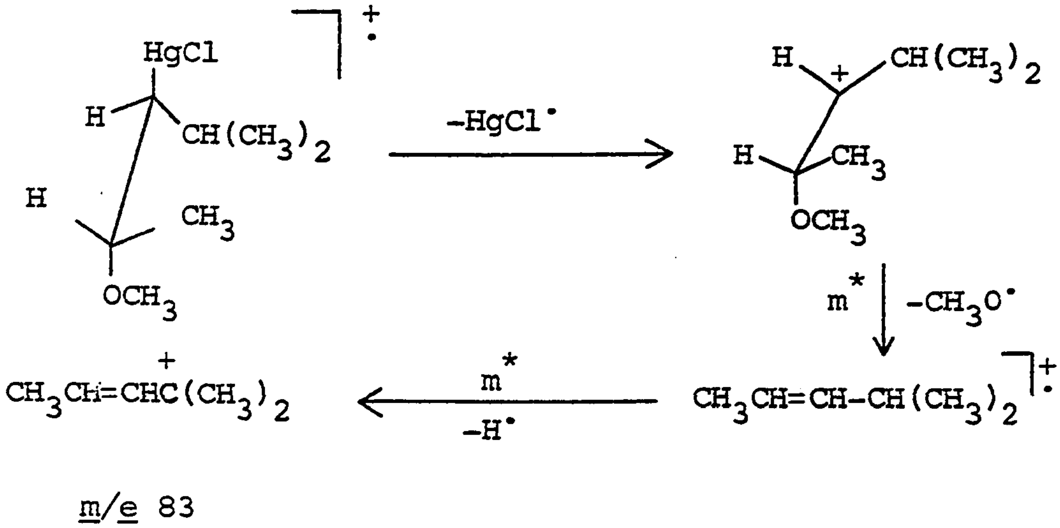
A variety of alternate fragmentations of the molecular ion are shown in Scheme 8, several of which necessitate rearrangement. Loss of mercury from the M-H ion is accompanied by chlorine migration to produce the *m/e* 104 ion.

A pair of diastereomers was next investigated in order to determine the applicability of mass spectrometry to structural analysis in this area of organomercury chemistry. The spectra of the methoxymercuric chloride adducts of *cis*- (11) and *trans*-4-methyl-2-pentene (12) turned out to be quite similar, both at high and low electron energies. Although disappointing, this was not a very surprising result since mass spectrometry has failed to distinguish many (27), but not all (28), isomeric systems. There are, however, certain intensity differences between the two compounds, and indeed the spectrum of 12 exhibits several mercury-containing ions that are completely absent in the spectrum of 11 (*m/e* 293, and *m/e* 217 CH_3Hg). At 70 eV the base peak in the spectrum of 11 is *m/e* 69, that of 12, *m/e* 59. (At 18 eV, they both exhibit base peak *m/e* 83, formed by successive loss of CH_3OH and HgCl).

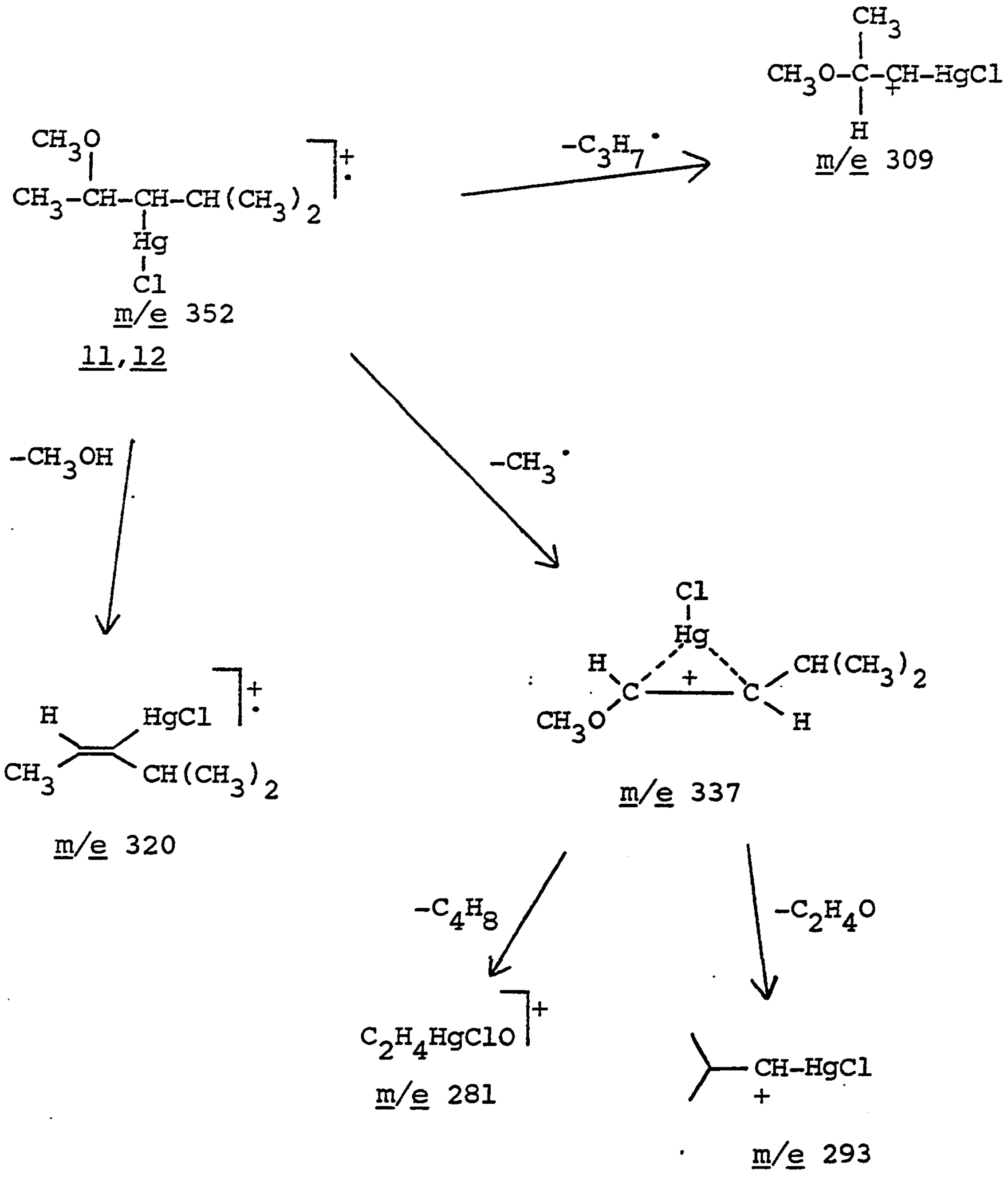
Simple *alpha* cleavage produces the *m/e* 59 ion, while *m/e* 69 is formed by a more complex pathway. Apparently the more crowded structure 11 prefers to fragment by initial loss of HgCl.



12



Other fragmentations of 11 and 12 are illustrated in Scheme 9. The structure suggested for the *m/e* 337 ion, although obviously conjectural, must at least be formed as a



Scheme 9. Fragmentation pattern of 11 and 12

transition state on the way to forming the m/e 281 and 293 ions. The formation of mercurinium ions in solution reactions has been postulated (29).

The synthetic importance and utility of a variety of organo-mercurials as halocarbene or halocarbenoid precursors has been well demonstrated by Seyferth (30).

Scheme 10 summarizes the fragmentations of phenyl (trichloromethyl)-mercury (13-a) and phenyl(bromodichloromethyl)mercury (13-b) observed in our investigations by which we have demonstrated the utility of mass spectrometry in structural and analytical analysis of such compounds. In each case the base peak is the phenyl cation, m/e 77. Both parent ions decompose through the metastable loss of the CXY_2 moiety yielding the phenyl mercury cation u. Molecular ion 13-a loses a chlorine radical producing the ion s which subsequently loses $:CCl_2$ in a metastable process giving u. For parent ion 13-b there are apparently two competing modes of fragmentation. The loss of $Br^\bullet$ generates s whereas the loss of $Cl^\bullet$ gives t. The ensuing loss of :CClBr from t would also produce the phenyl mercury cation. Elimination of either dichloromethylene from molecule ion 13-a or bromochloromethylene from 13-b gives rise to the phenylmercuric chloride molecular ion v.[1]

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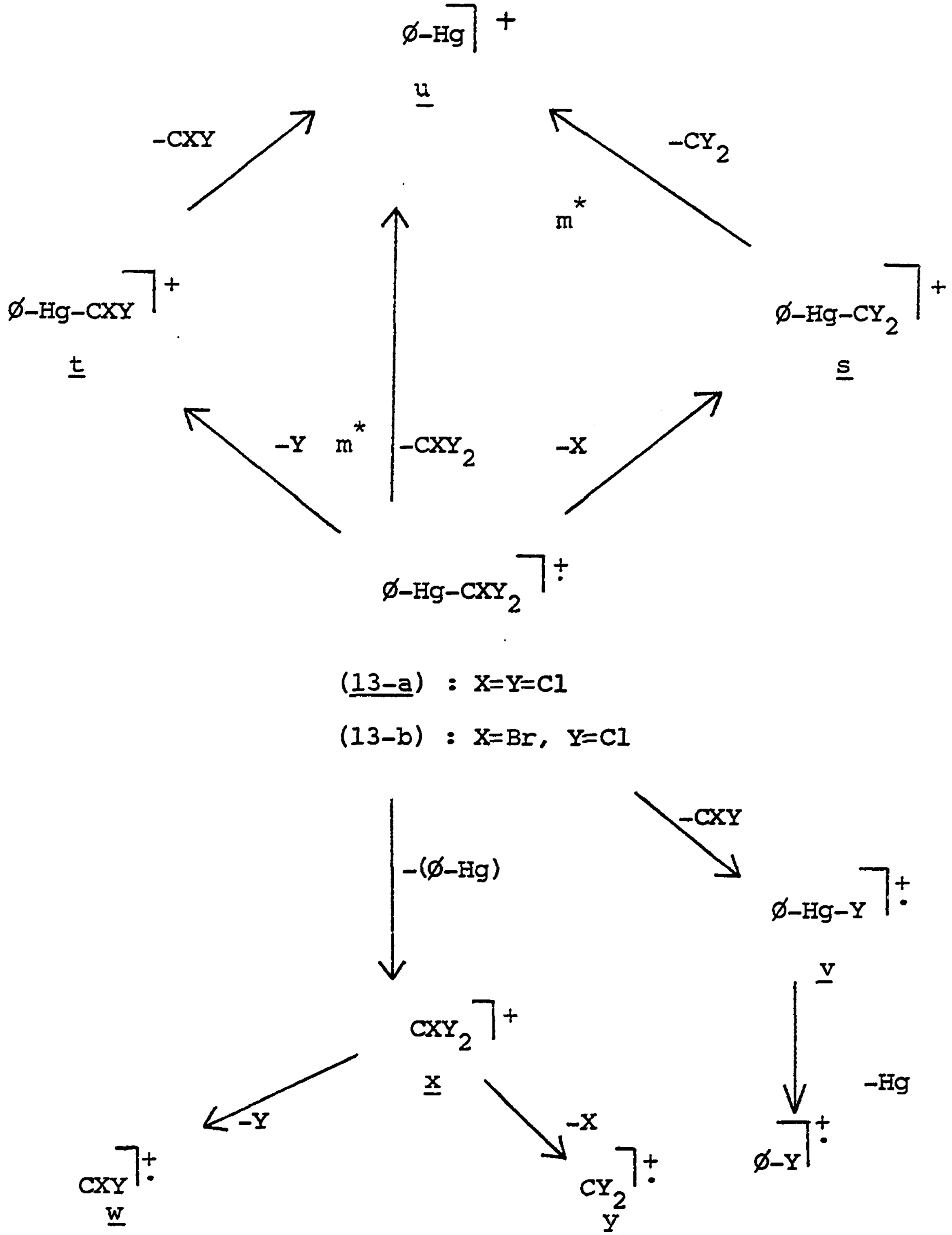
[1] High resolution data would be required to definitely confirm that m/e 358 is the phenylmercuric bromide molecule ion. This region of the spectrum is quite complex.



Scheme 10. Fragmentation pattern of 13-a and 13-b

In the spectrum of 13-a and 13-b, the trihalocarbonium ion x is observed. The bromodichlorocarbonium ion can lose either Cl• or Br• to generate ion w or y. Naturally, the trichlorocarbonium ion can only decompose to give y.

At 18 eV the molecule ion of 13-a is the base peak, but for 13-b the phenyl cation is still the most abundant ion. Ions s, t, and u are still observed, but v, x, w, and y are not present. In going from 18 to 16 eV ion u increases as the phenyl cation decreases in abundance. This is the only major change in the spectrum. Thus, it would appear that the phenyl cation is not formed directly from the molecule ion but from the phenylmercury cation.

SUMMARY

The mass spectrometric behavior of a variety of diaryl and dialkyl mercurials, aromatic and aliphatic mercuric chlorides have been studied. The utility of mass spectrometry for the structural and analytical analysis of organomercury compounds is demonstrated. These compounds give readily identifiable parent ions and the fragmentation patterns can be rationalized from the structural features of the molecules.[1]

In the fragmentation of simple dialkyl mercurials and alkyl mercuric chlorides there is a pronounced tendency toward charge retention on carbon rather than on mercury. However, with proper substitution the organomercury ions can be stablized. A number of mercury containing organic ions are observed and structural possibilities including cyclic mercurinium structures are discussed. In the aliphatic series the mercury atom gives rise to a prominent tendency toward *beta* cleavage. This could be rationalized in terms of the possible structures of the daughter ions. Rearrangement reactions involving mercury are discussed.

Several oxymercurated olefins including *cis*- and *trans*-4-methyl-2-pentene have been studied. It was not possible

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[1] Part I of this dissertation is in press--*J. Organometal. Chem.*

to readily distinguish between the diastereomeric adducts by analysis of the fragmentation patterns.

Two carbene precursors have been examined--phenyl (tri-chloromethyl) mercury and phenyl(bromodichloromethyl) mercury. The elimination of dihalocarbene from the molecule ions and the radical cations of the dihalocarbenes are observed. A novel elimination of methylene from 2-hydroxycyclooctylmercuric chloride might be indicative of interesting chemistry of this compound in solution.

EXPERIMENTAL

General Comments

All mass spectra were obtained using an Atlas CH4 spectrometer operated with a molecular beam inlet system. The electron energy was varied between 16 and 70 eV. An accelerating potential of 3000 volts and electron currents of 1-10 μa were employed.

Diphenylmercury and phenylmercuric chloride were obtained from Eastman Organic Chemicals and after recrystallization (methanol) had melting points in agreement with accepted literature valves.

The following compounds were prepared by well-established Grignard procedures: di-p-trifluoromethylphenylmercury, methanol [142-3°C]; dibenzylmercury, methanol [107.5 - 108.5, lit. 111° (31)]; di-n-butylmercury [b.p. 121-2° at 23 mm, lit. 120-23° at 23 mm (32)]. The following compounds were prepared by Grignard techniques, except that inverse addition was employed: n-butylmercuric chloride, methanol [m.p. 125.5 - 126.5°, lit. 125.5° (31)]; n-amylmercuric chloride, methanol [m.p. 123-4°, lit. 110° (31)].

Table 1. Mass spectra of 1-a, 1-b, and 1-c

m/e	Relative intensity (70 eV)		
	1-a	1-b	1-c
492			9.18
473			3.00
384		92.4	
356	44.7		
347			11.1
293		18.3	
290			0.48
279	21.2		
182		0.72	
181		1.58	
167		2.53	
165		2.15	
154	4.15		
153	2.52		
152	2.64		
145			100.
144			1.55
143			0.92
127			1.98
126			22.3
125			12.3
119			1.76
107			1.95
95			15.5
92		19.80	
91		100.	
81			1.10
78	7.36		
77	100.		

Table 1 (Continued)

m/e	Relative intensity (70 eV)		
	1-a	1-b	1-c
76			4.60
75			14.9
74			3.44
69			3.32
65		24.8	
63		5.87	
57			10.3
52	1.75		
51	31.8		5.30
50	7.95		9.09
43		33.1	

Table 2. Mass spectra of 2

m/e	Relative intensity	
	70 eV	16 eV
384	5.82	100.
202	1.24	
182	7.01	93.5
181	0.44	
104	1.32	9.35
103	0.22	
92	7.32	3.06
91	100.	41.1
90	2.10	
89	3.64	
66	0.72	

Table 2 (Continued)

m/e	Relative intensity	
	70 eV	16 eV
65	87.6	
64	1.04	
63	2.97	
51	1.78	
41	1.36	
39	4.34	

Table 3. Mass spectrum of 3

m/e	Relative intensity (70 eV)
316	11.8
287	0.77
256	2.28
230	1.22
216	trace
202	1.11
57	100.
56	11.6
42	27.2
40	4.65

Table 4. Mass spectra of 4-a, 4-b, 4-c, and 4-d

m/e	Relative intensity (70 eV)			
	4-a	4-b	4-c	4-d
388				100.
348			100.	
328		81.3		
314	87.4			
313			15.1	
309				11.9
293		4.70		
281				7.57
279	12.9			
237	16.5	2.56	2.21	
202	39.3	3.29	5.43	7.40
188				2.56
186				2.70
173				1.04
171				1.19
157				1.28
155				1.37
150			0.49	
149			1.47	
148			2.94	
146			4.24	
145				2.02
143				2.11
140				1.96
128		0.13		
126		0.39		
114	2.30		1.73	
113			14.4	
112	7.20		5.97	

Table 4 (Continued)

m/e	Relative intensity (70 eV)			
	4-a	4-b	4-c	4-d
111			44.3	
107				28.6
92				20.6
91		100.		
89		12.2		
78			14.9	
77	100.		4.47	25.7
76		0.74	12.9	
75		1.40	34.0	
74		1.80	14.4	
73			4.21	
65		2.90		12.0
64		3.80		4.55
63		12.8		
62		5.13		
61		1.80		
51	42.3	6.81	8.45	
50	24.3	6.86	22.8	
41				5.80

Table 5. Mass spectra of 5-a and 5-b

m/e	Relative intensity (70 eV)	
	5-a	5-b
386		26.5
371		1.18
355		1.18
328	70.5	
313	10.4	
309		10.2
293	4.77	
281		5.13
237	2.76	
202	4.77	15.40
186		trace
157		2.70
155		3.08
143		2.36
128	0.55	
126	1.38	
107		33.0
92		33.7
91	100.	
89	12.6	
79		24.80
77	2.90	100.00
76	1.34	
75	2.12	
74	2.67	
65	29.7	
64	4.25	16.1
63	4.17	21.6
62	5.94	

Table 5 (Continued)

m/e	Relative intensity (70 eV)	
	5-a	5-b
61	2.37	
51	9.56	13.7
50	9.41	12.3
43	3.08	
42	3.88	
41	5.06	
40	1.90	
39	18.5	
38	4.24	

Table 6. Mass spectrum of 6

m/e	Relative intensity (70 eV)
330	100.
295	42.20
294	20.7
237	4.35
202	12.6
94	18.2
93	24.4
92	59.5
65	43.4
64	39.6
63	45.6

Table 7. Mass spectra of 7-a and 7-b

m/e	Relative intensity (70 eV)	
	7-a	7-b
308		12.6
294	12.1	
279		2.65
273		2.00
265	59.8	17.7
259	1.34	
237	17.5	11.7
230	4.54	3.08
216	1.34	0.80
202	14.6	9.44
71		100.
65	3.11	2.00
63	9.46	5.73
57	100.	
56	12.2	
55	12.7	17.8
43		94.1
41	56.8	60.5

Table 8. Mass spectra of 8-a and 8-b

m/e	Relative intensity (70 eV)	
	8-a	8-b
350		4.03
336	0.64	
335	0.44	
318	8.16	5.71
315		3.09

Table 8 (Continued)

m/e	Relative intensity (70 eV)	
	8-a	8-b
307		trace
301	2.18	
293	6.77	
237	5.93	2.89
202	12.9	3.36
113		18.0
99	20.2	
98	3.24	
97	2.24	
85		1.50
84		2.84
83	9.04	1.90
82	46.4	14.0
81	100.	100.
80	3.33	1.20
79	9.01	5.18
78	2.25	
77	3.31	1.80
72		1.60
71	1.50	33.6
70	7.52	
69	11.6	2.00
68	3.01	
67	34.8	9.90
66	1.59	
65	1.88	
63	0.83	
58	1.89	
57	44.6	
56	3.84	

Table 8 (Continued)

m/e	Relative intensity (70 eV)	
	8-a	8-b
55	23.6	7.08
54	18.9	5.50
53	9.91	6.09
52	1.81	
51	3.36	
50	1.81	
43	16.9	
42	11.4	
41	32.2	
40	3.31	
39	18.7	

Table 9. Mass spectra of 9

m/e	Relative intensity	
	70 eV	18 eV
364	0.30	5.72
350	1.49	7.38
329	0.41	
318	1.92	11.5
307	0.25	
277	0.26	
237	0.43	
202	8.75	14.1
113	17.4	18.8
110		24.4
109		17.4
85	2.25	

Table 9 (Continued)

m/e	Relative intensity	
	70 eV	18 eV
84	4.04	
83	2.96	
82	17.7	31.3
81	100.	100.
80	1.70	
79	5.25	
72	2.79	
71	34.5	5.22
68	2.88	3.00
67	17.0	
62		8.70
58	2.75	
57	4.00	
56	1.93	
55	8.28	
54	9.82	
53	5.89	
52	1.30	
51	2.29	
50	1.30	
45	16.1	
43	5.08	
42	2.86	
41	22.4	
40	1.81	

Table 10. Mass spectrum of 10

m/e	Relative intensity (70 eV)
324	0.60
323	1.44
306	0.31
288	27.1
281	100.
265	1.25
255	1.03
245	29.3
237	4.43
216	1.50
202	5.81
106	0.20
104	0.63
70	8.93
69	30.50
59	0.39
58	3.53
55	17.2

Table 11. Mass spectrum of 11

m/e	Relative intensity (70 eV)
352	trace
336	0.58
320	2.40
309	4.67
115	14.2
99	5.93

Table 11 (Continued)

m/e	Relative intensity (70 eV)
84	43.9
83	98.9
72	56.8
69	100.
67	7.14
59	67.6
55	37.1

Table 12. Mass spectrum of 12

m/e	Relative intensity (70 eV)
352	0.17
337	0.81
320	4.13
309	8.23
293	0.17
281	1.78
237	2.92
217	4.03
212	3.80
99	5.90
84	3.02
83	73.4
73	7.30
72	35.0
69	63.9
67	6.94
59	100.
55	34.3
53	5.59

Table 13. Mass spectra of 13-a and 13-b

m/e	Relative intensity (70 eV)	
	13-a	13-b
440		4.50
405		1.11
396	23.3	
361	15.0	3.16
314	4.10	0.08
279	53.4	25.1
249		0.42
237	0.12	0.27
202	0.62	
165		0.61
163		1.40
161		1.01
128		0.82
126		0.67
121	0.61	
119	1.82	
117	1.86	
114	0.45	
112	1.30	1.33
84	1.45	
82	2.12	1.90
77	100.	100.
51	30.8	
50	14.2	34.70
47	2.78	

Preparation of compounds

Ortho- and Para-methoxyphenylmercuric Bromide were prepared by the Grignard procedure from ortho- and para-bromoanisole and $HgCl_2$. Using the ortho-isomer for an example, the product isolated was a mixture of ortho-methoxyphenylmercuric chloride and ortho-methoxyphenylmercuric bromide which was converted to pure ortho-methoxyphenylmercuric bromide by heating with a large excess of NaBr dissolved in DMSO on a steambath overnight. At the end of this period the mixture was poured into 100 ml of H_2O saturated with NaBr. The product was isolated by ether extraction, the combined extracts back-extracted with H_2O, dried ($MgSO_4$) and the ether removed under reduced pressure. Subsequent recrystallization from methanol yielded a white solid [4-d, m.p. 187°, lit. 187° (32)]; [5-b, m.p. 182.5 - 184°, lit. 183° (32)].

Ortho- and para-tolymercuric chloride and para-chlorophenylmercuric chloride were prepared by the method of Whitmore (33). Ortho-tolylmercuric chloride, ethanol [m.p. 229.5 - 30.5°]; para-tolylmercuric chloride, methanol [m.p. 234-5°; lit. 233 (31)]; para-chlorophenylmercuric chloride [m.p. 238-9°, lit. 225° (32)]. Ortho-chloromercuriphenol was prepared by the method of Whitmore and Middleton (31) [m.p. 146.5 - 47.5°, lit. 152.5° (32)].

Addition compounds of olefins and mercury salts The hydroxymercuric chlorides of cyclohexene, cyclooctene and 1-pentene and the methoxymercuric chlorides of cyclohexene and *cis* and *trans*-4-methyl-2-pentene were prepared by standard procedures for oxymercuration: 2-methoxycyclohexylmercuric chloride [m.p. 114-115° from benzene-hexane]; 2-hydroxycyclohexylmercuric chloride [m.p. 148.5° from benzene-hexane, lit. 153.0 - 153.6° (34)]; 2-hydroxycyclooctylmercuric chloride [m.p. 89-90° from methanol]; 2-hydroxy amyl mercuric chloride [m.p. 61-2° from chloroform-hexane]; methoxymercuric chloride of *cis*-4-methyl-2-pentene [m.p. 40.5 - 41.5° from methanol]; methoxymercuric chloride of *trans*-4 methyl-2-pentene [m.p. 70.5 - 71.5° from methanol].

Methylene transfer reagents Phenyl(trichloromethyl)mercury [m.p. 116-7°, lit. 115-7° (35)] was prepared by the method of Seyferth and Burlitch (35) as was phenyl(bromodichloromethyl)mercury[1] [m.p. 110° - dec., lit. 110°-11°-dec. (35)].

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[1] The author wishes to thank Richard Fugiel for supplying the sample utilized in this study.

PART II: MASS SPECTROSCOPY OF ORGANOGERMANES

INTRODUCTION

Site-specific hydrogen transfer processes occurring in odd-electron ions have received a great deal of attention in recent years. The McLafferty rearrangement of a gamma-hydrogen to an unsaturated center accompanied by the expulsion of an olefinic fragment provides an excellent example (36; 6, p. 155). Grubb and Meyerson examined the mass spectrum of 1-phenylbutane-3-d and found that 48.6% of the C_7H_8+ ions were labeled. In addition, study of 1-phenylbutane-4-d showed that 2.3% of the C_7H_8+ ions were labeled (37, p. 509). Thus, these authors were able to conclude that greater than 95% of the migrating hydrogen atoms originated from the gamma-carbon. The highly selective nature of this hydrogen

$$C_6H_5\text{-}CH_2CH_2CHDCH_3\rceil^{+\cdot} \longrightarrow C_7H_7D\rceil^{+\cdot} \qquad (48.6\%)$$

$$C_6H_5\text{-}CH_2CH_2CH_2CH_2D\rceil^{+\cdot} \longrightarrow C_7H_7D\rceil^{+\cdot} \qquad (2.3\%)$$

abstraction process has been studied and discussed by several workers in terms of the importance of localized radical character at the receptor site (38, 39, 40, 41).

Another example of site-specificity in the elimination of neutral molecules from odd-electron ions comes from the work of Benz and Biemann (42) and from the work of Meyerson and Leitch (43). These authors studied the electron-impact induced loss of water from a series of deuterium labeled aliphatic alcohols. Benz and Biemann examined a series of alcohols (n-butyl through n-heptyl) with a CD_2 group in consecutive positions (C-1 through C-5) and concluded that 90% of the abstracted hydrogen came from C-4 with the remainder coming from C-3 and C-5. Meyerson and Leitch worked with a series of n-hexyl alcohols (4-d_2, 5-d_2, and 6-d_3) and concluded that the loss of water was a 1,4 elimination process rather than a 1,2 elimination. They found that 91% of the abstracted hydrogen originated from C-4 with the remaining 9% coming from a carbon nearer the hydroxyl group. Recently Brown, Albert, and Pettit have published evidence for a 1,5-hydrogen(deuterium) abstraction in the loss of water from the molecule ion of 26-hydroxy-5alpha-furostan (44). This reaction, however, is in competition with a 1,4 elimination process.[1]

Not all odd-electron ions show this high degree of selectivity for hydrogen abstractions accompanying the loss of neutral molecules. Benz and Beimann found that the loss of acetic acid from the molecular ion of a series of labeled n-heptyl acetates involved the C-2 and C-3 hydrogens--55 and 45% respectively (42). The loss of water from cyclic alcohols (55) and the loss of HX from n-alkyl halides does not

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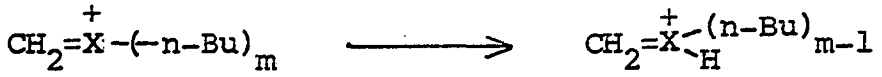
[1] There are a growing number of reports of eliminations of small neutral molecules through cyclic transition states larger than six members (45-54).

proceed in a site-specific manner (55).

Hydrogen abstraction processes occurring in even-electron ions are also known. Several of these reactions



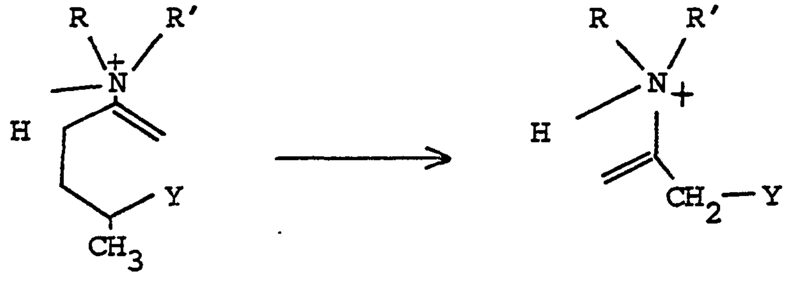
$$CH_2=\overset{+}{X}-(n\text{-}Bu)_m \longrightarrow CH_2=\overset{+}{X}\genfrac{}{}{0pt}{}{(n\text{-}Bu)_{m-1}}{H}$$

14-a: X=O; m=1
14-b: X=S; m=1
14-c: X=N; m=2

15-a: X=O; m=0
15-b: X=S; m=0
15-c: X=N; m=1

were originally formulated as site-specific abstractions but were later shown to be nonsite-specific [for example 14-a-c ⟶ 15-a-c] (56, 57, 58, and 59). The loss of water from even-electron ions is also a nonsite-specific hydrogen abstraction process (54). Kraft and Spiteller examined 2-methylhexan-2-ol-5,5-d_2 and observed the loss of water from the M-CH_3 ion. Approximately 30% of the eliminated water molecules were DHO.

Djerassi and coworkers (38) published the first report of a site-specific hydrogen abstraction in an even-electron ion (Reaction 4). The transferred hydrogen came entirely



(4)

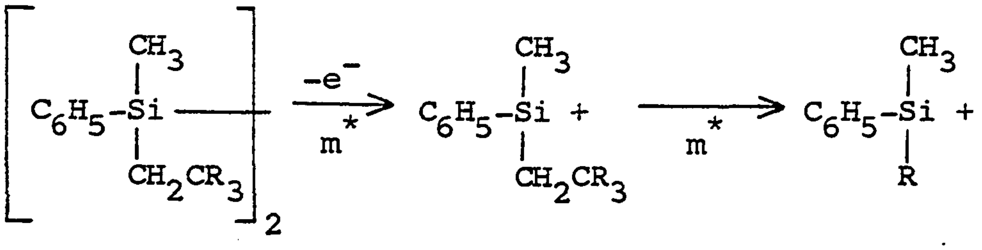
u

v

R = Me or H
R'= Me
Y = H(D)

from the *gamma*-carbon as evidenced by deuterium labeling. Unfortunately, ions *u* and *v* were of "extremely low intensity" so that this is not a particularly good example.

The work of Kinstle, Ihrig, and Goettert involving the loss of olefins from R_3Si^+ cations provides the best evidence published to date for site-specific hydrogen abstractions in even-electron ions (60). Olefin elimination accompanied by hydrogen rearrangement from R_3Si^+ ions is a well known process (61) but until these authors undertook the appropriate labeling studies, the origin of the abstracted hydrogen was only postulated to be from the *beta*-position. The cation *x* was generated by electron impact on the appropriate disilane and the loss of ethylene to give ion *y* was observed. When the specifically deuterium labeled disilane



$$\left[C_6H_5-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2CR_3}{Si}}- \right]_2 \xrightarrow[m^*]{-e^-} C_6H_5-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2CR_3}{Si}}{}^+ \xrightarrow[m^*]{} C_6H_5-\overset{\displaystyle CH_3}{\underset{\displaystyle R}{Si}}{}^+$$

x: R=H(D) *y*

was used and the loss of ethylene from ion *x* (R=D) studied, there was a clean shift of ion *y* from *m/e* 121(R=H) to *m/e* 122(R=D). The calculated site-specificity was greater than 98%.[1] This observation is particularly noteworthy in view

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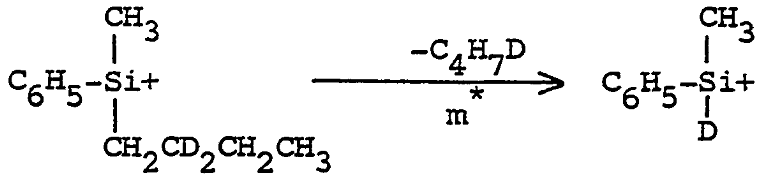
[1] Determined at 20 eV.

of the fact that ion y is the base peak in the spectrum. At 70 eV the calculation of label retention in y was complicated by the subsequent loss of H(D) from this ion but the site-specificity was still greater than 90%. In order to eliminate any question of the importance of chain length, ion z was generated in a similar manner and the loss of

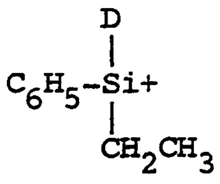


$$C_6H_5\text{-}\overset{CH_3}{\underset{CH_2CD_2CH_2CH_3}{Si+}} \xrightarrow[m^*]{-C_4H_7D} C_6H_5\text{-}\overset{CH_3}{\underset{D}{Si+}}$$

z a'

butene studied. Ion aa was again the base peak in the spectrum. The site-specificity of the hydrogen transfer was found to be greater than 95%.

Finally, Kinstle, Ihrig, and Goettert examined several silicon hydrides. They found that there is no scrambling of hydrogens in ion bb prior to the elimination of ethylene.



$$C_6H_5\text{-}\overset{D}{\underset{CH_2CH_3}{Si+}}$$

b'

Migrations to siliconium centers are well known. These rearrangements were originally detected during studies of the general fragmentation patterns of organosilanes and numerous reviews appear in the literature (6, p. 654; 62 through 75). However, little was known about the detailed mechanisms of these processes until labeling work was undertaken (50, 76).

The object of this current study was to extend the work begun by Kinstle and Ihrig to other Group IV organometallic systems--specifically those involving germanium. This was done in an attempt to establish that site-specific hydrogen rearrangements do occur in other even-electron systems and to examine the effect of altering the size of the metal atom in the R_3M^+ cations. It has been suggested that the size of the silicon atom is important in determining the high degree of specificity of the hydrogen rearrangements and that increasing the size of the M atom will increase the tendency for hydrogens atoms nearer the abstracting atom to be involved in the reaction (60; 76, p. 142). Quite recently Green _et_ _al_. (77) have published a restatement of this postulate. The possible relationship between hetero-atom size and site-specificity will be discussed in some detail. Finally, it was of interest to determine what effect, if any, would be noted when the substituents on the M atom are changed. Perhaps the site-specificity of the rearrancement would be influenced by altering the electronic nature of one of the substituents. To this end certain alkyl germanium halides were studied.

The germanium analogs were selected for study because the necessary background fragmentation studies have been done (61-74; 78-81; 82, p. 21). Furthermore the germanium containing ions exhibit a clean, easily recognizable isotope pattern more suitable for study than does tin with ten isotopes.

RESULTS AND DISCUSSION

Mass spectroscopic examination of germanium compounds is complicated by the polyisotopic nature of the metal--Table 14 (72). Interpretation of a spectrum can be difficult when there are overlapping isotope patterns from ions of similar mass to charge ratios. However, when the molecular ions and fragment ions are sufficiently isolated so that this overlapping does not occur, interpretation of the spectrum is relatively simple. Indeed, valuable information concerning ion composition can be obtained from the low resolution data. Each ion containing one germanium atom, and no other significant polyisotope elements, produces a characteristic pattern as shown in Figure 1a. For ions

Table 14. Mass and abundance of germanium isotopes

Isotope	Mass(^{12}C scale)	Abundance	
		percent	relative
^{70}Ge	69.924277	20.56	100.
^{72}Ge	71.921740	27.42	133.
^{73}Ge	72.923360	7.79	38.0
^{74}Ge	73.921150	36.47	178.
^{76}Ge	75.921360	7.76	37.9

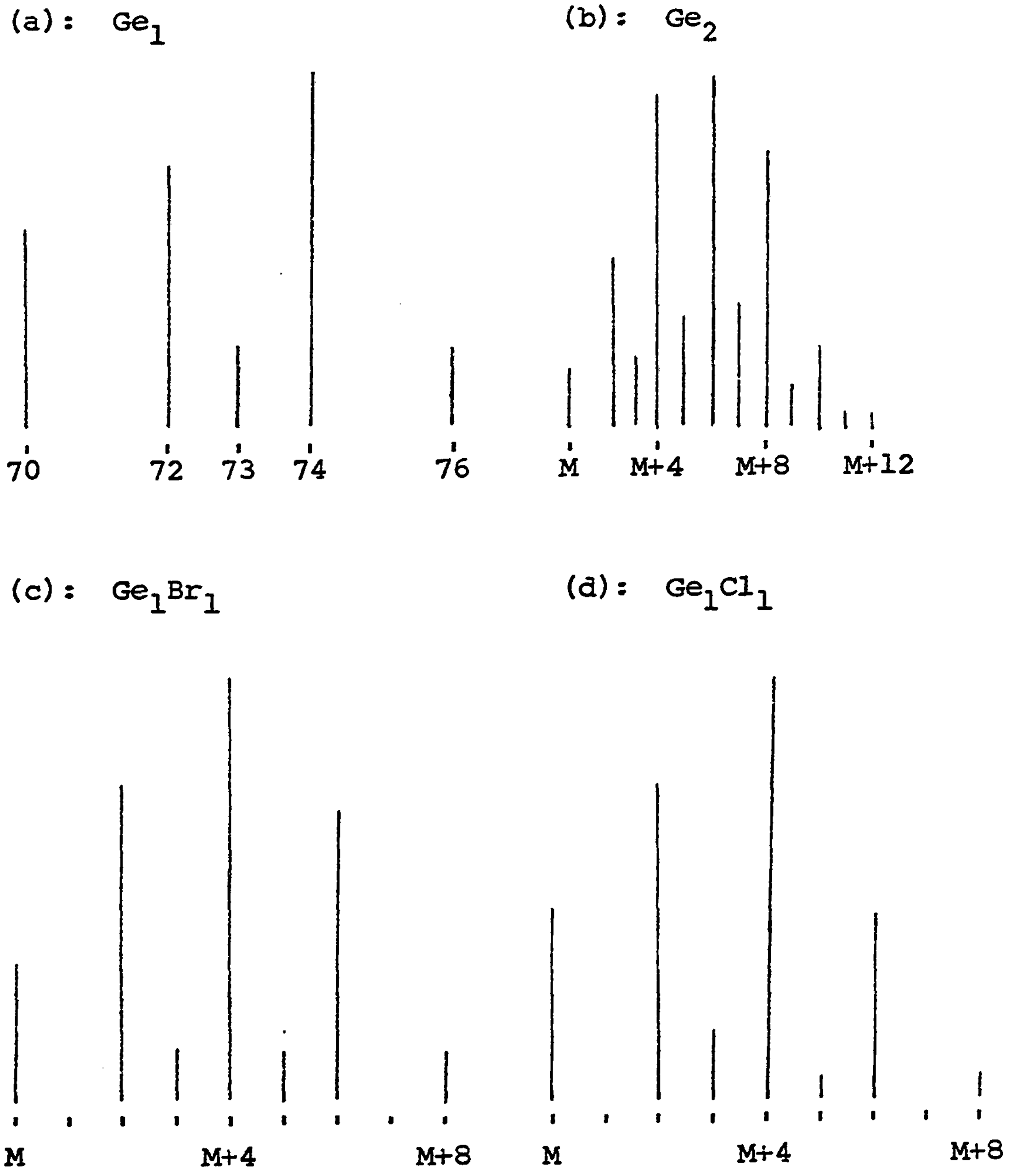


Figure 1. Isotope patterns for germanium-containing ions

containing more than one germanium atom, or more than one polisotopic atom, the pattern changes in a way that can assist in the identification of species under low resolution. In Figure 1b the isotope pattern expected for an ion containing two germanium atoms is given. Figure 1c presents the isotope pattern calculated for an ion containing one germanium and one chlorine atom.

Thus, from an examination of Figure 1 it is obvious that the elemental composition of a germanium-containing ion has a distinct effect on the isotope pattern appearing in the mass spectrum. This proved to be an invaluable aid in the identification of products isolated in the preparative procedures employed during this work. In Table 15 is displayed the experimental, relative abundances for several germanium-containing ions and the corresponding theoretical abundances. Ions containing the ^{70}Ge, ^{72}Ge, ^{74}Ge, and ^{76}Ge isotopes are tabulated. The ^{73}Ge containing ions have been disregarded because of the low abundance of ^{73}Ge.

With regard to the information given in this table in many instances there is excellent agreement between the experimentally determined relative abundances and those calculated from the known isotopic abundances of germanium (and bromine where appropriate). In general there is a tendency for the agreement to be less exact for ions such as $R_2Ge\text{-}H(D)^+$ and $R\text{-}GeH_2(D_2)^+$ than for the molecular ions,

Table 15. Theoretical and experimental abundances of selected germanium-containing ions

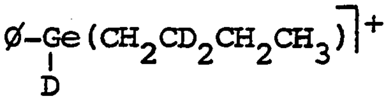
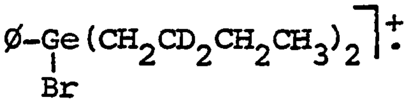
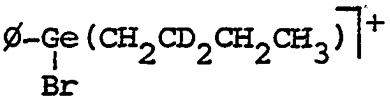
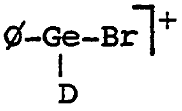
Ion	m/e	Abundance	
		experimental	theoretical
Ø-Ge$(CH_2CD_2CH_2CH_3)_3]^{+\cdot}$	330	39.0	37.9
	328	174.	178.
	326	139.	133.
	324	100.	100.
Ø-Ge$(CH_2CD_2CH_2CH_3)_2]^{+}$	271	47.4	37.9
	269	186.	178.
	267	139.	133.
	265	100.	100.
 Ø-$\underset{D}{\underset{\mid}{Ge}}(CH_2CD_2CH_2CH_3)]^{+}$	214	38.5	37.9
	212	172.	178.
	210	135.	133.
	208	100.	100.
 Ø-$\underset{Br}{\underset{\mid}{Ge}}(CH_2CD_2CH_2CH_3)_2]^{+\cdot}$	352	35.4	36.9
	350	210.	211.
	348	318.	308.
	346	227.	231.
	344	100.	100.
 Ø-$\underset{Br}{\underset{\mid}{Ge}}(CH_2CD_2CH_2CH_3)]^{+}$	293	38.3	36.9
	291	206.	211.
	289	302.	308.
	287	229.	231.
	285	100.	100.
 Ø-$\underset{D}{\underset{\mid}{Ge}}\text{-}Br]^{+}$	236	32.9	36.9
	234	168.	211.
	232	254.	308.
	230	203.	231.
	228	100.	100.
$R_3Ge\text{-}GeR_3]^{+\cdot}$ $R = CH_2CD_2CH_2CH_3$	504	126.	120.
	502	371.	359.
	500	514.	494.
	498	487.	467.
	496	255.	252.
	494	100.	100.

Table 15 (Continued)

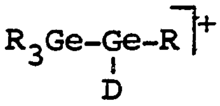
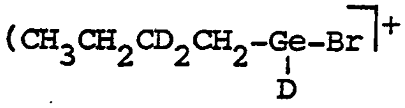
Ion	m/e	Abundance	
		experimental	theoretical
$R_3Ge\text{-}GeR_2]^+$	445	113.	120.
$R = CH_2CD_2CH_2CH_3$	443	360.	359.
	441	490.	494.
	439	462.	467.
	437	245.	252.
	435	100.	100.
 $R_3Ge\text{-}\underset{D}{Ge}\text{-}R]^+$	388	121.	120.
	386	346.	359.
	384	479.	494.
$R = CH_2CD_2CH_2CH_3$	382	452.	467.
	380	255.	252.
	378	100.	100.
$R_3Ge\text{-}GeD_2]^+$	331	145.	120.
$R = CH_2CD_2CH_2CH_3$	329	345.	359.
	327	469.	494.
	325	446.	467.
	323	245.	252.
	321	100.	100.
$(CH_3CH_2CD_2CH_2)_3Ge\text{-}Br]^+$	334	40.9	36.9
	332	198.	211.
	330	287.	308.
	328	221.	231.
	326	100.	100.
$(CH_3CH_2CD_2CH_2)_2Ge\text{-}Br]^+$	275	33.2	36.9
	273	198.	211.
	271	279.	308.
	269	222.	231.
	267	100.	100.
 $(CH_3CH_2CD_2CH_2\text{-}\underset{D}{Ge}\text{-}Br]^+$	218	25.4	36.9
	216	149.	211.
	214	241.	308.
	212	195.	231.
	210	100.	100.

Table 15 (Continued)

Ion	m/e	Abundance	
		experimental	theoretical
$(CH_3CH_2CH_2CD_2)_4Ge]^{+\cdot}$	312	38.2	37.9
	310	182.	178.
	308	136.	133.
	306	100.	100.
$(CH_3CH_2CH_2CD_2)_3Ge]^{+}$	253	37.7	37.9
	251	182.	178.
	249	140.	133.
	247	100.	100.
$(CH_3CH_2CH_2CD_2)_2Ge\text{-}H]^{+}$	195	38.0	37.9
	193	176.	178.
	191	135.	133.
	189	100.	100.
$CH_3CH_2CH_2CD_2\text{-}GeH_2]^{+}$	137	32.5	37.9
	135	157.	178.
	133	129.	133.
	131	100.	100.

$R_4Ge]^{+\cdot}$, or the M-R ions--$R_3Ge]^{+}$. The reason for the poorer agreement is due in part to the question of site-specificity of the elimination reaction (for example see Reaction 3). This aspect will be discussed below in greater detail.

$$(CH_3CH_2CH_2CH_2)_3Ge]^{+} \xrightarrow{-C_4H_8} (CH_3CH_2CH_2CH_2)_2Ge\text{-}H^{+} \qquad (3)$$

Secondly, when an ion such as $R\text{-}GeD_2{}^{+}$ is found only in low abundance in the mass spectrum, some error is introduced when attempting to tabulate the relative abundances of the various isotopes as opposed to those cases in which the ions involved are present in high abundance.

In the preparation of tri-(2,2-dideuteriobutyl)-phenylgermane (<u>14</u>) from bromotri-(2,2-dideuteriobutyl)-germane (<u>15</u>) and phenylmagnesium bromide, two molecular ion clusters were observed in the mass spectrum of the crude product. From the available information of germanium-carbon bond formation reactions it was possible that the second molecular ion cluster could have been unreacted bromotri-(2,2-dideuterio-butyl)-germane for it was known that introduction of the fourth alkyl (or aryl) group is rather difficult.[1] However, comparison of the isotope pattern and examination of the mass to charge ratios identified the side produce as bromo-(2,2-di-deuteriobutyl)-phenylgermane (<u>16</u>). An alternate possibility considering the mass to charge ratios of the molecule ions, bis-(2,2-dideuteriobutyl)-diphenylgermane was easily rejected by this process.

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[1] Although relative (numerical) rates are not known, there is a considerable body of evidence that the first two or three R groups are introduced more readily than the fourth (82). It is often necessary to replace part of the ether by a higher-boiling solvent, such as benzene or toluene, in order to effect the fourth alkylation or arylation.

Alkene Eliminations

For several years it has been known that alkylgermanes possessing the grouping R_2CHCH_2-Ge exhibit the loss of alkenes from even electron ions (82). For each alkyl group cleaved in this manner, one germanium-hydrogen bond is formed (Reaction 3).[1] These transitions are commonly accompanied by the appropriate metastable ions. Alkene eliminations occur from a wide variety of organogermanes as indicated by the data in Table 16. Polyalkylgermanes such as tetrabutylgermane and hexaethyldigermane exhibit an interesting sequence of alkene eliminations. The fragmentation pattern of hexaethyldigermane is presented in Scheme 11.

The alkene expulsions observed from even-electron ions in the mass spectra of organogermanes has been postulated to occur via a 1,2-elimination mechanism (82). Until this work was undertaken, however, the necessary evidence was not available to confirm or reject this prediction.

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[1] For alkylphenylgermanes it might be argued that the hydrogen is transferred from the alkyl to the phenyl group in a manner analogous to a McLafferty reaction. But since the alkene elimination also occurs in tetraalkylgermanes the phenyl moiety cannot be required for the rearrangement and logical receptor site is the germanium atom.

Table 16. Alkene eliminations from organogermanes

Compound	Transition	$(m^*)^a$
Et_6Ge_2 Et_4Ge Et_6Ge_2O	$Et_3Ge^+ \rightarrow Et_2GeH^+ + C_2H_4$	110.0
	$Et_2GeH^+ \rightarrow EtGeH_2{}^+ + C_2H_4$	83.0
	$EtGe^+ \rightarrow GeH^+ + C_2H_4$	54.6
$\emptyset_3GeEt$ $\emptyset_2GeEt_2$	$\emptyset_2GeEt^+ \rightarrow \emptyset_2GeH^+ + C_2H_4$	204.1
$(\emptyset CH_2)_3GeEt$	$(\emptyset CH_2)_2GeEt^+ \rightarrow (\emptyset CH_2)_2GeH^+ + C_2H_4$	231.8
$\emptyset GeEt_3$ $\emptyset_2GeEt_2$	$\emptyset GeEt_2{}^+ \rightarrow \emptyset Ge(H)Et^+ + C_2H_4$	156.8
Et_3GeCl Et_3GeBr	$Et_2GeCl^+ \rightarrow EtGe(H)Cl^+ + C_2H_4$	115.7
	$Et_2GeBr^+ \rightarrow EtGe(H)Br^+ + C_2H_4$	158.7
$(Et_3Ge)_2O$	$Et_5Ge_2O^+ \rightarrow Et_4Ge_2(H)O^+ + C_2H_4$	253.7
	$Et_4Ge_2(H)O^+ \rightarrow Et_3Ge_2(H)O^+ + C_2H_4$	225.9
	$Et_3Ge_2O^+ \rightarrow Et_2Ge_2(H)O^+ + C_2H_4$	196.1
	$Et_2GeOH^+ \rightarrow EtGe(H)OH^+ + C_2H_4$	98.3
	$EtGe(H)OH^+ \rightarrow H_2GeOH^+ + C_2H_4$	71.5

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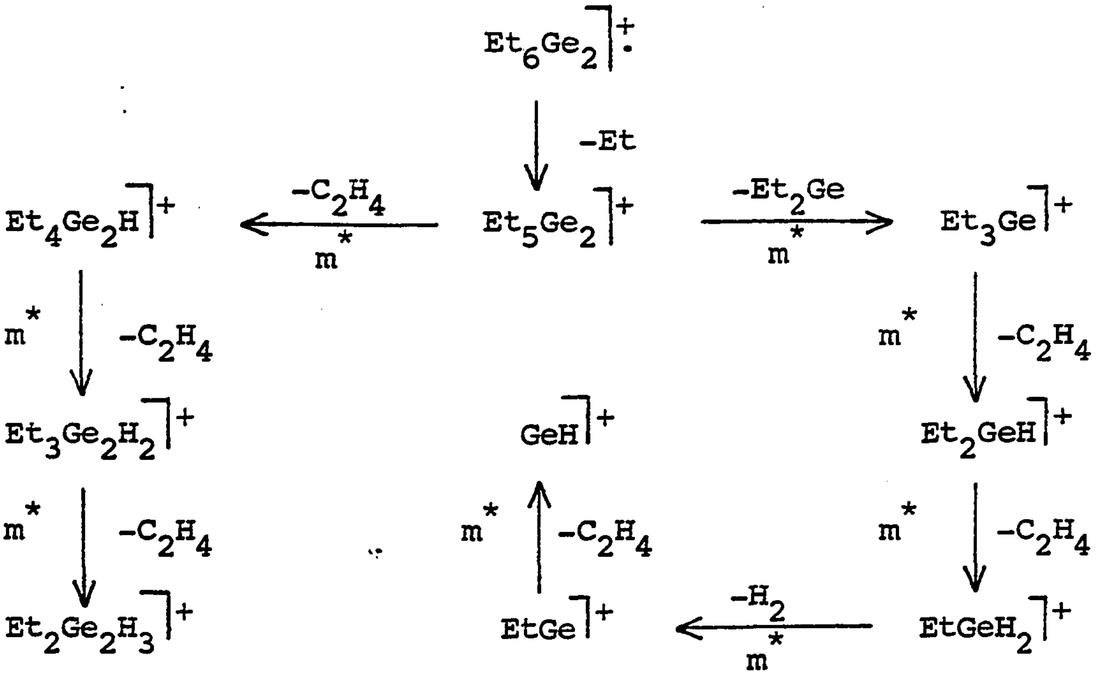
[a] Metastable ion.

Table 16 (Continued)

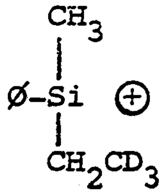
Compound	Transition	$(m^*)^a$
i-Bu_4Ge i-Bu_6Ge_2	i-$Bu_3Ge^+ \longrightarrow$ i-$Bu_2GeH^+ + C_4H_8$	145.8
	i-$Bu_2GeH^+ \longrightarrow$ i-$BuGeH_2{}^+ + C_4H_8$	93.5
i-Bu_6Ge_2	i-$Bu_5Ge_2{}^+ \longrightarrow$ i-$Bu_4GeH^+ + C_4H_8$	326.2
	i-$Bu_4Ge_2H^+ \longrightarrow$ i-$Bu_3Ge_2H_2 + C_4H_8$	271.3
	i-$Bu_3Ge_2H_2{}^+ \longrightarrow$ i-$Bu_2Ge_2H_3{}^+ + C_4H_8$	216.8
	i-$Bu_2Ge_2H_3{}^+ \longrightarrow$ i-$BuGe_2H_4{}^+ + C_4H_8$	162.9



Scheme 11. Fragmentation pattern of 17 (74)

Alkene Eliminations--Labeled Compounds

Kinstle and Ihrig first observed the alkene elimination accompanied by hydrogen rearrangement from a <u>beta</u>-position in the fragmentation of dialkylphenylsiliconium ion, <u>z</u>. In order to determine if the germanium systems



$$\phi\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2CD_3}{Si}}\ \oplus$$

<u>z</u>

would show similar behavior, ion <u>a</u>' was generated by electron impact induced ionization of <u>15</u>. The molecule ion <u>15</u> expelled a butyl radical yielding the dibutylphenylgermanium

$$\begin{tikzcd}
\underset{\underline{15}}{\phi\text{-}Ge(CH_2CD_2CH_2CH_3)_3} \arrow[r, "-e^-"] & \phi\text{-}Ge(CH_2CD_2CH_2CH_3)_3]^{+\cdot} \arrow[d, "-C_4H_7D_2"] \\
\underset{\underline{b}'}{\phi\text{-}Ge(D)CH_2CD_2CH_2CH_3]^+} & \underset{\underline{a}'}{\phi\text{-}Ge(CH_2CD_2CH_2CH_3)_2]^+} \arrow[l, "-C_4H_7D", "m^*"']
\end{tikzcd}$$

cation <u>a</u>'. The ensuing loss of butene from <u>a</u>' gave <u>b</u>'. Analysis of the isotope pattern of ion <u>b</u>' disclosed that this ion was 98% d_3 (at 70 eV). Consideration of the probable errors inherent in the calculation led us to believe that this number was accurate to within two percent. Subsequent butene loss from ion <u>b</u>' produced the dideuteriophenylgermanium cation, *c*'. This ion was determined to be

$$\underset{\underline{b}'}{\phi\text{-Ge(D)CH}_2\text{CD}_2\text{CH}_2\text{CH}_3\rceil^+} \xrightarrow{-C_4H_7D} \underset{\underline{c}'}{\phi\text{-GeD}_2\rceil^+}$$

83% d_2.[1] Ion *c*' was present only in low abundance in the spectrum hence the calculation of deuterium content was less accurate than that for ion *b*'. The error analysis indicated that the calculated label retention in ion *c*' was accurate to within 6%. Thus, in this first example of an alkene elimination from a specifically labeled organogermane, it has been observed that the first alkene loss involves a highly site-specific hydrogen(deuterium) transfer but that the second elimination proceeds in a somewhat less specific manner. The process, however, does remain highly site-selective at 70 eV. Tri-(2,2-dideuteriobutyl)-phenylgermane provided an excellent system for determining the origin of the hydrogen(deuterium) transferred during the alkene elimination because both *a*' and *b*' are very prominent ions in the spectrum. Indeed *a*' is the base peak and ion *b*' is only slightly less intense.

In studying the losses of alkenes from organosilanes Kinstle and Ihrig determined the site-specificity values at

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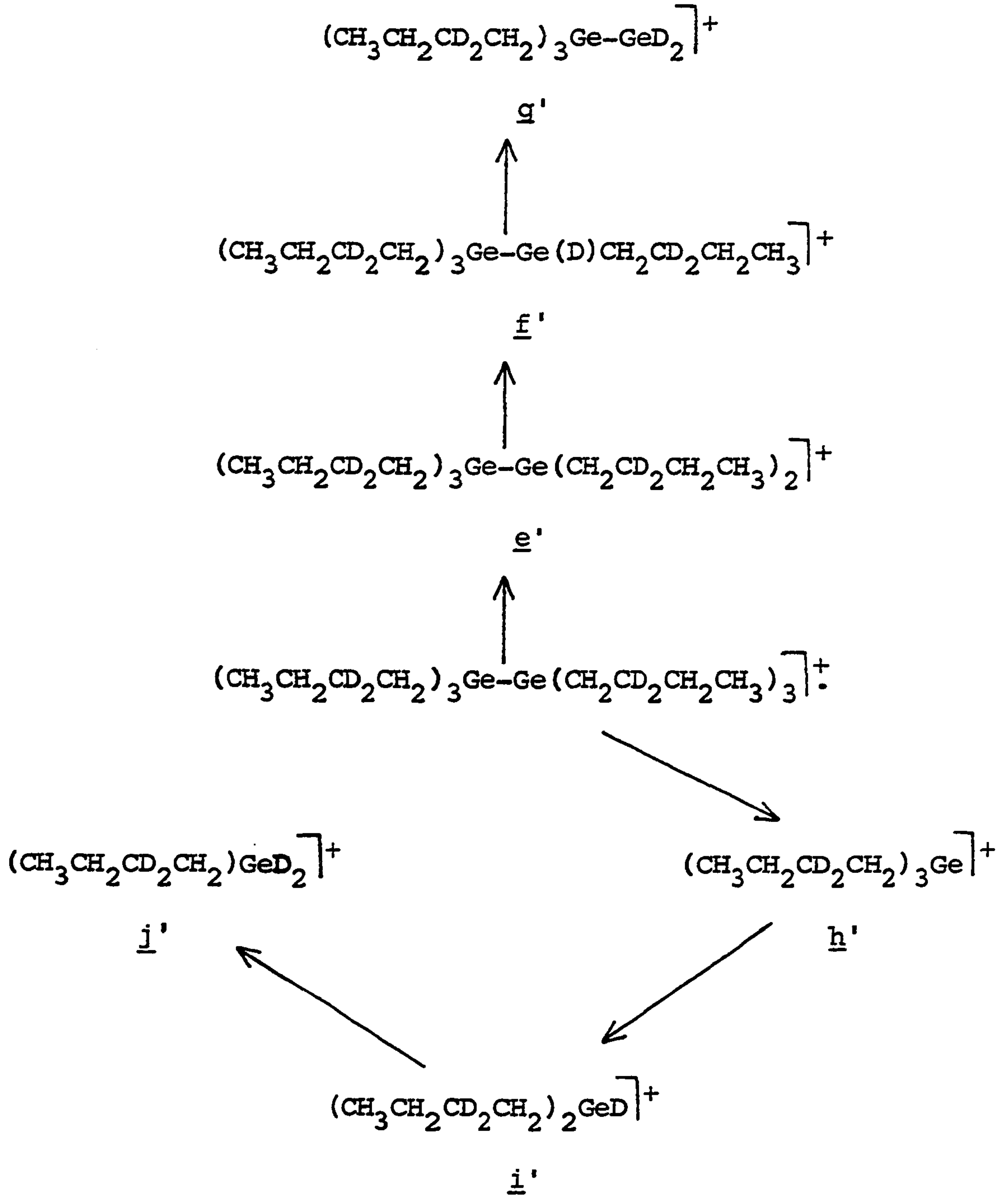
[1] In an independent run ion *c*' was found to be 83% d_2 indicating that the reproducibility of these values was quite good.

20 eV. It should be noted that the values reported above for 15 were determined at 70 eV. At low electron voltage, 20 eV, loss of butene from ion a' was still observed but ion c' was no longer present in the spectrum. The site-specificity of the a' to b' transition was found to be 99% under these conditions. Thus, there was no significant change from the 70 eV data.

Electron impact induced ionization of hexa-(2,2-dideuteriobutyl)-digermane (18) and loss of a butyl radical from the molecule ion produced ion e' (Scheme 12). Two sequential butene losses from this ion were observed and analyzed. The first butene elimination with the concomitant hydrogen(deuterium) transfer to the germanium atom was found to be 100% site-specific at 70 eV(ion f' was 100% d_9). The butene elimination from f' to give g' was calculated to be 97% site-specific. Data collected from the 20 eV spectrum showed that the site-specificity of these transitions was essentially the same as observed in the 70 eV spectrum.

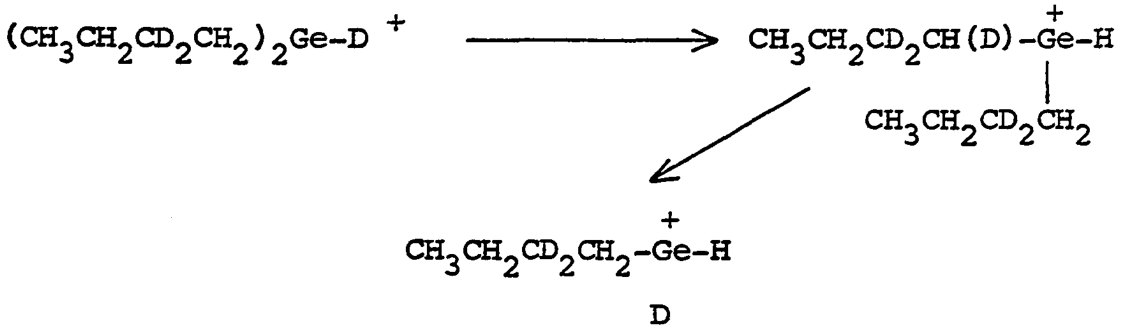
Cleavage of the germanium-germanium bond gave the tri-(2,2-dideuteriobutyl)-germanium cation, h'. Two subsequent, sequential losses of butene were studied. The first hydrogen(deuterium) transfer (h'→i') occurred in a highly site-selective manner--93% at 70 eV and 98% at 20 eV. The second hydrogen(deuterium) transfer, however, was not a highly



Scheme 12. Fragmentation of 18

site-selective process (*i*'→*j*'). Indeed the *i*' to *j*' transition was found to be the least site-selective of any rearrangement examined in this study. Ion *j*' was found to be 62% d_4 at 70 eV and was not observed at low electron energies.

It is interesting to speculate why the site-selectivity for the alkene loss from ion *i*' is so low. Several explanations can be proposed. First, hydrogen-deuterium radomization may occur in ion *i*' prior to the loss of butene thus making the site-selectivity appear to be low. However, if this is the case, why is randomization not observed in the *h*' ion? There are two major differences between these ions. They differ in energy content and ion *h*' does not possess a germanium-deuterium bond as does ion *i*'. The energy content of *i*' is lower than that of *h*' and may be a significant factor for it is known that lower energy ions have longer lifetimes (83). The longer lifetime may give the ion sufficient time to undergo some hydrogen-deuterium rearrangements. But the longer lifetime cannot be the sole controlling factor. Recall the data presented above for the formation of ion *f*' from *e*'. When this transition was observed at electron-beam energies varying between 70 and 16 eV there was no significant change in the calculated site-specificity even though there was a change in energy content and consequently a change in lifetime. Thus, if hydrogen-deuterium randomization occurs and is responsible for the lower site-selectivity observed in the i' to j' transition, then the deuterium bonded to the germanium atom must be important. A mechanism such as proposed in Scheme 13 could explain the lower site-selectivity observed in the i' to j' transition. The germanium deuterium could be scrambled with some hydrogens in the butyl chain--perhaps at the alpha position--followed by transfer of a beta deuterium to the germanium atom and concomitant elimination of butene. Assuming that the alpha hydrogens and the germanium deuterium become completely scrambled then the alkene elimination would produce two ions having the composition $C_4H_8D_3Ge$ and $C_4H_7D_4Ge$. If the loss of either alkyl moiety is equally probable, then approximately 66% of the ions formed by the loss of butene will have the composition $C_4H_7D_4Ge$ and 33% will have the composition $C_4H_7D_4Ge$. This analysis is close to the experimental data which shows that 62% of the ions contain four deuterium atoms. Loss of the tri-(2,2-dideuteriobutyl)-



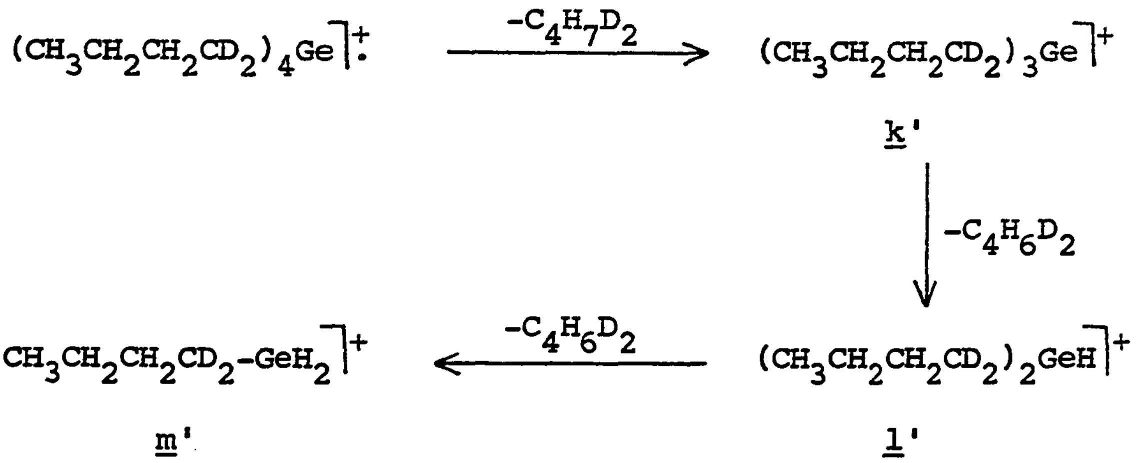
Scheme 13. Postulated hydrogen-deuterium randomization mechanism

germanium radical from the molecule ion may carry away sufficient energy to increase the lifetime of ion <u>i</u>' allowing the proposed scrambling to occur before the second loss of butene. All of the transferred hydrogen(deuterium) may still come from the <u>beta</u> position.

A simpler explanation for the decreased site-selectivities observed during the second butene losses can be suggested. Perhaps randomization does not occur and hydrogens are being transferred from some other position--such as the <u>alpha</u> carbon. The mechanism then would involve two competing reactions one being quite rapid occurring from the <u>beta</u> position and a second slower transfer involving the <u>alpha</u>, <u>gamma</u>, or <u>delta</u> hydrogens. However, this proposal does not adequately explain why the lower site-selectivities are only observed in the transitions such as <u>i</u>' to <u>j</u>' and not the <u>h</u>' to <u>i</u>' processes.

Examination of several different systems shows that there is a general tendency for the site-selectivity accompanying the second alkene elimination to be lower than that for the first. In some instances the difference is small but never-the-less there is a difference. Organosilanes present an interesting contrast to this behavior. The mass spectrum of tri-(2,2-dideuteriobutyl)-methylsilane has been studied and it was found that the loss of butene from $(CH_3CH_2CD_2CH_2)_2SiCH_3]^+$ occurs with a site-selectivity of 92%. The second, subsequent loss of butene produces two ions ($CH_3SiD_2]^+$ and $CH_3Si(D)H]^+$) in almost equal proportions. There is no selectivity accompanying the second hydrogen transfer (84).

Scheme 14 contains the fragmentation pathways for tetra-(1,1-dideuteriobutyl)-germane (19). The loss of butene



Scheme 14. Fragmentation pathways for tetra-(1,1-dideuteriobutyl)-germane (19)

from the $M\text{-}C_4H_7D_2$ ion, k', yields ion l' which is 98% d_4. Thus the alpha hydrogens (deuteriums) are not significantly involved in the butene elimination at 70 eV. At 20 eV ion l' was found to be 100% d_4 which is within experimental error of the 70 eV data. The subsequent loss of butene from l' gives ion m'--97% d_2 (70 eV). In the 20 eV spectrum m' was calculated to be 84% d_2. The alpha hydrogens (deuteriums) are involved to a substantial extent in the reaction pathway during the second elimination of butene. As the energy of the electron beam was lowered from 70 eV to 20 eV there was no significant change in the composition of ion <u>l</u>'. Again it would seem that the germanium-hydrogen bond of the precursor ion is a prerequisite to involvement of at least the <u>alpha</u> hydrogens(deuteriums).

Thus far it is evident that most of the hydrogen (deuterium) transferred in the alkene elimination originates from the <u>beta</u> carbon and that there is a small but significant involvement of the <u>alpha</u> hydrogens(deuteriums). The question then arises concerning the possible involvement of the <u>gamma</u> or <u>delta</u> hydrogens. To determine this, tetra-(3,3-dideuterio-butyl)-germane (<u>20</u>) was prepared and subjected to mass spectral investigation. Electron bombardment of <u>20</u> produced ion <u>n</u>' which underwent the elimination of

$$\underset{\underline{n}'}{(CH_3CD_2CH_2CH_2)_3Ge]^{+}} \xrightarrow{-C_4H_6D_2} \underset{\underline{o}'}{(CH_3CD_2CH_2CH_2)_2GeH]^{+}}$$

$$\underset{\underline{o}'}{(CH_3CD_2CH_2CH_2)_2GeH]^{+}} \xrightarrow{-C_4H_6D_2} \underset{\underline{p}'}{CH_3CD_2CH_2CH_2\text{-}GeH_2]^{+}}$$

butene to give ion <u>o</u>'. At 70 eV <u>o</u>' was calculated to be 98% d_4 thus indicating that mainly hydrogen and not deuterium was implicated in the mechanism. At low electron energies the results were quite analogous to that for 19. Ion o' was calculated to be 100% d_4 and p' to be 87% d_4. Ion p' was found to be 96% d_4 at 70 eV. Hence, the gamma as well as the alpha hydrogens are involved in the alkene elimination from cations of the general structure R_2Ge-H. It cannot be stated positively that the randomization mechanism suggested previously is operative but the apparent necessity of a germanium-hydrogen(deuterium) bond and the demonstrated involvement of the alpha, beta, and gamma hydrogens might best be explained in this manner. Obviously however, the simple situation considered before in which the germanium-deuterium and the alpha hydrogens become completely scrambled does not adequately explain the observations.

Two possible explanations have been presented for the lower site-selectivity observed. One involves two competing unimolecular decomposition reactions and involves transfer of hydrogen(deuterium) from different positions along the alkyl chain. The second involves transfer of hydrogen (deuterium) only from the beta carbon and utilizes hydrogen-deuterium randomization to explain the decrease in deuterium content of the daughter ion. How might one experimentally distinguish between the two mechanisms? The question of the occurrence and timing of hydrogen and skeletal scrambling has become one of the most interesting problems in mass spectrometry. However, the labyrinth nature of this question is worthy of Daudalus himself and hence precludes any definitive answer at this time. The following paragraphs will attempt to summarize briefly what is known about randomization reactions but the author does not feel that he can improve on the truly excellent reviews by R. G. Cooks and the interested reader is encouraged to see his papers (85, 86, 87).

Again, the question that is mainly of interest here is related to the type of experimental evidence that can be obtained to support a randomization mechanism. It is often assumed that an average molecular ion possesses 5 eV (115 Kcal/mole) of internal energy. If most of this energy can take the form of vibrational energy associated with the electronic level from which fragmentation occurs, the probability that all of the vibrational energy accumulates in a particular bond in low. Obviously the greater the number of atoms and bonds in the molecule the lower the probability of a given fragmentation occurring. Rearrangement reactions (hydrogen scrambling) however do not deplete the energy content of the ion in question for the process involves both bond breaking and bond formation. Thus, the occurrence of these reactions is not surprising.

The rates of unimolecular fragmentation processes depend on the energies and entropies of activation. The most successful treatment developed for mass spectral reactions is the quasi-equilibrium theory (88). The expression for the rate constant (k) is given where E is the internal energy

$$k = \nu \left[\frac{E - E_a}{E} \right]^{s - 1}$$

of the ion, E_a is the activation energy, ν is a frequency factor, and s is the number of effective oscillators in the ion. In attempting to determine whether or not hydrogen randomization occurs in a particular system the important components are the frequency factors and the activation energies. At high energy the average internal energies of ions will be high and differences in activation energies for competitive processes will be less important than differences in frequency factors. Hence, processes with low frequency factors (rearrangements) can be distinguished from simple cleavages by their greater importance in the low energy spectra (89).[1]

There are other important consequences of the relationship between internal energies of ions, lifetimes, and the relative probabilities of rearrangements and simple fragmentations. Ions of sufficiently long lifetime fragment only

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[1] The rate of increase of k with E is smaller for processes with low frequency factors than for high frequency factors and examples of calculated k vs E curves for unimolecular mass spectrometric and thermolytic reactions substantiate this (85).

after leaving the source and the corresponding daughter ions may be detected either as normal or "defocused" metastable ions.[1] Since rearrangements are more likely to occur in ions of longer lifetimes it is not surprising that rearrangement processes are often accompanies by abundant metastables.

$$D_1^{\,+} \xleftarrow{\quad m_1^{*} \quad} M^{+} \xrightarrow{\quad m_2^{*} \quad} D_2^{\,+}$$

Suppose that an ion M^+ undergoes two competing unimolecular decompositions giving $D_1^{\,+}$ and $D_2^{\,+}$ and that the appropriate metastables m_1^* and m_2^* are observed. The relative intensities of m_1^* and m_2^* reflect the relative activation energies for the two processes under consideration. For example Cooks <u>et al</u>. studied the loss of ethylene from thiophene-2,5-d_2 and 2,3-d_2. In both instances the relative

$$M]^{+\cdot} \longrightarrow M\text{-}C_2H_2]^{+\cdot} + M\text{-}C_2HD]^{+\cdot} + M\text{-}C_2D_2]^{+\cdot}$$

abundances of the metastable ions were 1:4:1 at low energies. At higher energies the ratio changed. These results are

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[1] The term "defocused" is quite deceptive here. In fact the metastable ions are focused and one obtains a spectrum that contains only metastable ions. This is done by adjusting the electrostatic analyzer in such a way that only metastable ions pass through the slits. As a result these ions appear in focus, more intense and as sharper peaks (86).

consistent with a mechanism in which the hydrogens and deuteriums are scrambled and the degree of randomization increases to 100% at lower energies. This example illustrates the technique involved in obtaining evidence consistent with hydrogen scrambling. One selects a fragmentation exhibiting the appropriate metastable ion then observes the process from a suitably labeled sample. The metastables for the loss of labeled and unlabeled fragments are observed at both high and low energies and their relative intensities should change to reflect the increased scrambling at lower energies. It is better to observe metastable ions rather than daughter ions. The abundance of a metastable is influenced by the following factors: (1) internal energy distribution in the parent ion, (2) activation energy of the process, (3) the frequency factor, and (4) the nature of the process and particularly the timing of the metastable transition. Daughter ion intensities are influenced by additional factors: (1) one ion may be formed <u>via</u> a greater number of pathways, and (2) one ion may decompose at a different rate than another.

Finally, the question on interest is whether or not this technique could be applied to the germanium systems to obtain evidence consistent with the proposed randomization mechanism. Unfortunately the answer at this time is no. It may be possible in the future but in any event it will be difficult for one is attempting to distinguish between rearrangement with and without randomization--a situation more complex than distinguishing between cleavage and rearrangement. The technique utilized can not be done on an instrument like the Atlas CH-4. A high resolution instrument is needed which has a computer printout. This is necessary because of the close spacing of the metastables due to the five isotopes of germanium. Table 17 contains the metastable ions for the b' to c' transition. Under high resolution the metastables could probably be separated and analyzed. However, in the low resolution spectrum the metastable appears as a continuous clump extending over nearly ten mass units.

Table 17. Metastable ions for the b' to c' transition

isotope	m/e(b')	m/e($c'-d_2$)	m/e($c'-d_1$)	$m^*(c'-d_2)$	$m^*(c-d_1)$
^{76}Ge	214	157	156	115.2	113.7
^{74}Ge	212	155	154	113.3	111.9
^{73}Ge	211	154	153	112.4	110.9
^{72}Ge	210	153	152	111.5	110.0
^{70}Ge	208	151	150	109.6	108.2

In order to determine whether or not electronic effects were important in regard to the site-selectivity of the hydrogen transfer, bromotri-(2,2-dideuteriobutyl)germane (*21*) was prepared. Ion *q'* was generated by electron impact induced ionization of *21* followed by loss of a butyl

$$(CH_3CH_2CD_2CH_2)_2Ge\text{-}Br\rceil^{+} \xrightarrow{-C_4H_7D} CH_3CH_2CD_2CH_2\text{-}Ge(D)Br\rceil^{+}$$

q' *r'*

radical from the molecule ion. At 70 eV the site-selectivity of the hydrogen rearrangement accompanying butene elimination was calculated to be 84%. The site-selectivity at 20 eV was 82%, but an experimental error of ±2% must be considered so the difference is insignificant. The loss of butene from *r'* was not observed and it was not possible to determine if the site-selectivity for the hydrogen abstraction accompanying the second butene loss would be lower.

The mass spectrum of bromobis-(2,2-dideuteriobutyl)phenylgermane (*22*) was run and the site-selectivity for Reaction 4 calculated. At 70 eV it was found to be 75%.[1]

$$\text{Ø}\text{-}Ge(Br)CH_2CD_2CH_2CH_3\rceil^{+} \xrightarrow{-C_4H_7D} \text{Ø}\text{-}Ge(Br)D\rceil^{+} \qquad (4)$$

s' *t'*

---

[1] The formation of *t'* was not observed at 20 eV.

Comparison of this result with that previously discussed for the loss of butene from ion b' (decomposition pathway of 14) reveals that the site-selectivity of the hydrogen abstraction was decreased by substitution of bromine for one of the butyl groups. The electron withdrawing nature (-I effect) of the bromine atom would be expected to remove electron density from the germanium center thereby altering the reactivity of the precursor ion s'. Thus ion s' should possess a more reactive germanium cation and it would be reasonable to expect the hydrogen abstraction to be less selective. This argument may be connected with one involving the size of the germanium atom. Substituents like bromine, which withdraw electron density from the germanium center, may in effect decrease its size thereby influencing the site-selectivity of the hydrogen abstraction as has been previously proposed (42). Benz suggested that as the size of the heteroatom increased the tendency for involvement of hydrogens located nearer to the heteroatom would increase.

Table 18 contains data on the relative sizes of the group IV atoms as calculated from Pauling covalent radii (90). Germanium is 1.14 times as large as silicon whereas tin is 1.52 times as large as germanium and 1.72 times as large as silicon. However, as the results of this study indicate there is no pronounced effect observed on the site-specificity due to replacing silicon by germanium for the

Table 18. Relative size of group IV atoms

Atom	Covalent Radii (A)	Volume (A^3)
C	0.77	1.91
Si	1.17	6.70
Ge	1.22	7.60
Sn	1.40	11.5

first alkene loss. Perhaps germanium is just not large enough to demonstrate the effect. A tetraorganostannane was therefore selected as a better system for attempting to observe the importance of heteroatom size. To this end tetra-(2,2,2-trideuterioethyl)-stannane (<u>22</u>) was prepared and its mass spectral fragmentation pattern studied. Interpretation of the spectrum was somewhat less than trivial due to the ten isotopes (see Table 19) of tin. This much however is clear. The molecular ion, <u>u</u>', of <u>22</u> exhibited an isotopic distribution expected for an organostannane as did the M-$C_2H_2D_3$ ion, <u>v</u>'. The ion generated by the loss of ethylene from <u>v</u>' did not possess an isotopic pattern similar

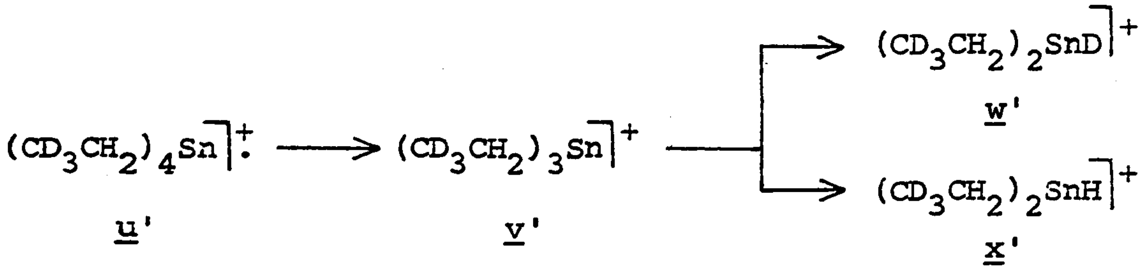


Table 19. Abundance of tin isotopes

Isotope	Relative abundance
^{112}Sn	0.95
^{114}Sn	0.65
^{115}Sn	0.34
^{116}Sn	14.24
^{117}Sn	7.57
^{118}Sn	24.01
^{119}Sn	8.58
^{120}Sn	32.97
^{122}Sn	4.71
^{124}Sn	5.98

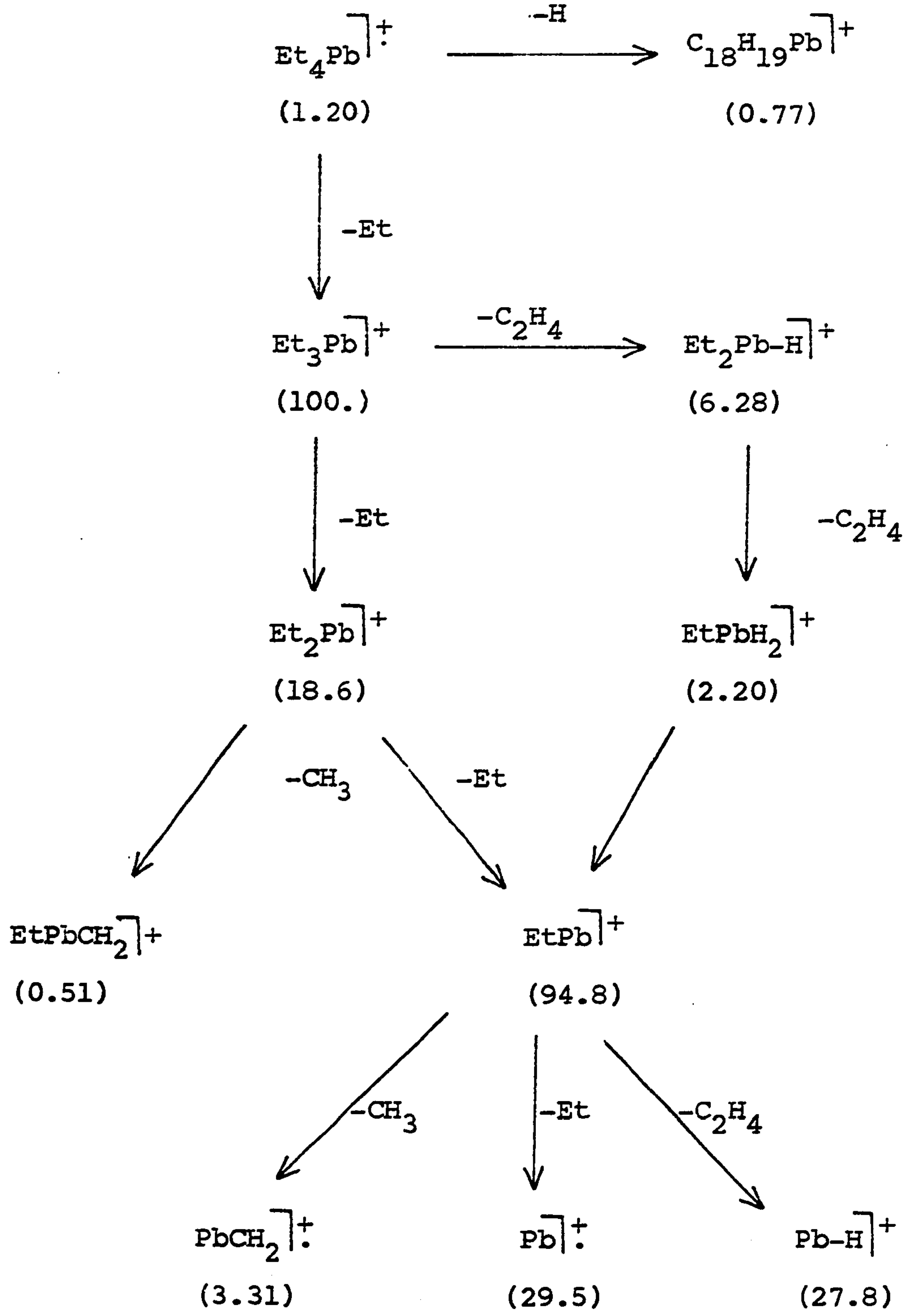
to the precursor ion v'. Evidently this was due to the formation of two ions, w' and x', concomitant with the elimination of ethylene. From an analysis of the isotope pattern of the v'-ethylene ions it was determined that 83% of the ions had the composition $C_4H_4D_7Sn$.

A second loss of ethylene could be observed from the v'-ethylene ions but it was impossible to make a quantative analysis of the isotope pattern due to the formation of three product ions from this reaction: $C_2H_2D_5Sn^+$, $C_2H_3D_4Sn^+$, and $C_2H_4D_3Sn^+$.

One might suggest that a deuterium labeled tetraorganoplumbane could be a better system to examine in an attempt to observe any effects of heteroatom size on site-selectivity. Lead is larger than tin, has only four isotopes, and therefore should give a simpler spectrum than a stannane. Examination of the spectrum of tetraethylplumbane (23) revealed, however, that the mode of fragmentation was significantly different from the analogous silanes, germanes, and stannanes. Scheme 15 presents the fragmentation patterns of tetraethylplumbane. The numbers in parentheses under the ions give the relative intensities. The Et_3Pb^+ cation fragments via several pathways. The loss of ethylene from Et_3Pb^+ is not the more favorable fragmentation mode and the $Et_2Pb\text{-}H^+$ cation has a low abundance compared to analogous ions formed from organosilanes, germanes and stannanes. In addition, this region of the spectrum is obscured by the Et_2Pb^+ ion. Thus if one were to generate ion y' and attempt to observe the loss of ethylene to form ion z', it would be impossible

$$\underset{\underline{y}'}{\left.(CD_3CH_2)_3Pb\right]^+} \longrightarrow \underset{\underline{z}'}{\left.(CD_3CH_2)_2Pb\text{-}D(H)\right]^+}$$

to determine if ion z' were $(CD_3CH_2)_2Pb\text{-}D$ or $(CD_3CH_2)_2Pb\text{-}H$ or a mixture of the two because of the complications presented by the overlapping $(CD_3CH_2)_2Pb^+$ ions.



Scheme 15. Fragmentation pattern of <u>23</u>

SUMMARY

Alkylgermanes possessing the grouping R_2CHCH_2-Ge exhibit the loss of alkenes from even electron ions when subjected to mass spectral analysis. For each alkyl group cleaved in this manner, one germanium-hydrogen bond is formed (Reaction 5). Certain deuterium labeled organogermanes have been prepared and their mass spectra studied

$$(R_2CHCH_2)_3Ge]^+ \xrightarrow{-R_2C_2H_2} (R_2CHCH_2)_2Ge{-}H]^+ \qquad (5)$$

in order to determine the origin of the hydrogen transferred concomitant with the alkene loss.

This study has ascertained that organogermanes, like organosilanes, undergo a site-specific hydrogen rearrangement during the first alkene elimination (Reaction 6). This

$$R(CH_3CH_2CD_2CH_2)_2Ge]^+ \xrightarrow{-C_4H_7D} R(CH_3CH_2CD_2CH_2)Ge{-}D]^+ \qquad (6)$$

observation is quite important because very few site-specific rearrangements are known to occur in even electron ions. Prior to the work of Kinstle and Ihrig there were no examples in the literature. However, site-specific hydrogen transfers were known to occur in odd electron ions and mechanistic speculation has over estimated the importance of radical character in explaining these processes.

Accompanying the second alkene loss a hydrogen rearrangement occurs which is site-selective but not site-specific. Contrasts with the behavior of organosilanes are drawn.

Arguments concerning the importance of heteroatom size and electronic effects are discussed.

EXPERIMENTAL

Instruments and Methods

All mass spectra were obtained using an Atlas MAT model CH4 single focusing mass spectrometer. The germanes were absorbed on crushed molecular serves and inserted into the ion source via the vacuum lock. The source was maintained at ambient temperatures. An ionizing current of 3-10μA and an accelerating potential of 3000 volts were employed. The electron energies reported are nominal values.

All gas liquid partition chromatography (glpc) analyses and purifications were carried out on an Aerograph 200 dual column instrument. Carrier gas (helium) flow rates of 30-80 ml/min were used, and the thermal conductivity detector block and injector ports were maintained at 25-50° above the column oven temperature. Individual analyses are reported in the following manner: (column length, liquid phase, oven temperature). The purity of samples collected by preparative glpc was verified by glpc analysis.

Microanalyses were performed by Chemalytics, Inc., Tempe, Arizona.

Preparation of Compounds

1-Bromobutane-2,2-d_2

Following the procedure of Djerassi (91), 40 g of sodium were cut into small pieces and added to 200 g of D_2O, cooled to 0° and mechanically stirred, over a three hour period. The solution was heated under reflux and diethylethylmalonate (50 g) added by means of a dropping funnel. The ethanol liberated in the saponification was removed by distillation until the vapor temperature was 98°. The reactants were cooled to 0° and cautiously treated with phosphorous trichloride (128 g). The resulting solution was heated under reflux for 24 hours and then distilled to near dryness. Deuterium oxide (40 g) was added and the distillation to near dryness repeated. The combined distillates were subjected to continuous ether extraction for 24 hours, the etheral solution dried ($MgSO_4$) and added to a slurry of lithium aluminum hydride (16 g) in anhydrous ether. This reaction mixture was heated under reflux for 10 hours, cooled, and worked up in the usual manner. The crude butanol obtained in the above steps was treated with 50 ml of a 4:1 mixture (v/v) of 48% hydrobromic acid and 98% sulfuric acid. The resulting mixture was heated at 120° and the product collected in a Dean-Stark trap. Distillation afforded 23.3 g (63% based on diethylethylmalonate) of 1-bromobutane-2,2-d_2, bp 100-103° [lit. (92) pb 104°]. Low voltage mass spectrometry showed that the material was 95.4% d_2, 4.6% d_1.

Hexabutyldigermane

To the Grignard reagent formed from 5.0 g (0.035 mole) bromobutane and excess magnesium was added 2.5 g of tetrachlorogermane at 0°. The reaction mixture was allowed to stir for 24 hours. Water (25 ml) was added and the product isolated by ether extraction, dried ($MgSO_4$), and the solvent removed under reduced pressure leaving 5.8 g (0.012 mole) of hexabutyldigermane, bp 147°, 1.0 mm [lit. (93) bp 131°, 0.2 mm].

Anal. Calc. for $C_{24}H_{54}Ge_2$: C, 59.08% H, 11.16%. Found: C, 59.11%; H, 11.20%.

Bromotributylgermane

Hexabutyldigermane (2.0 g, 0.0041 mole) was dissolved in 20 ml of carbon tetrachloride and treated with 22 g of a 3% solution of bromine in carbon tetrachloride. Removal of the solvent under reduced pressure yielded 1.3 g (0.0040 mole) of bromotributylgermane, bp 154, 2.5 mm [lit. (94) bp 176, 7.0 mm].

Anal. Calc. for $C_{12}H_{27}BrGe$: C, 44.50%; H, 8.40%. Found: C, 44.28%; H, 8.28%.

Tributylphenylgermane

Bromotributylgermane 1.3 g, (0.0040 mole) was dissolved in 20 ml of anhydrous di-n-butyl ether and treated with an excess of phenyl lithium. The reaction mixture was heated to 120° for 12 hours, cooled to room temperature and the excess phenyl lithium destroyed with water. The product was isolated by ether extraction, dried ($MgSO_4$), and the mixture subjected to molecular distillation. The product thus obtained was analyzed by glpc (8' SE-30, 205). The major component was collected and subjected to mass spectral and elemental analysis. The mass spectrum was entirely consistent with that expected for the desired product.
Anal. Calcd. for $C_{18}H_{32}Ge$: C, 67.34%; H, 10.05. Found: C, 67.39%; H, 10.12%.

Bromobis-(2,2-dideuteriobutyl)-phenylgermane

To the Grignard reagent formed from 7.00 g (0.053 mole) of 1-bromobutane-2,2-d_2 and excess magnesium was added 3.24 g (0.015 mole) tetrachlorogermane in 30 ml of anhydrous ether. The resulting suspension was stirred by means of a magnetic stirrer and heated under reflux overnight, phenylmagnesium bromide (5.2 ml, 2.94 M) was added dropwise and the ethyl ether gradually replaced by anhydrous di-n-butyl ether. The reaction mixture was heated under reflux for 15 hours, cooled, and quenched with water.

Isolation by ether extraction and distillation yielded a light yellow liquid (bp 80-100°, 0.05 mm) which was collected and analyzed by glpc (8' SE-30, 200°). The major component was collected and subjected to mass spectral investigation which indicated that two components were present; tri-(2,2-dideutrio)-butylphenylgermane and bromobis-(2,2-dideuteriobutyl)-phenylgermane. Separation was achieved by glpc analysis (8' Apiazon, 180°).

Anal. Calc. for $C_{14}H_{19}D_4GeBr$: C, 61.08%; H_{total}, 9.88%.
Found: C, 61.13%; H_{total}, 9.79%.

Hexa-(2,2-dideuteriobutyl)-digermane

This compound was prepared and purified by the method described for the preparation of hexabutyldigermane using bromobutane-2,2-d_2. Identification was achieved by comparing retention time with that of an authentic sample (8' SE-30, 200°).

Bromotri-(2,2-dideuteriobutyl)-germane

This compound was prepared and purified by the method described for the preparation of bromotributylgermane using the bromobutane-2,2-d_2. Identification was achieved by comparison of retention times (8' SE-30, 210°).

Tri-(2,2-dideuteriobutyl)-phenylgermane

The compound was prepared and purified by the method described for the preparation of tributylphenylgermane using bromobutane-2,2-d_2.

Anal. Calcd. for $C_{18}H_{26}D_6Ge$: C, 66.13%; H_{total}, 11.66%.
Found: C, 66.28%; H_{total}, 11.87%.

Bromobutane-1,1-d_2

To 2.46 g of lithium aluminum deuteride in anhydrous ether was added 7.60 g (0.0864 mole) butyric acid in a dropwise manner. Following the addition the reaction mixture was heated under reflux for 12 hours, cooled, and worked up in the usual fashion. The crude butanol thus obtained was treated with 50 ml of a 4:1 mixture (v/v) of 48% hydrobromic acid and 98% sulfuric acid. The resulting mixture was heated at 120 and the product collected in a Dean-Stark trap. Distillation afforded 6.35 g (0.0426 mole) of bromobutane-1,1-d_2. Low voltage mass spectrometry showed the compound to be 2.8% d_1, 97.2% d_2.

Tetra-(1,1-dideuteriobutyl)-germane

To the filtered Grignard reagent formed from 5.00 g (0.0350 mole) bromobutane-1,1-d_2 (THF) was added 2.50 g (0.0177 mole) tetrachlorogermane. The reaction mixture was heated under reflux for two hours, then allowed to stand overnight. The product was isolated by ether extraction and distillation bp 81-82° (20 mm) lit. (95) 178-180° (733 mm). A sample for mass spectral study and analysis was collected by glpc (8' Apiezon L, 165°).

Anal. Calc. for $C_{12}H_{28}D_8Ge$: C, 62.19%; H_{total}, 14.56%. Found: C, 62.13%; H_{total}, 14.81%.

Bromobutane-3,3-d_2

To 3.75 g of lithium aluminum deuteride suspended in 100 ml of anhydrous ether was added 7.15 g (0.119 mole) glacial acetic acid in 50 ml of anhydrous ether. The reaction mixture was heated under reflux overnight, cooled and worked up in the usual manner. To the etheral layer was added an equivalent volume of water and the ether removed by fractional distillation. The temperature of the distillation flask was raised and the fraction boiling between 70-100° collected, then added to 50 ml of a 4:1 mixture (v/v) of 48% hydrobromic acid and 98% sulfuric acid. This mixture was heated to 100° and the product collected in a Dean-Stark trap. Ethyl bromide thus obtained was dissolved in anhydrous ether, dried ($MgSO_4$) and converted to the Grignard reagent. The reaction flask was cooled in an ice-salt bath and fitted with a dry-ice condenser and an excess of ethylene oxide added while the reaction mixture stirred (10 hours) and the temperature kept near 0°.

Finally, the reaction was quenched with water and the product isolated by ether extraction. An equivalent volume of water was added to the ether layer and the ether removed by fractional distillation. A butanol-water mixture boiling between 80-100° was collected and the crude butanol brominated employing the procedure outlined above. The yield of bromobutane-3,3-d_2 was 8.28 g (0.0595 mole).

Low voltage mass spectrometry showed the product to be 95.3% d_2, 4.7% d_1.

Tetra-(3,3-dideuteriobutyl)-germane

This compound was prepared and purified by the procedure given for tetra-(1,1-dideutrio)-butylgermane using bromobutane-3,3-d_2. Identification was achieved by comparison of retention times with the tetra-(1,1-dideutrio)-butylgermane(8' Apiezon L, 165°).

Bromoethane-2,2,2-d_3

To 3.44 g (0.0860 mole) lithium aluminum hydride suspended in 100 ml anhydrous ether was added 3.67 g (0.0574 mole) of acetic acid-d_4. Following the addition, the reaction mixture was heated under reflux for 10 hours, cooled, and worked up in the usual manner. To the ether layer was added 50 ml of water and the resulting mixture fractionated. The azeotropic mixture containing the ethanol-d_3 was collected and brominated by the same procedure given for the preparation of bromobutane-2,2-d_2. The yield of bromoethane-2,2,2-d_3 was 6.0 g (0.0545 mole)--95%.

Tetra-(2,2,2-trideuterioethyl)-stannane

To 5.87 g (0.0134 mole) stannic bromide dissolved in 25 ml of anhydrous benzene was added the filtered Grignard reagent formed from 6.0 g (0.0545 mole) bromoethane-2,2,2-d_3 and excess magnesium. Following the addition, the reaction mixture was heated under reflux for 12 hours, cooled, and poured into 100 ml of 1 N sodium hydroxide. The organic layer was separated and the aqueous layer extracted several times with ether and the extracts added to the previously separated organic phase. The ether-benzene layer was dried ($MgSO_4$) and fractionated giving tetra-(2,2,2-trideuterioethyl)-stannane, bp 105°; 76 mm [lit. (96) 180; 760 mm].

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