SECTION C

Organic Chemistry

The Mass Spectra of Organomercury Compounds

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The fragmentation of a number of organomercury compounds under electron impact has been examined. In the symmetrical diarylmercury compounds it seems that the first fragmentation is loss of aryl radical to form arylmercury cation which then loses mercury to give aryl cation. Another important fragmentation is the extrusion of mercury from the parent ion to give a biaryl-type system. Fragmentation of the substituted aromatic compounds before C–Hg bond fission is also observed. In dialkylmercury compounds the dominant path is fission of the C–Hg bond even when an alternative path leading to a very stable cation ($C_7H_7^+$) is available.

In the α-halogenomercurated carbonyl compounds examined the dominant structural feature determining the direction of fragmentation is the carbonyl group, *e.g.* in α-chloromercuryacetone α fission leads to acetyl and α-chloromercuryacetyl ions of similar intensity. Di-(α-ethoxycarbonylbenzyl)mercury shows only Hg^+ and mercury-free organic ions formed by extrusion of mercury and subsequent fragmentation of the extrusion product.

When pairs of symmetrical diaryl and dialkyl mercury compounds were introduced into the mass spectrometer, ions of the type R^1–Hg–R^2 have been observed to accompany R^1_2Hg and R^2_2Hg. This exchange was confirmed by the appearance of mixed extrusion products R^1–R^2.

THE mass spectra of organomercury compounds has received comparatively little attention considering their widespread use and availability. Apart from the early study of Dibeler and Mohler[1] of the fragmentation of three dialkylmercurials, most of the work on organomercury compounds dealt with ionisation potentials and appearance potentials of simple fragments formed by carbon–mercury bond cleavage.[2] While this manuscript was in preparation, Bryant and Kinstle[3] published a report on the mass spectra of some aromatic and aliphatic mercury compounds paralleling some of our results. We have examined a number of aliphatic and aromatic mercury compounds containing a variety of functional groups with a view to identifying general features associated with their mass spectra.

Diarylmercury Compounds.—A series of symmetrical

cenyl-mercury (see Table 1), including compounds containing electron-withdrawing substituents and compounds containing electron-releasing substituents on the phenyl groups. The most important features of the mass spectra of these compounds are shown in Table 1. The general fragmentation of diarylmercury compounds can be described as:
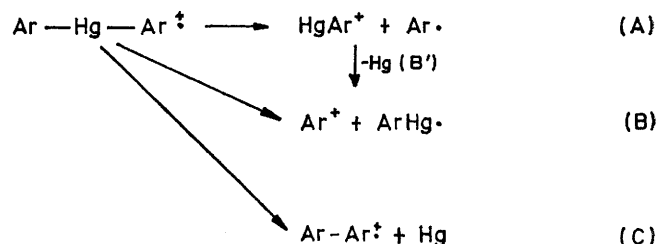
$$\text{Ar}-\text{Hg}-\text{Ar}^{+\cdot} \longrightarrow \text{HgAr}^+ + \text{Ar}\cdot \qquad (A)$$

$$\downarrow{-\text{Hg (B')}}$$

$$\text{Ar}^+ + \text{ArHg}\cdot \qquad (B)$$

$$\text{Ar}-\text{Ar}^{+\cdot} + \text{Hg} \qquad (C)$$

TABLE 1

Ar–Hg–Ar Fragmentation

Ar	% Relative abundances					Other significant ions (rel. abundances)
	$M^{+\cdot}$	$ArHg^+$	$Ar_2^{+\cdot}$	Ar^+	$Hg^{+\cdot}$	
Phenyl (1)	28	20	9	100	5	
α-Naphthyl (2)	20	1	10	100	4	
p-Methoxyphenyl (3)	30	15	87	100	86	
p-Aminophenyl (4)	22	2	9	42	24	ArH(100)
p-Dimethylaminophenyl (5)	8	0	100	55	17	$Ar_2 - 15(28)$, $Ar_2 - 31(10)$
p-Ethylphenyl (6)	23·5	10·5	30	100	23	$M - 15(5·5)$, $Ar_2 - 15(50)$
p-Chlorophenyl (7)	30	36	19	100	8	$C_{12}H_8(6)$, $C_6H_3(31)$
p-Bromophenyl (8)	80	50	80	100	65	$C_{12}H_8(65)$, $C_6H_4(64)$
p-Nitrophenyl (9)	35	35	100	61	70	$M - 46(10)$
Ferrocenyl (10)	100	0	10·5	26	5	$Ar_2 - C_5H_5(16)$ m/e 129 (31)

diarylmercury compounds (1)—(10) were prepared by standard methods,[4] ranging from diphenyl- to diferro-

All the compounds examined show significant molecular ions, in one case (10) this is the most abundant ion in the

[1] V. H. Dibeler and F. L. Mohler, *J. Res. Nat. Bureau Stand.*, 1951, **47**, 337.

[2] B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, 1962, **66**, 155; B. G. Gowenlock, R. M. Haynes, and J. R. Majer, *Trans. Faraday Soc.*, 1962, **58**, 1905; R. E. Dessy, I. Kaplan, G. R. Coe, and R. M. Salinger, *J. Amer. Chem. Soc.*, 1963, **85**, 1191.

[3] W. F. Bryant and T. H. Kinstle, *J. Organometallic Chem.*, 1970, **24**, 573.

[4] L. G. Makarova and A. N. Nesmeyanov, 'The Organic Compounds of Mercury,' North Holland Pub. Co., Amsterdam, 1967, and references therein.

spectrum. The simplest fragmentation of the molecular ion is the cleavage of the carbon–mercury bond, and judging by relative abundances the major process appears to be (B) with retention of the positive charge on the aryl group.[3] However, examination of the metastable peaks casts doubt on this interpretation, and suggests that process (B) is a minor path if it is at all significant, and that the major decomposition leads to the formation of an aryl mercury cation (A) followed by the loss of a mercury atom (B') to give the aryl cation. Not all the spectra contain metastable peaks but in those where they do appear they support process (A) in five cases [(1), (4), (7), (8), (9)], process (B') in four cases [(1), (4), (7), (8)]; in no case did a metastable peak correspond to process (B). The fact that the aryl mercury ion is very scarce in some cases [(2), (4)] and is totally absent in some others [(5), (10)] need not contradict this interpretation since the abundance of a particular fragmentation depends on the rate of its formation and the rate of its decomposition. In these cases the decomposition leading to the aryl cation and neutral mercury (process B') may be particularly favoured and any arylmercury cations that are formed in the first step immediately fragment further. This preferred fragmentation to aryl via arylmercury cation has also been observed in the case of di(pentafluorophenyl)-mercury where the assignment of fragmentations was supported by appearance of the corresponding metastable peaks.[5]

The other major fragmentation of the diarylmercurials is the loss of mercury from the molecular ion with the formation of an odd-electron ion (process C) the structure of which may be of the biphenyl type. This process which we wish to call 'extrusion' has been observed by Dibeler and Mohler[1] in the mass spectra of some dialkylmercury compounds as well as by Bryant and Kinstle[3] in diarylmercury compounds but not in di(pentafluorophenyl)mercury.[5] Bryant and Kinstle assigned the biphenyl structure to the product of fragmentation 'C' by the use of the 'external standard' method; they compared the mass spectrum 4,4'-bitolyl with the spectrum of di-p-tolylmercury below m/e 182 and found the same metastable peaks with the same shape and intensity. We have also examined a number of 'external standards': 4,4'-dimethoxybiphenyl, benzidine, 4,4'-dichlorobiphenyl, 4,4'-dibromobiphenyl, and 4,4'-dinitrobiphenyl; the mass spectra in all cases follow very closely the corresponding regions in the diaryl-mercurials, but the correspondence is not complete which is not entirely surprising if one considers that the comparison is between the fragmentation of ions formed in one case by direct ionisation, and in the other by the fragmentation of another ionic species. This is, in fact,

the basic objection to the use of the 'external standard' method,[6] and this reservation must be borne in mind in discussion of fragmentation and assignment of structures to ions in the middle of a fragmentation sequence. In four cases [(2), (8), dibenzylmercury and di-(2-phenylethyl)mercury] we have observed a metastable peak corresponding to the extrusion process, which quite clearly is an important fragmentation path (see Table 1) although no clear trend emerges when one looks for the effect of electron-releasing or electron-withdrawing substituents on the formation of the bisaryl system. The extrusion of the metal as a neutral entity is a rare process among organometallics. The single-step loss of two phenyl groups has been observed in the mass spectra of some Group IV tetraphenyls[7] but in these cases the charge is generally carried by the metal containing fragment. A rare exception to this is the fragmentation in which the metal-free biphenyl ion retains the charge.[8]

$$Ph_3GeX^{+\bullet} \longrightarrow Ph_2^{+\bullet} + PhGeX$$

In some of the diarylmercurial molecular-ions fragmentation involving the substituents on the aryl groups was observed. In the dinitro-compound (9) peaks corresponding to $M - 16$ (1%), $M - 30$ (1.2%), and $M - 46$ (10%) representing the loss of O, NO, and NO_2 respectively from the molecular ion, fragmentations that are common in nitroaromatics.[9] Similarly, in the di(p-ethylphenyl)mercury (6) we observed a peak corresponding to $M - 15$ (5.5%) suggesting loss of a methyl radical to form an ion which could have the structures

(11a)

or

(11b)
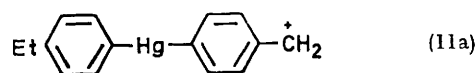
(11a) or (11b). Analogy to simpler systems suggests that the second (11b) is more likely.[10]

It is possible to write a detailed fragmentation path for the diarylmercury compounds, the individual steps are often confirmed by metastable peaks. Generally the fragmentations proceed by steps well known from the study of metal-free systems, the presence of mercury does not seem to affect materially the rest of the molecule. As an example the proposed fragmentation path of di-(p-nitrophenyl)mercury (9) is shown in the Scheme. The sequence described is as observed at 70 eV ionisation energy. At 15 eV the spectrum is considerably simplified; although the mercury extrusion product is still the base peak, the molecular-ion abundance is increased to

[5] S. C. Cohen and E. C. Tifft, *Chem. Comm.*, 1970, 226; M. I. Bruce, *J. Organometallic Chem.*, 1968, **14**, 461.
[6] T. W. Bentley and R. A. W. Johnstone, *Adv. Phys. Org. Chem.*, 1970, **8**, 194, and references therein.
[7] D. B. Chambers, F. Glockling, and M. Weston, *J. Chem. Soc. (A)*, 1967, 1759.
[8] F. Glockling and J. R. C. Light, *J. Chem. Soc. (A)*, 1968, 717.

[9] H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967, p. 516.
[10] H. M. Grubb and S. Meyerson, in 'Mass Spectrometry of Organic Ions,' ed. F. W. McLafferty, Academic Press, New York, 1963, p. 493.

80% and the abundance of ions at the low m/e end of the spectrum are either diminished or disappear altogether.

An interesting phenomenon was observed in the mass spectra of two diarylmercury compounds, di(bromo-phenyl)mercury (8) and di(nitrophenyl)mercury (9). In both compounds with the general formula R_2Hg low-intensity ions were observed with the formula $R_3-(H)$. In the nitro-compound (9) the abundance was 2% in the

cases the aromatic ring carried electron-withdrawing substituents. In two other compounds (3) and (5) where the extrusion product intensity is high this triaryl ion is not observed; in these cases the substituents are strongly electron releasing (OMe and NMe_2).

Dialkylmercury Compounds.—We have also examined the fragmentation of a number of simple dialkylmercury compounds: diethylmercury, dipropylmercury, di-s-

SCHEME

bromo-compound (8) 0·21% and this was accompanied by an ion formed by the loss of a bromine atom (abund-ance 0·8%, fragmentation confirmed by a metastable peak). The structure of these ions could be terphenyl-like (12):

(12)

and we feel that their formation is the likely result of bi-molecular reactions in the mass spectrometer. We note that in both cases when these ions appear, the mercury extrusion product is a very intense ion reflecting high concentration of that species in the ion source; in both

butylmercury, dibenzylmercury, and diphenethyl-mercury. Previous workers [1,3] on the fragmentation of dialkylmercury compounds reported that in R_2Hg the base peak was R^+, most of the ion current was carried by mercury-free ions, and some fragmentation of the alkyl group before cleavage of the mercury carbon bonds was also observed. Dibeler and Mohler [1] reported the presence of HgH^+ ions in the dialkylmercury mass spectra as well as low-intensity ions corresponding to hydrocarbons obtained by the extrusion of mercury. Neither of these features were observed by Bryant and Kinstle [3] under their operating conditions. In our study we found HgH^+ ions and mercury extrusion products, confirming the findings on these and other essential points, of the first workers. The mass spectrum we ob-tained for dibenzylmercury is in complete agreement with the one reported recently [3] except that we observed a metastable ion for the mercury extrusion process. Our

purpose in the study of diphenethylmercury was to see whether the dominant feature of dialkylmercury fragmentation, *i.e.* cleavage of the weak alkyl–mercury bond will be observed here, or whether a carbon–carbon bond will break preferentially to give a benzyl (tropylium) cation of known great stability.[10] In the event the peak at m/e 91 was quite small (2%) and the phenethyl cation (m/e 105) was the base peak. Both the molecular ion and the mercury extrusion product were of low intensity (1—2%). Further fragmentation of the mercury extrusion product (13) showed an interesting cleavage in which a benzyl radical was formed with the C_9 fragment

$$[Ph-CH_2-CH_2-CH_2-CH_2Ph]^{+\cdot} \xrightarrow{\quad*\quad}$$
$$(13) \quad m/e\ 210$$
$$[PhCH_2-CH_2-CH_2]^+ + PhCH_2\cdot$$
$$m/e\ 119 \qquad\qquad m/e\ 91$$
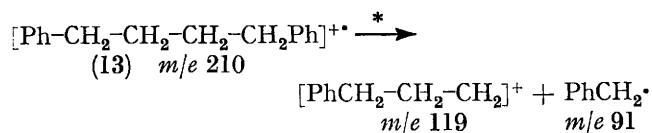
carrying the positive charge. In view of the known great stability of the C_7H_7 cation, this is surprising.

α-Mercurated Carbonyl Compounds.—In the mass spectra of α-chloromercuryacetaldehyde (14) and diacetaldehydemercury (15) * the highest molecular weight ion is formed by the loss of a hydrogen atom by α cleavage from the molecular ions. The fragmentation of both compounds follows familiar paths, since the possibility for the loss of stable, neutral fragments such as CO, keten, and atomic mercury is particularly favoured by the structure of the compounds. As in the dialkylmercurials, the $(HgH)^+$ ion is observed here, and in the chloromercuryacetaldehyde (14) the extrusion process is found to operate in the transition

$$Cl-Hg-CH_2-CO^+ \longrightarrow Cl-CH_2-CO^+ + Hg^\circ$$
$$m/e\ 279\ \text{and}\ 281 \qquad m/e\ 77\ \text{and}\ 79$$
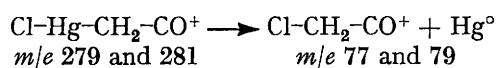
In the mass spectrometric fragmentation of the α-chloromercuryacetone (16) it is evident that the dominant feature determining the direction of the fragmentation is the keto-group of the acetone moiety. The spectrum shows clearly that the two possible products of the α cleavages are by far the most important ions in the spectrum. The base peak is formed by the loss of CH_3 from the molecular ion and to the best of our knowledge this is the first reported instance of the preferential cleavage of a strong carbon–carbon bond leading to the most important ion the mass spectrum of an organomercury compound, leaving a much weaker carbon–mercury bond unbroken. The extrusion of mercury from the molecular ion was not observed but the pair of peaks at m/e 77 and 79 can arise from $Cl-HgCH_2-CO^+$ by the loss of mercury. In contrast to α-chloro-

mercuryacetaldehyde (14), in α-chloromercuryacetone (16) the molecular ion is quite significant which is all the more surprising since in metal-free systems the loss of a hydrogen atom from aldehydes by α-cleavage is less favoured than the corresponding loss of alkyl groups in ketones.[11] Since the abundance of an ion is indicative of its stability the approximately equal intensity of the acetyl and chloromercury acetyl ions would suggest that the stability of an acetyl cation is not significantly affected by the presence of an α-chloromercury substituent.

The mass spectrum of 2-bromomercurycyclopentanone (17) adds further support to the observation that the presence of a halogenomercury group in a ketone need not cause the fragmentation to be very different from that of the parent compound. The base peak in this spectrum is the ion at m/e 55 with structure $CH_2=CH-C=O^+$ which is also the base peak in the mass spectrum of cyclopentanone and cyclohexanone.[12] The other possible unsaturated acylium ion containing the bromomercury substituent is also observed but with a much lower intensity. The other major decomposition path of cyclic ketones, the loss of CO and C_2H_4 as neutral fragments is also observed giving rise to the ions at m/e 309 and 311. The simple cleavage of the carbon–mercury bond, which is the dominant fragmentation in alkyl- and aryl-mercury compounds is observed, as is the mercury extrusion process to give a very weak ion at m/e 162 (abundance 0·8%).

The mass spectrum of di-(α-ethoxycarbonylbenzyl)-mercury (18) is unusual in the sense that no ions containing both carbon and mercury appear in it. The highest molecular weight ion corresponds to the mercury extrusion product, and the spectrum, apart from the intense $Hg^{+\cdot}$ ion, appears to be simply that of diethyl 2,3-diphenylsuccinate. This can be rationalised as meaning that the extrusion process is favoured over all other modes of decomposition (even at 15 eV) of the ions formed by the initial electron impact, and further fragmentation follows from there. There is, however, another possible explanation for these observations, namely that under the conditions prevailing in the ion source or in the inlet system, a pyrolytic loss of mercury occurs and by the time the molecules reach the electron beam, this pyrolysis is complete. There is some analogy for this in solution chemistry, because when dibenzylmercury was heated to 190 °C in solution, this pyrolysis was essentially complete after three minutes, the products being mercury and 1,2-diphenylethane.[13] In a parallel experiment diphenylmercury was pyrolysed and even under more vigorous conditions no biphenyl formation was observed. This thermal rearrangement in the di-(α-ethoxycarbonylbenzyl)mercury could be essentially complete in the mass spectrometer before ionisation.

* The mass spectra of compounds (14)—(18) are deposited as Supplementary Publication No. SUP 20222 (6 pp., 1 microfiche). For details of Supplementary Publications see *J. Chem. Soc. (A)*, 1970, Issue No. 20 (items less than 10 pp. will be supplied as full page copies). In these spectra in the interest of clarity Hg is represented by the most abundant one of its seven isotopes, ^{202}Hg but the intensity shown represents a summation of the total mercury-containing ion intensity in order to represent true abundances. For chlorine and bromine containing ions both isotopes are shown.

[11] Ref. 9, p. 129.
[12] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Appl. Spectroscopy*, 1960, **14**, 95; P. Natalis, *Bull. Soc. chim. belges*, 1958, **67**, 599.
[13] K. C. Bass and P. Nababsing, *J. Chem. Soc. (C)*, 1966, 1184.

We favour the former explanation, *i.e.* mercury extrusion *after* ionisation, largely because it is unlikely that thermal extrusion would be complete, and one would expect some organomercury ions to appear, however, in the absence of metastable peaks for the mercury extrusion process we cannot be certain of the correct explanation.

Another example of the extreme lability of the α-ethoxycarbonylbenzylmercury system is the mass spectrum of α-ethoxycarbonylbenzylmercuric bromide. The spectrum clearly shows it to be a mixture of the compound introduced and of the symmetrical disproportionation products mercuric bromide and di-(α-ethoxycarbonylbenzyl)mercury. The fragmentation of each clearly identifiable compound followed unexceptionable steps closely analogous to those observed in other, similar systems. In the α-ethoxycarbonylbenzylmercuric bromide, ions arising from the fragmentation of the ethoxycarbonylbenzyl group before loss of mercury make a substantial contribution to the ion current.

Alkyl Exchange Reactions in the Mass Spectrometer.—Mixtures of two symmetrical dialkylmercury compounds in one of which the mercury was labelled, were found to undergo exchange reactions in which the labelled mercury was redistributed between the two symmetrical dialkyl compounds.[14] The mechanism of this reaction is still

$$R^1_2Hg + R^2_2{}^*Hg \rightleftharpoons R^1_2{}^*Hg + R^2_2Hg$$

in some doubt, the simplest transition state proposed postulates a four-centre exchange[15] involving the intermediacy of unsymmetrical species of the R^1–Hg–R^2

type. The weakness of this interpretation lies in the failure of previous investigators to isolate any of the unsymmetrical dialkylmercury compounds. In view of the high sensitivity of the mass spectrometer towards minor constituents in a mixture we decided to use it to analyse for the presence of the species R^1–Hg–R^2 in the exchange reactions. We examined many pairs of compounds in solution and the results are shown in Table 2. Observation of exchange means that a significant intensity ion was observed at the position R^1–Hg–R^2 which was absent in both the pure components. In some instances the unsymmetrical ion was more intense than one of the symmetrical ones, but in all cases the symmetrical and unsymmetrical dialkyl/aryl mercury ions were of comparable intensity. A further indication that the exchange had taken place was the observation in many cases of ions corresponding to the extrusion of mercury from the unsymmetrical species, followed by the

$$[R^1\text{–Hg–}R^2]^{+\bullet} \longrightarrow [R^1\text{–}R^2]^{+\bullet} + Hg$$

fragmentation of the mixed extrusion products by steps familiar from the study of the symmetrical compounds.

In order to confirm that this is reliable evidence for the occurrence of the exchanges in solution and not something that happens in the mass spectrometer, we put solid samples of two symmetrical diarylmercury compounds as far as possible without mixing into a crucible which was

TABLE 2

Mass spectroscopic analysis of mixtures of two diorganomercurials

Diorganomercurial reactants		Exchange	Mixed extrusion product
$(C_6H_5)_2Hg$	$(C_6H_5CH_2)_2Hg$	+	+
$(BrC_6H_4)_2Hg$	$(CH_3OC_6H_4)_2Hg$	+	+
$(BrC_6H_4)_2Hg$	$(C_6H_5CH_2)_2Hg$	−	−
$(BrC_6H_4)_2Hg$	$(H_2NC_6H_4)_2Hg$	+	+
$(C_6H_5CH_2)_2Hg$	$(CH_3OC_6H_4)_2Hg$	−	−
$(C_6H_5)_2Hg$	$(CH_3OC_6H_4)_2Hg$	+	+
$(C_6H_5)_2Hg$	$(H_2NC_6H_4)_2Hg$	+	+
$(H_2NC_6H_4)_2Hg$	$(CH_3OC_6H_4)_2Hg$	+	−
$(H_2NC_6H_4)_2Hg$	$(NO_2C_6H_4)_2Hg$	+	+
$(CH_3OC_6H_4)_2Hg$	$(NO_2C_6H_4)_2Hg$	+	+
$(Ferr)_2Hg$	$(C_6H_5)_2Hg$	+	−
$(Ferr)_2Hg$	$(C_6H_5CH_2)_2Hg$	+	−
$(C_2H_5)_2Hg$	$(n\text{-}C_3H_7)_2Hg$	+	−
$(C_2H_5)_2Hg$	$(s\text{-}C_4H_9)_2Hg$	+	−
$(C_3H_7)_2Hg$	$(s\text{-}C_4H_9)_2Hg$	+	−

All substituted aromatic species refer to the *para*-isomer. Ferr represents the ferrocenyl group.

introduced into the ion source *via* the direct insertion probe. The mass spectrum clearly showed the same exchange as was observed when the two compounds were allowed to 'react' in solution. Re-examination of the exchange data by the introduction of solid samples without mixing showed that all the exchange reactions observed (Table 2) took place in the inlet system or in the ion source. Since these exchanges must proceed through bimolecular collisions their occurrence is more likely in the inlet system, where the pressure and hence the number of collisions is higher. We attempted to establish the location of the exchange by another experiment in which we introduced dipropylmercury *via* the heated reservoir inlet and diphenylmercury *via* the direct insertion probe. The two inlets introduce the stream of molecules from diametrically opposite sides of the ionisation chamber, therefore the only possible site for mixing was in the ion source. Under these circumstances exchange, *i.e.* Ph–Hg–Pr$^{+\bullet}$, ion was observed but with an intensity orders of magnitude less than when both compounds are introduced *via* the same inlet. The memory effect of molecules adsorbed on the walls can be excluded because removal of the probe or shutting off the leak from the reservoir leads to the disappearance of the exchange product.

[14] O. A. Reutov, H. Hunveng, and T. A. Smolina, *Izvest. Akad. Nauk, S.S.S.R., Otdel. khim. Nauk,* 1959, 559.
[15] D. S. Matteson, *Organometallic Chem. Rev.,* 1969, *A*4, 263.

EXPERIMENTAL

The organomercury compounds were prepared by standard methods and had physical properties in agreement with published data.[4] The mass spectra were determined on a Varian MAT CH7 mass spectrometer operating at 70 eV (unless otherwise stated) and a source temperature of 160—180 °C. The solid samples and solid mixtures were introduced *via* a direct insertion probe, and the liquid samples *via* the heated inlet system.