Mass Spectra of Some Alkynylmercury Compounds

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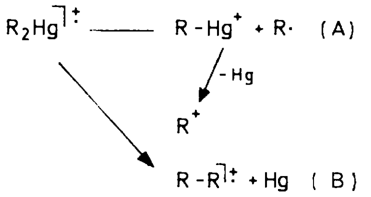
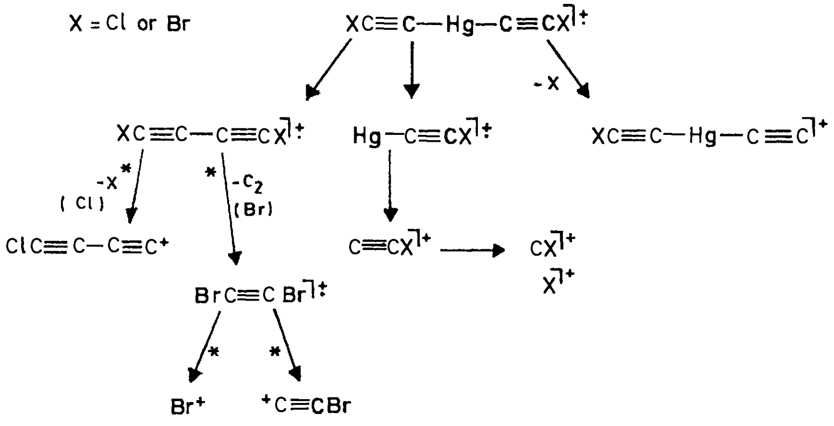
The fragmentation, under electron impact, of eleven halogenated, aliphatic, and aromatic alkynylmercury compounds of general structure $(XC{\equiv}C)_2Hg$ has been examined. The dominant fragmentation of organomercury compounds, namely the fission of the carbon–mercury bond, has been observed. The organic fragments formed either by direct fission or by extrusion of mercury fragmented in ways familiar from metal-free systems; losses of C_2H_4, C_2H_2, and H_2 were commonly seen, the proposed fragmentation pathways being supported by the observation of numerous metastable ions. Comparison of the relative metastable ion intensities suggests that the mercury extrusion products from the compounds with X = Et, Pr, and Bu^t decompose through the same structures as are formed from the higher alkylbenzenes. Fragmentation of the organic portion competes effectively with mercury–carbon bond cleavage in the mass spectra of the compounds with X = Bu^t and p-$MeOC_6H_4$. The loss of $HgCl_2$ from bis-(p-chlorophenylethynyl)mercury is also observed. In the mass spectrum of bis-(p-methoxyphenyl)-mercury and bis-(4-phenylbutadiynyl)mercury metastable ion peaks were found corresponding to fragmentations from doubly charged parent ions to doubly charged daughter ions.

THE past few years have seen an upsurge of interest in the mass spectra of organomercury compounds. Studies have appeared reporting the mass spectra of a wide variety of alkyl- and aryl-mercury compounds [1-5] as well as perhalogenoaryl- and alkenyl-mercury compounds both as the positive and as the negative ions.[6-9] In these studies it was generally observed that mercury–carbon bond cleavage is the most common feature in the fragmentation of these compounds and this can lead to a number of different products. The pathway of the major fragmentations of compound R_2Hg is shown in Scheme 1 [2] and the further fragmentations of R^+ and R_2^+ are usually very similar to analogous structures obtained directly in a metal-free system. Frequently fragmentations in the organic portion without prior loss of the metal were observed when the functional groups present offered the possibility of the formation of particularly stable ionic or neutral products.[1,2,8,9]



SCHEME 1



SCHEME 2

We have examined the mass spectra of a series of dialkynylmercury compounds of the general structure $(XC{\equiv}C)_2Hg$ in which X is halogen, alkyl, aryl, and PhC≡C. All the compounds had very well defined molecular ions; in many instances this was the base peak, undoubtedly owing to the high stability conferred on the system by the unsaturation of the acetylenic group and its substituents. The general pattern depicted in Scheme 1 was found to be an accurate representation of the major fragmentations. In most compounds fragmentation (A) was confirmed by a metastable ion, as was extrusion [2] (B) except where the high rate of further decomposition of $R_2^{+\cdot}$ led to very low abundances for those ions. All the spectra showed strong $Hg^{+\cdot}$ ions and when X = alkyl, this was accompanied by ions corresponding to HgH^+. The most intense metal-free ions were usually R^+ or R_2^+, and these generally fragmented with successive losses of C_2H_2 as neutral fragments

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

[2] S. W. Breuer, T. E. Pear, P. H. Lindsay, and F. G. Thorpe, *J. Chem. Soc.* (*C*), 1971, 3519.

[3] J. Lorberth and I. Weller, *J. Organometallic Chem.*, 1971, **32**, 145.

[4] G. Ahlgren, B. Akermark, and M. Nilsson, *J. Organometallic Chem.*, 1971, **30**, 303.

[5] A. K. Mal'tsev, R. G. Mikaelyan, and O. M. Nefedov, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim*, 1971, 1179.

[6] S. C. Cohen and E. C. Tifft, *Chem. Comm.*, 1970, 226.

[7] M. I. Bruce, *J. Organometallic Chem.*, 1958, **14**, 461.

[8] S. C. Cohen, *J. Chem. Soc.* (*A*), 1971, 632.

[9] S. C. Cohen, *J. Chem. Soc.* (*A*), 1971, 1571.

where this was possible. Apart from these common features, the various alkynyl compounds showed special characteristics which can be discussed conveniently for each different type of X.

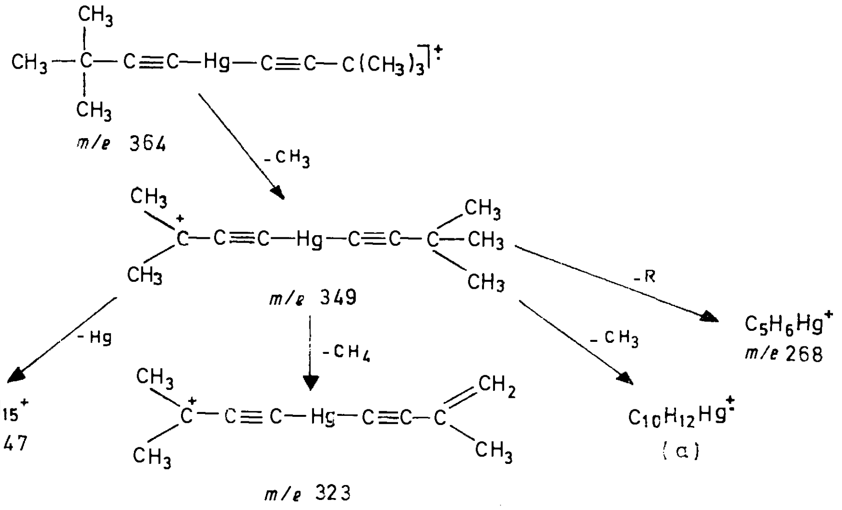
X = *Halogen*.—The two compounds examined had X = Cl and Br. The mass spectra of both were very similar, and exceedingly simple, with the bulk of the ion current being carried by ions containing mercury. Scheme 2 illustrates the major fragmentation pathways for both compounds, common in the early stages, but diverging later, particularly after the extrusion of mercury. On the whole the chloro-compound showed much more abundant metastable ions for more of the early processes than the bromo-compound.

X = *Alkyl*.—Four compounds were examined with X = Me, Et, Pr^n, and Bu^t. All these compounds showed numerous metal-free ions which carried most of the ion current. In all compounds the ion R^+ was very intense, and both it and $R_2^{+\cdot}$ gave rise to a series of fragmentations often accompanied by metastable ions. The hydrocarbon ions probably underwent extensive isomerisations since in the Et, Pr^n, and Bu^t compounds a series of interrelated ions were observed, derivable from the secondary fragments $C_8H_9^+$ and $C_7H_7^+$ which further fragmented with successive losses of H_2 or C_2H_2. The same ions, the same metastable ions, and therefore in all probability the same ion structures decomposing *via* the same mechanisms, were observed in the mass spectrum of ethylbenzene, see Table. The presence of the same metastable ions is held to be a reliable indication of identical ion structures decomposing *via* identical pathways,[10] and the relationship found here with respect to ethylbenzene suggests that the acetylenic extrusion products rapidly isomerise to common structures[11] of much greater stability in a manner very similar to that found with a range of alkylbenzenes.[12] The formation of the ions $C_8H_9^+$ and $C_7H_7^+$ from the extrusion products involves losses of H or Me when X = Et; Et or Pr when X = Pr^n; Me and C_3H_6 or C_2H_4 twice in succession when X = Bu^t. Most of these fragmentations are confirmed by the presence of the appropriate metastable ions. When X is Me, the extrusion product is an ion of composition $C_6H_6^{+\cdot}$. Its fragmentation was quantitatively different from that of benzene, showing many ions of the same composition and possibly structure, albeit of very different abundances.

Metastable ion abundance relative to peak of *m/e* 46·5

	PhEt	$(EtC{\equiv}C)_2Hg$
101·1 (105 ⟶ 103)	0·6	0·5
78·2 (106 ⟶ 91)	*	*
59·4 (105 ⟶ 79)	0·5	0·46
57·5 (105 ⟶ 77)	0·1	0·1
46·5 (91 ⟶ 65)	1	1
33·8 (77 ⟶ 51)	0·1	0·1
23·5 (65 ⟶ 39)	<0·1	<0·1

* Difficult to estimate because of the presence of intense peak at *m/e* 78.



SCHEME 3

For all four compounds with X = alkyl the R^+ ion (Scheme 1) gave a very intense peak. In X = Me, the ion at *m/e* 39 did not undergo further decomposition quite probably owing to the extremely stable, aromatic cyclopropenium structure that it can assume. The other three compounds, however, underwent extensive further fragmentations by the successive losses of H_2 or C_2H_2 or C_2H_4.

All four 'alkyl' compounds show fragmentations from the molecular ion at the carbon atom α to the acetylenic group. For X = Me this is merely a loss of a hydrogen atom to give a relatively weak ion. In the higher alkyl compounds however, these fragmentations are of increasing significance, *e.g.* when X = Et there is a sizeable $M - 15$ peak (accompanied by a metastable ion) and when X = Pr^n, the $M - 15$ and $M - 29$ ions

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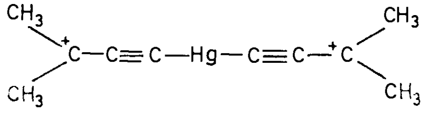
[10] T. W. Shannon and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1966, **88**, 5021; H. M. Rosenstock, V. H. Dibeler, and F. N. Harllee, *J. Chem. Phys.*, 1964, **40**, 591.

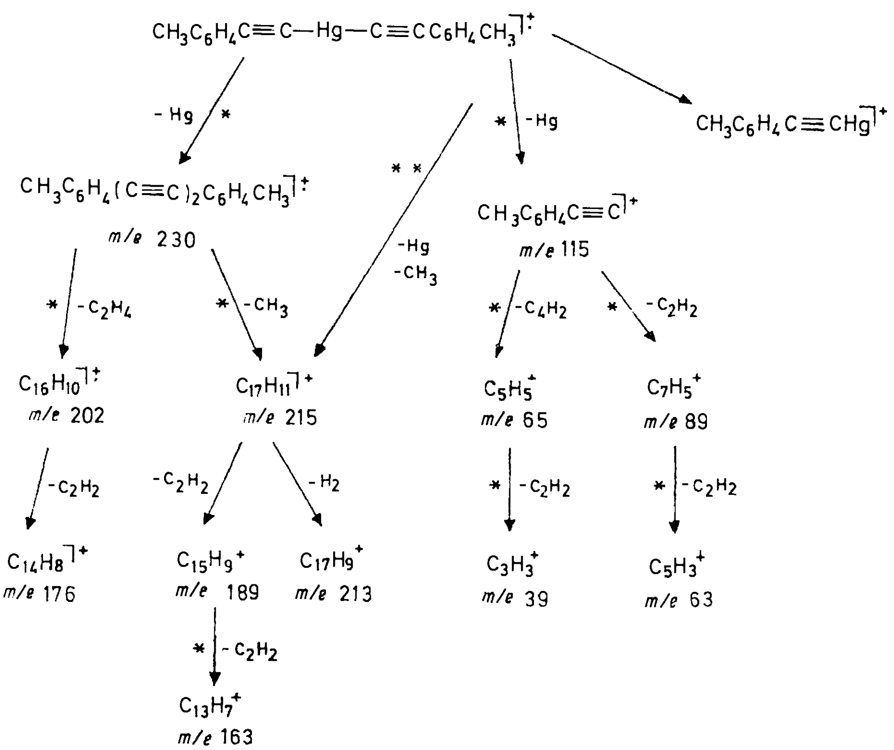
[11] H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967, p. 74.

[12] H. M. Grubb and S. Meyerson in 'Mass Spectrometry of Organic Ions,' ed. F. W. McLafferty, Academic Press, New York, 1963. p. 516.

are comparable in intensity with the molecular ion. This trend further increases for X = Bu^t; in the mass spectrum of this compound the $M - 15$ ion is comparable in intensity with the base peak and it undergoes a series of other fragmentations, as shown in Scheme 3.* It is interesting to note that ion (a), formed by the loss of a second methyl group from the ion at *m/e* 349, shows relatively strong doubly charged ions, the only organomercury species to do so in the alkyl series, apart from the molecular ion of the methyl compound (X = Me). For ion (a) one can draw close analogies with condensed phase carbonium ion structures indicating reasons why this ion may be particularly stable with a double positive charge. In this structure both the inductive effect of the methyl groups and the mesomeric effect of the acetylenic group can help to stabilise the double tertiary carbonium ion.



(a)



SCHEME 4

X = *Aryl*.—Four compounds of this general structure were examined with X = Ph, 4-ClC_6H_4, 4-MeC_6H_4, and 4-$MeOC_6H_4$. For all four compounds the molecular ion was either the base peak, or very near in intensity to the base peak, and the fragmentation pattern described in Scheme 1 was generally observed, most individual steps being supported by the appearance of the corresponding metastable ions. The fragmentations, apart from those involving mercury–carbon bond cleavage, followed along lines familiar from metal-free systems.[13]

When X = Ph the spectrum obtained was very simple, the only metal-containing ions being $R_2Hg^{+\cdot}$ and RHg^+. Extrusion of mercury led to a prominent ion PhC≡C–C≡CPh$]^{+\cdot}$ which in turn lost H_2 to give an ion of composition $C_{16}H_8$. The only other major series of metal free ions was based on the fragmentation products PhC≡CH$]^{+}$ and PhC≡C$]^{+\cdot}$ The latter, corresponding to R^+ in Scheme 1, was comparatively weak and fragmented further to give an intense ion at *m/e* 75 (C_6H_3) with concomitant loss of acetylene.

The *p*-tolyl compound (X = 4-MeC_6H_4) showed rather more extensive fragmentations mostly in the metal free ions. The only major mercury containing ion was M^+ and its first fragmentations involved breaking the carbon–mercury bonds. The main breakdown pattern is shown in Scheme 4. It is interesting to note than an intense metastable ion was observed for the process involving the consecutive losses of Hg and CH_3 by extrusion followed by fragmentation from the molecular ion to give $C_{17}H_{11}^+$ at *m/e* 215. (The stepwise loss of the same fragments is also accompanied by metastable ions.) The phenomenon of metastable ions associated with consecutive fragmentations is well known,[14] but not, so far as we are aware, in organometallic systems.

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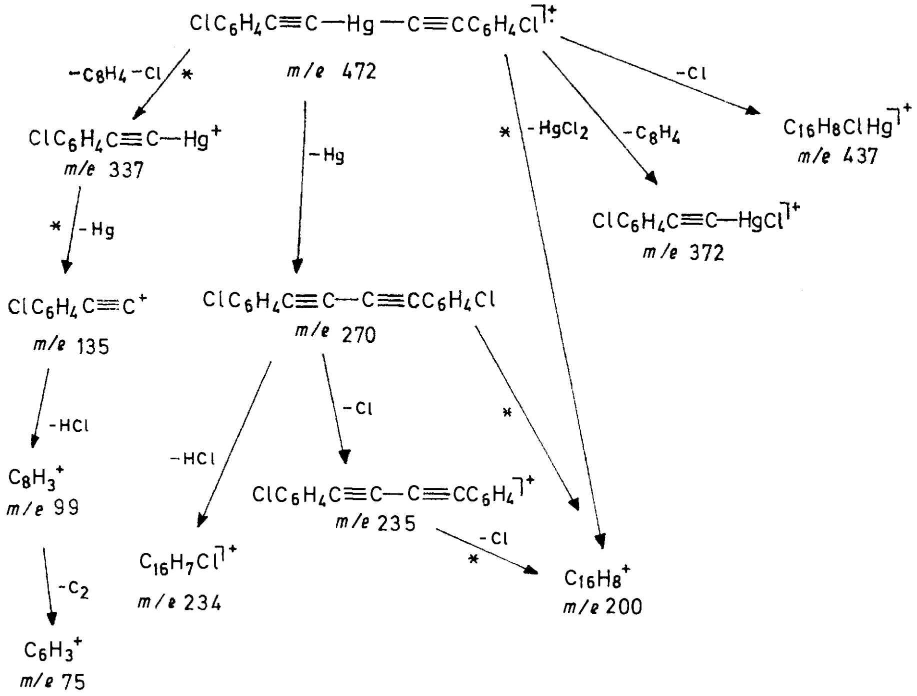
* In order to simplify the *m/e* quoted for mercury-containing ions in Schemes 3—7 the only mass quoted is the one corresponding to ^{202}Hg, the most abundant of the seven mercury isotopes.

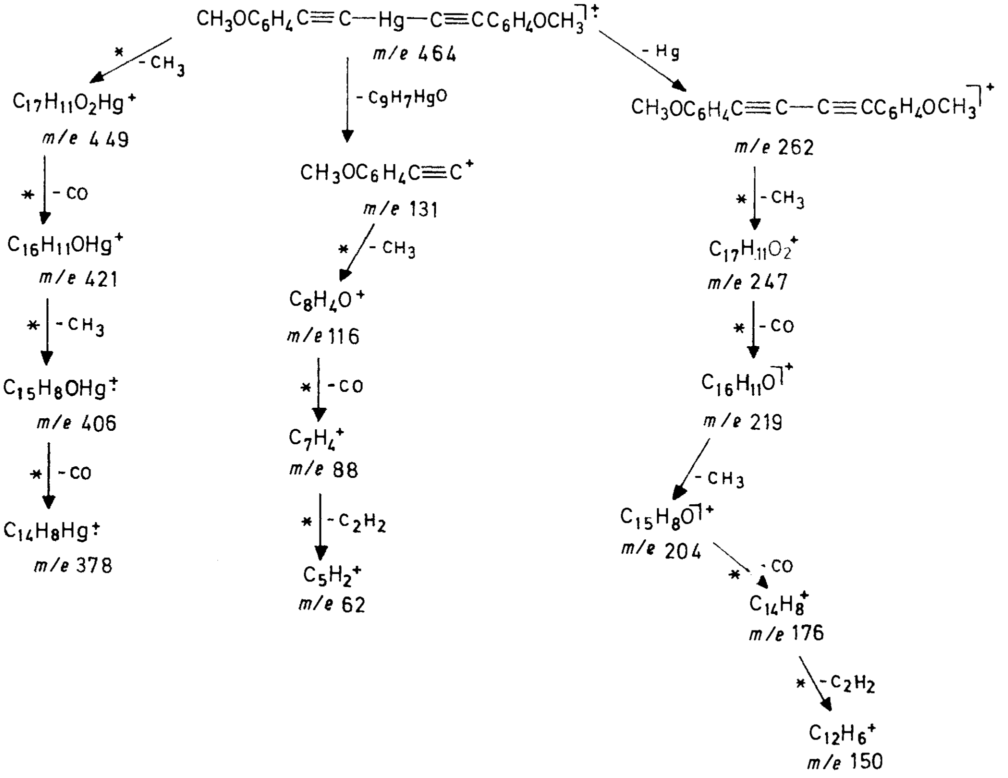
[13] Ref. 11, chs. 1, 6, and 12.

[14] J. L. Holmes and F. M. Benoit in 'Mass Spectrometry,' M.T.P. International Review of Science, ed A. Maccoll, Butterworths, London, 1972, vol. 5, p. 259 and references therein.

The mass spectrum of the chloro-compound (X = 4-ClC_6H_4) was very much simpler, the bulk of the fragmentations involving either cleavage of the carbon–mercury bond (as in Scheme 1) or losses of Cl or HCl. The molecular ion was by far the most intense peak in the spectrum and an unusual fragmentation for this type of compound was seen in the loss of $HgCl_2$ from the molecular ion to form $C_{16}H_8^{+\cdot}$ (but see ref. 8). The geometry of the parent molecule is linear, so this fragmentation must indicate a drastic reorganisation of the molecule



Scheme 5



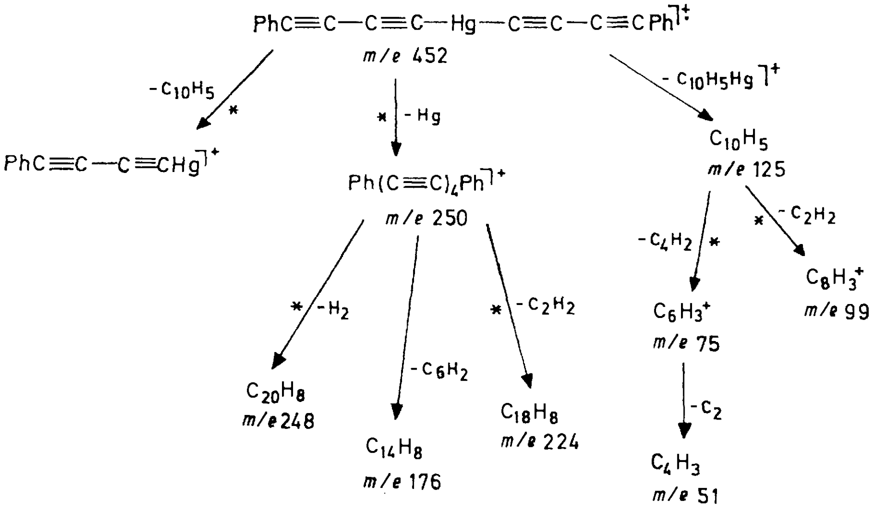
Scheme 6

to make possible the loss of $HgCl_2$ as a discrete unit. The breakdown pathway of the chloro-compound is shown in Scheme 5.

The mass spectrum of the *p*-methoxyphenyl compound ($X = 4\text{-}MeOC_6H_4$) is dominated by fragmentations associated with the methoxyphenyl group. The most common fragmentation pathway of the anisole system is loss of Me, followed by loss of CO, and these features are observed in the breakdown of the molecular ion and the various primary fragmentation products, as seen in Scheme 6. The ability of the methoxyphenyl system to stabilise a positive charge is reflected in the appearance of a sizeable doubly charged molecular ion, which undergoes fragmentation in the organic portion in exactly the same way as the singly charged molecular ions and medium intensity metastable ions are observed [reaction (C)] for these fragmentations. Metastable transitions in

$$M^{2+} \xrightarrow{*} (M - 15)^{2+} + CH_3 \xrightarrow{*} [M - (15 + 28)]^{2+} + CO \qquad (C)$$

which both the parent and the daughter ion carries a double positive charge are rare, but not unknown, in mass spectrometry. Beynon observed such peaks in the mass spectrum of anthraquinone [15] and of course metastable ions corresponding to the fragmentation of a doubly charged ion to two singly charged species are frequently observed.



SCHEME 7

The most important fragmentations of the diacetylenic compound ($X = PhC{\equiv}C$) are those which follow the general pattern described in Scheme 1. The great stability of the highly conjugated **R** group results in comparatively little fragmentation of the organic portion apart from mercury–carbon bond cleavage. The molecular ion is the base peak, and it is also the only mercury containing ion of any significance apart from Hg^+. RHg^+ is very weak, although its formation is accompanied by a metastable peak. Scheme 7 shows the fragmentation of the compound. As in the previous compound, a metastable ion was observed for the decomposition of doubly charged molecular ion according to equation (D)

$$(C_{20}H_{10}Hg)^{2+} \xrightarrow{*} (C_{20}H_{10})^{2+} + Hg \qquad (D)$$

EXPERIMENTAL

The acetylenic compounds $(XC{\equiv}C)_2Hg$ were all prepared by the described synthetic procedures [16–21] and had physical properties in agreement with published data.

The mass spectra were determined on a Varian MAT CH7 mass spectrometer operating at 70 eV and a source temperature of 160—180°. All samples were introduced *via* a direct insertion probe. Details of mass spectra are given in Supplementary Publication No. SUP 20963 (14 pp., 1 microfiche).*

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* For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1972, Index Issue.

[15] J. H. Beynon, 'Mass Spectrometry and its Application to Organic Chemistry,' Elsevier, Amsterdam, 1960, p. 261.

[16] K. A. Hofmann and H. Kirmreuther, *Ber.*, 1909, **42**, 4232.

[17] L. A. Bashford, H. J. Emeléus, and H. V. A. Briscoe, *J. Chem. Soc.*, 1938, 1359.

[18] J. R. Johnson and W. L. McEwen, *J. Amer. Chem. Soc.*, 1926, **48**, 469.

[19] T. H. Vaughan, *J. Amer. Chem. Soc.*, 1933, **55**, 3453.

[20] I. Iwai and Y. Yura, *Takamine Kenkyusho Nempo*, 1958, **10**, 30 (*Chem. Abs.*, 1961, **55**, 4400f).

[21] M Nakagawa, *J. Chem. Soc. Japan*, 1951, **72**, 561.