The Mass Spectra of Polychlorinated Biphenyls

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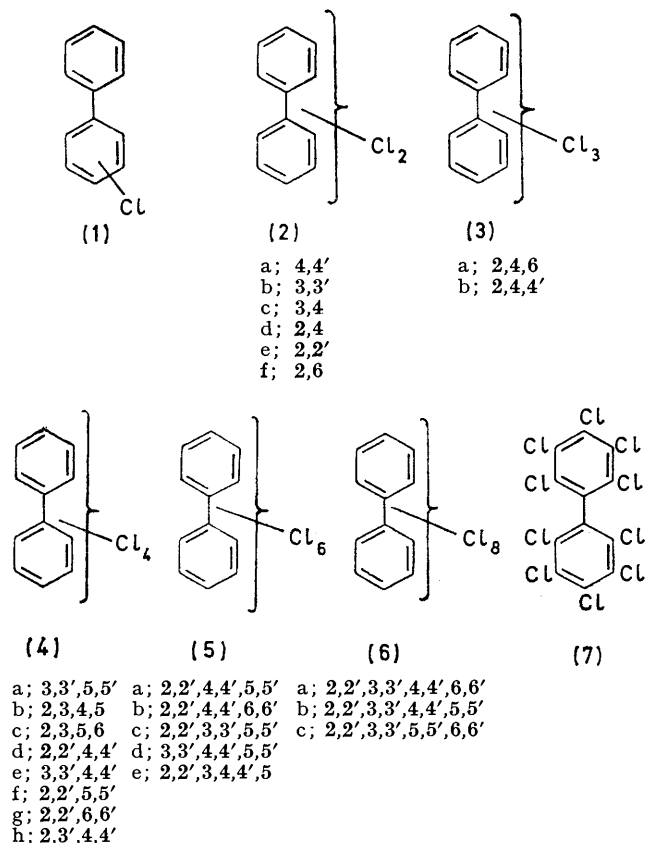
The mass spectra of several di- and tetra-chlorobiphenyls suggested randomization of chlorine over both phenyl rings in the molecular ion prior to fragmentation. The exceptions, 2,2'- and 2,6-dichloro-, 2,2',4,4'-, 2,2',5,5'-, 2,3,5,6-, and 2,2',6,6'-tetrachloro-biphenyls, all contain two or more chlorine atoms *ortho* to the Ph–Ph bond and their metastable ion intensities which result from the $M \longrightarrow M - Cl_2$ reaction are markedly different from those of the other isomers. The primary ion spectra of most isomeric compounds are similar, with successive losses of Cl· from the molecular ion. This process is often accompanied by expulsion of HCl from the lower chlorine homologues (2)—(5) but only the reactions which expel Cl· are accompanied by metastable ions. The ion kinetic energy spectra of the di- and tetra-chloroisomers confirm the suggested fragmentation pathways.

THE mass spectra of aromatic compounds provide evidence that extensive skeletal rearrangements, in which carbon and hydrogen atoms are rapidly equilibrated, occur upon electron impact. Monocyclic aromatic compounds (*i.e.* benzene,[1] halogenobenzenes,[2,3] phenylpropyne,[4] phenyl azide,[5] furan,[6] |and benzonitrile [7]) exhibit considerable H–D randomization in the molecular ion prior to fragmentation. Recently two groups [8,9] have investigated the fragmentation of [2]H- and ^{13}C-labelled benzene and concluded that both carbon and hydrogen atoms are equilibrated in the molecular ion. Bicyclic compounds such as biphenyl,[10] benzothiophen,[11] substituted diphenylacetylenes,[12] and stilbene [13] also show considerable H–D equilibration either in the molecular ion or some subsequent decomposition ion.

The mechanisms involved in the extensive atomic randomizations upon electron impact have not been fully ascertained although clearly they must involve a variety of processes in which both carbon–carbon and carbon–hydrogen bonds are broken. It has been proposed that photochemical-like scrambling in which only carbon–carbon bond fission occurs is a possible pathway, but studies [8,9] indicate that carbon–hydrogen bond cleavage must also be an important process.

Recently it has also been shown that o-, m-, and p-monohalogentoluenes [14] and dihalogenobenzenes [3] lose positional identity upon electron impact. The halogen atom in monosubstituted halogenobiphenyls [15] is also equilibrated in the molecular ion prior to fragmentation. In the monosubstituted biphenyls (1) it was not possible to distinguish between substituent scrambling over the two aromatic rings and scrambling only in the substituted ring. If the latter process occurred then the photochemical analogy of randomization is a possible explanation for the simi equilibration of the halogen atom. It was therefore of interest to examine the mass spectra of isomeric polyhalogenated biphenyls, which might

distinguish between the photochemical-like process and other alternatives such as the formation of acyclic ions by both carbon–carbon and carbon–chlorine bond fission.

(1)

(2)
a; 4,4'
b; 3,3'
c; 3,4
d; 2,4
e; 2,2'
f; 2,6

(3)
a; 2,4,6
b; 2,4,4'

(4)
a; 3,3',5,5'
b; 2,3,4,5
c; 2,3,5,6
d; 2,2',4,4'
e; 3,3',4,4'
f; 2,2',5,5'
g; 2,2',6,6'
h; 2,3',4,4'

(5)
a; 2,2',4,4',5,5'
b; 2,2',4,4',6,6'
c; 2,2',3,3',5,5'
d; 3,3',4,4',5,5'
e; 2,2',3,4,4',5

(6)
a; 2,2',3,3',4,4',6,6'
b; 2,2',3,3',4,4',5,5'
c; 2,2',3,3',5,5',6,6'

(7)

The mass spectra of a series of polychlorinated biphenyls (PCBs) were investigated to determine the extent

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of chlorine randomization.[16] Since PCB mixtures are ubiquitous environmental pollutants [17] their general fragmentation pattern and spectral characteristics are also of considerable interest from an analytical point of view. The major ions in the primary ion spectra of six isomeric dichlorobiphenyls (2a—f) are shown in Table 1a. The ion abundance data for all the isomers are similar except that compounds (2c) and (2f) have slightly more abundant ions at m/e 187 and 152 corresponding to loss of Cl· from the molecular ion and $M - Cl$ ion respectively. The fragmentation pathway (Scheme 1) shows

20 eV (Table 1a). The results indicate that for the isomers (2a—d) their decomposing molecular ions (a) and $M - Cl$ ions (b) have similar energy distributions and structures. Since the chlorine atoms of compounds (2a—d) are located both in the same ring as well as in both phenyl rings the results suggest randomization of the chlorine atoms over the 12 carbon atoms of the biphenyl system. This conclusion would not be consistent with chlorine equilibration by simple valence-bond isomerism encountered in photochemical reactions. Ring cleavage resulting in the formation of an array of

TABLE 1a

Relative ion abundances (%) [a] and [metastable ion] : [daughter ion] ratios for the dichlorobiphenyls (2a—f)

| Compound	M	$M - Cl$	$M - HCl$	$M - Cl_2$	$\dfrac{[m_1{}^*]}{[m/e\ 187]} \times 10^3$		$\dfrac{[m_2{}^*]}{[m/e\ 152]} \times 10^5$	
					70 eV	20 eV	70 eV	20 eV
(2a)	100	1·4	6·0	38	15·5	13·5	2·1	1·7
(2b)	100	1·4	6·1	38	15·5	12·0	2·2	1·5
(2c)	100	1·5	6·7	35	16·0	13·0	2·3	1·5
(2d)	100	1·5	7·2	39	17·0	14·0	2·3	1·7
(2e)	100	2·8	7·5	79	5·1	4·0	180	110
(2f)	100	2·4	6·3	35	100	27·0	100	100

Recorded at 70 eV.

TABLE 1b

Ion kinetic energy data for the dichlorobiphenyls (2a—f)

	$m/e\ 222 \rightarrow m/e\ 187$		$m/e\ 187 \rightarrow m/e\ 152$		$m/e\ 222 \rightarrow m/e\ 152$	
Isomer	V_x/V_i [a]	m_x/m_i [b]	V_x/V_i	m_x/m_i	V_x/V_i	m_x/m_i
(2a)	84·4	84·2	81·5	81·3	68·5	68·5
(2b)	84·2	84·2	81·3	81·3	68·3	68·5
(2c)	84·1	84·2	81·1	81·3	68·0	68·5
(2d)	84·3	84·2	81·3	81·3	68·3	68·5
(2e)	84·5	84·2	81·3	81·3	68·2	68·5
(2f)	84·3	84·2	81·2	81·3	68·2	68·5

[a] V_x is observed voltage and $V_i = 400$ V for the Dupont 21–110B model.   [b] m_x = Mass of daughter ion and m_i = mass of parent ion.

loss of both Cl and HCl from the molecular ion followed by expulsion of Cl· from the $M - Cl$ ion to give a strong

SCHEME 1
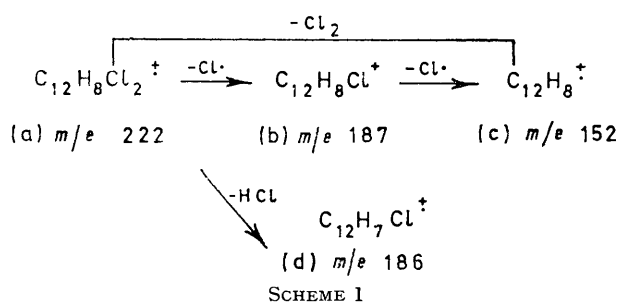
peak at m/e 152. Intense metastable peaks were observed at m/e 157·7 $(m_1{}^*)$ and 122·7 $(m_2{}^*)$ for the reactions (a) ⟶ (b) and (b) ⟶ (c) respectively. Using the kinetic approach [18] the $[m_1{}^*] : [b]$ and $[m_2{}^*] : [c]$ ratios for the above reactions were determined at both 70 and

linear polyunsaturated ions is a possible explanation, since these linear ions could readily facilitate chlorine randomizations by a series of reciprocal electron shifts within the extensive π system. For the ions (a) and (b) produced by isomers (2a—d) upon electron impact the ionic intermediates would thus have the same average energy distributions and kinetic energies.

We have also examined the ion kinetic energy (i.k.e.) spectra of the dichlorobiphenyls. The i.k.e. spectra show the ion decompositions which occur in the first field-free region of the mass spectrometer following acceleration of the ion beam and prior to its impinging upon the beam monitor electrode.[19-21] For the Dupont CEC 21-110B mass spectrometer the electrostatic sector is scanned and the daughter ion peaks are thus recorded. The ratio of the voltage at which the daughter ion appears (V_x) to the voltage of the focused beam (V_i) is directly proportional to the daughter ion : parent ion

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[18] (a) T. W. Shannon and F. W. McLafferty, J. Amer. Chem. Soc., 1966, 88, 5021; (b) M. M. Bursey and F. W. McLafferty, ibid., p. 529; (c) P. Brown, Org. Mass Spectrometry, 1970, 3, 639.
[19] J. H. Beynon, J. W. Amy, and W. E. Baitinger, Chem. Comm., 1969, 723.

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[21] E. M. Chait and W. B. Askew, Org. Mass Spectrometry, 1971, 5, 149.

ratio $(m_x : m_i)$. The results obtained for the dichlorobi-phenyls (2a—f) (Table 1b) confirm the fragmentation reactions (a) ⟶ (b), (b) ⟶ (c), and (a) ⟶ (d) suggested in Scheme 1. The use of i.k.e. spectrometry as a quantitative tool in distinguishing between isomers is currently under investigation, with PCBs and other isomeric compounds as models.

The tetrachlorobiphenyls (4a—h) exhibit remarkably similar primary ion mass spectra (Table 3a) and appear to fragment as shown (Scheme 3). Only the spectrum of isomer (4f) is sufficiently different to distinguish it from the other compounds. Metastable ions are observed at m/e 227·1, 189·8, 155·7, and 166·8 for the reactions (k) ⟶ (l), (l) ⟶ (m), (m) ⟶ (n), and (k) ⟶ (m).

TABLE 2

Mass spectral data of tri-, hexa-, octa-, and deca-chlorobiphenyls

Mass	Relative abundances (%)										
	(3a)	(3b)	(5a)	(5b)	(5c)	(5d)	(5e)	(6a)	(6b)	(6c)	(7)
M^+	100	100	100	100	100	100	100	100	100	100	100
$M^+ - 35$	1	1	2	1	2	1	5	3	6	8	1
$M^+ - 36$	5	4	3	1	1	15	2	11	11	6	~0
$M^+ - 70$	36	35	52	56	54	31	36	38	53	45	65
$M^+ - 71$	2	2	~0	~0	~0	~0	~0	0	~0	~0	~0
$M^+ - 105$	6	7	5	7	3	3	3	3	4	4	8
$M^+ - 106$	10	9	7	5	7	6	5	2	4	3	~0
$M^+ - 140$			22	19	22	15	17	24	33	29	5
$M^+ - 141$			2	2	3	3	2	1	2	~1	~0
$M^+ - 175$			a	a	a	a	a	3	4	3	9
$M^+ - 176$								3	5	2	~0
$M^+ - 210$								a	a	a	32
$M^+ - 211$											~0

^a Doubly charged ions make measurements difficult below this mass.

The primary ion mass spectra of the two trichlorobi-phenyls (3a) and (3b) were also similar (Table 2). The main fragmentation pathway was loss of Cl· and HCl from the molecular ion (e) and subsequent loss of Cl· from both the $M - Cl$ (f) and $M - Cl_2$ (g) ions (Scheme 2).

SCHEME 2

An abundant metastable ion was observed at m/e 190·8 (m_3*) for the reaction (e) ⟶ (f) and the [m_3*] : [m/e 221] ratios for the isomers (3a) and (3b) were 9·4 × 10⁻² and ca. 6·0 × 10⁻² with the metastable ion peak of (3b) much broader than that of the ion from (3a). These characteristics of the metastable ions were the only features of the mass spectral data which distinguished between isomers (3a) and (3b). The remaining metastable ions at m/e 156·5 and 135·1 for the reactions (f) ⟶ (g) and (e) ⟶ (g) were of low abundance and not amenable to measurement.

Examination of the metastable ions in more detail revealed both similarity and diversity between the tetra-chloro-isomers. The metastable ion peaks for the reactions (k) ⟶ (l) and (l) ⟶ (m) were somewhat broadened and [metastable ion] : [daughter ion] ratios were not readily calculated. The metastable ion peak at m/e 166·8 (m_4*) was relatively sharp and intense and the ratio for the reaction (k) ⟶ (m) has been obtained for all the isomers (4a—h) (Table 3a). The ratios for this reaction indicate that for the isomers (4a, b, e, and h) their respective decomposing molecular ions have similar structures, whereas for the other isomers the decomposing molecular ions have different structures. As in the case of the dichlorobiphenyls, the tetrachloro-isomers which have two or more chlorine atoms ortho to the Ph–Ph bond [i.e. (4c, d, g, and f)] decompose in an energetic pathway different from the isomers containing less than two chlorine atoms at these positions [i.e. (4a, b, e, and h)]. The latter isomers thus appear to have all four chlorine atoms equilibrated over the 12 carbon atoms of the biphenyl system, whereas for the other isomers the chlorine substituents are not fully equilibrated. The spectra of all the isomers (4a—h) also show a strong metastable ion peak at m/e 155·5 (m_5*) for the reaction (m) ⟶ (n). The [m_5*] : [m/e 185] ratio for all the isomers is 6·4—6·8 × 10⁻³ (Table 2), indicating that the structures of the decomposing $C_{12}H_6Cl_2$ ions (m) formed by tetrachlorobiphenyl isomers upon electron impact are similar and that the two remaining chlorine atoms are scrambled. The orientation effects of the two ortho-chlorine atoms in (4c), (4d), (4f), and (4g) which were observed in the [m_4*] : [k] ratios are absent from their respective $C_{12}H_6Cl_2$ ions. These data suggest that the ortho-substituents might be preferentially eliminated prior to complete chlorine equilibration.

TABLE 3a

Relative ion abundances (%) [a] and [metastable ion] : [daughter ion] ratios for the tetrachlorobiphenyls (4a—h)

| Compound	M	$M - Cl$	$M - HCl$	$M - Cl_2$	$M - Cl_3$	$M - (Cl_2 + HCl)$	$\dfrac{[m_5{}^*]}{[m/e\ 185]} \times 10^3$		$\dfrac{[m_4{}^*]}{[m/e\ 290]} \times 10^3$	
							70 eV	20 eV	70 eV	20 eV
(4a)	100	1·0	5·0	33	4·5	8·5	6·7	6·6	0·75	0·75
(4b)	100	1·0	4·0	38	4·0	7·5	6·7	6·9	0·8	0·8
(4c)	100	1·5	3·0	44	4·5	9·5	6·8	6·8	0·2	0·2
(4d)	100	4·0	2·5	56	5·0	9·5	6·6	6·6	<0·01	<0·01
(4e)	100	0·5	1·0	30	5·0	7·5	6·6	6·6	0·8	0·8
(4f)	100	13	5·0	71	8	11	6·5	6·9	<0·01	<0·01
(4g)	100	2·0	2·0	75	8	12	6·5	6·7	<0·01	<0·01
(4h)	100	0·5	2·0	35	3	7	6·4	6·6	0·8	0·8

[a] Recorded at 70 eV.

TABLE 3b

Ion kinetic energy data for the tetrachlorobiphenyls (4a—h)

Isomer	$m/e\ 290 \rightarrow m/e\ 255$		$m/e\ 255 \rightarrow m/e\ 220$		$m/e\ 220 \rightarrow m/e\ 185$		$m/e\ 185 \rightarrow m/e\ 150$		$m/e\ 290 \rightarrow m/e\ 220$	
	V_x/V_i [a]	m_x/m_i [b]	V_x/V_i	m_x/m_i	V_x/V_i	m_x/m_i	V_x/V_i	m_x/m_i	V_x/V_i	m_x/m_i
(4a)	87·3	87·9	85·7	86·2	83·3	84·0	80·0	81·0	75·0	76·1
(4b)	88·2	87·9	86·4	86·2	84·3	84·0	80·3	81·0	76·5	76·1
(4c)	88·1	87·9	86·5	86·2	84·4	84·0	80·4	81·0	76·3	76·1
(4d)	88·0	87·9	86·2	86·2	83·8	84·0	80·9	81·0	75·5	76·1
(4e)	87·6	87·9	85·8	86·2	83·8	84·0	80·5	81·0	75·6	76·1
(4f)	87·8	87·9	86·1	86·2	83·5	84·0	80·4	81·0	75·4	76·1
(4g)	87·9	87·9	86·2	86·2	84·2	84·0	80·9	81·0	75·8	76·1
(4h)	88·0	87·9	85·9	86·2	84·2	84·0	80·8	81·0	75·9	76·1

[a] V_x is observed voltage and $V_i = 400$ V. [b] m_x = Mass of daughter ion and m_i = mass of parent ion. Ratio was calculated by averaging the molecular weights of the isotopic species.
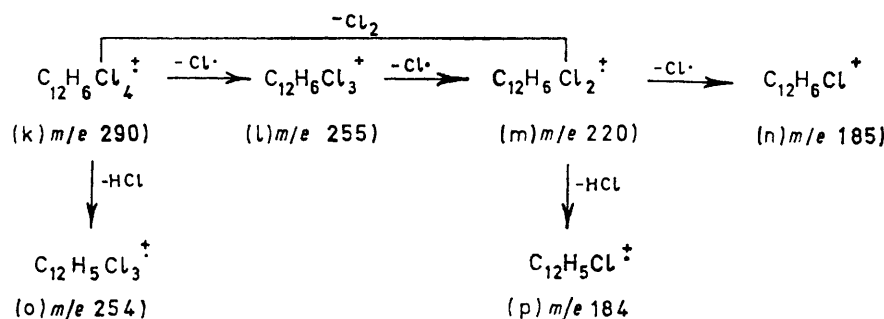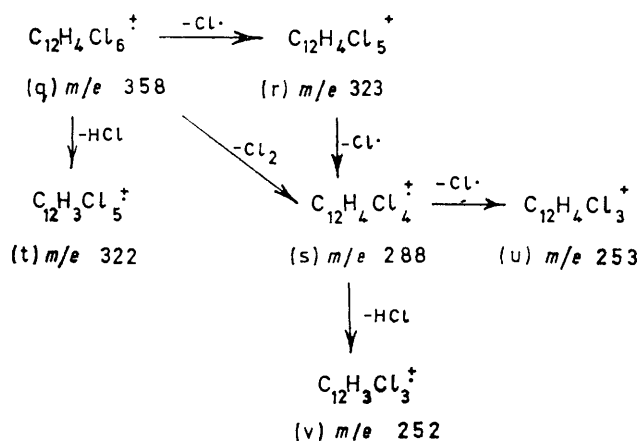

SCHEME 3

The i.k.e. spectra of the tetrachlorobiphenyls (4a—h) have also been recorded and the results are shown in Table 3b. The data confirm that the decompositions (k) $\longrightarrow$ (l), (l) $\longrightarrow$ (m), (m) $\longrightarrow$ (n), and (k) $\longrightarrow$ (m) which are apparent in their primary ion spectra also occur in the first field-free region of the mass spectrometer.

The primary ion mass spectra of the five hexachlorobiphenyls (5a—e) are similar, with only minor intensity variations (Table 2). The fragmentation pattern (Scheme 4) is typical of PCBs with successive loss of Cl· atoms accompanied by metastable ions for these reactions. Many of the ions lose HCl but no apparent metastable ions are detected for the transitions. Owing to the multiplicity of isotopes, the more intense higher mass metastable ion peaks are somewhat broadened, and the [metastable ion] : [daughter ion] ratios were not readily obtained; the lower mass metastable ion peaks are too weak to permit any accurate estimation of the ratio.

The remaining compounds (6a—c) and (7) contain

eight and ten chlorine atoms respectively; their relative ion intensities are given in Table 2. These data are comparable with the lower homologues in the series, and

SCHEME 4

successive loss of Cl· is the predominant feature of their fragmentation pattern although some expulsion of HCl was also noted with the isomers (6a—c). Compounds (5)—(7) also exhibit strong doubly charged ion peaks in the lower mass region of their mass spectra.

The primary ion spectra of polychlorinated biphenyls reveals several important features. In the predominant fragmentation pathway successive loss of Cl· occurs. In the lower homologues each loss of Cl· is often accompanied by expulsion of HCl, although only the former process exhibits a detectable metastable ion. The decomposition pathway for the di- and tetra-chlorobiphenyls has been confirmed by examination of their i.k.e. spectra. In most cases the molecular ion also expels a chlorine molecule and this is accompanied by a metastable ion. The kinetic approach using the tetrachloro- and dichloro-isomers as models reveals that in most isomers the chlorine atoms are scrambled over both atomatic rings, implying the formation of symmetrical intermediates formed by processes other than or in addition to photochemical-type equilibration. It is clear that both carbon–carbon and carbon–chlorine bond fission must occur and the intermediacy of linear acyclic ionic species is a possibility. The exceptions, compounds (2e and f) and (4c, d, f, and g), contained two or more chlorine atoms *ortho* to the Ph–Ph bond and although their fragmentation patterns were similar to those of the other isomers some of their metastable ion intensities were markedly different. These results also indicate that in most cases the primary ion mass spectra of polychlorinated biphenyls do not distinguish between isomers which are inseparable by g.l.c. and this is an important consideration in analysis of PCBs.

EXPERIMENTAL

For the syntheses of chlorobiphenyls, straightforward procedures were used. The replacement of amino-groups by chlorine (Sandmeyer reaction) and hydrogen atoms was carried out as previously described [22,23] except that larger amounts of conc. hydrochloric acid were usually employed. Sulphuric acid was preferable to hydrochloric acid for diazotations of amino-groups with two *ortho*-chlorine atoms. Chlorination of 2,2′,5,5′-tetrachlorobenzidine was carried out at −30° in dichloromethane solution with unprotected amino-groups, a procedure described for the preparation of pentachloroaniline.[24] The chlorine atom in the 2,2′,3,3′,5,5′-hexachlorobenzidine so obtained and the nitro-groups in 2,2′,4,4′,5,5′-hexachloro-3,3′-dinitrobiphenyl were shown to be in the positions given because both compounds were symmetrical (n.m.r.) and could be converted into 2,2′,3,3′,-4,4′,5,5′-octachlorobiphenyl, a new compound, different from the only other two existing symmetrical octachlorobiphenyls.[22] The nitration of 2,2′,4,4′,5,5′-hexachlorobiphenyl and the reduction of the resulting dinitro-compound

were carried out as described for an isomeric hexachlorobiphenyl.[25] 2,2′,3′,4,4′,5′-Hexachlorobiphenyl was prepared by the general peroxide method of Hey *et al.*[26,27]

A compound assigned the structure 2,2′,4,4′,5,5′-hexachlorobiphenyl, m.p. 137—138°, was previously reported to be formed by the decomposition of 3-(9,10-dihydroxyanthracen-1-yl)-1-(*p*-tolyl)triazene in 1,2,4-trichlorobenzene.[28] Our compound, prepared by an unambiguous route, has m.p. 103—104°.

N.m.r. spectra were recorded on a Varian A60 spectrometer for carbon tetrachloride solutions with tetramethylsilane as internal standard except where indicated otherwise. Analytical t.l.c. was carried out on Merck prepared silica plates (F-254; 0·25 mm) and preparative t.l.c. on 20 × 100 cm plates coated with Merck silica (F-254; 0·9 mm). Silica for column chromatography was supplied by Koch–Light (100—200 mesh).

Mass spectral data were obtained with a Dupont/CEC 21-110B double-focusing instrument equipped with an electron-impact ion source. The source temperatures for the di-, tri-, and tetrachloro-compounds were 10—80° and the temperatures for the hexa-, octa- and decachloro-compounds were 90—190°.

The purity of all compounds was checked by g.l.c. using a Hewlett–Packard 5750 instrument equipped with a 6 ft × ⅛ in stainless steel column packed with 6% QF-1 and 4% SE-30 on Chromosorb W. Helium was the carrier gas and oven temperatures ranged from 150 to 225°.

2,2′,5,5′-Tetrachlorobenzidine was obtained from Pfalz and Bauer Inc. 2,4-Dichlorobenzoyl peroxide was prepared by the method described for the 3,4-isomer.[29] 2,3′,4,4′-Tetrachlorobiphenyl was prepared by the method of Saeki *et al.*[30] All other chlorobiphenyls whose synthesis is not described in this paper were prepared as previously described.[22]

2,2′,5,5′-*Tetrachlorobiphenyl*.—A mixture of 2,2′5,5′-tetrachlorobenzidine (26 g) and conc. hydrochloric acid (85 ml) was heated to 70° and, after cooling, diazotized at 0—5° with sodium nitrite (16 g) in water (32 ml). The mixture was then stirred for 45 min at the same temperature and filtered, and the filtrate was added slowly to boiling ethanol (600 ml). The solution was boiled for an additional 15 min, the solvent was removed by distillation, and the residue was extracted with warm hexane (2 × 50 ml). The hexane solution was subjected to column chromatography on silica (100 × 12 cm), eluting with hexane. Fractions (100 ml) were collected and examined by t.l.c. (hexane). Fractions 11—20 contained pure 2,2′,5,5′-tetrachlorobiphenyl (R_F 0·65); they were combined and evaporated to dryness, and the residue was recrystallized (13·5 g, 57%), m.p. 86·5—87° (from ethanol) (lit.,[31] 84—85°).

2,2′,4,4′,5,5′-*Hexachlorobiphenyl*.—The clear solution of diazotized 2,2′,5,5′-tetrachlorobenzidine described above was added dropwise to a stirred solution of copper(I) chloride (17 g) in conc. hydrochloric acid (150 ml). After stirring for 2 h, the mixture was filtered, and the solid was washed with conc. hydrochloric acid and water. This

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crude product was extracted with hexane and purified on a silica column as described above. Fractions 18—26 contained only material of R_F 0·72. Evaporation and recrystallization gave the *product* (11·5 g, 39%), m.p. 103—104°, τ (CDCl$_3$) 2·38(s) and 2·63(s) (Found: C, 40·05; H, 1·05; Cl, 58·65. C$_{12}$H$_4$Cl$_6$ requires C, 39·95; H, 1·1; Cl, 58·95%).

2,2′,4,4′,5,5′-Hexachloro-3,3′-dinitrobiphenyl.— Finely powdered 2,2′,4,4′,5,5′-hexachlorobiphenyl (1 g) was added in portions to fuming nitric acid (*d* 1·50; 10 ml) at 0°. The mixture was warmed to 40° during 1 h and then poured onto ice. The *precipitate* was filtered off and purified by recrystallization from ethanol–ethyl acetate and benzene–hexane (0·85 g, 68%), m.p. 262—263°, τ (C$_6$D$_6$) 3·70(s), R_F (hexane–acetone, 4 : 1) 0·74 (Found: C, 31·75; H, 0·6; Cl, 46·95; N, 6·3. C$_{12}$H$_2$Cl$_6$N$_2$O$_4$ requires C, 31·95; H, 0·45; Cl, 47·2; N, 6·2%).

3,3′-Diamino-2,2′,4,4′,5,5′-hexachlorobiphenyl.—A paste of zinc dust (2 g), a few crystals of copper(II) sulphate, and water (2 ml) was gradually added to a boiling solution of 2,2′,4,4′,5,5′-hexachloro-3,3′-dinitrobiphenyl (600 mg) in glacial acetic acid (20 ml). The reaction was completed by boiling, with vigorous stirring, for 60 min. The mixture was then filtered and water (*ca.* 5 ml) was added to the hot filtrate. The *crystals* which appeared on cooling were filtered off and recrystallized from aqueous ethanol (410 mg, 79%), m.p. 191—192° (Found: C, 36·85; H, 1·6; Cl, 54·2; N, 6·9. C$_{12}$H$_6$Cl$_6$N$_2$ requires C, 36·85; H, 1·55; Cl, 54·4; N, 7·15%).

2,2′,3,3′,5,5′-Hexachlorobenzidine.—A vigorous stream of chlorine was bubbled through a filtered solution of 2,2′,5,5′-tetrachlorobenzidine (10 g) in dichloromethane (1·2 l) at −30°. Precipitation immediately commenced and the reaction was complete after 15 min. The crude brownish product, which was removed by filtration and washed with several portions of cold dichloromethane, was chromatographically homogeneous (hexane–acetone, 2·5 : 1; R_F 0·68) and pure enough to be used in the next step (7·6 g, 57%). Recrystallization from ethanol and benzene–hexane gave a *sample* of m.p. 186—187° (Found: C, 36·75; H, 1·55; Cl, 54·2; N, 7·25. C$_{12}$H$_6$Cl$_6$N$_2$ requires C, 36·85; H, 1·55; Cl, 54·4; N, 7·15%).

2,2′,3,3′,4,4′,5,5′-Octachlorobiphenyl.—(a) *From* 3,3′-di-amino-2,2′,4,4′,5,5′-hexachlorobiphenyl. A suspension of 3,3′-diamino-2,2′,4,4′,5,5′-hexachlorobiphenyl (300 mg) in conc. sulphuric acid (6 ml) and water (1·5 ml) was diazotized at −5° with sodium nitrite (300 mg) in water (3 ml). After stirring for 30 min at 0—5° the filtered mixture was added to a solution of copper(I) chloride (180 mg) in conc. hydrochloric acid (3 ml). The mixture was filtered after it had been stirred for 60 min and was washed with conc. hydrochloric acid and water. The crude product was dissolved in benzene; this solution was streaked onto a preparative t.l.c. plate and developed with hexane. The band at R_F 0·82 was removed, extracted with benzene, and after removal of the solvent, the *product* crystallized from ethanol (145 mg, 44%), m.p. 156—157° (Found: C, 33·85; H, 0·5; Cl, 65·7. C$_{12}$H$_2$Cl$_8$ requires C, 33·55; H, 0·45; Cl, 66·0%).

(b) *From* 2,2′,3,3′,5,5′-*hexachlorobenzidine.* Octachlorobiphenyl, m.p. 155—156° (1·3 g, 39%), was obtained from 2,2′,3,3′,5,5′-hexachlorobenzidine (3 g) by the procedure described under (a).

2,2′,3,3′,5,5′-Hexachlorobiphenyl.—The clear diazonium solution from 2,2′,3,3′,5,5′-hexachlorobenzidine (3 g), obtained as described above, was slowly added to boiling ethanol. After work-up in the usual manner, preparative t.l.c. (R_F 0·70) and recrystallization from ethanol gave the *product* (1·1 g, 40%), m.p. 128—129° (Found: C, 39·8; H, 1·1; Cl, 58·6. C$_{12}$H$_4$Cl$_6$ requires C, 39·95; H, 1·1; Cl, 58·95%).

2,2′,3,4,4′,5-Hexachlorobiphenyl.— 2,4-Dichlorobenzoyl peroxide (5 g) and 1,2,3,4-tetrachlorobenzene (100 g) were heated with stirring at 100° overnight. The mixture was then distilled over a short column and the fraction containing 2,2′,3,4,4′,5-hexachlorobiphenyl (b.p.135—150° at 1 mmHg) was further purified by preparative t.l.c. (benzene; R_F 0·85). Evaporation of the solvent and recrystallization of the residue from ethanol and hexane (−80°) gave the *product* (1·1 g, 21%), m.p. 77—78° (Found: C, 39·8; H, 1·2; Cl, 58·7. C$_{12}$H$_4$Cl$_6$ requires C, 39·95; H, 1·1; Cl, 58·95%).