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Isolation, Identification, and Chromatographic Characterization of Some Chlorinated C₁₀ Hydrocarbons in Technical Chlordane

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With the help of column chromatography, three new substances, 1-*exo*,4,5,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (8), 1-*exo*,2-*exo*,4,5,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (15), and 1-*exo*,2-*exo*,4,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (16), were isolated from technical chlordane and were identified by spectroscopic methods (mass spectrometry, infrared, and ¹H NMR). These compounds could be synthesized by photochemical dechlorination of heptachlor (11) and of α - (or *cis*-) chlordane (17) in methanol. In addition, the mixture was investigated by capillary gas chromatography and by combined gas chromatography and mass spectrometry. The data obtained were used to characterize the composition of technical chlordane.

Technical chlordane is an insecticidal mixture of C₁₀ components formed by chlorinating chlordene (6). The earliest publications about the composition of technical chlordane deal with the isolation and identification of the main components of the mixture (Vogelbach, 1951; March, 1952; Riemschneider, 1951, 1955). Later work is concentrated mainly on the gas chromatographic separation of the mixture. Polen (1966) succeeded in characterizing 11 compounds, while Saha and Lee (1969) identified 14 different compounds. Use of the polar phases in gas chromatography led to the recognition of 26 compounds (Cochrane and Greenhalgh, 1976) and of 45 compounds (Sovocool et al., 1977) subsequently. Additional work dealt mainly with the structural elucidation of the substances isolated from the mixture (Gäß et al., 1976, 1977a,b; Cochrane et al., 1975; Wilson and Sovocool, 1977). The present paper describes the isolation, identification, and synthesis of three new chlorinated tetrahydromethanoindanes from technical chlordane. In addition an attempt is made to obtain an improved characterization of the mixture with the help of chromatographic and spectroscopic data.

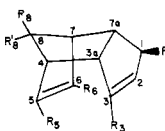
MATERIALS AND METHODS

Technical chlordane, chlordene, (6), heptachlor (11), α - (or *cis*-) chlordane (17), γ - (or *trans*-) chlordane (18), α - (or *trans*-) nonachlor (23), α -chlordene (24), β -chlordene (25), and γ -chlordene (26) and also compound C (27) and

compound K (28) were kindly made available by the Velsicol Co., Chicago, Ill. Compounds 1 and 2 were prepared by photodechlorination of 4,5,6,7-tetrachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (3), which is readily obtained from tetrachlorocyclopentadiene and cyclopentadiene (Hustert et al., 1975). Compounds 4 and 5 are prepared from 4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (6) (Parlar, 1970). Compound 9 was obtained by Diels-Alder reaction of pentachlorocyclopentadiene and cyclopentadiene in xylene (Cochrane, 1974). 1-*exo*,4,5,6,7,8-*exo*-Hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (10) could be isolated in small quantities after dechlorination of heptachlor (11) with lithium aluminium hydride and cobaltous nitrate (Bieniek et al., 1970). Compound 12 was formed on reacting 4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1-one with phosphorus pentachloride in carbon tetrachloride (Parlar and Korte, 1977). 4,5,6,7,8,8-Hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (13) was obtained by catalytic hydrogenation of 6 (Parlar and Korte, 1977), which reacted with HCl directly to β -dihydroheptachlor (14) (Falbe and Schulze-Steinen, 1966). Compound 19 was prepared by Büchel et al. (1966). Compounds 20 and 21 were obtained in minor quantities from this reaction (Gäß and Parlar, 1977). 1-*exo*,2-*exo*,3-*exo*,4,5,6,7,8,8-Nonachlor-3a,4,7,7a-tetrahydro-4,7-methanoindane (22) was isolated from technical chlordane with the help of column chromatography (Cochrane, 1974). Tables I, II, and III show the *R_f* values, relative retention times (*t_R*) relative to 4,5,6,7-tetrachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (3) and percentages of the individual compounds (determined gas chromatographically with a maximum error of $\pm 10\%$) in technical chlordane. All solvents used were of analytical reagent quality. Petroleum ether (bp 60–90 °C) was purified by distillation.

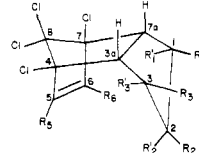
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Table I. Physical Data of Chlorinated Tetrahydro-4,7-methanoindene Derivatives and Their Proportion in Technical Chlordane



compound	R ₁	R ₃	R ₅	R ₆	R ₈	R ₈ '	t _R	R _f	% in techn. chlordane
4,5,7-trichloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (1)	H	H	Cl	H	H	H	0.55	0.48	
4,6,7-trichloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (2)	H	H	H	Cl	H	H	0.50	0.49	
4,5,6,7-tetrachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (3)	H	H	Cl	Cl	H	H	1.00	0.55	
4,5,7,8,8-pentachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (4)	H	H	H	Cl	Cl	Cl	1.90	0.50	
4,6,7,8,8-pentachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (5)	H	H	Cl	H	Cl	Cl	1.80	0.53	
4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (6)	H	H	Cl	Cl	Cl	Cl	2.20	0.61	0.9
1- <i>exo</i> ,4,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (7)	Cl	H	H	Cl	Cl	Cl	2.15	0.45	
1- <i>exo</i> ,4,5,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (8)	Cl	H	Cl	H	Cl	Cl	2.00	0.47	2.0
1- <i>exo</i> ,4,5,6,7,8- <i>endo</i> -hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (9)	Cl	H	Cl	Cl	H	Cl	4.80	0.23	
1- <i>exo</i> ,4,5,6,7,8- <i>exo</i> -hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (10)	Cl	H	Cl	Cl	Cl	H			
1- <i>exo</i> ,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (11)	Cl	H	Cl	Cl	Cl	Cl	2.40	0.51	8.1
1- <i>exo</i> ,3,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (12)	Cl	Cl	Cl	Cl	Cl	Cl	7.20	0.32	

Table II. Physical Data of Chlorinated Tetrahydro-4,7-methanoindane Derivatives and Their Proportion in Technical Chlordane



compound	R ₁	R ₁ '	R ₂	R ₂ '	R ₃	R ₃ '	R ₅	R ₆	t _R	R _f	% in techn. chlordane
4,5,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (13)	H	H	H	H	H	H	Cl	Cl	2.10	0.46	
2- <i>exo</i> ,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (14)	H	H	Cl	H	H	H	Cl	Cl	4.90	0.40	
1- <i>exo</i> ,2- <i>exo</i> ,4,5,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (15)	Cl	H	Cl	H	H	H	Cl	H	12.50	0.22	3.0
1- <i>exo</i> ,2- <i>exo</i> ,4,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (16)	Cl	H	Cl	H	H	H	Cl	Cl	12.50	0.20	
1- <i>exo</i> ,2- <i>exo</i> ,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (17)	Cl	H	Cl	H	H	H	Cl	Cl	8.20	0.28	13.0
1- <i>exo</i> ,2- <i>endo</i> ,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (18)	Cl	H	H	Cl	H	H	Cl	Cl	9.40	0.25	17.5
1- <i>exo</i> ,3- <i>exo</i> ,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (19)	Cl	H	H	H	Cl	H	Cl	Cl	5.10	0.45	
1- <i>exo</i> ,3- <i>endo</i> ,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (20)	Cl	H	H	H	H	Cl	Cl	Cl	4.70	0.48	
1,1,3- <i>exo</i> ,4,5,6,7,8,8-nonachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (21)	Cl	Cl	H	H	Cl	H	Cl	Cl	5.40	0.40	
1- <i>exo</i> ,2- <i>exo</i> ,3- <i>exo</i> ,4,5,6,7,8,8-nonachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (22)	Cl	H	Cl	H	Cl	H	H	Cl	12.30	0.76	3.7
1- <i>exo</i> ,2- <i>endo</i> ,3- <i>exo</i> ,4,5,6,7,8,8-nonachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (23)	Cl	H	H	Cl	Cl	H	Cl	Cl	10.60	0.35	8.1

Chromatography. Routine investigations were performed with a Packard gas chromatograph, Model 417 (glass column, length, 2 m; i.d., 4 mm; 3% OV-1 on Chromosorb W-AW-DCMS (80–100 mesh); injection port temperature, 250 °C; FID detector, 300 °C; column

temperature, 140 °C; carrier gas, nitrogen; flow rate, 40 mL/min). For thin-layer chromatography, TLC plates (Merck Silica 60 F 254) with a layer thickness of 0.25 mm were used; after developing (petroleum ether, bp 60–90 °C) the plates were sprayed with 1% diphenylamine solution

Table III. Physical Data of Other Chlorinated C₁₀ Hydrocarbons and Their Proportion in Technical Chlordane

structure	compound	t _R	R _f	% in techn. chlordane
	1,2,3,5- <i>exo</i> ,7,8-hexachloro-1,3a,4,5,6,6a-hexahydro-1,4-ethenopentalene (24)	2.60	0.50	2.7
	2,3,3a-4,5,7-hexachloro-3a,6,7,7a-tetrahydro-1,6-methano-1 <i>H</i> -indene (25)	3.90	0.47	7.3
	2,3,3a,4,5,8-hexachloro-3a,6,7,7a-tetrahydro-1,6-methano-1 <i>H</i> -indene (26)	3.70	0.47	9.0
	3a,4,5,5a,5b,6- <i>exo</i> ,hexachloro-1a,2,3,3a,5a,5b-hexahydro-1 <i>H</i> -cyclobuta[<i>cd</i>]pentalene (27)	1.80	0.49	7.1
	2,4,4,5,6,6,7,8-octachloro-2,3,3a,4,5,7a-hexahydro-1,4-methano-1 <i>H</i> -indene (28)	15.5	0.12	3.0

and irradiated with UV light for about 5 min (λ 254 nm) to detect the substances. A Carlo Erba 2200 gas chromatograph equipped with a linearized ⁶³Ni detector and a Hewlett Packard 3380 A integrator was employed for the capillary GC investigations (SE 30 WCOT-column, length, 30 m; i.d., 0.24 mm; injection port temperature, 250 °C; detector temperature, 300 °C; column temperature, 190 °C; carrier gas, nitrogen; flow rate, 1 mL/min).

Spectroscopy. The mass spectra of the gas chromatographically pure compounds were obtained by direct inlet and those of the mixtures by GC/MS on a LKB 9000 S (column length, 2 m; i.d., 4 mm; 3% OV-1 on Chromosorb W-AW-DMCS). The electron energy was 70 eV. The MS data were processed by a digital computer (IBM 1130) via an interface made by the WDV Company (Munich). The elementary composition of the molecule and fragment ions was based on the first peak in each Cl cluster. The ¹H NMR spectra (CDCl₃, Me₄Si) were recorded by a Perkin-Elmer R-32 90-MHz spectrometer. Infrared spectra were obtained with KBr disks of the sample using a Perkin-Elmer Model 577 instrument.

Isolation of Compounds 8, 15, and 16 from Technical Chlordane. Technical chlordane (15 g) was separated into 45 fractions of 80 mL each by column chromatography (length, 1.5 m; i.d., 7 cm). Silica gel (Merck, grain size 0.2–0.06 mm) served as the adsorbent and petroleum ether (bp 60–90 °C) was used for elution (elution speed, 0.75 mL/min).

Petroleum ether–benzene (1:1) was used for eluting the last 10 fractions. Compound 8 was isolated in the ninth fraction. Compounds 15 and 16 were obtained as a mixture in the 37th fraction, but could be separated by “thick-layer” chromatography carried out subsequently with hexane.

Preparation of 1 and 2 from 4 and 5 by Reduction with Zinc Dust. A solution of 0.2 g of starting material (4 or 5) in 50 mL of glacial acetic acid was prepared and

1 g of Zn powder was added. The mixture was refluxed for 5 h, cooled, and filtered.

Water (100 mL) was added to the filtrate and extracted twice with 50 mL of CCl₄. The combined CCl₄ extracts were dried with CaCl₂ and evaporated. Crystallization from methanol gave pure compounds.

Preparation of 1 and 2 by Photodechlorination of 3. Compound 3 (0.5 g) was dissolved in analytical grade methanol and irradiated through quartz glass with wavelengths above 230 nm for 240 min (HPK 125 W, Philips high-pressure mercury lamp). The solvent was removed under reduced pressure and the compounds (1 and 2) were isolated in pure form with the aid of a silica gel column (i.d., 3 cm; length, 70 cm). Petroleum ether (bp 60–90 °C) served as the eluant.

Reaction of 7 and 8 with Silver Carbonate. A solution of 0.2 g of the relevant compound (7 or 8) in 100 mL of methanol/water (8:2) was prepared. After adding 3 g of Ag₂CO₃ the solution was boiled under reflux for 24 h. The product (7a or 8a) was evaporated to dryness, the residue was taken up in 100 mL of diethyl ether, briefly heated, and filtered. After concentrating to 5 mL, the filtrate was taken up in 20 mL of hexane. The crystals formed after a short time were recrystallized from carbon tetrachloride.

Oxidation of 4 and 5 to 7a and 8a with Selenium Dioxide. A solution of 0.1 g of starting material (4 or 5) in 25 mL of glacial acetic acid was refluxed with 0.5 g of selenium dioxide. After the completion of the reaction (4 h) 100 mL of water was added and the products 7a and 8a (together with the acetates) were extracted with 250 mL of hexane. Separation was achieved by column chromatography (silica gel column, i.d., 3 cm; length, 70 cm; eluant, petroleum ether (bp 60–90 °C)/acetone, 10:1).

Preparation of 7, 8, 15, and 16 from Heptachlor (11) and α -Chlordane (17) by UV Irradiation. Heptachlor (11) or α -chlordane (17) was dissolved in analytical grade

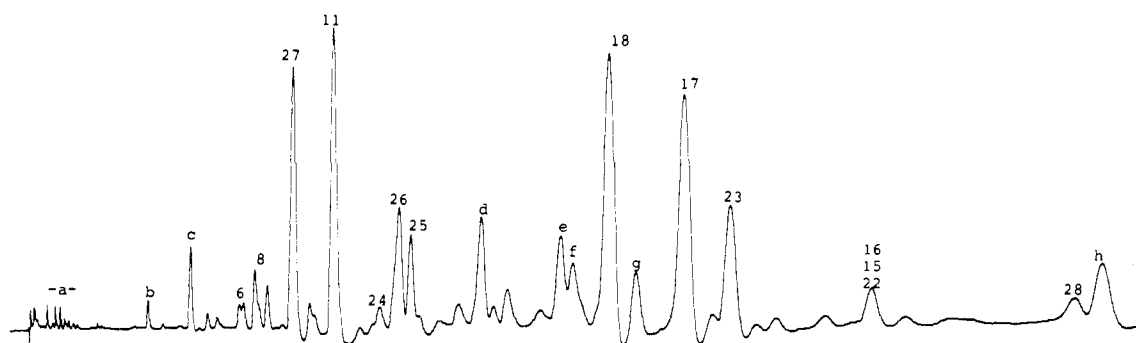




Figure 1. Capillary chromatogram of technical chlordane (SE 30 WCOT column length, 30 m; i.d., 0.24 mm; column temperature, 190 °C; flow rate, 1 mL/min).

Table IV. Important Fragment Ions of the Compounds 7, 8, 11, 15, 16, and 17

compound	M ⁺	rel. intensity	no. of Cl atoms	(M - Cl) ⁺	rel. intensity	no. of Cl atoms		rel. intensity	no. of Cl atoms		rel. intensity	no. of Cl atoms
7	336	12	6	301	53	5	236	100	5	100	20	1
8	336	15	6	301	50	5	236	100	5	100	20	1
11	370	10	7	335	46	6	270	100	6	100	31	1
15	372	8	7	337	70	6	236	100	5			
16	372	8	7	337	70	6	236	100	5			
17	406	6	8	371	60	7	270	100	6			

methanol (1 g in 100 mL) and a quartz, water-jacketed cooling finger containing a Hg high-pressure lamp (HPK 125 W Philips, wavelengths above 230 nm) was placed in the solution. Irradiation times were 180 min. Separation of the photoproducts (7 and 8) was carried out on a 100-g silica gel column (i.d., 3 cm; length, 100 cm), which was eluted with petroleum ether (bp 60–90 °C). By contrast, the reaction products 15 and 16 formed by the irradiation of α - (or *cis*-) chlordane (17) were obtained as a mixture by recrystallization of the oily reaction product. Separation of the two isomers was performed by means of "thick layer" chromatography (hexane/acetone, 20:1).

RESULTS

The capillary GC and GC-MS investigations show that technical chlordane contains at least 50 compounds (see Figure 1), which in the majority of cases belong to the tetrahydromethanoindene or tetrahydromethanoindane system. The principal representatives are heptachlor (1-*exo*,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene) (11), α - (or *cis*-) chlordane (1-*exo*,2-*exo*,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane) (17), γ - (or *trans*-) chlordane (1-*exo*,2-*endo*,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane) (18), α - (or *trans*-) nonachlor (1-*exo*,2-*endo*,3-*exo*-4,5,6,7,8,8-nonachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane) (23), and β - (or *cis*-) nonachlor (1-*exo*,2-*exo*,3-*exo*-4,5,6,7,8,8-nonachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane) (22). In addition, α -chlordene (1,2,3,5-*exo*,7,8-hexachloro-1,3a,4,5,6,6a-hexahydro-1,4-ethenopentalene) (24), β -chlordene (2,3,3a,4,5,7-hexachloro-3a,6,7,7a-tetrahydro-1,6-methano-1*H*-indene) (25), γ -chlordene (2,3,3a,4,5,8-hexachloro-3a,6,7,7a-tetrahydro-1,6-methano-1*H*-indene) (26), compound C (3a,4,5,5a,6-*exo*-hexachloro-1a,2,3,3a,5a,5b-hexahydro-1,4-methano-1*H*-cyclobuta[*cd*]pentalene) (27), and compound K (2,4,4,5,6,6,7,8-octachloro-2,3,3a,4,5,7a-hexahydro-1,4-methano-1*H*-indene) (28) are contained in the mixture.

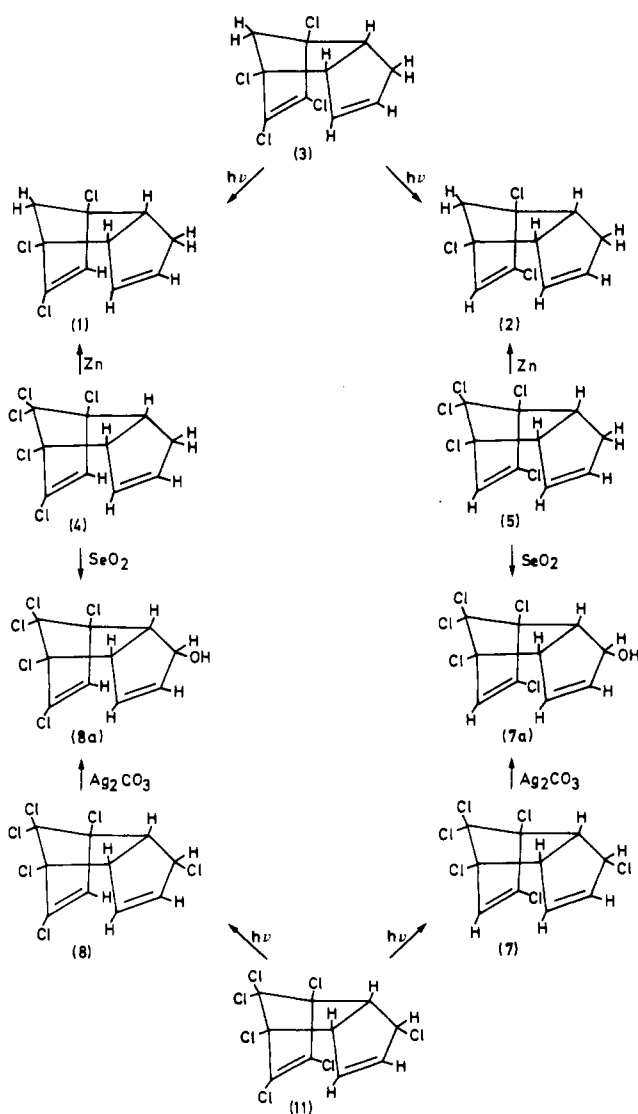
Along with the main components were found: unreacted chlordene (6) and several volatile chlorinated hydrocarbons such as trichlorocyclopentenes, tri- and tetrachloro-

cyclopentanes, penta- and hexachlorocyclopentadiene (Figure 1, zone a) and octachlorocyclopentane (Figure 1, peak b). Furthermore, several C₁₀ hydrocarbons with three–five chlorine atoms were detected, which according to GC-MS data apparently possess the tetrahydro-4,7-methanoindane or the hexahydro-1*H*-cyclobuta[*cd*]pentalene structure (Figure 1, peak c). However, their properties do not agree when compared to those of the corresponding synthetic compounds, e.g., the *R_f* values are different. In addition, fragmentation patterns are also different from those of compounds 1–5. The compounds 9 and 10 which were prepared for the comparison of peak d (Figure 1) and also the hexa- and heptachlorotetrahydromethanoindanes 13 and 14 were not found in technical chlordane. The mass spectra of octachlorotetrahydromethanoindane 19 and 20 correspond partially to those of peaks e and f (Figure 1), but are clearly different as to their peak positions from capillary gas chromatography. A possible nonachlor isomer (1,1,3-*exo*,4,5,6,7,8,8-nonachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane) (21) was also not found in technical chlordane. The peaks g and h (Figure 1) represent nonachlor and decachlor derivatives with the composition C₁₀H₅Cl₉ and C₁₀H₄Cl₁₀ whose structures have not yet been conclusively elucidated. On the other hand, the compounds 1-*exo*,4,5,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (8), 1-*exo*,2-*exo*,4,5,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (15), and 1-*exo*,2-*exo*,4,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane (16) correspond to the monodechlorinated derivatives of heptachlor (11) and α -chlordane (17).

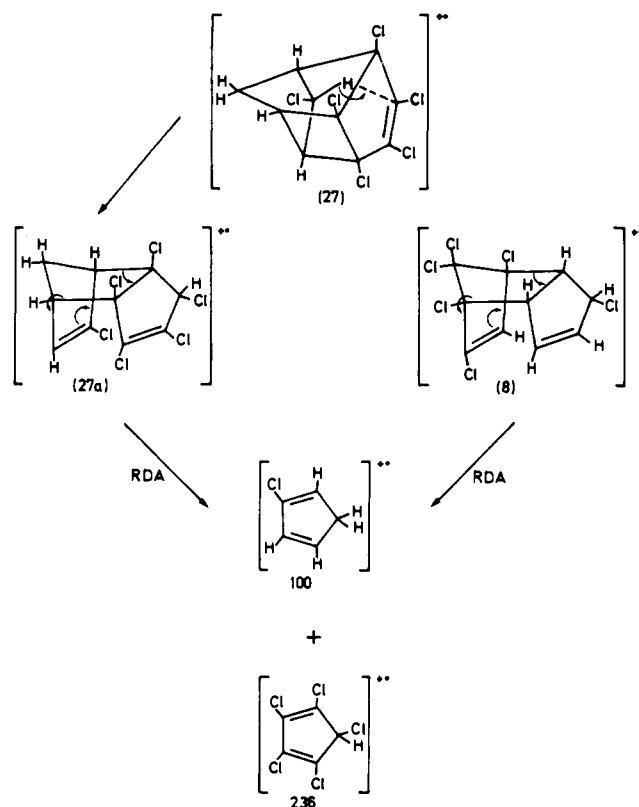
Structure Elucidation of the Compounds 8, 15, and 16 Isolated from Technical Chlordane. The MS (Table IV), the ¹H NMR spectra (Table V), and the IR spectra ($\nu_{\text{C}=\text{CH}} = 1595 \text{ cm}^{-1}$) support the proposed structures. UV irradiation of the relevant compounds was used to prepare the polychlorotetrahydro-4,7-methanoindenes monodechlorinated at the C₅ or C₆ position. Since both heptachlor (11) and α -chlordane (17) represent asymmetric compounds, there are principally two monodechlorinated compounds (7, 8, and 15, 16) which cannot easily be

Table V. ^1H NMR Data of the Compounds 7, 8, 11, 15, 16, and 17 (in ppm)

compd	^1H NMR
7	1 H (3.58, dd), 1 H (4.05, dd), 1 H (4.62, dd), 2 H (5.90, s), 1 H (5.97, s)
8	1 H (3.56, dd), 1 H (4.00, dd), 1 H (4.70, dd), 3 H (5.90, s)
11	1 H (3.58, dd), 1 H (4.27, dd), 1 H (4.90, dd), 2 H (6.06, s)
15	1 H (1.95, m), 1 H (2.40, m), 1 H (3.55, m), 1 H (3.68, dd), 1 H (3.96, m), 1 H (4.45, m), 1 H (6.35, s)
16	1 H (1.95, m), 1 H (2.40, m), 1 H (3.55, m), 1 H (3.68, dd), 1 H (3.96, m), 1 H (4.45, m), 1 H (6.18, s)
17	1 H (1.80, m), 1 H (2.38, m), 1 H (3.55, m), 1 H (3.68, dd), 1 H (3.95, m), 1 H (4.38, m)

**Figure 2.** Chemical reactions for the structure determination of 7 and 8.

distinguished by spectroscopic methods. Compounds 15 and 16 could both be isolated from the mixture; in contrast, only one of the possible monodechlorinated heptachlor compounds (7 or 8) was obtained. It was therefore of interest to determine which of the possible structures applies to the isolated compound. This assignment was

**Figure 3.** Important fragmentation pathways of compound C (27).

performed as follows (Figure 2): 4,5,6,7-tetrachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (3) was dechlorinated photochemically yielding compounds 1 and 2 whose structures had been determined before (Hustert et al., 1975). These compounds could, moreover, be obtained from the pentachlorotetrahydro-4,7-methanoindenes 4 and 5, which are photodechlorination products of chlordene (6), by reduction with zinc powder. Selenium dioxide oxidation of the same products in glacial acetic acid gives the hydroxy compounds 7a and 8a, which were obtained also by hydrolysis of 7 and 8 with silver carbonate. This procedure shows that the hexachlorotetrahydro-4,7-methanoindene isolated from technical chlordane unambiguously has the assigned structure 8.

Mass Spectroscopic Studies on 7, 8, 15, and 16. The relative intensities of selected fragments of compounds 7, 8, 15, and 16 as well as of compounds 11 and 17 are compiled in Table IV. The ions C_5HCl_5^+ or C_6Cl_6^+ were used as reference fragment ions with an intensity of 100. The fragmentation is characterized by elimination of small groups such as Cl or HCl. In addition, the retro-Diels-Alder cleavage (RDA) of these compounds is of great importance. An example is the fragmentation of 7, 8, 15, and 16 to fragment ion 236 with five chlorine atoms or in the case of compounds 11 and 17, 270 with six chlorine atoms. It can be seen, that the compounds 7, 8, 15, and 16, unlike compounds 11 and 17 with six chlorine atoms in the higher-chlorinated ring contain only five chlorine atoms. Although the RDA cleavage may be of considerable assistance in the mass spectroscopic identification of tetrahydro-4,7-methanoindanes and tetrahydro-4,7-methanoindenes, it must be pointed out that it does not suffice for the spectroscopic identification of this class of compounds. Under certain circumstances it may even lead to false conclusions. For example, compound C displays a peculiar mass spectroscopic behavior (Figure 3). By means of a hydrogen abstraction via an energetically very

avored six-membered ring transition state, this compound is intermediately transformed into an "isochlordene" derivative (27a) in the mass spectrometer. The decomposition of this intermediate is controlled mainly by the retro-Diels-Alder reaction. However, the intense RDA fragments would lead to an erroneous interpretation, because one could conclude that a tetrahydro-4,7-methanoindane derivative is responsible for the RDA fragment 236 and 100. Thus, in the mass spectrometric identification of components of technical chlordane and of their transformation products, it is advisable to adduce other spectroscopic methods as well, especially ¹H NMR spectroscopy.

¹H NMR Spectroscopic Observations on 7, 8, 15, and 16. Table V surveys ¹H NMR spectroscopic data of the compounds 7, 8, 15, and 16 relative to those of 11 and 17. The spectra of compounds 7 and 8 and of 15 and 16 correspond approximately to those of 11 and 17. Olefinic protons with signals between δ 5.90–6.35 are observed additionally. The signals of the olefinic protons H₂ and H₃ of the compounds 7 and 8 appear at δ 5.90.

As the signal of H₆ of compound 8 is also recorded at δ 5.90, all three olefinic protons of compound 8 appear as a singlet. Furthermore, compounds 7 and 8 show a chemical shift in the opposed H₂ and H₃ of 0.17 ppm relative to the olefinic protons of heptachlor (11), while the 1,2- and 3-endo protons of compounds 15 and 1 are unaffected.

DISCUSSION

Isolation of 8, 15, and 16 from technical chlordane shows that the hexachlorocyclopentadiene employed in the technical process contains pentachlorocyclopentadiene as an impurity which reacts with cyclopentadiene to form pentachlorotetrahydro-4,7-methanoindenes (e.g., 4 and 5). These compounds are unstable under the reaction conditions and react with chlorine to produce the components 8, 15, and 16. They contain monochlorinated double bonds and are thus the dechlorination products of heptachlor (11) and α-chlordane (17). Due to the absence of the chlorine atom at the double bond, they are capable of undergoing many reactions, especially oxidations and reductions, and are chemically more reactive than compounds 11 and 17.

Capillary gas chromatographic and mass spectroscopic investigations have shown that technical chlordane is a rather complicated mixture mainly of highly chlorinated C₁₀ components. A total of six different C₁₀ skeletons have been identified in the following proportions: tetrahydro-4,7-methanoindene, 11%; tetrahydro-4,7-methanoindane, 45.3%; tetrahydro-1,6-methanoindane, 16.3%; hexahydro-1H-cyclobuta[cd]pentalene, 7.1%; hexahydro-1,4-methano-1H-indene, 3%; and hexahydro-1,4-ethanopentalene, 2.7%.

Until now 85.4% of the compounds contained in technical chlordane are structurally known. The remaining 14.6% consist mainly of higher chlorinated C₅ and lower chlorinated C₁₀ hydrocarbons, of which the latter probably do not represent more than 1% of the mixture.

Furthermore, it becomes apparent through this work that the structure of the components in technical chlordane

cannot be reliably established solely from the fragmentations observed in the mass spectrometer. The typical RDA fragments, which for many years were regarded as specific for tetrahydro-4,7-methanoindene and tetrahydro-4,7-methanoindane, need to be evaluated with some care. Compound C (27), a hexahydro-1H-cyclobuta[cd]pentalene, which has also been identified in technical chlordane, shows the same behavior. The mass spectrometric fragmentation of some of the synthesized hexahydro-1H-cyclobuta[cd]pentalenes confirms these observations (Parlar, 1978).

From the analytical and spectroscopic data described in this work an improved characterization of the composition of technical chlordane is obtained. The data presented may be utilized for interpreting substances isolated from technical chlordane and potential chemical, photochemical, and biological transformation products.

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