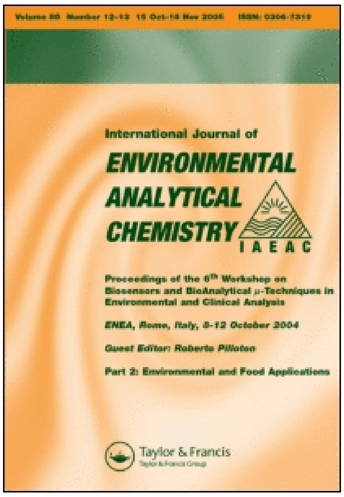

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Analysis of Chlorinated Aromatic Hydrocarbons by Exhaustive Chlorination: Qualitative and Structural Aspects of the Perchloro-Derivatives of Biphenyl, Naphthalene, Terphenyl, Dibenzofuran, Dibenzodioxin and DDE

O. Hutzinger[a]; S. Safe[a]; V. Zitko[b]
[a] Atlantic Regional Laboratory, National Research Council of Canada, hali, Nova Scotia, Canada [b] Environment Canada, Fisheries Services, St. Andrews, New Brunswick, Canada

To cite this Article Hutzinger, O. , Safe, S. and Zitko, V.(1972) 'Analysis of Chlorinated Aromatic Hydrocarbons by Exhaustive Chlorination: Qualitative and Structural Aspects of the Perchloro-Derivatives of Biphenyl, Naphthalene, Terphenyl, Dibenzofuran, Dibenzodioxin and DDE', International Journal of Environmental Analytical Chemistry, 2: 2, 95 — 106

To link to this Article: DOI: 10.1080/03067317208073249

URL: http://dx.doi.org/10.1080/03067317208073249

Intern. J. Environ. Anal. Chem., 1972, Vol. 2, pp. 95–106

Analysis of Chlorinated Aromatic Hydrocarbons by Exhaustive Chlorination: Qualitative and Structural Aspects of the Perchloro-Derivatives of Biphenyl, Naphthalene, Terphenyl, Dibenzofuran, Dibenzodioxin and DDE†

O. HUTZINGER, S. SAFE
Atlantic Regional Laboratory, National Research Council of Canada, Halifax, Nova Scotia, Canada

and

V. ZITKO
Environment Canada, Fisheries Services, St. Andrews, New Brunswick, Canada

(*Received April 17, 1972*)

A number of reagents for the exhaustive chlorination of aromatic compounds were investigated. Antimony pentachloride-iodine, and the BMC reagent (sulfuryl chloride-aluminum chloride-disulfur dichloride) were found to be the most effective and convenient reagents. They are liquids which can be used without special precautions to prepare the perchloro-derivatives of biphenyl, terphenyl, naphthalene, dibenzofuran, dibenzodioxin and DDE. The structures, mass spectra and GLC properties of these compounds are discussed

Polychlorinated biphenyls (PCB) and some related classes of chloroaromatic compounds are complex mixtures which consist of positional isomers of different degrees of chlorination for each corresponding parent hydrocarbon.

---

† Issued as NRCC No. 12731.

These highly heterogeneous mixtures often pose problems in identification and quantitative analysis and frequently interfere with the analysis for other compounds such as the chlorinated insecticides.

To simplify the analytical problem and to eliminate the interferences an approach was recently suggested[1] in which all compounds in a particular mixture are converted to a single derivative. This can be achieved by removing all chlorine atoms to obtain the parent hydrocarbon[1,2] or through exhaustive chlorination to give the fully chlorinated (perchloro-) hydrocarbon. The latter approach is preferable since sensitivity to the electron-capture detector is usually increased with more highly chlorinated derivatives.[3] Perchlorination has recently been used for the analysis of PCB,[2] for a screening method to detect chlorodibenzodioxins,[4] and as a confirmatory test for chloroterphenyls found in the environment.[5]

Since the present methods for perchlorination (antimony pentachloride in sealed vials[2] or gaseous chlorine[4]) are unusual operations in analytical laboratories we have investigated a number of perchlorination reagents. In this communication we describe some of these reagents and discuss conditions of formation as well as some of the properties of a number of perchloroderivatives.

MATERIALS AND METHODS

Gas Chromatography

A Packard A7901 gas chromatograph with a glass column (6 ft × 4 mm), containing 3% OV-210 (Pierce Chemical Co.) on Chromosorb WAW 60/80, operated at 200°C, was used. Injector and detector (^3H) were kept at 210°C. D.C. voltage in the electron-capture detector was 80 V and meter sensitivity was 3×10^{-9} amp. Solutions of perchlorinated compounds in pesticide-grade benzene were injected.

Thin-layer Chromatography

Merck precoated silica thin-layer plates (F-254, 0.25 nm) and hexane as developing solvent were used. The compounds were detected as quenched spots by viewing the plates with a 'short wave' u.v. (mineralight) lamp.

Mass Spectrometry

Spectra were obtained on a DuPont/CEC 21-110B double-focussing instrument. Samples were introduced directly into the ion source.

Chemicals

Aroclor 1254 and 5460 (Monsanto), Halowax 1014 (Koppers) and p,p'-DDE (Analabs) were used as received from the commercial sources. Dibenzofuran (Eastman) was recrystallized (ethanol) before use. Dibenzodioxin was prepared as described.[6]

Perchlorination Reactions

(1) *With the BMC Reagent*

The reagent was prepared by mixing equal volumes of the following two solutions prior to use: (*a*) sulfur monochloride (S_2Cl_2; 5g) in sulfuryl chloride (500 ml), and (*b*) powdered anhydrous aluminum chloride (2.5 g) in sulfuryl chloride (500 ml).

General procedure The substrate to be perchlorinated (100 mg) was dissolved in the BMC reagent (10 ml) and the mixture was heated for 2 hr in a loosely capped (aluminum foil) flask. The temperature was kept near the boiling point of sulfuryl chloride (69°) and was controlled in such a way that ca. two thirds to three quarters of the SO_2Cl_2 had evaporated after the 2-hr period. Several of the perchloro-derivatives had precipitated from the solution at this stage. 25% hydrochloric acid (30 ml) was then added and the mixture which consisted of two layers was heated (60–80°; 10–60 min) until the perchloro-derivative had separated out in solid form. After the mixture had cooled, the compound was recovered by filtration and washed with 25% HCl and water. Most compounds showed a melting point close to that of the purified derivative. Final purification was achieved by recrystallization from toluene, benzene or benzene-hexane mixtures.

(2) *With Antimony Pentachloride-Iodine*

The reagent was prepared by dissolving iodine (0.5 g) and antimony pentachloride (10 ml) in sulfuryl chloride (90 ml).

General procedure The substrate to be perchlorinated (100 mg) was dissolved in the SO_2Cl_2–$SbCl_5$–I_2 reagent (10 ml). The temperature was then gradually raised to 120–130° (the SO_2Cl_2 evaporated during this period) and maintained for 2 hr. 25% hydrochloric acid (10 ml) was then cautiously added and the mixture was warmed (60°) for 10 min. The solid compounds were recovered and purified as given under (1).

Reaction (2) can be carried out with similar results without SO_2Cl_2 (i.e., neat $SbCl_5$–I_2). Since $SbCl_5$ is very sensitive to moisture it is more conveniently handled in SO_2Cl_2 solution. Furthermore, reactions with more reactive nuclei (e.g. naphthalene, dibenzodioxin) tend to be too vigorous with undiluted $SbCl_5$.

The perchloro-derivatives obtained from the procedures given above can also be recovered (particularly for small samples) by extraction with boiling benzene.

For the study of completeness of reactions and formation of by-products the crude product, either the solid or a benzene solution, was used for TLC, GLC and mass spectral work.

RESULTS AND DISCUSSION

Reagents

Mechanistic and practical aspects of the chlorination of aromatic compounds are discussed in references 7–11. Since gaseous chlorine was considered impractical for use in analytical applications, metal chlorides, some of which are known to effectively chlorinate aromatic compounds,[12] and catalyzed surfuryl chloride reactions were investigated in an empirical fashion. The metal chlorides used were antimony trichloride, antimony pentachloride, aluminum trichloride, titanium tetrachloride, ferric chloride, tin tetrachloride and zinc dichloride. Most reactions were carried out in sulfuryl chloride or carbon tetrachloride at reflux temperatures and the metal chlorides were used alone or in combination with either S_2Cl_2 or iodine. Examination of reaction yields and products for the chlorination of Aroclor 1254 indicated that the BMC-mixture, $SbCl_5$–I_2 were the preferred reagents and these were subsequently used for all other compounds.

The BMC (sulfuryl chloride, sulfur monochloride and anhydrous aluminum chloride) reagent[13,14] which has been used for exhaustive (per-) chlorination of polycyclic and other strained molecules[13,14–19] is a variation of a nuclear chlorination reagent introduced by Silverrad 50 years ago (*cf.* ref. 20). This reagent gives excellent results and no major by-products in the preparation of octachlorobenzodioxin, octachlorodibenzofuran and decachlorobiphenyl. Decachloro-1,4-dihydronaphthalene was formed under these conditions in excellent yield, but two major spots each were observed on TLC of reaction mixtures of BMC with Aroclor 5460 and DDE. The latter compound has previously been shown to yield perchloro-DDE as well as a dimeric product on treatment with the BMC reagent.[17] In several cases, chlorinolysis of highly strained molecules was reported in the literature. The completeness of reaction and, to a certain extent, products formed seems to depend on the reaction time and concentration and ratio of S_2Cl_2 and $AlCl_3$.

Antimony pentachloride-iodine seems to be the most powerful perchlorination reagent. It can be used at lower temperatures than antimony pentachloride alone (*cf.* refs. 2, 21, 22), and at atmospheric pressure, which would

TABLE I

Properties of perchloro-derivatives

Compound	m.p. (lit. m.p.; ref.)	Analyses[a] C	Analyses[a] Cl	Retention times[b]	Method of preparation
Octachlorodibenzofuran (I)	256–7[c]	32.43	63.96	2.55[d]	BMC
		32.69	63.41		
Octachlorodibenzodioxin (II)	328	—[e]	—	2.60[d]	BMC
	(330; 23)				
Octachloronaphthalene (III)	196–7	29.70	70.30	1	SO_2Cl_2–$SbCl_5$[f]
	(From 197 to 202; 24)	30.00	70.23		
Decachloro-1,4-dihydronaphthalene (VII)	208	25.26	74.74	1	BMC
	(208; 25)	25.26	74.20		
Decachlorobiphenyl (IV)	304	—[e]	—	1	BMC and $SbCl_5$–I_2
	(305–6; 21)				
Dodecachloro-DDE (V)	> 360°	28.28	71.72	1.9, 2, 2.9	$SbCl_5$–I_2
		28.27	70.87	3.6, 4.7, 5.9	
Tetradecachloroterphenyl (VI)	from 290 to > 360[g]	30.29	69.71	11.9, 19.2	$SbCl_5$–I_2
		29.91	69.15	22.2[g]	

[a] Calculated over found. Values for chlorine are consistently low for most of these perchloro-derivatives, possibly due to incomplete decomposition.

[b] Retention time relative to decachlorobiphenyl.

[c] Identical to a sample provided by Dr. Pohland.

[d] Identical to samples provided by Dr. Firestone.

[e] Samples were identical to those prepared by the methods described in the literature.

[f] Halowax or naphthalene was heated, under reflux, in a mixture of sulfuryl chloride and antimony pentachloride 9: 1 (v/v) for one hour an the octachloronaphthalene was recovered as described for the other perchloro-compounds. Heating with neat $SbCl_5$ or SO_2Cl_2–$SbCl_5$–I leads to extensive decomposition.

[g] This product changes m.p. on crystallization. It probably consists of a mixture of *o*-, *m*- and *p*-perchloroterphenyl.

facilitate routine analytical use. This reagent cannot be used, however, with more sensitive nuclei such as dibenzofuran, dibenzodioxin and naphthalene because extensive decomposition of these systems occurs, particularly at higher temperatures.

Perchloro-derivatives

Some data for the perchloro-compounds prepared in this study are reported in Table I. GLC and mass spectra are discussed in the following sections.

Perchlorodibenzofuran (octachlorodibenzofuran; I in Figure 1). Perchlorodibenzofuran had not previously been described in the literature. The sample prepared from dibenzofuran and the BMC reagent was identical to a preparation obtained from Dr. Pohland.

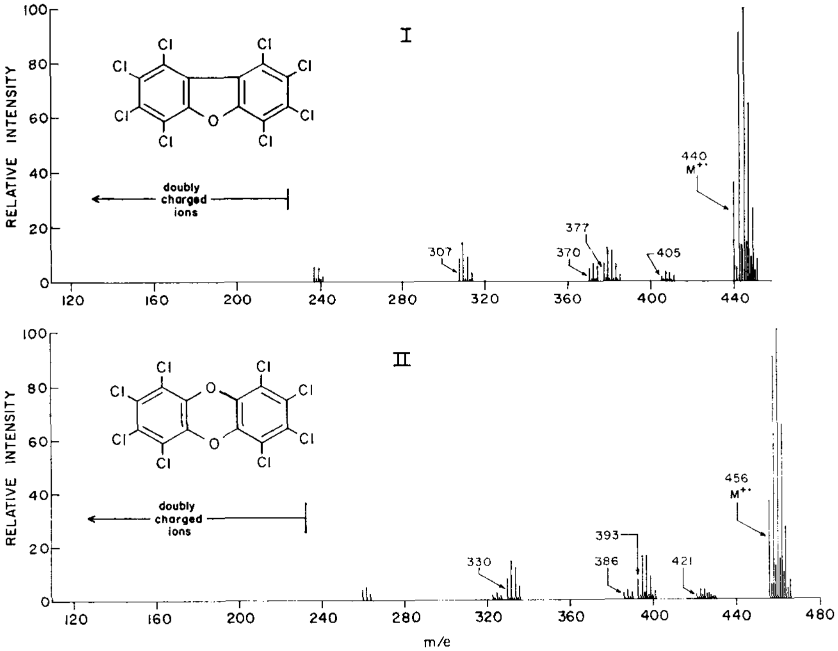

FIGURE 1 70 eV mass spectrum of octachlorodibenzofuran (I) and octachlorodibenzodioxin (II). Ionizing chamber temperatures 160° (I), 210° (II).

Perchlorodibenzodioxin (octachlorodibenzodioxin; II in Figure 1). This compound is obtained in good yield from dibenzodioxin and the BMC reagent. The properties of the product so obtained are identical to those described in the literature.[23]

Perchloronaphthalene. Under vigorous conditions of chlorination, octachloronaphthalene (III, Figure 2) as well as decachloro-1,4-dihydronaphthalene (VII) and perchloroindane (VIII) were reported to be formed (Figure 3; ref. 25).

(i) *Octachloronaphthalene* (III in Figures 2 and 3) was obtained in colorless needles from Halowax 1014 and $SbCl_5$ in sulfuryl chloride. $SbCl_5$ at higher temperatures and $SbCl_5$–I_2 apparently lead to extensive decomposition of the naphthalene ring.

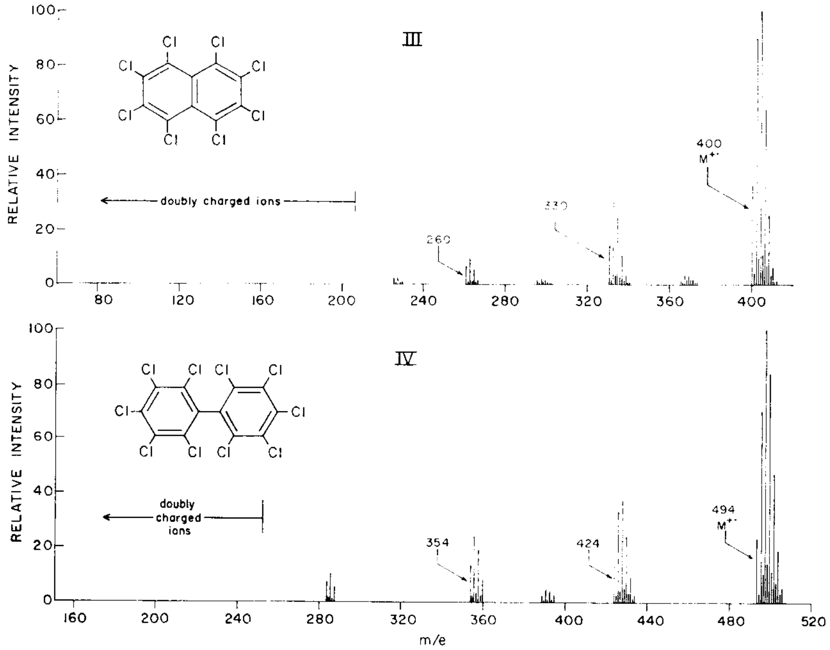

FIGURE 2 70 eV mass spectrum of octachloronaphthalene (III) and decachlorobiphenyl (IV). Ionizing chamber temperatures 130° (III), 190° (IV).

(ii) *Decachloro-*1,4*-dihydronaphthalene* (VII in Figure 3) as colorless prisms, was obtained in good yield from Halowax 1014 and the BMC reagent. It was previously reported that this reagent forms decachloro-1,4-dihydronaphthalene from a 1-phenylmethylnaphthalene derivative.[17]

When decachloro-1,4-dihydronaphthalene is heated above its melting point (208°), octachloronaphthalene is formed (*cf.* ref. 25). A thermal reaction may also account for the fact that both compounds give an identical mass spectrum (corresponding to octachloronaphthalene) and also have identical retention times.

Perchlorobiphenyl (decachlorobiphenyl; IV in Figure 2). This compound was obtained, in good yield, with both the BMC and $SbCl_5$–I_2 reagents. The sample was identical to the one prepared previously.[21]

Perchloro-DDE (dodecachloro-DDE; 1,1-dichloro-2,2-bis-(pentachlorophenyl)ethylene; V in Figure 4). Perchloro-DDE had previously been prepared[17] by chlorination of DDE with the BMC reagent. Full details on preparation and properties were not given and a dimeric product was also reported to be formed during this reaction. A product giving the expected mass spectrum (Figure 4) was obtained in good yield by the chlorination of p,p′-DDE with the $SbCl_5$–I_2 reagent.

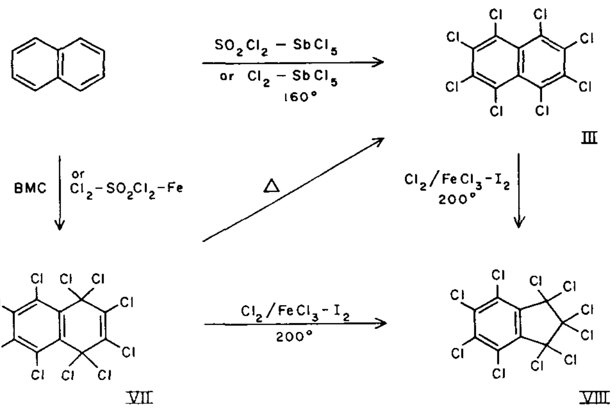

FIGURE 3 Products formed by the chlorination of naphthalene under vigorous conditions.

Several major peaks were observed in the gas chromatogram of crude as well as recrystallized perchloro-DDE. The possibility that thermal decomposition had occurred was not further investigated.

Perchloroterphenyl (tetradecachlorobiphenyl; VI in Figure 4). Only one (the p-) of the three possible isomers had previously been prepared[22] but no details were given. "Perchloroterphenyl" has been mentioned in the literature[26,27] but again no details were described. This compound seems to require the most vigorous conditions for its preparation. This preparation probably consists of a mixture of the three possible (*o*-, *m*- and *p*-) perchloroterphenyls. This is indicated by the change in the melting point on repeated recrystallization of an apparently pure sample (mass spectrum) and the three peaks in the gas chromatogram.

Aldrin, Dieldrin and Chloroparaffins

The BMC and $SbCl_5$–I_2 perchlorinating reagents decompose the two cyclodiene insecticides into several products and all three compounds yielded "polar products" which remained at the origin in a silica gel-hexane thin-layer system.

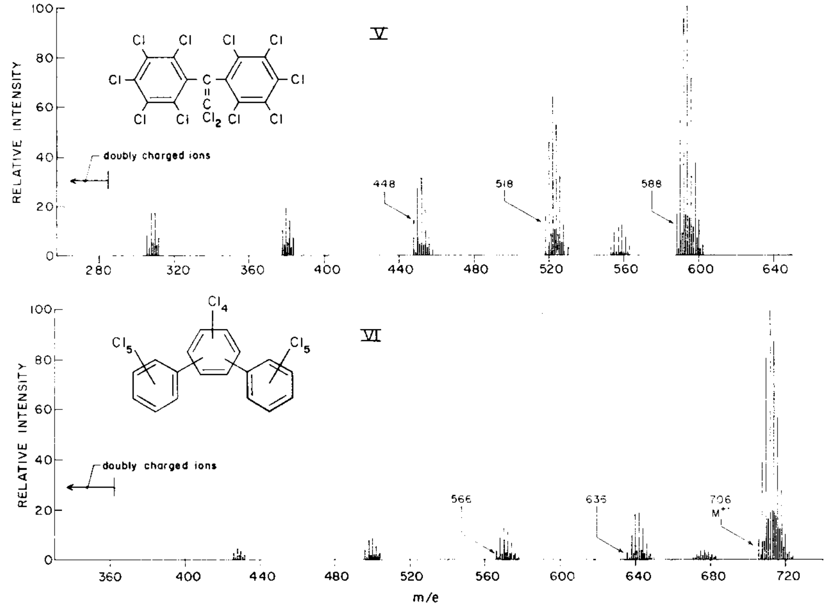

FIGURE 4 70 eV mass spectrum of dodecachloro–DDE (V) and tetradecachloroterphenyl (VI). Ionizing chamber temperatures 195° (V), 180° (VI).

Gas Chromatography

Retention times of the perchlorination products are presented in Table I. Perchloro-DDE gave several peaks of approximately equal size which may be due to thermal decomposition. Since p,p′-DDE is the major chlorinated hydrocarbon encountered in environmental samples, it is important to note that none of the peaks would interfere with the peaks of octachlorodibenzofuran and octachlorodibenzodioxin, respectively. Perchlorination of dibenzofuran yielded a single peak corresponding to an authentic sample of octachlorodibenzofuran. Dibenzodioxin yielded octachlorodibenzofuran and two minor peaks with shorter retention times. Octachloronaphthalene and decachloro-1,4-dihydronaphthalene both gave one peak with the same retention time. This may be due to thermal conversion of the latter into octachloronaphthalene (see discussion of perchloronaphthalenes). Decachlorobiphenyl gives one peak with a retention time identical to the perchloronaphthalenes. Perchloroterphenyl shows two major peaks with retention times of 19.2 and 22.2 relative to decachlorobiphenyl and a smaller peak with a retention time of 11.9 (*cf.* ref. 5), possibly corresponding to the three isomeric perchloroterphenyls.

Mass Spectrometry

The molecular ion is the most intense peak in the mass spectrum of all the perchlorinated compounds discussed followed by relatively abundant M-70 ions. This result facilitates identification of chloroaromatic compounds present in natural samples at low concentrations.

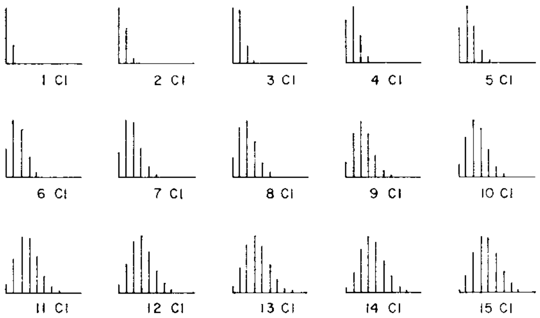

FIGURE 5 Isotopic abundance ratios for one to fifteen chlorine atoms.

Since isomer abundance ratios, particularly for higher numbers of chlorine atoms, are not easily accessible in conveniently readable bar chart form a graphic presentation up to Cl_{15} is given in Figure 5.

The general fragmentation pattern for perchloro-biphenyl, terphenyl, -naphthalene and -DDE features successive loss of both Cl_1 and Cl_2 from the molecular ion and the subsequent decomposition ions and in most cases the odd electron (i.e. $M^{+\cdot}$ and $[M\text{–}Cl_2]^{+\cdot}$) mass ions are the more intense species. Both perchlorodibenzofuran and dibenzodioxin also fragment as above; however, loss of CO from their M–Cl ions was also evident and in addition a further CO moiety is expelled from the m/e 393 ion of perchlorodibenzodioxin.

CONCLUSIONS

The reagents antimony pentachloride-iodine and BMC can be conveniently used for the exhaustive chlorination of aromatic compounds. These methods have been shown to be applicable to the preparation of perchloro-derivatives of several industrial chlorinated hydrocarbons and highly toxic by-products as well as to the insecticide decomposition product, DDE.

The advantages and possible analytical applications of this approach are as follows:

i) industrial chlorinated hydrocarbons which are sometimes complicated mixtures (e.g. PCB) are converted to one single derivative.

ii) analysis by GLC is therefore simplified and sensitivity is improved since all chloro-derivatives appear in one peak.

iii) sensitivity in GLC analysis is increased further since response to the electron-capture detector in chloroaromatic compounds usually increases with chlorine content.[3,28]

iv) identification of chlorinated hydrocarbons by mass spectrometry is simplified by having to deal with only one group of ions, which is particularly important when low levels in crude extracts are to be identified by high-resolution photoplate methods.[29,30]

v) exhaustive chlorination can be used as confirmatory test for single derivatives such as DDE.

In some cases, however, it may be important to determine the chlorinated hydrocarbons actually present in the sample, such as the pattern of PCB peaks in relation to commercial PCB preparations, or the presence of 2,3,7,8-tetrachlorodibenzodioxin. In such cases perchlorination obviously cannot be used.

The perchlorination reagents examined do not appear to give reasonably defined derivatives with aliphatic compounds.

Acknowledgments

Thanks are due to Monsanto and Koppers companies for samples of Aroclor and Halowax. We are indebted to Dr. W. D. Jamieson for writing the computer program used in the calculation of isotopic abundance ratios for chlorine, to Dr. Pohland for a sample of octachlorodibenzofuran and to Dr. Firestone for samples of octachlorodibenzofuran and octachlorodibenzodioxin.

References

1. O. W. Berg and G. A. V. Rees, 2nd Seminar on Pesticide Residue Analysis (Eastern Canada), Ottawa, May 22 (1970).
2. O. W. Berg, P. L. Diosady, and G. A. V. Rees, *Bull. Environ. Contam. Toxicol.* (1972) in press.
3. V. Zitko, O. Hutzinger, and S. Safe, *Bull. Environ. Contam. Toxicol.* **6**, 160 (1971).
4. D. T. Williams and B. J. Blanchfield, *J. Ass. Offic. Anal. Chem.* **55**, 93 (1972).
5. V. Zitko, O. Hutzinger, W. D. Jamieson, and P. M. K. Choi, *Bull. Environ. Contam. Toxicol.* **7**, 200 (1972).

6. H. Gilman and J. J. Dietrich, *J. Amer. Chem. Soc.* **79,** 1439 (1957).
7. P. B. D. De La Mare and J. H. Ridd, *Aromatic Substitution* (Butterworths Scientific Publications, London, 1959).
8. R. Stroh and W. Hahn, in *Methoden der Organischen Chemie*, edited by E. Müller G. Thieme Verlag, Stuttgart, 1962), Vol. **V/3,** p. 503.
9. H. P. Braendlin and E. T. McBee, in *Friedel-Crafts and Related Reactions*, edited by G. A. Olah (Interscience Publishers, New York, 1964), Vol. **III/2,** p. 1517.
10. R. O. C. Norman and R. Taylor, in *Benzenoid Compounds* (Elsevier Publishing Co., Amsterdam, 1965).
11. W. J. Feast and W. K. R. Musgrave, in *Rodd's Chemistry of Carbon Compounds*, edited by S. Coffey (Elsevier Publishing Co., Amsterdam, 1971), Vol. **III,** Part A, p. 241.
12. P. Kovacic, in *Friedel-Crafts and Related Reactions*, edited by G. A. Olah (Interscience Publishers, New York, 1965), Vol. **IV,** p. 111.
13. M. Ballester, C. Molinet, and J. Castañer, *J. Amer. Chem. Soc.* **82,** 4254 (1960).
14. L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis* (Wiley, New York, 1967), p. 1131.
15. M. Ballester, *Bull. Soc. Chim.* **7** (1966).
16. M. Ballester, *Pure Appl. Chem.* **15,** 123 (1967).
17. M. Ballester, J. Castañer, and J. Riera, Synthesis and properties of alkylaromatic chlorocarbons. Clearinghouse Fed. Sci. Tech. Inform 1968, AD 672319. *Chem. Abstr.* **70,** 46980 (1969).
18. M. Ballester, J. Castañer, and J. Pujadas, *Tetrahedron Lett.* 1699 (1971).
19. M. Ballester, J. Riera, J. Castañer, C. Badia, and J. M. Monsó, *J. Amer. Chem. Soc.* **93,** 2215 (1971).
20. R. Stroh and W. Hahn, reference 8, pp. 887–889.
21. O. Hutzinger, S. Safe, and V. Zitko, *Bull. Environ. Contam. Toxicol.* **6,** 209 (1971).
22. V. Merz and W. Weith, *Ber.* **16,** 2869 (1883).
23. A. E. Pohland and G. C. Yang, 162nd Meeting of the American Chemical Society, Pesticide Chemistry Division Paper No. 77 (Manuscript) (1971).
24. E. H. Huntress, *Organic Chlorine Compounds* (J. Wiley, New York, 1948), p. 461.
25. R. Stroh and W. Hahn, reference 8, pp. 670 and 671.
26. F. B. Stilmar, W. S. Struve, and W. V. Wirth, *Ind. Eng. Chem.* **39,** 348 (1947).
27. U. Kuhlmann, *Fr. Patent Addn.* **92,** 074 (1968) and **94,** 467 (1969); *Chem. Abstr.* **71,** 125–422 (1969); and **72,** 110994 (1970).
28. B. J. Gudzinowicz, *Gas Chromatographic Analysis of Drugs and Pesticides* (Marcel Dekker Inc., New York, 1967), p. 514.
29. O. Hutzinger and W. D. Jamieson, *Bull. Environ. Contam. Toxicol.* **5,** 587 (1970).
30. O. Hutzinger and W. D. Jamieson, *Pesticide Chemistry*, Proc. 2nd International IUPAC Congress, edited by A. S. Tahori, Vol. **4** (1971), p. 7.