

Polyquinanes

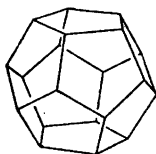
A Simple Synthesis of Tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene

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A convenient high-yield synthesis of the hitherto not described tricyclo[5.2.1.0^{4,10}]decane, as well as a simple transformation of this hydrocarbon into tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene, have been achieved.

Since all the ethanoid hydrocarbon fragments, into which the practically single strain-free,¹ rigid, polyhedral molecules of the hydrocarbon dodecahedrane * (I) may be divided, are necessarily equivalent and perfectly eclipsed, some valuable information (which does not seem to be obtainable with comparable accuracy in other ways) concerning the magnitudes of the changes in the heights of the potential energy barriers to internal rotation in ethane on vicinal substitution of its hydrogens by saturated carbons, should be derivable from the thermodynamic properties of the compound.



I

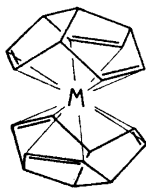
More purely chemical investigations of I, furthermore, would be expected to yield some additional aspects on the effects of strain and electronic factors upon the reactivity at saturated carbon.

The dodecahedrane also poses an intricate problem of organic synthesis. In the present studies of the problem, derivatives of tricyclo[5.2.1.0^{4,10}]decane were regarded to be among the more attractive starting materials

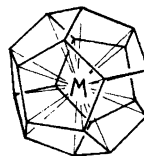
* *i.e.* undecaacyclo[15.3.0.0.^{2,15} 0.^{3,13} 0.^{4,20} 0.^{5,12} 0.^{6,19} 0.^{7,11} 0.^{8,18} 0.^{9,16} 0^{10,14}]icosane.

for the experiments, and a search for methods which would permit an easy entry into this series of tricyclic compounds was undertaken.* The result of these efforts, to be reported here, is a convenient high-yield synthesis of the hitherto not described tricyclo[5.2.1.0^{4,10}]decane, as well as a simple transformation of this parent hydrocarbon into tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene¹ (Scheme I).

The latter hydrocarbon seemed interesting, not only as a useful compound in experiments towards the dodecahedrane synthesis, but also because of its potential ability to form octahedral 2:1 π -complexes, II,**,*** with certain



II



III

transition metals for which the carbon-metal bond distances to be expected in this kind of compound probably permit non-bonded interactions between the olefinic hydrogens of the two organic entities (and carbon-metal non-bonded interactions at the methine-groups) to remain relatively small. Furthermore, the possibility seems not to be excluded at present that another 2:1 complex structure, in which the central atom is bonded to the same degree to all the methine groups of a dodecahedrane-like carbon skeleton, may prove to be (electronically) favourable in the case of some of those metal atoms whose bond radii in reasonably similar compounds seem to be compatible with the geometry of III.

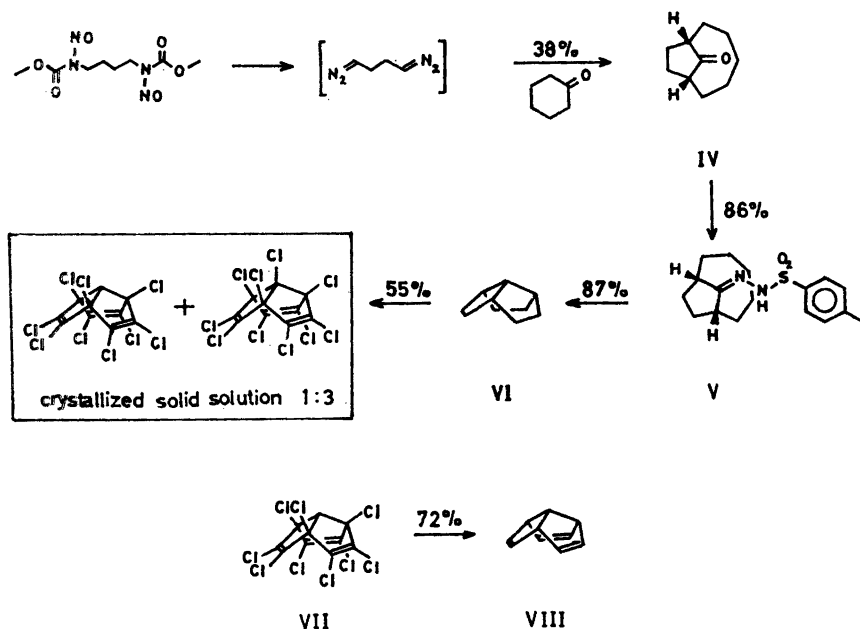
SYNTHESES AND STRUCTURAL PROOFS

A. *Tricyclo[5.2.1.0^{4,10}]decane*. 10-Ketobicyclo[5.2.1]decane (IV) was discovered more than twenty-five years ago³ as one of the products of the reaction between 1,4-bisdiazobutane and cyclohexanone. It has been further investigated later,⁴⁻⁶ and its structure seems to be well established.⁴ The pure ketone, however, was obtainable in reasonable amounts from the complex crude product (*cf.* Ref. 4) only by use of chromatographic methods. The problem of finding a relatively abundant source of starting material for the route planned in the present investigation was overcome, nevertheless, when it was found that the *p*-tosylhydrazone of IV (V) could be prepared in good

* The present investigation was started (though interrupted later for a considerable time) independently, before the earlier communication¹ on this subject appeared.

** possibly exhibiting the phenomenon of valence tautomerizations *via* a highly symmetrical intermediate reminiscent of III.

*** For an illustration of the behaviour of a triene having a related arrangement of the double-bonds, *cf.* Ref. 2.

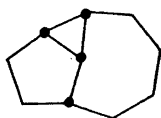


SCHEME I

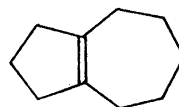
yield and in a state of high purity directly from this crude product (preferably obtained from a slightly modified ketone synthesis), without the use of such methods.

10-Carbenabicyclo[5.2.1]decane, generated thermally in a relatively aprotic medium from the anion of the tosylhydrazone, underwent transannular cyclization to produce tricyclo[5.2.1.0^{4,10}]decane (VI) as the principal product.* Under suitable conditions, the process worked to give a high hydrocarbon yield and a higher specificity of the reaction than seems to have been observed in any predominantly non-1,3-insertional, transannular carbene reaction hitherto investigated. This should very likely be satisfactorily interpretable in terms of restricted conformational mobility of the eight-membered ring of the bicyclic carbene, and strain in the various alternative products.

* About the same product-mixture was obtained in hexadecane¹⁵ and in the acetamide medium (which should be preferable from the preparative point of view) described in the experimental section. Since the procedure involving the former medium should rather efficiently suppress anything but typical carbenoid modes of reactions of the intermediate diazoalkane, only such courses of the reaction will be considered in the following brief discussion.



IX



X

Besides the hydrocarbon just mentioned, there was obtained 4 % (by GLC) of a liquid having a strong, disagreeable, olefinic odour as the only additional volatile product. The latter compound was isolated by means of preparative scale gas chromatography, and its molecular formula, $C_{10}H_{16}$, was determined by mass spectrometry. The NMR spectrum was devoid of absorptions ascribable to olefinic protons, nor did it seem to be compatible with the rearranged olefinic structure X. Since the minor product added bromine (for various reasons the more orthodox test for cyclopropane rings by means of acid treatment was not used) to yield a material which on qualitative scale dehydrobromination and dehydrogenation afforded a mixture containing azulene, a saturated, cyclopropanoid, tricyclic structure, derived from a hydrogenated azulene, was thus the most reasonable one. The only hydrocarbon of this kind which could be formed in a favourable reaction from 10-carbenabicyclo[5.2.1]decane should be tricyclo[7.1.0.0^{4,10}]decane (IX).

Since a transannular insertion in the eight-membered ring of this bicyclic carbene, leading to the formation of a cyclobutane ring, did seem still less likely than such a process in the ring of the monocyclic analog (*cf.* Ref. 7), it did, furthermore, appear plausible to assume that the non-cyclopropanoid, saturated [according to the bromine test, infrared (Fig. 1), and NMR (Fig. 2) spectra], principal product of the reaction was * the hydrocarbon VI. The $C_{10}H_{16}$ molecular formula was ascertained by elemental analysis and from the mass spectrum. The detailed structure as tricyclo[5.2.1.0^{4,10}]decane (VI; also fitting

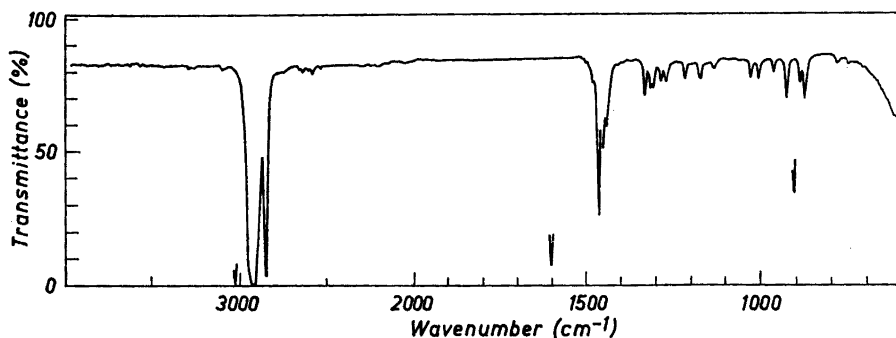


Fig. 1. Infrared spectrum of tricyclo[5.2.1.0^{4,10}]decane (solid film).

* all alternative saturated structures producible without unlikely rearrangements thus being excluded.

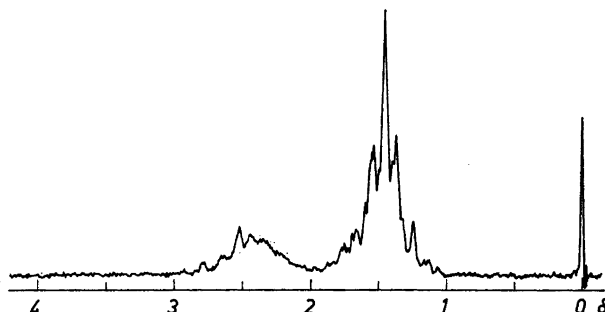
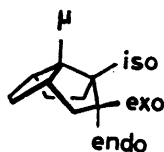


Fig. 2. NMR spectrum at 60 Mc. of tricyclo[5.2.1.0^{4,10}]decane in CDCl₃ with tetramethylsilane as internal reference.

the NMR spectral intensity ratio, methylene to methine protons of 3:1), as thus deduced essentially from the argument of the most likely course of the carbene reaction, was supported by the further transformations of the product, described below.

B. Transformation of tricyclo[5.2.1.0^{4,10}]decane into tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene. Extensive photochlorination of the principal product of the carbene reaction, under what seemed to be optimum conditions, gave a yield of about 55 % of a well crystallized solid solution, consisting of two components, viz. 1,2,3,4,5,6,7,8,9-nonachlorotricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (NCT; VII) and perchlorotricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (PCT; XII); this certainly being the result most expected for the complete radical chlorination of VI considering the analogous behaviour of cyclopentane⁸ under similar conditions in conjunction with the fact, that all other positions of the double-bonds required to attain stability in the tricyclic polychlorinated compounds, would result in more strained structures.

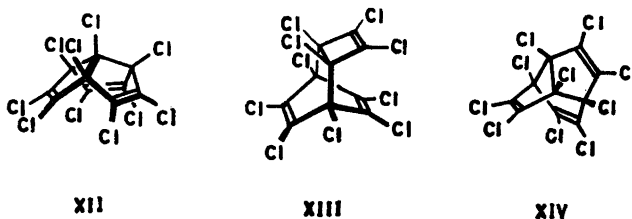


XI

Whereas the yield of the solid solution varied within wide limits with the amount of radiation used, the NCT:PCT ratio in the reaction products was rather constant at about 1:3 (by GLC), even after those prolonged experiments, in which yields decreased because of the chlorinolysis of the products, and NCT should thus be practically inert towards further chlorination to PCT. This fact could also be rationalized in a simple way, since the homolytic reactivity of the μ -hydrogen (see formula XI) in derivatives of tricyclo[5.2.1.0^{4,10}]decane bearing two or three chlorines on the adjacent iso-positions should be

cumulatively decreased, because of steric hindrance. On the other hand, introduction of one, two, or even three chlorines at the iso-positions should not be effectively hindered by the presence of a similar atom at the μ -position, because of the spontaneous introduction of 2,5,8-unsaturation during the course of the chlorination.

The PCT was obtained in a pure state from the solid solution by selective resinification of the latter with base, and the molecular formula, $C_{10}Cl_{10}$, was established by means of mass spectrometry. The ultraviolet spectrum of the product accommodated three unconjugated dichloroethylene groups in each molecule, proving the compound to be tricyclic. The infrared spectrum, furthermore, was devoid of the characteristic absorptions of the symmetrical and antisymmetrical carbon-chlorine stretching vibrations of dichloromethylene groups, thus making the number of possible product structures very limited; if a few alternatives which for various reasons would not be stable under the conditions of the photochlorination were excluded, only three



$C_{10}Cl_{10}$ structures remained, which were compatible with these findings, *viz.* XII, XIII, and XIV. The chlorocarbon isolated, however, lost four chlorines in a smooth reaction with zinc in tetrahydrofuran-ethanol (*vide infra*) to yield a dimeric compound,* having the molecular formula $C_{20}Cl_{12}$. Because of the partial and nearly complete skeletal inflexibility of XIII and XIV respectively, neither of these structures could reasonably account for that behaviour,** and the most likely formulation of the $C_{10}Cl_{10}$ product was thus perchlorotricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (XII), which should possess the required skeletal properties to a considerable extent.

The NCT was isolated from the solid solution by means of preparative gas chromatography, and the molecular formula, $C_{10}HCl_9$, was determined from the mass spectrum as in the preceding case. A chlorinated tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene structure seemed to be the most probable one, since the product had those infrared and ultraviolet spectral characteristics which were just mentioned, for the perchlorocompound. Great structural similarity between these two compounds was furthermore necessary to account for the

* This compound was essentially inert to further reaction with zinc under the conditions used.

** XIII could possibly eliminate two allylic halogen atoms at the cyclobutane ring. (For the reaction between zinc and chlorinated cyclobutanes, *cf.* Ref. 9). However, no mono- or dimeric products from that reaction seem probable which could react further, with the formation of some $C_{20}Cl_{12}$ product. Other elimination reactions of XIII and XIV, furthermore, seem unlikely, as do also other modes of reactions giving the specific result just mentioned.

fact that they form solid solutions in each other. The location of the hydrogen on one of the bridgehead positions of the nonachlorocompound was inferred from inspection of the NMR spectrum (singlet, τ 5.23 in CDCl_3). However, since PCT had two strong, sharp infrared absorptions at 1614 and 1626 cm^{-1} in the region of the carbon-carbon double-bond stretching modes and, in the case of the nonachlorocompound, only two and quite similar bands, with about the same intensity ratio, appeared in this region at 1601 and 1613 cm^{-1} , all three dichloroethylene groups of a molecule were likely to suffer the same environmental change when going from the perchloro- to the nonachlorocompound. The latter was thus formulated as 1,2,3,4,5,6,7,8,9-nonachlorotricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (VII). This interpretation derives some uncertainty from the fact, that more detailed assignments of the two bands in the double-bond stretching region are not known for either of the compounds. Nevertheless, also chemical arguments speak strongly in favour of the μ -H formulation of the nonachlorocompound (*cf.* the discussion of the chlorination reaction).

Reduction of the NCT-PCT solid solution with lithium and tertiary butanol in a rather diluted * tetrahydrofuran solution furnished a high yield (calculated on the nonachlorocompound used) of tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (VIII) when butyl chloride was present in the reaction mixture.** Attempts to reduce the pure PCT produced polymeric materials only, even in the presence of butyl chloride (one experiment), and it may thus be very likely concluded that NCT was the exclusive source of VIII in the experiments with the solid solution.

The tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene, obtained by the above over-all procedure from tricyclo[5.2.1.0^{4,10}]decane, was identical in all respects (*cf.* experimental section) with triquinacene, synthesized recently by Woodward and his co-workers.¹ For a discussion of the spectroscopic properties of this compound, see Ref. 1.

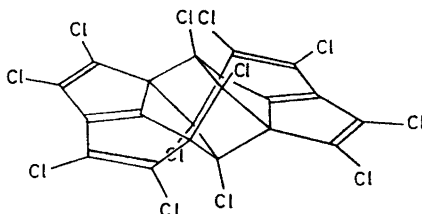
APPENDIX

Dimer of hexachloroacepethylene. A stable, yellowish-white powder, easily purified by recrystallizing its acetone solvate from chloroform-acetone, was isolated in 74 % yield from the reaction between zinc powder and PCT, or the NCT-PCT solid solution, in a refluxing ethanol-tetrahydrofuran solution

* For the original conditions of this reaction, see Ref. 10.

** In the absence of this additive, only traces of VIII were obtained. By way of preliminary considerations of the few facts known of the process at present, the butyl chloride seems to act as a rather short-lived metal-halogen exchange catalyst for the rapid, transient metalation of allylic positions of NCT. The resinification of the latter compound in the absence of the additive is presumed to be initiated either by reactions with tertiary butoxide, or by a reductive elimination in which two electrons are taken up at two different, allylic positions of a molecule. Removal of allylic chlorines from NCT by means of a transmetalation (in which two electrons may be regarded to be efficiently transferred to the same carbon) would make reactions competing with those giving resinous end-products more favourable, since allylic lithium derivatives, still bearing chlorines on one or two allylic positions, are likely to be stable enough towards elimination of chloride ion to react preferentially in other ways under the conditions used. A similar relatively good stability appears improbable for the transient products of a metalation of allylic positions of PCT.

containing some zinc iodide. The product was homogeneous by gas chromatography at 260°C, and the molecular formula, $C_{20}Cl_{12}$, was in agreement with the elemental analysis and the mass spectrum. The further information



XV

obtainable from the ultraviolet and infrared spectra did not seem to be sufficient for definite conclusions to be drawn concerning the detailed structure of the compound solely from the physical data so far collected. Arguments based upon considerations (not to be outlined in this brief account of the compound) of strain in possible isomers built up from two $C_{10}Cl_6$ units containing unrearranged tricyclo[5.2.1.0^{4,10}]decane carbon skeletons, and of most likely reaction paths in the formation of the $C_{20}Cl_{12}$ compound, as well as of some chemical properties of the latter did, however, appear to make XV (an analog of Prins' chlorocarbon $C_{10}Cl_{12}$ ¹¹) the best structural proposal, which accommodated the ultraviolet spectrum ($\lambda_{max} = 294 m\mu$, in hexane). In the region 600–800 cm^{-1} the infrared spectrum had only two absorptions of appreciable intensity. Because of a strong first overtone band (giving a seemingly correct unharmonicity) at 1559 cm^{-1} (vs), intensified by Fermi resonance with some of the adjacent coupled double-bond stretching vibrations, one of these (sharp band at 784 cm^{-1} (m)) could be assigned to a carbon-chlorine stretching fundamental of olefinic chlorine. Although other assignments could not be excluded, the other one (sharp band at 692 cm^{-1} (ms)) is also likely to be due to a carbon-chlorine stretching vibration. The fact that structure XV would thus, however, probably necessitate the exact coincidence of the absorptions from carbon-chlorine stretching vibrations of two non-equivalent chlorines does not, nevertheless, appear to be a very weighty argument against it.

However, no attempts to give any relatively conclusive structural proof for the compound seem possible at present, and the discussion of it is thus intended to be confined to the report of the above data, some of which seemed to be appropriate for the structural evidence given in section B of the present paper.

EXPERIMENTAL

The spectroscopic data were collected by means of the following instruments: a Perkin-Elmer grating infrared spectrophotometer, Model 257, a Perkin-Elmer infrared spectrophotometer, Model 221, a Unicam SP. 800 ultraviolet-visible spectrophotometer, and a 60 Mc. Varian Associates A-60 nuclear magnetic resonance spectrometer.

Mass spectra were obtained on a LKB mass spectrometer, Type 9000 A. All samples were introduced into the mass spectrometer from the gas chromatograph (column: 3.0 mm \times 3 m; 2 % silicon rubber, SE 30, on silanized Chromosorb W, 100–120 mesh), and spectra were recorded with 70 eV electrons.

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

Most gas chromatographic work was done on an Aerograph Autoprep preparative gas chromatograph, Model A-700, containing a 3/8" \times 6 m column with 20 % silicon rubber SE 30 on Chromosorb. A small-scale preparative separation of the C₁₀ chlorinated hydrocarbons was achieved by means of a 1/4" \times 1.8 m column with 5 % silicon rubber SE 30 on silanized Chromosorb W, 60–80 mesh. The walls of the latter column were preferably made of glass.

10-Ketobicyclo[5.2.1]decane (IV). 90 g (0.344 mole) of dimethyl 2,7-dinitroso-2,7-diazaoctanedioate* (recrystallized from ethanol) was dissolved in one litre of tetrahydrofuran-methanol (1:1). After cooling to room temperature and mixing with 33.7 g (0.344 mole) of cyclohexanone, the solution was added at a uniform rate during 8–10 h to an efficiently stirred mixture of some anhydrous potassium carbonate, 2 g of cyclohexanone, and 200 ml of tetrahydrofuran-methanol (1:1). The temperature in the reaction mixture was kept between +10° and –10° during the entire addition. Stirring at this temperature range was continued after all had been added until the solution was practically colourless (ca. 2 h). The undissolved potassium carbonate was then removed and most of the solvent was distilled off at atmospheric pressure (The solvent thus recovered was used directly for further runs). Remaining amounts of solvent were eliminated by raising the temperature of the stirred solution to about 120°. After cooling, the residue was mixed with 50 ml of petroleum ether (b.p. 40–60°). The precipitated potassium carbonate was filtered off and the solution shaken with 10 g of Na₂S₂O₅ in 40 ml of water. (This treatment removed almost completely about 2 g of cyclohexanone but practically no IV). After filtering off small amounts of emulsifying impurities, the layers were separated. The organic layer was washed with dilute aqueous potassium carbonate and water. After drying with magnesium sulfate, the petroleum ether was distilled off, until the temperature of the stirred liquid rose to about 120°. There was obtained about 49 g of a crude product, which contained about 40 % (as estimated from GLC data) of 10-ketobicyclo[5.2.1]decane. The pure ketone, m.p. 113–115° (lit.⁴ m.p. 113–115°) was isolated by means of preparative gas chromatography. The NMR spectrum was identical to that published.⁴ IR spectrum [CCl₄]: ν_{\max} 1731 cm⁻¹.

p-Tosylhydrazone of 10-ketobicyclo[5.2.1]decane (V). (A) *From the pure ketone IV*. A mixture of 0.93 g (5 mmole) of *p*-tosylhydrazine, 20 ml of 99.5 % ethanol, 0.15 ml of concentrated hydrochloric acid, and 0.53 g (3.5 mmole) of pure IV, obtained from the crude product above by preparative scale gas chromatography, was refluxed for 3 h. After standing at room temperature overnight, the product was collected and recrystallized from 99.5 % ethanol, giving 0.92 g (82 %) of V (*vide infra*).

(B) *From the crude ketone IV*. A mixture of 59. g (0.32 mole) of *p*-tosylhydrazine, 1.2 l of 99.5 % ethanol, 9 ml of concentrated hydrochloric acid, and 48 g of crude ketone IV, obtained as described above and containing about 40 % of IV, was refluxed for 3 h, after which 1.2 l of water was added to the boiling, hot, dark solution. After standing at room temperature overnight, the product was collected, washed with ethanol and dried, giving 35 g (86.5 %) of practically pure V. Recrystallization from 99.5 % ethanol gave

* The bisnitrosourethane was prepared by standard methods (*cf.* Ref. 12) from commercial 1,4-diaminobutane (Fluka AG, Buchs SG, Schweiz), by reaction with methyl chloroformate in the presence of aqueous potassium carbonate and subsequent nitrosation (74 % over-all yield in the two steps after recrystallization from ethanol). The presence of some ethanol in the recrystallized product proved to increase its stability to storage in the refrigerator considerably.

colourless cubes which were dried over P_2O_5 before analysis. (Found: C 63.5; H 7.29; N 8.84; S 10.1. Calc. for $C_{17}H_{24}N_2O_2S$: C 63.72; H 7.55; N 8.74; S 10.00).

The recrystallized tosylhydrazones prepared by the procedures (A) and (B) had superimposable infrared and NMR spectra. On being rapidly heated the tosylhydrazone decomposed at about 185°. There were no signs of melting.

Tricyclo[5.2.1.0^{4,10}]decane (VI). Acetamide* (360 g) was melted completely in an 1-l round-bottomed flask fitted with an efficient, not too narrow reflux condenser, and a thermometer that reached down into the contents. Sodium metal (9 g) was then added in small pieces under a stream of nitrogen, the temperature being kept at 90–100°. After all the metal had dissolved, the temperature was adjusted to about 90°, and the flow of nitrogen was discontinued. Dry, finely powdered tosylhydrazone V (30 g; 93.7 mmole) was then added quickly, in one portion. After the tosylhydrazone had been brought into solution completely by swirling the flask, the temperature was increased. Appreciable evolution of nitrogen started at about 110°. The temperature was rapidly increased further to about 175° and was maintained there for 5–7 min. The reaction mixture was then allowed to cool to 80–90° when 300 ml of water was added through the condenser with careful mixing. After cooling to 15–20°, 120 ml of pentane was added through the condenser as well, and the mixture was shaken and separated. The aqueous layer was extracted with one more portion of pentane. The combined organic solution was dried with magnesium sulfate and the pentane was distilled off at atmospheric pressure, until the temperature of the residue rose to about 170°. From the semi-solid mass thus obtained, the $C_{10}H_{16}$ hydrocarbons were removed by sublimation at 1 mm and 30–45° (a second sublimation proceeded easily at a considerably lower temperature) into a receiver cooled with dry ice-acetone. The sublimed product weighed 11.6 g (91 % yield of $C_{10}H_{16}$ hydrocarbons) and consisted of 96 % VI and 4 % IX (by GLC). The small viscous residue contained the azine $C_{20}H_{32}N_2$ and probably the dimeric alkene $C_{20}H_{32}$, as shown by mass spectrometry. Final purification of the sublimed product was achieved by means of preparative gas chromatography to yield the pure tricyclo[5.2.1.0^{4,10}]decane (VI), m.p. 66°, b.p. 188°/760 mm (Found: C 88.3; H 11.90. Calc. for $C_{10}H_{16}$: C 88.16; H 11.84).

Mass spectrum; Isotopic abundance ratio of the 136, 137, and 138 *m/e* molecular ion peaks: Found (at a relative intensity of the 136 peak of 0.344), 100:11.12:0.58; Calc. for $C_{10}H_{16}^+$, 100:11.06:0.55.

IR Spectrum: Fig. 1. NMR spectrum: Fig. 2.

Photochlorination of tricyclo[5.2.1.0^{4,10}]decane.** *Apparatus*: The photochlorination was performed in an all-glass apparatus consisting of a 500-ml three-necked round-bottomed flask of Pyrex glass, a gas inlet tube extending to the bottom of the flask, an efficient cooling-coil also extending to the bottom of the flask, and a gas outlet tube connected to a calcium chloride tube. During the entire experiment a rather rapid stream of cold (about +10°) water was run through the cooling coil. The source of irradiation was a Philips 250 W external type mercury vapour arc lamp type 11855/73, discharge-tube type U34/35. The shortest distance between the surface of the flask and the surface of the discharge-tube was adjusted to 30 mm. The wall-thickness of the flask was 2.0 mm at the point where most of the radiation passed into the reaction mixture.

Procedure: Pure VI (2.72 g; 0.02 mole) or 2.84 g of sublimed $C_{10}H_{16}$ mixture, obtained as described above and containing 96 % VI, was dissolved in 400 ml of carbon tetrachloride and 24 g (0.34 mole) of dry chlorine was introduced into the solution under irradiation during 30–60 min. A known weight of the halogen was conveniently obtained by condensing dry gaseous chlorine*** in a weighed flask (containing some phosphorus pentoxide) immersed in a dry ice-acetone bath. The chlorine was then introduced into the reaction mixture at a suitable rate by spontaneous volatilization. The irradiation was continued, after all the halogen had been introduced, for periods varying from 3 to 30 h. It proved to be essential for elemental chlorine to be present in the reaction mixture in

* This reaction medium was adopted from Ref. 13.

** Warning: The experiment should be carried out in an efficient hood. There are furthermore some indications that the chlorinated reaction products (including NCT and PCT) are toxic and precautions should thus be undertaken to prevent skin-contact and inhalation of vapours. GLC experiments should obviously be carried out in the hood.

*** Obtained from commercial compressed liquid chlorine.

reasonable amounts (as indicated by a strong yellowish-green colour of the solution) during the entire time of this irradiation. When this requirement was not fulfilled, most of the chlorinated tricyclic products were decomposed by the radiation in a few hours. With a satisfactory cooling coil in the reaction mixture, the amount of chlorine indicated above, however, sufficed even for prolonged experiments, and no introduction of additional amounts during later stages of the experiment was necessary. After the irradiation was completed, most of the carbon tetrachloride was distilled off at atmospheric pressure, the recovered solvent-chlorine solution being used directly in further runs. Evaporation of the residue at reduced pressure in a rotating evaporator yielded a white viscous mass, adhering to the walls of the flask. Acetone (10 ml) was added and the closed flask was swirled gently at room temperature until the white mass had gone into solution (30–60 min). Simultaneously as the mass dissolved, small white crystals separated from the liquid phase. The crystallization was completed in the refrigerator overnight. Concentration of the mother liquor yielded a second, somewhat less pure crop of crystals. In all experiments where appreciable yields were obtained, the NCT:PCT ratio (= the VII:XII ratio) of the first crop was about 1:3 and of the second crop slightly higher (by GLC). Under the conditions specified above, the optimum yield was obtained after about 15 h total time of irradiation (First crop: 3.7 g. Second crop: 1.4 g. Combined yield: 55 %, as calc. for the product composition NCT:PCT = 1:3). Recrystallization of the product from acetone-chloroform (1:1) yielded the pure two-component NCT-PCT solid solution as colourless rhomboids, m.p. 229°, having about the same 1:3 NCT:PCT ratio (concordant results by GLC and elemental analysis; Found: C 25.8; Cl 74.1).

1,2,3,4,5,6,7,8,9-Nomachlorotricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (NCT; VII). Small amounts of this component were isolated from the solid solution just mentioned by means of preparative scale gas chromatography.

Mass spectrum; Isotopic abundance ratio of the 436–450 *m/e* molecular ion peaks: Found (at a relative intensity of the 440 peak of 0.0787), 26.9:2.85:77.7:8.37:100:11.0:73.7:7.98:38.9:4.74:12.4:1.89:2.80:0.33:0.48; Calc. for C₁₀HCl₉⁺, 25.98:2.93:76.44:8.58:100:11.20:76.37:8.52:37.53:4.17:12.32:1.36:2.70:0.30:0.38.

NMR spectrum [CDCl₃]: singlet, $\tau = 5.23$ ppm. IR spectrum [KBr]: ν_{\max} (cm⁻¹), 1613 (ms), 1601 (s), 1254 (s), 1177 (ms), 1028 (ms), 901 (vs), 699 (m), 603 (m).

Perchlorotricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (PCT; XII). This component was isolated from the solid solution mentioned above, without using chromatographic methods, by selective resinification of the two-component product with sodium hydroxide suspended in boiling tetrahydrofuran.

Mass spectrum; Isotopic abundance ratio of the 470–484 *m/e* molecular ion peaks: Found (at a relative intensity of the 474 peak of 0.0688), 22.8:2.41:68.3:7.18:100:10.8:89.8:9.44:50.0:5.68:19.3:3.14:5.78:0.87:0.90; Calc. for C₁₀Cl₁₀⁺, 20.79:2.34:67.96:7.63:100:11.20:87.24:9.75:49.98:5.56:19.66:2.18:5.38:0.59:1.01.

IR spectrum [KBr]: ν_{\max} (cm⁻¹), 1626 (ms), 1614 (s), 1213 (m), 1161 (ms), 1157 (s), 1034 (m), 1025 (m), 919 (m), 724 (vs), 609 (ms;br). UV spectrum [cyclohexane]: λ_{\max} (μ), 218* (ϵ 23 300), 228 (shoulder; ϵ 20 600).

Superposition of weighed contributions of the above NCT and PCT infrared spectra yielded the infrared spectrum of the solid solution, thus showing that the components of the latter were unchanged when separated from each other by the methods used.

Tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene. Triquinacene (VIII). To a mixture of 8 g of butyl chloride, 24 g of *tert*-butanol, and 320 ml of tetrahydrofuran (distilled over lithium aluminium hydride), in which 5 g of the NCT-PCT (1:3) solid solution described above ** had been dissolved, was added 4.2 g of lithium sheet-metal of 0.4 to 0.5 mm thickness. A slow stream of dry nitrogen was passed over the mixture which was immediately heated to reflux. A vigorous reaction ensued, during which the boiling mixture occupied

* The position of the 218 μ maximum coincides with that estimated for 1,2,3,4,5-pentachlorocyclopentene, according to the rules given by McBee.¹⁴

** Reductions of photochlorinated (above conditions; 15 h) reaction mixtures, from which no crystallized NCT-PCT solid solution was isolated after evaporating the solvent, were performed without changing the procedure described. The two-component hydrocarbon product obtained had the same 9:1 composition (*cf.* the procedure given), and the over-all yield from VI was slightly improved.

a volume several times its original one. After the initial spontaneous reflux had subsided (5–10 min), refluxing was continued with external heating for an additional 3 h. The mixture was then allowed to cool and about 150 ml of water was added. After small amounts of unreacted lithium had dissolved, the tetrahydrofuran layer, salted out by the hydroxide, was separated and concentrated to a volume of about 50 ml at atmospheric pressure. To the dark, brownish-black residual solution there was immediately added 150 ml of water (At this stage, dark polymeric materials were practically quantitatively converted into a hydrophilic, pentane-insoluble suspension in the aqueous solution). The resulting mixture was extracted with two 150-ml portions of pentane. (In a few experiments, in which some of the conditions indicated above were not fulfilled, an emulsion was formed at this stage. It was broken by dissolving magnesium sulfate in the aqueous phase and filtering). After drying with magnesium sulfate, the practically colourless pentane extract was concentrated to a small volume at atmospheric pressure. Besides remaining amounts of the three low-boiling components (pentane, THF, *t*-BuOH) and traces of resin, the residual solution contained nothing but VIII and another hydrocarbon C₁₀H₁₂ (by mass spectrometry) in the ratio of 9:1 (by GLC). Hence, by working on a larger scale, crude VIII of about 90 % purity should be easily obtainable without appreciable losses from this solution by distillation. On the scale indicated, however, final purification was most conveniently achieved by preparative scale gas chromatography directly of the concentrated solution (containing a yield of 265 mg* of VIII, *i.e.* 72 %, calc. on the NCT used), to give the pure tricyclo[5.2.1.0^{4,10}]deca-2,5,8-triene (VIII), m.p. 18° (lit.¹ m.p. 18.1–19.1°). The C₁₀H₁₀ molecular formula was determined from the mass spectrum. IR spectrum [liquid film]: ν_{\max} (cm⁻¹), 3050 (s), 2964 (m), 2882 (ms), 1611 (wm), 1347 (m), 1281 (w), 1270 (w), 972 (vs), 862 (ms), 812 (ms), 747 (s), 743 (s), 699 (vs). The infrared spectrum was identical in all details to that published.¹ NMR spectrum [CDCl₃]: two sharp, symmetrical peaks, $\tau = 4.32$ and 6.23 ppm; intensity ratio, 3:2. No fine structure was discernible in either peak under conditions of optimum resolution.

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* Concordant results from determinations by means of the GLC detector and from the yield isolated in the preparative purification (185 mg) corrected for losses in the gas chromatograph.