Organic and Biological Chemistry

Decachlorotetracyclo$[5.2.1.0^{2,6}.0^{3,10}]$deca-4,8-diene. A New Tetracyclic Ring System

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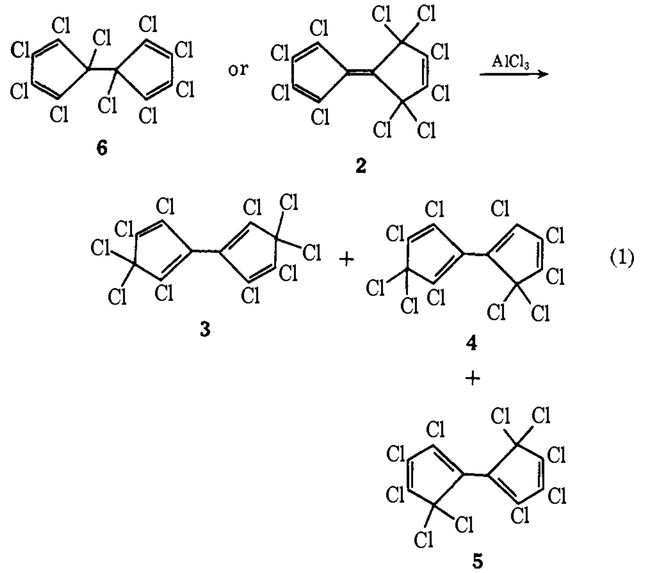
Abstract: Treatment of decachloro-1,1′-dihydrofulvalene with 2–3 equiv of $SbCl_3$ and a trace of $SbCl_5$ in dichloromethane at room temperature for 3–4 days gives a new $C_{10}Cl_{10}$ isomer, **1**, mp 173–174°, to which the decachlorotetracyclo$[5.2.1.0^{2,6}.0^{3,10}]$deca-4,8-diene structure is assigned on the basis of spectral and chemical evidence. Photolytic chlorination of **1** leads stereospecifically to the known *endo*-dodecachlorodicyclopentadiene (**7**). Catalytic hydrogenation of **1** gives a 90–95% yield of 1,2,3,6,7,10-hexachlorotetracyclo$[5.2.1.0^{2,6}.0^{3,10}]$decane (**8**), whose spectral and physical properties are fully consistent with the proposed structure. Treatment of **8** with Li–*tert*-BuOH–THF at reflux gives tetracyclo$[5.2.1.0^{2,6}.0^{3,10}]$decane (**9**) in 65% yield. Mechanisms for the formation of **1** and **7** are proposed and discussed.

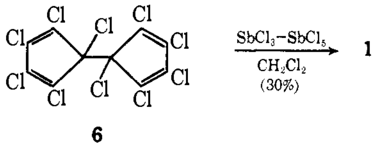
Recently we reported the thermal and Lewis acid catalyzed rearrangements of a number of $C_{10}Cl_{10}$ isomers, all having the dihydrofulvalene carbon skeleton, to give a mixture of other $C_{10}Cl_{10}$ isomers having the same carbon skeleton[2] (eq 1). During these studies we noted that increasing the amounts of Lewis acid could change the products obtained from a given isomerization. For example, whereas treatment of decachloro-2,5-dihydrofulvalene (**2**) with a catalytic amount of aluminum chloride led to the equilibrium mixture of $C_{10}Cl_{10}$ isomers **3**, **4**, and **5**, use of more than 1 equiv of catalyst led exclusively to **5**.[2a] The most interesting case in which this type of phenomenon occurred, however, was in the rearrangement of decachloro-1,1′-dihydrofulvalene (**6**). Treatment of this compound with more than 1 equiv of Lewis acid led to a new $C_{10}Cl_{10}$ isomer (**1**) whose structure was significantly different from those of the isomers isolated previously. The structure determination and chemistry of this interesting new isomer are the topics of this paper.



Isolation and Physical Properties

If **6** is treated with a catalytic amount of $AlCl_3$ in dichloromethane at room temperature for 1–2 days, and the reaction mixture is then hydrolyzed, a mixture of **3**, **4**, and **5** results.[2] When **6** is treated with 1 or more equiv of $AlCl_3$ under similar conditions, however, the oil obtained after hydrolysis shows a new band in the infrared spectrum at 1610 cm^{-1}, not present in the mixture of **3**, **4**, and **5**. Chromatography of this product mixture on neutral alumina with pentane leads to the isolation of a small amount ($\sim$5%) of a white crystalline $C_{10}Cl_{10}$ (**1**), mp 173–174°.

A number of Lewis acid–solvent mixtures were tried in order to improve the rather low yields of **1**. Because the formation of **1** from **6** seemed to require substantial ionization of **6**, strong, soluble Lewis acids were used which might increase cation formation. However, in most cases (BCl_3, $AlCl_3$–SO_2, $SbCl_3$–heat, $SbCl_3$–CH_2Cl_2, $SbCl_5$–CH_2Cl_2) either no improvement in yield occurred or the desired reaction did not take place at all. But with 2–3 equiv of $SbCl_3$ and a trace (0.05–0.10 equiv) of $SbCl_5$ in dichloromethane at room temperature for 3–4 days, the conversion to **1** was greatly improved to $\sim$30% compared with only $\sim$5% using $AlCl_3$ (based on rough quantitative infrared measurements). The only other material detected in the $SbCl_3$ reactions was the starting material **6**.



The infrared spectrum of **1** is unique for the known $C_{10}Cl_{10}$ isomers in that it shows a single olefinic absorp-

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(2) (a) R. M. Smith and R. West, *J. Org. Chem.*, **35**, 2681 (1970); (b) V. Mark and E. D. Weil, *ibid.*, **36**, 676 (1971).

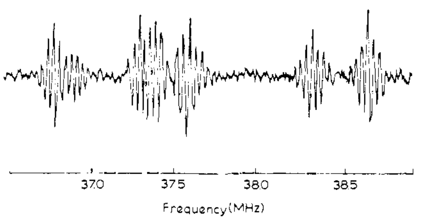


Figure 1. Nuclear quadrupole resonance spectrum of **1**.

tion band at 1610 cm^{-1} (*cf.* the spectra of **2**–**6**[2] which all show at least two olefinic absorptions), indicating a fairly high degree of symmetry in this molecule. In addition this band occurs at relatively high frequencies for chlorine-substituted double bonds, indicating the presence of only isolated olefinic moieties. Furthermore, **1** probably lacks *gem*-dichloride groups since the 750–850-cm^{-1} region of the spectrum is nearly devoid of absorptions.[2b]

In the ultraviolet, **1** shows only two bands, at 260 (log ε 3.54) and 220 nm (log ε 4.23). This spectrum is again unique for the known $C_{10}Cl_{10}$ isomers (**2**–**6** all have at least one λ_{max} above 300 nm) and suggests that **1** cannot possibly have the dihydrofulvalene skeleton. Instead this spectrum seems more consistent with a structure having isolated, olefinic linkages.[3]

The ^{13}C nmr spectrum of **1** (Table I) indicates the presence of five symmetry-different pairs of carbon atoms, two olefinic sets and three aliphatic sets. **1** therefore *must* be tetracyclic, and must have either C_s or C_2 symmetry. The ^{35}Cl nuclear quadrupole resonance (nqr) spectrum of **1** (Figure 1) which indicates the presence of five symmetry-different pairs of chlorines is consistent with this analysis. This spectrum is relatively complicated in the lower frequency region so that a more detailed analysis is not possible, but the resonant frequencies observed for **1** are consistent with a structure containing only vinylic and bridgehead chlorines, with no *gem*-dichloro groups.

Table I. Carbon-13 Nuclear Magnetic Resonance Spectra of Selected Chlorocarbons

Compd	Olefinic carbons[a]	Aliphatic carbons[a]
1	59.1, 64.1	101.6, 107.2, 112.0
5[b]	54.9, 54.5, 60.4, 64.7	109.4
6[b]	60.8, 61.8	119.7
C_5Cl_6	59.2, 63.8	110.6

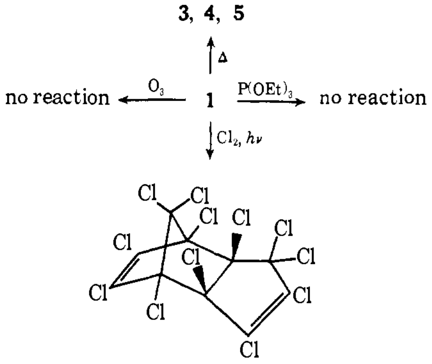
[a] Parts per million upfield from CS_2. [b] Reference 2b.

In view of the preceding evidence the mass spectrum of **1** is unexpected in that it is nearly identical with that of decachloro-3,3′-dihydrofulvalene (**3**). The cracking patterns shown by these two compounds are virtually identical, only the peak intensities being somewhat different.

Chemical Characterization

The similarity between the mass spectra of **1** and **3** led us to suspect that **1** was undergoing isomerization in the heated inlet of the mass spectrometer. A small amount of **1** was heated above its melting point (~200°) for 10–15 min. The infrared spectrum of the resulting yellow oil was identical with that of the previously reported[2] $C_{10}Cl_{10}$ isomer mixture. On the other hand, treatment of **1** with $AlCl_3$ (3.5 equiv) led only to some reversion to the starting material **6**. The spectral data for **1** thus require that this compound not have the dihydrofulvalene skeleton, but chemical evidence demands that **1** be closely related structurally to previously known $C_{10}Cl_{10}$ isomers.

Further chemical evidence supports the contention that **1** is not a decachlorodihydrofulvalene. For example, whereas triethyl phosphite readily converts **6** to octachlorofulvalene[4,5] and causes significant rearrangement to decachloro-1,2′-dihydrofulvalene[2a] to **3**, **4**, and **5**, $C_{10}Cl_{10}$ **1** is completely inert to this reagent under identical conditions. Furthermore, whereas **2** is destroyed by ozone at −78° in a few hours, **1** is totally unreactive under the same conditions. In fact, **1** does not even react with aqueous $KMnO_4$–KIO_4 in *tert*-BuOH over a period of 24 hr at room temperature.



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Photolytic chlorination of **1** in CCl_4 at room temperature provides *endo*-dodecachlorodicyclopentadiene[2b] (dodecachloro-*exo*-3a,4,7,*exo*-7a-tetrahydromethanoindene (**7**)) (60% after chromatography), further relating the structure of **1** to that of a known compound. No other chlorocarbon products (including the *exo*-perchlorodicyclopentadiene[2b]) were isolated or detected in this reaction. Since **7** might have resulted from photolytic rearrangement of **1** prior to attack by chlorine, **1** was irradiated in the absence of chlorine as well. Only **1** was recovered from the experiment.

1 reacts smoothly with hydrogen over Pd/C at room temperature and 900 psi over 50 hr to give a high yield (~90% after purification) of a white readily sublimable camphoraceous solid, $C_{10}H_8Cl_6$ (**8**) (mp 290–310° dec).

As expected **8** shows no olefinic absorptions either in the infrared or the ultraviolet, and the pmr spectrum of **8** (Figure 2) shows only a complex absorption pattern in the τ 7.4–8.1 region. At first glance the pmr spectrum of **8** seems consistent with a structure having isolated $-CH_2CH_2-$ groups and all of the chlorines attached at bridgehead positions (*cf.* the spectra of derivatives of 1,2,3,4,7,7-hexachloronorbornene[6]). More important is the fact that this spectrum is not symmetrical; thus the $-CH_2CH_2-$ groups in **8** (which could easily arise from hydrogenation and dechlorination of the isolated double bonds of **1**) do not give rise to an A_2B_2 or even an AA′-

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(3) Tricyclo[3.3.0.$0^{2,6}$]octa-3,7-diene shows uv absorption *above 300* nm, with log ε ~2 at 300 nm: J. Meinwald and H. Tsuruta, *J. Amer. Chem. Soc.*, 92, 2579 (1970).

(4) R. M. Smith and R. West, unpublished results, The University of Wisconsin.

(5) V. Mark, *Tetrahedron Lett.*, 333 (1961).

(6) K. L. Williamson, *J. Amer. Chem. Soc.*, **85**, 516 (1963).

BB′ pattern[7] as would be expected if the element of symmetry present in **1** (or in **8**) passed through the C=C (or $-CH_2CH_2-$) moieties. Hence *each proton in each of the* $-CH_2CH_2-$ *groups of* **8** *must be symmetrically distinct.*

The lack of double bonds in **8**, coupled with its known molecular formula, demands that **8** be tetracyclic. This evidence is important because a tetracyclic structure for **1** was also deduced from its ^{13}C nmr and nqr spectra. This suggests that no C–C bonds are broken during the hydrogenation of **1**. That **8** in fact has the same carbon skeleton as **1** is strongly implied from the mass spectra of these compounds, both of which show only C_{10} and C_5 fragments at higher *m/e* values. In the case of **8** rearrangement of the sample in the mass spectrometer cannot occur; heating a sample of **8** at 210° for 0.5 hr produced no change in its infrared spectrum.

Attempts to remove all of the chlorines originally present on **1** by reduction with Na-*tert*-BuOH–THF[8] failed, and only tarry materials were obtained even at temperatures below 0°. However, treatment of **8** with Li-*tert*-BuOH–THF[9] at reflux produced the desired saturated hydrocarbon $C_{10}H_{14}$ (**9**), bp 20° at 0.01 Torr, in good yield (65%).

Unfortunately little can be deduced about the structure of **9** from its spectral properties. The infrared spectrum of **9** shows primarily C–H stretching and bending modes, although bands of moderate intensity observed near 1300 and 1100 cm^{-1} are similar to those in the spectra of **8** and **1**, respectively. The mass spectrum of **9** shows progressive loss of one-carbon fragments as CH_3 or CH_2 units, unlike the behavior of **1** and **8**; however, the presence of chlorine on most fragments from the latter compounds may easily account for this difference. However, a symmetrical structure for **9** is suggested by the fairly strong (relative intensity, 60%) P/2 peak found.

Structure Determination and Mechanism of Formation

The structural evidence on **1** can be summarized as follows: (1) **1** is tetracyclic and has two isolated double bonds; (2) **1** probably has no highly strained bonds or *gem*-dichloride groups; (3) **1** has either C_2 or C_s symmetry, but the elements of symmetry do not pass through the double bonds; (4) **1** is structurally related to the known decachlorodihydrofulvalenes and to *endo*-perchlorodicyclopentadiene (**7**); (5) during catalytic hydrogenation only the double bonds of **1** are hydrogenated and dechlorinated. Although numerous structures for **1** fit these data, one seems most likely based on consideration of its probable mechanism of formation. This is shown in Scheme I.

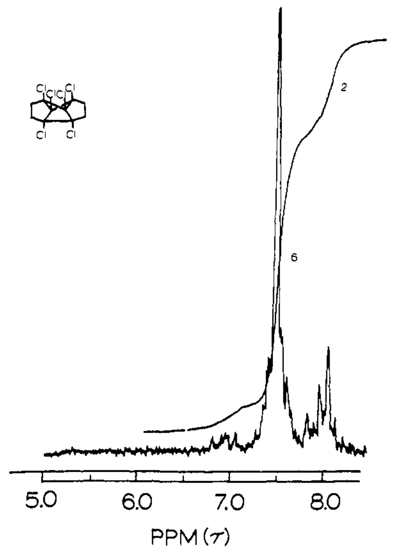
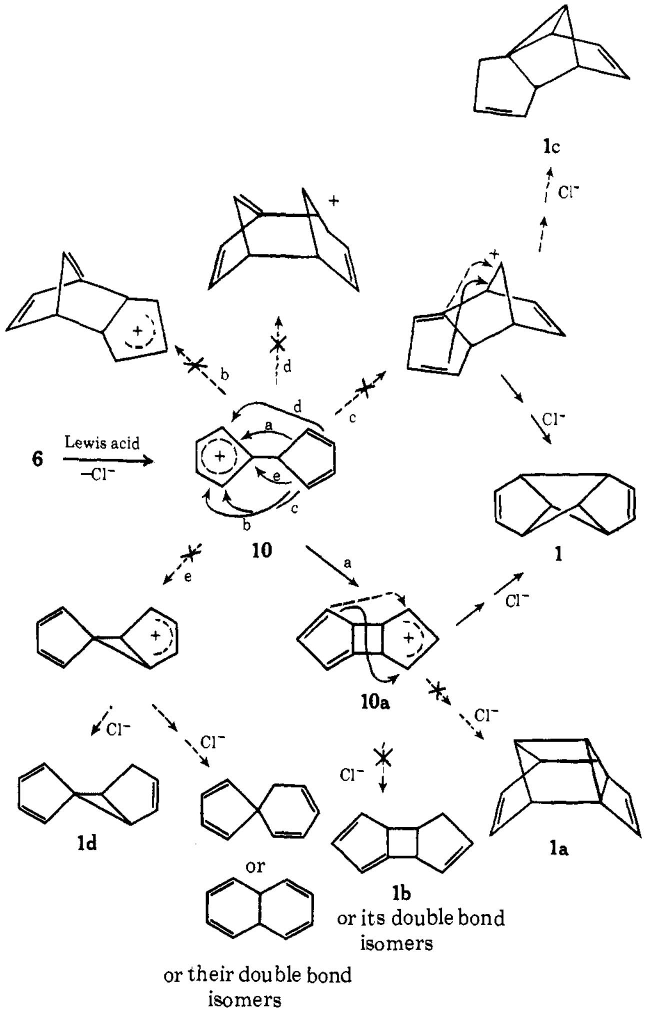


Figure 2. 60-MHz nmr spectrum of **8**.

Scheme I. Probable Mechanisms for the Formation of **1** (All Species are Fully Chlorinated)



Ring closure by paths b and d can be excluded since the product ions are in flagrant violation of Bredt's rule.[10] Closure *via* path c also seems unlikely, because the electron density at the "inside" positions of a 1,3-butadiene system is significantly less than at the "outside" positions;[11] thus, the "inside" positions are less likely to undergo electrophilic attack, especially if alternative reaction pathways for the molecule exist.

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[7] (a) K. B. Wiberg and B. J. Nist, "Interpretation of NMR Spectra," W. A. Benjamin, New York, N. Y., 1962, p 309 ff. (b) In particular the pmr spectrum of 1,4,7,7-tetrachloro-2,2,3,3-tetradeuterionorbornane is symmetrical even though this spectrum is very complicated: A. P. Marchand, N. W. Marchand, and A. L. Segre, *Tetrahedron Lett.*, 5702 (1969).

[8] P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

[9] P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind.* (*London*), 405 (1960).

[10] The most strained bicyclic hydrocarbon known having a double bond attached to a bridgehead position is bicyclo[3.3.1]non-1-ene: J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **89**, 5965 (1967); J. R. Wiseman, *ibid.*, **89**, 5966 (1967).

[11] A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 51.

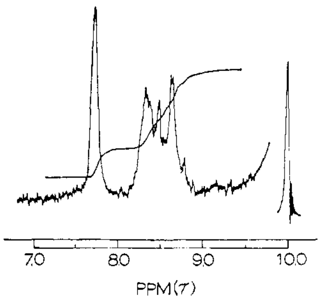


Figure 3. 60-MHz nmr spectrum of **9**.

Ring closure *via* path e is conceivable, although this leads to strained or extensively rearranged products *via* a highly strained intermediate ion. Both kinds of products obtained by this pathway appear to be inconsistent with all of the evidence listed above, so that this route is unlikely as well.

Ring closure by means of path a seems most reasonable. First, such a reaction appears to require the least motion[12] of the entire molecule. Second, a similar ring closure reaction (albeit *via* a free-radical intermediate) occurs in the photolytic chlorination of the starting material **6**.[2b]

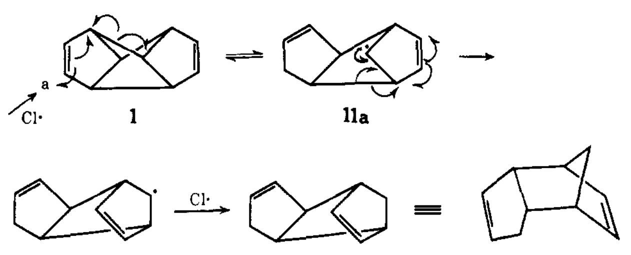
The intermediate cation **10a** has only three possible modes of reaction: (1) rearrangement and abstraction of chloride ion from the Lewis acid anion to give a tricyclic product **1b** or one of its double bond isomers; (2) closure at positions symmetrically related by the quasi-σ_v plane to give **1a**; or (3) closure at positions symmetry related by the quasi-C_2 axis to give **1**. Structures related to **1b** are inconsistent with the fact that **1** is tetracyclic. Structure **1a** is inconsistent with the ^{13}C nmr and nqr spectra of **1** in that it should show only three different types of carbon (and chlorine) atoms. Structure **1**, on the other hand, appears to be fully consistent with all of the spectral evidence presented; it has a single C_2 axis of symmetry, two isolated double bonds *which are not bisected by the axis of symmetry*, and no *gem*-dichloride groups.[13]

On the basis of this structure much of the chemistry of **1** is readily explainable. Thermal rearrangement of **1** to give a mixture of **3**, **4**, and **5** can occur *via* an essential reversal of the ring-closure reactions which led to its formation, since chlorocarbon **6** is known to yield readily this mixture of its double bond isomers.[2] The failure of **1** to react with triethyl phosphite is reasonable since there are no vicinal chlorines capable of being eliminated without substantial σ-bond breaking. Its failure to react with ozone indicates that both double bonds must bear chlorine substituents.[14]

The chlorination of **1** to give exclusively *endo*-perchlorodicyclopentadiene (**7**) is curious, because structure **1** would not be expected *a priori* to give rise only to the endo isomer. The most plausible point of attack by a chlorine atom on **1** is on either of its equivalent double bonds, since all sp^3 carbons occupy bridgehead positions. Attack on sp^2 carbon a (Scheme II, sequence A) allows bond rupture of the strained cyclobutane ring by a β scission step and results in the formation of species **11a**. In this the radical carbon points toward the inside of the molecule and so cannot capture chlorine from the outside to yield *exo*-dodecachlorodicyclopentadiene. To form the latter, inversion at the radical center would have to take place, passing through a strained, planar transition state. Instead, a second β scission followed by a bond shift to give **11b** may be more favored. The latter upon capturing chlorine gives **7**.

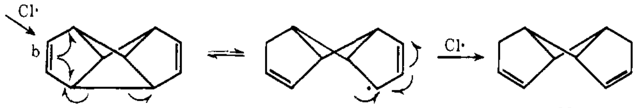
Scheme II. Alternate Pathways for the Chlorination of **1**

Sequence A



1 **11a** **11b** **7**

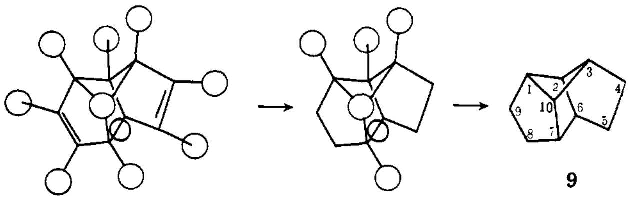
Sequence B (not observed)



1 **12**

The alternate path (Scheme II, sequence B) in which chlorine adds to the other sp^2 carbon, b, of the double bond would result in the formation of structure **12**, a known chlorocarbon.[2b] The complete absence of the latter in the chlorination mixture of **1** indicates that the exclusive photochlorination pathway is one which results in the disappearance of the most strained ring system, possibly as illustrated by sequence A of Scheme II.

Elimination of four of the chlorines of **1** upon hydrogenation is fully understandable on the basis of the proposed structure. Catalytic hydrogenation of **1** removes the vinylic chlorines and reduces both double bonds by a sequence of addition and elimination steps to give the expected $C_{10}H_8Cl_6$ (**8**). Similar behavior, in which the bridgehead chlorines also remain unaffected, is observed in the catalytic hydrogenation of 1,2,3,4-tetrachloronorbornene.[15] The physical properties of **8** (its high melting point and high volatility) as well as its pmr spectrum are consistent with this structure for **8**. The pmr spectrum (Figure 2) shows an unsymmetrical pattern (probably ABCD) and a lack of -CHCl- moieties. In addition, **8** shows no tendency to lose HCl either by treatment with methanolic KOH or in the mass spectrometer (the P − HCl peak from **8** is at least one order of magnitude less intense than either the P − Cl or the P − H$_2$Cl peaks).



1 **8** **9**

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[12] J. Hine, *J. Amer. Chem. Soc.*, **88**, 5525 (1966).

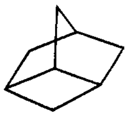
[13] Structure **1** is also less strained than the other possible tetracyclic structures **1a**, **1c**, or **1d**. The structure somewhat resembles a loving cup, and we suggest the trivial names "tropane" for the saturated hydrocarbon **9** and "perchlorotrophadiene" for **1**.

[14] W. K. Johnson and V. Mark, *J. Org. Chem.*, **26**, 4105 (1961).

[15] C. F. Wilson and J. C. Zajacek, *ibid.*, **29**, 2209 (1964).

Hydrogenolysis of **8** by more drastic means[8,9] apparently gives rise to the previously unknown hydrocarbon **9**, tetracyclo[5.2.1.$0^{2,6}$.$0^{3,10}$]decane. The pmr spectrum of **9** (Figure 3) is entirely consistent with the proposed structure. The broad singlet at τ 7.72 (4 H) must arise from the bridgehead protons at positions 1, 3, 6, and 7. Although these protons are not symmetrically equivalent, they are all essentially bridgehead protons on a "bicyclo[2.2.1]heptane" system, and would be expected to have similar chemical shifts. Moreover, they are clearly distinguishable from the bridgehead protons at positions 2 and 10. Absorptions in the same region for similar types of protons are observed in the pmr spectra of both **13** (τ 7.6–7.8)[16] and **14** (τ 7.62–7.95).[17] Furthermore, all of the bridgehead protons in **15** occur as a singlet, as observed here.[18] The lack of resolvable coupling (on the 500-cps scans) between the bridgehead and methylene protons in both **9** and **15** must arise[19] because of the large dihedral angles (60–90°) between the bridgehead protons and their immediate neighbors.

The multiplet occurring between τ 8.3 and 8.7 (10 H) in the spectrum of **9** must then be composed of absorptions from the methylene protons and the bridgehead protons at positions 2 and 10. These latter protons are expected at higher fields than those at the other bridgehead positions because they are more clearly "cyclobutane" protons. A similar shift is noted, for example, in comparing the pmr spectra of **14** and **15** (τ 7.8 *vs.* 8.18, respectively). Finally, the chemical shifts of the methylene protons in **9** are essentially the same as those observed in the spectra of **13**–**15**.[16–18]



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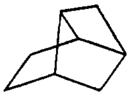

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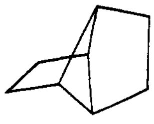

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Experimental Section

General. Decachloro-1,1′-dihydrofulvalene (**6**) was prepared by the method of McBee, Idol, and Roberts,[20] mp 122–123° (lit.[20] 122°). Infrared spectra were obtained in CCl_4 and CS_2 on Perkin-Elmer Model 237 and 437 recording spectrometers. Ultraviolet spectra were recorded in cyclohexane on a Cary Model 14 spectrophotometer. Nuclear quadrupole resonance spectra were obtained on a Wilks NQR-1A commercial spectrometer, using a Northeastern Model 14-21C electronic counter to measure frequencies. Proton magnetic resonance spectra were determined in CCl_4 on a Varian A-60A spectrometer, using tetramethylsilane (TMS) as internal standard. Mass spectra were recorded on a CEC Model 21-103C mass spectrometer equipped with heated inlet, and an AEI MS-902 high-resolution mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Decachlorotetracyclo[5.2.1.$0^{2,6}$.$0^{3,10}$]deca-4,8-diene (1). Decachloro-1,1′-dihydrofulvalene (22.0 g 0.046 mol) was dissolved in 80 g (60 ml) of dichloromethane and 30.0 g (0.131 mol) of *freshly opened* antimony trichloride was added. The mixture was stoppered and stirred until most of the $SbCl_3$ had dissolved. Antimony pentachloride (0.5 ml, 1.25 g, 0.004 mol) was added, whereupon the reaction mixture immediately turned dark. The reaction flask was quickly stoppered, and the mixture was stirred at room temperature for 3–4 days. At the end of this time approximately 150 ml of water was added with stirring until the entire reaction mixture took on the consistency of cottage cheese. An additional 50 ml of dichloromethane was then added, and the organic layer was decanted. The remaining semisolid material was extracted further with dichloromethane (~500 ml) until the organic portion was colorless. The dichloromethane solution was then washed with water and dried over anhydrous calcium chloride. Removal of the solvent by rotary evaporator gave a brownish-yellow solid which showed mainly bands due to starting material plus a prominent new band at 1610 cm^{-1} in the infrared. Pentane (22 ml) was added to this solid; 14 ml of the resulting solution was placed on a 3.5 ft × 0.75 in. column of neutral alumina (A. H. Thomas) and eluted with pentane. Preceding the yellow band due to **6** was **1**, average yield 0.6 g (mp 173–174°). Further pentane was added to the remaining solid, and chromatography was repeated three times. The total yield of **1** was 2.5 g (12% based on total starting material; 20% based on unrecovered starting material). The remaining solid was recrystallized and used again. *Anal.* Calcd for $C_{10}Cl_{10}$: C, 25.30; H, 0.00; Cl, 74.70. Found: C, 25.36; H, 0.00; Cl, 74.63. The mass spectrum of **1** showed a weak molecular ion peak at *m/e* 470; calcd intensities for 10Cl,[21] P + 2, 326; P + 4, 472; P + 6, 403; P + 8, 218; obsd intensities, P + 2, 346; P + 4, 520; P + 6, 406; P + 8, 220. Ir spectral data are: $\nu_{\max}$ (CCl_4,CS_2) 1612 (s), 1228 (s), 1194 (s), 1182 (s), 1163 (s), 1102 (s), 1097 (s), 1084 (s), 1062 (m), 1033 (s), 990 (m), 936 (m), 878 (w), 826 (w), 746 (w), 710 (s), 670 (m), 664 (m), 652 (s), 617 (s), and 552 (s) cm^{-1}. The nqr spectrum of **1** (Figure 1) showed resonances at 36.78, 37.30, 37.41, 37.62, 38.32, and 38.60 MHz in an approximate area ratio of 2:1:1:2:2:2.

1,2,3,6,7,10-Hexachlorotetracyclo[5.2.1.$0^{2,6}$.$0^{3,10}$]decane (8). **1** (1.0 g, 2.2 mmol), 2.0 g of sodium acetate, 0.5 g of 10% Pd/C, and 100 ml of absolute ethanol were placed in a high-pressure hydrogenation bomb (bomb volume, 300 ml), and the pressure was raised to 900 psi. The bomb was shaken for 50 hr at room temperature and emptied and washed thoroughly with absolute ethanol. The reaction mixture was filtered to remove catalyst, diluted with 200 ml of water, and extracted with 500 ml of pentane in small portions. The catalyst was washed with 100 ml of pentane and the organic layers were combined and washed with 250 ml of saturated NaCl solution, and then dried over anhydrous calcium chloride. Removing the solvent gave nearly 1 g of solid material, which was sublimed under high vacuum (~5 μ) at 50–60° to give 0.67 g (87%) of a colorless, waxy solid, **8**, mp 290–310° dec. *Anal.* Calcd for $C_{10}H_8Cl_6$: C, 35.15; H, 2.36; Cl, 62.49. Found: C, 35.08; H, 2.40; Cl, 62.49. The mass spectrum of **8** showed a molecular ion peak at *m/e* 338; calcd intensities for 6Cl,[21] P + 2, 196; P + 4, 160; P + 6, 70; obsd intensities, P + 2, 188; P + 4, 147; P + 6, 59. Ir spectral data are: $\nu_{\max}$ (CCl_4) 2995 (w), 2980 (w), 2954 (w), 2875 (w), 1456 (m), 1440 (m), 1313 (s), 1301 (w), 1287 (w), 1277 (m), 1248 (w), 1212 (m), 1157 (w), 1149 (w), 1134 (w), 1105 (m), 1091 (s), 1058 (s), 1047 (s), 991 (m), 979 (w), 949 (s), 780 (m), 755 (m), 710 (w), 690 (w), 648 (m), 611 (w), 598 (w), 527 (m), and 503 (m) cm^{-1}. **8** showed no absorptions in the ultraviolet above 200 nm, and attempts to obtain an nqr spectrum for this compound were not successful.

Photolytic Chlorination of 1. A solution of 0.5 g of **1** in 125 ml of CCl_4 was placed in a three-necked, 250-ml round-bottomed flask to which was attached a chlorine inlet and outlet and a stoppered reflux condenser. Chlorine was bubbled through the solution at a rate of 1–2 ml/sec, while the reaction flask was cooled in an ice–water bath and exposed to an external mercury vapor lamp. After 8 hr chlorine admission was stopped, and the solvent and excess chlorine were blown off under nitrogen. An oily, white solid remained (0.8 g) to which was added 5 ml of pentane. This solution was chromatographed on a 2 ft × 0.5 in. column of neutral alumina with pentane to give 0.33 g (58%) of **7** as white crystals, mp 237–240° (lit.[2b] 237–239°). The infrared spectrum of this product was identical with that of an authentic sample of *endo*-dodecachlorodicyclopentadiene, and a mixture of this product with authentic material showed no melting point depression.

Irradiation of 1. A solution of 0.35 g of **1** in 40 ml of CCl_4 was placed in a Vycor flask and irradiated with a 100-W G.E. mercury lamp, placed about 4 cm under the flask for 17 hr. Heat from the lamp kept the solvent refluxing during this period. On evaporation the resulting light amber solution yielded 0.32 g of residue, which gave an ir spectrum identical with that of **1**.

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Thermal Rearrangement of 1. About 20 mg of **1** was sealed in a melting point capillary and heated at 180° for 0.5 hr. The resulting yellow oil was extracted into dichloromethane, and the solvent was blown off. The infrared spectrum of this product was identical in every respect with those obtained from the thermal rearrangements of the decachlorodihydrofulvalenes.[2]

Isomerization of 1 by $AlCl_3$. To a solution of 0.2 g (0.4 mmol) of **1** in 2 ml of CH_2Cl_2 was added 0.2 g (1.4 mmol) of fresh $AlCl_3$, and the resulting solution was stirred for 18 hr at room temperature. The color of the solution turned amber, then gradually darker, and finally became deep purple. Water was added to the reaction mixture, causing the dichloromethane layer to turn amber again. Separation, washing, drying, filtering, and stripping the solvent resulted in the formation of a crystalline mass whose infrared spectrum indicated the presence of considerable amounts of **6** and lesser amounts of **3** and **4** in addition to a large amount of starting material.

Isomerization of 3 by $SbCl_3$. To a solution of 1.12 g of **3** and 1.5 g of $SbCl_3$ in 6.85 g of CH_2Cl_2 was added dropwise 0.18 g of $SbCl_5$, resulting in the formation of an orange colored solution. After standing at room temperature for 3 days, the reaction mixture was poured into water, extracted with CH_2Cl_2, washed, and dried, and the solution was evaporated to yield 1.02 g of a yellow solid, the ir of which indicated it to be a mixture of **3**, **4**, and **5**. No **1** was detectable in the crude reaction product, which was exactly identical with the one resulting when $AlCl_3$ was used as the Lewis acid.[2b]

Isomerization of 4 by $SbCl_3$. Repetition of the preceding experiment using **4** instead of **3** as the chlorocarbon substrate resulted in a reaction mixture identical with that given by **3**.

Attempted Dechlorination of 1. A solution of 0.4 g (0.9 mmol) of **1** and 0.15 g (0.9 mmol) of triethyl phosphite in a small amount of pentane was stirred at room temperature for 1 hr. Absolutely no color change was noted. Removing the solvent and the triethyl phosphite on a rotary evaporator gave a solid which was identified by infrared spectroscopy to be exclusively starting material. Two control experiments with decachloro-1,1′-dihydrofulvalene (**6**) and decachloro-1,2′-dihydrofulvalene[2a] gave rise to very marked color changes in a much shorter period of time. The reaction of **6** with $P(OEt)_3$ gave a good yield of octachlorofulvalene.[5]

Attempted Oxidation of 1. (A) By Ozone. Ozone (as a solution in Freon; Matheson Co.) was admitted to a solution of 0.5 g (1.1 mmol) of **1** in 80 ml of dichloromethane over a period of 4 hr while the reaction flask was cooled to −78° with a Dry Ice-acetone bath. During the fifth hour the temperature was allowed to warm slowly to −20°. The solution remained blue during the entire reaction. A solution of 0.5 g of sodium iodide in 10 ml of glacial acetic acid was then added slowly with stirring over 0.5 hr; during this time the temperature rose to room temperature. Excess aqueous sodium thiosulfate was then added. The organic layer was separated, washed with water, aqueous sodium bisulfite, and again with water, and then dried over anhydrous magnesium sulfate. Removing the solvent gave 0.45 g (90% recovery) of a white solid which was identical with starting material.

(B) By Aqueous Permanganate–Periodate. To a suspension of 0.50 g (1.1 mmol) of **1** in 450 ml of *tert*-butyl alcohol and 750 ml of water was added 300 ml of a stock solution of permanganate–periodate (11.2 g of potassium periodate and 0.20 g of potassium permanganate in 500 ml of water), followed by solid potassium carbonate until the pH of the solution (as measured by pH paper) was between 8 and 9. The reaction flask was stoppered, and the mixture was stirred at room temperature for 20 hr. Concentrated HCl (15 ml) was added, followed by solid sodium bisulfite until the color of the solution became light yellow. The solution was then made basic with sodium hydroxide, and the alcohol was distilled off under reduced pressure. Concentrated HCl was added to the residue until the solution became nearly colorless. This solution was extracted with 300 ml of pentane, which was subsequently washed with water and dried over anhydrous calcium chloride. Evaporation of the solvent gave an off-white solid (0.4 g, 80% recovery) which was identical with starting material.

Tetracyclo[5.2.1.$0^{2,6}$.$0^{3,10}$]decane (9). A solution of 1.0 g of **8** (3 mmol) and 2.6 g of *tert*-butyl alcohol (36 mmol) in 20 ml of tetrahydrofuran was prepared and stirred under argon. To this solution was added 0.72 g (90 mg-atom) of lithium wire which had previously been hammered as thin as possible. This mixture was refluxed under argon for 24 hr, and then stirred at room temperature for an additional 24 hr.

The reaction mixture developed a tan color. The product mixture was poured onto 100 ml of ice and then extracted with 300 ml of pentane in small portions. The pentane layer was washed with water and dried over anhydrous calcium chloride. Removing the solvent on a rotary evaporator gave 0.7 g of a yellow camphoraceous oil This oil was distilled under high vacuum (5–10 μ); two fractions were obtained: −80 to −20° (solvent) and −20 to +20° (0.28 g of volatile products). Gas chromatographic analysis (on a 25-ft SE-30 prep column, column temperature 150°) showed this latter fraction to consist of 92% **9**, 5% of an unidentified material, and 3% of a mixture of monochlorinated compounds (characterized only by mass spectroscopy). The yield of crude **9** was 0.26 g (65%). *Anal.* Calcd for $C_{10}H_{14}$: C, 89.5; H, 10.5. Found: C, 90.0; H, 9.8. The mass spectrum of **9** showed a molecular ion peak at *m/e* 134; calcd intensities for 10 C,[21] P + 1, 11.0; obsd intensities, P + 1, 11.6. Ir spectral data were: ν_{max} (CCl_4) 2940 (broad s), 2910 (s), 2870 (s), 1463 (m), 1449 (m), 1349 (w), 1328 (w), 1302 (m), 1298 (m), 1287 (m), 1265 (m), 1237 (w), 1209 (m), 1187 (w), 1089 (m), 1020 (w), 988 (w), 960 (w), 924 (w), 882 (w), 860 (w), 820 (w), 778 (w), 751 (m), 569 (w), 552 (w).

Attempted Reduction of 1. (A) With Na-*tert*-BuOH–THF. To a solution of 0.95 g of **1** (2 mmol) and 4.5 g (60 mmol) of *tert*-butyl alcohol in 15 ml of tetrahydrofuran was added, while cooling to −10° with an ice-acetone bath, 2.8 g (120 mg-atoms) of finely chopped sodium metal. This mixture was stirred under nitrogen for 18 hr at −10 to 0°; the reaction mixture was black in color. Absolute methanol (20 ml) was added to destroy the excess sodium, and after stirring at 0° for 1 hr the reaction mixture was poured onto 50 ml of ice. Extraction with 250 ml of cold pentane in small portions, washing the extract with saturated aqueous NaCl, and drying over anhydrous calcium chloride and removing the solvent on a rotary evaporator gave rise to a green semisolid material. This residue was distilled under high vacuum, and all materials volatile at −10 to +10° were collected. This fraction was redistilled to give a small, undetermined amount of product. The pmr spectrum of this material indicated the presence of vinylic protons; however, the ratio of aliphatic to olefinic protons was incorrect for any of the expected products. Since the yield of this material was so small (a number of other experiments gave no volatile products at all), it was not characterized further.

(B) With Bis(ethylenediamine)chromium(II).[22] Aqueous chromous perchlorate was prepared by dissolving 9 g of chromium metal (99.995%, Alfa Inorganics) in 156 ml of 20.4% perchloric acid. This mixture was stirred under nitrogen at room temperature until no further hydrogen evolution was noted (1.5–2 days). Ethylenediamine (11 ml, 0.16 mol) (distilled from over KOH under nitrogen) was dissolved in 100 ml of dimethylformamide (also distilled under nitrogen); to this solution was added 100 ml (large excess) of the chromous perchlorate solution. Finally, 0.75 g (1.6 mmol) of **1** was added, and the reaction mixture was stirred under argon for 48 hr at room temperature. No appreciable color change was noted during this time. The reaction mixture was then diluted with 200 ml of water and extracted with 250–300 ml of pentane. The organic layer was separated, washed with water, and dried over anhydrous calcium chloride. Removing the solvent at reduced pressure gave a light yellow solid whose infrared spectrum indicated mostly (~90%) starting material.

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