Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

MASS SPECTROSCOPY OF ORGANIC MERCURY COMPOUNDS

WILLIAM F. BRYANT AND THOMAS H. KINSTLE
Department of Chemistry, Iowa State University, Ames, Iowa 50010 (U.S.A.)

(Received January 16th, 1970; in revised form May 19th, 1970)

SUMMARY

The mass spectrometric behavior of a variety of diaryl- and dialkylmercurials, aromatic and aliphatic mercury chlorides has 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.

In the fragmentation of simple dialkylmercurials and alkylmercury chlorides there is a surprisingly pronounced tendency toward charge retention on carbon rather than on mercury. However, with proper substitution the organomercury ions can be stabilized. 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 β-cleavage. This is 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 to readily distinguish between the diastereomeric adducts by analysis of the fragmentation patterns.

Two carbene precursors have been examined, phenyl(trichloromethyl)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-hydroxycyclooctyl)mercury chloride might be indicative of interesting, but as yet uninvestigated, chemistry of this compound in solution.

INTRODUCTION

Organometallic compounds are currently an active area of interest in mass spectrometry[1]. Organomercurials, and indeed the Group IIB 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[2-4]. The only organomercury compounds previously subjected to fragmentation studies are dimethyl-, diethyl-, and di-n-butylmercury[5,6a]. Few other Group IIB 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* 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 usually do not contain mercury. This behavior is not consistent even within the Group IIB 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[6a] is the butyl cation. Because this behavior is quite unusual**, an investigation of a wider variety of organomercurials was initiated in order to determine the generality of these observations.

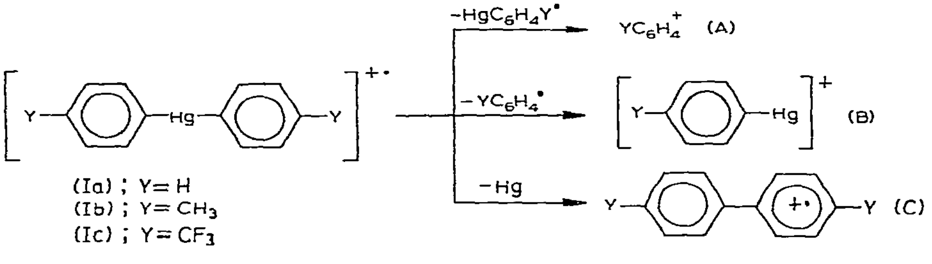
Also, we were interested in demonstrating the potential of mass spectrometry as a structural elucidation method for a variety of synthetically important organomercurials***. Determination of olefin stereochemistry via mass spectrometry of diastereomeric olefin–mercury salt adducts was also an initial 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 (methoxyalkyl)mercury chlorides, and mercury containing methylene transfer agents.

RESULTS AND DISCUSSION

Diarylmercury compounds

Scheme 1 summarizes the electron impact induced modes of fragmentation common to diphenyl-(Ia), di-*p*-tolyl-(Ib), and bis[*p*-(trifluoromethyl)phenyl]mercury (Ic).

SCHEME 1



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 (Ia), (Ib), and (Ic)

---

* For example, compounds of Ge[6b], Si[9], Sn[6c], Pb[6d], Fe[6e], Al[7,10], and Sb[7] have been studied.

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

*** 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[18-21] have appeared recently in the literature.

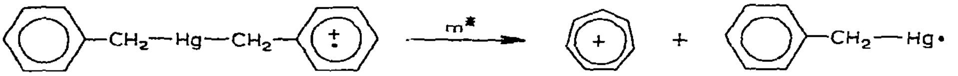
are present in the respective spectra but there is considerable variation in their abundances*. The molecule ion (Ib) has a relative abundance of 92.4%. Note, however, that the abundance of the parent ion of (Ic) is rather small (9.18%) and that the parent ion of (Ia) is of intermediate intensity (44.7%). The ions (B) are formed from the molecule ions (Ia), (Ib), and (Ic) 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 strong carbon–mercury bond[22].

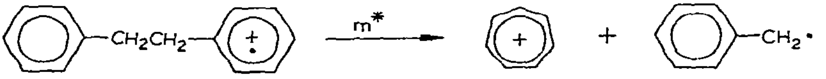
The structure of ion (C) is proposed to be a di-*p*-substituted biphenyl on the basis of comparisons of the mass spectra of 4,4′-bitolyl and (Ib). The *m/e* 182 ion from (Ib) and the 4,4′-bitolyl parent ion undergo the same fragmentations. Both spectra contain the same metastable peaks with the same shape and intensity. In the mass spectrum of (Ib), there is an ion at *m/e* 92 (19.8%) (toluene parent ion?) but no analogous ions are present in the spectra of (Ia) and (Ic). No metastable was found to correlate with its formation†.

Dialkylmercury compounds

Dibenzylmercury (II) is an isomer of (Ib). In the 70 eV spectrum the base peak is ion *m/e* 91 formed by cleavage of a carbon–mercury bond (eqn. 1) and from ion *m/e* 182 (eqn. 2). Both transitions show the appropriate metastable peaks. The *m/e* 182 ions found in the spectra of (II) and (Ib) are definitely different. In the spectrum of (II) loss of benzene is observed from ion *m/e* 182 to form *m/e* 104, probably the molecule ion of styrene.



(1)



(2)

Ion *m/e* 182 from (Ib) 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 (II).

At 16 eV the parent ion of (II) is the base peak in the spectrum. The rearrange-

---

[*] 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** 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.

[**] 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: (Ia) *m/e* 356; calcd. 44.7, found 45.8. (Ib) *m/e* 293; calcd. 18.3, found 18.6. (Ic) *m/e* 345, calcd. 11.1, found 11.6.

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

ment 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 its typical low frequency factor. The fragmentation of the m/e 182 ion from (II) to form m/e 104 is still pronounced and the appropriate metastable is observed.

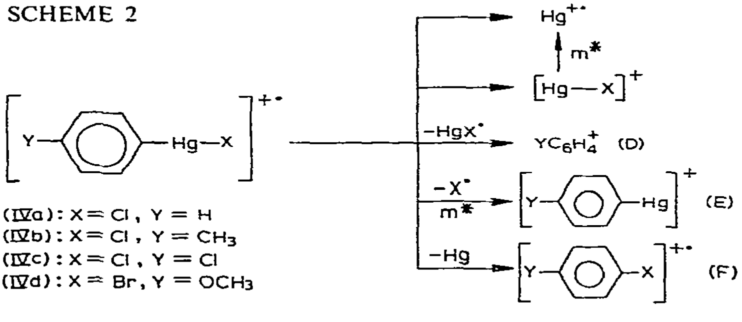
The mass spectrum of di-n-butylmercury (III) was rerun and is discussed here because of certain differences from the previously reported spectrum[5]. Furthermore, some of the organomercury ions have interesting compositions. At 70 eV the base peak is the butyl cation, m/e 57. The molecular ion is observed 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 concomittant difficulties in separating their contributions from the unavoidable mercury background in the spectrometer (from mercury vacuum pumps).

Arylmercuric halides

Another group of compounds investigated were arylmercuric halides. Scheme 2 summarizes the fragmentation behavior observed for phenylmercuric chloride (IVa),

SCHEME 2



p-tolylmercuric chloride (IVb), (p-chlorophenyl)mercuric chloride (IVc), and (p-methoxyphenyl)mercuric bromide (IVd) at 70 eV. All four compounds give intense peaks in the parent ion region. Indeed, in the spectrum of (IVc) and of (IVd) the parent ion is the most abundant ion observed. For (IVa) and (IVb), however, ion (D) forms the base peak. In every 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 (IVc) is the following transition

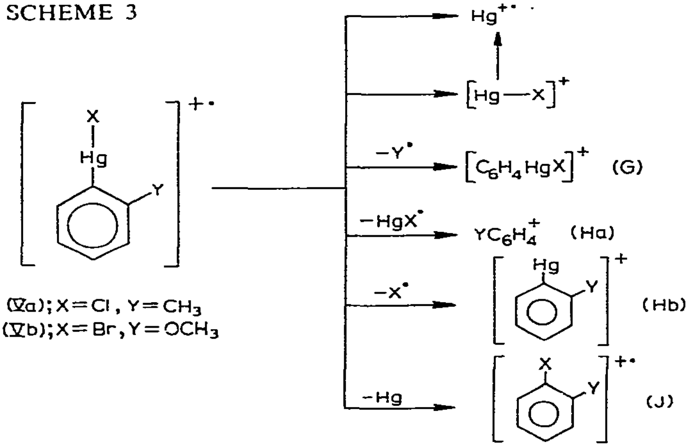
$$[Hg\text{–}X]^+ \rightarrow Hg^{+\cdot} + X^\cdot$$

substantiated by the appropriate metastable ion. $Hg^{+\cdot}$ 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 *o*-methylphenyl (Va), *o*-methoxyphenyl (Vb) and *o*-hydroxyphenyl (VI) groups. Scheme 3 summarizes the fragmentations of (Va) and (Vb), none of which are due to normal *ortho*-interactions. The base peak of (Va) is formed by cleavage of the carbon–mercury bond to give ion (Ha), while the base peak of (Vb) is the molecular ion. The elimination–rearrangement loss of mercury produces ion (J) in each case. A somewhat unique fragmentation of (Va) 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 observed, but ion (G) is still present.

SCHEME 3

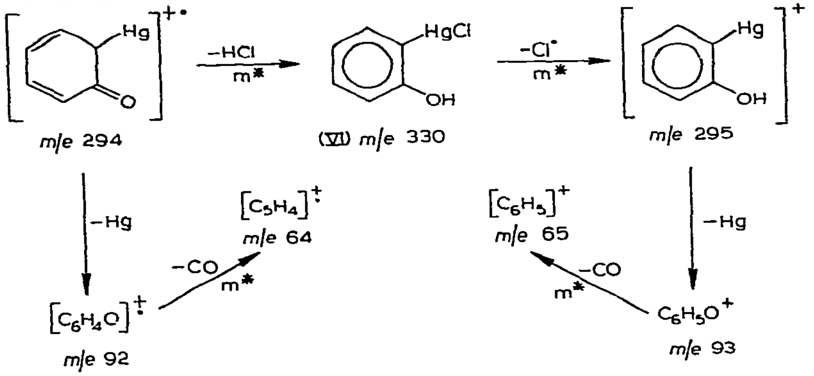


(*o*-Hydroxyphenyl)mercuric chloride (VI) exhibits behavior quite different from that of (Va) and (Vb). This is illustrated in Scheme 4. The molecular ion, which is also the base peak of the spectrum, loses both $Cl^\cdot$ and HCl* in metastable processes to generate the *m/e* 294 and *m/e* 295 ions, 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

---

* 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

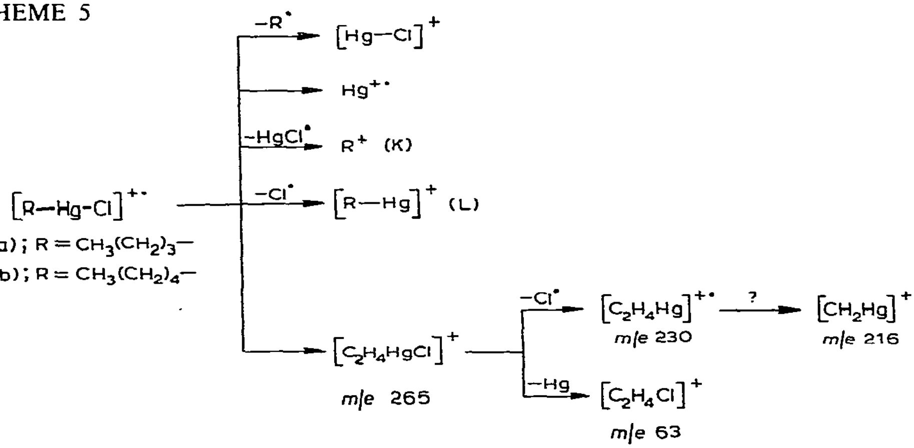


abnormally large, possibly due to some stabilizing interaction with the *ortho*-substituent. Another difference noted was the absence of an elimination–rearrangement loss of mercury from the molecular ion.

Alkylmercuric chlorides

Scheme 5 summarizes the fragmentation behavior of two primary alkylmercuric chlorides: n-butylmercuric chloride (VIIa) and n-amylmercuric chloride (VIIb). At 70 eV both compounds give parent ions of moderate intensity with base peaks due to the alkyl carbonium ions (K).

SCHEME 5

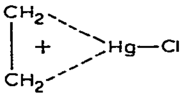


A variety of mercury-containing organic ions are observed. The alkylmercury ion (Hb) is observed but the intensity is quite low. The *m/e* 265 ion arises by cleavage β to the mercury atom. β-Cleavage predominates quite noticeably over α- or γ-cleavage [59.8% and 17.7% abundances of *m/e* 265 from (VIIa) and (VIIb), respectively]. No methyl loss occurs from the molecular ion of (VIIa) and methyl or ethyl loss from the molecular ion of (VIIb) is insignificant.

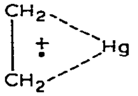
The *m/e* 230 and *m/e* 216 ions, which were observed in the spectrum of di-n-butylmercury, are also present in the spectra of (VIIa) and (VIIb) and along with the m/e 265 ion offer several interesting structural possibilities. They may be open chain species such as (M) and (N). But structures such as (O) and (P) might also account for

$$\underset{\text{(M)}}{[CH_2CH_2HgCl]^+} \qquad \underset{\text{(N)}}{[CH_2CH_2Hg]^{+\cdot}}$$

the predominance of β-cleavage. The importance of analogous bromonium ion participation in mass spectral ions has been the subject of several recent reports[23].



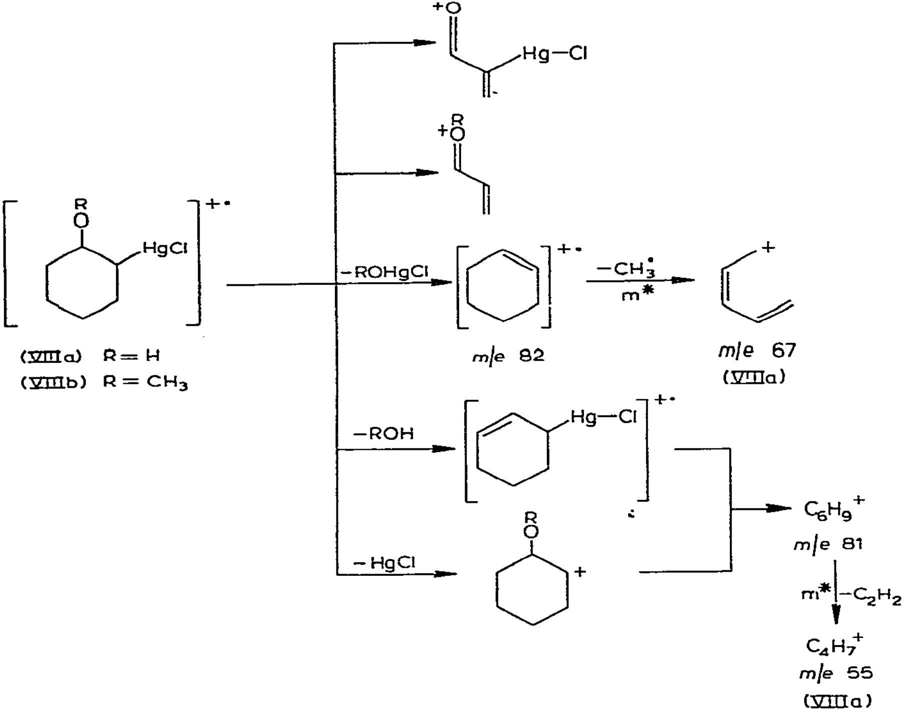
(O)



(P)

The alkyl ions (K) from (VIIa) and (VIIb) exhibit an interesting fragmentation. In the spectrum of (VIIa) there is a metastable for the transition from m/e 57 to m/e 41 and in the spectrum of (VIIb), 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[6g]. The reasons for their abundance in the spectra of (VIIa) and (VIIb) 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.

SCHEME 6

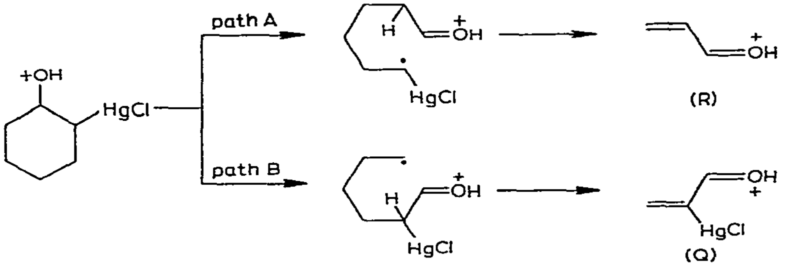


(2-Hydroxyalkyl)- and (2-methoxyalkyl)mercuric chlorides

In scheme 6 is outlined the 70 eV fragmentation behavior of (2-hydroxycyclohexyl)mercuric chloride (VIIIa) and (2-methoxycyclohexyl)mercuric chloride (VIIIb). In each spectrum only weak parent ions are observed.

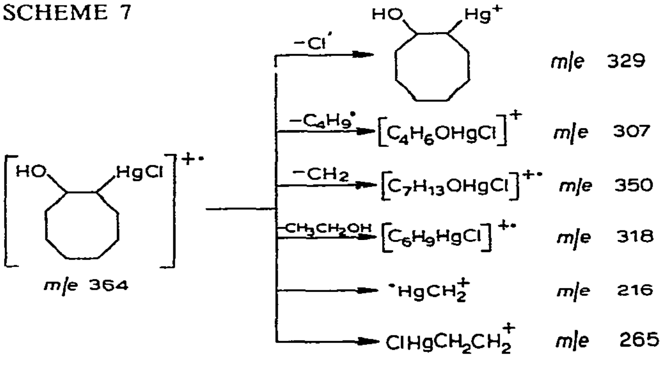
The base peak *m/e* 81 ion is formed through sequential loss of HgCl and ROH, in both orders. Formal reversal of the oxymercuration process occurs to produce the *m/e* 82 ion which decomposes further in a manner exactly analogous to cyclohexene[6f].

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 ($CH_2{=}CH{-}CH{=}O^+H$) which is formed by initial cleavage α 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 (VIIIa) and (VIIIb), respectively].



When the mercury-containing ions of (2-hydroxycyclooctyl)mercuric chloride (IX) (Scheme 7) are compared to the mercury-containing ions from (VIIIa), certain distinct differences are noted. The *m/e* 350, 318, and 307 ions are particularly interesting. The elimination of $:CH_2$ from the molecular ion to produce *m/e* 350* is one of the

SCHEME 7



---

* This observation raises the interesting possibility that (IX) 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 precursors is discussed later in this paper.

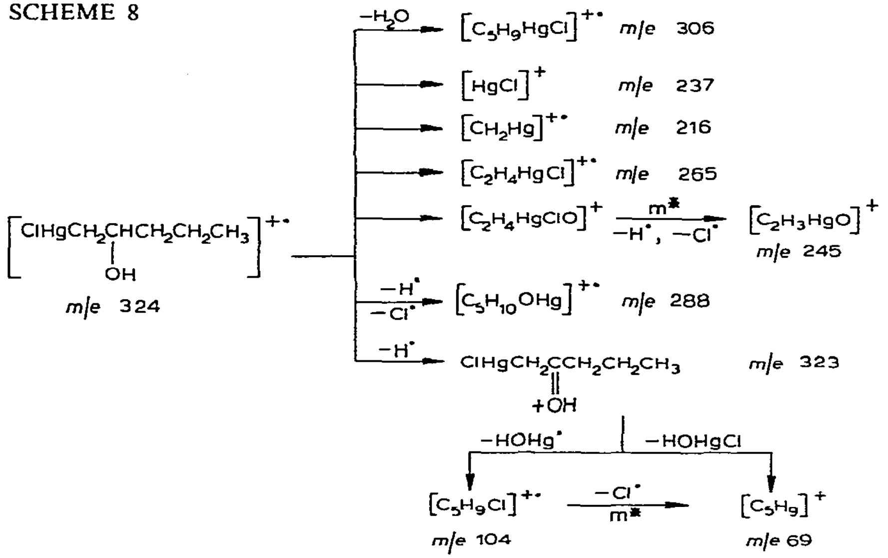
rare examples[24] of methylene elimination. The most often cited example of such a fragmentation, *i.e.* loss of $:CH_2$ from thioxanthene[25], has recently been shown to be non-repeatable[26].

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 (IX) is the hydrocarbon *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 an open chain olefin, that of 1-pentene (X), is shown in Scheme 8. The low intensity parent ion is cleaved very preferentially between carbons 2 and 3 to produce the base peak at *m/e* 281. In this process the usual cleavage *β* to mercury is reinforced by the tendency for cleavage *α* to a hydroxyl group. Subsequent metastable loss of HCl produces the abundant *m/e* 245 ion.

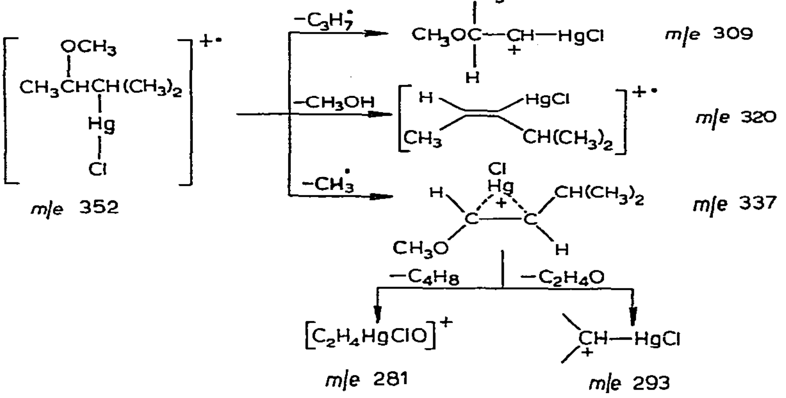
SCHEME 8



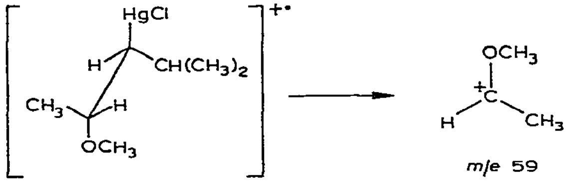
A variety of alternate fragmentations of the molecular ion are shown in Scheme 8, several of which necessitate rearrangement. Loss of mercury from the M−H ion is accompanied by chlorine migration to produce the *m/e* 104 ion.

A pair of diastereomers was next investigated in order to determine the applicability of mass spectrometry in structural analysis in this area of organomercury chemistry. The spectra of the methoxymercuric chloride adducts of *cis*- and *trans*-4-methyl-2-pentene (XI) and (XII) 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 (XII) exhibits several mercury-containing ions that are completely absent in the spectrum of (XI) [*m/e* 293, Scheme 9, and *m/e* 217 (CH_3Hg)]. At 70 eV the base peak in the spectrum of (XI) is *m/e* 69, that of (XII), *m/e* 59. (At 18 eV, they both exhibit base peak *m/e* 83, formed by successive loss of CH_3OH and HgCl).

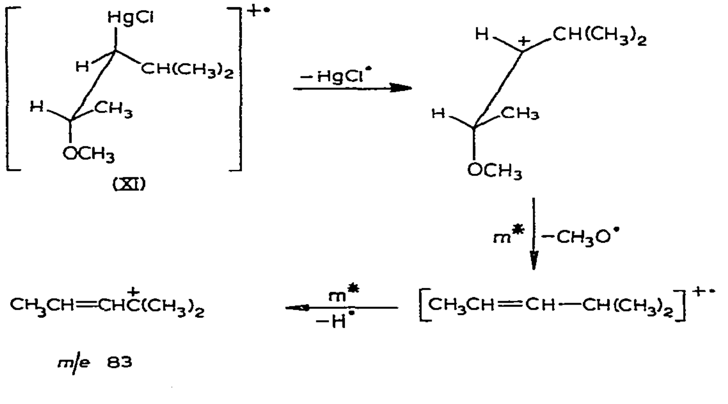
SCHEME 9



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



(XII)



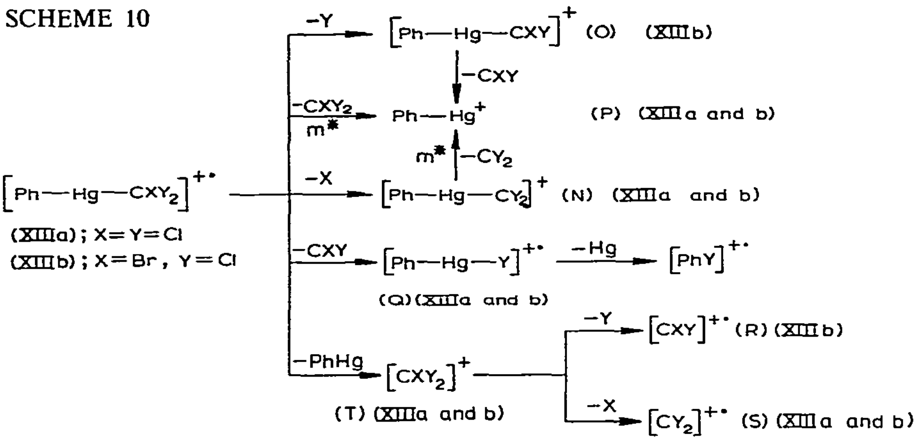
Other fragmentations of (XI) and (XII) are illustrated in Scheme 9. The structure suggested for the *m/e* 337 ion, although obviously conjectural, must at least be formed as a transition state on the way to forming the *m/e* 281 and 293 ions. The formation of mercurinium ions in solution reactions has been postulated[29]

Methylene transfer reagents

The synthetic importance and utility of a variety of organomercurials as halocarbene or halocarbenoid precursors has been well demonstrated by Seyferth[30].

Scheme 10 summarizes the fragmentations of phenyl(trichloromethyl)mercury (XIIIa) and phenyl(bromodichloromethyl)mercury (XIIIb) 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 phenylmercury cation (P).

SCHEME 10



Molecular ion (XIIIa) loses a chlorine radical producing the ion (N) which subsequently loses $:CCl_2$ in a metastable process giving (P). For parent ion (XIIIb) there are apparently two competing modes of fragmentation. The loss of Br• generates (N) whereas the loss of Cl• gives (O). The ensuing loss of :CClBr from (O) would also produce the phenylmercury cation. Elimination of either dichloromethylene from molecule ion (XIIIa) or bromochloromethylene from (XIIIb) gives rise to the phenylmercuric chloride molecular ion (G)*.

In the spectrum of (XIIIa) and (XIIIb), the trihalocarbonium ion (T) is observed. The bromodichlorocarbonium ion can lose either Cl• or Br• to generate ion (R) or (S). Naturally, the trichlorocarbonium ion can only decompose to give (S).

At 18 eV the molecule ion of (XIIIa) is the base peak, but for (XIIIb) the phenyl cation is still the most abundant ion. Ions (N), (O) and (P) are still observed, but (G), (T), (R) and (S) are not present. In going from 18 to 16 eV ion (P) 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.

---

[*] 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.

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 V 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 values.

The following compounds were prepared by well-established Grignard procedures: bis[*p*-(trifluoromethyl)phenyl]mercury (m.p. 142–143°); dibenzylmercury (m.p. 107.5–108.5°, lit.[31] 111°); di-n-butylmercury (b.p. 121–122°/23 mm, lit.[32] 120–123°/23 mm).

The following compounds were prepared by Grignard techniques, except that inverse addition was employed: n-butylmercuric chloride (m.p. 125.5–126.5°, lit.[31] 125.5°); n-amylmercuric chloride (m.p. 123–124°, lit.[31] 110°).

o- and *p*-(*Methoxyphenyl*)*mercuric bromide* were prepared by the Grignard procedure from *o*- and *p*-bromoanisole and $HgCl_2$. Using the *ortho*-isomer for an example, the product isolated was a mixture of (*o*-methoxyphenyl)mercuric chloride and (*o*-methoxyphenyl)mercuric bromide which was converted to pure (*o*-methoxyphenyl)mercuric 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 (IVd) (m.p. 187°, lit.[32] 187°); (Vb) (m.p. 182.5–184°, lit.[32] 183°).

o- and *p*-Tolylmercuric chloride and (*p*-chlorophenyl)mercuric chloride were prepared by the method of Whitmore[33]. *o*-Tolylmercuric chloride (m.p. 229.5–230.5°, from ethanol); *p*-tolylmercuric chloride (m.p. 234–235°; lit.[31] 233°); (*p*-chlorophenyl)-mercuric chloride (m.p. 238–239°, lit.[32] 225°). (*o*-Hydroxyphenyl)mercuric chloride was prepared by the method of Whitmore and Middleton[31] (m.p. 146.5–147.5°, lit.[32] 152.5°).

Addition compounds of olefins and mercury salts

The mercuric chlorides of hydroxycyclohexene, -cyclooctene and -1-pentene and the mercuric chlorides of methoxycyclohexene and -*cis*- and -*trans*-4-methyl-2-pentene were prepared by standard procedures for oxymercuration: (2-methoxycyclohexyl)mercuric chloride (m.p. 114–115° from benzene/hexane); (2-hydroxycyclohexyl)mercuric chloride (m.p. 148.5° from benzene/hexane, lit.[34] 153.0–153.6°); (2-hydroxycyclooctyl)mercuric chloride (m.p. 89–90° from methanol); (2-hydroxyamyl)mercuric chloride (m.p. 61–62° from chloroform/hexane); mercuric chloride of *cis*-2-methoxy-4-methyl-2-pentene (m.p. 40.5–41.5° from methanol); mercuric chloride of *trans*-2-methoxy-4-methyl-2-pentene (m.p. 70.5–71.5° from methanol).

Methylene transfer reagents

Phenyl(trichloromethyl)mercury (m.p. 116–117°, lit.[35] 115–117°) was prepared by the method of Seyferth and Burlitch[35]. Phenyl(bromodichloromethyl)-mercury* [m.p. 110° (decomp.), lit.[35] 110–111° (decomp.)].

MASS SPECTRA

The information is presented in the following form: ion *m/e* (rel. intensity in %).

(Ia) (70 *eV*): 356 (44.7), 279 (21.2), 154 (4.15), 153 (2.52), 152 (2.64), 78 (7.36), 77 (100), 52 (1.75), 51 (31.8), 50 (7.95).

(Ib) (70 *eV*): 384 (92.4), 293 (18.3), 182 (0.72), 181 (1.58), 167 (2.53), 165 (2.15), 92 (19.8), 91 (100), 65 (24.8), 63 (5.87), 43 (33.1).

(Ic) (70 *eV*): 492 (9.18), 473 (3.00), 345 (11.1), 290 (0.48), 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), 81 (1.10), 76 (4.6), 75 (14.9), 74 (3.44), 69 (3.32), 57 (10.3), 51 (5.30), 50 (9.09).

(II) (70 *eV*): 384 (5.82), 202 (1.24), 182 (7.01), 181 (0.44), 104 (1.32), 103 (0.22), 92 (7.32), 91 (100), 90 (2.10), 89 (3.63), 66 (0.72), 65 (87.6), 64 (1.04), 63 (2.97), 51 (1.78), 41 (1.36), 39 (4.34).

(16 *eV*): 384 (100), 182 (93.5), 104 (9.35), 92 (3.06), 91 (41.1).

(III) (70 *eV*): 316 (11.8), 287 (0.77), 259 (2.28), 230 (1.22), 216 (trace), 202 (1.11), 57 (100), 56 (11.6), 42 (27.2), 40 (4.65).

(IVa) (70 *eV*): 314 (87.4), 279 (12.9), 237 (16.5), 202 (39.3), 114 (2.30), 112 (7.20), 77 (100), 51 (42.3), 50 (24.3).

(IVb) (70 *eV*): 328 (81.3), 293 (4.70), 237 (2.56), 202 (3.29), 128 (0.13), 126 (0.39), 91 (100), 89 (12.2), 76 (0.74), 75 (1.40), 74 (1.80), 65 (2.90), 64 (3.80), 63 (12.8), 62 (5.13), 61 (1.80), 51 (6.81), 50 (6.86).

(IVc) (70 *eV*): 348 (100), 313 (15.1), 237 (2.21), 202 (5.43), 150 (0.49), 149 (1.47), 148 (2.94), 146 (4.24), 114 (1.73), 113 (14.4), 112 (5.97), 111 (44.3), 78 (14.9), 77 (4.47), 76 (12.9), 75 (34.0), 74 (14.4), 73 (4.21), 51 (8.45), 50 (22.8).

(IVd) (70 *eV*): 388 (100), 309 (11.9), 281 (7.57), 202 (7.40), 188 (2.56), 186 (2.70), 173 (1.04), 171 (1.19), 157 (1.28), 155 (1.37), 145 (2.02), 143 (2.11), 140 (1.96), 107 (28.6), 92 (20.6), 77 (25.7), 65 (12.0), 64 (4.55), 41 (5.80).

(Va) (70 *eV*): 328 (70.5), 313 (10.4), 293 (4.77), 237 (3.76), 202 (4.77), 128 (0.55), 126 (1.38), 91 (100), 89 (12.6), 77 (2.90), 76 (1.34), 75 (2.12), 74 (2.67), 65 (29.7), 64 (4.25), 63 (4.17), 62 (5.94), 61 (2.37), 51 (9.56), 50 (9.41), 43 (3.08), 42 (3.88), 41 (5.06), 40 (1.90), 39 (18.5), 38 (4.24).

(Vb) (70 *eV*): 386 (26.5), 371 (1.18), 355 (1.18), 309 (10.2), 281 (5.13), 202 (15.4), 186 (trace), 157 (2.70), 155 (3.08), 143 (2.36), 107 (33.0), 92 (33.7), 79 (24.8), 77 (100), 64 (16.1), 63 (21.6), 51 (13.7), 50 (12.3).

(VI) (70 *eV*): 330 (100), 295 (42.2), 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).

(VIIa) (70 *eV*): 294 (12.1), 265 (59.8), 259 (1.34), 237 (17.5), 230 (4.54), 216 (1.34), 202 (14.6), 65 (3.11), 63 (9.46), 57 (100), 56 (12.2), 55 (12.7), 41 (56.8).

(VIIb) (70 *eV*): 308 (12.6), 279 (2.65), 273 (2.00), 265 (17.7), 237 (11.7), 230 (3.08), 216 (0.80), 202 (9.44), 71 (100), 65 (2.00), 63 (5.73), 55 (17.8), 43 (94.1), 41 (60.5).

(VIIIa) (70 *eV*): 336 (0.64), 335 (0.44), 318 (8.16), 301 (2.18), 293 (0.77), 237 (5.93), 202 (12.9), 99 (20.2), 98 (3.24), 97 (2.24), 83 (9.04), 82 (46.4), 81 (100), 80 (3.33), 79 (9.01),

---

* The authors wish to thank Richard Fugiel for supplying the sample utilized in this study.

78 (2.25), 77 (3.31), 71 (1.50), 70 (7.52), 69 (11.6), 68 (3.01), 67 (34.8), 66 (1.59), 65 (1.88), 63 (0.83), 58 (1.89), 57 (44.6), 56 (3.84), 55 (23.6), 54 (18.9), 53 (9.91), 52 (1.81), 51 (3.36), 50, (1.81), 43 (16.9), 42 (11.4), 41 (32.2), 40 (3.31), 39 (18.7).

(*VIIIb*) (70 *eV*): 350 (4.03), 318 (5.71), 315 (3.09), 307 (trace), 237 (2.89), 202 (3.36), 113 (18.0), 85 (1.50), 84 (2.84), 83(1.90), 82 (14.0), 81 (100), 80 (1.20), 79 (5.18), 77 (1.80), 72 (1.60),71 (33.6), 69 (2.00), 67 (9.90), 55 (7.08), 54 (5.50), 53 (6.09).

(*IX*) (70 *eV*): 364 (0.30), 350 (1.49), 329 (0.41), 318 (1.92), 307 (0.25), 277 (0.26), 237 (0.43), 202 (8.75), 113 (17.4), 85 (2.25), 84 (4.04), 83 (2.96), 82 (17.7), 81 (100), 80 (1.70), 79 (5.25), 72 (2.79), 71 (34.5), 68 (2.88), 67 (17.0), 58 (2.75), 57 (4.00), 50 (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).

(18 *eV*): 364 (5.72), 350 (7.38), 318 (11.5), 202 (14.1), 113 (18.8), 110 (24.4), 109 (17.4), 82 (31.3), 81 (100), 71 (5.22), 68 (3.00), 62 (8.70).

(*X*) (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 (30.5), 59 (0.39), 58 (3.57), 55 (17.2).

(*XI*) (70 *eV*): 352 (trace), 336 (0.58), 320 (2.40), 309 (4.67), 115 (14.2), 99 (5.93), 84 (43.9), 83 (98.9), 72 (56.8), 69 (100), 67 (7.14), 59 (67.6), 55 (37.1).

(*XII*) (70 *eV*): 352 (0.71), 337 (0.81), 320 (4.13), 309 (8.23), 293 (0.17), 281 (1.78), 237 (2.92), 217 (4.03), 202 (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).

(*XIIIa*) (70 *eV*): 396 (23.3), 361 (15.0), 314 (4.10), 279 (53.4), 237 (0.12), 202 (0.62), 121 (0.61), 119 (1.82), 117 (1.86), 114 (0.45), 112 (1.30), 84 (1.45), 82 (2.12), 77 (100), 51 (30.8), 50 (14.2), 47 (2.78).

(*XIIIb*) (70 *eV*): 440 (4.50), 405 (1.11), 361 (3.16), 314 (0.08), 279 (25.1), 249 (0.42), 237 (0.27), 165 (0.61), 163 (1.40), 161 (1.01), 128 (0.82), 126 (0.67), 112 (0.41), 84 (1.33), 82 (1.90), 77 (100), 50 (34.7).

REFERENCES

1 D. B. Chambers, F. Glockling and J. R. C. Light, *Quart. Rev., Chem. Soc.*, 22 (1968) 317.
2 M. I. Bruce, *Advan. Organometal. Chem.*, 6 (1968) 273.
3 B. G. Gowenlock, R. M. Haynes and J. R. Majer, *Trans. Faraday Soc.*, 58 (1962) 1905.
4 B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, 66 (1962) 155.
5 V. H. Dibeler and F. L. Mohler, *J. Res. Nat. Bur. Stand., Sect. A*, 47 (1951) 337.
6 H. Budzikiewicz, C. Djerassi and D. H. Williams, *Mass Spectrometry of Organic Compounds*, Holden-Day, San Francisco, Calif., 2nd. ed. (1967): (a) p. 654, (b) p. 654, (c) p. 655, (d) p. 655, (e) p. 657, (f) p. 26, (g) p. 429.
7 R. E. Winters and R. W. Kiser, *J. Organometal. Chem.*, 10 (1967) 7.
8 L. F. Hatch, G. Sutherland and W. J. Ross, *J. Org. Chem.*, 14 (1949) 1130.
9 G. H. Draffan, R. N. Stillwell and J. A. McCloskey, *Org. Mass Spectrom.*, 1 (1968) 669.
10 D. B. Chambers, G. E. Coates, F. Glockling and M. Weston, *J. Chem. Soc. A.*, (1969) 1712.
11 D. B. Chambers, F. Glockling and M. Weston, *J. Chem. Soc. A*, (1967) 1759.
12 D. Seyferth and R. J. Spohn, *J. Amer. Chem. Soc.*, 91 (1969) 3037, 6192.
13 A. L. Kurts, I. P. Beletskaya, I. A. Savchenko and O. A. Reutov, *J. Organometal. Chem.*, 17 (1969) P21.
14 J. H. Robson and G. F. Wright, *Can. J. Chem.*, 38 (1960) 21.
15 H. C. Brown and Min-Hon Rei, *J. Amer. Chem. Soc.*, 91 (1969) 5646.
16 H. C. Brown and J. T. Kurek, *J. Amer. Chem. Soc.*, 91 (1969) 5647.
17 *Fr. Pat.* 1, 524, 639; *Chem. Abstr.*, 71 (1969) 13967m.
18 D. Seyferth and W. Tronich, *J. Organometal. Chem.*, 18(1969) P8.

19 D. Seyferth, M. E. Gordon, J. Y. P. Mui and J. M. Burlitch, *J. Amer. Chem. Soc.*, 89 (1967) 959.
20 D. Seyferth, S. P. Hopper and T. F. Jula, *J. Organometal. Chem.*, 17 (1969) 193.
21 D. Seyferth, S. B. Andrews and H. D. Simmons, Jr., *J. Organometal. Chem.*, 17 (1969) 9.
22 J. H. Beynon, R. A. Saunders and A. E. Williams, *The Mass Spectra of Organic Molecules*, Elsevier, New York, N. Y., 1968.
23 R. H. Shapiro, *Org. Mass Spectrom.*, 1 (1968) 907.
24 R. G. Cooks, *Org. Mass Spectrom.*, 2 (1969) 481.
25 B. D. Tilak, K. G. Das and H. M. Ei-Namaky, *Experientia*, 23 (1967) 609.
26 J. Heiss and K. P. Zeller, *Org. Mass Spectrom.*, 2 (1969) 1039.
27 P. Natalis, *Bull. Soc. Chim. Belg.*, 75 (1966) 668.
28 S. Meyerson and A. W. Weitkamp, *Org. Mass Spectrom.*, 1 (1968) 659.
29 W. L. Waters and E. F. Kiefer, *J. Amer. Chem. Soc.*, 89 (1967) 6261.
30 D. Seyferth, S. P. Hopper and K. V. Darrach, *J. Amer. Chem. Soc.*, 91 (1969) 6536.
31 *Dictionary of Organic Compounds*, Oxford University Press, New York, N.Y., 4th ed., 1966.
32 A. E. Goddard and D. Goddard, in J. N. Friend (Ed.), *A Text-Book of Inorganic Chemistry*, Charles Griffin and Co., London, 1928, Part XI.
33 F. C. Whitmore, F. H. Hamilton and N. Thurman, *Org. Synth.*, 3 (1923) 99.
34 O. W. Berg, W. B. Lay, A. Rodgman and G. F. Wright, *Can. J. Chem.*, 36 (1958) 358.
35 D. Seyferth and J. M. Burlitch, *J. Organometal. Chem.*, 4 (1965) 127.