Spectroscopic Characterization of 7*b*,8*c*,9*c*-Trichlorocamphene-2-one Formed from Toxaphene Components in an Anaerobic Soil

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A cyclic ketone, formed from the toxaphene components Toxicant A (Parlar No. 42) and Toxicant B (Parlar No. 32) in a flooded loamy silt in laboratory experiments, has been isolated, and its structure has been characterized. The product has been shown to have a camphenone skeleton, possibly formed via a Wagner−Meerwein rearrangement. The structure has been identified as 7*b*,8*c*,9*c*-trichlorocamphene-2-one. This is the first time that an oxygen-containing product as conversion product of a toxaphene component has been isolated. Comparison with the behavior of single toxaphene components in autoclaved soil points out that the 7*b*,8*c*,9*c*-trichlorocamphene-2-one is the result of biotransformation.

Keywords: *Toxaphene degradation; chlorinated camphenone; biotransformation*

INTRODUCTION

Toxaphene is a complex insecticidal mixture consisting of more than 200 polychlorinated monoterpenes with an average element composition of $C_{10}H_{10}Cl_8$, predominantly chlorinated bornanes (Saleh, 1991; Zhu et al., 1994; Muir and de Boer, 1995). Until now, about 50 toxaphene components have been isolated and structurally identified by spectroscopic techniques and, in some cases, by X-ray crystallography (Anagnostopoulos et al., 1974; Khalifa et al., 1974; Turner et al., 1975; Chandurkar et al., 1978; Parlar, 1991; Stern et al., 1992; Vetter and Oehme, 1993; Burhenne et al., 1993; Frenzen et al., 1994; Tribulovich et al., 1994; Nikiforov et al., 1995; Hainzl et al., 1993, 1995; Coelhan and Parlar, 1996). From these components, more than 90% have a bornane skeleton. Prior to its ban in many countries in the 1980s, toxaphene was widely used on a large scale as an insect control agent primarily on cotton and several other crops (Korte et al., 1979; Bidleman et al., 1988; Saleh, 1991). Within the past 40 years, global production has been estimated to 1.33 megatons (Voldner and Li, 1993). Because of its high persistence, formerly a desirable property of insecticides, and its high tendency to distribution, it is now present in essentially all parts of the environment (Zell and Ballschmiter, 1980; McConnell et al., 1993; Muir et al., 1995; Bidleman et al., 1989, 1995).

It is well-known that the environmental fate of toxaphene depends strongly on the structure of the individual component. Some components are transformed rather quickly while others are extremely stable. Two important and highly toxic components are Toxicant B (2,2,5-*endo*,6-*exo*,8*c*,9*b*,10*a*-heptachlorobornane, Parlar No. 32) and Toxicant A (2,2,5-*endo*,6-*exo*,-8*b*,8*c*,9*c*,10*a*- and 2,2,5-*endo*,6-*exo*,8*c*,9*b*,9*c*,10*a*-octachlorobornane, Parlar No. 42) (Khalifa et al., 1974). Hence, their degradation and metabolism have been investigated in various systems. In nearly all cases formerly examined, the major reaction has been reductive dechlorination. In both components, a chlorine from the geminal dichloro group in the six-membered ring is removed reductively, yielding isomeric hexachlorobornanes for Toxicant B and heptachlorobornanes for Toxicant A (Ohsawa et al., 1975; Khalifa et al., 1976; Saleh and Casida, 1978; Chandurkar and Matsumura, 1979a,b; Fingerling, 1995; Fingerling et al., 1996). In some systems, dehydrochlorination resulting in the formation of bornene derivatives has also been observed, while oxidation products were assumed but could not be confirmed. In no case an oxidation product could be isolated and confirmed in its structure.

The present paper reports on an oxygen containing product, a camphenone, formed from the toxaphene components Toxicant A and Toxicant B in a flooded soil in laboratory experiments. The identification of this product was carried out by means of MS, FTIR, and ^{1}H-NMR structure analysis.

EXPERIMENTAL PROCEDURES

Materials. The toxaphene components Parlar No. 32 (2,2,5-*endo*,6-*exo*,8*c*,9*b*,10*a*-heptachlorobornane) and Parlar No. 42 (2,2,5-*endo*,6-*exo*,8*b*,8*c*,9*c*,10*a*- and 2,2,5-*endo*,6-*exo*,8*c*,9*b*, 9*c*,10*a*-octachlorobornane) (Figure 1) were isolated from technical toxaphene by column chromatography as described previously (Hainzl et al., 1995; Burhenne et al., 1993). The soil, a loamy silt (pH 6.5; 1.8% organic carbon), was collected from a field in the surroundings of the city of Kassel. It has been chosen because of its lack of any organochlorine contamination. The soil was air-dried and passed through a 2 mm sieve prior to use.

Incubation of Toxaphene Components with Soil and Sample Preparation. Anaerobic soil systems were established in 250 mL Erlenmeyer flasks containing 100 g of soil and 200 mL of distilled water. The flasks were shaken vigorously and subsequently flushed with nitrogen gas for 30 min to remove dissolved O_2. Afterward, the soil solutions were spiked with the toxaphene components as follows: two replicates were spiked with 2 mg of Parlar No. 32 dissolved in 1 mL of acetone to give a final concentration of 20 mg/kg for soil. Furthermore, two replicates were spiked with 600 μg of Parlar No. 42 dissolved in 1 mL of acetone to give a final concentration of 6 mg/kg. Immediately after spiking, the flasks were capped with glass stoppers and incubated in the dark at 35 ± 3 °C. Additionally, nonsterile blanks without Parlar No. 32 and 42 and autoclaved biological controls, one for each toxaphene component, were prepared. Sterilization

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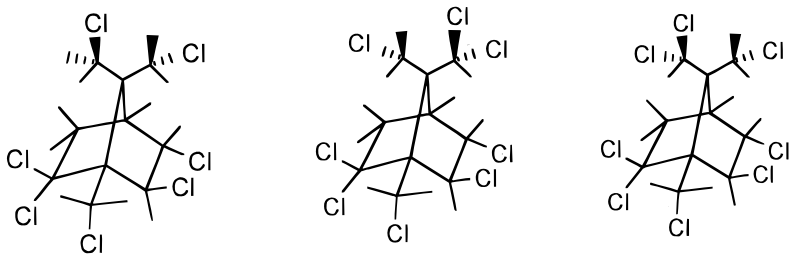

2,2,5-*endo*,6-*exo*,8c,9b,10a-heptachlorobornane (Tox B), Parlar No. 32

2,2,5-*endo*,6-*exo*,8b,8c,9c,10a-octachlorobornane (Tox A_1), Parlar No. 42a

2,2,5-*endo*,6-*exo*,8c,9b,9c,10a-octachlorobornane (Tox A_2), Parlar No. 42b

Figure 1. Names and chemical structures of the investigated chlorobornanes.

of the samples was performed by autoclaving (121 °C, 15 psi) for two 1 h periods at intervals of 24 h before adding each compound with a sterile syringe.

Extraction and Isolation of the New Degradation Product. From each sample, the supernatant liquid was decanted and extracted three times with 60 mL of petroleum ether (40−60 °C)/acetone (1:2) in an ultrasonic bath for 30 min. All extracts from one sample were combined and quantitatively transferred to a 500 mL separatory funnel containing 150 mL of distilled water. After vigorous shaking for 5 min and separation of the phases, the aqueous phase was discharged. The remaining petroleum ether layer (60 mL) was dried over sodium sulfate and checked for its peak profile with GC-ECD. Those organic phases which showed identical peak patterns were combined, concentrated to about 2 mL, and finally applied to a silica gel column (column 100 × 1.2 cm, 50 g of silica gel 60, 70−230 mesh). All compounds not being oxidized were eluted with approximately 2000 mL of petroleum ether (40−60 °C), whereas the oxygen containing product eluted only after changing the eluent from pure petroleum ether to petroleum ether/diethyl ether (8:2) with a purity of approximately 95%. However, its amount formed from Parlar No. 32 was too small to allow crystallization for X-ray analysis, and, in the case of the product formed from Parlar No. 42, not even ^{1}H-NMR measurements were possible.

Gas Chromatography. All routine measurements were performed on a Varian 3400 gas chromatograph; 30 m DB-5, fused silica, i.d. 0.25 mm; thickness 0.32 μm; EC detector 280 °C. N_2 was used as carrier gas (~1 mL/min). The samples were split injected at 230 °C. The GC oven program was as follows: 120 °C (0 min); 20 °C/min to 200 °C (0 min); 5 °C/min to 230 °C (1 min); and then 1.5 °C/min to 250 °C (10 min).

Mass Spectrometry. The MS experiments were carried out using a Hewlett-Packard (HP) 5890/5988A GC/MS system [column: 25 m HP-5, i.d. 0.2 mm; film thickness 0.33 μm; carrier gas He, 1 mL/min; temperature program was 140 °C (3 min) to 250 °C (20 min) at a rate of 4 °C/min; splitless (0.5 min)/split injection; injection block and transfer lines, 280 °C]. The temperature of the ion source was 100 °C for the negative ionization mode (ECNI/MS), with methane as moderating gas. The emission current was ca. 200 μA. Electron impact ionization (EI) was performed at 70 eV and 200 °C ion source temperature. Mass spectra were recorded within a mass range of m/z 40−500.

FTIR Spectroscopy. An HP 5890/5965 GC/FTIR system was used to record the IR spectra [column: HP-5, i.d. 25 m × 0.32 mm, film thickness 0.52 μm; carrier gas: He, 1 mL/min; temperature program was 140 °C (3 min) to 250 °C (20 min) at a rate of 4 °C/min; transfer lines, 250 °C; light pipe, 280 °C].

^{1}H-NMR Spectroscopy. Proton NMR spectra were recorded with a Bruker AC 400 spectrometer (nominal frequency 400.13 MHz) at 303 K in $CDCl_3$ (δ 7.25 ppm) using a 5 mm broadband inverse geometry probe (90°, 8.5 μs). DQF-COSY and NOE difference spectra (mixing time, 1 s) were performed using Bruker standard software, employing 90° pulses (8.5 μs).

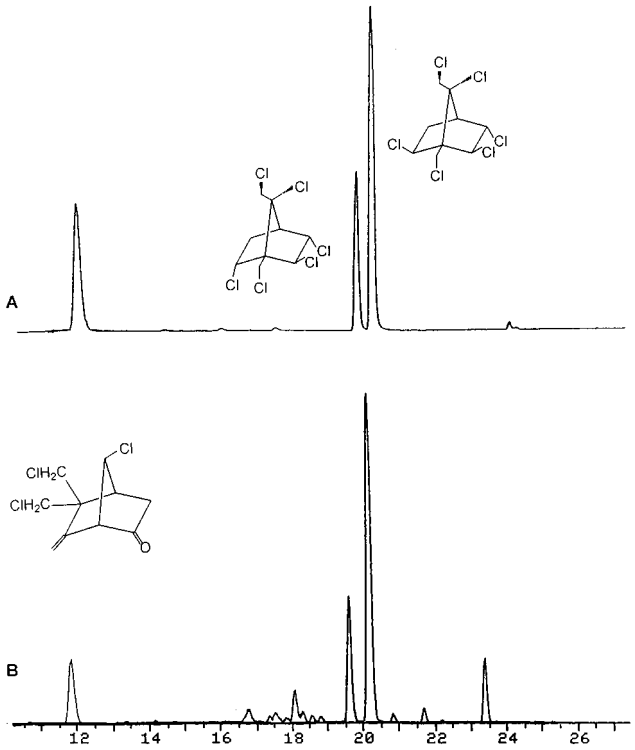

Figure 2. GC−ECNI chromatograms of transformation products from Parlar No. 32 (a) and Parlar No. 42 (b) in a flooded soil after 18 weeks.

RESULTS AND DISCUSSION

The fate of the toxaphene components Toxicant A (Parlar No. 42) and Toxicant B (Parlar No. 32) was investigated in an anaerobic soil over a period of 18 weeks. In Figure 2, the ECNI chromatograms of their transformation products are shown. No degradation is visible in chromatograms of the autoclaved controls which indicates that the transformation is mediated preferentially by microorganisms. Main reaction in the nonsterile samples was reductive dechlorination. This shows, that from each geminal dichloro group in the molecule (Parlar No. 32 has only one of these groups and Parlar No. 42 has two) one chlorine has been substituted by a hydrogen. The two major products were identified as 2-*exo*,5-*endo*,6-*exo*,8*c*,9*b*,10*a*- and 2-*endo*,5-*endo*,6-*exo*,8*c*,9*b*,10*a*-hexachlorobornane (Fingerling et al., 1996). Surprisingly, a further main product was formed from the parent components which did not elute from the silica gel column with pure petroleum ether (PE) like all other products. Only by changing the eluent PE of PE/diethyl ether (8:2) the

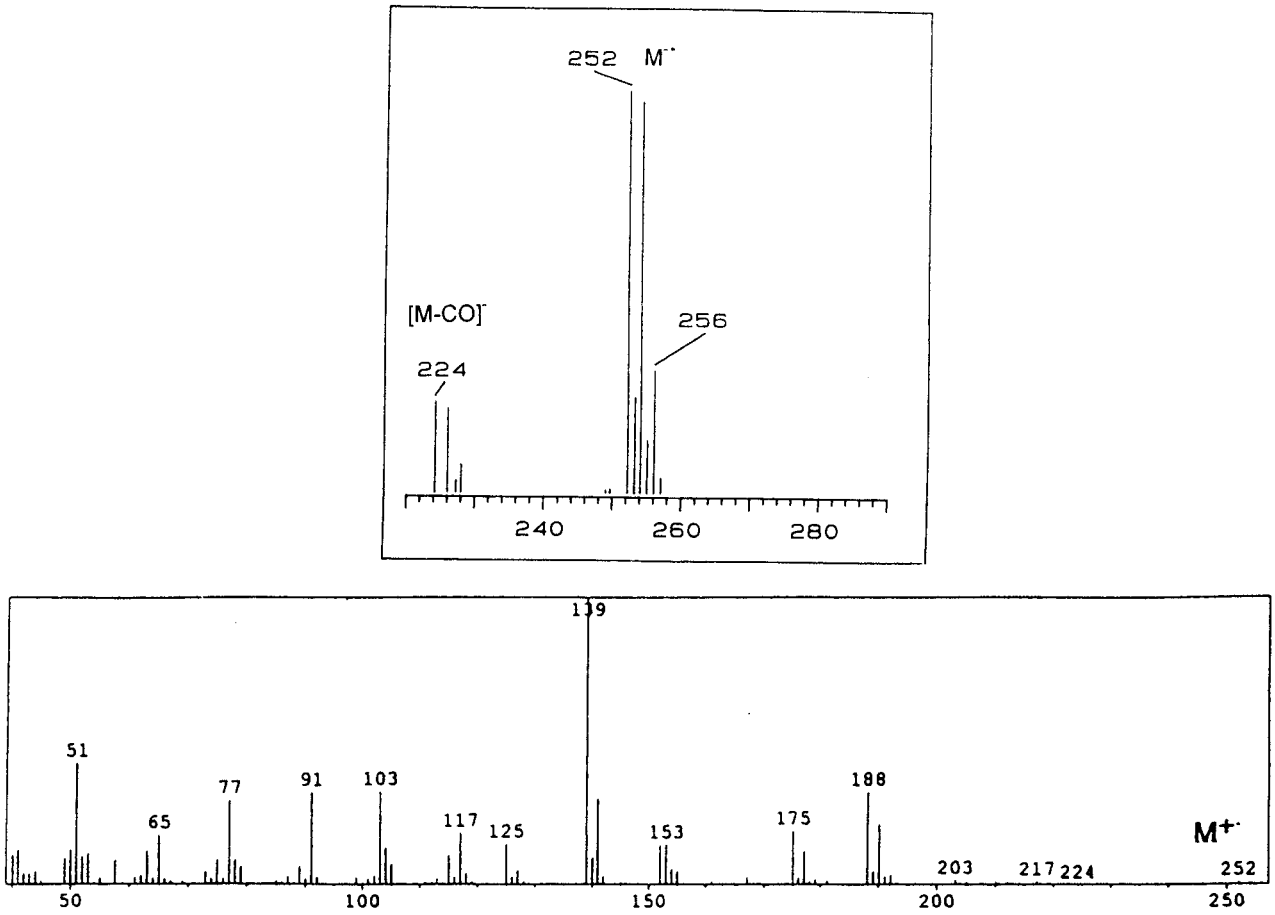

Figure 3. ECNI mass spectra (a) and EI mass spectra (b) of 7*b*,8*c*,9*c*-trichlorocamphene-2-one.

product was eluted. Because of the identical retention times of the respective peak in all measurements and, additionally, the similar MS and FTIR spectra it can be assumed, that the product is the same in all experiments.

The ECNI and EI-MS spectra of the isolated metabolite are shown in Figure 3. From the mass spectroscopic data the empirical formula $C_{10}H_{11}Cl_3O$ can be deduced. The most abundant ion cluster in the ECNI mass spectrum is the molecular ion $[M]^{\cdot -}$ at *m*/*z* 252, which suggests the presence of three chlorine atoms in the molecule. Furthermore, the ion *m*/*z* 224 results from the elimination of CO. The lack of the cleavage of H_2O confirms the assumption, that possibly a bicyclic ketone has been isolated. In the EI mass spectrum, the molecular ion is detected with low intensity. The weak signals at *m*/*z* 224, 217, and 203 correspond to the ions $[M - CO]^+$, $[M - Cl]^+$, and $[M - CH_2Cl]^+$, respectively. No loss of HCl is observed in this mass spectrum which is in agreement with the fragmentation of several chlorinated camphenes, while chlorinated bornanes generally eliminate HCl (Hainzl et al., 1995). The peak at *m*/*z* 188 results from the elimination of a neutral specimen, with a mass of 64 Da which may correspond to HCOCl. Presumably, it has been eliminated during a complex rearrangement of the molecular ion to a quite stable fragment, which, after the cleavage of a CH_2Cl group, finally forms the base peak at *m*/*z* 139. These decompositions may involve ring expansion, possibly to give a stable tropylium analogue, which is prominent in fragmentation processes of chlorinated bornanes, bornenes, and also camphenes (Parlar et al., 1977; Stern et al., 1993; Conacher et al., 1994; Hainzl, 1994; Hainzl et al., 1995). With the ketone, additional stable ions, like tropylium (*m*/*z* 91) and phenyl fragments (*m*/*z* 77), are formed. However, the information obtained from the mass spectra is not sufficient for an unambiguous prediction of the structure of the metabolite.

The FTIR spectrum (Figure 4) shows two characteristic bands, one at 1779 cm^{-1} and another at 1648 cm^{-1}, resulting from the C=O and the C=C valence vibration, respectively. However, in relation to the vibration band of a normal cyclic ketone in a six-membered ring (~1750 cm^{-1}) this band is considerably shifted to higher frequencies. This seems to be more in concordance with a cyclic ketone in a five-membered ring, where the vibration bands appear at approximately 1770 cm^{-1}. Hence, it can be assumed that an increased ring tension may occur, possibly due to the bridge, which is also observed with camphor, where the C=O valence vibration is detected at ~ 1760 cm^{-1}. The C=C valence vibration at 1648 cm^{-1} is in concordance with that found in chlorinated camphenes (Hainzl, 1995). In comparison to the vibration band of the semicyclic double bond in the camphene, the corresponding band of the cyclic double bond of polychlorobornanes appears at significantly lower frequencies, i.e., 1597 cm^{-1} for 2,5-*endo*,6-*exo*,8*b*,8*c*,9*c*,10*a*,10*c*-octachloroborn-2-ene (Burhenne, 1993) and 1596 cm^{-1} for 2,5-*endo*,6-*exo*,8*b*,9*a*,10*a*-hexachloroborn-2-ene (Fingerling, 1995). The strong band at 1296 cm^{-1} seems to be not very characteristic, for it is also found with high intensity in polychlorinated camphenes as well as in bornanes and bornenes (Hainzl, 1995; Burhenne, 1993).

The ^{1}H-NMR spectrum of the metabolite is shown in Figure 5 while Table 1 lists chemical shifts, signal forms, and coupling constants, respectively. The spectrum reveals the presence of eleven protons, with two

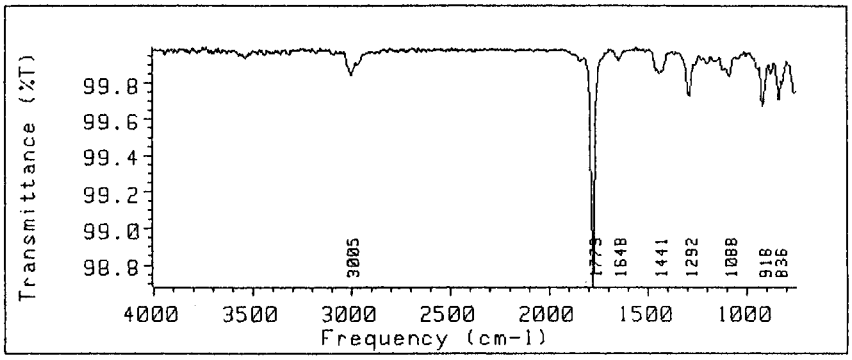

Figure 4. IR spectrum of 7*b*,8*c*,9*c*-trichlorocamphene-2-one.

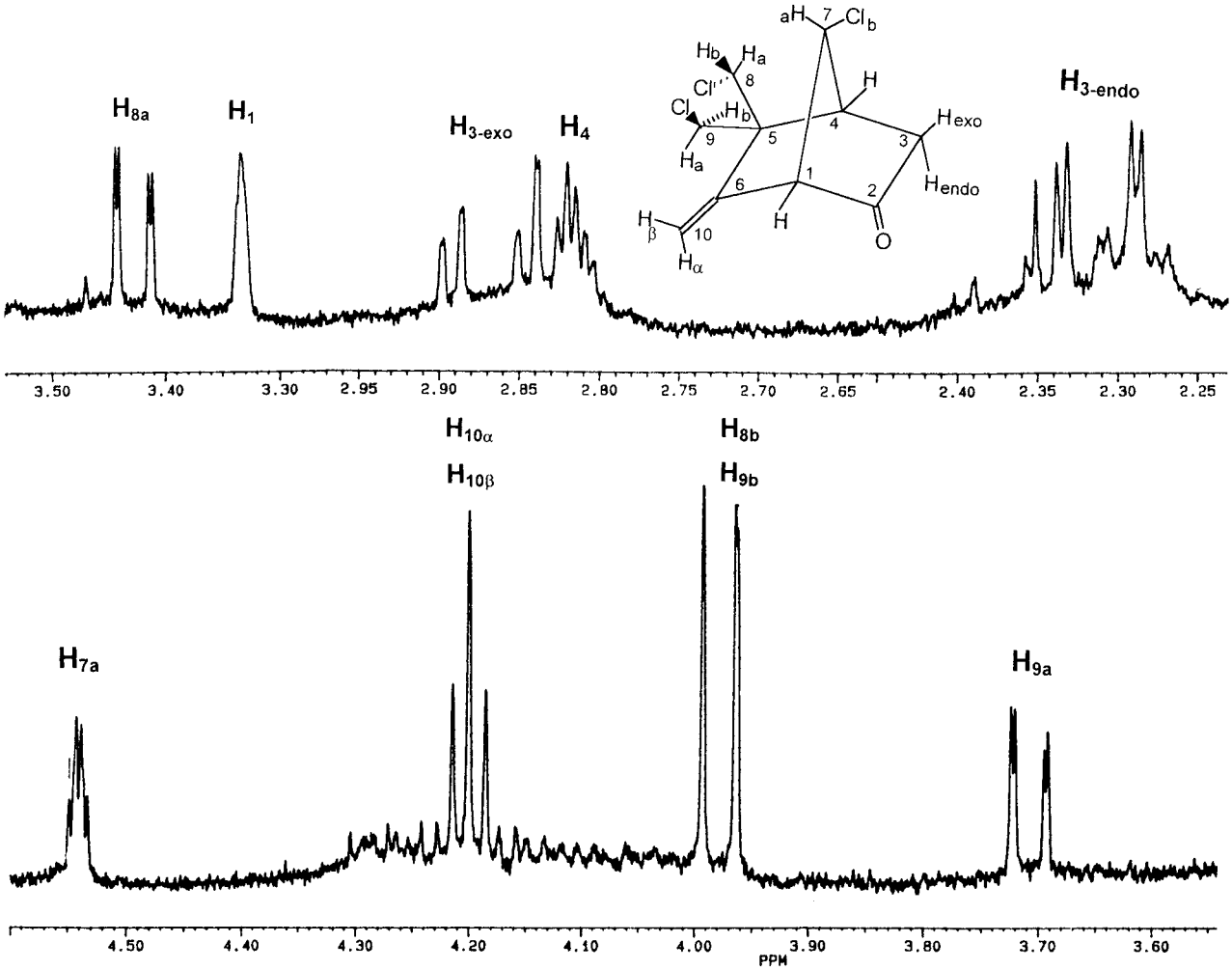

Figure 5. ^{1}H-NMR spectrum of 7*b*,8*c*,9*c*-trichlorocamphene-2-one.

of the signals overlapping. The signal at 2.32 ppm (H_{3-endo}) exhibits a geminal coupling of 18.2 Hz to the signal at 2.87 ppm (H_{3-exo}), which belongs to geminal protons at the six-membered ring. These couplings are in agreement with geminal ring protons of chlorobornanes (16−18 Hz), because ^2J couplings in CH_2Cl-groups show smaller values of about 11 to 14 Hz. Moreover, the geminal ring protons on C-3 are coupling with H_4, whereas the coupling constants differ considerably (H_{3-exo}/H_4 = 4.4 Hz; $H_{3-endo}/H_4 \sim$ 0.4 Hz) due to the dihedral angles of approximately 30° and 90°, respectively (Günther, 1992). Furthermore, the HH-COSY spectrum indicates an M-path long-range coupling between H_{3-endo} and H_{7a} (3.1 Hz). The significant downfield shift of H_{7a} and the lack of a geminal coupling of this proton points to the fact that a chlorine is located on C-7. Owing to the M-path long-range coupling of H_{3-endo} and H_{7a}, the C-7 chlorine must be located above the carbon pairs C-2 and C-3, otherwise no coupling would be observed. Though the signal at 3.33 ppm reveals a complex multiplet, the HH-COSY cross peaks with H_1, H_4, H_{7a}, and H_{10} imply that this signal corresponds to proton H_1. As expected, the small coupling of 5.7 Hz and, additionally, the chemical shifts of 4.18 and 4.22 ppm of the two olefinic protons are observed. Therefore, these signals are assigned as $H_{10\alpha}$ and $H_{10\beta}$.

The signals H_{8a} and H_{8b} or H_{9a} and H_{9b}, respectively, belong to CH_2Cl groups with characteristic geminal couplings of 11.6 Hz. Whereas H_{8b} and H_{9b} show only a geminal coupling, the proton H_{8a} additionally couples with H_{9a} (1.3 Hz) by a long-range M-path coupling,

Table 1. ^{1}H-NMR Data of 7*b*,8*c*,9*c*-Trichlorocamphene-2-one

protons	chemical shift (ppm)	multiplicity[a]	coupling constants (Hz)
H1	3.33	m	
H3-*endo*	2.32	ddd	18.2; 3.1; 0.4
H3-*exo*	2.87	ddd	18.2; 4.4; 0.6
H4	2.82	qui (ddd)	4.4; 2.3; 2.2
H7a	4.54	dd	3.1; 2.3
H8a	3.71	dd	11.6; 1.3
H8b	3.98	d	11.6
H9a	3.43	dd	11.8; 1.3
H9b	3.98	d	11.8
H10α	4.19	d	5.8
H10β	4.21	d	5.8

[a] Key: m = multiplet, d = doublet, dd = doublet of doublets, and ddd = doublet of doublets of doublets.

which allows the conclusion that the CH_2Cl groups are hindered in rotation. These results imply, that the two CH_2Cl groups must be located at the same carbon in the six-membered ring. The fact that no further coupling is observed points to the carbon C-5. With these two additional chlorines on C-8/C-9, all three chlorines in the metabolite are fixed unequivocally in the molecule skeleton. Therefore, the most likely position of the carbonyl group is C-2. It may be possible to find additional structures concurrent with the spectroscopic data, but it seems that the proposed structure is the most probable.

From the spectroscopic data it can be presumed, that the formed metabolite has a camphenone skeleton, indicating that during the transformation of the parent bornanes a rearrangement must have taken place. With respect to the toxaphene components, this is the first time that a product was isolated which has been formed via a rearrangement, obviously a Wagner−Meerwein rearrangement.

The question about the formation of this product is of scientific interest, but the results available do not suffice for exact elucidation of its transformation pathway. The anaerobic degradation of organochlorines is of particular interest, since this class has been the most ubiquitous and problematic of those chemical classes that contaminate the environment. In earlier experiments, microbial degradation of toxaphene in a flooded soil system has led to a partly dechlorinated mixture (Parr and Smith, 1976; Murthy et al., 1984). Reductive dechlorination and dehydrochlorination have been the predominant reactions, but no attempts were made to characterize the major products. The fact, that reductive dechlorination is preferred in such a system, can partially be explained by thermodynamical reasons. In general, polychlorinated compounds are more susceptible to anaerobic dechlorination due to their high oxidation state, while less chlorinated products are more susceptible to aerobic dechlorination. Therefore, less chlorinated toxaphene components can be degraded oxidatively in an aerobic environment while higher chlorinated ones are not. A good example is the compound 2,10-dichlorobornane, which is transformed only under aerobic conditions (Esaac and Matsumura, 1980). Correspondingly, the formation of 7*b*,8*c*,9*c*-trichlorocamphene-2-one from Parlar No. 32 and Parlar No. 42 in an anaerobic soil possibly depends on these special redox conditions. This means, that the bornane derivatives first must be partly dechlorinated and afterwards oxidative degradation can take place.

It seems unlikely that the camphenone is formed from one of the two main hexachlorobornane products. This can be predicted from previous studies on the behavior of Parlar No. 32 and Parlar No. 42 in an anaerobic soil environment which have shown that the two hexachlorobornanes increase when the parent components decrease (Fingerling, 1995). Because of the lack of any maximum in the degradation curve of the two hexachlorobornanes it is probable that both products will not be further degraded under these conditions. On the other hand, a possible precursor of the camphenone could be the dehydrochlorination product 2,5-*endo*,6-*exo*,8,9,10-hexachloroborn-2-ene, which is formed as a small byproduct from Parlar No. 32 as well as from Parlar No. 42. This assumption is based on the fact that its concentration does not increase with time, whereas the camphenone continuously increases in concentration and the parent components decrease. Presumably, the chlorobornene reacts via hydrolysis by forming a geminal chlorohydrin at C-2 which is rather unstable. As a result of this, HCl will be eliminated spontaneously to form a carbonyl group. Probably, this reaction is accompanied by a rearrangement forming the obviously more stable camphenone skeleton. Furthermore, other transformation processes could be also be involved initiating the rearrangement. Whether this conformation step is mediated by microorganisms or chemically is not clear. Presumably, both processes are involved in the observed degradation. Whereas some transformation steps are performed by microorganism others perhaps will be mediated chemically. The insertion of the oxygen atom into the molecule by an oxidative process seems rather unlikely because of the absence of oxygen in the flooded soil system. Therefore, the most possible step may be hydrolysis. To form the 7*b*,8*c*,9*c*-trichlorocamphene-2-one from Parlar No. 32 and 42, the bond between C-1 and C-2 must be broken, while a new bond between C-2 and C-6 must be formed. This may occur by a Wagner−Meerwein rearrangement. However, it seems probable that this reaction can only occur, if the chlorobornane possesses a characteristic chlorine substitution at the six-membered ring. In analogy to photodechlorination, it may be assumed that one chlorine must be located at C-6, possibly in *exo*-position, while a geminal dichloro group must be substituted at C-2.

In this connection it has been shown that the identified camphenone was also detected in small amounts when soil contaminated with technical toxaphene was incubated for six months under the same conditions as used in this study (Fingerling and Parlar, in preparation). Apparently, the chlorinated camphenone is an important intermediate playing a significant key role during the extensive degradation of some toxaphene components in anaerobic environments. Though it cannot be said with certainty from these experiments, the same degradation pathway may be expected in inoculated, anaerobic water.

The significance of this product is based on the fact, that during its formation oxygen has been inserted in the molecule. As a result of this process, the product becomes much more polar than the parent compounds. Because of its higher water solubility, it is more susceptible for a subsequent oxidative degradation. In this respect it would be of scientific concern to satisfactorily clarify its formation step. Hence, work is in progress to investigate the intermediates of this product which may help to elucidate the transformation pathway. Perhaps with these results it will be possible to

predict which of the toxaphene components may be a precursor of the camphenone.

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