

2,3,4-Trichloropentacyclo[6.4.0.0^{2,4}.0^{3,10}.0^{5,9}]dodeca-6,11-diene^{1a}

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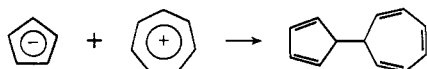
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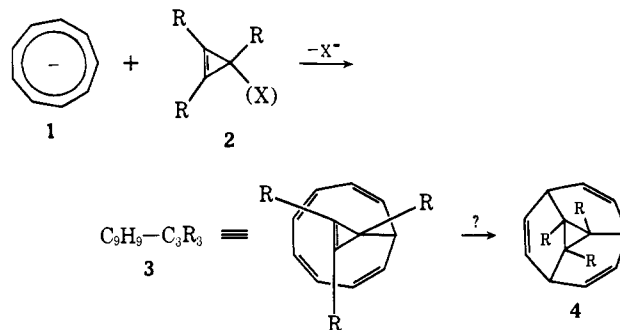
Abstract: Reaction between lithium cyclononatetraenide and tetrachlorocyclopropene gave the title compound as an unanticipated product. The structure was elucidated by X-ray crystallography and nmr spectroscopy. A probable sequence of reactions, involving the intermediacy of a cyclopropenyldihydroindene, has been devised to explain the formation of the observed substance.

The (CH)₁₂ hydrocarbons are expected to show a diversity of chemical properties as broad as that of the (CH)₁₀ hydrocarbons^{2,3} (of which bullvalene is the stellar performer) and perhaps surpassing them in theoretical significance.⁴ This paper describes a novel ring system which was obtained as an unanticipated product of the attempted synthesis of a key member of the (CH)₁₂ family.

One of the earlier preparations of a (CH)₁₂ hydrocarbon involved the reaction of the tropylium ion (C₇H₇⁺) with the cyclopentadienide ion (C₅H₅⁻).^{4a,b} The product was formulated as a cyclopentadienylcycloheptatriene. We reasoned that reaction between the known



higher and lower congeners of these 6π electron aromatic ions, namely between the cyclononatetraenide (1) and cyclopropenium ions, should likewise produce a (CH)₁₂ species. For reasons to be given we elected to work with perhalocyclopropenyl substances (2, R, X = Cl). We were particularly intrigued by the possibility that the anticipated initial product 3, which should be a highly reactive species, would readily undergo an internal Diels-Alder reaction to produce tetracyclododecaene 4.⁵ Hence, the latter substance was antici-



pated as the isolable product of such a reaction. Evidence to be presented justifies the expectation that 3 would indeed be produced, but it appears that 3 finds another fate than the production of 4.

Results

Synthesis. Tetrachlorocyclopropene⁶ was selected as the "cyclopropenium" component of the reactants for several reasons: (a) for its ready availability, (b) because of the known avidity of perhalocyclopropenes as dienophiles,⁷ and (c) for the favorable physical properties to be conferred on the desired product by the introduction of the chlorines (in comparison with other potentially available substituents).

Addition of a tetrahydrofuran solution of lithium cyclononatetraenide^{8,9} to an excess of tetrachlorocyclopropene gave, after work-up involving column chromatography on silicic acid and multiple sublimations and recrystallizations, approximately a 2% yield of a crystalline material, mp 152–154°. The new substance was shown to have composition C₁₂H₉Cl₃ by elemental analysis and by mass spectrometry, which fixed the molecular weight at 258 and confirmed the presence of three chlorines. The infrared spectrum of the new compound was relatively featureless insofar as recog-

considerations. Exploration of the energy surface with respect to just this mode of reactivity was the object of this project. We were especially interested in the possibility that the heptacyclic form might be modestly stabilized by extensive conjugative interactions attributable to the π character of the three-membered rings. We hope to elaborate upon the chemistry of this system elsewhere.

(6) S. W. Tobey and R. West, *J. Amer. Chem. Soc.*, **88**, 2481 (1966).

(7) D. C. F. Law and S. W. Tobey, *ibid.*, **90**, 2376 (1968).

(8) T. J. Katz and P. J. Garratt, *ibid.*, **86**, 5194 (1964); E. A. Lancette and R. E. Benson, *ibid.*, **87**, 1941 (1965); H. E. Simmons, D. B. Chesnut, and E. A. Lancette, *ibid.*, **87**, 982 (1965).

(9) It has recently been shown that *cis,cis,cis,trans*-cyclononatetraenide may be formed from chlorobicyclononatatriene under conditions of kinetic control: G. Boche, D. Martens, and W. Danzer, *Angew. Chem., Int. Ed. Engl.*, **8**, 984 (1969). Consequently, we are not certain that we were utilizing entirely the all *cis* isomer previously described.⁹

(1) (a) Previously reported in preliminary form: W. L. Mock, C. M. Sprecher, R. F. Stewart, and M. G. Northolt, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, ORGN 113; (b) Alfred P. Sloan Research Fellow, 1970–1972.

(2) For an interesting attempt at systematic classification of the (CH)_{2n} hydrocarbons (n = 1–5) see A. T. Balaban, *Rev. Roum. Chim.*, **11**, 1097 (1966).

(3) For references to known (CH)₁₀ species and their transformations the following papers may be consulted: (a) T. J. Katz and J. J. Cheung, *J. Amer. Chem. Soc.*, **91**, 7772 (1969); (b) R. T. Seidner, N. Nakatsuka, and S. Masamune, *Can. J. Chem.*, **48**, 187 (1970); (c) M. Jones, Jr., S. D. Reich, and L. T. Scott, *J. Amer. Chem. Soc.*, **92**, 3118 (1970); (d) L. A. Paquette and J. C. Stowell, *ibid.*, **92**, 2584 (1970); (e) K. Hojo, R. T. Seidner, and S. Masamune, *ibid.*, **92**, 6641 (1970); (f) T. J. Katz, J. J. Cheung, and N. Acton, *ibid.*, **92**, 6643 (1970); (g) W. G. Dauben, C. H. Schallhorn, and D. L. Whalen, *ibid.*, **93**, 1446 (1971).

(4) A few examples of (CH)₁₂ hydrocarbons have been described: (a) M. E. Vol'pin, I. S. Akhrem, and D. N. Kursanov, *Khim. Nauk. Prom.*, **2**, 656 (1957); *Zh. Obshch. Khim.*, **28**, 330 (1958); (b) W. v. E. Doering and H. Krauch, quoting unpublished work with R. S. Rouse: *Angew. Chem.*, **68**, 661 (1956); (c) J. N. Labows, Jr., J. Meinwald, H. Rottele, and G. Schröder, *J. Amer. Chem. Soc.*, **89**, 612 (1967); (d) L. A. Paquette and J. C. Stowell, *Tetrahedron Lett.*, 4159 (1969); (e) J. F. M. Oth, H. Rottele, and G. Schröder, *ibid.*, 61 (1970); J. F. M. Oth, J.-M. Gilles, and G. Schröder, *ibid.*, 67 (1970), and references cited.

(5) The geometry of 4 is favorable for an internal [$\pi 2_s + \pi 2_s + \pi 2_s$] cycloaddition leading to heptacyclo[5.5.0.0^{2,12}.0^{3,5}.0^{4,10}.0^{5,8}.0^{9,11}]dodecane. While this is formally a thermally allowed process, it might be expected to proceed only in retro fashion because of strain energy

Table I. Atomic Parameters^a

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11} (or <i>B</i>)	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(2)	0.3815 (2)	0.1935 (4)	0.8342 (7)	0.0029 (1)	0.0116 (5)	0.021 (2)	0.0000 (4)	-0.0002 (5)	0.0027 (8)
Cl(3)	0.4415 (2)	0.0675 (5)	0.4932 (9)	0.0023 (1)	0.0083 (5)	0.045 (2)	-0.0020 (3)	0.0009 (4)	-0.003 (1)
Cl(4)	0.3088 (2)	0.0770 (6)	0.5358 (9)	0.0028 (2)	0.0128 (7)	0.049 (3)	0.0023 (3)	0.0009 (5)	0.003 (1)
C(1)	0.3905 (7)	0.375 (1)	0.611 (2)	4.3 (5)					
C(2)	0.380 (1)	0.248 (1)	0.623 (3)	6.0 (5)					
C(3)	0.4045 (9)	0.187 (2)	0.451 (3)	3.8 (4)					
C(4)	0.3471 (9)	0.191 (2)	0.467 (3)	4.9 (5)					
C(5)	0.3224 (7)	0.260 (1)	0.309 (4)	3.9 (6)					
C(6)	0.2788 (8)	0.338 (1)	0.391 (2)	5.2 (5)					
C(7)	0.3052 (8)	0.424 (2)	0.464 (3)	6.1 (5)					
C(8)	0.3662 (9)	0.426 (1)	0.436 (2)	6.6 (5)					
C(9)	0.3716 (8)	0.342 (1)	0.274 (2)	4.4 (4)					
C(10)	0.4231 (7)	0.271 (1)	0.309 (4)	3.7 (6)					
C(11)	0.4647 (8)	0.344 (2)	0.403 (3)	5.0 (6)					
C(12)	0.4527 (8)	0.389 (1)	0.564 (3)	5.6 (6)					

^a Estimated standard deviations in parentheses refer to last decimal place.

nizable functionality, and the ultraviolet spectrum revealed only end absorption, attributable to the presence of halogen. Whereas the ir and uv were not indicative of structure, the proton magnetic resonance spectrum (see Figure 2) immediately revealed that the product lacked the symmetry of **4**. It was observed that each of the nine protons (four olefinic and five aliphatic) in the molecule was in a different environment, and that the resultant nine spin system was amenable to approximate first-order analysis. The chemical shifts and coupling constants were consistent with the structure given in

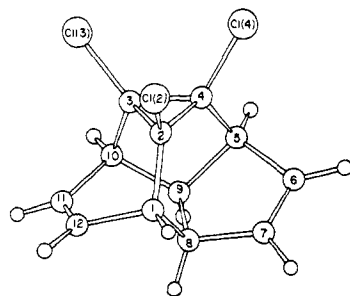


Figure 1. Perspective drawing of trichloropentacyclododecadiene based on the atomic coordinates in Table I. Hydrogens were generated with a standard bond length of 1.05 Å and with equal bond angles about the saturated carbon. For the olefinic hydrogens on C(12), C(11), C(6), and C(7) the hydrogen was constrained to lie in the plane of the unsaturated C atom and its two nearest neighbors.

Figure 1, which was adduced on the basis of mechanistic rationale. Consideration of the spectrum is deferred to the Discussion section. It was decided that such a structure could best be confirmed by X-ray crystallography, since intactness of the halocyclopropane ring could not be proven by spectroscopic results at hand.⁷ The results which follow provide this proof and describe the structure to which the nmr assignments are made.

Structure Solution and Refinement

Crystal and diffraction data are presented in the Experimental Section. Intensity measurements were reduced to relative structure factors by appropriate corrections for Lorentz and polarization effects. Absorption corrections were ignored. Normalized structure factors were computed after a scale factor and overall temperature parameter were determined from a Wilson plot. An $E^2 - 1$ Patterson map was com-

puted. The three chlorine atoms were clearly evident. One Cl-Cl vector was parallel to *a*. The *x* coordinate was determined from the intensity trends of the *h*00 reflections. With trial coordinates for the three Cl atoms, a structure factor calculation and subsequent Fourier synthesis of the data yield an electron density map that revealed the 12 carbon atoms. A structure factor calculation with all C atoms and Cl atoms had an agreement factor of 32%. Two cycles of least-squares with isotropic thermal parameters dropped the agreement factor, *R*, to 17%. Anisotropic thermal parameters for the Cl atoms were introduced and another two cycles of full-matrix least-squares dropped *R* to 0.157. The weighted *R* ($R_w = \{\sum w(F_o - F_c)^2 / \sum wF_o^2\}^{1/2}$) was 0.042. The rather poor signal to noise ratio for many of the reflections can account for the large difference between *R* and *R_w*. A final ΔF synthesis did not reveal any hydrogen atoms. At this stage of the refinement there were 76 parameters and only 520 reflections. In view of the poor quality of the data and an overdetermination of only 6.8 reflections per parameter, further refinement was terminated at this point. A pictorial representation of the resulting structure is given in Figure 1. The numbering system used corresponds to the nomenclature of the von Baeyer scheme. The scattering factors for Cl and C are from the International Tables¹⁰ and for H are from Stewart, *et al.*¹¹ For all calculations anomalous dispersion by Cl was ignored. All programs used in this work were from X-Ray-67.¹² Atomic positional and thermal parameters are listed in Table I. The atomic numbering is as shown in Figure 1.

Discussion

Crystallographic Structure. It should be emphasized at the outset here that radiation damage incurred by the crystal during diffraction measurements severely limits the accuracy of the crystal structure. The bond lengths and angles calculated from the final atomic positions are listed in Table II. A perspective drawing of the molecular structure is shown in Figure 1. The carbon-

(10) N. F. M. Henry and K. Lonsdale, Ed., "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, 1965, p 202.

(11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(12) J. M. Stewart, "X-Ray-67 Crystallographic Programming System," Computer Science Center Report No. 67-58, University of Maryland, College Park, Md., 1967.

chlorine bonds are normal (1.77 Å) except for C(2)–Cl(2). The C(6)–C(7) and C(11)–C(12) bond lengths are consistent with a C=C length of 1.33 Å. The saturated C–C bonds in the structure (excluding the cyclopropane ring) average to 1.57 Å. These bond lengths are rather long and probably reflect the radiation damage which took place. In the three-membered ring C(2) seems to have moved out since C(2)–C(3) and C(2)–C(4) are about 1.57 Å long. It may also be noted that the C(2)–Cl(2) bond has a rather short length of 1.66 Å. Examination of the unit cell reveals no interatomic distances between neighboring molecules within normal packing distances. A structure comparable to trichloropentacyclododecadiene is 3,4,5-trichlorotetracyclo[4.4.0.0^{3,9}.0^{4,8}]decan-2-one.¹³ For the latter crystal structure, the data were far more accurate and no radiation damage was reported. The C–Cl bonds were 1.77 Å and the average C–C bond was 1.54 Å with the largest at 1.57 Å.

The major strength of the present diffraction results is that the structure (Figure 1) produced (a) establishes the presence of the trichlorocyclopropane ring unequivocally, (b) is otherwise consistent with that rationalized on mechanistic grounds, and (c) is compatible with the high-resolution nmr results. The radiation damage limits the accuracy of the stereochemical structure, but the diffraction intensities were nevertheless of sufficient quality, in conjunction with the nmr results, to establish the structure of C₁₂H₉Cl₃ as trichloropentacyclododecadiene.

Table II. Bond Lengths and Angles^a

Bond	Length, Å	Angle	Degrees
Cl(2)–C(2)	1.66 (0.02)	C(10)–C(3)–Cl(3)	120 (1)
Cl(3)–C(3)	1.76 (0.02)	C(10)–C(3)–C(2)	110 (2)
Cl(4)–C(4)	1.77 (0.02)	C(10)–C(3)–C(4)	110 (2)
C(1)–C(2)	1.57 (0.02)	C(2)–C(3)–C(4)	62 (2)
C(1)–C(8)	1.54 (0.02)	C(5)–C(4)–Cl(4)	114 (1)
C(1)–C(12)	1.63 (0.03)	C(5)–C(4)–C(2)	121 (2)
C(2)–C(3)	1.58 (0.03)	C(5)–C(4)–C(3)	111 (2)
C(2)–C(4)	1.56 (0.03)	C(3)–C(4)–C(2)	63 (2)
C(3)–C(4)	1.47 (0.03)	C(4)–C(5)–C(6)	110 (2)
C(4)–C(5)	1.55 (0.03)	C(4)–C(5)–C(9)	98 (1)
C(5)–C(6)	1.58 (0.03)	C(9)–C(5)–C(6)	104 (1)
C(6)–C(7)	1.35 (0.03)	C(5)–C(6)–C(7)	105 (2)
C(7)–C(8)	1.57 (0.03)	C(6)–C(7)–C(8)	117 (2)
C(8)–C(9)	1.56 (0.02)	C(7)–C(8)–C(9)	100 (2)
C(9)–C(5)	1.63 (0.02)	C(7)–C(8)–C(1)	106 (2)
C(9)–C(10)	1.60 (0.02)	C(9)–C(8)–C(1)	109 (1)
C(10)–C(3)	1.52 (0.03)	C(8)–C(9)–C(5)	102 (2)
C(10)–C(11)	1.55 (0.03)	C(8)–C(9)–C(10)	109 (2)
C(11)–C(12)	1.32 (0.03)	C(5)–C(9)–C(10)	106 (1)
		C(9)–C(10)–C(3)	102 (2)
Angle	Degrees	C(9)–C(10)–C(11)	109 (1)
C(2)–C(1)–C(12)	107 (2)	C(3)–C(10)–C(11)	108 (2)
C(2)–C(1)–C(8)	112 (2)	C(10)–C(11)–C(12)	118 (2)
C(12)–C(1)–C(8)	100 (1)	C(11)–C(12)–C(1)	111 (2)
C(1)–C(2)–Cl(2)	116 (1)		
C(1)–C(2)–C(3)	110 (2)		
C(1)–C(2)–C(4)	119 (2)		
C(3)–C(2)–C(4)	56 (1)		

^a Esd are shown in parentheses.

Nmr Spectrum. The proton magnetic resonance spectrum, illustrated in Figure 2 (at 100 MHz), was the first clue to the structure of the reaction product, which was subsequently firmly established by crystallography.

(13) D. Schwarzenbach, *Acta Crystallogr., Sect. B*, **24**, 238 (1968).

Table III. Nmr Analysis of 2,3,4-Trichloropentacyclo[6.4.0.0^{2,4}.0^{3,10}.0^{6,9}]dodeca-6,11-diene (Spectrum, Figure 2)^a

δ (TMS) ^b	Atom position assignment	Proton positions to which coupled	Coupling constants, Hz ^c	Vicinal dihedral angle, deg ^d
2.050	8	1, 7, 9	$J_{1,8} = 1.5$	68
2.604	9	1, 5, 8, 10	$J_{1,9} = 1.5$	
2.929	1	8, 9, 11, 12	$J_{1,11} = 1.0$	
3.293	5	6, 9	$J_{1,12} = 6.3$	6
3.558	10	9, 11, 12	$J_{5,6} = 2.5$	30
5.871	7	6, 8	$J_{5,9} = 6.2$	38
6.178	6	5, 7	$J_{6,7} = 5.9$	4
6.345	11	1, 10, 12	$J_{7,8} = 2.8$	41
6.624	12	1, 10, 11	$J_{8,9} = 7.4$	29
			$J_{9,10} = 5.9$	33
			$J_{10,11} = 5.9$	4
			$J_{10,12} = 1.0$	
			$J_{11,12} = 7.5$	11

^a Line positions were measured in *ca.* 10% CDCl₃ solution at 100 MHz by the side-band technique with TMS as internal reference. ^b Chemical shifts given are approximately corrected for second-order perturbation effects and are considered accurate to $\delta \pm 0.005$. ^c All couplings are reciprocally consistent to within ± 0.2 Hz; most may be accepted within ± 0.1 Hz. ^d Calculated HCCH torsional angle—see text.

Proton assignments and a consistent set of spin-spin couplings are listed in Table III. Coupling constants were abstracted by first-order analysis and refined by hand computation. The numbering system is the same as that in Figure 1 (von Baeyer scheme). The larger coupling assignments were entirely confirmed by decoupling experiments at 60 MHz. Relative signs of J were not determined but are all expected to be positive with the possible exception of some of the allylic couplings (*ca.* 1 Hz). Among the five nonolefinic protons (those between δ 2 and 3.6) it will be noted that the higher field pair (2.050, 2.604) were assigned to positions (8 and 9, respectively) which are not vicinal to a chlorine atom. These may also be experiencing a specific anisotropy effect of the three-membered ring and the double bonds.¹⁴ The other three protons (2.929, 3.293, 3.558) were assigned to the remaining bridgehead positions (1, 5, and 10, respectively), where the inductive effect of the chlorines may be more strongly felt. The assignments do not depend upon the previous assumption, however, inasmuch as the mutual relationships of the coupling constants virtually rule out alternative assignments. Turning to the olefinic region, the high-field pair of protons (5.871, 6.178) were assigned (to 7 and 6, respectively) on the basis of their observed couplings to the adjacent bridgehead positions. Assignment of the remaining pair (6.345, 6.624) to their positions (11 and 12, respectively) on the other double bond required decoupling experiments, since the observed splittings were quite similar for both. The couplings previously alluded to were also confirmed in this manner. There are no unusual J values in the present assignment (as shown below). The only long-range coupling detected (*i.e.*, not involving a double bond) was between the 1 and 9 positions ($J = \pm 1.5$ Hz). These protons are separated by four bonds in an approximately planar zig-zag ("W") configuration (see Figure 1); this constitutes a favorable coupling path.

(14) Chemical shifts in the tricyclo[3.2.2.0^{2,4}]nonane system have received scrutiny: Y. E. Rhodes, P. E. Schueler, and V. G. DiFate, *Tetrahedron Lett.*, 2073 (1970).

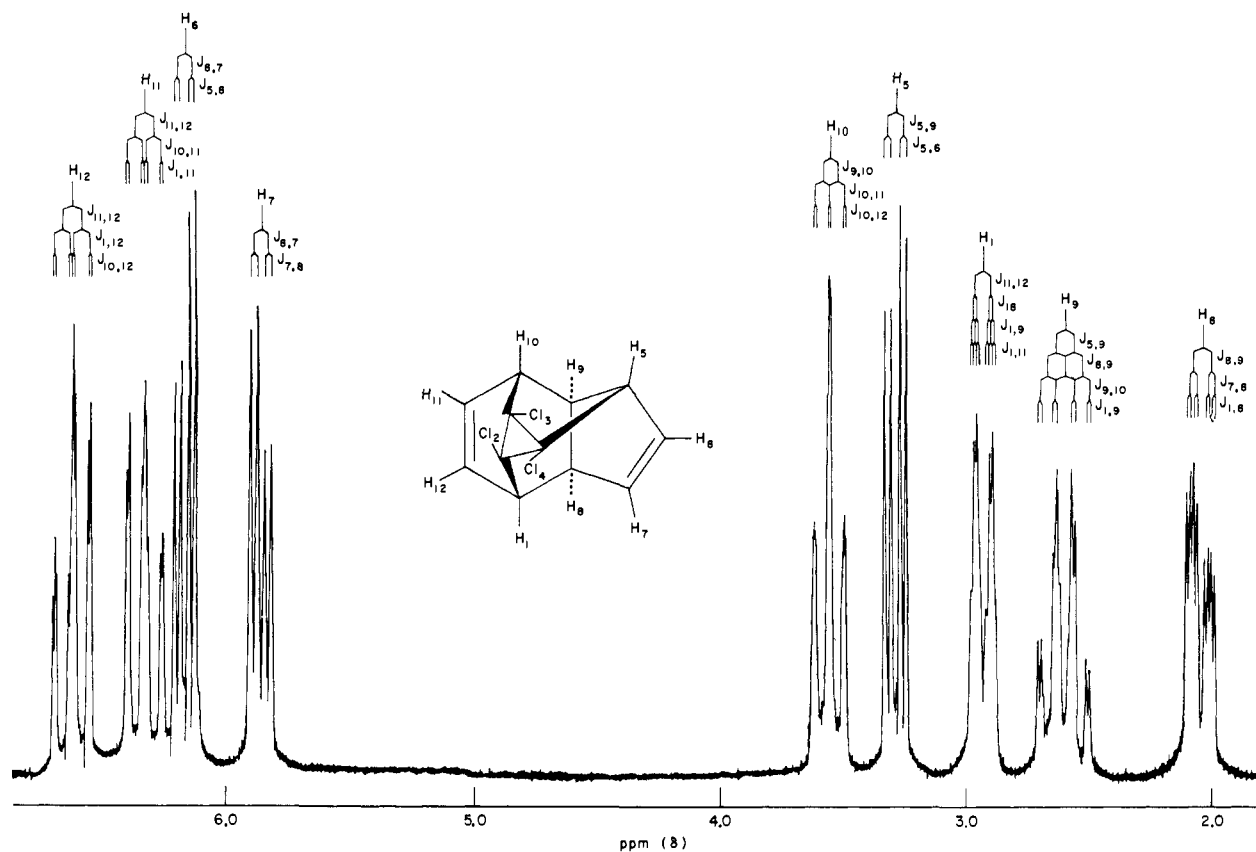


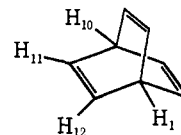
Figure 2. The 100-MHz nmr spectrum of 2,3,4-trichloropentacyclo[6.4.0.0^{2,4}.0^{8,10}.0^{5,9}]dodeca-6,11-diene in CDCl₃. Spectrum calibrated by the side-band technique.

Some care was taken in deriving the coupling constants in Table III, for the reason that this rigidly defined hydrocarbon skeleton provides an excellent calibration structure for determining the relationship between vicinal coupling and dihedral angle between adjacent CH bonds (the so-called Karplus relationship). There is need for empirical data to provide parameters for this correlation for strained systems.¹⁵ Regrettably, the crystallographic determination of this structure is not of sufficient quality to provide "experimentally measured" HCCH dihedral angles. We have, however, included in Table III calculated dihedral angles for adjacent sets of protons for comparison with the observed coupling constants. Caution should be exercised in accepting these numbers; the positions of the carbon atoms are poorly defined, as may be seen by inspection of bond lengths (Table II), and the protons were artificially positioned with equal bond angles to neighboring carbon atoms (Figure 1). The bias in this latter assumption is demonstrated in the computed 11° torsional angle about the C(11)-C(12) double bond; such strain is likely more easily accommodated by modest rehybridization of the atoms involved, producing a compensating adjustment in the real torsion about C(10)-C(11) and C(12)-C(1). The angles in the last column of Table III should be assumed accurate only to within $\pm 5^\circ$, at best.

The use of our nmr analysis for comparative purposes will be briefly demonstrated. The polycyclic ring system under investigation has embedded within it many bi- and tricyclic partial structures commonly encountered. For example, carbons 1-3 and 8-12 comprise a

(15) S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 236 (1969).

bicyclo[2.2.2]octene fragment. For barrelene, Zimmerman has given the coupling constants shown.¹⁶ In the figure the protons are numbered nonsystematically according to the similarly situated positions in trichloropentacyclododecadiene. The values in paren-



$$J_{1,12} = J_{10,11} = 5.5 \text{ Hz (5.9, 6.3)}$$

$$J_{11,12} = 6.3 \text{ Hz (5.7)}$$

$$J_{1,11} = J_{10,12} = 1.6 \text{ Hz (1.0)}$$

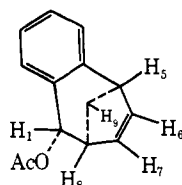
theses are the corresponding couplings for our substance. The differences in the two sets of parameters probably lie in the distortions which are induced into our system by the additional fused rings and which are not likely in barrelene.¹⁷

As a second example, carbons 1,2 and 4-9 comprise a bicyclo[3.2.1]octene fragment. A suitable analog structure, in which the constraint of the 2,4 fused cyclopropane ring is approximated by an aromatic ring, is the acetoxybicyclooctadiene shown.¹⁸ Again the numbering system identifies protons corresponding to those in our structure, from which couplings in paren-

(16) H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **91**, 2330 (1969).

(17) Coupling across the double bond in bicyclo[2.2.2]octenes is apparently more typically $J = 8-9$ Hz; F. W. Baker and L. M. Stock, *J. Org. Chem.*, **32**, 3344 (1967).

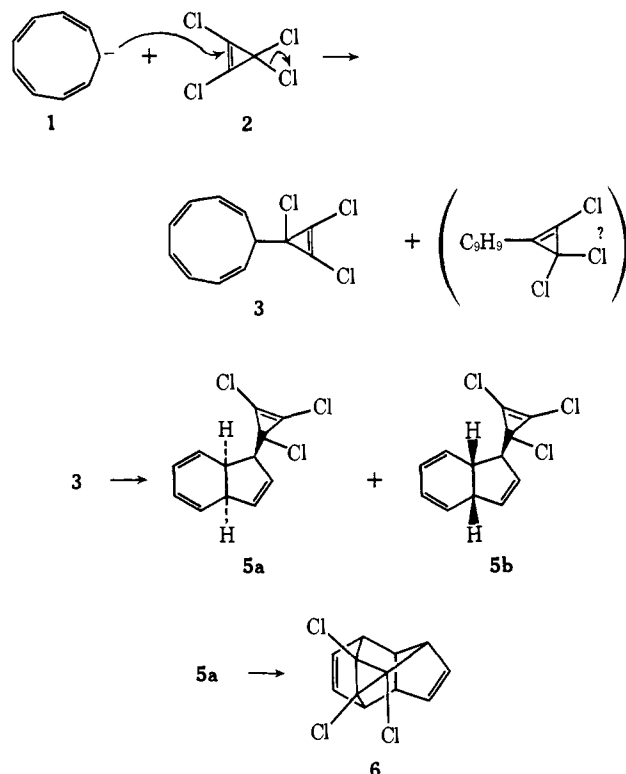
(18) H. Tanida, K. Tori, and K. Kitahonoki, *J. Amer. Chem. Soc.*, **89**, 3212, (1967); this bicyclooctane skeleton has also been examined by C. W. Jefford and K. C. Ramey, *Tetrahedron*, **24**, 2927 (1968).



$$\begin{aligned}
 J_{1,8} &= 2.0 \text{ Hz (1.5)} \\
 J_{5,6} &= 3.1 \text{ Hz (2.5)} \\
 J_{6,7} &= 5.8 \text{ Hz (5.9)} \\
 J_{7,8} &= 2.7 \text{ Hz (2.8)} \\
 J_{8,9} &= 4.7 \text{ Hz (4.7)} \\
 J_{5,9} &= 4.7 \text{ Hz (6.2)} \\
 J_{1,9} &= 0.8 \text{ Hz (1.5)}
 \end{aligned}$$

theses are derived. As before, it is suggested that such differences in coupling constants as are observed arise from subtle geometrical incongruities (with the understanding that this will also induce slightly different hybridizations, etc., at the carbon atoms concerned). Further exposition of the nmr spectral features of these and other analogous systems is beyond the intended scope of this paper.

Mechanism. It remains to provide a reasonable pathway by which the structure in Figure 1, 2,3,4-trichloropentacyclo[6.4.0.0^{2,4}.0^{3,10}.0^{5,9}]dodeca-6,11-diene (6), could arise from 1 and 2. The following sequence is considered most probable. Formation of 3 is



formulated as an SN2' displacement, although a direct SN2 displacement or the intervention of trichlorocyclopropenium ion (SN1) or something intermediate between these extremes cannot be excluded.¹⁹ Isomers of 3 may also be produced (as shown).²⁰ The interme-

(19) For analogous examples of nucleophilic attack by cyclononatetraene see ref 3a, e, f, and K. Hafner and H. Tappe, *Angew. Chem., Int. Ed. Engl.*, **8**, 593 (1969).

(20) Further elimination of hydrogen chloride from 3 to give dichlorocyclopropenylenecyclononatetraene is a plausible base-induced side reaction.¹⁹ Such a material was not isolated, and the experiment was designed to minimize its formation.

diate 5a (as well as 5b, most likely) may be produced by disrotatory ring closure of the anticipated initial product 3. There is ample evidence that this is a facile process which might precede intramolecular Diels-Alder addition (to give 4).⁸ Furthermore, there is evidence supporting the expectation that 5a should be a minor product relative to 5b.²¹ Only 5a can feasibly undergo an internal cycloaddition to give 6; the low yield observed is thus partially rationalized inasmuch as the balance of material presumably was converted to a polymeric substance which was indeed the major product. Recent results pertaining to the velocity of bridging in cyclononatetraene allow that the formation of 5a (5b) may represent the rate-limiting step in the overall formation of 6.²² On the other hand, a concerted ($\pi 2_s + \pi 2_s + \pi 2_s$) cycloaddition wherein 6 is formed directly from 3 cannot be ruled out. The fact that cyclononatetraene has an appreciable lifetime under the conditions occurring in this synthesis²² renders the latter pathway at least plausible.²³

A careful search of the chromatographic fractions in the region in which 6 was eluted failed to produce detectable amounts of 4 or any other tractable product. Examination of molecular models reveals that a concerted transition state leading to such a product is sterically difficult to achieve. We conclude that recourse to other synthetic approaches for the preparation of 4 is required.

Experimental Section

Synthesis. To a magnetically stirred mixture of 1.05 g of lithium (cut into small pieces in an argon stream and added directly to the reaction flask containing solvent and argon atmosphere) and 50 ml of tetrahydrofuran (freshly distilled from lithium aluminum hydride) was added 9.8 g (0.064 mol) of 9-chlorobicyclo[6.1.0]nona-2,4,6-triene⁹ in 30 ml of tetrahydrofuran. The ensuing reaction required intermittent cooling. The final black reaction mixture contained only a few particles of unreacted lithium. The above solution was added by means of a hypodermic syringe to a solution of 38.5 g of tetrachlorocyclopropane⁶ in 350 ml of tetrahydrofuran at 0° (ice bath, magnetic stirring, argon atmosphere) over a period of 15 min. The mixture was allowed to stand overnight, during which time the temperature gradually came to 25°, whereupon a few milliliters of ethanol was added and the solvent was removed on a rotary evaporator. The residual oil was treated with water and extracted with methylene chloride. The organic extract was dried with calcium chloride. It was evaporated under vacuum, and a small amount of residual tetrachlorocyclopropane was removed at 0.1 mm. The thick oily black residue was taken up in carbon tetrachloride and submitted to column chromatography on 80 g of silicic acid with carbon tetrachloride-chloroform gradient elution. Multiple fractions were taken at periodic time intervals; most failed to yield a characterizable component. However, several early fractions solidified upon evaporation. These were combined and recrystallized from hexane at -80° to give 0.4 g of crude product. Sublimation at 85° (0.1 mm) followed by recrystallization from pentane gave 0.35 g (2%) of 2,3,4-trichloropentacyclo[6.4.0.0^{2,4}.0^{3,10}.0^{5,9}]dodeca-6,11-diene: mp 152-154°; $\lambda_{\text{max}}^{\text{KBr}}$ 7.4 (m), 7.5 (m), 9.35 (m), 11.95 (m), 13.55 (s), 13.95 (s), and 14.2 (s) μ ; $\lambda_{\text{max}}^{\text{C}_6\text{H}_6}$ 210 nm ($\epsilon < 2500$); nmr (see Discussion section);²⁴ mass spectrum m/e (parent) 258 (260, 262, 264—Cl isotopes).

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Anal. Calcd for $C_{12}H_9Cl_3$: C, 55.53; H, 3.50; Cl, 40.98. Found: C, 55.55; H, 3.52; Cl, 40.87.

Crystal Data. Single crystals of trichloropentacyclododecadiene, $C_{12}H_9Cl_3$, were obtained by slow evaporation of solvent from ethanol solution. The crystals were needles along the b axis with prominent forms $\{010\}$ and $\{101\}$. Zero and higher level layer Weissenberg photographs about the b axis revealed systematic absences for which the space group was uniquely determined as $Pcab$. Accurate lattice parameters were determined by a least-squares analysis of 20 measurements with a General Electric quarter circle goniostat on an XRD-5 diffractometer. A density measurement of the crystals was made by flotation. There are eight units of $C_{12}H_9Cl_3$ per unit cell. A summary of crystal data is given in Table IV.

Table IV.

$a = 25.56 \pm 0.01 \text{ \AA}$	Habit
$b = 12.148 \pm 0.003 \text{ \AA}$	Needles along b
$c = 7.234 \pm 0.002 \text{ \AA}$	Prominent forms $\{010\}$, $\{101\}$
$\lambda(\text{Cu K}\alpha) = 1.5418 \text{ \AA}$	Absences
$V = 2246 \text{ \AA}^3$	$0kl; l = 2n + 1$
$\rho_{\text{calcd}} = 1.534 \text{ g cm}^{-3}$	$h0l; h = 2n + 1$
$\rho_{\text{measd}} = 1.539 \text{ g cm}^{-3}$	$hk0; k = 2n + 1$
$Z = 8$	Space group: $Pcab$

Intensity Measurements. Bragg intensities were measured on an XRD-5 G.E. diffractometer with Nb-filtered Mo $K\alpha$ radiation. The compound has a substantial vapor pressure; therefore, the crystal was coated with epoxy resin. As a result the background scatter was rather large and contributed strongly to an unfavorable signal to noise ratio for a number of weak reflections. Radiation damage was severe during data collection. Standard intensities changed systematically by as much as 50%. Data were collected for two crystals. A third set was collected with Cu $K\alpha$ radiation, but in this case radiation damage was intolerable; the crystal became a powder within 24 hr. The Mo $K\alpha$ radiation damage from these measurements dramatically limits the final accuracy of the

(24) Spectrum taken on a Varian HA-100 spectrometer operating in the frequency sweep mode.

structure. Diffraction intensity measurements were restricted to the upper octant (the crystal was mounted along b^*). The 2θ scan technique was employed.²⁵ Data were collected out to $2\theta = 42^\circ$ ($\sin \theta/\lambda = 0.5 \text{ \AA}^{-1}$). Three standard reflections were measured every hour. It was found that the different standards exhibited similar decreases in the net counts.

A quadratic function of time was determined from the distribution of standard reflections. The empirical curve was then used to scale the measured intensities as a function of their sequence. The procedure used here assumes that the standards are representative of the effect of radiation damage to the true structure factors. A preferable treatment has been reported by Ibers²⁶ where a scale factor for all reflections was given a quadratic time dependence and the corresponding parameters were refined along with the atomic structural parameters. At the time this structure was refined, however, the Ibers' procedure was not known to us. Although the conventional R factor would be probably lower by such a treatment, the gross structural results would indeed be the same. The intensity data of the two crystals were put on the same relative scale according to the method of Hamilton, *et al.*²⁷ Only reflections with net intensities 1.4 times the estimated standard error were used for the crystal structure analysis. Altogether 520 reflections were selected. The weights for each reflection were estimated by the procedure of Stewart and Jensen.^{28,29}

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Nuclear Magnetic Resonance Spectroscopy. Ring Inversion in 1,1-Difluorocyclodecane¹

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Abstract: Rates of ring inversion of 1,1-difluorocyclodecane were obtained from line-shape changes in the low-temperature ¹⁹F nmr spectra. At -135° , the free energy of activation was 5.7 kcal/mol. The results are interpreted in terms of a boat-chair-boat conformation. Possible pathways for effecting ring inversion are discussed.

Although nmr spectroscopy has been found to be well suited for conformational studies of many cyclic compounds,³ this method has been used in relatively few cases for the investigation of ten-membered

rings. Compounds which have been studied include *trans*-cyclodecene- d_8 ⁴ and several *cis,cis*-1,6-cyclodecadienes.⁵ The temperature dependence of the nmr spec-

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