The Fragmentation of Dibenzo-p-dioxin and Its Derivatives under Electron Impact

N. P. Buu-Hoï[+] and G. Saint-Ruf

Centre Marcel Délépine du C.N.R.S.
45-Orleans-La Source

and

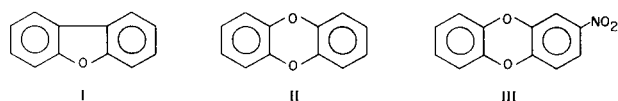M. Mangane

Institut Lannelongue de Recherches sur la Cancérogénèse chimique et hormonale
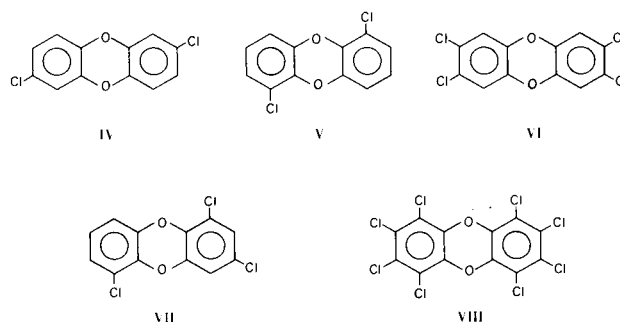45-Orlean-La Source and 92-Vanves, France

Whereas the behavior of benzofuran (I) and its derivatives under electron impact has been extensively investigated by two groups of authors (1,2), a similar general study on the closely related dibenzo-p-dioxin (II) has not been reported hitherto. Recently, mass-spectrometric data concerning 2,3,7,8- and 1,3,6,8-tetrachlorodibenzo-p-dioxin have been published by Baughman and Meselson (3) and by ourselves (4), but in these early spectra of ours, the relative abundances of several ions were distorted on account of catalytic decomposition in the spectrometer (probably suffered by the samples on a filament which had retained metal traces from previous measurements with organometallic derivatives) (5).

In the framework of our studies on the meso-heterocyclic analogs of anthracene and 9,10-dihydroanthracene (6), we were led to investigate more closely the dibenzo-p-dioxin series. The present paper deals with the behavior of dibenzo-p-dioxin itself, its 2-nitro derivative III, and five of its chloro derivatives (IV to VIII). The sub-
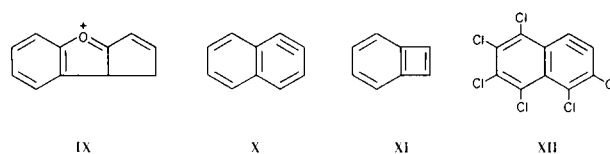
stances investigated have all been described previously in the literature (7,8) except for 1,6-dichlorodibenzo-p-dioxin (IV). We prepared all the chloro compounds by means of a recently reported procedure for the cyclization of o-chlorinated phenols (4), which is more convenient than Tomita's method (7) and also more satisfactory as regards the purity of the reaction-products. 2,7-Dichlorodibenzo-p-dioxin (V) was thus obtained by cyclization of 2,4-dichlorophenol in yields considerably

+ Deceased 28 January 1972.

higher than by the previously used halogenation of (I) (8) and in a purer state; a similar cyclization of 2,3-dichlorophenol readily afforded 1,6-dichlorodibenzo-p-dioxin. It should, however, be kept in mind that, as in many dehalogenation reactions induced by alkaline reagents, more or less extensive rearrangements cannot be ruled out in these cyclizations.

Dibenzo-p-dioxin showed considerable stability under electron impact, as witnessed by the presence of a prominent peak corresponding to the doubly charged molecular ion in its mass spectrum. As with dibenzofuran, the fragmentation pattern is relatively simple. The molecular ion (which corresponds to the base peak) extrudes successively carbon monoxide and hydrogen to give the stabilized species (VIII; m/e = 155) which loses carbon monoxide in its turn to give the naphthyl ion (m/e = 127); a second mode of decomposition of the molecular ion leads to the naphthalene species (m/e = 128) through the loss of 2 CO.
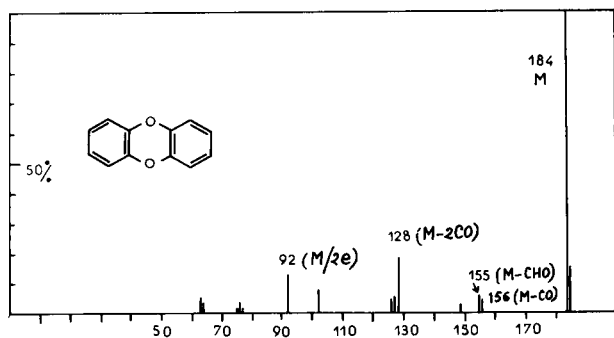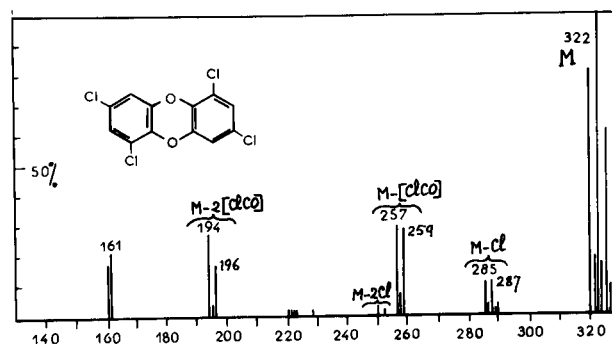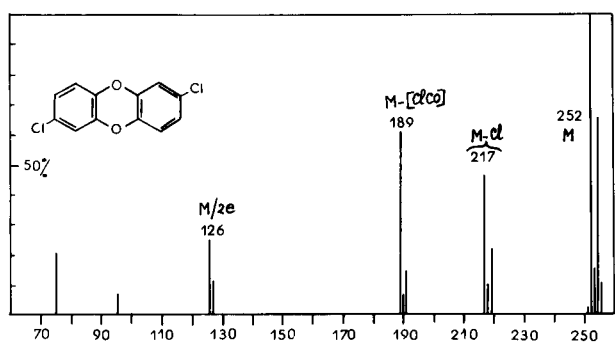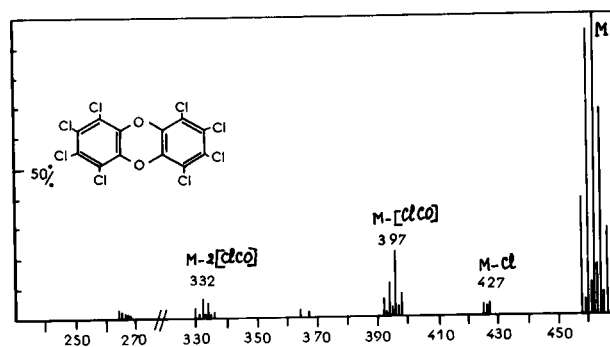
Figure 1

Figure 2

Figure 3

Figure 4
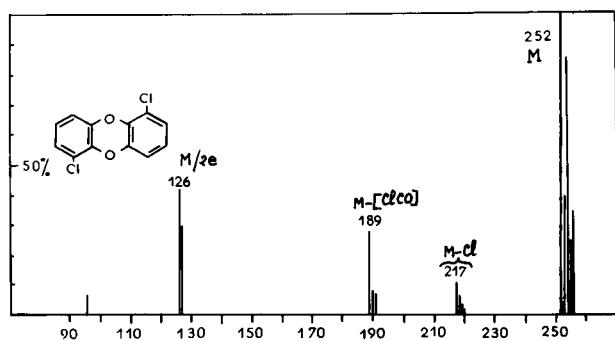

Figure 5
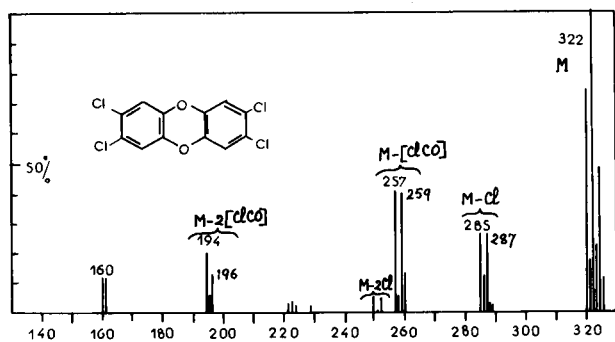

Figure 6

All these steps are authenticated by the presence of the following metastable peaks:

Transition	m* Calcd.	m* Found
184 → 128	89.04	89.1
184 → 156	132.26	132.4
156 → 155	154	154
156 → 128	105.02	104
155 → 127	104.05	106

Further peaks observed correspond to the decomposition of naphthalene to the cyclobutabenzene species (XI; m/e = 102) with loss of acetylene, and to the dehydrogenation of the naphthyl ion to naphthalyne (X; m/e = 126).

Similar fragmentation patterns are observed with the various chloro derivatives of dibenzo-p-dioxin, except that here, the decarbonylation ions extrude chlorine instead of hydrogen, and that in the case of the two dichloro compounds (IV; Figure 2) and (V; Figure 3), the second decarbonylation-dechlorination sequence is negligible. This is the more remarkable as this last sequence reappears with both the two tetrachloro compounds (VI; Figure 3)

and (VII; Figure 4) (with the formation of the corresponding dichloronaphthalyne species) and also in the case of octachlorodibenzo-p-dioxin (VIII; Figure 5) (with the formation of hexachloronaphthalyne (XII). In addition, all the chlorinated substances examined show more or less prominent peaks corresponding to a simple dechlorination of the molecular ion. Here again, the various fragmentation reactions reported are confirmed by the presence of the relevant metastable peaks.

2-Nitrodibenzo-p-dioxin (III) also conforms to the general fragmentation pattern outlined above, as shown in the following identifiable peaks:

m/e	Relative Abundance (%)	Nature of the ion (a)
229	100	molecular (M^+)
201	3	$[M\text{-}CO]^+$
200	8	$[M\text{-}CHO]^+$
183	44	$[M\text{-}NO_2]^+$
155	22	$[M\text{-}(NO_2+CO)]^+$
154	3	$[M\text{-}(NO_2+CHO)]^+$
128	12	$(C_{10}H_8)^+$
127	4	$(C_{10}H_7)^+$
126	2	$(C_{10}H_6)^+$
114.5	6	M^{2+}
76	12	benzyne $(C_6H_4)^+$

(a) No metastable peaks observed in this spectrum.

EXPERIMENTAL

Preparation of Substances.

Dibenzo-p-dioxin.

This compound was prepared by Gilman and Dietrich's method (8), crystallized from aqueous ethanol as colorless needles, m.p. 122°; lit. 118-119° (7); 120-122° (8).

1,6-Dichlorodibenzo-p-dioxin.

This compound was prepared in 50% yield by the following procedure: an intimate mixture of 2,3-dichlorophenol (1 mole) and anhydrous potassium carbonate (0.5 mole) was heated at 240-250° in a metal bath with catalytic amounts of copper powder in a reactor (1 l.) equipped with a sublimation device and a refrigerating column until sublimation subsided. The sublimate was dissolved in benzene, the benzene solution washed with 10% aqueous sodium hydroxide, then with water, dried (sodium sulfate) and the solvent distilled off; the residue recrystallized from ethanol as colorless needles, m.p. 190-191°.

Anal. Calcd. for $C_{12}H_6Cl_2O_2$: C, 56.9; H, 2.4. Found: C, 56.9; H, 2.6.

2,7-Dichlorodibenzo-p-dioxin.

This compound was similarly prepared from 2,4-dichlorophenol, had m.p. 206°; lit. 201-203° (8); yield, 50%. Gilman and Dietrich (8) obtained 0.2 g. of this compound starting from 4.6 g. of II; nmr spectrum in deuteriochloroform, a singlet (τ = 2.77) and a massif (centered at τ = 3.34).

Mass Spectrometry.

The mass spectrometer used was a high resolution Thomson TSN-218 apparatus (70 eV), with direct introduction. The experimental conditions used were: for compound (II), t° = 165° (10 Kv); for compound (III), t° = 165° (9 Kv); for compound (IV), 155° (10 Kv); for compound (V), t° = 140° (9 Kv); for compound (VII), t° = 150° (9.5 Kv), and for compound (VIII), t° = 190° (8 Kv).

REFERENCES

(1) B. Pring and N. E. St. Jernström, *Acta Chem. Scand.*, 22, 549 (1968).

(2) E. N. Givens, L. Alexakos, and P. B. Venuto, *Tetrahedron*, 25, 2407 (1969).

(3) R. W. Baughman and M. S. Meselson, paper presented at the American Chemical Society, 162nd National Meeting, Washington, D. C. (September 17, 1971).

(4) N. P. Buu-Hoï, G. Saint-Ruf, P. Bigot, and M. Mangane, *C. R. Acad. Sci.* (Paris), 273, [D], 708 (1971).

(5) We thank Professor M. S. Meselson and Dr. R. W. Baughman for having drawn our attention to these distortions. Further investigations on such catalytic decompositions and their possible use for analytical purposes are being carried out.

(6) For phenoxthiin derivatives, see E. Lescot, N. P. Buu-Hoï, and N. D. Xuong, *J. Chem. Soc.*, 2408 (1956); for phenothiazine, see N. P. Buu-Hoï and N. Hoán, *J. Chem. Soc.*, 1834 (1951); for phenoxazine and phenoselenazine, see P. Muller, N. P. Buu-Hoï and R. Rips, *J. Org. Chem.*, 24, 37, 1699 (1959); for phenarsazine, see N. P. Buu-Hoï, M. Mangane, and P. Jacquignon, *J. Heterocyclic Chem.*, 3, 149 (1966).

(7) M. Tomita, *J. Pharm. Soc. Japan*, 52, 49 (1952); M. Tomita, S. Ueda and M. Narasida, *Yakugaku Zasshi*, 79, 186 (1959); *Chem. Abstr.*, 53, 13152f (1959).

(8) H. Gilman and J. J. Dietrich, *J. Am. Chem. Soc.*, 79, 1439 (1957).