Organic Mass Spectrometry, 1970, Vol. 3, pp. 51 to 62. Heyden & Son Limited. Printed in Northern Ireland

THE MASS SPECTRA OF SOME CHLORINATED AROMATIC PESTICIDAL COMPOUNDS*

J. A. Sphon and J. N. Damico

Division of Food Chemistry and Technology, Bureau of Science, Food and Drug
Administration, Department of Health, Education and Welfare, Washington D.C.
20204, USA

Abstract—Mass spectral studies of some chlorinated aromatic pesticidal compounds are reported. The compounds studied include substituted diphenyl derivatives of methane, ethene and methanol.

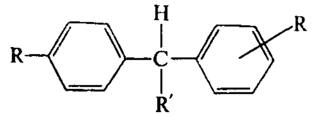
The diphenylmethanes are characterized by a relatively intense peak at *m/e* 165. Comparison of their low voltage spectra with 9-dichloromethylfluorene indicates that this ion has a fluorenyl ion structure.

The structure of the base peak (*m/e* 246) of the diphenylethenes was investigated by comparing competitive metastable transitions with 9-dichloromethylenefluorene and utilizing defocusing metastables. Additional studies of model compounds suggest that the *m/e* 246 ion is very complex and is probably comprised of a number of structures.

The mass spectra of the diphenylmethanols are significantly different from the other two groups. The hydroxyl group markedly affects the fragmentation process for these compounds; the characteristic peak is presumably the chlorobenzoyl ion and is probably precursor for other fragment ions.

Mass spectral correlations of pesticidal compounds of similar structure are needed to obtain enough background to facilitate interpretation of the mass spectra of their metabolites. Furthermore, such studies make feasible the identification of characteristic product ions formed by rearrangement processes during ionization of organic molecules in the gas phase. This information can be a nucleus for correlating the other significant mass spectral data of an unknown compound. Intensive studies of carbamates,[1] organophosphorus[2] and bridged polycyclic chlorinated pesticidal[3] compounds were invaluable in identifying metabolites of the aforementioned pesticides.[4,5,6] The compounds in this

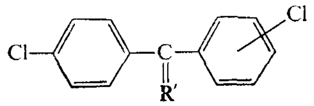
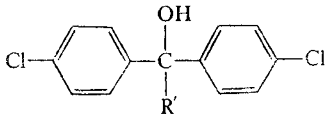
Table 1. Compounds examined

	Group I. Diphenylmethane derivatives				
Chemical name	Other name	Source	Mol. Wt.	Purity	Figure
					
1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane	*p,p'*-DDT	FDA	352	99^{+}*	1
1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)-ethane	*o,p'*-DDT	FDA	352	99^{+}*	2
1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane	*p,p'*-DDD	FDA	318	99^{+}*	3
1,1-dichloro-2-(*o*-chlorophenyl) 2-(*p*-chlorophenyl)ethane	*o,p'*-DDD	FDA	318	99^{+}*	4
1,1-dichloro-2,2-bis(*p*-ethylphenyl)ethane	Perthane	FDA	306	99^{+}*	5
1,1,1-trichloro-2,2-bis(*p*-methoxyphenyl)ethane	Methoxychlor	FDA	344	99^{+}*	6

---

* Presented at the 4th Middle Atlantic Regional Meeting of the American Chemical Society, Washington, D.C., February 12–15, 1969.

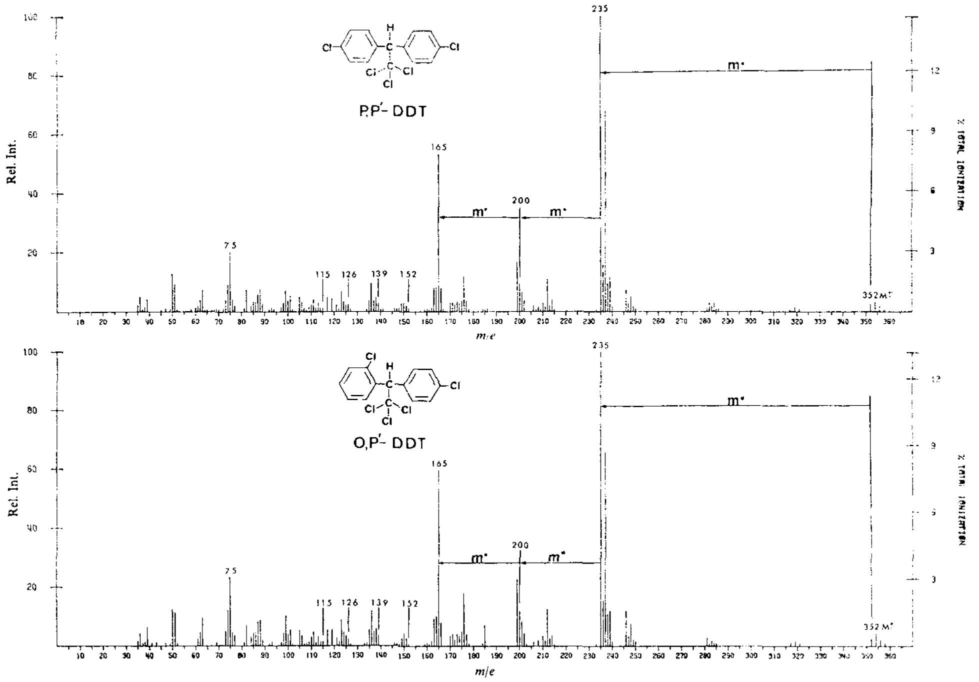
TABLE 1. (*Continued*)

Group II. Diphenylethylene derivatives					
					
1,1-dichloro-2,2-bis(*p*-chlorophenyl) ethylene	*p,p'*-DDE	FDA	316	99+*	7
1,1-dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)ethylene	*o,p'*-DDE	FDA	316	99+*	8
Group III. Diphenylmethanol derivatives					
					
Bis(*p*-chlorophenyl)methyl carbinol	Dimite	Syn.	266		9
1-Ethoxymethyl-1,1-di(*p*-chlorophenyl)carbinol	Etoxinol	Syn.	310		10
Ethyl 4,4'-dichlorobenzilate	Chlorobenzilate	FDA	324	99+	11
1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol	Kelthane	FDA	368	98	12

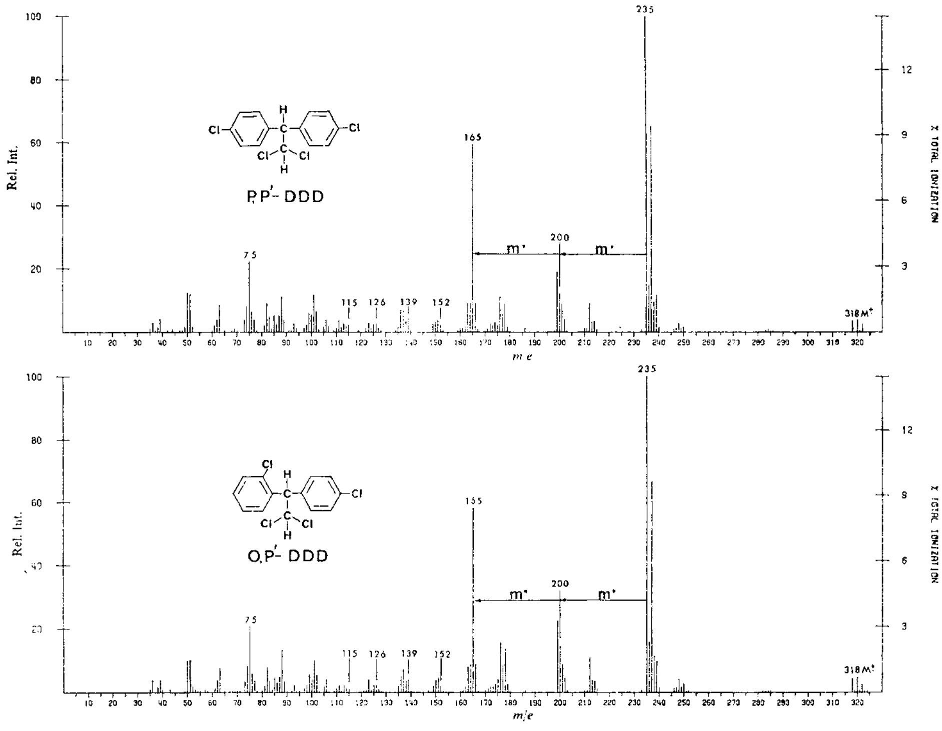
* FDA Primary Std.

work are chlorinated aromatic pesticidal compounds which consist of a diphenylmethane, a diphenylethylene, or a diphenylmethanol structure. The compounds p,p'-DDT and *p,p'*-DDE were briefly discussed by Jorg, Houriet and Spiteller.[7] The compounds examined are listed in Table 1.

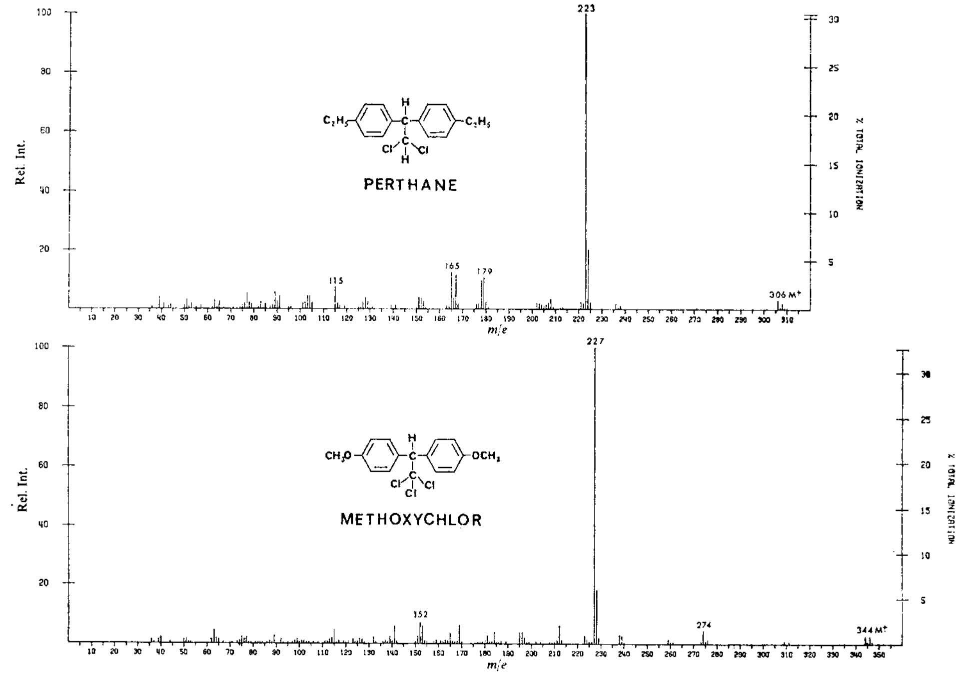
Treatment of data. The mass spectra of the pesticides are presented as bar graphs in Figs 1 to 12.



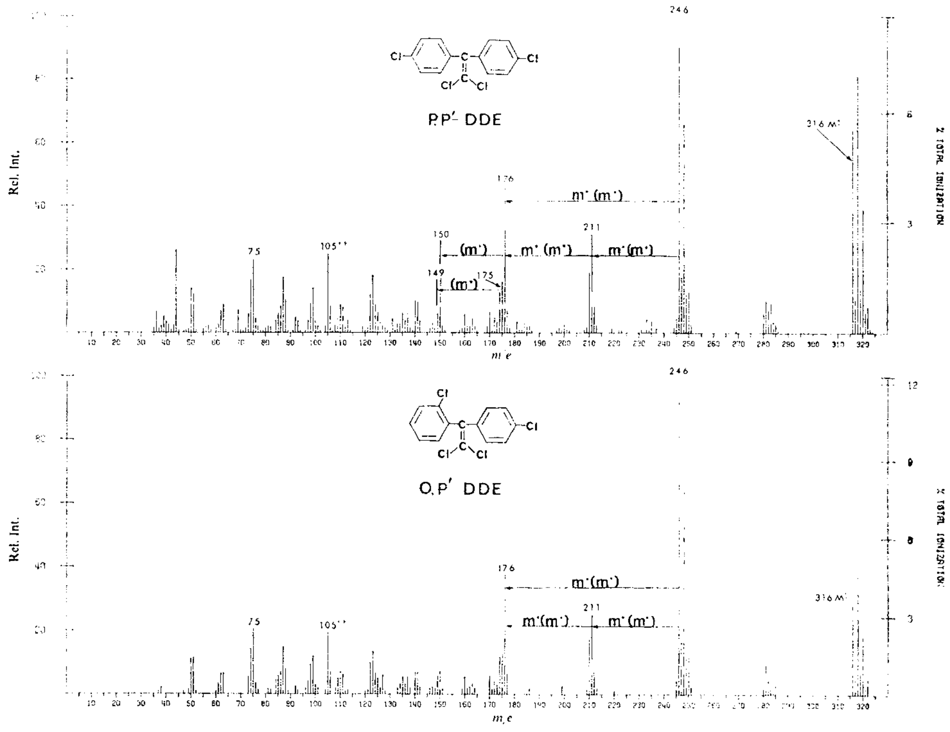
FIGS. 1 and 2



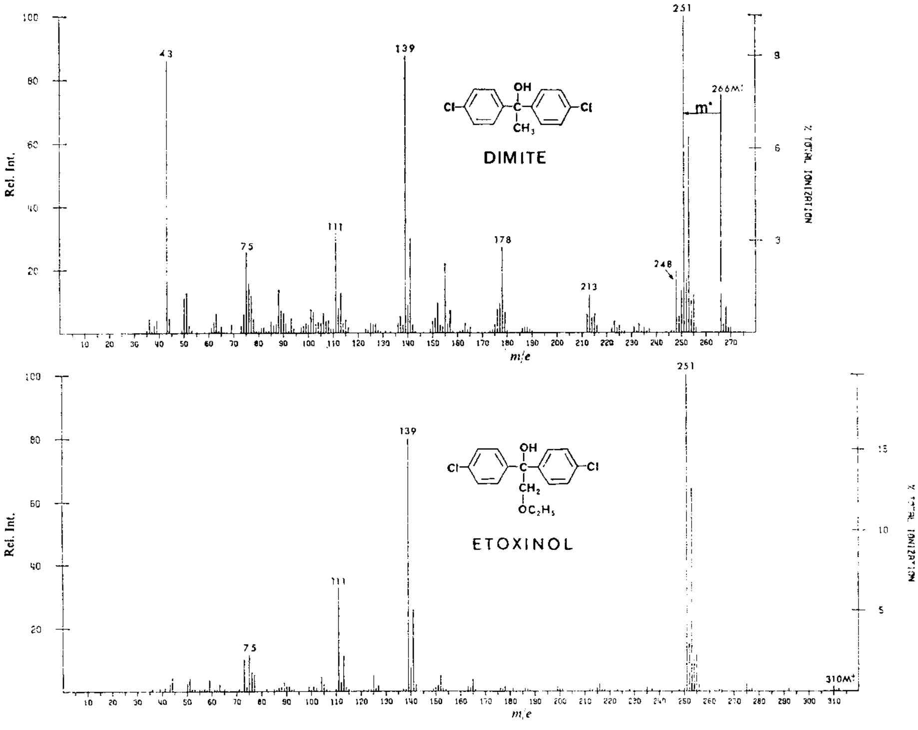
Figs. 3 and 4



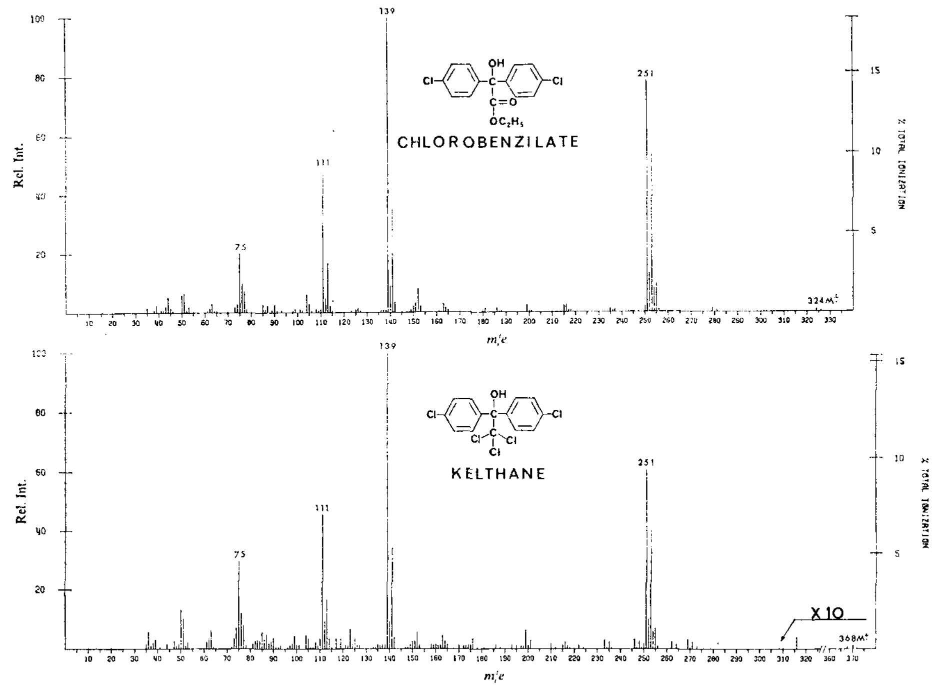
Figs. 5 and 6



Figs. 7 and 8



Figs. 9 and 10



FIGS. 11 and 12

If a metastable peak is observed, the metastable transition is indicated by m* on the figures and also by (m*) when confirmed or identified using the defocusing technique.[8] Since the relative abundances of the metastable peaks for these compounds are very small (<0·1%) no special effort was made to establish their presence unless they were pertinent.

DISCUSSION

EXAMINATION of the spectra discloses that the R′ group is labile for all the compounds with the exception of the DDE isomers. The DDE isomers do not fragment by rupture of the double bond, which is not surprising since fragmentation generally occurs alpha or beta to the double bond. Accordingly, the R′ group is not lost from the molecular ion; this is why the molecular ion of each DDE isomer is much more intense than it is for the other pesticides.

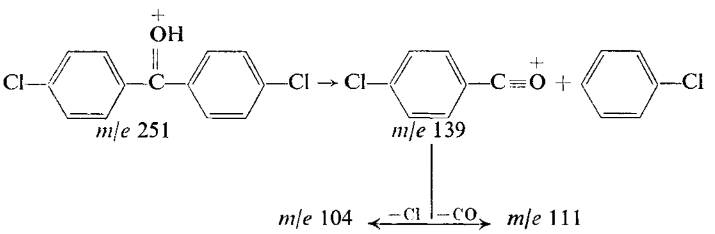
A substituted phenyltropylium ion could be a structure for the *m/e* 235 ion of the DDT and DDD isomers and for the *m/e* 227 ion and the *m/e* 223 ion of methoxychlor and Perthane, respectively, as suggested for *p,p′*-DDT by Jorg *et al.*[7] Meyerson *et al.*[9] postulated the phenyltropylium ion for the structure of the [M — 15] ion of ortho substituted diphenylmethanes. Williams *et al.*[10] used deuterium labeling studies of diphenylmethanol to show that hydrogen scrambling between phenyl rings occurs through reversible ring expansion to yield a cycloheptatriene structure. The larger percent total ion current (*ca.* 31·5%) observed for methoxychlor (*m/e* 227) and Perthane (*m/e* 223), as compared to *ca.* 14% for the DDT (*m/e* 235) and DDD (*m/e* 235) isomers, could be attributed to stabilization of the product ion by the methoxy and ethyl groups of methoxychlor and Perthane, respectively.

Metastable peaks indicate that the second most abundant ion (*m/e* 165) of the DDT and DDD isomers results from stepwise decomposition of the two R groups from the *m/e* 235 ion mentioned above. This process is of only minor significance for methoxychlor and Perthane. The structure of the *m/e* 165 ion will be discussed later.

The DDE isomers yield abundant ions by stepwise cleavage of two chlorine atoms from the molecular ion. The [M — 2Cl] ion (*m/e* 246) is the base peak, and its structure will also be discussed later.

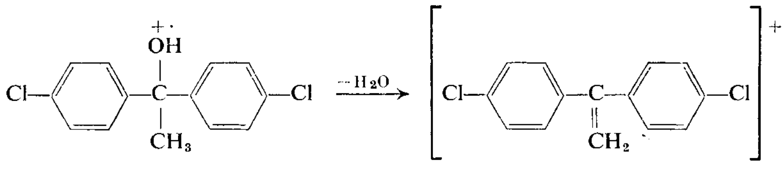
The DDT isomers can be distinguished because there are subtle differences in their mass spectra. The *o,p*-isomer yields an ion by loss of HCl from the [M — Cl] ion, which is more significant than the [M — 2 Cl] ion. For the *p,p'*-isomer, the [M — 2 Cl] ion is more significant. The DDE isomers can be distinguished by significant differences in the percent total ion current of several characteristic peaks (*m/e* 316, *m/e* 246, *m/e* 210, *m/e* 176). As is frequently the case in mass spectrometry, however, the DDD isomers cannot be readily distinguished by their spectra.

Fragmentation of the compounds in Group III is markedly affected by the hydroxyl group. The [M — R'] product ion does not subsequently lose the R substituent as is observed for the DDT and DDD isomers, but could fragment by the scheme below for Kelthane.



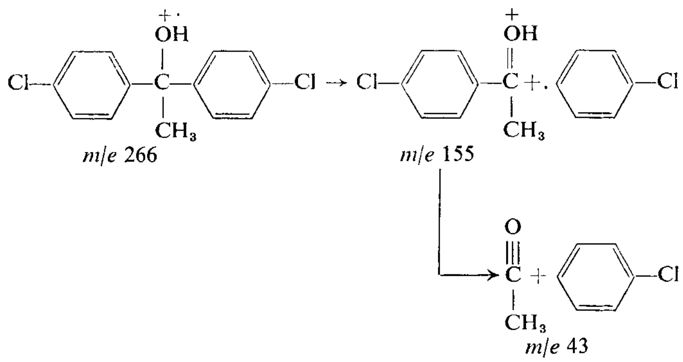
An alternative pathway for the chlorobenzoyl ion instead of the 4-center hydrogen transfer shown above could result also by two separate cleavages with the formation of the chlorobenzene and hydrogen radicals.

The R' substituent significantly affects the fragmentation of Dimite, the only compound of this group that undergoes dehydration of the molecular ion. A metastable peak is not observed.



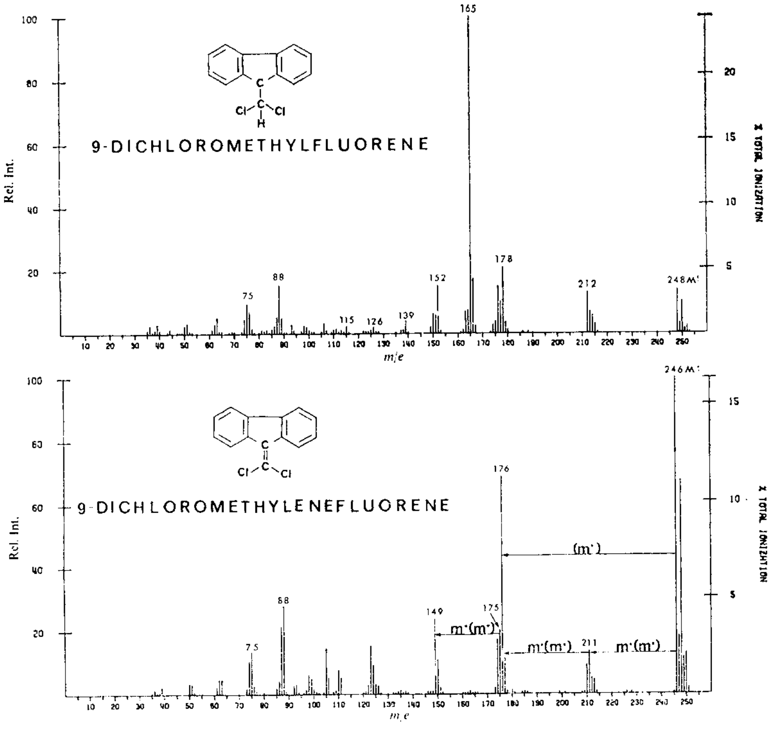
The *m/e* 248 ion subsequently loses Cl to yield abundant ions at *m/e* 213 and *m/e* 178. Dimite also undergoes fragmentation by cleavage between the aliphatic carbon and the ring to form the *m/e* 155 ion, which subsequently decomposes to form the acetyl ion.

The identification of gaseous ions produced by electron-impact is a formidable task. Furthermore, the literature is replete with examples of ionic species whose structures seem obvious but which upon closer scrutiny are quite different from what they seem.[11] The fluorenyl ion[7] was said to be obviously the structure of the *m/e* 165 ion of *p,p'*-DDT. Bowie *et al.*,[12] using deuterium labeling, showed evidence for the



formation of the m/e 165 ion from substituted oxazoles, which they indicated was the fluorene cation. In order for the DDT and DDD isomers to have the fluorenyl ion structure, hydrogen scrambling must occur. It has been demonstrated by deuterium labeling studies that hydrogen scrambling occurs during the fragmentation of diphenylmethanol and diphenylmethylchloride.[10] Hydrogen scrambling could also account for the similarities in the spectra of the DDT isomers and in the spectra of the DDD isomers.

Since four pesticides in this study yield an abundant common m/e 165 ion, this offers an excellent system for elucidating the identity or non-identity of the common m/e 165 ion by comparison with 9-dichloromethylfluorene (9-DCMF) (see Fig. 13).



FIGS. 13 and 14

It seems plausible that the *m/e* 165 ion of 9- DCMF would have the fluorenyl structure, because its formation involves only the loss of the $HCCl_2$ moiety from the molecular ion by simple bond cleavage.

The *m/e* 165 ions of the DDT and DDD isomers did not yield any metastable peaks. Accordingly, the metastable ratio method[13] is not applicable in elucidating the identity or non-identity of this ion. It should be mentioned that a metastable transition is not observed for the *m/e* 165 ion of 9-dichloromethylfluorene as precursor.

Since completely identical breakdown patterns[14] imply a common structure and internal energy distributions, a logical approach would be to compare the significant portions of the spectra of the pesticides with the spectrum of 9-DCMF. Inspection of the 70 eV spectra of *o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDD, and *p,p'*-DDD, and of 9-DCMF (see Figs. 1 to 4, 14) show that the spectra below *m/e* 165 are very similar. If the structures are identical, however, they should also be similar at the lower beam energies. Accordingly, the spectra of the pesticides and 9-DCMF were recorded at various electron energies. The ions which are of major significance at the lower beam energies are listed in Table 2. Even though several of these peaks are as little as 0·1 %, these measurements are significant because the signal to noise ratio was at least 7/1. Furthermore, the spectrum of each compound was obtained several times and on various days with essentially the same results as shown in Table 2.

Table 2. Significant mass spectral data for relevant pesticides and 9-dichloromethylfluorene (9-DCMF) recorded at various electron energies

Intensity normalized to *m/e* 165 = 100										
	70 eV					27 eV				
m/e	DDT *p,p'*	DDT *o,p'*	DDD *p,p'*	DDD *o,p'*	9-DCMF	DDT *p,p'*	DDT *o,p'*	DDD *p,p'*	DDD *o,p'*	9-DCMF
152	1·2	2·3	2·6	3·6	3·1	0·9	1·3	1·8	2·9	3·3
151	3·5	4·5	5·2	6·4	4·4	1·1	1·5	2·1	3·2	3·1
139	3·2	3·4	5·6	5·7	2·6	0·9	1·0	2·9	3·1	1·4
126	2·4	3·0	2·7	3·0	1·4	0·2	0·3	0·2	0·5	0·3
115	1·6	1·7	1·0	1·9	1·8	0·5	0·5	0·6	0·7	1·0
	30 eV					25 eV				
152	1·0	1·6	2·4	3·3	3·9	0·5	1·0	1·3	2·1	2·6
151	2·2	2·6	3·3	4·4	4·4	0·7	1·0	1·3	2·1	2·2
139	1·5	1·6	4·1	4·2	2·1	0·5	0·6	2·3	2·7	1·0
126	0·4	0·7	0·4	0·7	0·5	0·1	0·3	0·1	0·3	0·2
115	0·8	0·9	0·9	1·0	1·4	0·3	0·3	0·3	0·4	1·0

Inspection of the data in Table 2 shows that the intensities are also similar at the lower beam energies except for the intensities of the *m/e* 152 ions. Furthermore, at 30 eV the relative intensity of the *m/e* 152 ion of 9-DCMF increases; this is not observed in the pesticide spectra. In addition, the intensity of the *m/e* 152 ion of 9-DCMF at 27 eV is greater than that of the *m/e* 151 ion; whereas the intensity of the *m/e* 151 ion of the pesticides is always greater than the intensity of the *m/e* 152 ion. These subtle differences in intensities could be attributed to a multiple pathway for the *m/e* 152 ion of 9-DCMF. The *m/e* 152 ion of 9-DCMF could arise also by the loss of acetylene from the *m/e* 178 ion [M − 2 Cl]. The increase at the lower electron energy could be due to the lower activation energy for the loss of acetylene. These observations suggest that the *m/e* 165 ion of the pesticides and of 9-DCMF are of a common structure.

Elucidation of the identity or non-identity of the *m/e* 246 ion of the DDE isomers was also undertaken. It is conceivable that this ion could have the 9-dichloromethylene fluorene (9-DCMeF) structure, which is closely related to the fluorenyl ion structure. Since the *m/e* 246 ion of both isomers and of 9-DCMeF gives two competing metastable transitions, the metastable ratio method[13] can be used to characterize this ion directly. Accordingly, the metastable ratios obtained for the two DDE isomers were compared with the ratio obtained for 9-DCMeF; the values are listed in Table 3. Inspection of the data in Table 3 shows that the ratio values for the two competing metastable transitions for both pesticides are similar at 70 eV and 30 eV. Although the ratio values are not the same at the two beam energies, they are not significantly different. In a recent review,[13] it was pointed out that if the metastable abundance ratio does not change significantly with beam energy the metastable ratio method is valid for establishing the identity or non-identity of a given ion. Note that the metastable ratio obtained for 9-DCMeF is significantly different from the ratios obtained for the DDE isomers. This does not exclude the possibility, however, that some of the *m/e* 246 ion of the DDE isomers might have the 9-DCMeF structure.

TABLE 3. METASTABLE RATIO VALUES FOR *o,p′*-DDE, *p,p′*-DDE AND 9-DICHLOROMETHYLENEFLUORENE

	70 eV R	30 eV R
o,p′-DDE	2·31 ± 0·03*	2·63 ± 0·04*
	2·34 ± 0·02†	2·69 ± 0·01†
	2·34 ± 0·05*	2·40 ± 0·06*
p,p′-DDE	2·25 ± 0·02*	2·49 ± 0·05*
	2·09 ± 0·01*	2·55 ± 0·03‡
	2·28 ± 0·02*	2·32 ± 0·03*
9-DCMeF	5·04 ± 0·09	5·54 ± 0·11

* 10 observations.
† 15 observations.
‡ 5 observations.

$$R = \frac{\text{relative abundance of m* for } 246^{+\cdot} \rightarrow 211^{+}}{\text{relative abundance of m* for } 246^{+\cdot} \rightarrow 176^{+\cdot}}$$

Note: Ratio calculated using equation (4.1) and the error using equation (4.2) p. 190, N. H. Hansen, W. M. Hurwitz and W. G. Madow, *Sample Survey Methods and Theory*, Vol. I, John Wiley, New York, 1953.

The mass spectrum of 1,1-dichloro-2,2-bis(phenyl)ethylene (see Table 4) indicates that the *m/e* 246 ion of the DDE pesticides is comprised of isomers. This compound loses two chlorine atoms from the molecular ion, which indicates that for the DDE isomers it is possible to lose the chlorines from the unsaturated carbon atom as well as from the rings in forming the *m/e* 246 ion.

TABLE 4. SELECTED PEAK INTENSITIES OF 1,1-DICHLORO-2,2-BIS-(PHENYL) ETHYLENE

m/e	Rel. int.-%	*m/e*	Rel. int.-%
88	22·7	165	5·5
93	11·8	176	30·0
106*	11·4	177	25·4
125	5·4	178 [M − 2Cl]	100
135	3·6	212 [M − HCl]	24·5
137	4·5	213 [M − Cl]	14·5
150	8·2	214	8·2
151	11·8	215	5·4
152	10·9	248	50·0
		250	32·7

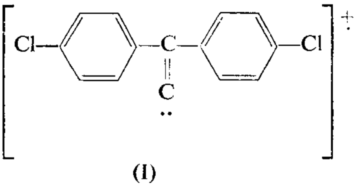
* Doubly charged ion.

The mass spectrum of 1,1-dichloro-2,2-bis(*p*-bromophenyl)ethylene revealed some very interesting features. This compound yields appreciable ion current (see Table5).

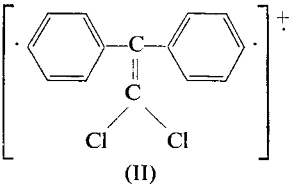
TABLE 5. SELECTED PEAKS OF 1,1-DICHLORO-2,2-BIS(*p*-BROMOPHENYL)ETHYLENE

m/e	Fragment	Intensity normalized to 10 for *m/e* 334
334	[M − 2Cl]	10
290	[M − BrCl]	25
246	[M − 2Br]	45

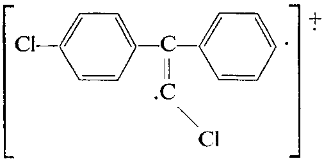
due to the loss of two bromine atoms from the rings, the loss of a bromine and chlorine atom and the loss of two chlorine atoms from the unsaturated carbon. Since the Hammett substituent constants[15] for the *p*-Br and *p*-Cl are about the same, it is valid to infer[16] that for the *p,p'*-DDE isomer the *m/e* 246 ion might be comprised of the following structures* and that they possibly form in about the same proportions,† as shown for the compound listed in Table 5. The *o,p'*-isomer could have two additional structures, assuming that hydrogen scrambling does not occur.



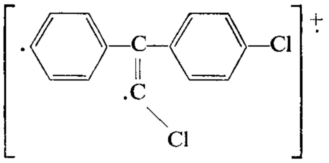
(I)



(II)



(III)



(IV)

---

* These structures as shown serve only to demonstrate the number of possibilities and are not intended to be representative of the actual structures.

† Since structures III and IV [M − BrCl] cannot be distinguished in the gas phase, the proportionate amount of each cannot be determined.

CONCLUSION

Our experimental data support the fluorenyl ion structure for the structure of the *m/e* 165 ion of the subject pesticides. The studies on the identity of the *m/e* 246 ion of the DDE isomers show that the structure elucidation for this ion is even more complex than that for the *m/e* 165 ion. The experimental data indicate that the *m/e* 246 ion of the DDE isomers is probably comprised of more than one structure.

EXPERIMENTAL

Recording technique. The spectra were recorded with an Atlas CH4-mass spectrometer equipped with a probe inlet system.[17] With the compounds studied, use of the probe was necessary to avoid thermal degradation in heated reservoirs. The following conditions apply to the Atlas spectra: ion source regulation at 250°C, electron energy of 70 volts, magnetic scanning and accelerating potential of 3 kV. The temperatures of the samples during evaporation ranged from 20°C for methoxychlor and Dimite to 62°C for Kelthane. The metastable transitions determined by the defocusing technique were obtained with an AEI MS-9 mass spectrometer. The bar graph data presented in Figs. 1 to 14 were obtained using a Calcomp plotter.

Dimite, $C_{14}H_{12}Cl_2O$, was prepared by the addition of *p*-chlorophenyl magnesium bromide to ethyl formate. The product was recrystallized from ligroin (b.p. 100 to 115°C); m.p. 66°C.

Etoxinol, $C_{16}H_{16}Cl_2O_2$, was prepared by a published method;[18] m.p. 58 to 59°C.

9-Dichloromethylfluorene, $C_{14}H_{10}Cl_2$, was prepared by the addition of dichlorocarbene, prepared from sodium trichloroacetate,[19] to fluorene. The product was recrystallized from ligroin (b.p. 65 to 75°C); m.p. 101°C.

9-Dichloromethylenefluorene, $C_{14}H_8Cl_2$, was prepared by the reaction between 9-fluorenone, carbon tetrachloride and triphenylphosphine.[20] The product was recrystallized from methanol; m.p. 134°C.

1,1-Dichloro-2,2-bis(*p*-bromophenyl)ethylene, $C_{14}H_8Br_2Cl_2$, was prepared by a published method;[21] m.p. 118 to 119°C.

The i.r. and n.m.r. spectra of the aforementioned compounds were consistent with the proposed structures.

Acknowledgments—The authors are grateful to the Pesticide Standards Branch, Division of Pesticides, Food and Drug Administration for the purified pesticides listed in Table 1. The authors thank Albert E. Pohland for assistance in synthesizing compounds listed under Experimental, Jo-Yun T. Chen and her group for the i.r. data, and Ernest Lustig and his group for the n.m.r. data of the synthesized compounds (all of the Division of Food Chemistry and Technology). The authors thank Henry Fales and Eli Gilbert, respectively, of the National Institutes of Health, Bethesda, Maryland, for the defocusing studies and for the bar graph data (Figs. 1 to 14), and Henry Rosenstock and Vernon Dibeler of the National Bureau of Standards, Gaithersburg, Maryland, for helpful suggestions.

REFERENCES

1. J. N. Damico and W. R. Benson, *J. Assoc. Offic. Agr. Chemists* **48,** 344 (1965).
2. J. N. Damico, *J. Assoc. Offic. Anal. Chemists* **49,** 1027 (1966).
3. J. N. Damico, R. P. Barron, and J. M. Ruth, *Org. Mass Spectrom.* **1,** 331 (1968).
4. R. L. Baron, J. A. Sphon, J. T. Chen, E. Lustig, J. D. Doherty, E. A. Hansen and S. Kolbye, *J. Agr. Food Chem.* **17,** 883 (1969).
5. J. R. Pardue, Abstracts of Papers, 156th National Meeting of the American Chemical Society, Atlantic City, NJ, 8th to 13th September 1968, Abstract No. 143 AGFD.
6. J. N. Damico, J. T. Chen, C. E. Costello and E. O. Haenni, *J. Assoc. Offic. Anal. Chemists* **51,** 48 (1968).
7. J. Jorg, R. Houriet and G. Spiteller, *Monatsh. Chem.* **97,** 1064 (1966).
8. (a) M. Barber and R. M. Elliot, ASTM Committee E-14, 12th Annual Conference on Mass Spectrometry and Allied Topics, Montreal, June 1964; (b) J. H. Futrell, K. R. Ryan and L. W. Sieck, *J. Chem. Phys.* **43,** 1832 (1965); (c) K. R. Jennings, *J. Chem. Phys.* **43,** 4176 (1965); (d) K. R. Jennings in R. Bonnett and J. G. Davis (Eds), *Some Newer Physical Methods in Structural Chemistry*, United Trade Press, London, 1967, p. 105; (d) T. W. Shannon, T. E. Mead, C. G. Warner and F. W. McLafferty, *Anal. Chem.* **39,** 1784 (1967).

9. S. Meyerson, H. Drews and E. K. Fields, *J. Am. Chem. Soc.* **86,** 4964 (1964).
10. D. H. Williams, R. S. Ward and R. G. Cooks, *J. Chem. Soc.* (*B*) 522 (1968).
11. S. Meyerson and J. L. Corbin, *J. Am. Chem. Soc.* **87,** 3045 (1965).
12. J. H. Bowie, P. F. Donaghue and H. J. Rodda, *Tetrahedron* **24,** 3965 (1968).
13. R. G. Cooks, I. Howe and D. H. Williams, *Org. Mass Spectrom.* **2,** 137 (1969).
14. D. H. Williams, R. G. Cooks and I. Howe, *J. Am. Chem. Soc.* **90,** 6759 (1968).
15. J. Hine, *Physical Organic Chemistry*, 2nd Edn, McGraw-Hill, New York, 1962, p. 87.
16. M. M. Bursey, *Org. Mass Spectrom.* **1,** 31 (1968).
17. C. Brunnee, ASTM Committee E-14, 14th Annual Conference on Mass Spectrometry and Allied Topics, Dallas, Texas, 22nd to 27th May 1966, p. 410.
18. F. Hafliger, U.S. Patent 2,654,688 (to J. R. Geigy A-G) 6th October 1953.
19. E. K. Fields, U.S. Patent 3,230,267 (to Standard Oil Co., Chicago, Ill.) 20th March 1962.
20. R. Rabinowitz and R. Marcus, *J. Am. Chem. Soc.* **84,** 1312 (1962).
21. O. G. Backeberg and J. L. C. Marais, *J. Chem. Soc.* 803 (1945).