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CHARACTERIZATION OF THE PHOTOISOMERS FROM *CIS*- AND *TRANS*-CHLORDANES, *TRANS*-NONACHLOR AND HEPTACHLOR EPOXIDE

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Abstract—Irradiation of acetone solutions of *trans*-chlordane (**4a**) and *trans*-nonachlor (**4b**) with UV light produces new half-cage photoisomers (**5a** or **6a** and **5b** or **6b**, respectively) with bridging that differs from that of the photoisomers (**2** and **8a**) obtained from *cis*-chlordane (**1b**) and heptachlor epoxide (**7**). A new photoisomer (**10**) obtained from heptachlor epoxide is transformed into photoisomer **8a** on further irradiation. Detailed PMR and ^{13}C-NMR studies establish the structures of the new photoisomers and permit a decision between alternative formulations for the structures of the half-cage photoisomers of heptachlor epoxide and *cis*-chlordane.

INTRODUCTION

An understanding of the photolytic behaviour of the chlorinated methanoindane constituents of the commercial insecticides chlordane and heptachor and of their environmental transformation products, including heptachlor epoxide, is of chemical interest and toxicological importance. It is known that some of these compounds form half-cage photoisomers while others bridge to cage structures; in addition, photodechlorination can occur with or without the bridge formation.[1-6]

The previously-known half-cage photoisomers in this series have been derived in high yields from exposure of acetone solutions of β-dihydroheptachor (**1a**), *cis*-chlordane (**1b**) and heptachor epoxide (**7**) to UV light.[1-4] Previous attempts to obtain photoisomers from *trans*-chlordane (**4a**) and *trans*-nonachlor (**4b**) were unsuccessful even though *trans*-chlordane was noted to undergo partial decomposition.[4] However, we have recently found that single half-cage photoisomers are formed with the *trans*-series.[7] These transformations occur in low yields under similar photolytic conditions to those used for the *cis*-series and adequate recoveries are obtained only with more extended irradiation periods.[7] Further, we have obtained a new photoisomer from the irradiation of heptachor epoxide in acetone solution, one that forms more rapidly than the previously-reported half-cage photoisomer and that can be converted to the half-cage photoisomer on further irradiation. This new photoisomer is formed from heptachlor epoxide exposed to sunlight on bean leaves only in the presence of a photosensitizer and the subsequent conversion to the half-cage photoisomer does not require a photosensitizer.[7]

Korte *et al.*[1-3] have assigned structures **3** and **9** to the half-cage photoisomers of *cis*-chlordane and heptachlor epoxide, respectively, although they have not presented supporting evidence. On the other hand, Benson *et al.*[4] were unable to distinguish these proposed structures from the respective alternative formulations, **2** and **8a**. In this paper, we present spectral data and mechanistic considerations bearing on the structures of these two known compounds and on the structures of the three new photoisomers mentioned above. For ease of discussion, the two photoisomers of heptachlor epoxide are referred to as photoheptachlor epoxide A and photoheptachlor epoxide B in the order of their formation from heptachlor epoxide.

RESULTS AND DISCUSSION

The transformation of chlorinated cyclodiene insecticide chemicals into half-cage photoisomers is accompanied by characteristic changes in the IR and PMR spectra. Thus an IR peak near 1600 cm^{-1} due to the stretching vibration of the dichloroethylene moiety is lost while the PMR spectrum gains a sharp one-proton signal at low field ($\sim 5\delta$) due to the resonance of the migrated H atom. These spectral changes occur in the photoisomerization of *cis*-chlordane (**1b**) and heptachlor epoxide (**7**) (in forming photoheptachor epoxide B) and it has been proposed[1-4] that the resulting photoproducts have half-cage structures in which the bridging is from C_2 to C_5 or C_6 (Figs 1 and 2). We observe similar spectral changes on conversion of *trans*-chlordane (**4a**) and *trans*-nonachlor (**4b**) into their photoisomers which therefore must also have

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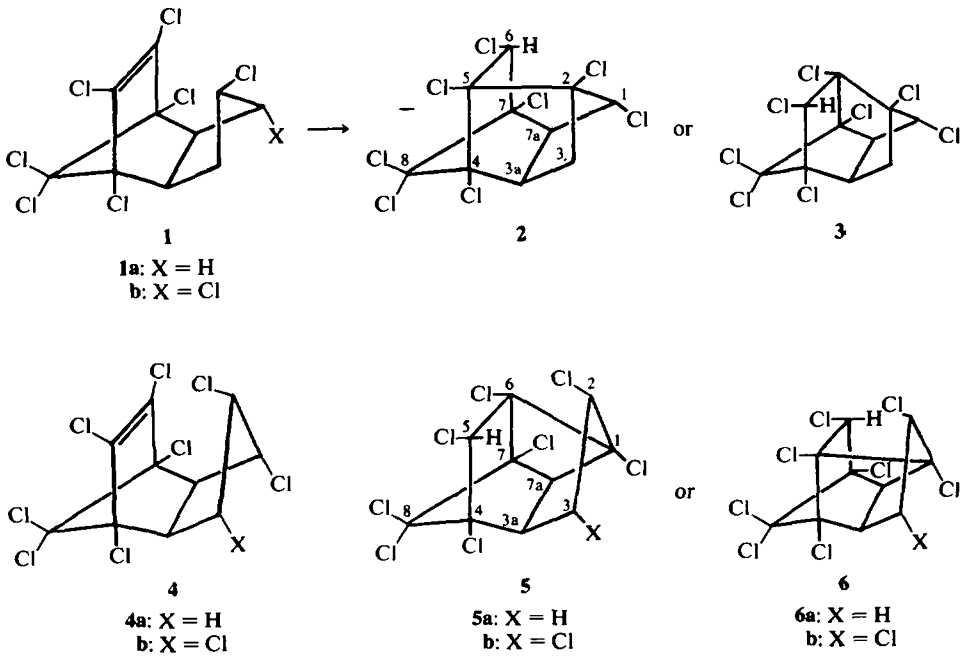
1
1a: X = H
b: X = Cl
2
or
3
4
4a: X = H
b: X = Cl
5
5a: X = H
b: X = Cl
or
6
6a: X = H
b: X = Cl

Fig 1.

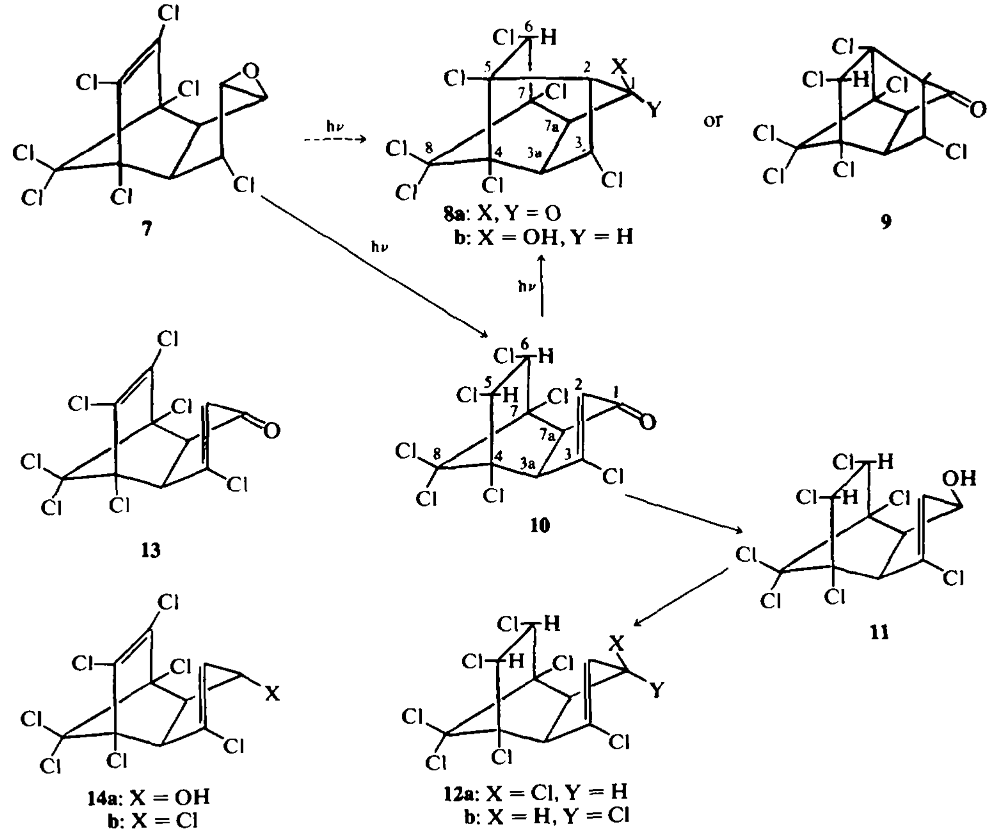
7
hν
8a: X, Y = O
b: X = OH, Y = H
or
9
hν
hν
13
10
11
14a: X = OH
b: X = Cl
12a: X = Cl, Y = H
b: X = H, Y = Cl

Fig 2.

half-cage structures (Fig 1). This observation is of particular interest because, in contrast to the above compounds, the *trans*-precursors have *endo*-chlorine substituents. This suggests that the two photoisomers from *trans*-chlordane and *trans*-nonachlor have structures with bridging from the 1-position (**5a** and **5b** or **6a** and **6b**) or alternatively, in the case of photo-*trans*-nonachlor, from the 3-position (the corresponding structures with 3→5 or 3→6 bridging).

Photoheptachor epoxide A*, on the other hand, is not a half-cage photoisomer because its PMR spectrum lacks the characteristic sharp one-proton resonance at low field. The IR spectrum has absorptions at 1565 and 1700 cm^{-1} (Nujol) which are assigned to an α,β-unsaturated ketone grouping. This chromophore is also evident from UV absorption at 241 nm ($\epsilon = 10{,}133$). Similar IR[8] and UV spectral absorptions are found with the α,β-unsaturated ketone (**13**) derived from heptachlor epoxide by isomerization and oxidation[8] (ν_{max} 1578, 1707 cm^{-1}; λ_{max} 220 nm, shoulder 234 nm, $\epsilon = 12{,}000$ and 9,984 respectively). Thus, it is clear that the new photoisomer is of a type unrelated to the photoisomers previously reported in this series and is closely related to compound **13**.

Several derivatives have been formed from photoheptachlor epoxide A and photoheptachlor epoxide B (Fig 2) to assist in structural studies. Both photoisomers give a single alcohol (**11** and **8b**) from reaction with $NaBH_4$; it is considered in each case that the reducing species approaches from the less-hindered side to give the product with the *endo*-configuration of the OH group. On further reaction with thionyl chloride, the alcohol obtained from photoheptachlor epoxide A is converted into epimeric chloro-derivatives (**12a** and **12b**) which are designated in the order of increasing mobility on TLC. Neither of the chloro-derivatives is identical to *cis*-, *trans*- or δ-chlordane (**15**)[9] which shows that, barring skeletal rearrangement, the new photoisomer is not simply a product of isomerization of the epoxide functionality to a ketone group.

The mass spectra (MS) of alcohol **11** and one of the chloro-derivatives **12a** indicate that they are dichloroethane rather than dichloroethylene compounds; both have an abundant pentachloro ion *m/e* 236 which probably results from initial dehydrochlorination (either thermally or from electron impact) followed by a retro-Diels Alder fragmentation,[10] forming ionised 1,2,4,5,5-pentachlorocyclopenta-1,3-diene or its equivalent. (This *m/e* 236 ion is weak in the MS of chloro-derivative **12b** and is essentially absent from the spectrum of photoisomer A). In comparison the MS of photoheptachlor epoxide B and of some related unbridged compounds[10] have ions at *m/e* 235; these ions probably have a related structure although they are usually of low abundance.

Analysis of PMR spectra. PMR spectra have been measured for photo-*cis*-chlordane (**2**), photo-*trans*-chlordane (**5a** or **6a**), photo-*trans*-nonachlor (**5b** or **6b**), photoheptachlor epoxide A (**10**) and B (**8a**), the various derivatives obtained from the latter two photoisomers (**11**, **12a**, **12b** and **8b**) and a related series of compounds (**13**, **14a** and **14b**). The spectra were measured at 100 MHz with CD_3SOCD_3 solutions except with photo-*trans*-nonachlor for which a $CDCl_3$ solution was used at 60 MHz. For comparison purposes, additional incompletely-analyzed spectra were obtained with photo-*trans*-chlordane and photo-*cis*-chlordane using $CDCl_3$ solutions.

The detailed analysis of the spectra has generally necessitated only first order and AB considerations of well-resolved signals. However, in several cases mentioned in the following discussion, multispin interactions have been analyzed through combining these simple considerations with an ABX analysis. It is possible that small errors have been introduced by these analyses although this has been minimized, wherever possible, by analyzing the patterns from decoupled spectra. The decoupling experiments (and couplings which have been confirmed through these experiments) are summarized in Table 4 (Experimental). Tables 1 and 2 summarize the assignments for the chemical shifts and coupling constants obtained from the spectra. These assignments are firmly-based on the considerations outlined below except in a few cases which do not affect the structural assignments. Spectra have been reported previously for photo-*cis*-chlordane[4] and photoheptachlor epoxide B[4] and compounds **13**, **14a** and **14b**[8,11] but these have been only partially analyzed.

*Photo-*cis*-chlordane and photoheptachlor epoxide B.* The PMR spectra of photo-*cis*-chlordane (**2**), photoheptachlor epoxide B (**8a**) and the derived alcohol (**8b**) show the expected correlations with one another and with the spectrum of photodieldrin.[12,13] The main point of comparison centers on the signals for the ring-junction hydrogens (H_{3a},H_{7a}). In the spectrum of photo-*cis*-chlordane the signals of these hydrogens form an AB pattern which has a small extra splitting on the low-field arm due to coupling with H_{3exo}. With photoheptachlor epoxide B and the derived alcohol, on the other hand, the patterns are more complex, in part because H_2,H_{3a} and H_{7a} in these compounds have similar chemical shifts and are mutually coupled. The parameters for this set were determined from consideration of the patterns obtained after decoupling the H_3 interaction in the former compound and after separately

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*It is possible that earlier workers[3,4] failed to observe the formation of this new product because of an unfavourable irradiation time or because this compound has a surprisingly low mobility on TLC and fails to yield an observable peak on GLC under usual conditions for this series.[7]

Table 1. PMR spectra—chemical shifts (δ values) and multiplicities of signals

Compound	H_1	H_2	H_3	H_{3a}	H_{7a}	H_5 and/or H_6
2	5·67 (d)	—	*exo* 2·79 (dd) *endo* 2·24 (dd)	3·38 (dd)	3·29 (d)	5·89 (s)
2*	4·66 (s)†	—	*exo* ~ 2·60 (m) *endo* 2·38 (d)	~ 3·28 (m)	~ 3·14 (m)	4·90 (s)
5a or **6a**	—	4·89 (dd)	*exo* 2·72 (ddd) *endo* 2·04 (dd)	3·83 (m)	3·77 (m)	6·12 (s)
5a or **6a***	—	4·66 (dd)	*exo*, *endo* 2·1–2·9 (m)	3·88 (m)	3·24 (d)	6·10 (s)
5b or **6b***	—	4·40 (d)	4·66 (d)†	4·00 (d)†	3·40 (d)	6·00 (s)
8a‡	—	3·43 (m)	4·85 (m)	3·67 (ddd)	3·38 (m)	5·05 (s)
8b	5·00 (dd)	2·99 (m)	4·49 (dd)	3·30 (ddd)	3·16 (ddd)	6·84 (s)
10	—	6·73 (d)	—	4·26 (dd)	3·82 (d)	4·84 (s)
11	5·07 (m)	6·14 (dd)	—	3·73 (m)	3·66 (m)	4·90, 5·80 (ABq)
12a	5·50 (m)§	6·26 (dd)	—		3·98 (d)§	5·00, 5·52 (ABq)
12b	5·58 (m)	6·28 (m)	—	4·31 (ddd)	3·68 (dd)	4·71, 5·12 (ABq)
13	—	6·73 (d)	—	4·38 (dd)	3·87 (d)	—
14a	4·38 (m)	6·02 (m)	—	4·07 (ddd)	3·26 (dd)	—
14b	4·82 (m)	6·26 (m)	—	4·43 (ddd)	3·74 (dd)	—

*60 MHz spectrum with $CDCl_3$ solution. All others are 100 MHz spectra with CD_3SOCD_3 solutions. Chemical shifts estimated to the nearest 0·02 and 0·01 ppm respectively.

†Broadened.

‡At 80°.

§Centre of signal.

Table 2. PMR spectra—coupling constants (Hz)[a]

Compound	$J_{1,2}$	$J_{1,3a}$	$J_{1,7a}$	$J_{2,3a}$	$J_{2,3n}$[b]	$J_{3a,3n}$	$J_{3a,7a}$	Others[b]
2	—	0	0	—	—	*c*	7·0	$J_{1,3n} = 1·3$ $J_{3a,3x} = 2·8$ $J_{3x,3n} = 12·0$ $J_{1,6} = 0·7$[d]
5a or **6a**	—	—	—	0	6·9	0	3·5	$J_{2,3x} = 12·0$ $J_{3a,3x} = 5·8$ $J_{3x,3n} = 15·0$
5b or **6b**	—	—	—	—	5	*c*	3	
8a	—	—	—	2·8	*e*	1·5	5·8	$J_{2,7a} = 2·8$
8b	1·0	0	5·8	2·8	2·3	0·8	5·8	$J_{2,7a} = 2·8$
10	—	—	—	1·8	—	—	8·5	$J_{5,6}$[f]
11	2·3	< 1	9·5	1·0	—	—	10·0	$J_{5,6} = 9·0$
12a	2·3		11·3	1·3	—	—	*f*	$J_{5,6} = 9·0$
12b	2·3	2·8	1·5	1·8	—	—	10·0	$J_{5,6} = 8·0$
13	—	—	—	1·3	—	—	6·0	
14a	2·5	2·8	1·8	1·5	—	—	7·8	
14b	2·5	3·0	2·0	1·5	—	—	7·8	

[a] CD_3SOCD_3 solutions estimated to 0·3 Hz except for photo-*trans*-nonachlor (**5a** or **6a**, $CDCl_3$ solution, estimated to nearest 1 Hz).

[b] x refers to *exo*, n refers to *endo*.

[c] Small unresolved coupling (< 1 Hz).

[d] Observed by associates of Perkin-Elmer Co. using degassed $CDCl_3$ solution.

[e] $J_{2,3} + J_{3,7a} = 2·0$.

[f] Not determined.

decoupling the H_1 and H_3 interactions in the latter compound. From these patterns, values for the chemical shifts (3·16–3·67δ) and mutual coupling constants (5·8–7·0 Hz) have been obtained which are closely comparable with those obtained with photodieldrin.[13] Furthermore, the magnitudes of the long-range H_2–H_{3a} and H_2–H_{7a} couplings deduced for photoheptachlor epoxide B and the derived alcohol have close analogy in the spectrum of photodieldrin.[13] The chemical shift of H_2 in these compounds is unexceptional.

The signals due to the hydrogens on C_1 and C_3 are assigned from general chemical shift considerations. The assignment for H_1 in the alcohol is confirmed by the loss of a coupling on the H_1 signal after D_2O exchange of the OH proton. The signals for the methylene hydrogens of photo-*cis*-chlordane, which have a typically large geminal coupling, are distinguished on the basis of a small additional coupling of one of the signals to H_1: this coupling is attributed to the interaction of H_1 and H_{3endo} because these two hydrogens have the appropriate W-relationship. Although photodieldrin apparently does not show a corresponding coupling between H_3 and H_6,[13] there is ample analogy for this coupling in bridged structures.[14]

With the exception of H_1 in photo-*cis*-chlordane, the 1- and 3-hydrogens of the three compounds each have vicinal couplings to the neighbouring 3a- or 7a-protons. In the case of photoheptachlor epoxide B and the derived alcohol, the couplings have been confirmed by the decoupling experiments previously mentioned. No clear evidence has been obtained with the *endo*-hydrogen signals for the existence of the complementary long-range couplings to the ring-junction hydrogens whereas a small coupling between H_3–H_7 (but not H_6–H_8) has been observed in the spectrum of photodieldrin.[13] However, for photoheptachlor epoxide B, the values of $J_{2,3}$ and $J_{3,7a}$ could not be separately determined leaving open the possibility for a long-range coupling in this compound. If, however, $J_{3,7a}$ is small or zero the remaining value for $J_{2,3}$ (~ 2 Hz) is comparable with that in the alcohol (2·3 Hz). These couplings (and the H_1–H_2 coupling in the alcohol) are unexceptional.

The coupling of the 3-*endo*-hydrogen of photo-*cis*-chlordane to H_{3a} is revealed only as a broadening of the signals whereas the 3-*exo*-hydrogen has a clearly-resolved larger coupling. The corresponding couplings of H_3 in photoheptachlor epoxide B and the derived alcohol appear to be more closely comparable to the former coupling and consequently the *endo*-configuration is assigned for the 3-hydrogen of these two compounds; this stereochemistry is in accord with mechanistic considerations. Also noteworthy for the vicinal couplings of the ring-junction hydrogens is the order of the magnitudes: $J_{1exo,7a} > J_{3exo,3a} > J_{3endo,3a} > J_{1endo,7a}$ (~ 0). This is in accord with the respective dihedral angles and it is noticeable that the *endo*-couplings have close analogy in the H_3–H_8 and H_6–H_7 couplings in photodieldrin.[13]

Although these *vicinal* couplings can be taken as evidence for $C_2 \rightarrow C_5$ (rather than $C_2 \rightarrow C_6$) bridging in the three compounds, more compelling evidence is offered by PMR effects associated with the environment of the migrated hydrogens (H_6). An important difference for the two bridgings is that the $C_2 \rightarrow C_5$ bridged structures for the alcohol (**8b**) and photo-*cis*-chlordane (**2**) have the migrated hydrogen (H_6) in close proximity to the 1-*endo*-OH and the 1-*endo*-H respectively whereas the alternative $C_2 \rightarrow C_6$ bridged structures (**9**, 1-*endo*-OH and **3**) have the migrated hydrogen (H_5) close to the 3-*endo*-hydrogens. The PMR signal for the migrated hydrogen in the alcohol is at an extremely low-field position; it is deshielded by 1·79 ppm relative to the corresponding resonance in the spectrum of photoheptachlor epoxide B. This deshielding is attributable to the close proximity of the OH group[15] and provides clear evidence for $C_2 \rightarrow C_5$ bridging in photoheptachlor epoxide B and the derived alcohol. Evidence for the bridging in photo-*cis*-chlordane was sought in a nuclear Overhauser effect.[16] Measurements carried out by associates of the Perkin Elmer Co. using a Perkin-Elmer R32 (90 MHz) spectrometer with a degassed $CDCl_3$ solution of **2** showed that careful irradiation at the resonance frequency of the migrated hydrogen (H_6) gives a 30% enhancement of the signal due to H_1 and no change in the signal due to H_{3endo}. Irradiation at the H_1 resonance frequency likewise enhances the H_6 signal. Also observed in these measurements with degassed solutions was a small coupling (0·7 Hz) between H_1 and H_6 which is analogous to the H_6–H_{12} coupling reported with photodieldrin and attributed to a through-space interaction.[12] Thus the migrated hydrogen of photo-*cis*-chlordane is in close proximity to H_1 indicating that this compound has $C_2 \rightarrow C_5$ bridging.

The photoisomers obtained from *trans*-chlordane and *trans*-nonachlor have bridging from C_1 to C_5 or C_6 (see next section) and the question arises whether photoheptachlor epoxide B and photo-*cis*-chlordane have analogous structures. This possibility is readily excluded by consideration of the foregoing data which is entirely in accord with the assigned structures (**8a** and **2** respectively).

Photo-trans-*nonachlor and photo*-trans-*chlordane.* A consideration of the usual structural modifications involved in half-cage formation suggests four alternative structures for photo-*trans*-chlordane (**5a** and **6a** and the related pair with bridging to C_3) and two for photo-*trans*-nonachlor (**5b** or **6b**). The PMR spectrum of photo-*trans*-chlordane has signals for two hydrogens, which, from their chemical shift and mutual coupling, are clearly attributable to a methylene group. Hence the structural alternatives with bridging to C_3 are excluded from consideration. The remaining structural alternatives for the two compounds, however, can each be reconciled with the respective PMR spectra. Although we were originally inclined to favour the $C_1 \rightarrow C_6$ bridged structures[7] our view now is that there is insufficient basis for a decision between the alternative bridgings.

The CD_3SOCD_3 spectrum of photo-*trans*-chlordane has well-resolved signals for each of the protons with the exception of those due to H_{3a} and H_{7a} which form a narrow five-line pattern centred at

3·80δ. Irradiation at this position with a decoupling field collapsed an eight-line pattern assigned to H_{3exo} into four lines but no other changes in the spectrum were discerned. Consequently the parameters for H_{3a} and H_{7a} were determined by an ABX analysis assuming that the only additional coupling interaction is with H_{3exo}. This analysis reveals that the two hydrogens resonate at lower field and have a smaller coupling than do the ring-junction hydrogens of photo-*cis*-chlordane and other related bridged structures. The differences are not surprising in view of the distortions in the alternative structures proposed for photo-*trans*-chlordane. The separate assignments for the ring-junction hydrogens rest on the magnitude of the coupling between the signals attributed to H_{3a} and H_{3exo} which dictates that the interacting hydrogens have a vicinal relationship. In turn, the basis for the assignment of the H_{3exo} signals in distinction to the H_{3endo} signals is that the H_{3exo} couplings to H_2 and H_{3a} have larger magnitudes than the corresponding couplings to H_{3endo} in accord with dihedral angles measured from **5a** and **6a**.

The $CDCl_3$ spectrum of photo-*trans*-nonachlor shows H_{3a}–H_{7a} and H_2–$H_{3(endo)}$ couplings which have similar magnitudes to those in the CD_3SOCD_3 spectrum of photo-*trans*-chlordane. The low-field arms of the AB patterns for the two pairs of hydrogens in the former compound are each broadened suggesting that, in contrast to photo-*trans*-chlordane, H_{3a} and $H_{3(endo)}$ in photo-*trans*-nonachlor have a small coupling. This observation is the basis for the separate assignments of H_{3a} and H_{7a} and of H_2 and H_3. The chemical shifts of H_2, H_{3a} and H_{7a}, not unexpectedly, differ slightly from the corresponding chemical shifts for photo-*trans*-chlordane in $CDCl_3$ solution.

The migrated hydrogens of the two photoisomers resonate as sharp singlets at low-field positions. For $CDCl_3$ solutions, the resonances are deshielded in excess of 1 ppm relative to the corresponding signals for photo-*cis*-chlordane (4·90δ) and photodieldrin (4·87δ).[13] This observation is of considerable interest because an inspection of molecular models of the alternative structures proposed for the *trans*-photoisomers suggests that the chemical shifts of the migrated hydrogens are the PMR parameters which are most likely to differ substantially for the two bridgings; this is suggested because these structures differ importantly in the environment of the migrated hydrogens. Unfortunately the factors influencing chemical shifts are not sufficiently well understood to permit the alternative structures for the *trans*-photoisomers to be reliably differentiated at this time on the basis of estimated chemical shifts. The known factors[17, 18] which may account for the deshielding in photo-*trans*-chlordane relative to photo-*cis*-chlordane are the magnetic anistropy and electrostatic effects of bonds and the effects of hybridization and steric compression. Zurcher[18] has suggested that allowance also needs to be made for the displacement of solvent molecules in considering the effects of bonds on chemical shifts in rigid structures. There is analogy to suggest that hybridization effects[17] in the strained ring systems of **5a** and **6a** will cause a small deshielding of the migrated hydrogen in these two structures relative to H_6 in photo-*cis*-chlordane and that steric compression[15] in **5a** (interaction of H_5 with H_{3endo} and the 2-chlorine) and in **2** (H_1–H_6 interaction) will have a substantial net deshielding effect in Va and a smaller net shielding effect in **6a** relative to **2**. The effects of the remaining bonds in the three structures have been assessed using "apparent" magnetic anisotropy values[19, 20] coupled with geometrical parameters obtained from Dreiding models (but ignoring differences due to differing distortions of the hexachlorocyclopentane rings). The calculations suggest that these interactions have a net shielding effect in **5a** (~ 0·4 ppm) and a net deshielding effect in **6a** (~ 0·8 ppm) with respect to **2**. Unfortunately these calculations are open to considerable question[17–21] and furthermore it is difficult to assess the magnitudes of the steric compression and the hybridization effects more precisely. The general impression is that the migrated hydrogens of both **5a** and **6a** can be expected to resonate at lower field than in **2** although the observed chemical shift difference between photo-*trans*-chlordane and photo-*cis*-chlordane appears to be larger than expected from the above analysis.

In connection with an assignment for bridging in the *trans*-photoisomers, it is also interesting to note the deshielding of H_{3a} in photo-*trans*-chlordane relative to photo-*cis*-chlordane for both $CDCl_3$ and CD_3SOCD_3 solutions. This possibly can be reconciled with the closer proximity of an 8-chlorine atom and the larger dihedral angle with the 4-chlorine atom[17, 18] in structure **6a**.

Photoheptachlor epoxide A. Photoheptachlor epoxide A (**10**) and its derivatives (**11**, **12a**, **12b**) show spectra which are closely related to those of **13**, **14a** and **14b** (Tables 1 and 2). This latter group of compounds was prepared through an unambiguous route by Cochrane[8] and consequently the close correlations that have been observed between the spectra is taken as evidence for the structures of photoheptachlor epoxide A and its derivatives.

The major difference between the spectra of the two sets of compounds lies in the additional signals for H_5 and H_6 with **10**, **11**, **12a** and **12b**; these signals appear as a singlet in the spectrum of the photoisomer but as clear AB quartets in the spectra of its derivatives. The magnitude of the mutual coupling (7·8–9·0 Hz) shows that these vicinal hydrogens have a *cis*-relationship because a *trans*-relationship would be expected to give a smaller coupling.[17] The *endo*-configurations are assigned from mechanistic considerations. With the exception of this difference the spectra of the photoisomer (**10**) and the related α,β-unsaturated ketone (**13**) are almost identical. In each case H_{3a} and H_{7a} give an AB pattern, the low-field arm of which has an additional fine splitting due to coupling of one of the hydrogens with the vinyl proton. A similar fine coupling is observed in the spectra of the various derivatives of these compounds which suggests that it is H_{3a} rather than H_{7a} that has the long-range coupling to H_2. This allylic coupling[14] is the basis for the assignment of the H_{3a} resonances in distinction to the H_{7a} resonances in all seven spectra of this group.

The spectra of the derivatives of the two α,β-unsaturated ketones are influenced by the stereochemistry at C_1: the patterns due to H_1, H_2, H_{3a} and H_{7a} are similar in the *endo*-substituted series (**11**. **12a**) and in the *exo*-substituted series (**12b**, **14a**, **14b**) although the alcohols (**11**, **14a**) in each case have an extra coupling on H_1 due to interaction with the OH proton. With the two *endo*-compounds, H_{3a} and H_{7a} differ little in chemical shift but, whereas the signals due to H_1, H_{3a} and H_{7a} in the alcohol could be analyzed as an ABX pattern after decoupling the interactions with H_2 and the OH proton (which give superimposed signals), the corresponding pattern in the spectrum of the chloro-compound presented insufficient data to calculate all the parameters. The couplings assigned to $J_{2,3a}$ in these cases are on the assumption that the H_2–H_{7a} interactions do not make an important contribution to the splitting of the H_2 signals. The spectra of the three 1-*exo*-substituted compounds on the other hand, have more widely-separated resonances and only first order and AB considerations were necessary for the analysis of these spectra; for **14a** and **14b** the analysis was aided by a set of decoupling experiments.

These analyses demonstrate that the spectra of the *endo*-substituted compounds differ from those of the *exo*-compounds principally in the magnitude of the coupling between H_1 and the adjacent H_{7a}. The larger coupling in the *endo*-series is consistent with the dihedral angles between H_1 and H_{7a} which an inspection of models suggests is small for the *endo*- and close to 90° for the *exo*-substituted compounds. The actual value of $J_{1,7a}$ for the low R_f chlorination product (**12a**) could not be separately determined but the value of $J_{1,3a}+J_{1,7a}$ (11·3 Hz) plainly indicates that it has a large magnitude because H_1–H_{3a} coupling in the *endo*-alcohol (**11**) has a small or zero value. In comparison the spectra of the *exo*-substituted compounds each show a substantial long-range coupling between H_1 and H_{3a}.

The chemical shifts of the ring-junction hydrogens show interesting variations. For the H_{7a} resonance, the following order for functionalities at the 1-position leads to decreasing shielding: 1-*exo*-OH, 1-*endo*-OH ~ 1-*exo*-Cl, 1-keto, 1-*endo*-Cl. For the H_{3a} resonance the order is: 1-*endo*-OH, 1-*exo*-OH ~ 1-*endo*-Cl, 1-keto ~ 1-*exo*-Cl. These orders are in general accord with the observed spatial effects of the Cl, OH- and CO groups.[17, 21] It is interesting to note that the H_{3a} and H_{7a} chemical shift differences for **10** → **11**, perhaps fortuitously, parallel the differences for photoheptachlor epoxide B (**8a**) → the corresponding alcohol (**8b**).

Another chemical shift effect is revealed by a comparison of the position of the H_5 and H_6 resonances in the spectra of the photoheptachlor epoxide A derivatives (**11**, **12a**, **12b**). In the spectra of the two *endo*-substituted compounds (**11**, **12a**), the resonance of one of these hydrogens is at markedly lower field (5·80 and 5·52δ respectively) than either resonance in the *exo*-substituted compound. This resonance is attributed to H_6 in each case because it is likely that the *endo*-substituents will have a deshielding influence on this hydrogen. It is not clear however, whether H_5 also experiences a small deshielding in the two *endo*-substituted compounds.

Finally, there is evidence that the dichloroethylene group in **14b** exerts a diamagnetic effect on the 1-*endo*-hydrogen. This effect is indicated by the fact that the two chloro-compounds (**12a**, **12b**) derived from photoisomer A have similar chemical shifts for H_1 whereas the corresponding signal in the spectrum of **14b** is at markedly higher field position. The two alcohols (**11**, **14a**) have a chemical shift difference for the H_1 resonances which is in the same direction and of a similar magnitude.

Analysis of ^{13}C-*NMR spectra.* The ^{13}C-NMR spectra of photo-*trans*-chlordane, photo-*cis*-chlordane and photoheptachlor epoxide B are consistent with the assigned structures **5a** or **6a**, **2** and **8a** respectively; those of photoheptachlor epoxide A provide strong support for the assigned structure **10**. Table 3 presents a partial assignment of the signals in the spectra. All signals are completely resolved in the fully-decoupled spectra with the exception of the pairs C_{3a} and C_{7a} and C_5 and C_6 in the spectrum of photoheptachlor epoxide A. The selective decoupling experiments allow the signals of the carbons bearing hydrogen substituents to be differentiated from the signals of the fully-substituted carbons; these observations are in accord with the Overhauser enhancement of the former set of signals in the fully-decoupled spectra.

In the spectra of the four compounds the dichloromethane carbon (C_8) resonates at only slightly different position and consequently its signal is readily identified in each case. The remaining fully-substituted carbons, however, resonate at varying positions in the different spectra. With the exception of the spectrum of photoheptachlor epoxide A, a separate assignment of these signals was not attempted although some correlations between the spectra are evident.

Most of the signals in the spectra of photoheptachlor epoxide A (**10**) are assignable simply from a consideration of the chemical shifts;[22] these considerations clearly identify the resonances of C_1, C_2, C_3 and C_8. The signals for C_4 and C_7 appear as singlets

Table 3. ^{13}C-NMR—Chemical shifts (ppm downfield from TMS) and major multiplicities of signals

Compound	Protons decoupled	C_1	C_2	C_3	C_{3a}	C_6	C_{7a}	C_8	Unassigned
2	All	63·5 or 63·8	†	37·5	50·8	63·5 or 63·8	57·2	96·8	C_2,C_4,C_5,C_7: 72·0, 79·4, 83·4 or 87·0
	H_3 (partially), H_{3a},H_{7a}	d		t		d			
	H_1,H_6			t	d		d		
6a (or **5a**)‡	All	†	63·3	29·8	51·5	71·9	65·1	100·4	C_1,C_4,C_5,C_7: 68·8, 79·7, 82·0 or 84·2
	H_2			t	d	d	d		
	H_6		d	t	d		d		
8a	All	199·1	†	70·3 or 71·6	†	70·3 or 71·6	†	96·9	C_2,C_{3a},C_{7a}: 53·7, 56·1 or 58·8 C_4,C_5,C_7: 72·4, 75·5 or 83·7
10	All	198·6	138·2	165·3	57·7	62·3	57·7	99·9	C_5: 62·3§ C_4,C_7: 75·7 or 76·2
	None		d		d	d	d		

*CD_3SOCD_3 solutions. Singlets unless otherwise indicated.
†See unassigned column.
‡Structure **5a** has reversed C_5 and C_6 assignments.
§Doublet in undecoupled spectrum.

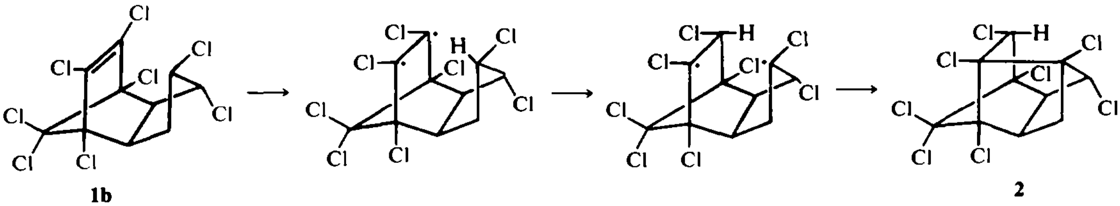
in the un-decoupled spectrum allowing their assignment. Of the remaining carbons, C_{3a} and C_{7a} are considered likely to resonate at a higher field position than C_5 and C_6 but no attempt has been made to confirm this by an appropriate decoupling experiment.

Selectively-decoupled spectra of photo-*cis*-chlordane and photo-*trans*-chlordane each show a triplet signal from one ^{13}C nucleus which readily identifies the signals for the methylene carbons in these compounds. The resonance of C_2 and C_6 in photo-*trans*-chlordane (**6a**; or C_2 and C_5 for **5a**) and of the C_1, C_6 pair in photo-*cis*-chlordane (**2**) and the C_{3a},C_{7a} pair in both photo-*trans*-chlordane and photo-*cis*-chlordane are also identified from the multiplicities of the signals in selectively-decoupled spectra (Table 3). Although the decoupling experiments do not distinguish between the signals due to the ring-junction carbons (C_{3a} and C_{7a}), these are assigned in each case from the consideration that C_{7a} will be more strongly deshielded by the extra substitution on the adjacent C_1;[22] as is to be expected, the effect is greater for photo-*trans*-chlordane than for photo-*cis*-chlordane. No decision was possible for assignment of the closely-spaced signals due to C_1 and C_6 in the spectrum of photo-*cis*-chlordane.

Photoheptachlor epoxide B was not subjected to selective decoupling experiments partly because of its limited solubility at room temperature in CD_3SOCD_3. Chemical shift considerations and Overhauser effects in the spectrum allow unique assignments for the C_1 and C_8 signals and suggest limiting assignments for the other signals (Table 3).

The sensitivity of ^{13}C-NMR spectra to steric interactions[22] is evident from a comparison of the photo-*cis*-chlordane and photoheptachlor epoxide B spectra. The greater shielding of C_6 in the former compound is attributed to the H_1–H_6 steric interaction. This effect is of particular interest in connection with the differing steric environments of the migrated hydrogen in the alternative structures proposed for photo-*trans*-chlordane (**5a** or **6a**) because it offers a possible means for distinguishing between these structures. Structure **5a** has the 2-chlorine and the 3-*endo*-hydrogen within the van der Waal radii of H_5 whereas **6a** has much less severe interactions with H_6. Consequently the resonance of the carbon bearing the migrated hydrogen in photo-*trans*-chlordane should be at a high-field position if the former structure applies and at a more normal position if the latter structure applies. It appears, from a comparison with the C_6 resonances of photo-*cis*-chlordane and photoheptachlor epoxide B, that the resonance for photo-*trans*-chlordane is at a normal field position and consequently the latter structure is favoured. However, more extensive studies with closely-related compounds are necessary to confirm this observation.

Mechanistic considerations. The formation of half-cage photoproducts appears to involve intramolecular hydrogen transfer as is illustrated for the formation of photo-*cis*-chlordane in Scheme 1.



SCHEME 1

This is in accord with the stereochemistry of photodieldrin[12] and with the results of isotopic studies.[3] For chlordane derivatives it has previously been considered[4] that only a hydrogen in the 2-*endo*-position can migrate in such photochemical transformations (Scheme 1) but the finding, reported here, that *trans*-chlordane and *trans*-nonachlor form half-cage photoproducts invalidates this proposal; these compounds have chlorine substituents in the 2-*endo*-positions and it is the hydrogen from the 1-*endo*-position which is transferred. Presumably for the photoisomerization of *trans*-chlordane this hydrogen migrates in preference to the 3-*endo*-hydrogen because the geminally-located chlorine atom has a labilizing influence. In view of the structure of photo-*cis*-chlordane however, it is apparent that transfer of the 2-*endo*-hydrogen normally is preferred for the photoisomerizations of chlordane derivatives. This is also evidenced by the greater ease with which a half-cage photoisomer is formed from *cis*-chlordane than from *trans*-chlordane or *trans*-nonachlor.

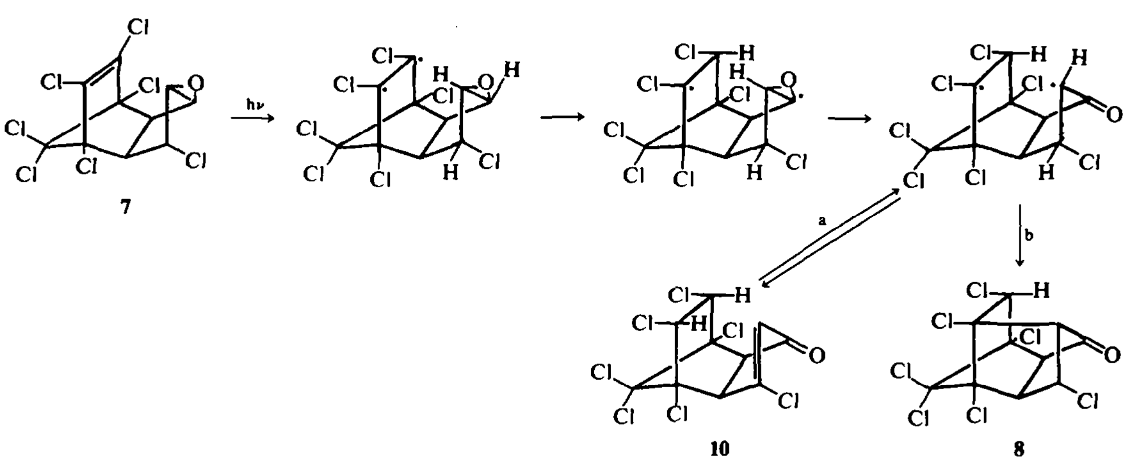
The structure established for photo-*cis*-chlordane (**2**) demonstrates that, in the photoisomerization of *cis*-chlordane, the abstracted hydrogen (H_2) is transferred to C_6. The reason for the preference of C_6 over C_5 is unclear because the two carbons appear to have equal separations from the 2-*endo*-hydrogen. However, the 1-*endo*-hydrogen is located much closer to C_6 than C_5 and consequently, in the photoisomerization of *trans*-chlordane, it might be expected that the former carbon would abstract the 1-*endo*-hydrogen more readily than would the latter carbon. Subsequent coupling of C_1 to C_5 would then form structure **6a**. An analogous process would form structure **6b** from *trans*-nonachlor. If, on the other hand, these photoisomers have structures **5a** and **5b** they must arise from transfer of the 1-*endo*-hydrogen to the more remote dichloroethylene carbon atoms (C_5 in *trans*-chlordane) with subsequent C–C coupling. The C_5–H_1 separations seem rather large for the transfer to occur directly whereas an unprecedented indirect transfer of the hydrogen via C_6 appears feasible only if the pathways to the two differently bridged structures have favourable equilibria or favourable transition state energies for the C–C couplings. For this to occur it seems that structures **5a** and **5b** must be thermodynamically more stable than **6a** and **6b**. Unfortunately neither skeleton has been reported previously, but it is worth noting that the tricyclo[3.2.1.0^{3,6}]octane skeleton is formed more readily than the tricyclo[3.3.0.0^{3,7}]octane skeleton[23] and that 2-tricyclo[3.2.1.0^{3,6}]octyl carbonium ions are more stable than 2-tricyclo[3.3.0.0^{3,7}]octyl carbonium ions.[24,25]

The photolytic conversion of heptachlor epoxide into photoheptachlor epoxide A (**10**) appears to be a unique transformation but previous reports have appeared of transformations analogous to the conversion of heptachlor epoxide into photoheptachlor epoxide B (**8a**)[26] and for conversion **10**→**8a**.[27,28] The photoisomerization of heptachlor epoxide may proceed by pathways in which the excited dichlorethylene group abstracts either H_1 or the somewhat closer H_3. After abstraction of H_1, divergent pathways (a and b, Scheme 2) would lead to photoheptachlor epoxide A and photoheptachlor epoxide B. The former pathway must be faster to account for the more rapid formation of photoisomer A and spin-states may be important in this regard. The alternative formulation for the photoisomerization pathway in which H_3 is the first hydrogen abstracted (followed by H_1) requires that photoisomer A, in a ground or excited electronic state, be an obligatory intermediate in forming photoisomer B. It is worthwhile noting in this respect that, on structural grounds, the half-cage photoendrin cannot be formed from its epoxide precursor, endrin,[26] with an α,β-unsaturated ketone in the ground state as an intermediate; on the other hand, a pathway analogous to that in Scheme 2 (excluding step a) is quite satisfactory. However, the separations between the dichloroethylene group and the candidate hydrogens are not closely comparable for endrin and heptachlor epoxide.

The orientation of the bridging in photoheptachlor epoxide B (C_2→C_5) is consistent with either pathway on the assumption that hydrogen migrations occur over the shortest distance. Furthermore, the *exo*-configuration can be expected for the 3-chlorine in photoheptachlor epoxide B if an intramolecular hydrogen-transfer mechanism applies.

EXPERIMENTAL

60 MHz and 100 MHz spectra were recorded respectively with a Varian T60 spectrometer and with a modified Varian HA 100 spectrometer. ^{13}C-NMR spectra were recorded at 22·63 MHz with a Brucker 90 spectrometer with



Scheme 2

Digilab modifications for recording by the Fourier transformation method.

The 100 MHz PMR spectra were subjected to extensive decoupling experiments and the more useful results are summarized in Table 4.

Mass spectra were determined with a Consolidated Electrodynamics Corp. model type 21-103 C with a direct insertion probe heated to the minimum temperature necessary for obtaining a useful ion abundance.

Table 4. Decoupling experiments

Compound	Proton(s) Irradiated	Coupling(s) confirmed
5a or **6a**	H_{3a}, H_{7a}	H_{3a}–H_{3exo}
8a	H_3	H_3–H_{3a}, H_2–H_3
8b	H_1	H_1–H_2, H_1–H_{7a}
11	H_{3a}, H_{7a}	H_2–H_{3a}
	H_2, OH	H_1–H_2, H_1–OH, H_2–H_{3a}
12a	H_{3a}, H_{7a}	H_2–H_{3a}, H_1–H_{7a}
14a	H_1	H_1–H_2, H_1–H_{7a}, H_1–OH
	H_2	H_1–H_2, H_2–H_{3a}
14b	H_2	H_1–H_2, H_2–H_{3a}
	H_{7a}	H_1–H_{7a}

M.ps were determined on samples sealed in capillary tubes and heated in a sulphuric acid bath.

Characterization of photoisomers. The photoisomers were prepared by irradiation of acetone solutions of the precursors with a pyrex-filtered high pressure mercury-vapor lamp and then isolated by Florisil chromatography according to the earlier-reported procedures.[7] A summary of the recrystallizing solvents, melting points and elemental analysis data is presented in Table 5.

Interconversion of photoheptachlor epoxide A and photoheptachlor epoxide B. A stirred soln of photoheptachlor epoxide A (100 mg) in acetone (165 ml) was irradiated with a 450 watt high-pressure quartz mercury-vapor lamp equipped with a pyrex absorption sleeve. After 2 hrs, photoisomer A had almost completely disappeared (TLC). The recovered material was photoheptachlor epoxide B (70 mg) based on TLC, GC, IR and MS comparison.

Reduction of heptachlor epoxide photoisomers

(i) Photoheptachlor epoxide A (1·0 g) in methanol (30 ml) was stirred with an excess of $NaBH_4$ in an ice-bath. After 90 min the product (950 mg) was isolated by elution from a dry Florisil column with petroleum ether : ether (2 : 1). Several crystallizations from ether-hexane

Table 5. Characteristics of photoisomers

Compound	Recrystallizing Solvent	Melting Point	Formula	—	Elemental Composition % C	H	Cl
2	hexane	148·5–151°	$C_{10}H_6Cl_8$	Calc.	29·3	1·5	69·2
				Found	29·5	1·6	69·3
5a or **6a**	hexane	168·5–170°	$C_{10}H_6Cl_8$	Calc.	29·3	1·5	69·2
				Found	29·2	1·6	69·4
5b or **6b**	hexane	154–155·5°	$C_{10}H_5Cl_9$	Calc.	27·0	1·1	71·8
				Found	26·8	1·3	71·9
8a	$CHCl_3$–hexane	208–9°	$C_{10}H_5Cl_7O$	Calc.	30·8	1·3	63·8
				Found	30·9	1·2	63·9
10	$CHCl_3$–hexane	178·5–181·5°	$C_{10}H_5Cl_7O$	Calc.	30·8	1·3	63·8
				Found	30·9	1·6	63·7

gave the alcohol, m.p. 149–150°. (Found: C, 30·8; H, 2·1; Cl, 63·2. Calc. for $C_{10}H_7Cl_7O$: C, 30·7; H, 1·8; Cl, 63·4%).

(ii) Photoheptachlor epoxide B (0·9 g) in EtOAc (50 ml) was stirred at room temp with an excess of $NaBH_4$. After 39 hr the alcohol (675 mg) (m.p. 185–7°) was isolated by elution from a dry Florisil column with chloroform–petroleum ether mixtures (1:4 and 5:2) and crystallized from ether–hexane. It gave a single spot on TLC. (Found: C, 31·2; H, 1·8; Cl, 63·2. Calc. for $C_{10}H_7Cl_7O$: C, 30·7; H, 1·8; Cl, 63·4%).

Chlorination of the alcohol (**11**) *derived from photoheptachlor epoxide A*. The alcohol (500 mg) in dry benzene (5 ml) was refluxed for 30 min with $SOCl_2$ (184 μl) and pyridine (2 drops). After evaporation of the volatile materials, the residue was chromatographed several times on a dry column of Florisil. Elution with light petroleum ether (2:1) gave the two chloro-compounds as pure materials (TLC).

The high R_f chloro-compound (194 mg) was crystallized from hexane as colourless crystals m.p. 176–8°. (Found: C, 29·4; H, 1·5; Cl, 69·2. Calc. for $C_{10}H_6Cl_8$: C, 29·3; H, 1·5; Cl, 69·2%).

The low R_f chloro-compound (298 mg) was crystallized from hexane as colourless crystals m.p. 168·5–172°. (Found: C, 29·5; H, 1·5; Cl, 69·0. Calc. for $C_{10}H_6Cl_8$: C, 29·3; H, 1·5; Cl, 69·2%).

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