Photodegradation Aroclor-1016

Date	Elapsed Days	Sample Extract (Red)	µg
6-9-72	addition		21.68
	seal bulbs	3, 12 (controls)	20.46, 22.11
		1*, 7*, 15*	22.50, 24.71, 18,57
		2	2.17
		4	24.71
		5	26.75
		6	19.94
		8	19.72
		9	21.46
		10	22.54
		11	16.69
		13	18.21
		14	

Return of sample extracts

DSW 152944

Photodegradation

Standards 0.867 x 10^{-6} g/ml

ul	area
2	419
3	673
4	783
5	1039
6	1124
7	1381
8	1408

Samples

R-3	5ul	5ml	2:10	955	(4.72)	20.461 ug
R-12	5ul	5ml	2:10	1035	(5.10)	22.109 ug
R-1	5ul	5ml	2:10	1052	(5.19)	22.499 ug
R-7	5ul	5ml	2:10	1155	(5.70)	24.710 ug
R-15	3ul	5ml	4:1	1041	(5.14)	18.568 ug
R-2	5ul	5ml	2:1	1011	(5.00)	2.168 ug
R-4	5ul	5ml	2:10	1153	(5.70)	24.710 ug
R-5	5ul	5ml	2:10	1253	(6.17)	26.747 ug
R-6	5ul	5ml	2:10	936	(4.60)	19.941 ug
R-8	5ul	5ml	2:10	928	(4.55)	19.724 ug
R-9	5ul	5ml	2:10	1004	(4.95)	21.458 ug
R-10	5ul	5ml	2:10	1056	(5.20)	22.542 ug
R-11	5ul	5ml	2:10	783	(3.85)	16.690 ug
R-13	5ul	5ml	2:10	831	(4.20)	18.207 ug

Standards for R-14

ul	area
2	1262
3	1736
4	2183
5	2394

DSW 152945

Samples

R-14	5ul	5ml	2:10	1580	(2.75)	11.921 ug
R-14	5ul	5ml	2:10	1729	(3.07)	13.308 ug

Calculations

R-3 5ml 5ml 2:10 (4.72)

$$\frac{4.72 \times .867 \times 5 \times 10}{5 \times 2} = \frac{204.610}{10} = 20.461 \text{ mg}$$

R-12 5ml 5ml 2:10 (5.10)

$$\frac{5.10 \times .867 \times 5 \times 10}{5 \times 2} = 22.109 \text{ mg}$$

R-1 5ml 5ml 2:10 (5.19)

$$\frac{5.19 \times .867 \times 5 \times 10}{5 \times 2} = 22.499 \text{ mg}$$

R-7 5ml 5ml 2:10 (5.70)

$$\frac{5.70 \times .867 \times 5 \times 10}{5 \times 2} = 24.710 \text{ mg}$$

R-15 3ml 5ml .4:1 (5.14)

$$\frac{5.14 \times .867 \times 5\text{ml} \times 1}{5 \times .4} = \frac{22.282}{1.2} = 18.568 \text{ mg}$$

R-2 5ml 5ml 2:1 (5.00)

$$\frac{5.00 \times .867 \times 5\text{ml} \times 1}{5 \times 2} = 2.168 \text{ mg}$$

R-4 5ml 5ml 2:10 (5.70)

$$\frac{5.70 \times .867 \times 5\text{ml} \times 10}{5 \times 2} = 24.710 \text{ mg}$$

DSW 152946

Photodegradation calculations (cont.)

R-5 5ml 5ml 2:10 (6.17)

$$\frac{6.17 \times .867 \times 5 \times 10}{5 \times 2} = 26.747 \text{ ug}$$

R-6 5ml 5ml 2:10 (4.60)

$$\frac{4.60 \times .867 \times 5 \times 10}{5 \times 2} = 19.941 \text{ ug}$$

R-8 5ml 5ml 2:10 (4.55)

$$\frac{4.55 \times .867 \times 5 \times 10}{5 \times 2} = 19.724 \text{ ug}$$

R-9 5ml 5ml 2:10 (4.95)

$$\frac{4.95 \times .867 \times 5 \times 10}{5 \times 2} = 21.458 \text{ ug}$$

R-10 5ml 5ml 2:10 (5.20)

$$\frac{5.20 \times .867 \times 5 \times 10}{5 \times 2} = 22.542 \text{ ug}$$

R-11 5ml 5ml 2:10 (3.85)

$$\frac{3.85 \times .867 \times 5 \times 10}{5 \times 2} = 16.690 \text{ ug}$$

R-13 5ml 5ml 2:10 (4.20)

$$\frac{4.20 \times .867 \times 5 \times 10}{5 \times 2} = 18.207 \text{ ug}$$

DSW 152947

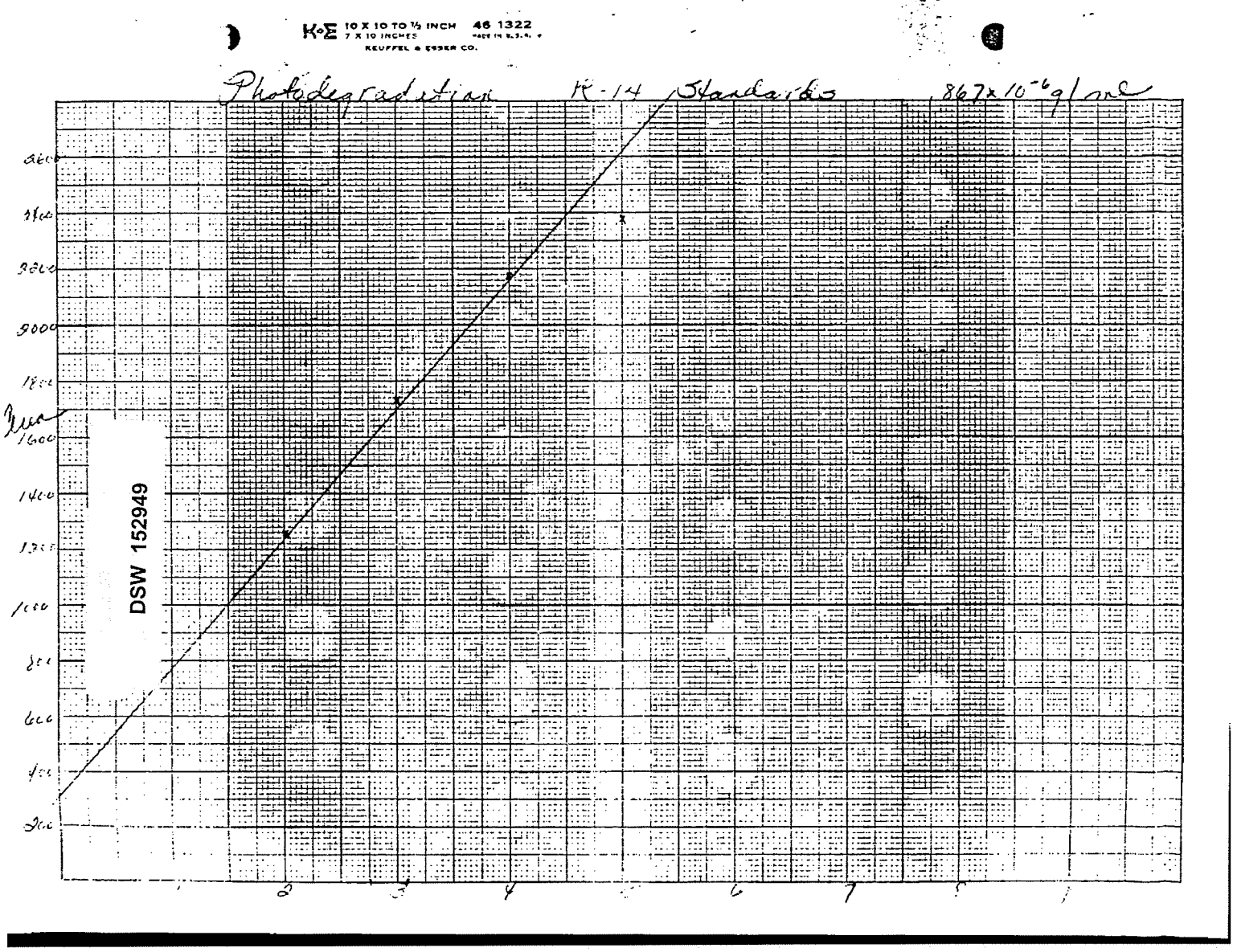
R-14 5 ml 5 ml 2:10 (2.75)

$$\frac{2.75 \times .867 \times 5 \times 10}{5 \times 2} = 11.921 \text{ mg}$$

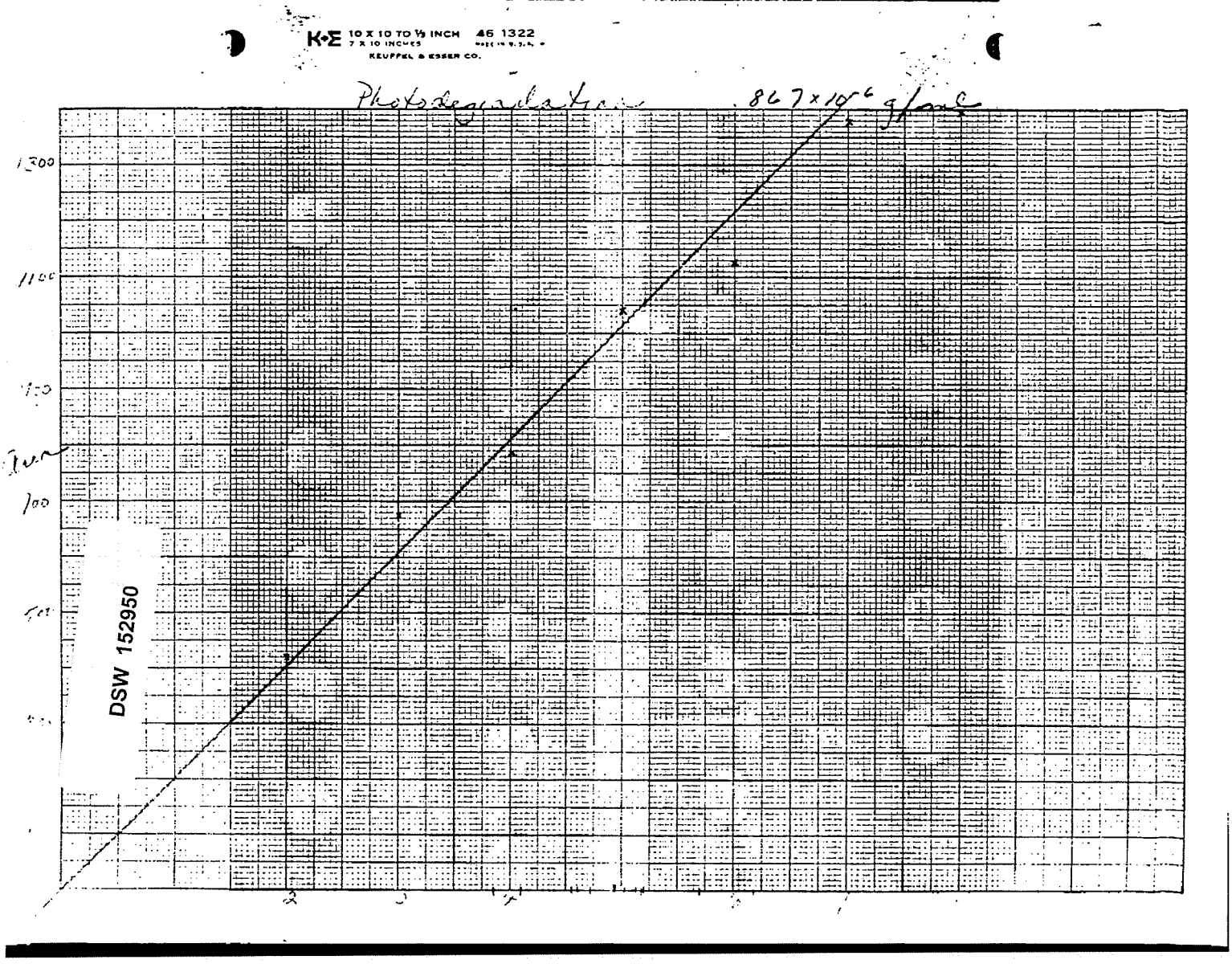
R-14 5 ml 5 ml 0:10 (3.07)

$$\frac{3.07 \times .867 \times 5 \times 10}{5 \times 2} = 13.308 \text{ mg}$$

DSW 152948



STLCOPCB4040295


K+E 10 X 10 TO ½ INCH 46 1322
7 X 10 INCHES
KEUFFEL & ESSER CO.
Photodegradation
.867 x 10^-6 g/ml
1300
1100
700
DSW 152950

Photodegradation Aroclor 1016

Date	Elapsed Days	Samp Ident. (Red)	µg
6-9-72	addition		21.68
	seal bulbs	3, 12 (cont no exp?)	17.39, 17.18
6-20-72	0	1*, 7*, 15*	21.68, 16.26, 17.61
6-21-72	1	2	14.90
6-22-72	2	4	16.80
6-23-72	3	5	18.04
6-24-72	4	6	15.99
6-27-72	7	8	14.90
6-30-72	10	9	16.91
7-5-72	15	10	15.55
7-11-72	21	11	13.98
7-18-72	28	13	11.92
8-18-72	59	14	

No significant change in isomer distribution

DSW 152951

STLCOPCB4040297

MONSANTO CHEMICAL COMPANY
ORGANIC CHEMICALS DIVISION - RESEARCH DEPARTMENT

№ 88982

1348006	PREPARED BY (SIGNATURE) C. S. Tucker	DATE 2-8-72

Photo decomposition of Aroclor 1016

(lot KA 708)

~~41.1484~~ 41.1487
41.0500
.0987 g/100 ml nanograde hexane

9.87×10^{-2} g/100 ml $\times 10^{-3}$ ml/ul = 9.87×10^{-7} g/ul

10/25 = 3.95×10^{-7} g/ul

Six pyrex 500 ml RB flask spiked ~ 25 ml of a hexane soln containing 3.95×10^{-7} g/ul = 9.87×10^{-6} g Aroclor 1016 in each. Flasks sealed after evaporation of hexane. Heated to ~ 80°C for 15 minutes and placed equidistant from a 100 watt mercury vapor lamp (pyrex env.) — exposure started 4:00 pm 2-8-72 at ambient temperature — one flask stored in dark for use as a reference. First flask to be analyzed 2-14-72 (~ 160 hrs)

flask No	exposure (hrs)		
1	4:00 PM	2-10-72	48 hrs.
2	4:07 PM	2-14-72	144 hrs.
3	4:00 PM	2-22-72	336 hrs.
4	4:00 PM	4-1-72	528 hrs.
5	4:00 PM	4-1-72	528 hrs

Sample #3 was pulled but not transferred.

READ AND UNDERSTOOD BY	DATE

DSW 152952

STLCOPCB4040298

K&E 10 X 10 TO ½ INCH 46 1322
7 X 10 INCHES MADE IN U.S.A.
KEUFFEL & ESSER CO.

Aroclor 1016 Photodegradation

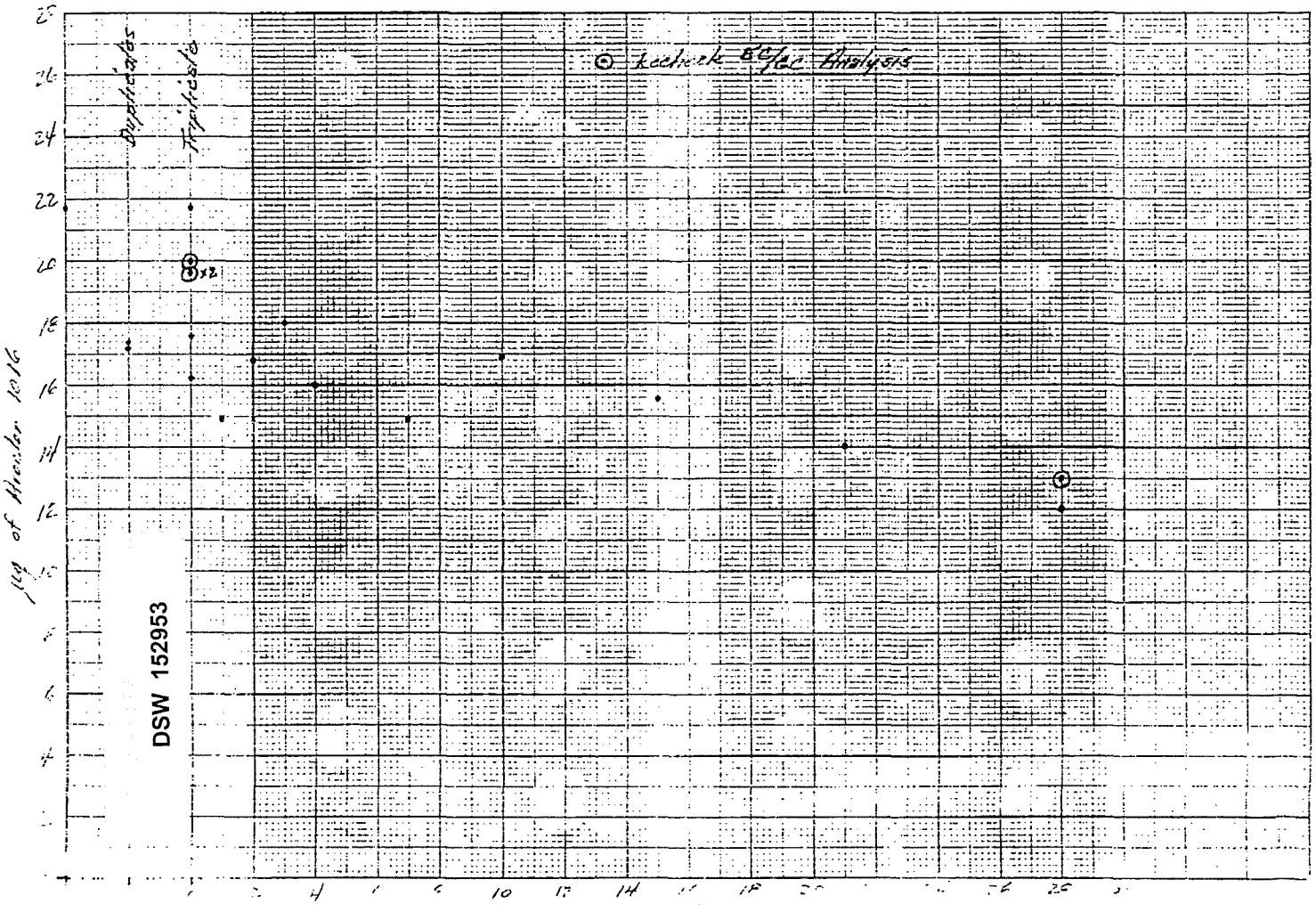


Photo deg. exps

	ug Found	T (hrs)	
#1	7.05	48	
#2	5.16	144	
#3	3.30	336	
#4	3.95	528	(22 d.)
Blk (Stored in Dark)	8.60	528	

theo. amt added = 9.87×10^{-6} g

—"—

added to bulbs 6-9-72 stored in dark refrig.

RFD order add block order sealed

	T (days)	
1*	0	
2	1	6/21 Wed
3	Control	
4	2	6/22 Thurs
5	3	6/23 Fri
6	4	6/24 Sat ✓
7*	0	
8	7	6/27 Tues
9	10	6/30 Fri
10	15	7/5 Wed
11	21	7/11 Tues
12	Control	
13	28	7/18 Tues
14	59	8/18 Fri.
15*	0	

Samples to be in red order.

on @ 2:30 PM 6-20-72

Dwyh

Aroclor 1016

56.2665
56.1798
0.0867 g/100 mL × 10^{-3} mL/µL × 25 µL

21.68 µg

Same to 5 mL
dilute 1/10

DSW 152954

STLCOPCB4040300

Aroclor 1016	Aroclor 1242 Hill	Aroclor 1242 Webb
56.2665	54.6932	56.4472
56.1798	54.6171	56.3550
.0867	.0761	.0922

$.0877\,g/100ml \times 10^{-3}\,ml/ul = 8 \times 10^{-7}\,g/ul = .8\,ug/ul$

$25ul = 20ug$

$\frac{20 \times 10^{-6}\,g}{5ml} \times 10^{-3}\,ml/ul \times 5ul = 20 \times 10^{-9}\,g/5ul$

$\frac{7.61 \times 10^{-2}\,g}{100ml} \times 10^{-3}\,ml/ul = 7.61 \times 10^{-7}\,g/ul \times \frac{1}{100}$

$\rightarrow 7.61 \times 10^{-9}\,g/ul \times 1/10 = .761 \times 10^{-9}\,g/ul$

DSW 152955

Std	Peak Height mm
1	18.6
2	30.9
4	37
5	49.8
6	53.8
7	68.0
8	70.5

(Ad)

c	3	42.8	50.1		
c	12	50	52		
0	1	50.4	53.6		30.7
0	7	55.6	58.3		32.8
0	15	86	87	52	31
1	2	50.5	54		
2	4	55.3 (54.7)	57.1		
3	5	61	63.8		
4	6	45	46.8		
7	8	42	42.6		
10	9	42.8	44.9		
15	10	45.6	47.6		
21	11	35.5	36		
28	13	33.9	36		21.9
59					

5 µl	3 µl	7 µl
2:10		1:10

DSW 152956

STLCOPCB4040302

$\frac{31}{7} \times \frac{\cancel{25}}{1} \times \cancel{14} = \frac{\cancel{50.4}}{\cancel{5}} \times \cancel{2} \times \cancel{5}$

(4.43) 5.04 $\frac{.61}{4.43}$

$\frac{21.9}{7} \quad \frac{\cancel{10}}{1} \quad \cancel{5} = \frac{84}{5} \times \cancel{2} \times \cancel{5}$

3.12 3.40 $\frac{.28}{3.12}$

13.

17.3

$\frac{52}{3} \times \frac{1}{\cancel{12}} \times \cancel{2} \times \frac{10}{10}$

.3

5.8

4.3

DSW 152957

MCC 1016 .867 ng/mL

Standards

mL	area
2	1127
4	2639
6	3953
8	5159

Samples

R-1 B-10 7 mL of 5.0 mL 1:10 2235 (3.50)

R-2 B-11 8 mL of 5.0 mL 1:10 1726 (2.75)

R-3 B-15 8 mL of 5.0 mL 1:10 2038 (3.21)

R-4 B-12 8 mL of 5.0 mL 1:10 1962 (3.10)

R-5 B-13 8 mL of 5.0 mL 1:10 2120 (3.35)

Calculations

R-1 B-10 $\frac{3.50 \times .867 \times 5 \times 10}{7 \times 1} = \frac{151.7250}{7} = 21.675$ ng

R-2 B-11 $\frac{2.75 \times .867 \times 5 \times 10}{8 \times 1} = \frac{119.213}{8} = 14.902$ ng

R-3 B-15 $\frac{3.21 \times .867 \times 5 \times 10}{8 \times 1} = \frac{139.114}{8} = 17.389$ ng

DSW 152958

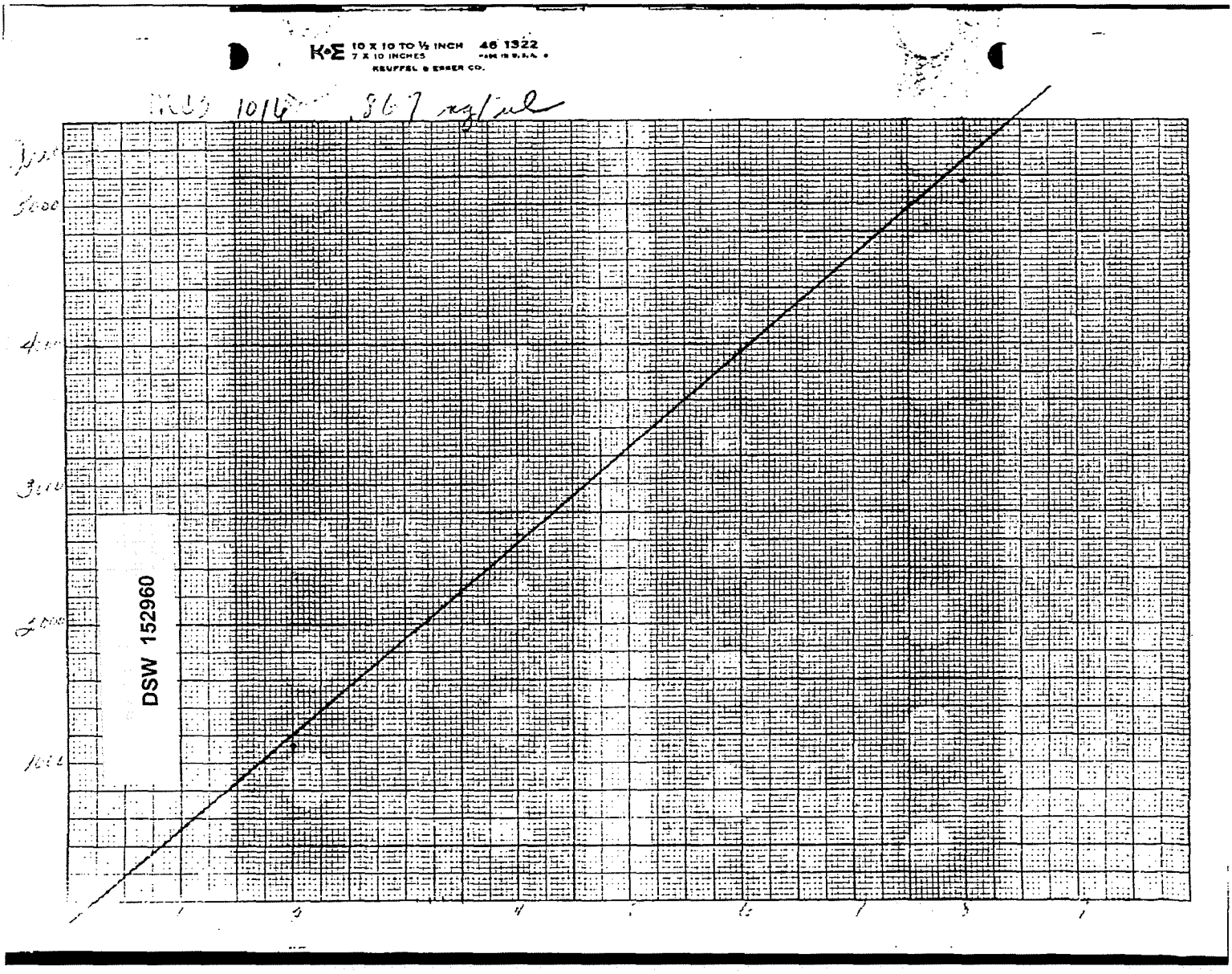
MCS 1016

R-4 B-12 $\frac{3.10 \times .867 \times 5 \times 10}{8 \times 1} = \frac{134.385}{8} = 16.7$ ug

R-5 B-13 $\frac{3.33 \times .867 \times 5 \times 10}{8 \times 1} = \frac{144.355}{8} = 12.04$ ug

ug

DSW 152959


K&E 10 X 10 TO ½ INCH 46 1322
7 X 10 INCHES
KEUFFEL & ESSER CO.
DSW 152960

WCO 1016 .1867 mg/mL

Standards

ml	area
2	1516
3	1992
4	2650
5	3977
6	4068
7	4896
8	5123

Samples

P-6 E-7	8 ml of 5.0 mL	1:10	1995	(2.95)
R-7 B-8	8 ml of 5.0 mL	1:10	2031	(3.00)
R-8 B-7	8 ml of 5.0 mL	1:10	1867	(2.75)
R-9 B-11	8 ml of 5.0 mL	1:10	2173	(3.17)
R-10 B-5	8 ml of 5.0 mL	1:10	1948	(2.87)
R-11 B-6	8 ml of 5.0 mL	1:10	1756	(2.58)
R-12 B-1	8 ml of 5.0 mL	1:10	2164	(3.17)
R-13 B-2	8 ml of 5.0 mL	1:10	1509	(2.23)

DSW 152961

MCS 1016 (cont)

R-15 B-3 [illegible] 5.0 [illegible] [illegible] [illegible] (3.[illegible]

Calculations

* R-6 B-9 $\frac{2.95 \times .867 \times 5 \times 10}{8 \times 1} = \frac{127.885}{8} = \underline{15.986}$ [illegible]

R-7 B-8 $\frac{3.00 \times .867 \times 5 \times 10}{8 \times 1} = \frac{130.050}{8} = \underline{16.[illegible]}$

R-8 B-7 $\frac{2.75 \times .867 \times 5 \times 10}{8 \times 1} = \frac{119.215}{8} = \underline{14.900}$ [illegible]

R-9 B-14 $\frac{3.12 \times .867 \times 5 \times 10}{8 \times 1} = \frac{[illegible]}{8} = \underline{[illegible]}$

R-10 B-5 $\frac{2.87 \times .867 \times 5 \times 10}{8 \times 1} = \frac{124.415}{8} = \underline{15.552}$ [illegible]

R-11 B-6 $\frac{2.58 \times .867 \times 5 \times 10}{8 \times 1} = \frac{111.845}{8} = \underline{13.981}$ [illegible]

R-12 B-4 $\frac{3.17 \times .867 \times 5 \times 10}{8 \times 1} = \frac{137.420}{8} = \underline{17.178}$ [illegible]

R-13 B-2 $\frac{2.20 \times .867 \times 5 \times 10}{8 \times 1} = \frac{95.370}{8} = \underline{11.921}$ [illegible]

R-15 B-3 $\frac{3.25 \times .867 \times 5 \times 10}{8 \times 1} = \frac{140.890}{8}$ [illegible]

DSW 152962

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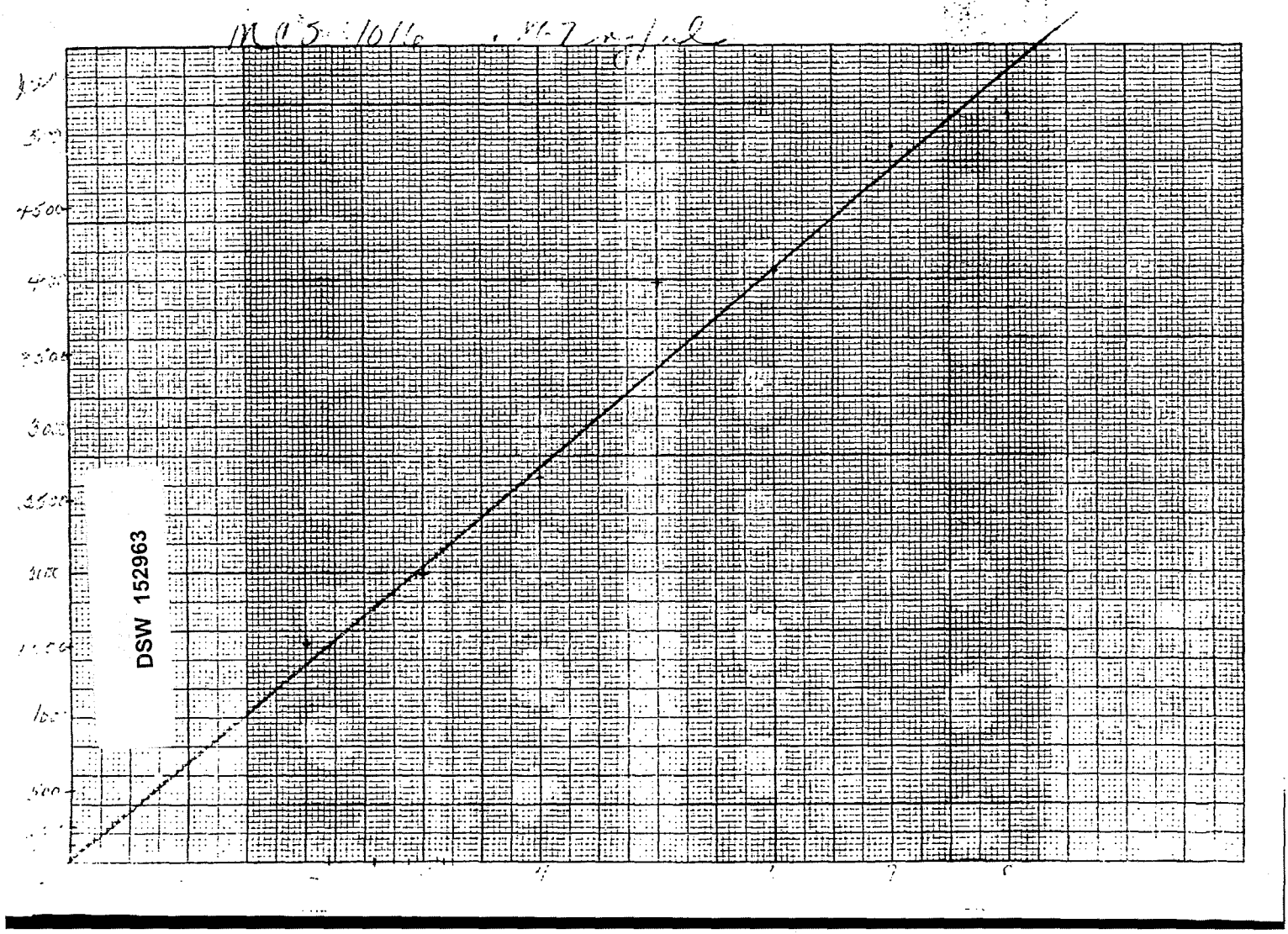
K•E 10 X 10 TO ½ INCH 46 1322
7 X 10 INCHES
KEUFFEL & ESSER CO.
DSW 152963

E. P. Wheeler

Photodecomposition of Chlorinated Biphenyls and Dibenzofurans

by
DONALD G. CROSBY and KENNETH W. MOILANEN
Department of Environmental Toxicology
University of California
Davis, Calif. 95616

The polychlorinated biphenyls (PCB's) have been widely detected throughout the world's aquatic environments (DUKE et al. 1970, VIETH and LEE 1970, SCHMIDT et al. 1971, HARVEY et al. 1973). They are accumulated by aquatic organisms (DUKE et al. 1970, ZITKO 1970, RISEBROUGH and de LAPPE 1972, STALLING and MAYER 1972) and so present concern not only for their acute and chronic toxic effects (DUKE et al. 1970, ZITKO 1970, HANSEN et al. 1971, STALLING and MAYER 1972) but also because of the probability of their transmission in food chains.

PCB's do not appear to be particularly toxic to higher animals (PANEL 1972). In fact, several effects including chloracne, hepatotoxicity, and prophyria originally attributed to PCB exposure later were ascribed to contained chlorinated dibenzofurans (PANEL 1972, KIMBROUGH 1972). Although toxicity measurements with pure PCB isomers appear not to have been reported, limited data with Arochlors indicate that maximum acute toxicity resides in the di-, tri-, and perhaps tetrachloro compounds (MURGAN 1972, STALLING and MAYER 1972, MAYER 1973).

The chlorinated biphenyls, like chlorinated hydrocarbon insecticides, are highly hydrophobic and may be expected to occur in lipid phases such as the organic films sometimes found on the surface of natural waters (DUCE et al. 1972). However, the aqueous solubility of the lower chlorinated members is surprising; water saturated with the commercial Arochlor 1221 was claimed (ZITKO 1970) to contain 5 mg/liter, although other data indicate lower values (PANEL 1972).

Recent laboratory investigations (MOILANEN and CROSBY 1973) show that DDT and DDE are converted, in part, to di-, tri-, and tetrachlorobiphenyls under simulated atmospheric irradiation conditions; these biphenyls would be expected to precipitate in rainfall (TARRANT and TATTON 1968) if they were to form in the atmosphere or be selectively volatilized from surfaces. Consequently, the possible degradative effects of the ultraviolet (UV) component of sunlight on the low-molecular weight PCB isomers is of particular interest and was the subject of this investigation.

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DSW 152964

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Materials and Methods

Materials. Pure standards of chlorinated biphenyl isomers were purchased from Aldrich Chemical Co. (Milwaukee, Wisc.) and Analabs, Inc. (North Haven, Conn.) and were homogeneous upon gas chromatography (glc). 2-Chloro- and 2,8-dichlorodibenzofuran were prepared by the method of GILMAN et al. (1934). Methanol was redistilled reagent-grade and acetone-free (Mallinckrodt Chemical Co.), and other reagents were pure grades used as received.

Irradiation. The chlorinated biphenyl (1 or 10 mg/l) in a small volume (0.3-2 ml/l) of methanol was suspended in distilled water; one liter of suspension was held in the dark, while another was irradiated for 15-26 summer days in Davis, Calif., or for 1-2 weeks in an aerated, sunlight-simulating, laboratory photoreactor (CROSBY and TANG 1969). The suspensions were extracted exhaustively with benzene, the extracts dried and vacuum-evaporated to 0.5 ml, and aliquots subjected to glc after methylation with ethereal diazomethane.

The chlorinated dibenzofurans were dissolved in purified methanol (10-100 mg/l) and irradiated in the photoreactor. Aliquots were removed at intervals and subjected directly to glc.

Chromatography. The biphenyls were chromatographed on a 180 x 0.2 cm column of 2% Carbowax 20M on 60/80 Chromosorb G, temperature-programmed 150-250°C at 10°C/min, TC detector. Fractions were collected from the effluent gas in glass capillary tubes, purified by rechromatography, and their spectra compared with those of authentic specimens where possible.

For mass spectrometry, the collected fractions were rechromatographed on a 180 x 0.2 cm column of 2% OV-1 on 60/80 Chromosorb G, temperature-programmed 150-250°C at 10°C/min, and detected with a Finnigan Model 3000 mass spectrometer detector (GC/MS).

The dibenzofurans were chromatographed on a similar 5% SE-30 column at 195°C (EC detector) or 5% XE-60 at 190° (FID detector).

Results and Discussion

Previous work in this laboratory demonstrated that chlorinated aromatic compounds are reductively dechlorinated readily in organic solvents when irradiated with UV light at sunlight wavelengths (CROSBY and HAMADMAD 1971). Under similar conditions, irradiation in aqueous media results in replacement of the chlorine by hydroxyl as well as by hydrogen (CROSBY and LEITIS 1969, MOILANEN and CROSBY 1972).

Several authors (SAFE and HUTZINGER 1971, HERRING et al. 1972, HUSTERT and KORTE 1972, HUTZINGER et al. 1972, RUZO et al. 1972) recently have reported that simple chlorinated biphenyls as well

DSW 152965

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as the complex PCB mixtures of commerce likewise underwent photoreduction in hexane solution. In aqueous suspension, our irradiation experiments also showed dechlorination (Table I);

TABLE I

Photolysis of Chlorobiphenyls in Water

Chlorobiphenyl[a]	Irradiation[b] (hrs) A	B	Reduced Product (m/e)	Hydroxylated Product[c] (m/e)
2,4-Cl_2	312	135	none	218
2,5-Cl_2	189	180	188	218[d]
3,4-Cl_2	192	135	none	none
4,4'-Cl_2	168	135	188	218
2,4,5-Cl_3	240	135	none	none
2,2',3,3'-Cl_4	216	235	257	287
2,2',4,4'-Cl_4	264	235	none	none
2,2',5,5'-Cl_4	168	200	257	287[d]

[a] 10 mg/l suspension indoors, 1 mg/l outdoors.
[b] F40BL lamp (A) or summer sunlight, Davis, Calif. (B).
[c] Methylated.
[d] 2-Chlorodibenzofuran detected by GC/MS.

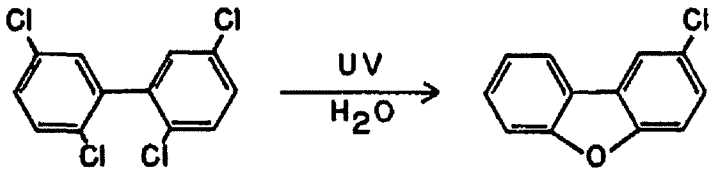
for example, 4,4'-dichlorobiphenyl formed 4-chlorobiphenyl and 4-chloro-4'-hydroxybiphenyl, as expected, although at a relatively slow rate. The higher chlorinated isomers and polymers reported previously (HUSTERT and KORTE 1972, HUTZINGER et al. 1972) were not observed, and in each instance only a reduced product containing one less Cl and a single (unidentified) product with Cl replaced by OH were detected by GC/MS. Indoor and outdoor results were identical.

Treatment of 2,2'-dichloro- or 2-chloro-2'-hydroxybiphenyl with aqueous base, or simply boiling 2,2'-dihydroxybiphenyls with water, is known to form dibenzofurans (CULLINANE et al. 1934, ZAHN and SCHIMMELSCHMIDT 1940, CASE and SCHOCK 1943), and the photochemical formation of dibenzofurans from 2-chlorobiphenyls represented a logical extension. Irradiation of chlorinated biphenyls dispersed in water (Table I), followed by GC/MS,

DSW 152966

STLCOPCB4040312

revealed identifiable traces of 2-chlorodibenzofuran as a photolysis product of 2,5-dichloro- and 2,2',5,5'-tetrachlorobiphenyl in roughly a 0.2% steady-state yield.



Similar irradiation of 2,8-dichlorodibenzofuran also resulted in slow dehalogenation, explaining the previous appearance of 2-chlorodibenzofuran. Irradiation in purified methanol under conditions similar to those which resulted in the rapid photoreduction of 2,7-dichlorodibenzo-p-dioxin (CROSBY et al. 1971) likewise caused disappearance of the dichlorodibenzofuran (Fig.1); like the 4-chlorobiphenyl (RUZO et al. 1972), the 2-chlorodibenzofuran remained almost unaffected by light. Decomposition in aqueous suspension was slow.

Although the environmental conversion of Arochlor constituents to dibenzofurans was predicted (RISEBROUGH and BERGER 1971), other investigators (HUTZINGER et al. 1972, MARTIN et al. 1972) have been unsuccessful in detecting the conversion of chlorinated biphenyls to dibenzofurans in light, perhaps due to the rapid decomposition under energetic (254 nm) irradiation conditions or the presence of sensitizers. The addition of the photosensitizer 4,4'-dichlorobenzophenone to a methanol solution of 2,8-dichlorodibenzofuran during irradiation (Fig.1) resulted in a sharp increase in the photolysis rate. Both natural and synthetic photosensitizers have been shown to affect other xenobiotics (LYKKEN 1972, ROSS and CROSBY 1973), and the environmental sensitization of dibenzofuran photolysis seems quite plausible.

The photodecomposition of the lower chlorinated PCB isomers in both polar and nonpolar solvents reveals the operation of environmental mechanisms which could effectively degrade these widespread contaminants. The recent report (HARVEY et al. 1973) that PCB mixtures occur dispersed in seawater at levels up to 150 ng/l indicates appropriate conditions for hydroxylation and dibenzofuran formation in addition to the probability of reductive dechlorination by organic matter in the sea. Indeed, the notable absence of the lower chlorinated biphenyls from most environmental samples (PANEL 1972) is suggestive of an important role of photodecomposition in the environmental fate of PCB's, the interpretation of their source and movement, and prediction of toxic effects on aquatic life.

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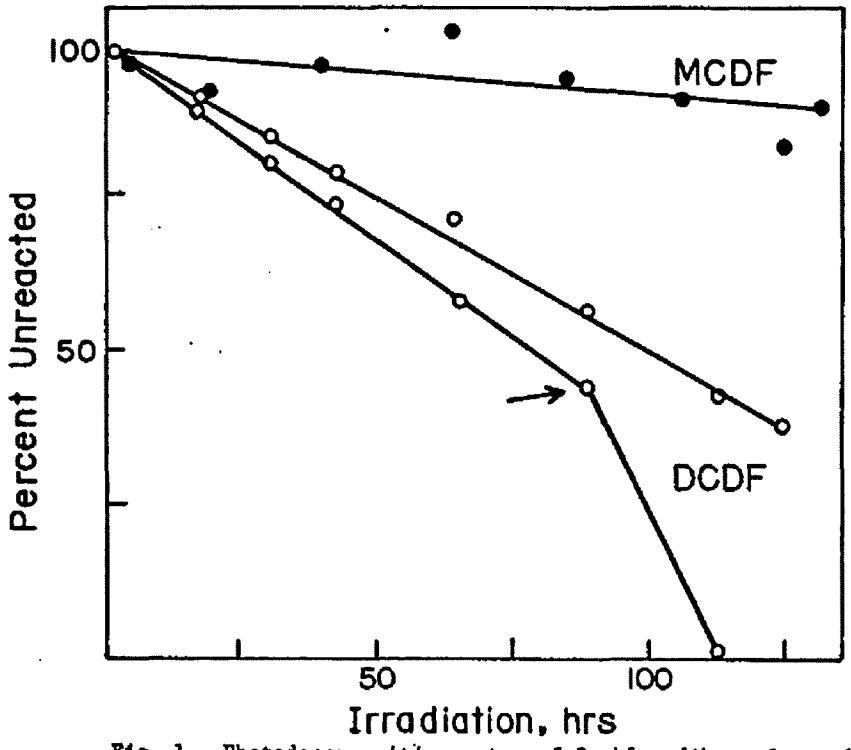

Fig. 1. Photodecomposition rates of 2-chlorodibenzofuran (MCDF) and 2,8-dichlorodibenzofuran (DCDF) in methanol at 30°C. 4,4'-Dichlorobenzophenone added as sensitizer (arrow).

Acknowledgement

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DSW 152968

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DSW 152969

STLCOPCB4040315

Photochemical Degradation of Chlorobiphenyls (PCBs)*

by O. Hutzinger and S. Safe† and V. Zitko**

Polychlorinated biphenyls (PCBs) are stable towards oxidation, hydrolysis and other chemical reactions which conceivably occur in the environment. Although there is little direct evidence available, it is generally assumed that PCBs, particularly those with a high chlorine content, are also quite resistant to metabolic change.

Over the past years photochemical degradation was shown to be a possible major route of environmental breakdown for a number of pesticides (1–4). Until relatively recently (5), however, simple chloroaromatic compounds have not received much attention. The limited interest of photochemists in compounds of this type can perhaps be explained by the commonly held view that there is generally little cleavage of the C–Cl bond in chloroaromatic compounds (6).

We have previously shown (7) that 2,2′,4,4′,6,6′-hexachlorobiphenyl, when irradiated at 3100 Å in hexane, photolyzes rather readily to give products which are formed by loss of chlorine, rearrangement and condensation. We now wish to present a first report of our studies on the photochemical stability of a number of chlorobiphenyl isomers in hexane as well as on the breakdown of chlorobiphenyls under natural and simulated "natural conditions", with particular emphasis on polar products.

Considerable experience in laboratory irradiations of pesticides has accumulated (1, 3, 8) and an elaborate "weathering chamber", which also allows controlled irradiation, has been described (9). "Natural conditions", however, are difficult to simulate for water-insoluble compounds such as the PCBs. Even in sunlight, irradiation experiments in solution are artificial since "unnatural" organic solvents have to be used. Irradiations of chlorobiphenyls in thin films, in the gas phase (both in the presence of water or water vapor) or in aqueous suspension are likely to be closer to the natural environmental conditions to which PCBs are actually exposed.

Equipment and Methods

Gas chromatographic (glc) separations were carried out with a Hewlett Packard model 5750 chromatograph using a flame ionization detector and an 8 ft × ¼ in stainless steel column containing 3% SE-30 on acid washed Chromosorb W (60/80 mesh). Temperature was isothermal or programmed as indicated. Quantitative data were obtained with a Packard A7901 gas chromatograph equipped with a 6 ft × ½ in 4% SE-30 column and an electron capture detector using the conditions previously described (10).

Combined glc mass spectral data were recorded with a Hewlett Packard model 5750 instrument, using a 6 ft × ⅛ in glass column, coupled to a DuPont/CEC 21-491 mass spectrometer via a single stage jet separator.

A DuPont/CEC 21-110B mass spectrometer equipped with a direct introduction-constant temperature probe (11) was used for obtaining spectra of individual samples.

The infrared (ir) spectra (thin films) were recorded on a Perkin Elmer 237 spectrophotometer.

Thin-layer chromatography (tlc) was carried out on precoated Merck silica thin layer plates (F-254) and plates (100×20 cm) coated with

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Merck silica gel (F-254; 0.9 mm thickness). Solvents used were: hexane and (A) 1,1,1-trichloroethane-hexane (5:1), (B) hexane–acetone (3:1), (C) benzene-ethyl acetate (12:1), (D) benzene–chloroform (2:3). The chlorobiphenyls were synthesized as described before (12,13). Aroclor 1254 was a gift of Monsanto Co.

Sources of ultraviolet light for the irradiation experiments were as follows:

(i) Sun: direct sunlight at Halifax, N.S. during the period July to September 1971.

(ii) Photochemical reactor: Rayonet (the Southern N.E. Ultraviolet Co.) using 16 R.P.R. 3100 lamps (3100 Å). The temperature was maintained at 14±2°.

(iii) Blacklight: four General Electric F40BL fluorescent lamps mounted with reflective backing ca. 15 cm above the samples. The temperature at this distance was 30–33°.

(iv) Sunlamp: General Electric 275 W "Sunlamp", one per dish at ca. 25 cm distance (temp. 35–40°). For irradiation of chlorobiphenylwater vapor, four lamps per 500 ml quartz tube were mounted horizontally at ca. 10 cm. distance.

Experiments and Results

Stabilities of Chlorobiphenyls at 3100 Å in Hexane Solution

Time study of 2,2',5,5'-tetrachlorobiphenyl decomposition—2,2',5,5'-Tetrachlorobiphenyl (50 mg) in hexane (300 ml) was irradiated in the Rayonet reactor with N_2 bubbling through the solution. 50 ml Aliquots were removed from the reaction vessel at 2, 4.5, 17, 41 and 89 h. Good quantitative data could not be obtained for the 89 h sample, probably because much of the material had polymerized. Chromatograms observed after injecting equal amounts of these aliquots and using a flame ionization (F.I.) detector are shown in Fig. 1. Percentages of starting material remaining after different irradiation times are also presented in Fig. 1. These data were obtained by measuring the area under the peak with retention time identical to the starting material

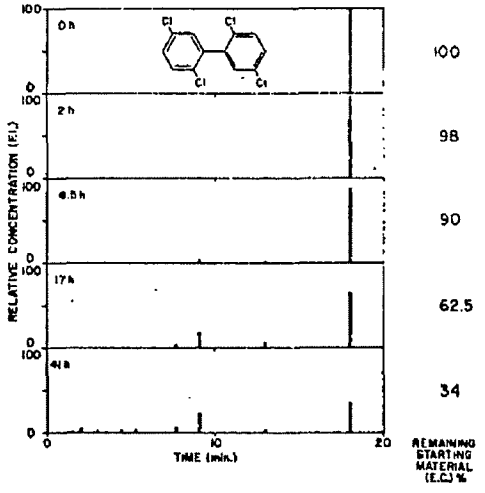

FIGURE 1. Irradiation of 2,2',5,5'-tetrachlorobiphenyl for different times; chromatograms and percent starting material remaining.

using an electron capture (E.C.) detector. Mass spectral and glc data for the 41 h sample are given in Fig. 2.

Comparative stability of chlorobiphenyl isomers—A 0.1% solution (3 ml) of the chlorobiphenyl hexane was flushed for 3 min with nitrogen, stoppered and irradiated in the Rayonet reactor for 24 h. The volume of the solution was removed from the quartz reaction cell and, after rinsing with hexane and evaporation of some of the solvent, adjusted to 3 ml. Equal amounts of the irradiated solution and the original solution

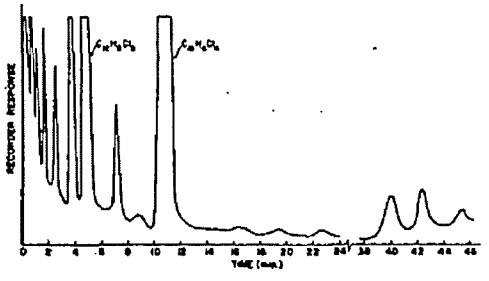

FIGURE 2. Chromatogram and mass spectral data for the 41 h sample. Oven temperature 150° isothermal, at 36 min beginning of programming (4°/min). A number of further peaks were observed after 46 min.

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Table 1. Relative Photochemical Labilities of some Chlorobiphenyl Isomers

Compound	Starting material remaining after 24 h at 3100 Å in Hexane
Tetrachlorobiphenyls	%
3,3′,4,4′-	32
2,2′,6,6′-	29
2,2′,5,5′-	33
2,2′,4,4′,5,5′-	3.8
Hexachlorobiphenyl	
2,2′,3,3′,4,4′,5,5′-	<1
Octachlorobiphenyl	

were injected into the gas chromatograph, and the areas under the peak corresponding to the starting material compared (Table 1). No immediate correlation can be seen between steric hindrance of *o*-chlorine substitution or uv spectra (14) and photochemical lability, although chlorobiphenyls with high chlorine content seem to degrade more rapidly.

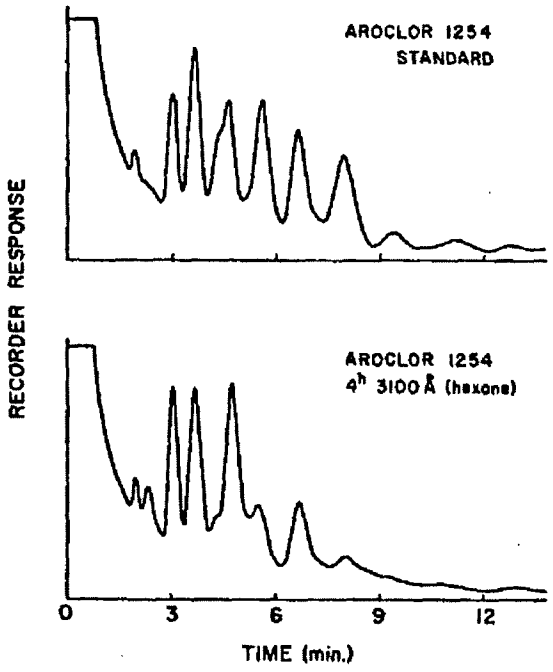
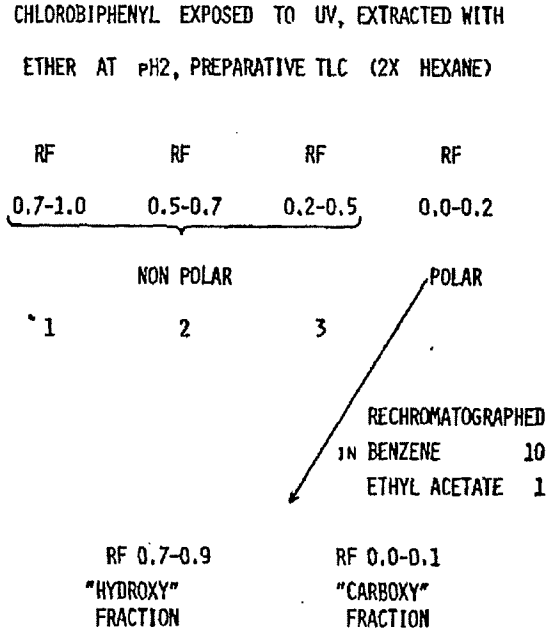


Figure 3. Chromatogram of Aroclor 1254 before and after irradiation. Glc conditions of (10).

Stability of Aroclor 1254—Aroclor 1254 (20 mg) in hexane (3 ml) was irradiated for 4 h at 3100 Å in the presence of air. Examination of the irradiated mixture and standard Aroclor 1254 by glc shows gross differences with tendencies toward shorter retention times (Fig. 3).

Irradiations in Sunlight; Under Simulated "Natural" Conditions and in Solvent Mixtures Containing Water

Aroclor 1254 I; Aqueous dioxane suspension at pH 9—A suspension of Aroclor 1254 (2 g) in a mixture of dioxane (150 ml) and water (350 ml) containing sodium bicarbonate (0.5 g) was irradiated in the Rayonet reactor for 24 h with air bubbling through the mixture. After this period another portion of sodium bicarbonate (0.5 g) was added, and the irradiation continued further for 24 h. The mixture was worked up as shown in Scheme 1. Preliminary mass spectral data for the crude nonpolar fractions one, two and three indicated the presence of only chlorobiphenyls since no ions containing oxygen corresponding to hydroxychlorobiphenyls or chlorodibenzofurans were detected. The mass spectrum of the crude



Scheme 1. Separation-scheme for irradiated chlorobiphenyls.

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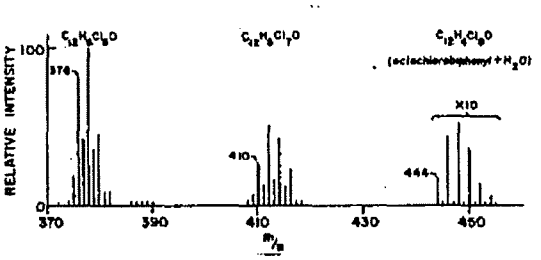

FIGURE 4. Partial mass spectrum (70 eV; probe temperature 35°) of "hydroxy" fraction from Aroclor 1254 irradiation experiment I. The chlorine isotope pattern for the Cl_5 and Cl_7 compounds are distorted due to impurities or fragment ions.

"hydroxy" fraction, part of which is shown in Fig. 4, indicated the presence of compounds formed by the addition of water to chlorobiphenyls. Hydroxy and carbonyl stretching frequencies in the infrared spectrum of the crude "carboxy" fraction (Fig. 5) are indicative of the type of compounds present in this mixture.

Aroclor 1254 II; Irradiation as thin film—Aroclor 1254 (0.5 g) was dissolved in benzene (3 ml), and this solution spread over a circular pyrex dish (diameter: 35 cm). The benzene was allowed to evaporate slowly in a way to ensure formation of a uniform Aroclor 1254 film. Water (3 ml) was added, and the dish was covered with plastic film. Water was frequently replaced during the Blacklight one-week irradiation. The irradiated product was fractionated according to Scheme 1. Preliminary mass spectra of the crude nonpolar fractions 1 and 2 (in this experiment no material

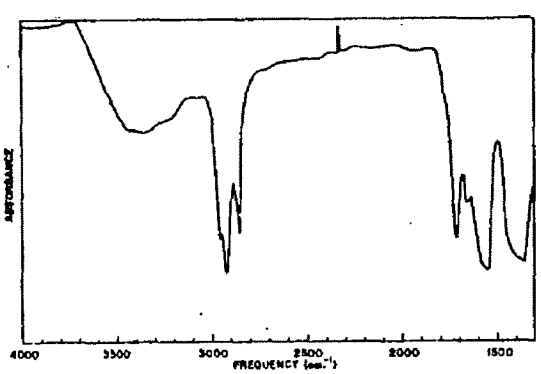

FIGURE 5. Partial infrared spectrum (thin film) of "carboxy" fraction from Aroclor 1254 irradiation experiment I.

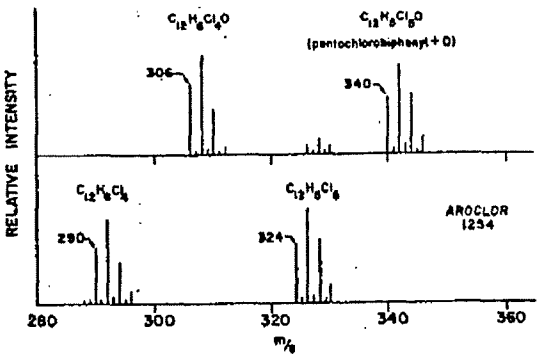

FIGURE 6. Partial mass spectra (70 eV; probe temperature 35°) of "hydroxy" fraction from Aroclor 1254 irradiation experiment II (top)) and standard Aroclor 1254 (bottom; ions <340 not shown).

corresponding to 3 was detected) showed only the presence of chlorobiphenyls. A mass spectrum of the crude "hydroxy" fraction (Fig. 6) showed ions which can be most easily explained as resulting from hydroxychlorobiphenyls. The ir spectrum of the crude "carboxy" fraction was almost identical to that from experiment I (Fig. 5).

Irradiations of 2,2',5,5'-tetrachlorobiphenyl—Some information on the types of products formed from 2,2',5,5'-tetrachlorobiphenyl on irradiation under a variety of conditions is given in Table 2. Samples were fractionated as

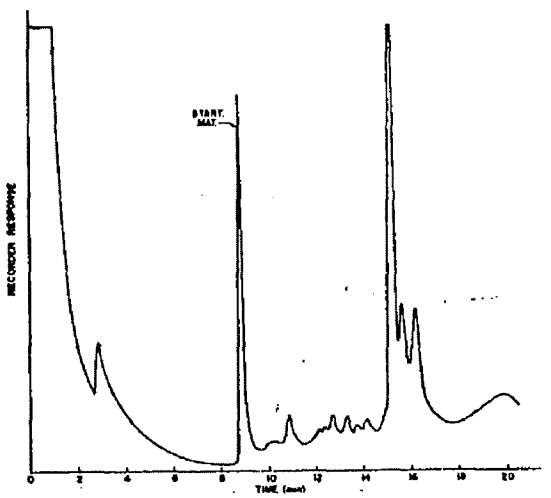

FIGURE 7. Chromatogram for 2,2',5,5'-tetrachlorobiphenyl irradiation experiment II. Oven temperature programmed from 150° at 10°/min until 310 . A number of further peaks were observed after 20 min.

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Table 2. Photochemical Decomposition of 2,2′,5,5′-Tetrachlorobiphenyl.

Experiment number	Irradiation conditions	UV source	Time	Types of products formed[a,b]			
				"Polar" products		"Nonpolar" products	
						Retention time[c]	
				"Hydroxy-"	"Carboxy-"	Short	Long
1	Aqueous suspension (+ emulsifier)	sun	2 mo	−	+	(+)	+
2	Thin film	sun	2 mo	(+)	+	(+)[d]	+[d]
3	Thin film	sun lamp	24 h	(+)	+	(+)	+
4	Thin film	black light	1 wk	(+)	+	(+)	+
5	Dioxan-2N NaOH solution	reactor	16 h	−	+	+	+
6	Aqueous dioxane solution + $FeCl_3$	reactor	16 h	(+)	+	+	+
7	Vapor (refluxing with water)	sun lamp	16 h	−	+	(+)	+

[a] + = present; (+) = present in small quantities; − = not detected.
[b] For further description of products, etc. see text.
[c] Glc retention time shorter or longer than starting material (2,2′,5,5′-tetrachlorobiphenyl).
[d] See Fig. 7.

described in Scheme 1. The nonpolar fraction was analyzed by glc (e.g. Fig. 7).

"Carboxy"-type compounds were indicated in all experiments by the chromatographic properties of a portion of the reaction products which were similar to the corresponding fractions from the Aroclor 1254 irradiation experiments I and II (i.e., $R_f < 0.1$ in solvents A–C; high R_f in aqueous methanol mixtures).

The presence of "hydroxy"-type compounds was indicated by:

(i) chromatographic comparison of the appropriate fractions with authentic hydroxy- and dihydroxybiphenyls in solvent systems A, (R_f 0.3–0.8); B, (R_f 0.3–0.7) and C, (R_f 0.4–0.8), and

(ii) by reacting the "polar" fractions with dansyl chloride (1-dimethylaminonaphthalene-5-sulfonyl chloride) and comparing the chromatographic properties (solvent D; R_f ca. 0.75 for monohydroxy and ca. 0.4 for dihydroxy compounds) and in situ fluorescence excitation (350 nm) and emission (525 nm) wavelength with those of dansyl derivatives of authentic hydroxy and dihydroxybiphenyls (see reference 15 for the general method).

Discussion

The photolysis of chlorobiphenyls reveals a number of degradative reactions which occur on irradiation in sunlight and a number of laboratory conditions. In hexane, the most prominent reaction was the progressive reductive dechlorination of these compounds as well as formation of polymeric materials. Irradiation of Aroclor 1254 in hydroxylic solvents at pH 9 yields compounds corresponding to the addition of water to the PCB molecules and a more polar carboxylic acid fraction. The same sample irradiated as a thin film does not yield the water-addition products, but mass spectrometry reveals the presence of new hydroxylated species. This experiment also gives a more polar "carboxylic" fraction. Data for a number of different irradiations of 2,2′,5,5′-tetrachlorobiphenyl indicate that dechlorination, formation of polymers, and carboxylic products as well as hydroxylation, does occur.

DSW 152974

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The present photolytic work thus reveals decomposition of PCBs by both oxidative and reductive pathways.

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DSW 152975

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BEITRÄGE ZUR ÖKOLOGISCHEN CHEMIE XXXVIII[x)]

Synthese polychlorierter Biphenyle und ihre Reaktionen bei UV-Bestrahlung

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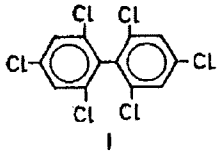
Organisch-Chemisches Institut der Universität Bonn

(Received in Germany 3 December 1971; received in UK for publication 10 December 1971)

Kommerzielle polychlorierte Biphenyle, PCB (Arochlor, Clophen) sind für die experimentelle Untersuchung ihrer chemischen Veränderungen in der Umwelt aufgrund ihrer komplexen Zusammensetzung nicht geeignet. Wir synthetisierten deshalb einige reine definierte PCB-Isomere. Durch Ullmannreaktion der entsprechenden Chlorjodbenzole erhielten wir 2, 4, 6, 2', 4', 6'-Hexachlorbiphenyl (I), 2, 4, 5, 2', 4', 5'-Hexachlorbiphenyl (II) und 2, 4, 2', 4'-Tetrachlorbiphenyl (III). 2, 5, 2', 5'-Tetrachlorbiphenyl (IV) entstand aus dem entsprechenden Tetrachlorbenzidin[1)].

Für UV-Bestrahlungsversuche wählten wir besonders das 2, 4, 6, 2', 4', 6'-Hexachlorbiphenyl sowie das 2, 5, 2', 5'-Tetrachlorbiphenyl.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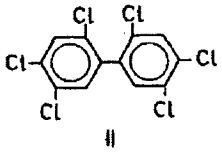
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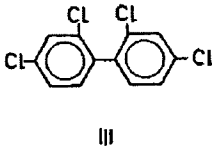
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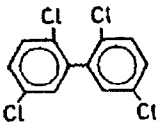
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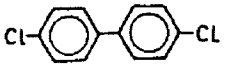
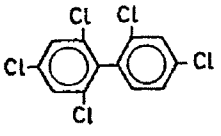
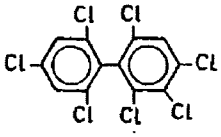

V


VI


VII

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No. 1

Als Lichtquelle wurde eine Quecksilberdampflampe benutzt, deren Emission oberhalb 230 nm beginnt. Das UV-Spektrum von 2, 4, 6, 2', 4', 6'-Hexachlorbiphenyl (I) zeigt erst unter 300 nm eine nennenswerte Absorption (dasselbe gilt für das Tetrachlorbiphenyl IV), weshalb die Bestrahlungen vorwiegend mit Quarzfiltern durchgeführt werden. Mit Pyrexfiltern konnte eine nur außerordentlich langsam verlaufende Photolyse beobachtet werden.

Bei Bestrahlung des Hexachlorbiphenyls I in Lösungsmitteln wurde eine Dechlorierung nachgewiesen, deren Geschwindigkeit in der Lösungsmittelreihe n-Hexan, Aceton, Methanol, Methanol/Wasser zunahm. Folgende Reaktionsprodukte konnten durch kombinierte Gaschromatographie/Massenspektrometrie im Reaktionsgemisch nachgewiesen werden: Pentachlorbiphenyl, Tetra-, Trichlor-, Dichlor- und Monochlorbiphenyl sowie Biphenyl. Bei Bestrahlungsdauer, z.B. in Methanol über 100 Stunden, waren die Reaktionsprodukte, vermutlich wegen Polymerisation, nicht mehr identifizierbar.

Zur Strukturaufklärung wurden die Hauptzwischenprodukte der Photolyse, 4, 4'-Dichlorbiphenyl (V) und ein Pentachlorbiphenyl, wahrscheinlich das 2, 4, 6, 2', 4'-Isomere (VI), isoliert. V entsteht z.B. bei 24-stündiger Bestrahlung von I in Methanol mit 20 %iger Ausbeute. Tri- und Tetrachlorbiphenyl treten nur in geringen Mengen auf, sodaß eine sichere Strukturaufklärung der Isomeren nicht möglich war. Die Nebenprodukte 4-Monochlorbiphenyl und Biphenyl wurden durch gaschromatographischen und massenspektrometrischen Vergleich mit authentischen Proben identifiziert.

Das Tetrachlorbiphenyl IV wurde in Methanol bestrahlt. Es erfolgte wie bei I zunächst Dechlorierung. Nach 70-stündiger Bestrahlung enthält das Reaktionsgemisch nur noch Polymere.

Bei der Bestrahlung von I in Methanol entstehen neben den erwähnten Produkten polare Substanzen, wahrscheinlich Phenole, von denen drei dünnschichtchromatographisch charakterisiert wurden. Wegen der geringen Ausbeute war bisher eine Isolierung jedoch nicht möglich.

Bei Bestrahlung von I in perfluoriertem Dimethylcyclohexan als Lösungsmittel ist die in anderen Lösungsmitteln beobachtete sukzessive Dechlorierung zurückgedrängt. Hier erfolgt hauptsächlich Isomerisierung und eine mit Dechlorierung verbundene Chlorierung, z.B. zu Heptachlorbiphenyl.

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Zur Bestrahlung in fester Phase wurde das Hexachlorbiphenyl I als Film auf die Wand des Bestrahlungsgefäßes aufgetragen. In geringer Ausbeute konnte Heptachlorbiphenyl (VII) sowie spurenweise Octachlorbiphenyl nachgewiesen werden.

Die Gasphasenbestrahlung wurde in einer größeren Apparatur bei 50°C mit Pyrexfiltern durchgeführt. Hier wurde nur das unveränderte Hexachlorbiphenyl I erhalten.

Diskussion der Ergebnisse:

Während in protonenhaltigen Lösungsmitteln Dechlorierung und Polymerisation zu beobachten ist, erhält man in perfluoriertem Kohlenwasserstoff (inertes Medium) und in fester Phase Isomerisierung und nachweisbare Chlorierung. Unsere Untersuchungen deuten darauf hin, daß unter Umweltbedingungen neben Photolyseprodukten mit niedrigerem Chlorgehalt [2] höherchlorierte Biphenyle, wenn auch in geringen Mengen, zu erwarten sind.

EXPERIMENTELLER TEIL:

2,4,6,2',4',6'-Hexachlorbiphenyl (I), 2,4,5,2',4',5'-Hexachlorbiphenyl (II) und 2,4,2',4'-Tetrachlorbiphenyl (III) wurden nach Ullmann synthetisiert [3]. Die hierzu notwendigen Chlorjodbenzole erhält man aus den entsprechenden Chloranilinen. Die Darstellung von 2,4,5,2',4',5'-Hexachlorbiphenyl (II) gelingt in höherer Ausbeute durch Sandmeyerreaktion aus 2,5,2',5'-Tetrachlorbenzidin. 2,5,2',5'-Tetrachlorbiphenyl (IV) wird durch Reduktion des Diazoniumsalzes von 2,5,2',5'-Tetrachlorbenzidin hergestellt. Durch NMR- und Massenspektren wurden die Strukturen der synthetisierten Verbindungen sichergestellt. Bei allen Bestrahlungen wurde mit einer Hg-Hochdrucklampe Philips, HPK 125 gearbeitet. Die Konzentrationen der bestrahlten Lösungen lagen bei ungefähr 10 mg/ml, das Lösungsmittelvolumen bei etwa 100 ml.

Gaschromatographie: Für gaschromatographische Analysen wurden ein Aerograph 200 (Varian MAT) und ein F & M, Modell 720 verwendet; Säulenmaterial: 5 % QF_1 auf Chromosorb W (5 feet, 1/8 inch) bzw. 10 % Carbowax 20 M auf Chromosorb WAW (2 feet); Trägergas: Stickstoff bzw. Helium; Detektor: Tritium-EC bzw. WLD; Säulentemperatur: 150°C isotherm bzw. ab 190°C temperaturprogrammiert; Dünnschichtchromatographie: Kieselgel G oder H; Laufmittel: n-Hexan; Sprühmittel: 0,5 g Diphenylamin in 80 ml Äthanol, 20 ml Aceton und 1,5 ml Paraffinöl (im UV-Licht entwickelt) [4].

Spektren: Die Kernresonanzspektren wurden mit einem Varian A 60-Gerät gegen TMS als internen Standard, die Massenspektren mit einem LKB 9000 A aufgenommen.

DSW 152978

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x) XXXVII. Mitteilg. M. Zimmer und W. Klein, vorstehend

DSW 152979

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621

UV Irradiation of Aroclor 1254[1,2]

by JEFFRY L. HERRING, ELLEN J. HANNAN, and DONALD D. BILLS
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Oregon State University
Corvallis, Ore. 97331

Although polychlorinated biphenyls (PCB's) have been shown to be widespread, highly persistent environmental contaminants occurring in numerous wildlife specimens and food samples (1,2,3), little is known about their fate in the environment. One proposed mechanism of breakdown is degradation by ultraviolet (uv) radiation from the sun (2). The degradation of PCB's by this means seemed feasible since their structure is similar to many of the chlorinated insecticides which are readily degraded by uv light (4,5,6). To study this possibility, solutions of a commercial PCB mixture (Aroclor 1254, Monsanto Chemical Co.) were irradiated with a laboratory uv lamp and sunlight.

EXPERIMENTAL

A solution of 200 ppm Aroclor 1254 (supplied by Monsanto Chemical Co.) in acetone was prepared and diluted 1:100 (2 ppm) with distilled water, hexane, and benzene. Three ml portions of each solution were placed in quartz cuvettes (Beckman standard 1 cm absorption cells) fitted with teflon caps. The samples, placed at a distance of 14 cm from the light source, were irradiated with a Hanovia Utility Quartz Lamp (100 watt) for 5, 15, 30 and 45 minutes. Control samples of each solvent system were not irradiated. The benzene and hexane samples were concentrated to one ml using a rotary evaporator. The water sample was extracted with two consecutive 10 ml portions of hexane in a separatory funnel. The extract was dried with anhydrous sodium sulfate and concentrated to 1 ml.

Hexane solutions of 1, 10 and 100 ppm in glass stoppered quartz test tubes were exposed to direct sunlight during the month of July and sampled weekly for three weeks.

All samples were analyzed using an F & M Model 810 gas chromatograph equipped with a tritium electron capture detector: carrier gas, 95% argon and 5% methane, 60 ml/min; injector, 200° C; column, 180° C; detector, 200° C. A glass column, 122 cm x 4 mm I.D., packed with 2% SE-30 and 2% QF-1 on Anakrom ABS 70/80 mesh was used.

[1]This investigation was supported in part by a Food and Drug Administration grant 5R01 FD 00033.

[2]Technical Paper No. 3279, Oregon Agricultural Experiment Station, Oregon State University, Corvallis, Oregon 97331.

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RESULTS AND DISCUSSION

Figure 1 represents a typical chromatogram of the unirradiated mixture. For purposes of following the pattern of degradation, only the first 10 major peaks, which represent tetra-, penta- and hexachlorobiphenyls, were examined. The Aroclor 1254 mixture was readily degraded in all three solvent systems but at different rates in each. Tables 1-3 present the percentages of each peak remaining, compared to the unirradiated sample, after varying lengths of irradiation with the Hanovia lamp.

In general, the PCB's degraded fastest in hexane, then water, and slowest in benzene. The fact that some peaks increased in size suggests that the more highly chlorinated PCB's were being dechlorinated to form PCB's with lower molecular weights and shorter retention times. It is also quite evident from the variations between each peak that the PCB's do not all degrade at the same rate.

There are two possible explanations for the effect of solvent on degradation rate. The most obvious is the transmission limit for uv radiation of the solvent. This limit is approximately 190 nm, 210 nm and 280 nm for water, hexane, and benzene, respectively. By comparing the rates in hexane and water to that in benzene, it would appear that the shorter wavelength, higher energy radiation is more effective. The second explanation could be that the solvent participates in the reaction, possibly as a hydrogen donor. In this case, both the reactivity and the polarity of the solvent would be important. One would expect benzene to be a relatively poor hydrogen donor which would explain its slower rate, while hexane and water would be more reactive, thus giving faster rates. The fact that the rate is slower in water than in hexane might be due in part to the relative insolubility of PCB's in water. Even at the low concentration of 2 ppm, it is not known whether PCB's exist in true solution or as a suspension in water.

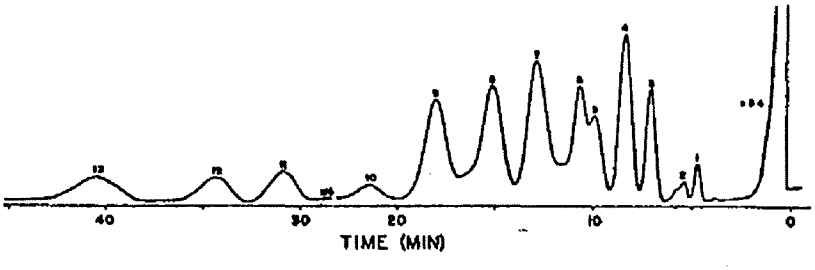

Figure 1. Chromatogram of Aroclor 1254 mixture.

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TABLE 1

Percent of each peak left after irradiation of hexane solutions with uv lamp.

Peak#	Time of Exposure (minutes)		
	5	15	30
1	104%	29%	0
2	275	83	0
3	99	0	0
4	62	0	0
5	0	0	0
6	140	75	0
7	9	0	0
8	28	0	0
9	7	0	0
10	0	0	0

The results of the sunlight (Table 4) and laboratory lamp irradiations agree fairly well except that peak 5 did not appear to degrade as readily. The overall rate of degradation was much slower due to the lower intensity and the lack of short wavelength radiation in sunlight compared to the laboratory lamp. There was a close correlation in the degradation patterns at all three concentrations which suggests the process is not concentration dependent.

From an environmental standpoint, the degradation of PCB's by sunlight is most significant. It should, however, be noted that little is known at this time of the products of the photolytic breakdown of PCB's, thus uv degradation may result in the production of at least transient quantities of more toxic compounds.

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TABLE 2

Percent of each peak left after irradiation of water mixture with uv lamp.

Peak #	Time of Exposure (minutes)			
	5	15	30	45
1	97	20	0	0
2	30	0	0	0
3	121	43	21	10
4	96	45	23	10
5	66	14	0	0
6	80	38	26	15
7	110	78	55	32
8	79	54	35	20
9	75	35	27	10
10	0	0	0	0

TABLE 3

Percent of each peak left after irradiation of benzene solution with uv lamp.

Peak #	Time of exposure (minutes)			
	5	15	30	45
1	104	72	31	55
2	116	48	30	43
3	94	73	57	60
4	96	77	31	55
5	106	61	26	44
6	99	67	43	47
7	75	47	22	15
8	90	68	46	40
9	90	64	45	44
10	106	71	67	63

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TABLE 4

Sunlight Irradiation of Aroclor 1254.

Initial Concentration of Aroclor 1254 in Hexane

	1 ppm			10 ppm			100 ppm		
	% remaining after			% remaining after			% remaining after		
Peak No.	1 week	2 weeks	3 weeks	1 week	2 weeks	3 weeks	1 week	2 weeks	3 weeks
1	97	109	143	65	104	104	85	131	139
2	111	137	161	111	140	180	114	164	184
3	74	76	79	113	94	88	110	110	101
4	83	104	109	127	108	143	92	99	120
5	103	89	87	98	96	94	118	70	63
6	181	211	196	210	206	241	157	205	218
7	58	51	36	68	58	40	68	58	42
8	84	89	75	111	98	90	105	96	80
9	66	47	30	53	44	44	80	56	47
10	62	47	41	49	50	59	80	64	54

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to minor changes in O and S substitution, which do not greatly affect MONITOR activity. Adverse effects are also apparent in acyl chain branching or cyclization despite the remarkable retention of high activity out to 18 carbon atoms.

20. STRUCTURE AND FUNGITOXICITY OF ORGANOPHOSPHORUS COMPOUNDS. Henry Tolkmith, Dorsey Mussell, Dow Chemical U.S.A., Midland, Michigan 48640.

A number of organic phosphorus compounds have been found to be active against fungi pathogenic for agriculturally important plants. Such compounds represent two separate classes of structure. One class comprises substances containing at least one sulfur atom attached directly at phosphorus. Organophosphorus fungicides of this kind belong to several types of compounds, viz., phosphonothioates, phosphorothiolates and phosphorothiolothionates. The other class comprises products that are phosphorus derivatives of N-heterocyclics, such as maleimide, imidazole, triazole and pyrazolopyrimidine. The antifungal activity and mammalian toxicity of the compounds indicated will be discussed.

TUESDAY MORNING - SECTION B - GENERAL - H. F. Enos, Presiding

21. VAPOR-PHASE PHOTODECOMPOSITION OF *p,p'*-DDT AND ITS RELATIVES. Kenneth W. Moilanen, and Donald G. Crosby, Department of Environmental Toxicology, University of California, Davis, Calif. 95616.

Investigations with the vapor-phase photoreactor described previously (Moilanen and Crosby, ACS Meeting, Boston, 1972) have been extended to the decomposition of DDT and its relatives. DDT was converted to DDE which underwent further decomposition to four electron-capturing, chlorinated photoproducts. In addition, 3,6-dichlorofluorenone was detected as a product of DDT photodecomposition taking place on the reactor walls. Several improvements in the photoreactor, including a new source of ultraviolet light, have been directed toward closer simulation of environmental conditions.

22. INVESTIGATION FOR BOUND RESIDUES IN TISSUES FROM CATTLE FED 2,4,5-T D. J. Jensen, P. W. Miller, L. F. Berhenke, Agricultural Department, Dow Chemical U.S.A., P. O. Box 1706, Midland, Michigan 48640.

Muscle, fat, liver, and kidney from animals fed various amounts of 2,4,5-T were assayed for 2,4,5-T and 2,4,5-trichlorophenol employing an extraction with 2% ammonium hydroxide in methanol. Other portions of these samples were subjected to hydrolysis with both 6N KOH and 6N H_2SO_4 before extraction to obtain the total residue and to compare the effects of both acid and alkali on the residues obtained. Still other portions of these samples were extracted with 2% ammonium hydroxide-methanol mixture and the extract and the extracted solids were hydrolyzed by both 0.5N KOH and 0.5N H_2SO_4. Interesting residue patterns were obtained.

23. DETECTION OF MAMMALIAN EXPOSURE TO CARBAMATE INSECTICIDES. Hazel C. Sullivan, T. Shafik, Perrine Primate Laboratory, Environmental Protection Agency, P. O. Box 490, Perrine, Florida 33157.

A method for the determination of low level exposure in mammals to three carbamate insecticides (Baygon, carbaryl, carbofuran) will be described. The procedure is based on the quantitation of the corresponding phenolic or hydroxylated metabolite in urine. Since in each case, the metabolite to be detected had poor electron capturing properties, the pentafluorobenzyl ether derivative was used to enhance the limits of detection. The urine from male rats fed at levels as low as 10^{-4} of the LD_{50} was analyzed using acid hydrolysis, extraction, derivatization, silica gel cleanup, and electron capture gas chromatography. Data will be presented which establishes the limits of detection and the rate of excretion of the three metabolites used as the index of exposure to these insecticides.

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various authors, and reviewed by Dubois (1961), is needed for the purpose of verifying whether potentiation resulting from the administration of pairs of organophosphorus insecticides to warm-blooded animals was at least in part attributable to impurities of the type under study and present in the products used.

ACKNOWLEDGMENT

The authors thank the following persons for their assistance: Roberto Guarnieri, Marco Radice, Guglielmo Galluzzi, Fiorenzo Vola Gera, Giannantonio Michieli, and Nicola Troiani, Istituto Ricerche Agrarie, Montecatini Edison S.p.A., Milano, Italy. Gratitude is expressed to Franco Santoro, Centro Ricerche, Montecatini Edison S.p.A., Bollate, Italy, for the mass spectra and their interpretation. Thanks are also due to the Agriculture Division, American Cyanamid Co., Princeton, N.J., for contributing samples of technical malathion.

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Photodecomposition of 3′,4′-Dichloropropionanilide (Propanil)

Kenneth W. Moilanen* and Donald G. Crosby

The action of sunlight on dilute aqueous solutions of 3′,4′-dichloropropionanilide (propanil) provided a large number of photodecomposition products separable by gas chromatography. 3′-Hydroxy-4′-chloropropionanilide, 3′-chloro-4′-hydroxypropionanilide, 3′,4′-dihydroxypropionanilide, 3′-chloropropionanilide, 4′-chloropropionanilide, propionanilide, 3,4-dichloroaniline, 3-chloroaniline, propionic acid, propionamide, 3,3′,4,4′-tetrachloroazobenzene, and a humic acid were identified. The tetrachloroazobenzene also resulted from the photolysis of a dilute aqueous solution of 3,4-dichloroaniline. The principal pathways of propanil photodecomposition were: replacement of chlorine substituents by hydroxyl groups; formation of propionamide; replacement of chlorine substituents by hydrogen; and hydrolysis of the amide. Propanil and its benzenoid photolysis products were not appreciably volatile, and only propanil was phytotoxic.

The anilide herbicide 3′,4′-dichloropropionanilide (propanil, I) is widely used for the selective control of broadleaf weeds in cultivated rice and as a postemergence herbicide in tomatoes. In 1968, a controversy developed over the use of propanil in the vicinity of prune orchards in several Northern California counties after some of the trees began to exhibit yellowing of the leaves allegedly due to incidental exposure to the herbicide following its use in nearby rice fields.

The purpose of the present investigation was to identify the products of propanil photodecomposition in aqueous solution, to propose a possible mechanism for their formation, and to determine whether or not the photodecomposition of propanil was related to prune tree damage.

EXPERIMENTAL

Synthesis of Photoproducts. 3′,4′-Dichloropropionanilide was received as a technical product, mp 85–89°C (Technical Stam, Rohm & Haas Co.). It was recrystallized twice from cyclohexane (charcoal) to a mp of 91–92°C [lit. 91–92°C (Good, 1961)].

3′-CHLOROPROPIONANILIDE (II). Propionyl chloride (0.92 g, 0.010 mol) was slowly added to a chilled suspension of 3-chloroaniline (Eastman Organic Chemicals) (1.28 g, 0.010 mol) in 6 ml of 10% sodium hydroxide solution to give 3′-chloropropionanilide (0.92 g, 50%) which was recrystallized twice from 3:1 water–ethanol; mp 85.5–86°C [lit. 88–89°C (Good, 1961)].

Anal. Calcd for $C_9H_{10}ClNO$: C, 58.85; H, 5.49; N, 7.65. Found: C, 59.00; H, 5.30; N, 7.70.

Infrared (ir) spectrum 3236 (NH) and 1667 (CO) cm^{-1}. Nuclear magnetic resonance (nmr) spectrum δ 8.80 (NH). Mass spectrum *m/e* 183 (parent), 127 (base, $ClPhNH_2$).

4′-CHLOROPROPIONANILIDE (III). The procedure was identical to that for 3′-chloropropionanilide except that 4-chloroaniline (Eastman Organic Chemicals) was used to give 4′-chloropropionanilide (0.84 g, 46%) which was recrystallized twice from benzene; mp 137.5–139°C [lit. 137°C (Good, 1961)].

Anal. Calcd for $C_9H_{10}ClNO$: C, 58.85; H, 5.49; N, 7.65. Found: C, 58.96; H, 5.39; N, 7.44.

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Ir spectrum 3333 (NH) and 1675 (CO) cm^{-1}. Nmr spectrum δ 9.20 (NH). Mass spectrum *m/e* 183 (parent), 127 (base, $ClPhNH_2$).

3′-Chloro-4′-hydroxypropionanilide (V). 2-Chloro-4-nitrophenol (Aldrich Chemical Co.) (10.0 g, 0.058 mol) in absolute ethanol (200 ml) was reduced to the corresponding amine with platinum oxide (Adams Catalyst) and hydrogen at ambient temperature and pressure. The resulting 2-chloro-4-aminophenol was propionylated at the amino group by dissolving it in propionic acid (120 ml) and adding a slight excess of propionic anhydride (7.2 ml). After heating on a steam bath for 1.5 hr, the mixture was poured over ice to give 3′-chloro-4′-hydroxypropionanilide (2.7 g, 23.5%) which was recrystallized twice from water; mp 140–141.5°C.

Anal. Calcd for $C_9H_{10}ClNO_2$: C, 54.26; H, 5.06; N, 7.03. Found: C, 54.14; H, 4.98; N, 7.04.

Ir spectrum 3413 (NH), 3205 (PhOH), and 1667 (CO) cm^{-1}. Nmr spectrum δ 8.68 (PhOH) and δ 9.17 (NH). Mass spectrum *m/e* 199 (parent), 143 (base, $ClPhNH_2OH$).

3′-Hydroxy-4′-chloropropionanilide (VI). A solution of 2-amino-5-nitrophenol (Eastman Organic Chemicals) (61.6 g, 0.400 mol) in concentrated hydrochloric acid (260 ml) was diazotized with sodium nitrite (28.8 g, 0.400 mol) in water (70 ml), and the diazonium salt was treated with cuprous chloride (40 g, 0.400 mol) in water (200 ml) to give 2-chloro-5-nitrophenol (3.4 g, 4.9%). This compound was catalytically hydrogenated, followed by propionylation at the amino group as described above to give 3′-hydroxy-4′-chloropropionanilide (1.5 g, 31%) which was crystallized twice from 4:1 water–ethanol; mp 206–207°C.

Anal. Calcd for $C_9H_{10}ClNO_2$: C, 54.26; H, 5.06; N, 7.03. Found: C, 54.19; H, 4.99; N, 7.06.

Ir spectrum 3344 (NH), 1661 (CO) cm^{-1}. Nmr spectrum δ 8.72 (PhOH) and δ 9.17 (NH). Mass spectrum *m/e* 199 (parent), 143 (base, $ClPhNH_2OH$).

3′,4′-Dihydroxypropionanilide (VIII). 4-Nitrocatechol (Aldrich Chemical Co.) (5.0 g, 0.032 mol) in absolute ethanol (100 ml) was catalytically hydrogenated and then propionylated at the amino group as described for the previous two compounds to give 3′,4′-dihydroxypropionanilide (4.7 g, 81%) which was recrystallized twice from water; mp 200°C (dec).

Anal. Calcd for $C_9H_{11}NO_3$: C, 59.64; H, 6.12; N, 7.73. Found: C, 59.45; H, 6.24; N, 7.58.

Ir spectrum 3390 (PhOH), 3344 (NH), and 1587 (CO) cm^{-1}. Nmr spectrum δ 8.72 (PhOH) and δ 9.48 (NH). Mass spectrum *m/e* 181 (parent), 125 (base, $PhNH_2(OH)_2$).

3,3′,4,4′-Tetrachloroazobenzene (XIV) was prepared by the method of Corbett and Holt (1963) and recrystallized twice from benzene–petroleum ether; mp 158–158.5°C. Standard humic acid (XII) was prepared by the method of Crosby and Tutass (1966).

Methods. All melting points were determined on a Hoover capillary melting point apparatus and are uncorrected. Ir spectra were measured in KBr micropellets with a Perkin-Elmer Model 337 grating spectrophotometer. Ultraviolet spectra were measured in aqueous solution on a Beckman DK-2A spectrophotometer. Nmr spectra were measured with a Perkin-Elmer Hitachi Model R-20 spectrometer as solutions in deuterated acetone or deuterated dimethylsulfoxide with a tetramethylsilane internal standard. Mass spectra were recorded with a Varian M-66 instrument. Elemental analyses were performed by the Microanalytical Laboratory of the Chemistry Department at the University of California, Berkeley, Calif.

Gas–liquid chromatographic (glc) analyses were accomplished with an F&M Model 720 instrument equipped with a thermal conductivity detector and 2-ft × $^1/_8$-in. i.d. stainless steel columns containing either 2% SE-30 silicone gum on 60/80 mesh acid-washed, DMCS-treated Chromosorb G, or 1% diethylene glycol adipate (DEGA) on 100/120 mesh acid-washed, DMCS-treated Chromosorb G (Perco Supplies, San Gabriel, Calif.). The initial column temperature was 50°C; final column temperature, 200°C (DEGA) or 280°C (SE-30); program rate, 10°C per min; injection port temperature, 250°C; detector temperature, 300°C; helium carrier gas, flow rate 40 ml per min. As it eluted, each compound was collected in a glass capillary tube, purified by rechromatography, and identified by comparison of its spectra, mp, and chemical properties with those of authentic specimens.

Thin-layer chromatography (tlc) was carried out on Brinkmann Silica Gel F-254 (0.5-mm thickness) containing 1% zinc orthosilicate:manganese phosphor using benzene–ethyl acetate–methylene chloride (9:7:3, v/v/v). Detection of phenolic compounds employed 1% *p*-nitrobenzenediazonium fluoborate in 20% aqueous sodium acetate. The R_f values for several of the photoproducts are: Compound II, 0.51; III, 0.49; V, 0.35; VI, 0.32; VII, 0.14; XIV, 0.77.

Standard solutions for irradiation were prepared by dissolving 200 mg of propanil in 1 l. of distilled water. A preparative-scale photoreactor which closely simulated the effects of sunlight was employed for laboratory irradiations (Crosby and Li, 1969; Crosby and Tang, 1969); samples for isolation and identification usually were prepared in this equipment.

Irradiations with sunlight were conducted with 200-ppm solutions prepared by dissolving 3.4 g of propanil in 17 l. of distilled water in a covered, 40-l. borosilicate glass bottle. To ensure aerobic conditions and agitation, filtered compressed air was bubbled in through a glass frit. The solution was allowed to remain outdoors for 6 months, and aliquots were analyzed at frequent intervals.

The irradiated solutions were adjusted to pH 11 with aqueous sodium hydroxide solution, extracted with three portions of ethyl ether, and the combined extracts were washed with a small amount of water, dried ($MgSO_4$), and evaporated to a small volume on a rotary evaporator. Each aqueous phase was acidified to pH 2 with a few drops of dilute hydrochloric acid and extracted in the same way. The volume of each concentrated extract was reduced further to about 0.5 ml in a centrifuge tube under a stream of nitrogen.

Toxicity Measurements. The phytotoxicity of irradiated propanil solutions was determined with 6-month-old prune trees (*Prunus domestica* L., var. French) grown outdoors in 5-gal cans. A 200-ppm propanil solution was stored in the dark as a control (Solution I), while an identical solution was exposed to sunlight for 3 days (Solution II) for formation of early photolysis products. (Some photolysis had occurred during the 3-day period, since the pH of the solution dropped from 7 to about 5.5, and a glc profile showed very small amounts of several of the characteristic peaks.) Another solution was exposed to sunlight for 1 month (Solution III) to obtain steady-state photolysis products.

To differentiate between volatile and nonvolatile photoproducts, 1 l. of a 200-ppm aqueous propanil solution, exposed to sunlight for 1 month, was evaporated to dryness in an all-glass rotary evaporator. The solid residue of nonvolatile products was redissolved in 1 l. of water (Solution V), while the condensate provided Solution IV.

The test solutions, containing 0.1% Triton 100 wetting

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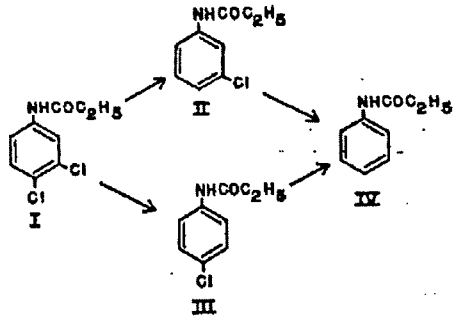

Figure 1. Photoreduction of propanil

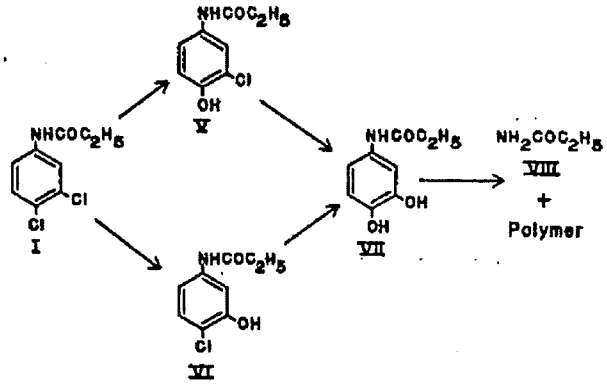

Figure 2. Formation of hydroxylated analogs of propanil

agent, were applied to each surface of the leaves with a cotton swab. Leaves of a separate tree received Triton 100 solution (Solution VI) as a control. After 5 weeks, the number of missing and damaged (yellow) leaves was recorded.

Volatility Measurements. To determine whether propanil itself codistilled with water, a 50-ppm solution contained in a 2-l. flask was immersed in a constant temperature bath at 35°C. The concentration of propanil was determined each day by measuring its ultraviolet spectrum.

To check for the possibility of volatile photolysis products, a stream of air was bubbled through the reactor and into a trap as photolysis took place. The trap consisted of several hundred milliliters of isopropyl alcohol immersed in a Dry Ice–propylene glycol cold bath. In each experiment the photolysis was conducted for 1 week, after which the isopropyl alcohol solution was evaporated to a small volume and analyzed for products by thin-layer and gas chromatography.

RESULTS AND DISCUSSION

Both in sunlight and in the laboratory, propanil solutions gradually became yellow and, eventually, dark brown. However, decomposition of the herbicide was slow, and 18% still remained unchanged after irradiation of a 200-ppm solution in the photoreactor for 34 days.

Comparison of the glc profiles of extractives from both outdoor and laboratory photolyses demonstrated the close simulation of sunlight conditions by the more controllable reactor. The profiles were unusually complex and changed rapidly as irradiation progressed. However, the accumulation of several major conversion products was evident; 3′-chloropropionanilide (II), 3-chloroaniline (XV), 3,4-dichloroaniline (XIII), and the rather volatile propionamide (VIII)

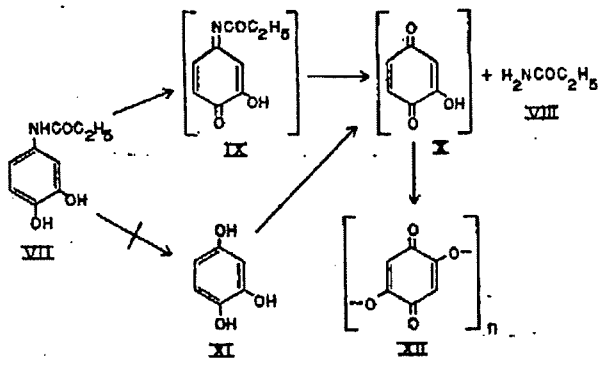

Figure 3. Proposed photooxidation of propanil. Compounds IX and X are hypothetical

were identified. Prolonged irradiation led to dark, unextractable materials.

The reductive formation of II was to be expected; similar examples of the replacement of ring halogens by hydrogen are well-known (Crosby and Li, 1969; Plimmer, 1970). Predictably (Plimmer, 1970), the 3-chloro isomer should be more stable than the 4′-chloropropionanilide (III) to further photolysis; examinations of the small glc fraction having the same retention time as authentic III confirmed that both isomers indeed were formed during photolysis. Further irradiation of 100-ppm solutions of either II or III produced unsubstituted propionanilide (IV) (Figure 1). Obviously, II is more stable than I toward light and is the principal photolysis product to accumulate, but it exhibits only 5.8% of the herbicidal activity of I (Good, 1961).

Previous experience also has shown the replacement of ring chlorines by hydroxyl to be a general reaction (Crosby and Li, 1969; Plimmer, 1970). The acidity of the propanil solution gradually increased from pH 7.5 to pH 2.8 as photolysis proceeded, and the precipitation of silver chloride upon addition of silver nitrate solution confirmed the dechlorination. Several phenolic products showing a yellow color with *p*-nitrobenzenediazonium fluoborate were detected on thin-layer chromatograms, but concentrations amounted to only 0.1 ppm. Using authentic 3′-chloro-4′-hydroxypropionanilide (V), 4′-chloro-3′-hydroxypropionanilide (VI), and 3′,4′-dihydroxypropionanilide (VII) for reference, these three possible dechlorinated products were isolated from the photolysis mixture and identified spectrometrically.

Irradiation of 100-ppm solutions of V and VI also produced detectable VII, but all three compounds were converted rapidly into VIII and dark insoluble matter, suggestive of their oxidation to quinones (Figure 2). VIII was detectable after 5 days of irradiation in the reactor, and its stability resulted in an eventual yield of 14% after 46% of the propanil had been photolyzed. The oxidation of other acylaminophenols with lead tetraacetate or chromium trioxide under very mild conditions results in the formation of the corresponding *p*-benzoquinone *N*-acylimides (Adams and Looker, 1951) which are spontaneously hydrolyzed in the presence of water to yield the quinone and amide. Consequently, as proposed in Figure 3, VII could undergo photooxidation to the transient quinone imide (IX) which would produce 2-hydroxy-*p*-benzoquinone (X) and VIII in the aqueous medium; X would be converted to a polymeric humic acid XII (Bremner, 1967; Crosby and Tutass, 1966; Ziechmann and Scholy, 1960) under the reaction conditions. In view of the well-known inhibition of photosynthesis by quinones (Zweig, 1969), it appears that the herbicidal activity of acyl-

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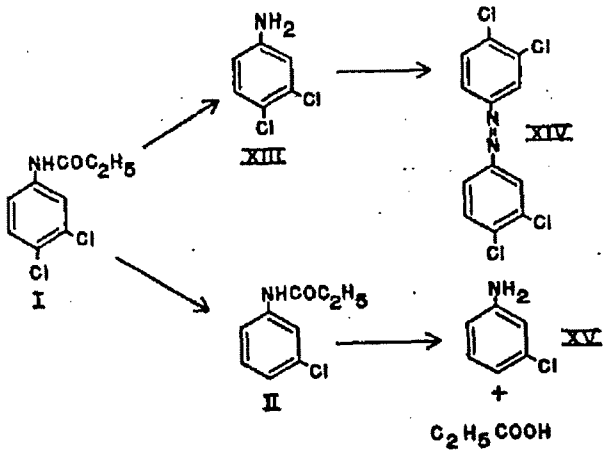

Figure 4. Formation and fate of chloroanilines

anilides such as propanil may lie in their ability to undergo metabolic conversion to chloroquinones within the plant.

The dark-insoluble substance isolated from the photolysis mixtures indeed exhibited an ir spectrum identical to that of synthetic humic acid prepared from 1,2,4-benzenetriol (XI), but attempts to detect XI itself (Crosby and Tutass, 1966) were consistently unsuccessful. Efforts to isolate IX are continuing.

Photolytic formation of anilines from corresponding amides and ureas has been reported (Crosby and Tang, 1969; Elad *et al.*, 1965), so the appearance of XIII and XV as major transformation products of propanil was not surprising (Figure 4). However, the irradiation of a 100-ppm solution of XIII resulted in rapid photodecomposition and isolation of 3,3′,4,4′-tetrachloroazobenzene ("TCAB"), presumably through the intermediate formation of 3,4-dichloronitrosobenzene. TCAB has been reported as a metabolite of propanil formed by soil microorganisms (Bartha and Pramer, 1967; Chisaka and Kearney, 1970), and also by the irradiation of XIII in the presence of sensitizers (Plimmer and Kearney, 1969; Rosen *et al.*, 1969).

Due to the fact that all of the photodecomposition products, except II, break down at a much faster rate than propanil, no mechanistic studies or quantitative data were obtained for the three pathways contributing to the total photolysis. Qualitatively, each of the pathways contributes significantly to the overall breakdown, since the concentrations of photolysis products arising from each correspond within one order of magnitude after steady state conditions are achieved.

The propanil solution held in the dark (Solution I) caused a high degree of phytotoxicity (Table I), and short-term irradiation caused little change (Solution II). However, a month's exposure to sunlight (Solution III) resulted in distinct reduction in effects, with all activity concentrated in the nonvolatile fraction (Solution V) rather than in the distillate (Solution IV).

The volatility measurements (Table II) revealed that the concentration of propanil increased as water evaporated. After 1 week, there was no detectable loss of propanil from the solution, indicating that it does not codistil with water.

Table I. Phytotoxicity of Propanil and Its Photoproducts

Solution no.	Leaves dropped, %	Remaining leaves, damaged, %	Total leaves affected, %
I (control)	53	17	70
II	51	13	64
III	37	9	46
IV	0	0	0
V	32	12	44
VI (control)	0	0	0

Table II. Attempted Volatilization of Propanil[a]

Time, days	Volume, ml	Propanil conc, mg/l.	Remaining propanil, mg
0	2000	50.0	100.00
1	1925	52.0	100.10
2	1838	54.5	100.17
3	1740	57.5	100.05
4	1620	61.7	99.95
5	1480	67.5	99.90
6	1283	78.0	100.07

[a] Initial amount was 100 mg.

No volatile aromatic photoproducts of propanil were ever detected.

The results show that the observed phytotoxicity in orchards can be attributed to propanil itself, probably in particulate form. Sunlight may act to reduce the effect through the photodecomposition of the herbicide, as the photolysis products are nontoxic to young prune trees.

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Photochemical Degradation of Isomerically Pure Di-, Tetra-, Hexa-, Octa- and Decachlorobiphenyls

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We have previously shown that photochemical changes occur in chlorinated biphenyls on irradiation with a number of light sources (1,2). This report deals with the behaviour of a number of chlorobiphenyls on exposure to natural sunlight.

Experimental

100 Milligrams each of 4,4'-dichlorobiphenyl (I), 3,3',4,4'-tetrachlorobiphenyl (II), 2,2',5,5'-tetrachlorobiphenyl (III) and 2,2',4,4',5,5'-hexachlorobiphenyl (IV) were dissolved in benzene and spread evenly on a pyrex dish (diameter: 35 cm) under a gentle flow of air to ensure uniform formation of a chlorobiphenyl film. Distilled water (5 ml) was added to the dishes which were then loosely covered with plastic material to prevent dust and rain to contaminate the chlorobiphenyl film but allow air to exchange (3). Dishes were exposed, on the laboratory roof, for the period June 24 to September 15, 1971. Total duration of bright sunshine was 612 hours (4).

After this period of exposure the contents of the dishes were dissolved in acetone and the solvent and residual water removed by evaporation. After weighing, the residue was redissolved in each case, streaked onto a preparative TLC plate (20 × 100 cm coated silica gel F-254) and the plate developed in hexane three times. Three bands were visible on the plates under U.V. illumination: band A at R_f 0.7-0.9 corresponding to the starting material; band B at R_f 0.4-0.7 which was usually weak and band C at the origin to approximately R_f 0.1. The bands were eluted with benzene-ethyl acetate (A,B) and ethyl acetate-acetone (C) with the addition of small amounts of water, the solvent removed and the crude extracts examined by mass spectrometry using a DuPont/CEC 21-110B double focussing instrument. The samples were slowly heated in the direct introduction probe and electrical scans as well as photoplate exposures obtained at different temperatures.

The polar fraction C was methylated with excess diazomethane.

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Results and Discussion

The main conclusions for the behaviour of the four compounds on exposure to natural sunlight (see table) are as follows:

(a) Loss of weight occurred presumably by evaporation of either the starting material or more volatile breakdown products. The amount of crude material recovered from the dishes was 4.8 mg (I); 7 mg (II); 17 mg (III) and 34 mg (IV). Future experiments will be conducted in closed quartz tubes.

(b) Contrary to irradiations in hexane where stepwise loss of chlorine was observed, irradiations in thin films produces chlorobiphenyls of higher chlorine content. In this case the substrate probably acts as scavenger ("solvent") for the Cl· produced. Under the present experimental conditions, however, extensive loss of compounds with lower vapour pressure (chlorobiphenyls containing less chlorine) is likely.

(c) A band corresponding to more polar products was observed on TLC in all cases. Mass spectra for definite compounds containing chlorine could not be obtained, however, which indicates the products to be either polymers or thermally labile compounds with little or no chlorine remaining.

(d) A number of peaks corresponding to chlorinated compounds other than PCB were observed. Among these were terphenyls and compounds whose compositions could not be deduced from the low resolution spectra. High resolution data from the photoplates are being processed. These data and information on other isomers will be available.

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4. Values from Canadian Force Base Shearwater, Halifax Co., N. S., supplied by Maritimes Weather Office, Atmospheric Environment Service.

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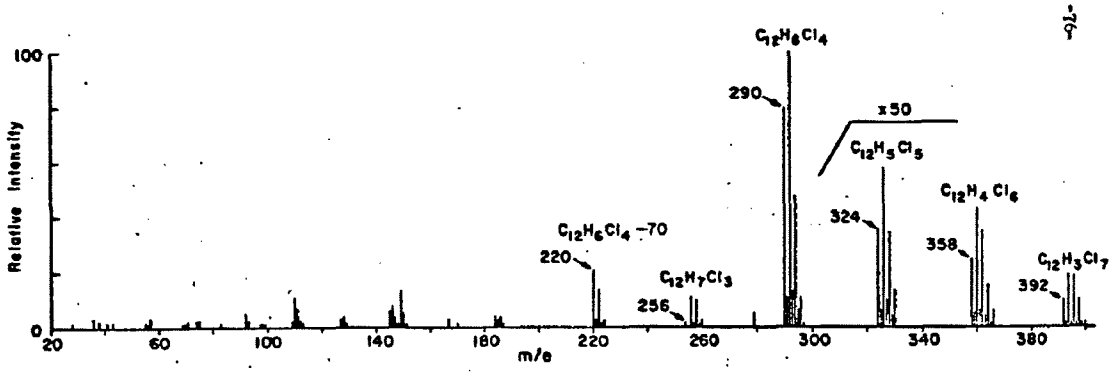

Figure 1. Mass spectrum of "TLC band A" from 3,3',4,4'-tetrachlorobiphenyl exposed to sunlight.

Mass Spectr

Band I

A Cl
trace
Cls,C

B m/e 4
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C
and methylated

Legend: + = Many peal
impuritic
apparent.
Cl4, Cls, etc

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TABLE

Mass Spectral Data on Compounds Formed by Irradiation

Band	Chlorobiphenyl irradiated			
	I	II	III	IV
A	Cl_2 trace Cl_4, Cl_5, Cl_6	Cl_3, Cl_4, Cl_5, Cl_6, Cl_7 (Fig. 1)	Cl_4, Cl_5, Cl_6, Cl_7	+
B	m/e 476, 509, 542	Chloroterphenyls (Fig. 2) trace Cl_4, Cl_5	-	m/e 248, 284, 320, 354, 412, 446, 480, 574 (Fig. 3) Different minor peaks at different probe temperatures
C and methylated	+	+	+	+

Legend: + = Many peaks due to either extensive decomposition of samples or impurities; no pattern characteristic for chlorine isotopes apparent.

Cl_4, Cl_5, etc. = tetra-pentachlorobiphenyl, etc.

Figure 1. Mass spectrum of "TLC band A" from 3,3',4,4'-tetrachlorobiphenyl exposed to sunlight.

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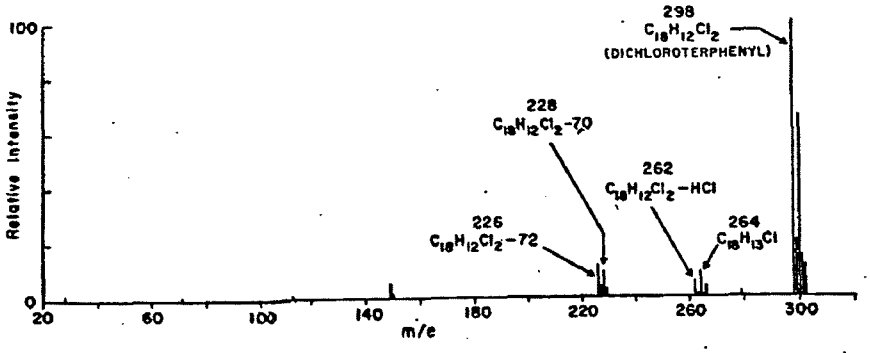

Figure 2. Mass spectrum of "TLC band B" from 3,3',4,4'-tetrachlorobiphenyl exposed to sunlight.

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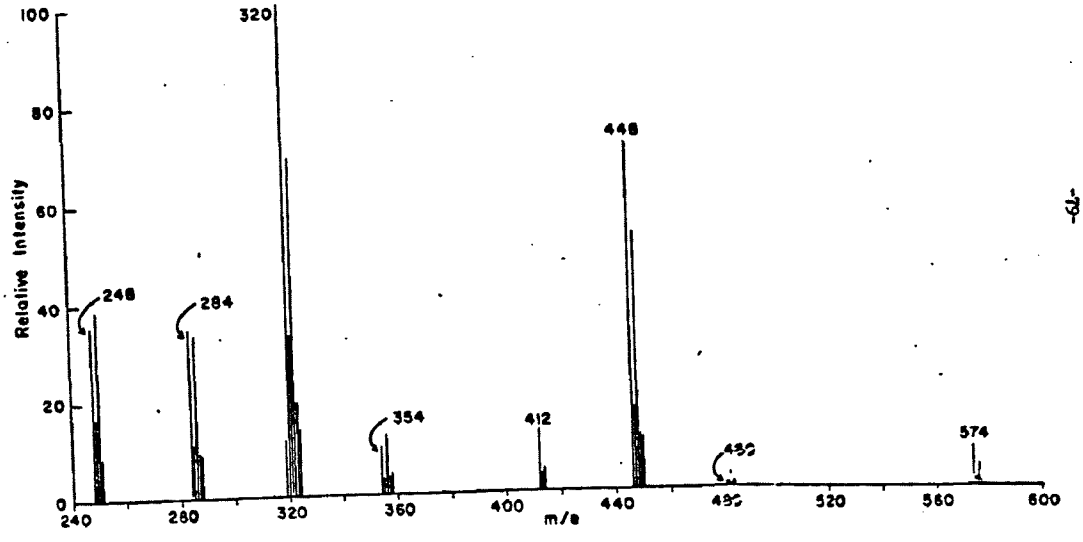

Figure 3. Mass spectrum of "TLC band B" from 2,2',4,4',5,5'-hexachlorobiphenyl exposed to sunlight.

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tions, which are stimulated to synthesize DNA by contact with antigen, enter a resting phase until stimulated to re-enter division by secondary exposure to the same antigen. By definition these would be memory cells. They apparently correspond to Mitchell and Miller's "educated T lymphocytes"[2], for they were only observed at a time when the mitotic response of thymus-derived lymphocytes is maximal[3]. We are currently seeking direct experimental proof of their identity. Previous attempts to establish this point[11] have failed, perhaps because of the use of *Salmonella* antigens, which are poor stimulators of thymus-derived cells[12]. Our finding implies that cell replication may serve as a means of enlarging and/or altering the pool of thymus-derived cells capable of reacting with certain antigens. Replication may not, however, be essential to the helper function of these cells[13].

At the peak of the secondary response to SRC 30–40% of the cells in mitosis in the spleen are thymus-derived[3]. Thus we were initially surprised to find only 8–9% of the spleen cells responding mitotically to a second injection of antigen which showed evidence of having responded in the earlier primary response. It is important to remember that the work delineating the time and magnitude of the response of thymus-derived cells to antigen was carried out in irradiated, thymus-grafted mice. Thus it is possible that there may be some differences in normal mice. If there should be any significant differences, however, there would probably be an increase of thymus-derived cells responding in normal mice. Davies *et al.* have shown that increasing the number of reconstituting thymus grafts up to a point increases the number of peripheral thymus-derived cells[3]. This increase does not, however, alter the percentage of thymus-derived cells responding to antigen in lymph nodes nor does it change the timing of their response. It is possible that some thymus-derived memory cells lost their label through division after the period of labelling. We are investigating the possibility of recruitment of thymus-derived cells by other thymus-derived cells responding specifically. The small number (0–1%) of labelled cells found in control animals may be due, at least in part, to the emergence and subsequent response of a few thymus-derived cells which were undergoing division in the thymus at the time of thymidine administration.

The chief conclusion we should like to draw from this experiment is that one result of the DNA synthesis which follows primary antigenic stimulation is the generation of memory cells. The ability to identify these cells should be of value in characterizing them further.

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Note added in proof: Since we submitted this manuscript, another report in which memory cells were identified by autoradiography, has appeared. Bosmann, C., and Feldman, J. D., *Clin. Exp. Immunol.*, 7, 565; 1970.

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Polychlorinated Biphenyls: Photolysis of 2,4,6,2′,4′,6′-Hexachlorobiphenyl

MANY aromatic organochlorine compounds are readily utilized or otherwise decomposed by a number of specific micro-organisms. In the environment, however, these compounds are relatively stable and resistant to general microbial breakdown. For many of these compounds photochemical degradation, induced by the ultraviolet content of the Sun's light, may be a major pathway of decomposition.

Because a large number of pesticides contain a chloroaromatic moiety as a primary structural feature, considerable attention has been paid to the photolysis of these compounds[1–7]. Photochemical decomposition of chlorobiphenyls may be a significant process in the environment because they absorb in that region of the ultraviolet (ref. 8 and our unpublished demonstrations) which is available in natural conditions (compare ref. 1) from sunlight.

Commercially available polychlorinated biphenyls (PCB) for example 'Aroclor', consist of a complex mixture of chlorinated biphenyls which can be resolved into more than fifty peaks by gas chromatography on 'Scot columns' (private communication from D. J. Sissons and G. M. Telling). As it is difficult to correlate data from such a complex mixture we have synthesized a series of isomeric di, tri, tetra, penta, hexa, octa and decachlorobiphenyls to facilitate fundamental studies on analytical, biological and chemical aspects of PCB (manuscript in preparation). We have also shown that all these compounds give strong molecular ions on electron

Table 1 GLC and Mass Spectral Data for Hexachlorobiphenyl Photolysis Products

	Retention time* (min)	*m/e* of M^+	Chlorine† content
TLC band I			
Peak 1	5.6	—‡	0
Peak 2	8.2	—‡	0
Peak 3	9.9	222	2
Peak 4	13.5	256	3
Peak 5	14.1	290 (256)	4, (3[tr])
Peak 6	19.0	324 (290)	5, (4[tr])
Peak 7	29.7	358	6
Peak 8	56.9	304	2
TLC band II			
Peak 1	19.6	290	4
Peak 2	26.8	324	5
Peak 3	35.2§	358	6

* Conditions: instrument, Hewlett-Packard 5750; column, 6% QF-1+4% SE30 on 'Chromosorb' (AW) 60–80 mesh 5′, 1/4″ outside diameter, glass; injection port temperature, 220° C; column temperature, 175° C; flame ionization detector temperature and collection port temperature, 240° C; helium flow rate, 40 ml./min.
† From isotope peak distribution; tr, trace.
‡ Hydrocarbon peaks, M^+ not identified.
§ Corresponding to starting material.

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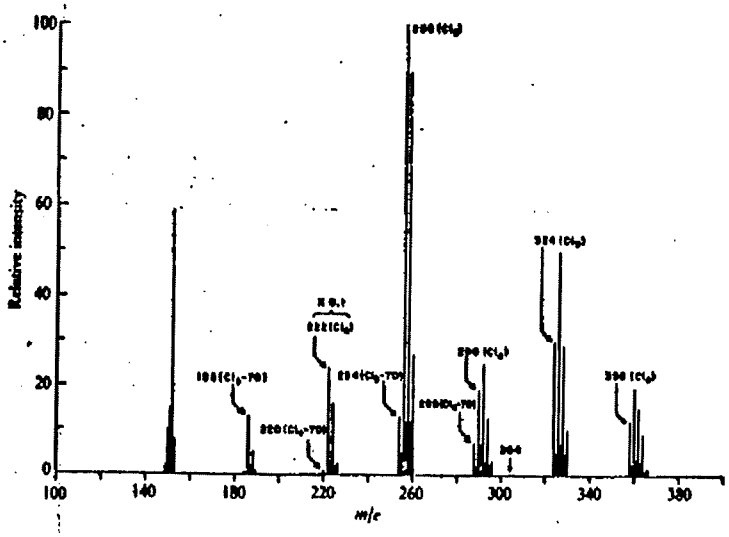

Fig. 1 70 eV mass spectrum (DuPont/CEC 21-110B instrument). The temperature of the sample, controlled independently from the source temperature[10], was 40° C. The intensity of ions corresponding to the components ($Cl_6 = C_{12}H_4Cl_6$, $Cl_5 = C_{12}H_5Cl_5$, and so on) in the mixture varies with sample temperature. Each isomer shows an M^+-70 ion as the most important fragment. These ions are indicated as Cl_6-70, Cl_5-70, and so on.

impact, followed by less intense ions resulting from successive loss of Cl and/or HCl (manuscript in preparation). As the general formula for PCB is $C_{12}H_{10-x}Cl_x$ the molecular ions of individual isomers are thus readily recognized in a mass spectrum of a mixture of these compounds (compare ref. 9).

We now wish to report the photochemical behaviour of 2,4,6,2′,4′,6′-hexachlorobiphenyl. A sample of 25 mg of this compound in 2.0 ml. of hexane was irradiated at λ_{max} 3100 Å for 100 min. Thin-layer chromatography, using 'Merck Silica Gel F-254' and hexane, revealed the presence of two major bands; band I (R_F 0.40) and band II (R_F 0.65, corresponding to starting material). The mass spectrum of band I (Fig. 1) indicated molecular ions corresponding to di, tri, tetra, penta and hexachlorobiphenyls. Gas liquid chromatography (GLC) of bands I and II revealed eight and three major peaks respectively. Retention times and mass spectra data for all peak components are reported in Table 1. When irradiation was carried out in methanol, similar results were obtained, but in addition a third and more polar band appeared, containing oxygenated polychlorinated compounds with structures which have not been investigated further.

Two conclusions can be drawn from the results of this study: (i) during photolysis, chlorine is removed rather readily from hexachlorobiphenyl yielding compounds of lower chlorine content; (ii) photochemical production of new compounds formed by loss of chlorine, rearrangement or condensation may lead to further complications in residue analysis with the possible appearance of chlorobiphenyls ("peaks") in environmental samples that are not present in commercial PCB mixtures.

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Selection for Resistance to Carbamate and Organophosphorus Insecticides in *Anopheles albimanus*

The development of resistance in anopheline mosquitoes to DDT, HCH, and cyclodienes, and the consequent set back in malaria eradication programmes has lent urgency to the search for alternative insecticides to replace the chlorinated hydrocarbons. During the past few years, more than 1,300 new insecticides, chiefly organophosphates and carbamates, have been tested under an international collaborative programme of the World Health Organization[1]. Testing consists of seven sequential stages and only insecticides that satisfy the criteria in all stages are recommended for use on a large scale.

One of the insecticides that satisfied the criteria of stage VI (operational evaluation) and has been found suitable for stage VII (epidemiological evaluation) is the carbamate, propoxur[2]. It is intrinsically more toxic to adults of many mosquito species than dieldrin, malathion, fenthion and fenitrothion, and as a residual spray has been found to be effective for 2 to 4 months against *Anopheles gambiae* and *A. funestus* in Africa, *A. stephensi* and *A. dthali* in Iran, and *A. albimanus* in El Salvador[2].

No case of resistance to carbamate or organophosphorus insecticides has yet been reported although tolerance to malathion has been suspected in *A. albimanus* in Guatemala and Nicaragua[3,4] and subsequently demonstrated in El Salvador[1,5]. In this communication we report the development of high degrees of carbamate and organophosphorus resistance in *A. albimanus* resulting from intensive selection pressure in the field, and subsequently in the laboratory.

Earlier attempts to induce carbamate resistance in *A. albimanus* by laboratory selection have been unsuccessful, although in *Culex pipiens fatigans* a 30× level of resistance to propoxur developed in larvae within twenty-five generations of selection pressure[5,6]. A strain of *A. albimanus* from Panama selected with *m*-isopropylphenyl methylcarbamate for fifty generations developed only a 2.8× increase in the LC_{50} level[7]. Another strain from Haiti, containing dieldrin-resistant individuals, when subjected to larval selection pressure by propoxur for nineteen generations and to adult pressure during the

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Polychlorinated Biphenyls: Photolysis of 3,4,3',4'-tetrachlorobiphenyl and 4,4'-dichlorobiphenyl in Solution

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INTRODUCTION

We wish to report the photoproducts of 3,4,3',4'-tetrachlorobiphenyl and 4,4'-dichlorobiphenyl in hexane solution at 300 nm.

The photolysis of 2,4,6,2',4',6'-hexachlorobiphenyl has been studied (1), but isomeric composition of the products has not been determined. Polychlorinated biphenyls have been found in the environment and are known to be toxic and resistant to microbial breakdown (2), therefore, photodecomposition may prove to be their major breakdown pathway.

In our study we have found that there is stepwise dechlorination upon photolysis and the products have been identified.

METHODS & MATERIALS

4,4'-Dichlorobiphenyl was obtained from Aldrich Chem. Co. 3,4,3',4'-tetrachlorobiphenyl was prepared by reacting 3,4-dichloro-1-iodobenzene in ether solution with magnesium metal to form the Grignard reagent and coupling was accomplished using cupric chloride. This is a modification of the procedure used by Tsutsui (3). The overall yield was 40% of theory. The product was characterized by its melting point and spectrometric methods (NMR, UV IR, Mass spec.).

10 mg of 3,4,3',4'-Tetrachlorobiphenyl in 10 ml of redistilled n-hexane and 10 mg 4,4'-dichlorobiphenyl in 10 ml n-hexane (spectrograde) were photolyzed in the ultraviolet (λ>286 nm, λmax 310 nm) for 36 hours and 150 hours respectively, in sealed borosilicate test tubes, using a Rayonette reactor equipped with RUL 3000, B1 lamps (The Southern N.E. Ultraviolet Co.).

Using an LKB 900 GC-mass spcetrometer equipped with a 6 ft stainless steel column of 3% OV-210 on gas chrom Q, temperature programmed 140-190°C the products were resolved and their mass spectra obtained.

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The products were also separated using a 6 ft stainless steel column of 3% Apiezon L on gas chrom Q, flow rate 35 $\frac{ml}{min}$ at 220°C for the dichlorobiphenyl and 240° for the tetrachlorobiphenyl irradiated solutions.

RESULTS

The retention times for the photoproducts of 3,4,3',4'-tetrachlorobiphenyl and 4,4'-dichlorobiphenyl were found to be identical with those of standards. The three peaks obtained (240°) with 3,4,3',4'-tetrachlorobiphenyl with retention times 5.27, 10.86, 22.83 min corresponded to those of standard 4,4'-dichlorobiphenyl (5.27 min) and 3,4,3',4'-tetrachlorobiphenyl (22.83 min). Mass spectrometry revealed a tetrachlorinated biphenyl at 22.83 min (m/e 290), a trichlorinated biphenyl at 10.86 min (m/e 256) and a dichlorinated one at 5.27 min (m/e 222). From these data and the fact that no photochemical rearrangements of chlorinated biphenyls have been observed we conclude that the peak at 10.86 min corresponds to 3,4,4'-trichlorobiphenyl and that 3,4,3'-trichlorobiphenyl is not formed in the reaction since no 3,3'-dichlorobiphenyl is found among the products.

The two peaks obtained from the 4,4'-dichlorobiphenyl photolysis with retention times 4.17 min and 9.60 min (220°C) corresponded with standard samples of 4-chlorobiphenyl and starting material.

SUMMARY

The large difference in retention times for the photoproducts of 3,4,3'4'-tetrachlorobiphenyl can be explained on the basis of their chlorine content and the effect of vicinal chlorosubstitution as observed by V. Zitko and coworkers (4).

The absence of biphenyl among the photoproducts of 4,4'-dichlorobiphenyl was not surprising since 4-chlorobiphenyl (λmax 203, 253) does not absorb at the wavelength of irradiation (λ>286), 4,4'-dichlorobiphenyl exhibits only marginal absorption at this wavelength (λmax 201, 259, 286) this explains the low yield of 4-chlorobiphenyl obtained (appx. .1%). The greater reactivity at the meta position may be the result of bond weakening due to steric interactions with the chlorine atom at the para position. Rate studies may provide an answer to this problem.

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The Photoreduction of Pentachlorobenzenes

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Ultraviolet (2537 Å) irradiation of the fungicides pentachloronitrobenzene (PCNB), pentachlorobenzene (PCB), and pentachlorophenol (PCP) in organic solvents resulted primarily in reductive dechlorination. The nitro group in PCNB also was removed to form PCB, but corresponding nitroanilines were not detected. Reduction occurred ortho and meta to the electron-withdrawing substituent, para to the electron-releasing group, and in para and meta positions where the substituent was H, indicative of either a free radical or hydride transfer mechanism. The compounds remained almost unchanged in sunlight, probably excluding photolysis as a major route of environmental loss.

Several pentachlorobenzenes have received wide use as pesticides. Pentachloronitrobenzene (PCNB), pentachlorophenol (PCP), hexachlorobenzene (perchlorobenzene), and pentachlorobenzene (PCB) are fungicidal, and PCP also acts as an insecticide (Martin, 1968). Application rates often are high; PCNB, for example, sometimes has been used at as much as 200 lb per acre (Thomson, 1967). The possibility that these quantities are necessary because of environmental inactivation led to an investigation of the effect of ultraviolet (uv) light on PCNB, PCP, and pentachlorobenzene.

EXPERIMENTAL

Materials. Technical pentachloronitrobenzene (Aldrich Chemical Co., Inc.) was crystallized four times from 95% ethanol to provide colorless needles, mp 143–144° C. Pentachlorophenol (Dow Chemical Co.), mp 189–190° C, was used without further purification. 2,3,4,5-, 2,3,5,6-, and 1,2,4,5-tetrachlorobenzene (Aldrich) were purified by preparative gas–liquid chromatography (glc) and were homogeneous.

Hexachlorobenzene, crystallized twice from benzene–ethanol, mp 225–226° C, was converted to pentachlorobenzene by the method of Rosenberg *et al.* (1957). The product was purified by preparative glc, mp 85–86° C (lit. 86° C; Holleman, 1920).

2,3,5,6-Tetrachlorophenol was prepared by reduction of 2,3,5,6-tetrachloronitrobenzene to the aniline by the method of Peters *et al.* (1943) and subsequent conversion of the amine to the corresponding phenol by the method of Holleman (1920). The product was purified by glc, mp 115° C (lit. 115° C; Holleman, 1921). Attempts to prepare the phenol by other routes were unsuccessful.

2,3,4,6-Tetrachloronitrobenzene was prepared from 1,3,5-trichlorobenzene (5.0 g, 0.028 mol) dissolved in 20 ml of carbon tetrachloride and treated with 0.2 g of amalgamated aluminum prepared by shaking aluminum foil with saturated aqueous mercuric chloride. The mixture then was heated to 80–90° C for 1 hr during which 0.8 g (0.011 mol) of chlorine gas was bubbled in and absorbed. After cooling, the crude reaction mixture was treated with 12 ml of fuming nitric acid, 5 ml of concentrated nitric acid, and 2 ml of 1 *M* sulfuric acid, boiled under reflux for 1.5 hr with stirring, cooled, and extracted repeatedly with water. The dried organic phase ($MgSO_4$) was subjected to preparative glc and provided pale yellow crystals, mp 20–21° C (lit. 21–22° C; Beilstein and Kurbatow, 1878).

Glc of the chlorinated mixture before nitration permitted isolation of pure 1,2,3,5-tetrachlorobenzene, mp 51° C, and a smaller proportion of pentachlorobenzene.

Equipment. Most glc was carried out with an F&M Model 720 chromatograph employing a thermal conductivity detector, linear temperature program (5° per min), and a 2-ft × 0.25-in. stainless steel column containing 20% DC-11 silicone oil on 60/80 mesh Chromosorb W (for PCNB experiments) or 10% SE-30 gum rubber on 60/80 mesh Chromosorb P. Preparative glc was accomplished with an Aerograph Model A-70 instrument equipped with a stream splitter, flame ionization detector, and an electrostatic precipitator (Fish and Crosby, 1968); the column was 6 ft × ⅜ in. stainless steel packed with 5% DC-11 on 60/80 mesh Chromosorb P. Specific detection of chlorinated compounds was made with a Dohrman Model G-100 gas chromatograph equipped with a microcoulometric detector and a 6-ft × 0.25-in. glass column packed with 10% SE-30 on 60/80 mesh Chromosorb W.

Infrared (ir) spectra were measured (KBr) with a Perkin-Elmer Model 337 or 421 spectrophotometer; all spectra were identical with those of the authentic standards.

Irradiation. Laboratory experiments were conducted in a water-cooled reactor (Henderson and Crosby, 1967) with a low-pressure mercury arc lamp radiating at 2537 Å (Nester-Faust Manufacturing Corp.). A solution of 1 g of the compound per liter of either redistilled hexane, cyclohexane, acetone, or 95% ethanol was irradiated at 25 ± 1° C under a slight positive pressure of either dry nitrogen or air. Aliquots were withdrawn at intervals and injected directly on the gas chromatograph for analysis.

At the termination of the experiment, the irradiated solution was concentrated under reduced pressure to about 5 ml, and aliquots were subjected to glc. (PCNB precipitated from its concentrated solutions and was removed by centrifugation prior to glc.) The photoproducts were trapped in glass

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Table I. Properties of Fractions Collected from glc

Compd irradiated	Elution temp, °C	mp, °C	Ir_{max}, cm^{-1}	Identity
PCNB (I)	160	139–40	1445, 1325, 1111, 1053, 881, 647	IV
	182	85–86	1401, 1333, 1163, 864, 823, 685	III
	190	20–21	1550, 1348, 1163, 909, 833, 633	V
	197	65–67	1546, 1529, 1337, 925, 791, 662	VI
	208	144	1563, 1368, 1333, 942, 793, 682	I
VII	114	140	1445, 1325, 1110, 1053, 880, 647	IV
	130	45–60	1543, 1447, 1366, 1183, 813	*a*
	145	99	1425, 1337, 1176, 1111, 885, 791	VII
PCB (III)	145	51[b]		VIII
	160	139–40	1445, 1325, 1110, 1053, 881, 647	IV
	180	85–86	1400, 1333, 1163, 865, 823, 685	III
PCP (II)	132	115	3484, 1553, 1408, 1289, 1220, 957	IX
	153	189–90	3425, 1418, 1385, 1309, 1220, 772	II

[a] Mixture of trichloronitrobenzenes. [b] Identification by melting point and elution temperature only.

capillary tubes as they emerged and were purified by repeated rechromatography. Quantitative measurements were taken from standard curves representing peak area.

Irradiation by sunlight was carried out during July and August in Davis, Calif. The hexane or methanol solutions were exposed in uncovered 21 × 34 cm borosilicate glass dishes over a period of 7 days, and fresh solvent was added, as needed, to maintain volume. Alternatively, 50 ml of a 1% solution of each compound in ether was caused to evaporate evenly on the bottom of the dish to form a thin solid film. This amount (7 g/m^2) corresponded roughly to the field application rate of PCNB (0.5 to 10 g/m^2). In both instances, homogeneous samples were taken at 1, 3, 5, and 7 days and examined chromatographically.

Thin-layer chromatography (tlc) employed silica gel G adsorbent (phosphor) on 20-cm square glass plates. Chromatograms were developed in hexane–acetone mixtures whose composition depended on the compounds under examination.

RESULTS

Upon exposure to sunlight for 7 days, solutions of PCNB or PCP became pale yellow. However, neither glc nor tlc revealed any decomposition products, and starting materials were recovered unchanged; pentachlorobenzene solutions did not even discolor. Thin films of these compounds behaved in the same way.

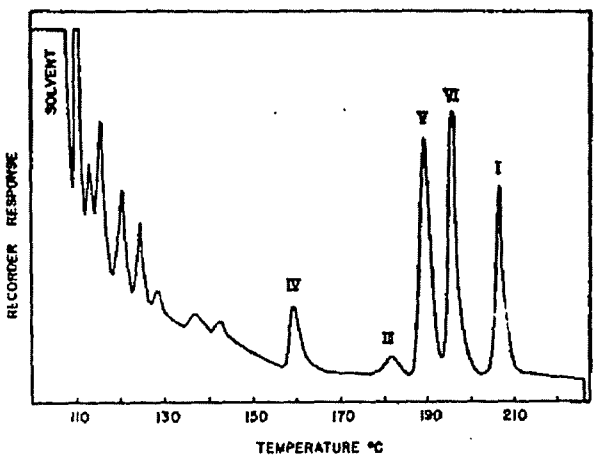

Figure 1. Typical gas chromatogram of irradiated PCNB

Irradiation of PCNB in hexane solution in the laboratory resulted in rapid discoloration, and glc (Figure 1) revealed the formation of four products in addition to unchanged starting material (Table I). The most volatile constituent of the mixture was 1,2,4,5-tetrachlorobenzene (IV); the next to elute was PCB (III), followed by 2,3,4,6-tetrachloronitrobenzene (V), 2,3,4,5-tetrachloronitrobenzene (VI), and finally PCNB itself. Unlike PCNB, V and VI were yellow and accounted in part for the color formed during irradiation.

Glc samples withdrawn at various intervals (Figure 2) revealed that III, V, and VI appeared in quantity after less than 5 min of irradiation. Their relatively constant proportions indicated steady state photolysis, although quantitative measurements showed that compounds III to VI represented 20–23% of the initial PCNB after 56 hr irradiation, while only 7% of the PCNB remained. Removal of the hexane solvent left a large proportion of dark nonvolatile tar. Increasing amounts of a number of chlorinated constituents eluting below 150° C also were observed, several of which corresponded

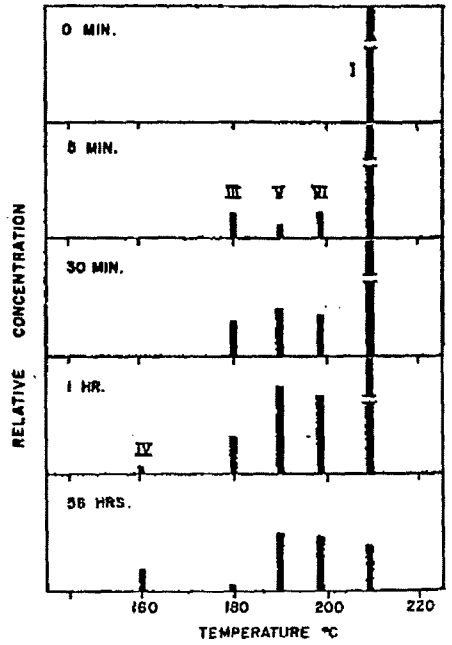

Figure 2. Time-course of PCNB photolysis (measured by glc). Bars represent peak areas

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in elution temperature to di- and trichlorobenzenes, although their isolation was not attempted.

Isothermal glc of the irradiated PCNB solution with a microcoulometric (chloride) detector (180° C, N_2 flow 80 ml per min) provided peaks at 5.0 (IV), 8.5 (III), 11.0 (V), 13.0 (VI), and 18.5 min (PCNB) as well as a small distinct peak at 3.5 min attributed to VIII and a very sharp spike at 1 min associated with low boilers. Glc at 75° C resolved the spike into three peaks of equal height corresponding to 2-chlorohexane (4.0 min), 3-chlorohexane (5.0 min), and 1-chlorohexane (6.5 min).

The slow disappearance of III, proportional to the formation of IV, suggested a direct relationship between the two. However, although no 2,3,5,6-tetrachloronitrobenzene (VII) could be detected in the photolysis mixture, the possibility remained that it was converted to IV as rapidly as it formed. Irradiation of VII produced a small amount of IV, but, in fact, by far the major product was a mixture of trichloronitrobenzenes which was completely absent in the PCNB photolysis mixture. VII was not a product of PCNB photolysis.

To establish the source of IV, the authentic specimen of III also was irradiated in hexane. IV (50%) and a small amount (13%) of the isomeric 1,2,3,5-tetrachlorobenzene (VIII), but no di- or trichlorobenzenes, were formed in 3 hr of irradiation. This evidence shows clearly that IV arises exclusively from III.

Similar irradiation of PCP (II) produced only a single major decomposition product. After 32 hr, unchanged starting material (60%) and 30% of 2,3,5,6-tetrachlorophenol (IX) were identified (Sloan, 1961); a small amount (about 10%) of another phenolic substance appeared as a high-temperature shoulder on the gas chromatogram of IX and was assumed to be an isomeric tetrachlorophenol.

Figure 3 summarizes the principal photolysis products of the pentachlorobenzenes. None of these were observed when a borosilicate glass filter absorbing below 2850 Å surrounded the arc lamp, which is consistent with the results of the sunlight experiments.

DISCUSSION

Although the photoreduction of chlorinated aromatic compounds has been reported on several recent occasions (Crosby, 1966; Plimmer and Hummer, 1968), the generality of the reaction has not been recognized. The apparent unreactivity of the *p*-chlorine substituent during photolysis of PCNB indicates that the familiar ground-state reactions of *p*-nitrophenyl halides are not operative. Instead, reduction occurred in positions ortho and meta to an electron-withdrawing substituent, para to an electron-releasing group, and in intermediate para and meta positions in the case of H.

The effect of the nonhalide substituent on the position of reduction, indeed, is consistent with a free radical hydrogen abstraction from the solvent (Wolf and Kharasch, 1965), stability of the electrically neutral aromatic radical being primarily influenced by induction (Stirling, 1965). A radical mechanism also is supported by observation of very similar proportions of identical products whether irradiation was conducted in hexane, cyclohexane, acetone, or ethanol. On the other hand, expected dimeric products such as dodecanes and biphenyls were not observed, the reaction was unaffected by either the presence or absence of oxygen, and alkylated products could not be detected after photolysis in acetone, hexane, or cyclohexane.

The observed products also could be rationalized through an ionic hydride transfer mechanism, involving excited inter-

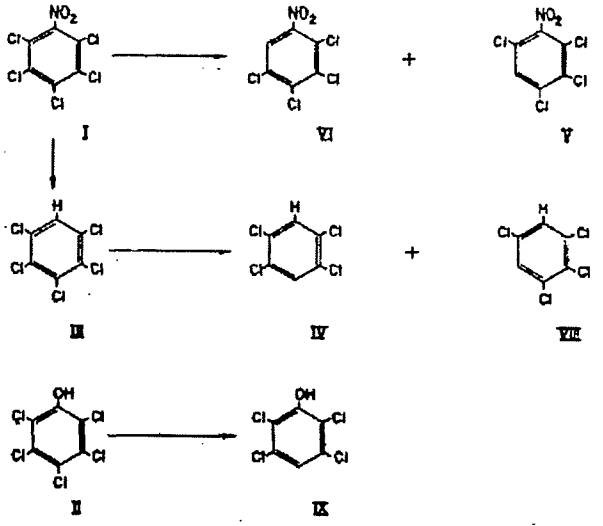
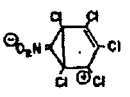


Figure 3. The photolysis of pentachlorobenzenes

mediates such as X (Zimmerman, 1963), analogous to similar photosubstitution reactions with cyanide ion (Letzinger and



X

McCain, 1966). The displacement of the nitro group to form IV also could be explained by either a free radical (Calvert and Pitts, 1967) or ionic mechanism (Letzinger *et al.*, 1965), although the absence of *N*-reduced products such as pentachloroaniline is contrary to the known affinity of the nitro group for hydride ions. However, present evidence favors the ionic mechanism.

Verification of chlorinated compounds with the element specific microcoulometric glc detector showed, in addition to the expected aromatic compounds, three low-boiling, chlorinated photolysis products corresponding to 1-, 2-, and 3-chlorohexane. These products account for the replaced chlorine atoms, and their appearance in equal quantity lends further support for radical formation; failure to observe other byproducts of free radical reactions could be justified on the basis of steric interference by adjacent chlorines which would restrict attack by all except the hydrogen atoms. Their presence together with the reduced (dechlorinated) aromatic compounds as the only detectable products of photolysis also demonstrates the important role which solvent may play in pesticide photolysis.

In contrast to the instability of the sodium salt of PCP (Kuwahara *et al.*, 1966) and many aromatic nitro compounds (Ellis and Wells, 1941), PCNB, PCP, and PCB underwent only very slow change in sunlight. Although definite photodecomposition of the first two was observed, both in solution and in solid films, light probably is relatively unimportant in the loss of this group of pesticides from the environment.

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Photodecomposition of Chlorobenzoic Acids

D. G. Crosby and Eriks Leitis

Ultraviolet irradiation of 2-, 3-, and 4-chlorobenzoic acids as aqueous solutions of their sodium salts led to replacement of the chlorine by hydroxyl and hydrogen to produce the corresponding hydroxybenzoic acids and benzoic acid itself. In the case of the 4-chloro isomer, conversions to benzoic acid reached 90%. A mixture of 4-acetylbenzoic acid and terephthalic acids also was formed. In sunlight, the monochlorobenzoic acids remained unaffected, while amiben (3-amino-2,5-dichlorobenzoic acid) decomposed rapidly.

Previous work (Crosby and Tutass, 1966) has demonstrated that the widely used herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) undergoes photodecomposition in aqueous solution. The key reaction in the eventual complete transformation of 2,4-D to polymeric humic acid was the photochemical replacement of the chlorine atoms of the aromatic ring by hydroxyl groups.

Although amiben (3-amino-2,5-dichlorobenzoic acid) is easily photolyzed in aqueous solution (Sheets, 1963), the chlorinated benzoic acids as a general class of herbicides similar to the phenoxy acids in many chemical and biological properties might be expected to have greater environmental stability due to deactivation of the ring by the carboxyl group. The present investigation was conducted to determine the stability of the otherwise unreactive ring chlorines of model chlorobenzoic acids under photolyzing conditions in aqueous solution in the laboratory and in sunlight.

EXPERIMENTAL

Materials. The halogenated benzoic acids and other standard organic compounds were reagent grade commercial products homogeneous on thin-layer chromatography. Organic solvents were redistilled shortly before use. Acids were esterified for gas chromatographic determination and comparison by reaction with an ethereal solution of diazomethane. Amiben (3-amino-2,5-dichlorobenzoic acid) was an analytical standard (Amchem Products, Inc., Ambler, Pa.).

4-Acetylbenzoic acid was prepared by reaction of a suspension of *p*-diacetylbenzene (Aldrich Chemical Company) in 10% aqueous sodium hydroxide solution with an excess of a reagent prepared by dissolving 9.0 grams of iodine and 18.3 grams of potassium iodide in 75 ml. of water. After 10 minutes, the homogeneous solution was made strongly alkaline with sodium hydroxide, filtered, the filtrate was extracted with chloroform, and the upper aqueous phase was decanted and acidified. A precipitate of highly-insoluble terephthalic acid was removed by filtration, this filtrate was extracted with several portions of ether, the decanted ether layer was evaporated to dryness, and the brown residue was triturated with chloroform to remove most of the color. The tan residue (m.p. 196° C.) was sublimed (*ca.* 200 Torr.) to provide a small yield of 4-acetylbenzoic acid, m.p. 207° to 209° C. (lit. 208°, Heilbron, 1965).

Irradiation. Solutions for irradiation were prepared by dissolving the desired acid in demineralized water, containing a small excess of sodium hydroxide, to provide a concentration of 100 mg. per liter. The pH of the solution was adjusted with a small amount of dilute sulfuric acid or aqueous sodium hydroxide if desired. Results were checked with solutions prepared from recrystallized sodium chlorobenzoates.

The solutions were irradiated in open dishes in outdoor sunlight or under a 360-watt mercury arc lamp as previously described (Crosby and Tutass, 1966). The temperature was maintained at 25 ± 2° C. by circulation of ice-cold water through immersed glass cooling coils or by an external cold bath. Alternatively, solutions were irradiated with a low-pressure mercury arc lamp in the reactor described by Henderson and Crosby (1967), the temperature being maintained at 25° C. by circulating water through the cooling jacket of the apparatus. In all cases, the solutions were continuously stirred magnetically. The duration of most indoor irradiations was three hours, while experiments in sunlight required up to 14 days. Unirradiated controls were examined in every instance.

Extraction and Separation. The irradiated solutions were extracted with ether, and the extracts were separated into acidic and neutral fractions as described previously. Ether extractables were subjected to thin-layer chromatography (TLC) on silica gel G plates developed with solvent A in the case of 2-chloro- and 3-chlorobenzoic acids and with solvent C in the case of 4-chloro- and 3-bromobenzoic acids. Strips of the developed plates were sprayed with diazonium reagent, and the detected phenolic bands were scraped off, eluted with acetone, and the eluates evaporated to dryness at ambient temperature. Ultraviolet-absorbing compounds also were detected on chromatoplates by their quenching of the fluorescence of the phosphor incorporated in the adsorbent.

Methylated acidic fractions and the neutral fractions were subjected to gas-liquid chromatography (GLC) on a 2-ft. by 1/8-in. column containing 20% Dow 11 silicone oil on 70- to 80-mesh Chromosorb W. Generally, an F and M Model 720 gas chromatograph with thermal conductivity detector was

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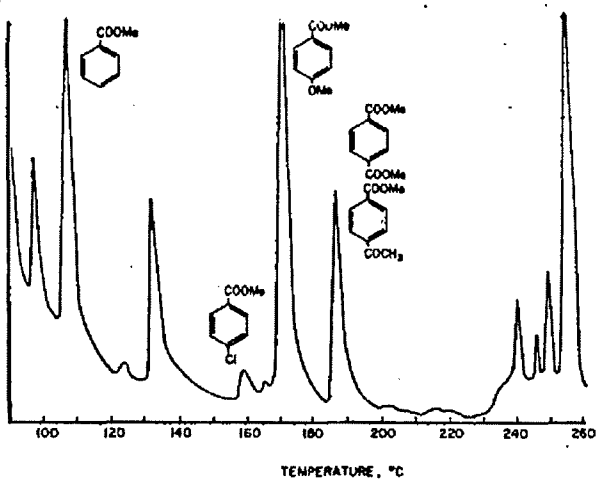


Figure 1. Gas chromatogram of methylated acidic ether extract from sodium 4-chlorobenzoate irradiated in aqueous solution

employed, and programmed-temperature measurements were made at an increase of 7.5° C. per minute. Some fractions also were checked for chlorinated constituents on a Dohrman Model G-100 gas chromatograph equipped with a microcoulometric detector and a 6-ft. by ¼-in. glass column containing 10% SE-30 gum rubber on 60- to 80-mesh Chromosorb W.

Individual constituents resolved by GLC were isolated by inserting the small end of a Pasteur pipet through a Neoprene septum into the exit port of the chromatograph as the desired fraction emerged. Collections were improved by heating the lower portion of the pipet on a warm hot-plate while chilling the top portion with solid carbon dioxide. Detector filaments generally were turned off during collections to avoid possible thermal decompositions. Collected fractions were purified by rechromatography, and their infrared spectra were measured in KBr disks with a Perkin-Elmer Model 337 Infrared Spectrophotometer and compared with those of known compounds also collected from the gas chromatograph under identical conditions.

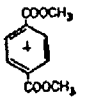
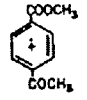
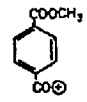
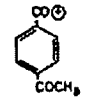
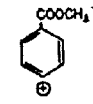
Mass spectra were measured with an AEI Model MS-9 high resolution mass spectrometer equipped with a heated inlet.

Thin-layer chromatography was conducted on silica gel G containing zinc silicate phosphor. Solvents were mixed according to volume: solvent A was toluene–dioxane–acetic acid (6:2:1); solvent B was hexane–acetone (4:1); solvent C was 1-butanol saturated at 25° C. with water; solvent D was benzene–acetic acid–water (2:2:1, upper phase); and solvent E was ethanol–ammonium hydroxide–water (20:1:4). Adsorbed compounds were detected by quenching of the fluorescence of the phosphor, by spraying with 1% aqueous potassium permanganate solution, or by spraying with a 1% solution of 4-nitrobenzenediazonium fluoborate in 20% aqueous sodium acetate.

RESULTS

None of the three isomeric chlorobenzoic acids gave rise to neutral or alkaline products upon irradiation with sunlight or ultraviolet light, although extracts were checked by TLC and by GLC with both thermal conductivity and microcoulometric detectors. TLC of the acidic extract in solvent A followed by treatment with diazonium reagent revealed a single yellow-brown band corresponding in R_f to the expected hydroxybenzoic acid in each instance. 3-Bromobenzoic acid gave results identical to those from its chloro analog.

Table I. Mass Spectrum of the 192° Fraction

Ion	Formula	Mass Calcd	Mass Found
	$C_{10}H_{10}O_4$	194.0579	194.0598
	$C_{10}H_{10}O_3$	178.0630	178.0630
	$C_9H_7O_3$	163.0395	163.0390
	$C_9H_7O_2$	147.0446	147.0456
	$C_8H_7O_2$	135.0446	135.0449

The methylated acidic fraction of photolyzed 4-chlorobenzoic acid was examined in detail by GLC. In addition to minor constituents, major fractions were eluted at 138°, 160°, 177°, and 192° C. (Figure 1). Other fractions were not explored. Comparison of elution temperatures and infrared spectra of each purified constituent showed the 138° C fraction to be methyl benzoate resulting from reductive dechlorination of the starting material to benzoic acid. The smaller 160° C. fraction represented the methyl ester of unreacted 4-chlorobenzoic acid, revealing that almost all of the starting material had been converted to other products during the 3-hour irradiation. The major fraction, eluted at 177° C., was identical with methyl 4-methoxybenzoate representing the 4-hydroxybenzoic acid formed by replacement of the ring chlorine by hydroxyl.

The fraction which was eluted at 192° C. was obtained as a white crystalline solid after repeated GLC purification. It melted over a narrow range, and the IR spectrum showed absorption frequencies representing two different types of carbonyl group (1730, 1680 $cm.^{-1}$), the first of which was characteristic of the expected methyl ester group. The high-resolution mass spectrum indicated a mixture of two compounds having respective masses of 178 and 194. Determination of the exact masses of several major fragments (Table I) revealed that the 192°C. fraction was a roughly 1:3 mixture of methyl 4-acetylbenzoate and dimethyl terephthalate. Methylation of various mixtures of the two acids followed by GLC provided only the single fraction which was eluted at 192° C.

This fraction was collected from GLC and subjected to TLC in solvent B. Ultraviolet-absorbing bands appeared at R_f 0.22 and 0.32, corresponding exactly with those produced by authentic methyl 4-acetylbenzoate and dimethyl terephthalate, respectively. Under the same conditions, methyl 4-chlorobenzoate appeared at R_f 0.75 and methyl 4-methoxybenzoate at R_f 0.64. The band at R_f 0.32, eluted from the TLC plate, provided an infrared spectrum and GLC elution temperature identical with those of dimethyl terephthalate; the R_f 0.22 band likewise was identical with authentic methyl 4-acetylbenzoate.

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To assure that these acids were not artifacts, the acidic extracts from each of several irradiation experiments with 4-chlorobenzoic acid were subjected to TLC in solvent C. The resulting bands, detected by fluorescence quenching, corresponded to terephthalic acid (R_f 0.04), 4-acetylbenzoic acid (0.26), 4-chlorobenozic acid (0.44), 4-hydroxybenzoic acid (0.49), and several minor unidentified compounds (0.09, 0.15). Identity was verified by rechromatography and comparison with standards in two additional solvents, D and E.

For comparison, an aqueous solution of amiben (sodium salt) rapidly became yellow-brown upon exposure to sunlight. GLC analysis of the methylated acidic extract produced only a single volatile product, which proved to be identical with amiben in its spectral and chromatographic characteristics. However, TLC of the photolysis mixture resulted in at least 12 colored bands upon treatment with the diazonium reagent (Crosby, 1966). Irradiation with the mercury arc caused destruction of amiben within a few minutes and no photodecomposition products could be resolved.

DISCUSSION

Among the economically important benzoic acid herbicides are TBA (principally 2,3,6-trichlorobenozic acids with smaller amounts of other chlorobenzoic acids), PBA ("polychlorobenzoic acids" containing 2 to 5 chlorines), amiben (3-amino-2,5-dichlorobenzoic acid) and dicamba (3,6-dichloro-2-methoxybenzoic acid); DCPA and Glenbar are esters of 2,3,5,6-tetrachloroterephthalic acid. The complexity of the potential photodecomposition products to be expected from these compounds suggested the prior investigation of simple models.

As observed previously with the chlorinated phenoxyacetic acids, irradiation of chlorobenzoic acid salts with ultraviolet light at 254 mμ brought about the replacement of the ring halogen by hydroxyl. The reaction was rapid in either the *o*-, *m*-, or *p*- position, and bromobenzoic acids responded in an identical manner. The absence of halobenzenes in the neutral fraction indicated that decarboxylation does not occur during photolysis of the monochlorobenzoic acids.

The photochemical reductive dehalogenation of chlorinated aromatic compounds in aqueous solution appears not to have been described prior to our initial report (Crosby, 1966), although the formation of chloride ions during irradiation of chlorobenzoic acids in alcohols (Szychlinski, 1960; Walczak and Szychlinski, 1963) could be due to this reaction. The requirement for light normally suggests the operation of a free-radical mechanism in which hydrogen atoms are transferred from solvent water; failure to detect chlorobenzene, 4,4′-dichlorobiphenyl, biphenyl-4,4′-dicarboxylic acid, or other products expected from a free-radical reaction may be due to the very large molar proportion of water compared to solute or, perhaps, to an ionic mechanism. Nonetheless, at alkaline pH the reduction product (benzoic acid) represented at least 90% of the total photolyzate mixture in the case of 4-chlorobenzoic acid and appeared to be stable to further photolysis under these experimental conditions (compare Joschek and Grossweiner, 1966).

Although always present in amounts far less than the hydroxylated and hydrogenated products, the presence of 4-acetylbenzoic acid and terephthalic acids in the reaction mixture is significant. In addition to the difficulties of identification raised by the consistent occurrence of these compounds or their methyl esters as a single, homogeneous substance, their formation demonstrates the possibility that completely unexpected products may result from photolysis. Although it is possible that terephthalic acid is derived from reaction of the aromatic halogen compound with carbonate ion in the surrounding medium, the source of the acetyl group in 4-acetylbenzoic acid is obscure even after extensive investigation.

Benzoates and their simple chlorinated and hydroxylated derivatives absorb ultraviolet light at wavelengths well below 290 mμ (Doub and Vandenbelt, 1947, 1949). While sufficient energy to break C—Cl bonds can be derived from sunlight, it is not surprising that the longer wavelengths reaching the earth's surface do not appear to affect sodium chlorobenzoate solutions. The herbicidal polychlorobenzoic acids such as TBA may be expected to be resistant to photolysis in aqueous solution in the environment; indeed, they remain impassive to light even in the presence of sensitizers such as riboflavin (Hamilton and Aldrich, 1953), and the persistence of this class in the greenhouse and field is notably greater than that of corresponding phenoxacetic acids (Minarik *et al.*, 1951; Sheets *et al.*, 1968).

A few herbicidal benzoic acid derivatives absorb ultraviolet light in the region about 290 mμ, however. Amiben, for instance, exhibits a wavelength maximum of 297 mμ in aqueous solution (Bailey and White, 1965); sunlight causes this herbicide to decompose readily in aqueous medium with the formation of reduced (and, probably, hydroxylated) products (Plimmer, 1967). Chlorobenzoic acids also are rapidly photoreduced in methanol solution, and amiben, TBA, and the related dichlobenil (2,6-dichlorobenzonitrile) were preferentially reduced in the 2-position (Plimmer and Hummer, 1968, 1969). Indeed, where multiple chlorines are present, replacement of either or both halogens by hydroxyl or hydrogen is to be expected, and the eventual formation of polyhedric phenols in this way finally leads to polymer formation, as was the case with 2,4-D.

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