

Polyquinanes

II.* Further Studies on the Chlorination of *all-cis*-Tricyclo[5.2.1.0^{4,10}]decane

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Forcing photochlorination of *all-cis*-tricyclo[5.2.1.0^{4,10}]decane in the presence of limited amounts of oxygen gives rise to crystallizable products. The crystalline material typically contains four compounds with molecular formulae C₁₀HCl₉ (NCT), C₁₀Cl₁₀ (PCT), C₁₀HCl₁₁ (UCTD), and C₁₀C₁₂ (PCTD). This material may be converted in high yield into pure PCT by an iodine-catalyzed thermal chlorination-dechlorination process. Methods for the preparation of pure NCT, UCTD, and PCTD are described. Evidence is presented that PCT is perchloro-*all-cis*-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene and that NCT is 10-H-nonachloro-*all-cis*-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene. The structures of UCTD and PCTD are likely to be 10-H-undecachloro-*all-cis*-tricyclo[5.2.1.0^{4,10}]deca-2,5-diene and perchloro-*all-cis*-tricyclo[5.2.1.0^{4,10}]deca-2,5-diene, respectively.

In the previous paper¹ in this series a simple synthesis of *all-cis*-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene was reported and the possible value of this hydrocarbon (as well as related compounds) as starting materials in a synthesis of the theoretically important hydrocarbon dodecahedrane** was pointed out. In order to make possible intensive study of the problem of the synthesis of dodecahedrane it was, however, necessary in particular to work out procedures that would easily give the tricyclic chlorinated compounds of Ref. 1 in a pure state in relatively large quantities. These compounds also needed improved structural proofs. The present paper reports proposals of solutions to these problems.

1. PHOTOCHELORINATION

In Ref. 1 a procedure was described for the photochlorination of *all-cis*-tricyclo[5.2.1.0^{4,10}]decane which involved irradiation by a mercury vapour

* Part I: see Ref. 1.

** Interest in the dodecahedrane molecule has been reported by a number of investigators during the last few years; cf., e.g., Refs. 2-6.

arc lamp of a solution in carbon tetrachloride of the hydrocarbon and excess chlorine. This procedure was reported to give rise to a crystalline product consisting of two chlorinated hydrocarbons, $C_{10}HCl_9$ (NCT), and $C_{10}Cl_{10}$ (PCT). Later studies of the system under consideration have shown its behaviour to be somewhat more complicated than was known or anticipated at the time of Ref. 1. The essential results are as follows.

1. If large amounts of air leak into the reaction mixture yields of crystalline product are zero. The reaction products are sirupy and show strong $\nu-C=O$ absorption.*

2. If photochlorination is carried out under rigorously oxygen-free conditions, chlorination stops virtually completely at a still quite hydrogen-rich, polychlorinated stage. (The corresponding reaction product is sirupy and noncrystallizable and shows strong $\nu-C-H$ absorption.) Chlorination beyond this stage is not possible even when excessive amounts of ultraviolet light are introduced into the reaction mixture.

3. When chlorination is carried out in the presence of limited amounts of oxygen, it proceeds to a crystallizable, polychlorinated material.

4. Crystallization of the material just mentioned from acetone typically gives rise to a crystalline product which contains four polychlorinated compounds $C_{10}HCl_9$ (NCT), $C_{10}Cl_{10}$ (PCT), $C_{10}HCl_{11}$ (UCTD), and $C_{10}Cl_{12}$ (PCTD).

5. If the dose of radiation fed into the reaction mixture is relatively low the crystalline material just mentioned contains only or almost only NCT and PCT, and is obtained as a solid solution of these compounds.

6. If the dose of radiation fed into the reaction mixture is high the crystalline material mentioned contains only or almost only UCTD and PCTD. Overdosage of radiation is of little importance under these conditions except that the UCTD:PCTD ratio decreases slowly (*cf.* section 5 on p. 2485).

7. NCT, PCT, UCTD, and PCTD are all extremely stable to ultraviolet irradiation (by sources of radiation used in the photochlorinations) in the absence of chlorine in carbon tetrachloride solution, provided that oxygen is absent. The addition of some acetone to the solutions as a sensitizer does not change this result.

8. A typical, good yield of the solid solution of NCT and PCT in the presence of a suitable amount of oxygen in the reaction chamber, during an optimum irradiation time, and with other conditions as reported in Ref. 1 is about 2.1 g from 2.72 g of *all-cis*-tricyclo[5.2.1.0^{4,10}]decane.**

9. A typical, good yield of UCTD and PCTD (conditions except time of irradiation as under point 8 above) is about 5.3 g from 2.72 g of *all-cis*-tricyclo[5.2.1.0^{4,10}]decane.

10. The times of irradiation necessary to obtain optimum yields of mixtures of NCT and PCT and of UCTD and PCTD vary somewhat from one experi-

* In Ref. 1 photochlorinations with long irradiation times were reported to give lowered yields of crystalline product. The cause of lowered yield was believed¹ to be chlorinolysis reactions. In retrospect it seems obvious that the actual cause was leakage of air into the reaction mixtures in experiments with long irradiation times, and/or incomplete crystallization of the products.

** In Ref. 1 a higher yield of the solid solution of NCT and PCT was reported. In retrospect it is obvious that the material obtained must have been contaminated by appreciable amounts of UCTD and PCTD.

ment to another. In practice it is necessary to follow the progress of the reaction by IR spectroscopy and/or (at advanced stages of the chlorination) GLC.

For large-scale preparation of crude chlorinated material, to be utilized merely as a source of pure NCT or PCT (*cf.* below), the photochlorination has been allowed to proceed to a point where the reaction mixture contains much UCTD and PCTD but still also some NCT and PCT. Yields of crystalline product are then good at relatively low input of time and electric energy (*cf.* Experimental).

That oxygen and moisture have a beneficial effect on certain photochlorinations is a well-established fact (for a recent report on the observation of this phenomenon, *cf.* Ref. 14). The mode of action of the oxygen is presumably that it gets incorporated into carbonyl compounds. The photochemically generated triplet carbonyl group may, furthermore, be a more efficient agent for abstraction of hydrogen atoms from a partially chlorinated hydrocarbon than chlorine atoms, in particular if the hydrogen is sterically hindered. This is due to the fact that the van der Waals radius of oxygen is smaller than that of chlorine. This interesting phenomenon would seem to deserve further attention.

2. PREPARATION OF PURE PCT

The problem of preparing pure PCT was first studied using the solid solution of NCT and PCT (*cf.* section 1) as starting material. It was found possible to obtain PCT in excellent yield from this material by heating with hexachloroethane and iodine in a sealed tube at 260° for 24 h. That chlorination of NCT to PCT took place in the experiment was obvious from the high yield (approximately quantitative) obtained when a solid solution of high purity was used as starting material. Furthermore, this was easily confirmed by carrying out the same experiment with pure NCT (prepared as described below), in which case a practically quantitative yield of PCT was also obtained.

Hexachloroethane is obviously the agent which donates the required chlorine (with formation of tetrachloroethylene). However, iodine is also a necessary ingredient of the reaction mixture. In the absence of iodine little reaction between NCT and hexachloroethane took place even after 24 h at 260°. Reasonably, the agent actually responsible for chlorination is iodine monochloride. The latter and tetrachloroethylene exist in equilibrium with iodine and hexachloroethane at the temperature of the chlorination procedure. Furthermore, it may be easily demonstrated that iodine monochloride actually chlorinates NCT rapidly to PCT at 260°. From the preparative point of view, the iodine-hexachloroethane mixture is, however, much to be preferred, owing to the hygroscopic nature of iodine monochloride. (If compounds containing reactive oxygen are introduced into the reaction mixture yields are greatly decreased.)

The problem next to be solved was preparation of PCT from the solid solution of UCTD and PCTD (for the origin of this product, see section 1). When this solid solution was heated with half its own weight of iodine at 260°

with a slow stream of nitrogen (atmospheric pressure) being passed over the reaction mixture, red fumes of iodine monochloride were carried away from the reaction mixture by the nitrogen. Heating was continued with the addition of fresh iodine as soon as the colour of the reaction mixture changed from dark red-violet to bright red (*i.e.* when only iodine monochloride remained in the solution; several times the theoretical amount of iodine was needed owing to losses caused by volatilization). After iodine monochloride was apparently no longer formed in appreciable quantities, which required about 20 min, heating was discontinued and the reaction mixture worked up. The product – after removal of some unreacted UCTD and PCTD by crystallizing NCT and PCT as the solid solution between the latter compounds – was a pure solid solution of NCT and PCT with an NCT : PCT ratio rather much lower than the UCTD : PCTD ratio of the starting material. (This was demonstrated by IR and GLC methods.) UCTD and PCTD are thus apparently both capable of chlorinating iodine to iodine monochloride, being reduced thereby to NCT and PCT.* Since NCT has been found to be rapidly chlorinated by iodine monochloride to PCT (*cf.* above) it was obvious that the same experiment carried out in a sealed tube would give pure PCT easily. This was found to be so. Heating at 260° a 1:1 mixture of UCTD and PCTD with an appropriate amount of iodine in a sealed tube for several hours gave PCT of high purity after work-up.

For practical preparation of pure PCT from crude, crystalline products, obtained from large-scale photochlorination of *all-cis*-tricyclo[5.2.1.0^{4,10}]decane, and containing UCTD and PCTD as well as smaller amounts of NCT and PCT and certain amounts of relatively hydrogen-rich impurities, the crude crystalline products were heated with iodine and hexachloroethane in sealed tubes for 24 h. PCT of excellent purity was obtained in an over-all yield (based on *all-cis*-tricyclo[5.2.1.0^{4,10}]decane) of 52 % (*cf.* Experimental).

Some study of the properties of PCT at high temperatures was necessary in the development of the procedures just described. Some results of this study of interest in this connection are included in section 4 of the present paper.

3. PREPARATION OF PURE NCT

Preparation of pure NCT from the solid solution of NCT and PCT was easily achieved by mild catalytic hydrogenation. Under these conditions PCT was converted to a complex mixture containing noncrystallizable, monomeric products including *all-cis*-tricyclo[5.2.1.0^{4,10}]decane itself as well as less volatile, sirupy, probably dimeric products and a sparingly soluble chloro-carbon C₂₀Cl₁₆. NCT remained unchanged under the same conditions. Work-up

* UCTD and PCTD are decomposed, at elevated temperatures, to NCT and PCT, even in the absence of iodine. Gas chromatography of relatively pure UCTD, with the injection block at 300° and the column at 230°, thus gave a chromatogram that exhibited large peaks due to both UCTD and NCT. When the temperature of the injection block was decreased to 230°, conversion of UCTD to NCT was no longer noticeable. Similar observations during GLC work have been made for PCTD. Pure PCTD has also been heated without additives in a sealed tube of relatively large volume at 260° for 24 h. The product contained PCT (48 % by weight) and PCTD (52 %). The atmosphere above the product contained molecular chlorine.

of the hydrogenated mixture by a combination of crystallization and sublimation was facile and gave NCT of excellent purity and in good yield.

Application of the procedure developed for the preparation of pure NCT from the solid solution of NCT and PCT to a pure solid solution of UCTD and PCTD and to NCT - PCT - UCTD - PCTD mixtures gave NCT of equally good purity and in good yield. Side-products were the same as in the catalytic hydrogenation of NCT - PCT mixtures, *i.e.* a sirupy mixture of relatively strongly hydrogenated products and the sparingly soluble chlorocarbon $C_{20}Cl_{16}$ mentioned above.

4. STRUCTURES OF NCT AND PCT

The problem of the skeletal structures of NCT and PCT needs careful consideration since both compounds are prepared by procedures that involve photochlorination of *all-cis*-tricyclo[5.2.1.0^{4,10}]decane, and since photochemical rearrangements of unsaturated chlorinated compounds under the reaction conditions are by no means excluded. The opinion that both compounds are actually formed during the photochlorination of *all-cis*-tricyclo[5.2.1.0^{4,10}]decane with *no* change of skeletal structure is, however, supported by the following facts.

1. Pure NCT and pure PCT may both be dechlorinated in moderate yield to triquinacene under the influence of lithium and tertiary butanol in tetrahydrofuran, provided that the reaction mixture contains certain amounts of water. (The earlier¹ claim that PCT fails to give triquinacene under conditions that yield triquinacene from a mixture of NCT and PCT is incorrect. The dechlorination of NCT and PCT will be considered in more detail in a subsequent paper⁷ in the present series.)

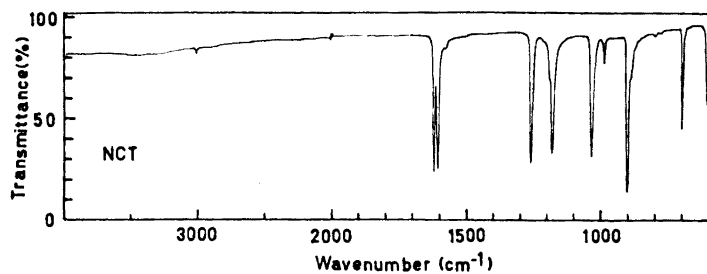
2. Under the influence of a new metal hydride reagent (obtained from lithium aluminium hydride and water at low temperature; lithium aluminium hydride itself is unsatisfactory) NCT and PCT may both be partially dechlorinated in high yield to a compound $C_{10}H_4Cl_6$ whose NMR spectrum shows the presence of four aliphatic protons which give rise to a strongly coupled AB_3 spectrum. $|J| = 9.55$ cps. The latter compound may be dechlorinated further to triquinacene. These dechlorinations will be described in the subsequent paper⁷ just mentioned.

3. NCT is convertible into PCT by chlorination (*cf.* section 2 and Experimental).

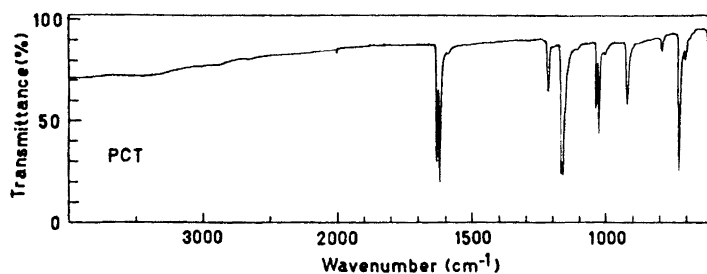
4. Mild catalytic hydrogenation of PCT yields a complex mixture containing a small amount of *all-cis*-tricyclo[5.2.1.0^{4,10}]decane (identified by GLC-mass spectrometry; *cf.* section 3 above).

Changes in skeletal structure, in particular during the dechlorinations by lithium and tertiary butanol mentioned above, would not seem to be entirely excluded. That such changes should also occur under the influence of a metal hydride reagent and, in particular, during catalytic hydrogenation seems, however, unlikely. NCT and PCT are thus reasonably both derivatives of tricyclo[5.2.1.0^{4,10}]decane.

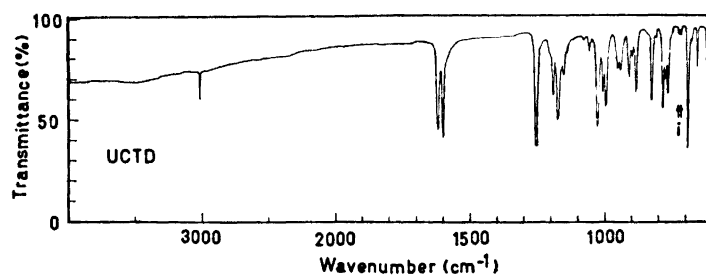
NCT and PCT are both unsaturated compounds, as indicated by the appearance of strong absorption bands in the neighbourhood of 1600 cm^{-1}



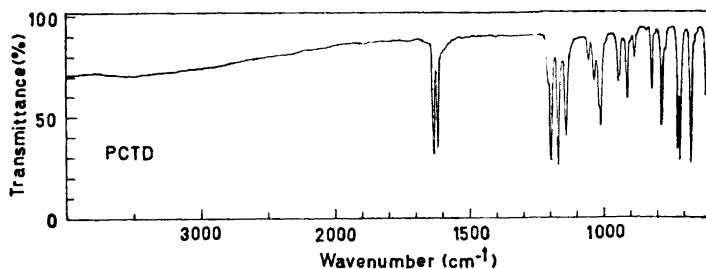
(a)



(b)



(c)



(d)

Fig. 1. Infrared spectra (all recorded on KBr discs) of a, 10-H-nonachloro-*all-cis*-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (NCT); b, perchloro-*all-cis*-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (PCT); c, 10-H-undecachloro-*all-cis*-tricyclo[5.2.1.0^{4,10}]deca-2,5-diene (UCTD; the two weak bands indicated by arrows and the letter *i* are due to a small amount of PCTD present as impurity in the sample); and d, perchloro-*all-cis*-tricyclo[5.2.1.0^{4,10}]deca-2,5-diene (PCTD).

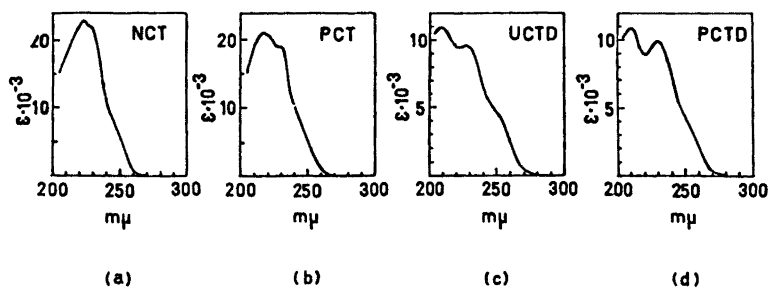


Fig. 2. Ultraviolet spectra (all recorded on solutions in 2,2,4-trimethylpentane) of a, 10-H-nonachloro-*all-cis*-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (NCT); b, perchloro-*all-cis*-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (PCT); c, 10-H-undecachloro-*all-cis*-tricyclo[5.2.1.0^{4,10}]deca-2,5-diene (UCTD); and d, perchloro-*all-cis*-tricyclo[5.2.1.0^{4,10}]deca-2,5-diene (PCTD).

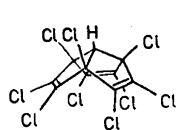
in the IR spectra¹ (*cf.* also Fig. 1, a and b). Accepting the tricyclic skeletal structure inferred above, the number of double bonds in a molecule of either compound must be three according to the molecular formulae, which are $C_{10}HCl_9$ and $C_{10}Cl_{10}$, respectively. The ultraviolet spectra of NCT and PCT (*cf.* Fig. 2, a and b), however, show that conjugation is absent. This leaves only two possible double bond arrangements, I and II, for NCT and PCT.



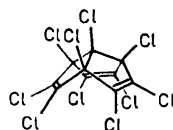
If NCT had the double bond arrangement I its aliphatic hydrogen (NMR, $\tau = 5.23$ ppm in $CDCl_3$) would be present either as a $CHCl$ group with *endo* or *exo* arrangement of hydrogen, or at the 10-position. In all three cases the hydrogen would be allylic and not strongly sterically hindered. The very considerable inertness of the hydrogen of NCT towards substitution by photochlorination is thus not understandable on the basis of this formulation and thus formulation II, with hydrogen at the 10-position and preferably with *all-cis*-stereochemistry (because in other stereoisomers a hydrogen at the 10-position is less effectively hindered by adjacent chlorines) is to be preferred. NCT is thus a 10-H-nonachlorotricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene.

Furthermore, if PCT did not also have the double bond arrangement II, almost quantitative rearrangement from arrangement II to I would have to be assumed during the chlorination of NCT to PCT, which seems most unreasonable. PCT is thus best formulated as a perchlorotricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene.

NCT has shown itself to be extremely stable under conditions that would be expected to permit equilibration of stereoisomers. It may thus be heated in an atmosphere of compressed, dry hydrogen chloride* in a sealed tube at 260° for 50 h practically without change. NCT was also recovered perfectly unchanged from heating in sealed nitrogen-filled tubes alone and with addition of iodine at 260° for 128 and 42 h, respectively. This makes the least strained formulation the most probable one. This is reasonably the *all-cis*-stereoisomer. NCT is accordingly assigned the structure 10-H-nonachloro-*all-cis*-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (III).



III



IV

A similar extremely high stability under conditions expected to cause equilibration of stereoisomers was found for PCT. The following experiments are illustrative:

1. Heating PCT without additives in a sealed, nitrogen-filled tube at 260° for 72 h produced no detectable change.
2. The above experiment repeated with the addition of iodine produced no detectable change.
3. Heating PCT in a sealed tube at 320° for 24 h led to the recovery of a slightly darkened product which was practically pure PCT.**
4. Heating PCT in an atmosphere of compressed, dry hydrogen chloride at 260° for 50 h, as described above for NCT, produced practically no change.
5. Heating 100 mg of PCT and 5 mg of anhydrous aluminium chloride in a sealed tube at 260° produced a homogeneous, intensely red, almost black melt. Continuation of the heating for 15 min followed by cooling and work-up led to the recovery of a crude product that consisted of almost pure PCT.***

This extremely high stability of PCT makes the least strained stereochemical formulation the most probable one. This would, in spite of the presence of eclipsing relatively bulky chlorine atoms at the bridgehead positions, reasonably be the *all-cis*-stereoisomer. This assignment has recently

* Hydrogen chloride was generated *in situ* by thermal decomposition of pentachloroethane. The hydrogen chloride partial pressure was estimated to be 43 atm. at 260°, assuming complete decomposition of the hydrogen chloride donor.

** Gas phase pyrolysis of PCT at still higher temperatures (about 600–650°) with short contact times will, on the other hand, bring about clean rearrangement-dechlorination to octachloronaphthalene. Similar reactions have been observed at elevated temperatures for NCT and triquinacene.

*** If this experiment is repeated with a much longer reaction time (48 h) PCT will, however, react with skeletal rearrangement, elimination of carbon tetrachloride, and dimerization, giving a chlorocarbon C₁₈Cl₁₂. On the basis of some chemical evidence and mass spectral, IR, and UV data this compound is preliminarily formulated as perchloro-2,7-dihydrocyclopenta[h,i]aceanthrylene.

been confirmed by single crystal X-ray diffraction studies of PCT (prepared as described in the experimental section of the present paper).⁸ PCT is thus perchloro-*all-cis*-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (IV).

5. PREPARATION OF UCTD (C₁₀HCl₁₁) AND PCTD (C₁₀Cl₁₂)

Forcing photochlorination of pure PCT in carbon tetrachloride solution in sealed tubes gave pure PCTD (C₁₀Cl₁₂). Chlorination beyond the PCTD stage failed under all conditions tried. PCTD was also highly stable to skeletal breakdown by photochlorination and was recovered in good yield even from the most vigorous of the photochlorination experiments. (The temperature was not above *ca.* 50° in any of these experiments.)

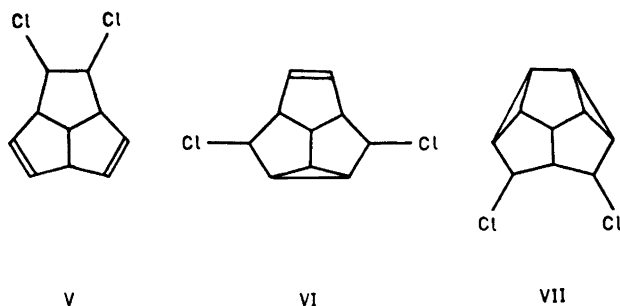
The preparation of UCTD (C₁₀HCl₁₁) requires somewhat more attention due to the possibility of substitution of hydrogen for chlorine by photochlorination. However, the very low reactivity of the hydrogen in UCTD (and NCT) makes the finding of suitable reaction conditions relatively easy. NCT was thus chlorinated in carbon tetrachloride-chlorine solution in sealed tubes of Pyrex glass kept at the same distance from the discharge-tube of a 250 W mercury vapour arc lamp. All experiments were essentially identical except with respect to the irradiation time. (Small amounts of oxygen were present above the reaction mixtures in all of these experiments as indicated by the formation of small amounts of oxygenated material; *cf.* also Experimental. The amount of oxygen might have differed somewhat in different experiments.) It was estimated that the ratio [supply of radiation energy of suitable wavelengths/(mol of C₁₀-compounds) × (time unit)] in these experiments was about 80 times larger than under the experimental conditions for photochlorination described in Ref. 1. Under these conditions NCT was only present in traces, just detectable by GLC but not by IR, in the crude reaction product after 67 min. UCTD isolated after recrystallization did not contain more than 4.7 % of PCTD. This is so far the purest sample of UCTD that has been prepared.

Increase of the time for photochlorination of NCT under forcing conditions in an otherwise essentially identical experiment to 37 h gave a mixture containing 96.4 % of PCTD and 3.6 % of UCTD. As expected neither NCT nor PCT was found. It may be concluded from these experiments and from the result of photochlorination of PCTD under forcing conditions that PCTD is the true end-product of photochlorination of *all-cis*-tricyclo[5.2.1.0^{4,10}]decane (at least when small amounts of oxygen are present in the reaction chamber). Photochlorination in the neighbourhood of room temperature beyond that stage is apparently not possible under any conditions of interest in the preparative laboratory.

6. STRUCTURES OF UCTD (C₁₀HCl₁₁) AND PCTD (C₁₀Cl₁₂)

As mentioned above (section 3) UCTD (C₁₀HCl₁₁) is converted to NCT upon mild catalytic hydrogenation. Similarly, the hydrogenation of PCTD (C₁₀Cl₁₂) under mild conditions may be made to yield PCT instead of the

chlorocarbon $C_{20}Cl_{16}$ mentioned above (section 3) if a quite short reaction time is used. This necessitates great structural similarity between NCT and UCTD, on the one hand, and between PCT and PCTD, on the other hand. In particular, these findings are not compatible with the migration of chlorines already present in NCT and PCT (resulting in migration of double bonds) concomitant with the formation of UCTD and PCTD from these compounds by photochlorination (*cf.* section 5). UCTD and PCTD are thus both formed by direct addition of chlorine to the 2,5,8-trienes with no rearrangements. Three types of adduct must then, primarily, be taken into consideration, *i.e.* the classical adduct V and the homoconjugate adducts VI and VII. (Chlorines not participating in the addition have been omitted from formulae V – VII for clarity.) Of these possibilities VII may immediately be excluded for both UCTD and PCTD, because both compounds have IR spectra (*cf.* Fig. 1, c and d) which show strong absorption in the $\nu-C=C$ region. The choice between V and VI seems to be less easy, however.



The strongest argument at present for structures of the type V and not VI for UCTD and PCTD seems to be obtained from the ultraviolet spectra. Structures of the type VI would presumably show only a single absorption maximum above $200\ m\mu$ and no relatively intense long wavelength shoulder. Thus octachlorocyclopentene, which may be chosen as a model compound for the olefinic groups in the structures of the type VI, shows only a single absorption maximum at $230\ m\mu$ and no long wavelength shoulder (*cf.* Ref. 9). The cyclopropane rings in the structures of the type VI are likely not to absorb appreciably above $200\ m\mu$ and seem to be too far removed from the double bonds of these structures to form cooperative electronic excited states. However, the ultraviolet spectra of UCTD (Fig. 2c) and PCTD (Fig. 2d) both show two maxima, at 209 and $227\ m\mu$, and at 210 and $230\ m\mu$, respectively. Relatively intense shoulders towards longer wavelengths are also found. Accepting structures of the type V for these compounds, at least part of these differences (as compared to the spectrum of octachlorocyclopentene) may be interpreted as due to the availability in the molecules of new cooperative electronic excited states due to the small distance between the two chromophoric groups within a molecule (*cf.* Ref. 12). The ultraviolet spectra of NCT (Fig. 2a) and PCT (Fig. 2b) show signs of the presence of similar double-maxima and long wavelength shoulders although the separation between the

maxima is smaller for these compounds. Triquinacene itself shows a relatively intense shoulder towards longer wavelengths.² This has been interpreted² as due to the availability of one or more transitions to cooperative electronic excited states in triquinacene and not to vibronic excitations. We tentatively interpret the long wavelength absorptions in the ultraviolet spectra of NCT, PCT, UCTD, and PCTD analogously.

EXPERIMENTAL

Spectroscopic data were obtained by means of the following instruments: a Perkin-Elmer grating infrared spectrophotometer, Model 257, a Unicam SP 800 ultraviolet-visible spectrophotometer, and a 60 Mc Varian Associates A-60 nuclear magnetic resonance spectrometer.

Mass spectra were recorded on an LKB mass spectrometer, Type 9000 A. The instrument was equipped with GLC and direct inlet systems. All samples introduced into the mass spectrometer through the gas chromatograph were passed through a column (3.0 mm \times 3 m) of 2.5 % silicon rubber OV-1 on silanized Chromosorb W, 100–120 mesh.

Elemental analyses were carried out by the Department of Analytical Chemistry at the University of Lund.

Most analytical GLC work was done on a Perkin-Elmer gaschromatograph Model 900, equipped with a flame ionization detector and a Varian-Aerograph electronic integrator Model 480. The column used in analytical gas chromatography of polychlorinated compounds was of the dimensions 2.5 mm \times 2.5 m and consisted of 3 % silicon rubber OV-1 on Chromosorb Q 100–120 mesh. In analyses of NCT–PCT–UCTD–PCTD mixtures a column temperature of about 230° was satisfactory. The integrated surface ratio of the peaks due to NCT, PCT, UCTD, and PCTD of any such mixture was found to be converted with relatively good precision to the weight ratio by multiplying the surfaces found by the numbers 0.877, 0.929, 1.00, and 1.06, respectively.

Melting points were determined in capillaries heated in a conventional metal block apparatus and are corrected, unless otherwise indicated.

Photochlorination. *all-cis*-Tricyclo[5.2.1.0^{4,10}]decane used in the photochlorination was a sublimed product, prepared essentially as described in Ref. 1 and purified further after sublimation by treatment with bromine in the dark followed by resublimation. Improvements in the procedures for preparation and purification of the hydrocarbon will be reported in a separate communication.¹¹

The quality of the solvent used in the photochlorinations must be adequately high. One sample of a lower, commercial grade of carbon tetrachloride was found to contain substantial amounts (estimated content 1 %) of hydrocarbon(s) which were photochlorinated with the formation of large amounts of a waxy product. Isolation of the desired tricyclic compounds from a reaction mixture containing this solvent was impossible.

(A) *Solid solution of NCT and PCT.* *all-cis*-Tricyclo[5.2.1.0^{4,10}]decane (2.72 g; 20 mmol) was photochlorinated in 400 ml of carbon tetrachloride containing excess chlorine during the entire reaction time. The procedure was in all essential details that described in Ref. 1. Leakage of large amounts of air into the reaction mixture was prevented by connecting the reaction flask with a relatively long (1.5 m) and narrow (4 mm internal diameter) gas outlet tube. [Whether or not this precaution is sufficient to prevent to a satisfactory extent air from being sucked back into the reaction chamber during the latter stages of the experiment, when evolution of hydrogen chloride is quite slow, is expected to depend upon the constancy of room temperature (and the constancy of the temperature of the cooling water) in the laboratory used. Under our working conditions the precaution has invariably been sufficient.] The small amount of air (about 100 ml, *cf.* Ref. 1) present at the beginning of the experiment above the surface of the reaction mixture was not flushed away by inert gas before introduction of chlorine and irradiation was started. Concerning the significance of this detail, *cf.* section 1 above. Progress of the reaction was followed by IR and GLC methods (*cf.* the preparation of solid solution of UCTD and PCTD below). In a typical experiment irradiation was continued for 20 h.

Work-up gave 2.1 g of a relatively pure solid solution of NCT and PCT. After one recrystallization from chloroform-acetone the material melted (on a Kofler "Heizbank") at 223°.

(B) *Solid solution of UCTD and PCTD. all-cis-Tricyclo[5.2.1.0^{4,10}]decane* (2.72 g; 20 mmol) was photochlorinated in 400 ml of carbon tetrachloride containing excess chlorine during the entire reaction time. The procedure was in all essential details that indicated above and in Ref. 1 for the preparation of the solid solution of NCT and PCT. The progress of the reaction was followed by removing small samples of the reaction mixture at suitable intervals, evaporating the solvent, and investigating the residue by IR and GLC methods. (The IR method is particularly valuable at early stages of the experiment. The ν -C-H and ν -C=C regions are revealing. The ν -C=O region should, furthermore, show only a relatively weak, broad absorption throughout the experiment. The GLC method, however, competes favourably with the IR method at advanced stages of the chlorination.) Irradiation was continued until NCT and PCT had practically disappeared from the reaction mixture. A typical experiment was continued for 100 h. Removal of excess chlorine and solvent and crystallization of the residue from acetone gave 5.3 g of crystalline material. This was a relatively pure solid solution (or possibly a mixture of crystals with similar appearance) of UCTD and PCTD (IR and GLC evidence), containing substantial amounts of both components. The exact UCTD:PCTD ratio was not determined. After one recrystallization from acetone the material melted (on a Kofler "Heizbank") at about 251°.

(C) *Large-scale photochlorination of all-cis-tricyclo[5.2.1.0^{4,10}]decane. Apparatus.* The experiment was performed in a 2 l, three-necked, round-bottomed flask of Pyrex glass equipped with a chlorine inlet tube and an efficient cooling-coil both of which extended to the bottom of the flask, and a long (3.5 m) and rather narrow (internal diameter 4 mm) gas outlet tube. The end of the gas outlet tube was bent downwards, so that drops of moisture, which generally collect there owing to the evolution of hydrogen chloride, could not run into the tube. Furthermore, the end of the tube was for obvious reasons placed inside a hood. The flask was mounted in the middle of a Rayonet 800 W photochemical reactor, Model RPR-208, equipped with eight discharge-tubes, type RUL 3500 A. Below the flask an electric fan was mounted which blew a stream of air against the flask during the entire reaction time. Cooling water was run through the cooling coil mentioned above during the entire operation as well. All parts of the apparatus which came into contact with hydrogen chloride and/or chlorine were made of glass and equipped with ground-glass joints.

Procedure. *all-cis-Tricyclo[5.2.1.0^{4,10}]decane* (13.1 g; 0.0963 mol) was dissolved in 1600 ml of carbon tetrachloride in the 2 l flask (*cf.* Apparatus). Dry chlorine (115 g) was then introduced into the solution under irradiation. (The air present in the chlorine inlet system and in the 2 l flask above the surface of the reaction mixture was not removed by inert gas at the beginning of the experiment.) The method of introduction of chlorine was that described in Ref. 1. After introduction of the chlorine, the inlet tube was removed and quickly substituted by an arrangement that permitted removal of small samples of the reaction mixture with no simultaneous leakage of air into the reaction chamber. The progress of the reaction was followed by IR and GLC methods, as indicated above in the preparation of the solid solution of UCTD and PCTD. Irradiation was continued for 102 h, after which the weight-ratio ($w_{\text{NCT}} + w_{\text{PCT}}$):($w_{\text{UCTD}} + w_{\text{PCTD}}$) of the reaction mixture was close to 1:6, as determined by GLC. Then the photochlorination was interrupted and most of the carbon tetrachloride-chlorine solution distilled off at atmospheric pressure. Residual solvent was removed in a rotating evaporator, finally at about 60° and 20 mm. The white, opaque, semi-solid, somewhat sticky residue was dissolved in 40 ml of hot acetone. The resulting solution was maintained first for several hours at room temperature (crystallization often begins only after a few hours, and seeding does not accelerate the process at this stage) and then at +5° overnight. Then the product was collected, washed portion-wise with a total of 35 ml of acetone and dried in air, finally at 70°. In this way 20.23 g of a white crystal powder containing NCT, PCT, UCTD, and PCTD in the weight-ratio 5.2:3.7:51.7:39.4 was obtained. The amount of impurities in the material was estimated to be 5%. Concentration of the mother liquor and washings gave a second crop of similar composition weighing 2.20 g. Additional quantities of crystalline product were isolated from the resulting mother liquor and washings by evaporation in the neighbourhood of room temperature in a rotat-

ing evaporator. (Crystallization from the viscous, concentrated, product-poor solution occurs particularly easily during this operation.) Crystalline product that separated was removed by filtration and washed with acetone. Mother liquor and washings were again concentrated in the evaporator, *etc.* Despite the fact that the volume of the solution during crystallization was about the same in all of these evaporations, six additional crops (total weight 6.94 g) of crystalline product were obtained in this manner. Dominating constituents in all of these crops were UCTD, PCTD, NCT, and PCT. NCT and PCT were relatively much more abundant than in the first and second crops. Impurities were also more important constituents in these materials than in the first and second crops. The dried crystalline material (first–eight crops) was combined (total yield 29.37 g) for transformation into pure NCT and PCT, as described below.

Perchloro-all-cis-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (PCT). Crude crystalline material (29.37 g), obtained from large-scale photochlorination of *all-cis-tricyclo[5.2.1.0^{4,10}]decane* as described above, hexachloroethane, and iodine were sealed in glass ampoules.* The charge in each ampoule consisted of photochlorinated product, *ca.* 1 g, hexachloroethane, 0.35 g, and iodine, 0.10 g. The ampoules were made from Pyrex glass tubing with 8 mm internal and 10 mm external diameter. All ampoules had an internal volume of about 3 ml after sealing. They were placed in an aluminium block containing channels, 11 mm in diameter, and steel plates were mounted against the ends of the block. The resulting device was placed in a thermostated electric furnace preheated to 260°, and a thermometer was mounted in a channel in the aluminium block. The temperature of the block rose from room temperature to 260° in about 3 h. 260° was maintained for additional 24 h, after which heating was discontinued. After cooling, the ampoules were removed from the aluminium block and broken. (Suitable precautions must be undertaken in this step owing to the high pressure inside the tubes.) The resulting mixture of glass powder and reaction mixture was spread on the bottom of an enamelled saucepan and heated gently in a slow stream of air until the iodine colour had disappeared. (Heating should not be so strong that the powdery organic part of the mixture melts, because then too much PCT volatilizes.) This treatment removed most of the iodine, iodine monochloride, hexachloroethane, and tetrachloroethylene from the product. The organic product was then dissolved in chloroform and the resulting solution filtered. A slight violet colour of the filtrate was removed by shaking with a little aqueous sodium sulfite solution. After drying with magnesium sulfate and filtration the solution was concentrated at atmospheric pressure until crystallization began from the hot solution. Crystallization was completed at room temperature. The product was collected, washed with some chloroform, and dried in air at 70°. It then weighed 15.2 g and was practically pure, slightly brownish PCT. Successive concentrations of the mother liquor and washings until crystallization began from the boiling solutions gave three additional almost equally pure crops. The combined yield was 23.65 g (52 % based on *all-cis-tricyclo[5.2.1.0^{4,10}]decane* used in the photochlorination). The combined crystalline material was subjected to sublimation at 0.25 mmHg (bath temperature 160–170°). There was only a small amount of residue after sublimation. The white, finely powdery sublimate was dissolved in chloroform and the product brought to crystallize by successive concentrations of the resulting solution, *etc.* This gave pure PCT, m.p. 239.4–240.1°, as snow-white, transparent, beautiful crystals. (The crystals belong to the orthorhombic system.¹⁵) Impurities were not detectable in the product by GLC. The yield of the sublimation-crystallization procedure was essentially quantitative. (Found: C 25.4, 25.4; Cl 74.7, 74.9. Calc. for C₁₀Cl₁₀: C 25.30; Cl 74.70.)

IR spectrum [KBr]; *cf.* Fig. 1b. IR band wave-numbers have been reported in Ref. 1. Unfortunately, the 609 cm⁻¹ band was characterized as (ms; br). The correct characterization should be (ms).

UV spectrum [2,2,4-trimethylpentane]: λ_{\max} (m μ), 217 (ϵ 21 100), 229 (shoulder; ϵ 18 900); *cf.* also Fig. 2b. The UV data reported here represent improvements compared with the data reported in Ref. 1.

Mass spectrum (GLC inlet, 70 eV electrons): Besides the molecular ion C₁₀Cl₁₀⁺ reported earlier,¹ and fragments thereof, this spectrum also shows dimeric ions, C₂₀Cl_n⁺,

* The convenience of the operation would obviously be considerably increased if it could be carried out in a suitably coated autoclave. Studies on the problem are at present being undertaken in this laboratory.

$n = 8, 9 \dots 16$. The relative intensity of the dimeric ions depends upon the concentration of sample in the ionization chamber, thus showing that these ions arise by a dimerization reaction which takes place in this chamber.

*10-H-Nonachloro-all-cis-tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (NCT), and a dimer of perchlorotricyclo[5.2.1.0^{4,10}]deca-1(10),2,5,8-tetraene.**

A. *NCT*. In a 100 ml round-bottomed, two-necked flask, equipped with a bent hydrogen inlet tube extending to the bottom of the flask (below the stirrer), a mechanical stirrer, and a reflux condenser, was placed 2.00 g of crude, crystalline, chlorinated material obtained from large-scale photochlorination as indicated above. Tetrahydrofuran (40 ml) was added and the solid dissolved. Then 100 mg of palladium on activated carbon (10 % Pd) hydrogenation catalyst (Fluka) was added and a quite slow stream of hydrogen bubbled through the mixture. Vigorous mechanical stirring was started and the mixture heated to reflux. Gentle reflux, with efficient stirring, and slow inlet of hydrogen, was maintained for 4 hours. Some tetrahydrofuran had to be added through the condenser during this time in order to keep the volume of the reaction mixture unchanged. At the end of the heating period and after cooling, the catalyst was filtered off and washed with some chloroform. The solvent was distilled off from the filtrate and the sirupy residue redissolved in some carbon tetrachloride. This brought about precipitation of a minute amount of suspended palladium which had passed through the filter in the first filtration. It was removed by filtration and washed with carbon tetrachloride. The filtrate was a clear, yellow solution. Its solvent was distilled off. The sirupy residue was dissolved in 1 ml of acetone. Crystallization started almost immediately. After standing at room temperature the product was collected and washed with three 1 ml portions of acetone. After drying in air at 100° the product weighed 536 mg. Concentration and preservation of the mother liquor and washings gave four more crops of crystalline product. The combined dried crops (1st–5th crops) weighed 704 mg. The entire material (which is essentially a mixture of NCT and a chlorocarbon C₂₀Cl₁₆) was subjected to sublimation at 0.25 mmHg (bath temperature 145–150°). The sublimed product was removed from the sublimation apparatus with a little chloroform. The solvent was distilled off and the residue recrystallized from acetone. This gave four almost equally pure crops of beautiful, colourless, transparent crystals. (The NCT crystals belong to the monoclinic system.¹⁵ It is interesting to note that NCT and PCT crystals are not isomorphous, despite the fact that the compounds form solid solutions in each other.) The combined yield was 542 mg (57 % based on the content of NCT and UCTD in the photochlorinated, crystalline starting material). Impurities were detectable in the material in trace amounts only, by GLC. One more recrystallization from acetone gave pure product, m.p. 177.1–177.9°. (Found: C 27.2; H 0.29; Cl 72.3, 72.7. Calc. for C₁₀HCl₅: C 27.28; H 0.23; Cl 72.49.)

IR spectrum [KBr]: A weak narrow band due to the ν -CH mode is seen at 3002 cm⁻¹. Wave-numbers of other important absorptions in the 600–4000 cm⁻¹ region have been reported in Ref. 1; cf. also Fig. 1a.

UV spectrum [2,2,4-trimethylpentane]: λ_{\max} (m μ), 222 (ϵ 23 050), 228 (shoulder; ϵ 21 900); cf. also Fig. 2a.

NMR spectrum [CDCl₃]: singlet, $\tau = 5.23$ ppm.

Mass spectrum (GLC inlet, 70 eV electrons): The molecular ion is C₁₀HCl₅⁺, as reported in Ref. 1. There are no signs of formation of dimeric ions even at high concentrations of sample in the ionization chamber (cf. the mass spectrum of PCT).

B. *Dimer C₂₀Cl₁₆*. The residue after the sublimation mentioned above was a white powder weighing 144 mg. It consisted of a chlorocarbon C₂₀Cl₁₆ contaminated by a certain amount of hydrogen-containing impurities. The compound C₂₀Cl₁₆ was obtained in a state of high purity by treatment of the residue under carefully controlled conditions with sodium hydroxide. Part of the chlorocarbon C₂₀Cl₁₆ was destroyed in this operation. However, no other method of purification which affords the chlorocarbon in a comparable state of purity has so far been found. The procedure was as follows. The sublimation

* Exactly the same experiment as that described here has also been carried out using a pure solid solution of NCT and PCT and a pure solid solution of UCTD and PCTD instead of the chlorinated material indicated here. Yields of NCT and dimer C₂₀Cl₁₆ comparable to those reported in this paper were obtained.

residue just mentioned was dissolved with heating in 35 ml of peroxidefree * tetrahydrofuran. After cooling to +20° a solution of 160 mg of sodium hydroxide in 40 ml of water (solution at 20°) was gradually added at a uniform rate with constant swirling. The time for addition was 3 min. The resulting mixture was allowed to stand an additional 5 min, after which the white powder that had separated was filtered with suction from the brownish solution and washed with 99.5 % ethanol. (Preservation of the mother liquor overnight yielded an additional crop of solid. This consisted of impure product.) The powder was dried in air at 100°. Yield of pure product: 66.6 mg (11 % based on the content of PCT and PCTD in the starting material). The product gradually decomposes at about 280 – 300° when heated in an evacuated tube. Decomposition is not preceded by melting. Decomposition products are a dark carbonized material and PCT[†] (IR evidence). Decomposition is accompanied by gradual liquefaction of the sample. The characteristic IR spectrum of the product was unchanged upon recrystallization from various solvents. An analytical sample was recrystallized once from chloroform, which gave a white, microcrystalline powder. (Found: C 29.7; Cl 70.1. Calc. for C₂₀Cl₁₆: C 29.74; Cl 70.26.) IR spectrum [KBr]: ν_{\max} (cm⁻¹), 1664 (m), 1645 (s), 1624 (s), 1608 (s), 1589 (s) (1300 – 4000 cm⁻¹ region reported only; the 600 – 1300 cm⁻¹ region contains an additional 29 bands).

UV spectrum [2,2,4-trimethylpentane]: λ_{\max} (m μ), 225 (ϵ 24 400), 297 (ϵ 6600).

Mass spectrum (direct inlet, 70 eV electrons): The molecular ion is C₂₀Cl₁₆⁺.

Perchloro-all-cis-tricyclo[5.2.1.0^{4,10}]deca-2,5-diene (PCTD). Carbon tetrachloride (4 ml), saturated at room temperature with chlorine, and PCT (200 mg) were sealed in an ampoule made of Pyrex glass tubing with 9.5 mm internal diameter and 1 mm wall-thickness. The internal volume of the resulting ampoule was 5.5 ml. (Only a quite small flame was used in the sealing operation and that part of the glass tube where sealing was to be made was strongly constricted (diameter about 2 mm) already before the reaction mixture was filled into the tube. Despite these precautions it was apparent that chlorine volatilized from the surface layer of the solution in the unsealed ampoule during this operation. This volatilization – when it occurs to a limited extent – may be regarded as advantageous since the air above the solution in the ampoule is largely removed.) After sealing, the ampoule was shaken in order to completely dissolve PCT. The ampoule was then mounted in the vicinity of the discharge-tube of a Philips 250 W mercury vapour arc lamp type 11855/73 (discharge-tube type U34/35) as shown in Fig. 3. The

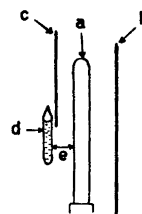


Fig. 3. a, discharge-tube; b, reflector; c, iron plate protecting against unwanted irradiation; d, ampoule with reaction mixture; e, distance (cf. text).

shortest distance between the ampoule and the discharge-tube (distance e in Fig. 3) was adjusted to 30 mm. An iron plate was placed according to Fig. 3, close to the ampoule but not in direct contact with the glass in order to avoid efficient heat transfer; the iron plate extended 6 mm "below" the surface of the liquid. In this way no radiation from the lamp could reach the ampoule above the surface of the liquid inside the ampoule. (If this precaution is not undertaken the ampoule walls above the surface of the liquid will soon be quite hot in the direction of the discharge-tube and there will be continuous evaporation with deposition of solid on this surface. Conversion of PCT into PCTD may be incomplete under these circumstances.) The reflector (b in Fig. 3) used was that provided with the lamp. The lamp was then put into operation. After full emission had

* This is highly important. The chlorocarbon C₂₀Cl₁₆ is very sensitive to oxidation by the peroxides present in deteriorated tetrahydrofuran. Solvent freshly distilled from lithium aluminium hydride was used.

been reached, which required about 20 min, irradiation was continued for 20 h. (A shorter time would have been sufficient, however.) The ampoule was then opened and carbon tetrachloride and chlorine were distilled off from the reaction mixture. The residue (in which no PCT was detectable by GLC) was recrystallized from acetone containing a little chloroform. This gave after drying 180 mg (yield 78 %) of practically pure PCTD as colourless crystals. The quality of the product was improved somewhat further by sublimation at 0.25 mmHg (bath temperature 180–190°). The residue after sublimation (*ca.* 1 mg) contained oxygenated material. The sublimed product was recrystallized once more from acetone–chloroform and dried in air at 100° before analysis, m.p. 271.6–272.6° (melting point recorded with rapid heating; slow heating yields lower melting points). (Found: C 21.8, 22.2; Cl 77.4. Calc. for $C_{10}Cl_{12}$: C 22.01; Cl 77.99.)

IR spectrum [KBr]: ν_{\max} (cm^{-1}), 1629 (s), 1614 (s); *cf.* also Fig. 1d.

UV spectrum [2,2,4-trimethylpentane]: λ_{\max} ($m\mu$), 210 (ϵ 10 900), 230 (ϵ 10 000); *cf.* Fig. 2d.

Mass spectrum (GLC inlet and direct inlet, 70 eV electrons): The molecular ion is $C_{10}Cl_{12}^+$. $C_{10}Cl_n^+$ ions with $n > 12$ were not detectable. The spectrum also shows formation of dimeric ions $C_{20}Cl_n^+$, $n = 8, 9, \dots, 16$ (*cf.* the mass spectrum of PCT).

10-H-Undecachloro-all-cis-tricyclo[5.2.1.0^{4,10}]deca-2,5-diene (UCTD). Carbon tetrachloride (4 ml), saturated at room temperature with chlorine, and NCT (48.0 mg) were sealed in an ampoule made of Pyrex glass tubing with 9.0 mm internal diameter and 1.0 mm wall-thickness. The internal volume of the ampoule was 5.5 ml. For suitable precautions in the sealing operation. *cf.* the preparation of PCTD. After sealing, the ampoule was shaken until the NCT had dissolved completely. The ampoule was then mounted in the vicinity of the discharge-tube of a Philips 250 W mercury vapour arc lamp type 11855/73 (discharge-tube type U34/35) as shown in Fig. 3. Unless otherwise indicated all arrangements in the experiment were the same as in the preparation of PCTD (*cf.* above). The distance *e* in Fig. 3 was 30 mm. An iron plate (in addition to the plate *c* in Fig. 3) was placed between the ampoule and the discharge-tube so that no radiation from the lamp could reach the ampoule. The lamp was then put into operation. After 20 min, when reasonably stable emission had been reached, the iron plate just mentioned was removed. Irradiation was continued for 67 min. The ampoule was then opened and carbon tetrachloride and chlorine evaporated from the reaction mixture. The white, crystalline residue was recrystallized from a small volume of chloroform–acetone and then sublimed at 0.25 mmHg (bath temperature 145–165°). Yield: 20.95 mg (38 %; the yield of the reaction was undoubtedly much better. Work-up, however, caused appreciable losses). M.p. 204.0–206.5°. The product contained 4.7 % PCTD and 93.5 % UCTD (by weight), as shown by GLC-electronic integrator. (Found: C 23.2; H 0.27; Cl 76.2. Calc. for $C_{10}HCl_{11}$: C 23.50; H 0.20; Cl 76.30.)

IR spectrum [KBr]: ν_{\max} (cm^{-1}), 3005 (m), 1616 (s), 1598 (s); *cf.* also Fig. 1c.

UV spectrum [2,2,4-trimethylpentane]: λ_{\max} ($m\mu$), 209 (ϵ 11 000), 227 (ϵ 9600); *cf.* Fig. 2c.

NMR spectrum [$CDCl_3$]: singlet, $\tau = 5.40$ ppm.

Mass spectrum (GLC inlet, 70 eV electrons): The molecular ion is $C_{10}HCl_{11}^+$. No ions $C_{10}HCl_n^+$ with $n > 11$ were detected. No dimeric ions were detectable even at high concentration of sample in the ionization chamber (*cf.* the mass spectra of NCT, PCT, and PCTD).

Transformation of pure NCT into PCT. NCT (50 mg), hexachloroethane (13.5 mg), and iodine (10 mg) were sealed under nitrogen in a small ampoule. The ampoule was heated at 260° for 24 h. It was then opened and the contents heated gently in a slow stream of air until iodine, hexachloroethane, *etc.* had volatilized. This gave a perfectly white, crystalline residue, which according to the IR spectrum was pure PCT. The yield of crude product was close to quantitative. The product was purified further by recrystallization and then melted at 239.5–240.5°.

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