

## Structural Elucidation of Compound C. A Chlordene Isomer Constituent of Technical Chlordane

The constituent of technical chlordane designated compound C is an isomer of chlordene ( $C_{10}H_6Cl_6$ ). This isomer is formed via the rearrangement of isochlordene by the action of chlorine or free-radical initiating agents, such as  $Bz_2O_2/CCl_4$ . By means of spectroscopic data (MS, IR,  $^1H$  NMR, and  $^{13}C$  NMR), it was shown that compound C does not possess the cyclodiene-type structure but corresponds to 3a,4,5,5a,5b,6-hexachloro-1a,2,3,3a,5a,5b-hexahydro-1,3-methano-1*H*-cyclobuta[*gh*]pentalene (III).

Technical chlordane is a complex mixture of compounds which is formed by chlorination of chlordene. The products are formed mainly by addition of chlorine (*cis*- and *trans*-chlordane), substitution by chlorine (heptachlor), or a combination of both reactions (*cis*- and *trans*-nonachlor) (Velsicol Chemical Corp., 1971). Another group of products, which includes  $\alpha$ -,  $\beta$ -, and  $\gamma$ -chlordene, results from a rearrangement of chlordene. These isomeric chlordenes ( $C_{10}H_6Cl_6$ ) do not possess the cyclodiene-type structure (Gäb et al., 1975, 1976; Cochrane et al., 1975; Wilson and Sovocool, 1977).

A constituent which appears as peak C (referred to as compound C) in the gas chromatogram of technical chlordane (Polen, 1966) was described as a monochlorinated derivative of the pentachlorocyclopentadiene-cyclopentadiene adduct (Polen, 1966; Saha and Lee, 1969; Cochrane et al., 1973; Sovocool and Lewis, 1975; Cochrane and Greenhalgh, 1976; Sovocool et al., 1977).

By these authors, the fragment ions at *m/e* 236 and *m/e* 100 in the mass spectrum of compound C (III) were assumed to be retro-Diels-Alder fragments and were considered sufficient evidence for the presence of the monochlorinated adduct. Since elucidation of the structure of III has not yet been reported, the present study was undertaken to determine the structure by means of a number of spectroscopic data.

### MATERIALS AND METHODS

Compound C was kindly supplied by the Velsicol Chemical Corporation, Chicago (mp 113–115 °C).

A Packard 417 gas chromatograph was employed for both qualitative and quantitative purposes. A glass column (diameter, 3 mm; length, 2 m) packed with 3% QF1 on Chromosorb W-AW-DMCS (80–100 mesh) was used. Temperatures were: inlet, 250 °C; detector, 300 °C; column, 180 °C. The nitrogen flow rate was 20 mL/min. For thin-layer chromatography, silica gel 60 TLC plates with a layer thickness of 0.25 mm (Merck, Darmstadt) were used, with *n*-hexane as developing solvent.

Table I gives the respective TLC and GLC characteristics of compounds I–IV.

Infrared spectra were recorded as KBr pellets on a Perkin-Elmer Model 577 grating spectrometer.  $^1H$  and  $^{13}C$  NMR spectra were recorded on a Varian CFT 20 (80 resp. 20 MHz) spectrometer.  $CDCl_3$  was used as solvent,  $(CH_3)_4Si$  as internal reference.

Mass spectra were measured with a LKB 9000S GC-MS combination operating at 70 eV.

**Chlorination of Chlordene (I) and Isochlordene (II).** In a typical chlorination experiment, 0.3 g of starting material (I or II) was dissolved in 50 mL of  $CCl_4$  and treated with  $Cl_2$  at room temperature. Each reaction was monitored by TLC or GLC until complete chlorination of the starting material was achieved (ca. 1 h). Excess chlorine was driven off with  $N_2$  and the solvent was removed under reduced pressure. The oily residue was

Table I. GLC and TLC Characteristics of Compounds I–IV

Compound	$R_f$ value	Rel retention time
Chlordene (I)	0.60	1.00
Isochlordene (II)	0.55	1.00 <sup>a</sup>
C (III)	0.49	1.50
Dichloroisochlordene (IV)	0.45	4.07

<sup>a</sup> At 180 °C isochlordene rearranges quantitatively to chlordene ( $t_R = 2.80$  min).

analyzed by GC and GC/MS.

### Reaction of Chlordene (I) and Isochlordene (II) with Benzoyl Peroxide in Carbon Tetrachloride.

Starting material (0.3 g) (I or II) was dissolved in 20 mL of  $CCl_4$ . A solution of 0.25 g of benzoyl peroxide in 20 mL of  $CCl_4$  was slowly added at 80 °C (to chlordene for 2 h and to isochlordene for 1 h). The two mixtures were then refluxed (the chlordene mixture for 3 h and the isochlordene mixture for 1 h) and cooled. The solvent was removed under reduced pressure and the oily residue was subjected to column chromatography on 20 g of silica gel and eluted with *n*-hexane. The obtained eluates were characterized by GC and GC/MS.

### RESULTS AND DISCUSSION

The set of  $^1H$  NMR parameters for compound C (III) (Table II) is characteristic of a five-membered ring having a methylene group,  $\delta_H$  2.38 and 2.46; a chloromethylene group,  $\delta_H$  3.63; and three methine protons at bridgeheads,  $\delta_H$  2.94, 3.11, and 3.35.

The vicinal coupling constants,  $J_{1,1a} = 5.2$  Hz,  $J_{1a,2} = 1.6$ –1.7 Hz,  $J_{1a,2'} = 1.4$  Hz,  $J_{3,6} = 1.6$  Hz,  $J_{2,3} = 1.6$ –1.7 Hz,  $J_{2,3} = 1.4$  Hz, and  $J_{1,6} = 0.4$  Hz, appear to have the Karplus dihedral angle dependence. For example, the coupling between H-1 and H-6 is very small, as expected from the dihedral angle of about 90° measured from the molecular model. The observed long-range couplings  $J_{1a,3} = 1.6$  Hz,  $J_{1,3} = 1.7$  Hz, and  $J_{2,6} = 0.6$  Hz are in accord with the approximately planar "u" orientation of the corresponding protons.

The  $^{13}C$  NMR data (Table II) show that III has one chlorine-substituted double bond, since there are two resonances in the  $sp^2$  carbon range, at  $\delta_C$  127.26 and 132.91. The resonances for the bridgehead chloromethine carbons C-3a, C-5a, and C-5b lie at  $\delta_C$  75.79, 82.67, and 82.96. Because of the lack of selective proton decoupling experiments, no unequivocal assignments could be made for the protonated carbons C-1, C-1a, C-3, and C-6. The resonance at 57.63 could probably be attributed to C-6, since the carbon of the  $CHCl$  group should be less shielded than the bridgehead methine carbons. The methylene group at  $\delta_C = 33.65$  is easily identified.

The mass spectrum of III shows the molecular ion,  $M^+$ , with six chlorine atoms at *m/e* 336. Elimination of Cl or

Table II.  $^1\text{H}$  and  $^{13}\text{C}$  NMR Characteristics of Compound C

Chemical shifts, $\delta$						Coupling constants, $J$ , Hz <sup>a</sup>
H-2 2.38	H-2' 2.46	H-3 2.94	H-1 3.11	H-1a 3.35	H-6 3.63	$J_{1,1a} = 5.2; J_{1,2} = 0.2; J_{1,2'} = 0.4;$ $J_{1,3} = 1.7; J_{1,6} = 0.4; J_{1a,2} = 1.6-1.7;$ $J_{1a,2'} = 1.4; J_{1a,3} = 1.6; J_{1a,6} = 0.2;$ $J_{2,2'} = 12.4; J_{2,3} = 1.6-1.7; J_{2,3} = 1.4;$ $J_{2,6} = 0.6; J_{3,6} = 1.6$
C-2 33.65	C-1, C-1a, C-3, C-6 46.23, 51.75, 55.89, 57.63					
C-3a, C-5a, C-5b 75.79, 82.67, 82.96	C-4, C-5 127.26, 132.97					

<sup>a</sup> The accuracy of the determination of coupling constants is  $\pm 0.1-0.2$  Hz.

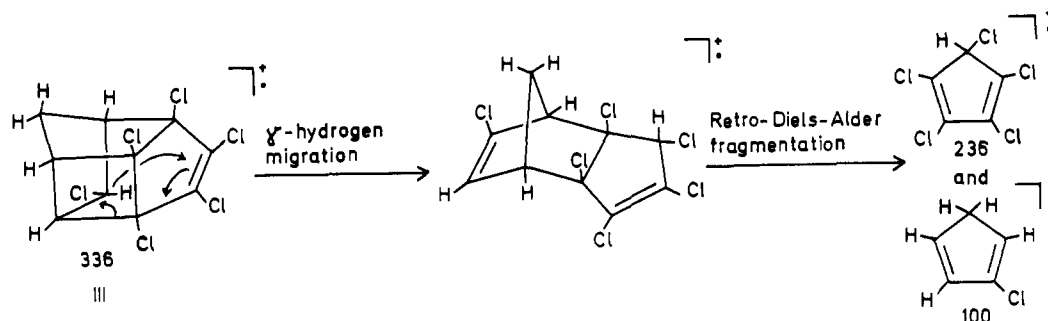


Figure 1. Possible fragmentation pathway of III.

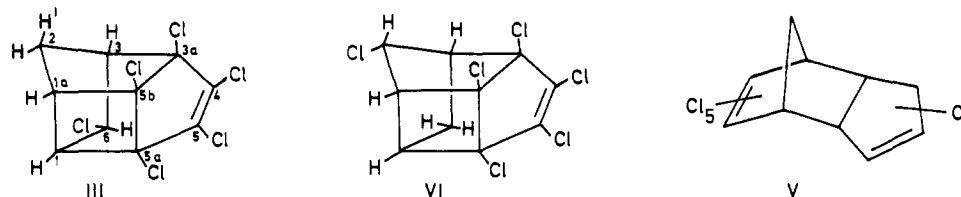


Figure 2. Structure of III and the alternatives V and VI.

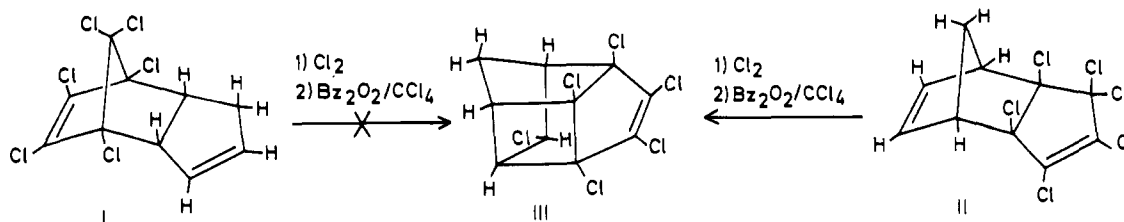


Figure 3. Routes of formation of III.

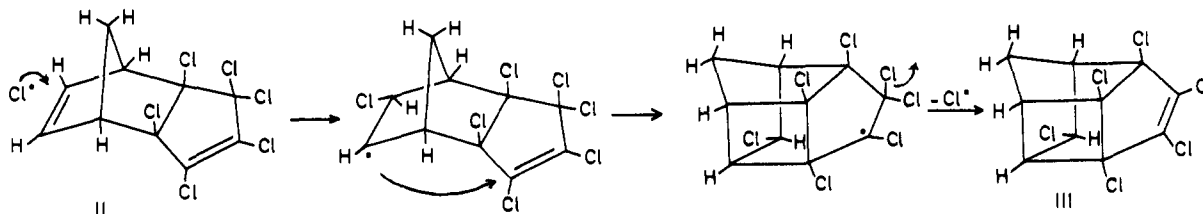


Figure 4. Postulated mechanism of formation of III from II by the action of chlorine radicals.

$\text{Cl}$  and  $\text{HCl}$  leads to fragment ions at  $m/e$  301, 266, 265, 230 and 196. The presence of fragment ions at  $m/e$  236 ( $\text{Cl}_5$ ) and 100 ( $\text{Cl}_1$ ) indicates a retro-Diels-Alder reaction of the molecular ion, which is characteristic of 4,7-methanoindene or -methanoindane derivatives (Chau et al., 1974). Since compound III does not have this structural feature, the occurrence of the pentachloro- and chlorocyclopentadiene ions at  $m/e$  236 and 100 can theoretically be explained by a  $\gamma$ -hydrogen migration, followed by a retro-Diels-Alder reaction (Figure 1).

From the spectroscopic data it can be concluded that III is not a chlorinated 4,7-methanoindene derivative, as was previously assumed. Data from  $^{13}\text{C}$  NMR and IR

( $\nu_{\text{C}=\text{C}} = 1580 \text{ cm}^{-1}$ ) unequivocally prove the presence of only one double bond in III, in contrast to two double bonds in V (Figure 2). In addition, the absence of olefinic resonances in the  $^1\text{H}$  NMR spectrum indicates a chlorinated double bond. The  $^1\text{H}$  NMR parameters agree well with the proposed structure of III but do not permit a clear distinction between the structures of III and VI (Figure 2). However, formation of III through chlorination of II, together with the proposed mechanism (Figures 3 and 4), can be taken as strong evidence for a fixation of the chlorine atom of the  $\text{CHCl}$  group in the 6-exo position rather than in position 2, as is the case in the structure of VI.

It seems an interesting fact that the formation of III was not observed during chlorination of I or heating of I with benzoyl peroxide-carbon tetrachloride. The chlorination of II yielded as main product, dichloroisochlordene (IV) (yield, ca. 50–60%,  $\nu_{C=C} = 1600 \text{ cm}^{-1}$ ) while III appeared as a by-product in a yield of about 5%. If II was treated with benzoyl peroxide, the main product was III (yield, ca. 25–30%).

It should be pointed out that the present investigations were not performed under the same conditions as used in the production of technical chlordane. Therefore, the possibility of I being a direct precursor of III in this process cannot be excluded. Also, the relatively high proportion of III in technical chlordane (approximately 6%, Parlar et al., 1977) cannot be assumed to be derived solely from reactions of II, although the latter is a possible by-product of the technical synthesis of I.

## ACKNOWLEDGMENT

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## CORRECTIONS

INDOLE ALKALOIDS FROM *BALANSIA EPICHLÖE*  
 (WEESE)

In this article by James K. Porter, Charles W. Bacon, Joe D. Robbins, David S. Himmelsbach, and Howard C. Higman, the compound referred to in fraction B and named 3-(3-indolyl)propane-1,2,3-triol should be changed to 1-(3-indolyl)propane-1,2,3-triol.

AMINO ACID ANALYZER STUDIES OF THE  
 PRODUCTS OF PEROXIDE OXIDATION OF CYSTINE,  
 LANTHIONINE, AND HOMOCYSTINE

In this article by Samuel H. Lipton, C. E. Bodwell, and Albert H. Coleman, Jr., on p 627, in the second line of the second full paragraph of the second column, the last word sulfoxide should read sulfone.