other Hercules samples but not necessarily to certain of the remaining chlorinated terpenes examined.

The toxicity of the toxaphene samples and related materials to mice and houseflies does not clearly correlate with their chlorine content, with the amount of components (including B and A) appearing in GLC peaks 9 or 16, or with the amount of any individual GLC peak. This suggests that the toxicity of such diverse samples may be due to many components which could vary with the manufacturing method or that it is due to relatively minor components not easily differentiated on examining such complex mixtures.

Methodology is now available to distinguish between toxaphene and related materials. These procedures may be useful in evaluating the chemical and environmental degradation of these insecticides and their residues.

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A Contribution to the Structure of the Toxaphene Components. Spectroscopic Studies on Chlorinated Bornane Derivatives

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The ir, MS, ^{1}H NMR, and ^{13}C NMR spectroscopic behavior of the synthetically produced low chlorinated bornane derivatives was studied. The obtained data were used for the spectral analysis of compound I, a substance isolated from technical toxaphene. It was further attempted to characterize the composition of technical toxaphene on the basis of spectroscopic data from defined toxaphene fractions.

Technical toxaphene is an insecticidal mixture of C_{10} components with 5–12 chlorine atoms, produced by chlorinating camphene in carbon tetrachloride under uv light. Toxaphene contains up to 70% chlorine and consequently conforms to the empirical formula $C_{10}H_{10}Cl_8$. So far only a few compounds have been isolated from the toxaphene mixture in pure form and studied in regard to their toxicological properties (Anagnostopoulos et al., 1974; Casida et al., 1974; Khalifa et al., 1974; Matsumura et al., 1975). In addition nearly 177 substances have been detected with the aid of GC–MS (chemical ionization) (Holmstead et al., 1974). Detailed reports have also been given on analytical methods for the determination of toxaphene components in environmental samples (Dolan et al., 1974). In the present work, the ir, ^{1}H NMR, ^{13}C NMR, and mass spectroscopic behavior of synthetically produced chlorinated bornane derivatives was investigated and compared with that of compound I, isolated from technical toxaphene (Anagnostopoulos et al., 1974). In addition, attempts were made to characterize the composition of the mixture on the basis of spectroscopic data

Table I. Physical Data of Chlorinated Bornane Derivatives

Compound	R_f	t_R	Mp, °C
2-*exo*,10,10-Trichlorobornane (**4**)	0.70	2.05	141.5
2-*exo*,10-Dichlorobornane (**5**)	0.60	1.23	122.5
2-*exo*,9,10-Trichlorobornane (**7A** or **7B**)	0.41	3.02	120
2-*exo*,3-*endo*,10-Trichlorobornane (**8**)	0.58	3.30	130 dec
2-*exo*,6-*endo*,10-Trichlorobornane (**9**)	0.72	1.64	18
2-*endo*,6-*endo*-Dichlorobornane (**10**)	0.40	1.00	177
2-*endo*,3-*exo*,5-*exo*,6-*endo*-Tetrachlorobornane (**11**)	0.51	3.00	115 dec

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of defined fractions from technical toxaphene.

MATERIALS AND METHODS

Chemicals. Technical toxaphene was kindly supplied by the Hercules Company. Its softening point was between 69 and 70 °C. Compound I, which was isolated by column chromatography on silica gel (petroleum ether, bp 60–90 °C), is representative of a typical member of the toxaphene mixture due to its carbon skeleton and its degree of chlorination. It has an LD_{50} value of 0.59 μg/female fly (LD_{50} for toxaphene = 2.1 μg/female fly), and a toxicity index of 7.3 (Parathion = 100) (Anagnostopoulos et al., 1974). Compounds **4**, **5**, **7A** or **7B**, **8**, and **9** were produced during careful chlorination of camphene (**2**), while compounds **10** and **11** were produced by chlorination of α-pinene (Parlar et al., 1976).

Table I shows the R_f values, the relative retention times, and the melting points of the chlorinated bornane derivatives.

Preparation of Toxaphene Fractions. Fifteen grams of technical toxaphene was separated by column chromatography (length, 1 m; φ, 4 cm) into eight fractions of 700 ml each. Silica gel from Merck Co. (grain size 0.20–0.06 mm) served as adsorbent, and petroleum ether (bp 60–90 °C) was used for elution. The elution speed was 0.75 ml/min. The last two fractions were eluted from the column by petroleum ether (bp 60–90 °C)/acetone (1:1).

Chromatography. Routine investigations were performed with a Packard gas chromatograph Model 417 (column length, 2 m; φ, 4 mm; 3% OV-1 on Chromosorb A W-AW-DMCS (80–100 mesh); injection port temperature, 250 °C; detector, 300 °C; column, 140 °C; carrier gas, nitrogen; flow rate, 40 ml/min). For thin-layer chromatography, TLC plates (Merck silica gel 60 F 254) with a layer thickness of 0.25 mm were used. Plates were sprayed after developing (petroleum ether, bp 60–90 °C) with 1% diphenylamine solution and irradiated with uv light for about 5 min (λ 254 nm) to detect substances.

Spectroscopy. The mass spectra of the gas chromatographically pure compounds were obtained by direct inlet and those of mixtures by GC/MS LKB 9000 S (column length, 2 m; φ, 4 mm; 3% OV-1 on Chromosorb A W-AW-DMCS). The electron energy was 70 eV. The MS data were processed by a digital computer IBM 1130 via an Interface of WDV Company (Munich, West Germany). The elementary composition of the molecule and fragment ions is based on the first peak in each Cl cluster. The ^1H NMR spectra ($CDCl_3$, Me_4Si) were recorded by a 90-MHz R-32 apparatus from Perkin-Elmer, and the ^{13}C NMR spectra ($CDCl_3$, Me_4Si) by a CFT-20 Pulse Fourier spectrometer of Varian. Infrared spectra were obtained with KBr disks of the sample using a Perkin-Elmer Model 577 instrument.

RESULTS

It is known that chlorination of camphene (**2**) with molecular chlorine under temperature-controlled conditions leads to a mixture of mono-, di-, and polychlorinated compounds (Tishchenko and Uvarov, 1953; Jennings and Herschbach, 1965). The intermediate **2a** is first produced by a Cl^+ attack and then reacts to form the main product 2-*exo*,10-dichlorobornane (**5**) in a Wagner–Meerwein rearrangement (see Figure 1). Stabilization of the cationic intermediate state (**2a**) by hydrogen elimination to the 8-chlorocamphene (**1**) or via the 10-chlorotricyclene (the rearrangement of tricyclene results from the attack of C-10 on C-3 and the breaking of the C-2–C-3 single bond) to 6-*exo*-chlorocamphene (**3**) is possible. Since the relative reactivities of primary, secondary, and tertiary carbons with chlorine are similar, further chlorination causes a more or less statistical attack which leads to isomers. It may be assumed that compounds **4**, **5**, **6**, and also the trichlorobornanes **7A** or **7B**, **8**, and **9** developed from 2-*exo*,10-dichlorobornane (**5**) are intermediates during the production of toxaphene. In order to obtain further substances for comparison with chlorinated bornane, the compounds **10** and **11** were produced by chlorinating α-pinene. The intermediate products **4**, **5**, and **6** together with the 10- and 2-exo-positioned chlorine atoms show common structural elements. The 4-positioned bridge hydrogen atom was substituted neither in toxaphene-isolated compounds (Khalifa et al., 1974; Anagnostopoulos et al., 1974) nor in the synthesized low-chlorinated bornane derivatives (Parlar et al., 1976). These positions can be determined as structural elements for all toxaphene components which possess bornane skeletons.

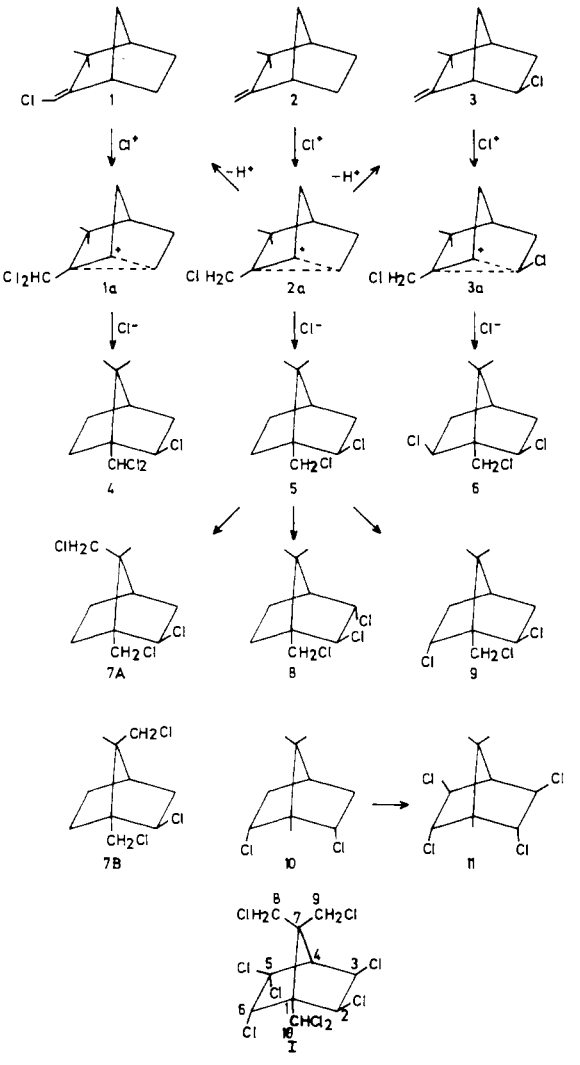

Figure 1. Chlorination pathway of the chlorinated bornane derivatives (**4–11**) and compound I.

Mass Spectroscopic Studies on Chlorinated Bornane Derivatives. The relative intensities of selected fragments of compounds (**4–11**) as well as of compound I are compiled in Table II. The intensity of $(M - HCl)^+$ was used as reference fragment ion with an intensity of 100. The mass number 35 was used for the chlorine atoms contained in the molecules and fragment ions. A suggested pathway for the fragmentation of the chlorinated bornane derivatives is given in Figure 2.

The fragmentation is characterized by elimination of small groups like Cl (path a), HCl (path b), CH_3, CH_2Cl, and $CHCl_2$ (path c or e). The compounds **7A** or **7B** and

Table II. Important Fragment Ions of the Chlorinated Bornane Derivatives

Compd	M^+	Rel intensity	No. of Cl atoms	$(M - CH_3)$	Rel intensity	No. of Cl atoms	$(M - Cl)$	Rel intensity	No. of Cl atoms	$(M - HCl)$	Rel intensity	No. of Cl atoms	$(M - Cl - HCl)$	Rel intensity	No. of Cl atoms
4	240	1.6	3	225	25.2	3	205	74.8	2	204	100.0	2	169	135.0	1
5	206	4.8	2	191	33.3	2	171	92.7	1	170	100.0	1	135	3400.0	0
7A or 7B	240	8.0	3	225	2.0	3	205	92.4	2	204	100.0	2	169	130.0	1
8	240	0.2	3	225	11.1	3	205	82.3	2	204	100.0	2	169	231.0	1
9	240	20.5	3	225	7.8	3	205	47.1	2	204	100.0	2	169	133.0	1
10	206	10.2	2	191	5.2	2	171	66.7	1	170	100.0	1	135	165.0	0
11	274	8.0	4				239	19.6	3	238	100.0	3	203	926.0	2
I				395 (CH_2Cl)	30.0	8	409	250.0	8	408	100.0	8	373	250.0	7

Table III. Composition of Individual Toxaphene Fractions (in Percent)

	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Fraction 6	Fraction 7	Fraction 8
Portion rel to total mixt.	39.7	17.7	9.9	8.3	8.5	8.3	4.2	1.4
$C_{10}H_{13}Cl_5$	0.1	0.1	0.1					
$C_{10}H_{12}Cl_6$	1.3	1.2	1.4	1.0	1.5	0.2	0.1	0.1
$C_{10}H_{11}Cl_7$	10.4	10.3	11.0	13.4	10.5	5.6	4.1	4.0
$C_{10}H_{10}Cl_8$	44.1	46.0	57.3	61.0	64.1	62.0	61.0	51.7
$C_{10}H_9Cl_9$	12.9	17.8	12.9	10.5	10.3	11.5	16.0	17.1
$C_{10}H_8Cl_{10}$	4.0	6.5	3.9	3.0	2.8	1.8	3.8	4.1
Others	27.2	18.1	13.4	11.1	11.3	18.9	15.0	23.0

Table IV. Ir Absorptions of the Chlorinated Bornane Derivatives[a]

Wavelength, cm^{-1}	C_1 position, CH_3 group	C_1 position, CH_2Cl group	C_1 position, $CHCl_2$ group	C_7 position, CH_3 group	C_7 position, CH_2Cl group	C_7 position, $CHCl_2$ group
1450	0	0	0	–	+	–
1435-1430	–	+	–	0	0	0
1390-1370	0	0	0	+	–	–
1350-1340	+	–	–	0	0	0
950-945	–	+	+	0	0	0
855-845	–	+	–	0	0	0

[a] +, present; –, not present; 0, not characteristic.

9 contain a CH_2Cl group as can be seen from the mass spectra. The fragmentation $(M - CH_2Cl)^+$ is observed with two chlorine atoms at *m/e* 191. This fragmentation is not only missing with compounds **10** and **11**, which do not possess a CH_2Cl group, but notably also with compounds **5** and 8.

Compounds 4 and I possess a $CHCl_2$ group at the C-1 position. The fragment ion $(CHCl_2)^+$ is recorded at *m/e* 83. The same elimination was found in the spectra of toxicants A (a mixture of 2,2,5-*endo*,6-*exo*,8,8,9,10-octachlorobornane and 2,2,5-*endo*,6-*exo*,8,9,9,10-octachlorobornane) and B (2,2,5-*endo*,6-*exo*,8,9,10-heptachlorobornane) (Holmstead et al., 1974). The fragment at *m/e* 83 can readily be associated with a $CHCl_2$ group. It cannot be explained why toxicant B, which does not possess the structural feature, results in such a fragmentation.

Important clues to structures in this class of compounds are obtained from characteristic fragmentation, e.g., the ions of *m/e* 161 with two chlorine atoms of compound 4 (path i); *m/e* 127 with one chlorine atom of compound **5** (path i); *m/e* 129 with one chlorine atom (path h) and *m/e* 139 with one chlorine atom (path k) of compound **7A** or **7B**; *m/e* 161 with two chlorine atoms (path i) of compound 8; *m/e* 127 with one chlorine atom (path i) of compound **9**; *m/e* 129 with one chlorine atom (path h) and *m/e* 127 with one chlorine atom (path i) of compounds **10** and **11**. The ions *m/e* 277 with five chlorine atoms (path g), *m/e* 243 with four chlorine atoms (path g), *m/e* 265 with five chlorine atoms (path h), *m/e* 263 with five chlorine atoms (path i), and *m/e* 207 with three chlorine atoms (path k) were formed by the fragmentation of compound I. From these ions, it can be postulated that the structure of compound I contains three CHCl groups in the 2(6), 3, and 5 positions and one CCl_2 moiety in the 2(6) position. The fragments [*m/e* 231 with four chlorine atoms (path h), *m/e* 195 with three chlorine atoms (path i), and *m/e* 173 with two chlorine atoms of toxicant A; *m/e* 209 with three chlorine atoms (path g), *m/e* 231 with four chlorine atoms (path h), *m/e* 195 with three chlorine atoms (path i), and *m/e* 173 with two chlorine atoms (path k) of toxicant B (Holmstead et al., 1974)] agree with the postulated fragmentation scheme.

Mass Spectroscopic Studies of Toxaphene Fractions (GC–MS). Each toxaphene fraction (1–8) was separated in several peaks by gas chromatography using packed columns. It was shown by repeated scannings that each peak represents a uniform isomer fraction and its quantitative measurements were determined over the peak areas. For peaks which could not be fully separated from one another, extrapolations of their theoretical distribution curves were done. Since the relative sensitivity of the single substances could not be determined due to the lack of comparison compounds a value for the absolute error is not given. Table III shows the composition of the individual fractions. The empirical formulas were obtained from the molecular ions or their $(M - Cl)^+$ fragments. Nearly half the compounds of the mixture possess the summation formula $C_{10}H_{10}Cl_8$ whereby compounds with the summation formulas $C_{10}H_{13}Cl_5$ and $C_{10}H_{12}Cl_6$ occur in very small quantities. Also considerable amounts of compounds with summation formulas $C_{10}H_{10}Cl_6$, $C_{10}H_9Cl_7$, $C_{10}H_8Cl_8$, and $C_{10}H_7Cl_9$ were found.

Ir Spectroscopic Studies of Chlorinated Bornane Derivatives. The characteristic absorption bands of low-chlorinated bornane derivatives (KBr) are given in Table IV, from the data available. In the range of

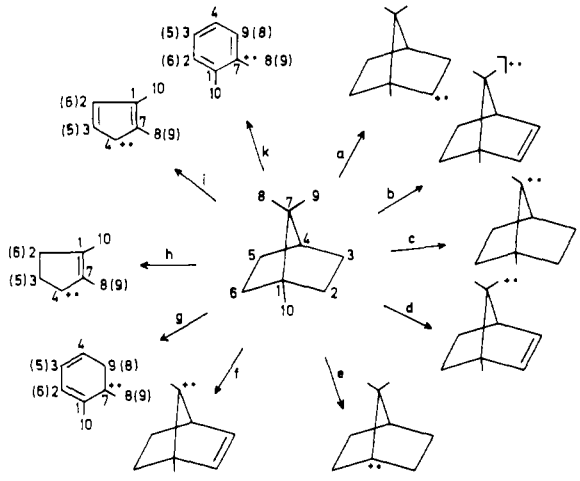

Figure 2. Postulated fragment ions formed by mass spectroscopy of present chlorinated bornane derivatives.

1290–1310 cm^{-1} all compounds have several absorption bands, which partially overlap and do not give characteristic information about the structural feature of bornane derivatives. Therefore, the suggestion that the absorption band at 1305 cm^{-1} is caused by a chloromethyl group (Khalifa et al., 1974) is questionable since compound I, which has two CH_2Cl groups, exhibits only a slight band at 1305 cm^{-1}, while compounds **4** and **10**, which contain no CH_2Cl group, show considerable absorption at 1305–1310 cm^{-1}.

^{1}H NMR Spectroscopic Studies of Chlorinated Bornane Derivatives. Table V gives a summary of the ^{1}H NMR data of compounds **4**–**11** and compound I. The chemical shifts of the C_{10}-positioned protons of compound I (δ 6.83) and compound **4** (δ 6.28) are comparable and indicate the presence of $CHCl_2$ groups. The fact that in compound I the protons at C_8 and at C_9 are not equivalent may be attributed to the blocking of the free rotation along the C_7–C_8 and C_7–C_9 axes, respectively, caused by Cl substitution. (The spatial arrangement of protons H_8 and H_9 in **1** causes a strong ^4J coupling.)

Protons H_2 and H_3 of compound I have the same chemical shift and appear as a singlet. Exchange of the 5-endo-positioned Cl and 2-endo-positioned hydrogen atoms in I leads to a conceivable structure in which, however, the vicinal coupling $J_{H_5H_6'}$ should appear. Nevertheless, this alternate structure cannot be excluded.

^{13}C NMR Spectroscopic Studies on Chlorinated Bornane Derivatives. Although a great number of ^{13}C NMR studies of norbornyl derivatives have been reported (Winkert et al., 1969; Olah and White, 1969; Lippman et al., 1970) little information on the behavior of chlorinated bornane derivatives is available. This is because of difficulties involved in the direct synthesis of these substances. The suggested structures **4**, **5**, **9**, **10**, and I are supported by the ^{13}C NMR data, even though the individual assignments of a few carbon atoms are not always free of doubt. Because of the unfavorable signal/noise ratio in spectrum I the absolute assignment of all observed signals was not possible. The assignment of C_4 and C_7 in **4**, **5**, **9**, and **10** may be assumed to be reliable when the relative shifts in bornane are compared. The absorption of C_7 in **9** and C_4 in **10** at a higher field than in **4** and **5** can be attributed to a sterically induced polarization caused by the γ-positioned chlorine atoms.

The carbon atoms of the $CHCl_2$ fragments in **4** and I might absorb at a lower field than C_2 in **4**, **5**, **9**, **10**, and I or C_6 in **9** and **10**. C_1 and C_7 in **4** allow easy assignment

Table V. ^{1}H NMR Data of Chlorinated Bornane Derivatives (δ in Parts per Million; J in Hertz)[a]

Compd	H_2	H_2'	H_3	H_3'	H_4	H_5	H_5'	H_6	H_6'	H_8	H_9	H_{10}
4	-	4.22, d of d, J = 5.0, 8.0			1.20–2.60, m					1.28, s	1.13, s	6.28, s
5	-	4.20, d of d, J = 5.5, 8.3	2.00–2.40, m		2.20, m		1.30–2.00, m			1.20, s	0.96, s	3.98, d, 3.55, d J = 11
7A or **7B**	-	4.25, d of d, J = 6.0, 8			1.15–2.30, m					3.58, d, 4.15, d J = 11	1.10, s	4.02, d, 3.51, d J = 11
8	-	4.23, d, J = 4.7	4.70, m	-		1.40–2.40, m				1.22, s	1.05, s	3.87, d, 3.50, d J = 11
9	-	4.40, m, J = 5.0, 7.5	1.80–2.10, m	2.68, d of d of d, J = 13, 2.2	1.60–2.10, m			4.30, s	-	1.13, s	1.02, s	4.05, d, 3.70, d J = 11
10	4.35, d of d, J = 10, 4.5	-	1.50–1.95, m, J = 12.5	2.63, m	1.82, m	See H_3	See H_3'	See H_2	-		0.95, s	1.10, s
11	4.50, d, J = 5	-	-	4.09, d	2.42 s	-	See H_3'	See H_2	-		1.30, s	1.18, s
I	-	3.66, s	-	3.66, s	3.20, s	-	-	5.70, s	-	5.08, d of d, J = 3, 13	4.20, d - 4.20, d, J = 12	4.65, d - 6.83, s -

[a] The protons H_2', H_3', H_5', and H_6' are in the endo position.

Table VI. ^{13}C NMR Data (δ in Parts per Million) of Chlorinated Bornane Derivatives[a]

Compd	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8 (C_9)	C_9 (C_8)	C_{10}
Bornane	47.0 (s)	36.8 (t)	28.7 (t)	46.3 (d)	28.7 (t)	36.8 (t)	45.3 (s)	19.2 (q)	19.2 (q)	15.8 (q)
4	59.15 (s)	66.75 (d)	41.21 (t)	49.12 (d)	28.10 (t)	26.19 (t)	50.11 (s)	23.86 (q)	20.19 (q)	75.79 (d)
5	54.16 (s)	64.12 (d)	41.80 (t)	47.56 (d)	26.48 (t)	32.89 (t)	48.69 (s)	21.01 (q)	20.31 (q)	45.72 (t)
9	59.34 (s)	58.90 (d)	34.49 (t)*	47.08 (d)	40.76 (t)*	70.33 (d)	39.47 (s)	23.19 (q)	30.02 (q)	44.59 (t)
10	52.98 (s)	63.98 (d)	40.19 (t)	43.23 (d)	40.19 (t)	63.98 (d)	49.52 (s)	20.47 (q)	20.47 (q)	11.86 (q)
I	+	70.35 (d)*	65.85 (d)*	+	+	70.48 (d)	+	47.53	49.25	77.15

[a] The asterisk indicates that the assignments are interchangeable.

because of the low signal intensity and the observed multiplicity. The low-field shift of C_1 in **4** and **9** may be due to the influence of the β-positioned chlorine atoms. The carbon atoms C_5 and C_6 in **4** show approximately the same chemical shift. The signal at δ 26.19 was assigned to C_6, since the γ-positioned $CHCl_2$ fragment should lead to an absorption at higher field. This effect is also observed with C_6 in **5**.

On the basis of the ^1H NMR spectrum an alternative structure (2,5,10-trichlorobornane) could be suggested for compound **9**, which, however, was excluded by the ^{13}C NMR spectrum. Considering the fact that C_1 in **4** absorbs at δ 59.15 and that this shift value is caused by three β-positioned chlorine atoms, the singlet at δ 59.34 can also be assigned to C_1 in the spectrum of **9**, since this situation is given by a chloro substitution at C-6, but not at C-5, as discussed in the alternative structure. The chemical shift of C_4 (δ 47.08) also excludes the presence of a 2,5,10-trichlorobornane because of the lack of a paramagnetic shift of C_4 caused by the chlorine atom at C_5. C_2 as well as C_7 in **9** are shifted to a higher field because of the 1,4-correlation of C_6- or C_{10}-positioned chlorine atoms.

The $CHCl_2$ fragment in I absorbs at δ 77.15 and is overlapped by the chloroform signal. The signals at δ 70.35, 65.85, and 70.48 in the "off-resonance" spectra each yielded a doublet and consequently were assigned to C_2, C_3, and C_6. Because of similar shifting of C_{10} in **5** and **9**, the strong signals at δ 47.53 and 49.25 were allocated to C_8 and C_9.

DISCUSSION

It is evident from the GC–MS spectra of the single fractions that not only bornane derivatives with the composition $C_{10}H_nCl_{18-n}$ (n = 6–12) are present in the mixture, but also those with the composition $C_{10}H_nCl_{16-n}$ are found, as confirmed by other investigators (Holmstead et al., 1974).

Furthermore, it is possible to characterize the chloro substitution at the methyl groups of the bornane derivatives from the ir spectra alone. Thus, compound I possesses two strong absorption bands at 1450 and 950 cm^{-1}, which are characteristic for the CH_2Cl at C_7 and the $CHCl_2$ group at C_1, respectively. Toxicant A (Khalifa et al., 1974) shows absorptions at 1435 and 845 cm^{-1}, caused by the CH_2Cl group at C_1 and also a band at 1450 cm^{-1} representing a CH_2Cl group at C_7. Toxicant B has absorptions at 1450 and 1435 cm^{-1}, which are assigned to a CH_2Cl at C_7 and a CH_2Cl group at C_1, respectively. From the ^1H NMR coupling constants of low chlorinated bornane derivatives it is possible to determine the positions of individual protons on the bornane skeleton. The coupling constants given in Table VI agree with coupling constants of the toxaphene isolated compounds (Anagnostopoulos et al., 1974; Matsumura et al., 1975).

From the given spectroscopic data of the low chlorinated bornane derivatives and of the toxaphene fractions the composition of technical toxaphene can be better resolved. The data can also be of use in the interpretation of toxaphene isolated compounds and of possible chemical, photochemical, and biological end products resulting from the toxaphene mixture.

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