# Applications of Nuclear Quadrupole Resonance to Organic Chemistry. II. The Chlorination of Octachlorofulvalene[1a]

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Chlorination of octachlorofulvalene (1) proceeds rapidly at room temperature to give two new $C_{10}Cl_{10}$ isomers: decachloro-2,5-dihydrofulvalene (6) and decachloro-1,2'-dihydrofulvalene (7) in 40 and 15–20% yields, respectively. The structures of these compounds are deduced from their $^{35}Cl$ nuclear quadrupole resonance (nqr), their ultraviolet spectra, and their chemistry. 6 and 7 rearrange upon heating or under the influence of Lewis acid catalysts to a complex mixture of three other $C_{10}Cl_{10}$ isomers 3, 4, and 5. The same isomeric mixture is obtained under similar conditions from decachloro-1,1'-dihydrofulvalene (2). Structures for 3–5 are proposed on the basis of their nqr and ultraviolet spectra and chemical evidence. Both 6 and 7 also undergo further chlorination: 6 adds chlorine in the absence of light to give a new $C_{10}Cl_{12}$ (50%) and a new $C_{10}Cl_{14}$ (25%) for which the structures 11 and 10, respectively, are suggested; 7, on the other hand, gives the known $C_{10}Cl_{14}$, 13, upon photolytic chlorination.

Recent studies in these laboratories[1b] on various polychlorinated hydrocarbons led to a convenient preparation of octachlorofulvalene[2] (1) in large quantities (Scheme I shows the chlorination of octachlorofulvalene and reactions of $C_{10}Cl_{10}$ isomers.) In the hope that octachlorofulvalene would exhibit interesting properties which might be characteristic of fulvalenes in general, we have undertaken a study of the chemistry of 1. This is the first in a series of papers dealing with that chemistry and is concerned with the chlorination of 1.
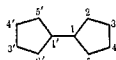
**Chlorination.**—1 reacts very readily with chlorine at room temperature in chloroform solution. The reaction is complete within 1.5–2 hr, as is evidenced by the change in color of the solution from blue to wine red. At least two new compounds 6 and 7, both $C_{10}Cl_{10}$ isomers, are formed in this reaction in 40 and 15–20% yields respectively. However, there are eight different $C_{10}Cl_{10}$ isomers (2–9) which could conceivably arise from chlorination of 1.



8                    9

Compound 6 is a deep violet solid, melting at 183–184°. The electronic spectrum of this compound immediately indicates a structure containing the 1,2,3,4-tetrachlorofulvenoid moiety, such as 6 or 8 (compare the spectra of 6 and hexachlorofulvene,[3] Figure 1).

Some twisting or stretching of the 1,1' double bond due to steric repulsions between chlorines in the 2 and 5' and 5 and 2' positions would be expected to occur in either 6 or 8, giving rise to the observed bathochromic shift[4] compared with hexachlorofulvene.

The most convincing evidence for the structure proposed for 6 comes from its $^{35}Cl$ nuclear quadrupole resonance (nqr) spectrum (Table I and Figure 2), which shows only four types of chlorines.[5] A comparison of this spectrum with that of 1, a model for the fulvenoid half of structure 6, allows assignment of the peaks at 36.41 and 37.90 MHz to the chlorines at positions 2', 3', 4', and 5'. The resonance at 37.14 MHz in the spectrum of 6 is comparable with the corresponding low-frequency resonances in the spectra of 1,2,3,3,5,5-hexachlorocyclopenten-4-one (14) and octachlorocyclopentene (15) (models for the chlorinated half of 6). This



14                    15                    16
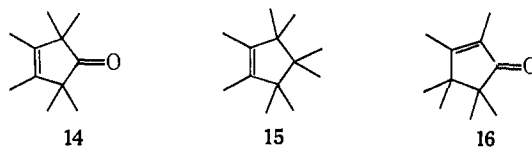
resonance, therefore, can be ascribed to the vinylic chlorines at positions 3 and 4. Finally, the resonances at 38.88 and 39.14 MHz may be assigned to the geminal chlorines at positions 2 and 5 by comparison with the corresponding absorptions in the spectrum of 14. In contrast, 1,2,4,4,5,5-hexachlorocyclopenten-3-one (16), a model for structure 8, shows a very complicated spectrum in both the vinylic and geminal chlorine regions. Thus 6 must have the decachloro-2,5-dihydrofulvalene[2] structure.

The infrared spectrum of 6 further supports this structural assignment with olefinic bands at 1656 (unconjugated double bond) and 1554 cm$^{-1}$ (conjugated double bond). The former band seems especially inconsistent with the alternative structure 8. In addition 6 shows an intense m/e 235 ($C_5Cl_5^+$) peak in its mass spectrum (Table II), which supports the proposed bicyclopentyl carbon skeleton.

(1) (a) Previous paper in this series: A. Roedig, R. Helm, R. West and R. M. Smith, *Tetrahedron Lett.*, 2137 (1969). (b) R. West and D. C. F. Law, unpublished work; D. C. F. Law, Ph.D. Thesis, The University of Wisconsin, 1966.

(2) The IUPAC name for 1 is 2,2',3,3',4,4',5,5'-octachlorobicyclopentadienylidene. To facilitate distinguishing among the numerous $C_{10}Cl_{10}$ isomers presented here without using cumbersome IUPAC nomenclature, yet without resorting to a nondescript tag such as a melting point, we are describing these isomers as fulvalene derivatives and retaining the name fulvalene in preference to bicyclopentadienylidene. The positions of saturation in the $C_{10}Cl_{10}$ isomers are designated using the accepted numbering system.



Thus, 5-(1,2,3,3,5,5-hexachlorocyclopenten-4-ylidene)-1,2,3,4-tetrachlorocyclopentadiene (6) is designated decachloro-2,5-dihydrofulvalene; 1-(1,3,-4,5,5-pentachlorocyclopentadien-2-yl)-2,3,4,5,5-pentachlorocyclopentadiene (4) is designated decachloro-2,3'-dihydrofulvalene, etc. Although this system differs from that used by some authors (*e.g.,* see ref 15), we feel that it is significantly easier for the reader to remember.

(3) A. Roedig, *Justus Liebigs Ann. Chem.*, **569**, 161 (1950).

(4) This type of phenomenon is responsible for the large bathochromic shifts exhibited by 1 and octabromofulvalene: R. West and P. T. Kwitowski, *J. Amer. Chem. Soc.*, **90**, 4697 (1968).

(5) Chlorines which are symmetrically equivalent in a given molecule often appear as doublets with splittings of 10–600 kHz due to asymmetric packing in the crystal lattice. For the fundamentals of nqr spectroscopy, see G. Semin and E. I. Fedin in V. I. Gol'danskii, "The Mössbauer Effect and Its Applications in Chemistry," Consultants Bureau, New York, N. Y., 1964, pp 68–119.
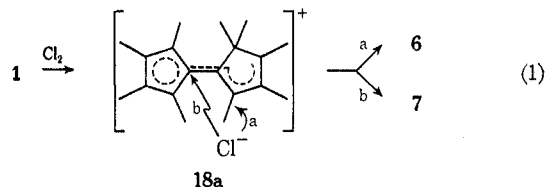
SCHEME I
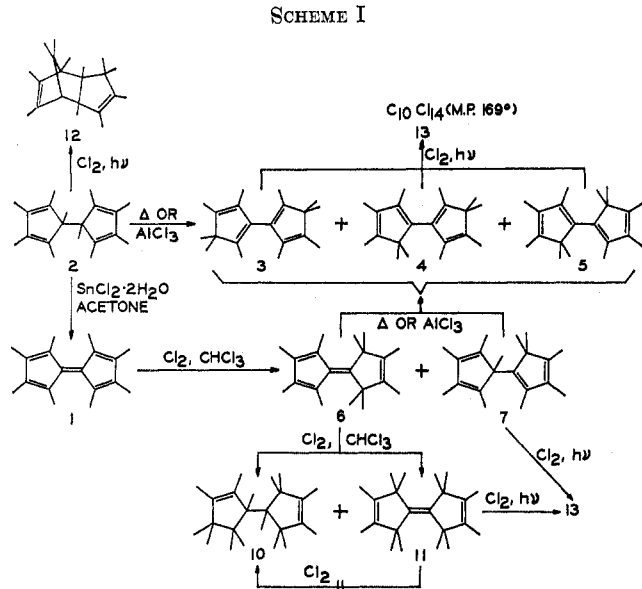


The structure of 6 is confirmed by its isomerization to 5 and by its chlorination, which are discussed below.

The other product, 7, obtained from chlorination of 1 is a tan to light yellow solid, mp 127–128°. The nqr spectrum of 7 (Table I and Figure 2) establishes the presence of a single tertiary (C-1) chlorine (39.75 MHz; *cf.* the spectrum of 2 which shows two such high-frequency resonances), which narrows the field of possible structures to 7 and 9. The remainder of the nqr spectrum (ratio of vinylic to geminal chlorines = 7:2) and other spectral data for this compound are also consistent with both structures 7 and 9. In the infrared olefinic bands are observed at 1618, 1607, and 1568 cm$^{-1}$, similar to those shown by 2 in this region (1598 and 1568 cm$^{-1}$).[1] Furthermore, the ultraviolet spectrum of 7 (Table III) is similar to that of hexachlorocyclopentadiene,[6] which confirms the presence of two isolated polychlorocyclopentadienyl fragments in 7. Finally, the mass spectra of 2 and 7 (Table II) are nearly identical above *m/e* 230. That these two compounds should have similar propensities toward fragmentation and dechlorination would be expected from either of the proposed structures.

The choice between the decachloro-1,2′-dihydrofulvalene[2] (7) and the decachloro-1,3′-dihydrofulvalene[2] (9) structures rests on the isomerization of this compound to 5 (*vide infra*).

The formation of 6 and 7 in this reaction may be rationalized in the following way. Extended HMO calculations[7] on 1 show that position 2 is the most susceptible to electrophilic attack (assuming an ionic pathway, which seems reasonable under the reaction conditions). Attack by chlorine then gives rise to cation 18a, followed by nucleophilic attack by chloride ion (predicted[8] to occur predominantly at positions 3, 5 and 1′) at positions 5 and 1′ to give the observed products (eq 1). The lack of 1,2 addition of chlorine (leading here

(6) E. T. McBee, J. D. Idol, Jr., and C. W. Roberts, *J. Amer. Chem. Soc.*, **77**, 4375 (1955).

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

(8) S. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Vol. I, Pergamon Press, Oxford, 1965, p 41.



$$1 \xrightarrow{Cl_2} \quad 18a \quad \xrightarrow{} \quad \begin{array}{c} a \\ b \end{array} \quad \begin{array}{c} 6 \\ 7 \end{array} \tag{1}$$

to 8) appears fairly general for polychlorinated fulvenes[9] and cyclopentadienes[10] and may be due to steric hindrance by the neighboring *gem*-dichloride group in the intermediate ion (or radical) to further attack by chloride ion (or Cl·).

**Isomerization of 6 and 7.**—Both 6 and 7 undergo facile rearrangement when heated to slightly above their melting points or when treated with aluminum chloride in chloroform solution at room temperature. Because the thermal and Lewis acid catalyzed isomerizations of decachloro-1,1′-dihydrofulvalene (2) were recently reported by Weil[11] to give a mixture of two new C$_{10}$Cl$_{10}$ isomers, whose structures would have an obvious bearing on the structures of 6 and 7, we undertook a study of these reactions.[12] During this study a third C$_{10}$Cl$_{10}$ isomer (5) was isolated from this mixture.

Not unexpectedly, the mixtures of C$_{10}$Cl$_{10}$ isomers obtained from the isomerizations of 2, 6, and 7 are identical (by infrared), indicating that complete equilibration has occurred (eq 2). This observation is confirmed by the rearrangement of 3, 4, and 5 to the same mixture and by the constancy in composition of the mixture upon prolonged heating. Semiquantitative infrared analysis shows that, at equilibrium, the three isomers (3–5) are present in the proportions 35–45% : 45–55% : 5–15% (3 : 4 : 5).

$$2 \longrightarrow 3 \rightleftharpoons 4 \rightleftharpoons 5 \underset{7}{\overset{6}{\rightleftharpoons}} \tag{2}$$
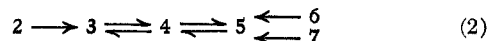
Compound 3, isolated by dissolving the reaction mixture in acetic acid and chilling[11] or by trituration and recrystallization from acetonitrile, is a light yellow solid (mp 110–111°). The ultraviolet spectrum of 3 (Table III) indicates a structure with separated, interacting, polychlorocyclopentadienyl fragments (*e.g.*, 2, whose rings probably interact in a "face-to-face" manner, has similar electronic absorptions Table III).[1] However, the nqr spectrum of this compound (Table I and Figure 3) immediately rules out structures 7 and 9 from consideration. Not only is a structure containing two *gem*-dichloride groups indicated, but the simplicity of the spectrum (showing only three kinds of vinylic chlorines) also excludes the unsymmetrical structure 4. Both spectra seem comparible only with the decachloro-3,3′-dihydrofulvalene[2] structure (3), which contains only cross-conjugation.

Compound 5 is a bright yellow solid melting at 113–114°, which like 4 is isolated from the reaction mixture by chromatography.[10,12] Although the ultraviolet spectrum of 5 (Table III) shows more conjugation than

(9) Hexachlorofulvene, for example, undergoes predominantly 1,4-chlorination under a variety of conditions: Cl$_2$ at 200° and PCl$_5$ in CCl$_4$ at 25°; bubbling Cl$_2$ through a solution of the fulvene at room temperature, however, has no effect at all.[8]

(10) V. Mark, personal communication.

(11) E. D. Weil, U. S. Patent 3,219,710 (Nov. 23, 1965); *Chem. Abstr.*, **64**, 3377 (1966).

(12) V. Mark and E. D. Weil have also studied these rearrangements in detail to determine product structures, obtaining results in good agreement with ours: V. Mark and E. D. Weil, *J. Org. Chem.*, in press.

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TABLE I

[35]Cl NUCLEAR QUADRUPOLE RESONANCE SPECTRA OF SELECTED CHLOROCARBONS

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| Compd | $T$, °K | Vinylic chlorine resonances[a] | Geminal chlorine resonances[a] | Tertiary chlorine resonances[a] |
|---|---|---|---|---|
| 1 | 298[b] | 36.17 (4),[c] 37.19 (2), 37.37 (2) | | |
| | 77[d] | 36.64 (4), 37.73 (2), 37.84 (2) | | |
| 2 | 298 | 36.34, 36.69, 37.04, 37.22 (8 complex[e]) | | 38.94 (1), 39.40 (1) |
| | 77 | 37.12, 37.20, 37.40, 37.56, 37.84, 38.10 (8 complex) | | 39.35 (1), 39.75 (1) |
| 3 | 298 | 36.21 (2), 36.52 (2), 36.73 (2) | 38.67 (2), 39.06 (2) | |
| | 77[d] | 36.77 (2), 37.02 (2), 37.35 (2) | 39.18 (2), 39.56 (2) | |
| 4 | 298 | 36.30 (1), 36.48 (1), 36.66 (2), 36.79 (1), 36.88 (1) | 38.47 (3 triplet[e]), 38.85 (1) | |
| | 77[d] | 36.82 (1), 37.01 (1), 37.09 (1), 37.19 (1), 37.23 (1), 37.42 (1) | 38.91 (1), 38.97 (1), 39.03 (1), 39.31 (1) | |
| 5 | 298 | 36.1 (2), 36.4 (1), 36.6 (2), 36.8 (1) | 38.3 (2 doublet[e]), 38.9 (1), 39.5 (1) | |
| | 77[d] | 36.65 (1), 36.92 (1), 37.17 (2), 37.22 (1), 37.26 (1) | 38.70 (1), 38.79 (1), 39.49 (1), 40.00 (1) | |
| 6 | 298 | 36.41 (2 doublet), 37.14 (2 doublet), 37.90 (2 doublet) | 38.88 (2 doublet), 39.14 (2 doublet) | |
| | 77[d] | 36.86, 36.93 (2); 37.52, 37.59 (2); 38.21, 38.45 (2) | 39.22, 39.39 (2); 39.49, 39.59 (2) | |
| 7 | 298 | 36.10 (4 triplet), 36.56 (3 doublet) | 39.03 (2) | 39.75 (1) |
| | 77 | 37.02 (4 triplet), 37.41 (3 doublet) | 39.77 (2) | 40.37 (1) |
| 11 | 298 | 37.4 (2), 37.5 (2) | 39.0–39.6 (8 complex) | |
| 14 | 298 | 37.05 (2) | 38.07 (2), 38.42 (2) | |
| | 77 | 37.83 (2) | 39.27 (2), 39.62 (2) | |
| 15 | 298 | 36.65 (1), 37.18 (1) | 38.72, 39.01, 39.4, 40.36 (6 complex) | |
| | 77 | 37.51 (1), 38.01 (1) | 39.45 (1), 39.70 (1), 39.85 (1), 40.07 (1), 40.28 (1), 41.25 (1) | |
| 16 | 77 | 37.33 (1); 37.75, 38.12 (1) | 39.23 (1), 39.56 (1); 40.2–40.4 (2 complex) | |
| 17 | 77[d] | 36.40, 36.43, 36.50 (2 complex); 36.84, 36.90, 37.04 (4 complex) | 38.29 (1), 38.33 (1) | |
| $C_5Cl_6$ | 77[f] | 36.95 (2), 37.28 (1), 37.45 (1) | 38.81 (1), 39.08 (1) | |

[a] Resonant frequencies measured in MHz. [b] All room temperature and some low temperature spectra were obtained on the Wilks NQR-1; frequencies are accurate to ±0.10 MHz. [c] Numbers in parentheses indicate relative number of chlorines. [d] Spectra obtained on Decca Radar spectrometer; frequencies accurate to ±0.01 MHz. [e] Complex, relative areas under and/or positions of peaks uncertain; doublet, frequency measured at center of two closely spaced peaks; triplet, frequency measured at center of three closely spaced peaks. [f] Hexachlorocyclopentadiene: H. O. Hooper and P. J. Bray, *J. Chem. Phys.*, **33**, 334 (1960).

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TABLE II

MASS SPECTRA OF $C_{10}Cl_{10}$ ISOMERS

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| Compd | $C_{10}Cl_{10}$·[+] | $C_{10}Cl_8$·[+] | $C_{10}Cl_6$·[+] | $C_{10}Cl_4$·[+] | $C_5Cl_6$·[+] | $C_5Cl_5$[+] |
|---|---|---|---|---|---|---|
| | | | Relative intensities[a] of high mass fragments | | | |
| 2 | <1% | 11.3% | 24.4% | 20.6% | 10.1% | 100.0% |
| 3 | <1% | 50.8% | 97.3% | 76.2% | 2.5% | 100.0% |
| 4 | <1% | 70.0% | 100.0% | 48.2% | 13.5% | 75.4% |
| 5 | <1% | 1.4% | 2.9% | 1.9% | 12.0% | 100.0% |
| 6 | <1% | 4.1% | 5.5% | 4.1% | 15.1% | 100.0% |
| 7 | <1% | 13.5% | 30.2% | 22.6% | 6.5% | 100.0% |

[a] Only the intensities of the first peak (lowest $m/e$) in each cluster are compared.

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TABLE III

ULTRAVIOLET SPECTRA OF SELECTED CHLOROCARBONS

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| Compd | $\lambda_{max}$, nm (log $\epsilon$) |
|---|---|
| 2[a] | 330 (3.47), 280 (3.32) |
| 3 | 328 (3.39), 274 (3.76) |
| 4 | 319 (3.60), 228 (sh) |
| 5 | 355 (3.44), 234 (3.86) |
| 6 | 512 (2.36), 302 (4.27), 227 (sh) |
| 7 | 324 (3.57), 228 (sh) |
| 17[a] | 380 (3.98), 292 (3.32) |
| $C_5Cl_6$[b] | 323 (3.17) |

[a] Reference 1. [b] Hexachlorocyclopentadiene.[6]

is present in **2**, **3**, **4**, and **7**, it is inconsistent with structures **6** and **8**, which contain the tetrachlorofulvenoid moiety. Similar low energy absorption is observed in **17**;[1] where the highest $\lambda_{max}$ is seen at 380 nm, indicating

that **5** also contains the four double bonds in conjugation. In the case of **5** steric repulsions undoubtedly cause the two rings to be significantly canted, causing the observed hypsochromic shift.
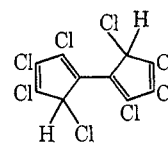


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The nqr spectrum of decachloro-2,2′-dihydrofulvalene[2] (**5**) (Table I and Figure 3) showing a ratio of six vinylic to four geminal chlorines, also lends support to the proposed structure. The large number of geminal chlorine resonances at first appears anomalous,
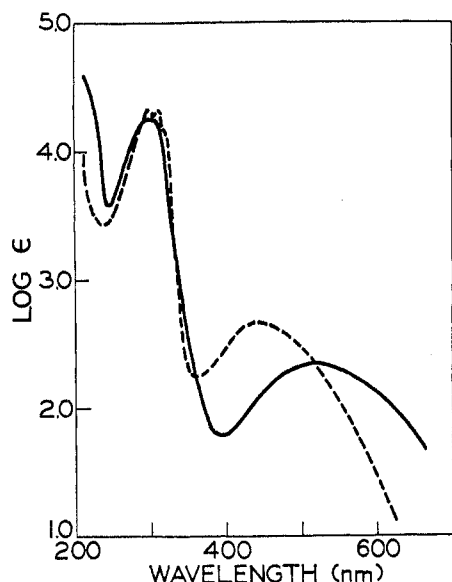
Figure 1.—Electronic spectra of 6 (———) and hexachlorofulvene (-----) in cyclohexane solution.
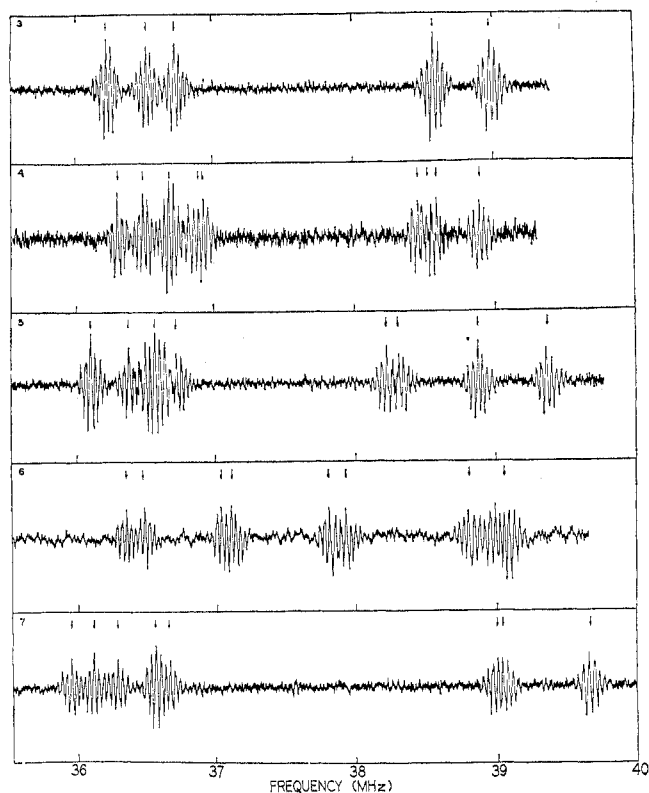


Figure 2.—Nuclear quadrupole resonance spectra of 3-7. Fine structure accompanying each resonance is due solely to the detection system and has no chemical significance.[5]

since 5 (like 3) is a symmetric structure. However, any twisting of the 1,1' bond induces an inherent non-equivalence to chlorines 2α (2'α) and 2β(2'β), causing first-order splitting; further splitting, however, must be ascribed to asymmetry in the crystal lattice.[5]
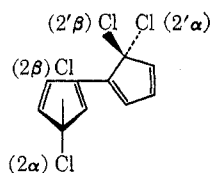


The nqr spectrum of 4, a beige to nearly colorless solid (mp 81–82°), is quite complex, showing ten separate absorptions (ratio of vinylic to geminal chlorines = 6:4) at −196°. This is good evidence in support of the unsymmetrical decachloro-2,3'-dihydrofulvalene[2] structure for this compound. On the other hand, the ultraviolet spectrum of 4 (Table III) is very deceiving, since it is nearly identical with that shown by 7. Models of 4, however, indicate that the 2, 5, 2', and 5' positions suffer severe steric repulsions in any configuration which even approaches coplanarity of the rings, so that substantial twisting of the 1,1' bond must occur and effectively isolate the rings.

Also consistent with the proposed structures are the mass spectra of 3-5 (Table II). All three compounds give intense $C_5Cl_5^+$ ($m/e$ 235) peaks, which is indicative of the bicyclopentyl carbon skeleton. [This fact has been substantiated by the chlorination and catalytic hydrogenation of these compounds[10-12] to the known[13] $C_{10}Cl_{14}$ (mp 169°) (13) and bicyclopentyl, respectively.] In addition, 3 and 4 exhibit a definite propensity toward dechlorination, as opposed to fragmentation to $C_5Cl_5^+$. Such behavior seems inconsistent with an alternative structure (9) in view of the mass spectral behavior of 2 and 7 (*vide supra*).

If the isomerizations of decachloro-2,5-dihydrofulvalene (6) and decachloro-1,2'-dihydrofulvalene (7) are followed more closely, the structures of these two compounds can be related to each other and to that of 5. If 6 is treated with excess aluminum chloride in chloroform solution for a short period of time (2–5 min; 10–24 hr are required for isomerization to the equilibrium mixture) and the reaction is hydrolyzed immediately, a nearly quantitative yield (>90%, by infrared) of 5 results. If 7 is treated similarly, infrared absorption bands due to 5 grow in over those of the starting material in preference to bands due to 3 and 4. We feel that 6 and 7, then, give rise to a common intermediate (cation 18b), which is hydrolyzed exclusively to 5 (eq 3).
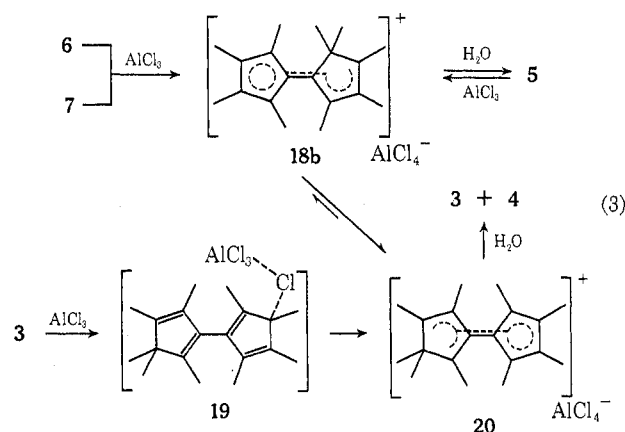


(The reaction of 7 is not so clean as that of 6, however, since the former compound has two nonequivalent sites at which ionization can occur.) 5, as expected, slowly regenerates 18b upon treatment with aluminum chloride. The reaction is sluggish, however, and is complicated by some rearrangement, possibly via an intermediate in which the migrating chlorine is only weakly

(13) E. T. McBee, J. D. Idol, Jr., and C. W. Roberts, U. S. Patent 2,911,448 (Nov. 3, 1959); *Chem. Abstr.*, 54, 4527 (1960).

bound to the aluminum chloride.[14] **3**, on the other hand, shows no tendency to form initially the green solution of **18b**, but instead rearranges rapidly *via* the bronze complex **19** and eventually gives what is probably the violet cation **20** in equilibrium with **18b**. Hydrolysis of this mixture of cations (the end product of all the aluminum chloride catalyzed rearrangements) leads to the observed mixture of **3**, **4** and **5**.

The formation of decachloro-2,2'-dihydrofulvalene (**5**) [instead of the 2,3' isomer (**4**) which is predicted on steric and electronic[8] grounds to be more favorable] upon hydrolysis of **18b** appears to be kinetically controlled by the extended conjugation present in **5**.[10] This is rather interesting, since cation **18a** (which has a different, and probably more closely associated, counterion) leads to **6** and **7** in a reaction which is also kinetically controlled.

A puzzling question concerning these isomerizations is the relative ratios of the three isomers present at equilibrium. As can be seen from the structures of the compounds obtained, no individual factor controls the isomer distribution. Although **3** suffers least from steric repulsions (the *gem*-dichloride groups are at the "outside" of the molecule), it lacks appreciable conjugation. On the other hand, **5** contains a fair amount of conjugation, but suffers seriously from steric interactions. A happy medium between these opposing factors appears to be reached in **4**.[15]

**Chlorination of 6 and 7.**—The chlorination of **6** proceeds with relative ease in the absence of light at room temperature in chloroform solution to give two new chlorocarbons, **10** and **11**, in 20–25% and 50% yields, respectively (see Scheme I). **11**, which precipitates from the reaction mixture as a white solid $C_{10}Cl_{12}$ (mp 227–228°), shows only a shoulder at 265 nm (log $\epsilon$ ~3.6) in the ultraviolet above 240 nm. This evidence excludes structures having the tetrachlorofulvenoid or even the polychlorocyclopentadienyl fragment of **6** still intact (both have $\lambda_{max}$ >300 nm). Not so easily excluded, however, are structures **21** and **22**.



21          22
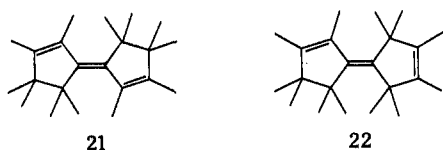
A comparison of the ultraviolet spectrum of octachloro-1,3,5-hexatriene [$\lambda_{max}$ 260–265 nm (shoulder, log $\epsilon$ ~3.85)[16]] with that of this compound offers evidence against structure **21**, which would be expected to give rise to a bathochromic shift over the corresponding absorption of its acyclic analog.[17] In choosing between structures **11** and **22**, however, the ultraviolet evidence

becomes ambiguous, since the contribution of the numerous steric factors involved here are unknown. However, the nqr spectrum of this compound (Table I) shows a closely spaced doublet in the vinylic chlorine region, which seems consistent only with the more symmetrical structure **11** (*cf.* the spectra of **14** and **16**, Table I). This structure, it must be noted, is consistent with the proposed structure of the starting material **6** (since **8** would be expected to give rise to **11** under the relatively mild reaction conditions) and with the observed predominance of 1,4- over 1,2-chlorination of the fulvene system (*vide supra*).

The mass spectrum of **11** indicates the unrearranged carbon skeleton to be present, showing major peaks at $m/e$ 400 ($C_{10}Cl_8 \cdot {}^+$), $m/e$ 330 ($C_{10}Cl_6 \cdot {}^+$), and $m/e$ 260 ($C_{10}Cl_4 \cdot {}^+$) and a base peak at $m/e$ 235 ($C_5Cl_5{}^+$). The chlorination of **11** under mild conditions to **13**, which is known to have the bicyclopentyl skeleton,[13,18] also confirms this point.

From the chloroform solution obtained in the chlorination of **6** one can isolate **10**, a white solid $C_{10}Cl_{14}$ (mp 186–187°). This compound shows only one ultraviolet absorption [230 nm (log $\epsilon$ 4.28)] whose position and intensity are consistent with two isolated double bonds. Preliminary considerations indicate that structure **10** is correct for this compound, since (1) it is compatible with the fact that **11** does not chlorinate to **10** under any conditions, (2) it is consistent with the structure of **6** and could be formed *via* the less favorable **22**, and (3) it contains two heptachlorocyclopentenyl fragments, which is consistent with the resistance of the latter system to further chlorination.[19] However, this structure, like that of **11**, must be considered only tentative.

The chlorination of **7** under light-induced conditions leads to **13**, although the intermediate $C_{10}Cl_{12}$ is not isolated here as it was in the case of **6**. This reaction is also consistent with the structure assigned to **7**. Decachloro-1,1'-dihydrofulvalene (**2**) chlorinates under identical conditions to give **12**,[6] which has a condensed carbon skeleton,[20] by means of proposed mechanism 4.



$$2 \xrightarrow{Cl \cdot} \quad \longrightarrow \quad \xrightarrow{Cl \cdot} 12 \quad (4)$$

(14) Similar complex formation followed by ionization, giving rise to a series of color changes, occurs in the reaction of hexachlorocyclopentadiene with AlCl₃: P. T. Kwitowski, Ph.D. Thesis, The University of Wisconsin, 1966.

(15) This product distribution is to be contrasted with that obtained in the thermal isomerization of 1,1'-dihydrofulvalene, the hydrocarbon analog of **2**. In that case the only product which is isolated is 2,2'-dihydrofulvalene, the analog of **5**, and conjugative effects can be invoked exclusively to account for the product ratio: E. Hedaya, D. W. McNeil, P. Schissel, and D. J. McAdoo, *J. Amer. Chem. Soc.*, **90**, 5284 (1968).

(16) A. Roedig, G. Voss and E. Kuchinke, *Justus Liebigs Ann. Chem.*, **580**, 24 (1953).
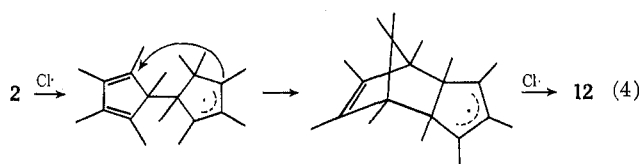
(17) R. B. Woodward, *J. Amer. Chem. Soc.*, **63**, 1123 (1941); **64**, 72, 76 (1942).

(18) The formation of **13** from **11** under relatively mild conditions indicates that these two compounds may be structurally related. However, the fact that **13** occurs as the product of so many of these reactions indicates that it also might be the thermodynamic sink for a series of labile C₁₀Cl₁₄ isomers. Unfortunately no data is available at present to help solve this problem, so that **i**, a likely structure for this compound, must be considered tentative at best.

i
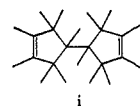
(19) J. A. Kritinsky and R. W. Bost, *J. Amer. Chem. Soc.*, **69**, 1918 (1947).

(20) V. Mark has suggested the structure ii for compound **12**. However, a mechanism analogous to that given here must be postulated for the formation of ii from **2**, so that our argument remains unchanged. See ref 12.

ii
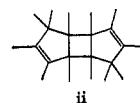
Now **3**, **4** and **5** cannot undergo this type of condensation and, in fact, do not[11,12] (*vide supra*). **7** cannot do this either with any facility (eq 5), but structure **9** (the
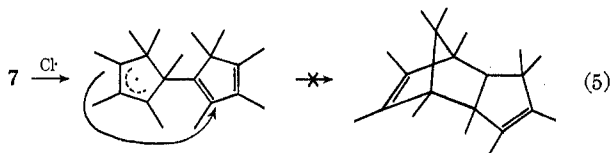


alternative to **7**) presumably could (eq 6). Since *both*
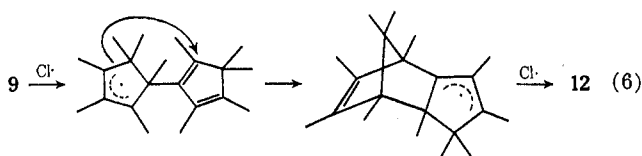


compounds **7** and **9** are not available, however, their relative behavior in this reaction is unknown; furthermore, the stabilities of the starting materials to the reaction conditions are questionable, so that the above argument is only indicative.

In contrast to the facile electrophilic addition of chlorine to octachlorofulvalene, this compound also exhibits interesting electron-deficient properties. These properties will be the subject of further communications on the chemistry of **1**.

### Experimental Section

Decachloro-1,1'-dihydrofulvalene (**2**) was prepared from commercial grade hexachlorocyclopentadiene according to the method of McBee and coworkers,[6] mp 122–123° (lit.[6] 122–122.5°).

The infrared spectra of pure solids were obtained on a Perkin-Elmer 237 spectrometer as mulls with mineral oil (Nujol) between sodium chloride disks. Ultraviolet spectra were taken on a Cary Model 14 recording spectrophotometer in 2-cm and/or 0.5-mm quartz cells, using Spectrograde cyclohexane as solvent unless otherwise indicated. Mass spectra were recorded on the CEC 21-103C spectrometer, equipped with heated inlet, and the AEI MS-902 high resolution mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preliminary nqr spectra were run on the Wilks NQR-1 commercial spectrometer with superregenerative oscillating detector, using a Hewlett-Packard Model 524B electronic counter to measure frequencies. Wherever the center of the envelope due to a single peak was obvious, the frequency at that point was measured with an accuracy of ±0.10 MHz. In cases where the center was not obvious owing to overlapping peaks, the frequency of the approximate center of that group of peaks was measured to the same degree of accuracy. A number of low temperature spectra were run on the Decca Radar commercial spectrometer with superregenerative oscillating detector and side band suppressor (which facilitated the location of individual peaks); these spectra are noted in Table I. The spectra which are reproduced in this paper were obtained on the Wilks NQR-1A commercial spectrometer. Samples that were solid at room temperature were slowly recrystallized from pentane to afford crystals as large as possible; sample sizes varied from 0.5–3.0 g. Liquid samples were slowly cooled to −20 or −80° before immersion in liquid nitrogen for low temperature spectra. Commercial grade octachlorocyclopentene and 1,2,4,4,5,5-hexachlorocyclopenten-3-one were used for nqr analysis, but 1,2,3,3,5,5-hexachlorocyclopenten-4-one was prepared by the method of McBee, *et al.*,[21] mp 87–89° (lit.[21] 91–92°).

Octachlorofulvalene (**1**).[1]—A solution of 12 g of tin(II) chloride dihydrate (0.053 mol) in 75 ml acetone was added dropwise to decachloro-1,1'-dihydrofulvalene[6] (25 g, 0.053 mol), dissolved

in 375 ml of refluxing acetone, over a period of 20–25 min with constant, vigorous stirring. The reaction mixture became green almost immediately. After an additional 5–10 min of refluxing, the contents of the flask were cooled to room temperature, and stirring was stopped. Decantation of the reaction solution uncovered 12.0 g (56.5%) of octachlorofulvalene, which was washed with small portions of acetone and air-dried. Recrystallization from hexane with activated charcoal yielded **1** as shiny, metallic-blue prisms (7.7 g, 36.1%), mp 200° dec (lit.[1,22] 200° dec). **1** is stored most conveniently at room temperature in a vacuum desiccator, as it appears to undergo slow oxidation in the air.

Chlorination of **1**.—Octachlorofulvalene, 20.0 g (0.050 mol), was placed in a 3-l., round-bottom flask, and 2500 ml of chloroform was added. Chlorine was admitted at a moderate rate (1–3 cc/sec) to the solution at room temperature *via* a gas dispersion tube while the solution was vigorously stirred. After 1.5–2 hr the color of the solution had changed from deep blue to wine red, at which time chlorine admission was stopped. The solvent was blown off under nitrogen over a period of 24 hr, leaving a black, gummy solid. Recrystallization of this solid from 1400 ml of acetone (four crops) gave 8.7 g (37.5%) of decachloro-2,5-dihydrofulvalene (**6**). A second recrystallization from hexane yielded a pure sample of **6** as violet prisms, mp 183–184°. *Anal.* Calcd for $C_{10}Cl_{10}$: C, 25.30; H, 0.00; Cl, 74.70. Found: C, 24.90; H, 0.05; Cl, 75.01. Although the mass spectrum of **6** shows no molecular ion peak (*m/e* 470), it does show a fairly intense peak at *m/e* 400. Calcd intensities for 8 Cl:[23] M + 2, 261%; M + 4, 298%; M + 6, 194%; M + 8 79.3%. Observed intensities: M + 2, 255%; M + 4, 278% M + 6, 174%; M + 8, 85.5%. Other important fragments in this spectrum appear in Table II. Ir: $\nu_{max}^{mull}$ 1656 (s), 1554 (m), 1275 (s), 1258 (s), 1203 (m), 1190 (m), 1093 (m), 990 (s), 944 (m), 875 (m), 845 (w), 806 (s), 757 (m), 726 (w), 680 (m), and 671 cm$^{-1}$ (m). Uv: $\lambda_{max}^{cyclohexane}$ 512 nm (log ε 2.36), 302 nm (4.27), and 227 nm (shoulder).

The filtrate remaining after recrystallization of **6** was taken to dryness, and the remaining solid was recrystallized from acetonitrile with decolorizing charcoal. Two crops of crystals were obtained: 3.0 g (13%) of decachloro-1,2'-dihydrofulvalene (**7**) as beige needles, mp 127–128°. *Anal.* Calcd for $C_{10}Cl_{10}$: C, 25.30; H, 0.00; Cl, 74.70. Found: C, 25.41; H, 0.05; Cl, 74.84. The mass spectrum of **7** shows a small, but visible, molecular ion peak at *m/e* 470. The first peak of major intensity, however, occurs at *m/e* 400. Calcd intensities for 8 Cl:[23] M + 2, 261%; M + 4, 298%; M + 6, 194%; M + 8, 79.3%. Observed intensities: M + 2, 252%; M + 4, 280%; M + 6, 178%; M + 8, 70.0%. Ir: $\nu_{max}^{mull}$ 1618 (m), 1607 (s), 1568 (m), 1260 (w), 1233 (s), 1225 (s), 1163 (m), 1007 (m), 970 (w), 954 (w), 940 (m), 846 (m), 800 (s), 725 (m), 719 (m), 670 (s), and 658 cm$^{-1}$ (s). Uv: $\lambda_{max}^{cyclohexane}$ 324 nm (log ε 3.57) and 228 nm (shoulder).

Chlorination of **6**.—Decachloro-2,5-dihydrofulvalene (**6**), 2.05 g (4.3 mmol), was chlorinated in 150 ml chloroform at room temperature. Vigorous stirring was maintained, and the reaction vessel was shielded from light with aluminum foil. After 24 hr the reaction solution had become yellow, and an off-white precipitate had formed. The solution was reduced to half-volume, and the solid was filtered off, 1.15 g (50%) of **11**. Recrystallization from chloroform with decolorizing charcoal produced **11** as fluffy, white needles, mp 227–228°. *Anal.* Calcd for $C_{10}Cl_{12}$: C, 22.02; H, 0.00; Cl, 77.98. Found: C, 21.91; H, 0.06; Cl, 78.19. **11** showed a small molecular ion peak at *m/e* 540, as well as small fragment ion clusters at *m/e* 505 ($C_{10}Cl_{11}^{+}$), *m/e* 470 ($C_{10}Cl_{10}\cdot^{+}$), *m/e* 435 ($C_{10}Cl_{9}^{+}$), but the first peak of major intensity again occurred at *m/e* 400. Calcd intensities for 8 Cl:[23] M + 2, 261%; M + 4, 298%; M + 6, 194%; and M + 8, 79.3%. Observed intensities: M + 2, 254%; M + 4, 288%; M + 6, 165%; and M + 8, 86.1%. Ir: $\nu_{max}^{mull}$ 1658 (m), 1650 (s), 1626 (w), 1197 (s), 1125 (w), 1045 (s), 1000 (m), 928 (m), 886 (m), 871 (s), 775 (s), 740 (m), 724 (m), and 645 cm$^{-1}$ (s). Uv: $\lambda_{max}^{CHCl_3}$ 265 nm (shoulder, log ε 3.61).

Taking the reaction solution to dryness yielded a colorless oil that, upon standing, solidified to give 0.6 g (23%) of **10**. Recrystallization from acetone led to **10** as fluffy, white needles, mp 186–187°. *Anal.* Calcd for $C_{10}Cl_{14}$: C, 19.79; H, 0.00;

(21) E. T. McBee, D. L. Crain, R. D. Crain, L. R. Belohlav, and H. P. Braendlin, *J. Amer. Chem. Soc.*, **84**, 3557 (1962).

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

(23) J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier, Amsterdam, 1960, p 298.

Cl, 80.21. Found: C, 19.65; H, 0.00; Cl, 80.62. Ir: $\nu_{max}^{mull}$ 1622 (m), 1573 (m), 1228 (m), 1180 (s), 1143 (m), 110 (w), 1054 (m), 1025 (m), 950 (w), 900 (m), 877 (m), 849 (m), 823 (m), 806 (w), 760 (s), 750 (s), 712 (w), 688 (m), and 663 cm$^{-1}$ (m). Uv: $\lambda_{max}^{cyclohexane}$ 230 nm (log $\epsilon$ 4.24).

**Chlorination of 7.**—A solution of 0.93 g (2.0 mmol) of decachloro-1,2'-dihydrofulvalene (7) in 125 ml of carbon tetrachloride was chlorinated using a gas dispersion tube for 20 hr. The reaction flask was irradiated during the reaction with a mercury vapor lamp, and a reflux condensor was utilized to minimize solvent loss. Upon completion of the reaction the solvent and excess chlorine were evaporated, and a colorless oil, which subsequently solidified, was obtained, 13 (1.25 g, >100%). Recrystallization of this solid from pentane gave 0.90 g (75%) of 13 as colorless needles, mp 166–167° (lit.[18] 168–169°). The infrared spectrum of this compound was superimposable upon that of 13 prepared by chlorination of 3,[11] and a mixture of these compounds showed no melting point depression.

**Chlorination of 11. A. In the Absence of Light.**—A suspension of 0.55 g of 11 (1.0 mmol) in 150 ml of chloroform was stirred vigorously for 48 hr, while chlorine was admitted via gas dispersion tube. The reaction flask was covered to exclude light. The solvent then was reduced to one-fourth of its original volume, and the existing precipitate was isolated and air-dried to give 0.45 g (82%) of unchanged 11, as shown by infrared.[24]

**B. In Diffuse Room Light.**—11 (0.50 g, 0.9 mmol) was placed in 150 ml of chloroform, and this suspension was chlorinated for 24 hr. In this case, light from the room was allowed to enter the reaction flask, although no ultraviolet irradiation was used. A clear, yellow solution resulted, which, after solvent removal, gave crystals of 13. These crystals were washed with acetone and isolated to give 0.2 g (32%) of 13. Recrystallization from pentane gave 13 as colorless needles, mp 162–166° (lit.[18] 168–169°). This product was shown to be identical by infrared spectroscopy and mixture melting point with 13 prepared by chlorination of 3.[11]

**Thermal Rearrangement of 2.**[11,12]—Decachloro-1,1'-dihydrofulvalene (2), 15.0 g (0.032 mol), was placed in a pyrex tube that was flushed with nitrogen and kept under a positive nitrogen pressure during the entire reaction. The tube was heated at 128–130° for 40 hr with an oil bath. At this point the yellow oil that had formed showed no signs of starting material, as evidenced by the disappearance of bands at 1568 and 1250 cm$^{-1}$ in the infrared. This oil, after cooling, was partially dissolved in 35 ml glacial acetic acid, and the resulting suspension was cooled for 3–4 hr in a refrigerator. The precipitate that had formed was filtered off and air-dried to give 5.30 g (34%) of decachloro-3,3'-dihydrofulvalene (3). Recrystallization from acetonitrile produced small, light yellow plates of 3, mp 109–110° (lit.[11] 110–111°). The infrared and ultraviolet spectra of this compound were identical with those reported in the literature.[11,12]

The acetic acid filtrate, after isolation of 3, was diluted with 150 ml of water, causing the chlorocarbon layer to oil out. The organic materials were extracted into dichloromethane, and this solution was washed with water and dried over anhydrous calcium chloride. Evaporation of the solvent led to an oil, which was placed on a 3.5 ft × ³/₄ in. column of neutral aluminum oxide and eluted with pentane. Initial fractions, analyzed by infrared, contained significant amounts of 3, whereas middle fractions were composed mostly of decachloro-2,3'-dihydrofulvalene (4). The final fractions, on the other hand, were predominantly decachloro-2,2'-dihydrofulvalene (5). The intermediate fractions were resubjected to chromatography (aluminum oxide–pentane) to give 0.5 g (3.3%) of pure 4 as a nearly colorless powder, mp 80–81.5° (lit.[11] 81–82°). The infrared spectrum of this compound was identical with that of a pure sample of 4.[25]

**Thermal Rearrangement of Other C₁₀Cl₁₀ Isomers.**—0.5 g samples of 3, 5, 6, and 7 were placed in Pyrex tubes and heated at 130–140° until constant infrared spectra were obtained. The times required for these reactions were as follows: 3, 2–2.5 hr; 5, 1.5–2 hr; 6, 36–48 hr (this reaction is accompanied by some

oxidation and proceeds much more rapidly above the melting point of 6); and 7, 10–20 hr. The infrared spectra of the oils obtained from these reactions were literally superimposable upon one another and upon that obtained from the thermal rearrangement of 2.

**Aluminum Chloride Catalyzed Rearrangement of C₁₀Cl₁₀ Isomers.**—Samples (0.5–1.0 g) of 2, 3, 5, 6, and 7 were stirred with 0.25–0.50 g of anhydrous aluminum chloride (~1.75 mol AlCl₃)/mol of substrate) in 10–20 ml of chloroform at room temperature for varying lengths of time: 2, 12–16 hr;[26] 3, 3–6 hr; 5, 3–6 hr; 6, 16–24 hr; and 7, 3–7 hr. The mixtures were hydrolyzed by addition of 25–50 ml of water. The organic layers were diluted with chloroform, separated, washed with water, and dried over anhydrous calcium chloride. Removing the solvent on a rotary evaporator produced oils similar to those obtained in the thermal isomerizations. The infrared spectra of these oils were superimposable upon one another and upon those obtained in the thermal rearrangements.

**Aluminum Chloride Catalyzed Rearrangement of 6 at Short Reaction Times.**—Decachloro-2,5-dihydrofulvalene (6) (1.35 g, 2.8 mmol) and anhydrous aluminum chloride (0.65 g, 4.7 mmol) were stirred vigorously in 10–15 ml of chloroform at room temperature. After 2–5 min, the color of the solution had changed from violet to yellow to deep green. When the green color had persisted for 1 min, 10–15 ml water was added with stirring. The organic layer was diluted with chloroform, washed with water, and dried over anhydrous calcium chloride. Evaporation of the solvent led to a viscous oil which solidified upon trituration with acetonitrile to give 1.30 g (96%) of decachloro-2,2'-dihydrofulvalene (5). The crude product was recrystallized from acetonitrile to give 0.75 g (60%) of 5 as bright yellow clusters, mp 113–114°. *Anal.* Calcd for C₁₀Cl₁₀: C, 25.30, H, 0.00; Cl, 74.70. Found: C, 25.13; H, 0.10; Cl, 74.50. The mass spectrum of 5 shows no appreciable peaks above $m/e$ 420, but exhibits an intense peak at $m/e$ 400. Calcd intensities for 8 Cl:[23] M + 2, 261%; M + 4, 298%; M + 6, 194%; M + 8, 79.3%. Observed intensities: M + 2, 254%; M + 4, 287%; M + 6, 183%; M + 8, 79.2%. Ir: $\nu_{max}^{mull}$ 1600 (s), 1543 (m), 1277 (w), 1230 (s), 1175 (w), 1156 (s), 992 (w), 965 (m), 902 (m), 805 (s), 725 (m), 699 (m), and 662 cm$^{-1}$ (m). Uv: $\lambda_{max}^{cyclohexane}$ 355 nm (log $\epsilon$ 3.44) and 234 nm (3.86). This compound was shown by infrared and mixed melting point to be identical with 5 obtained in low yield from the equilibrium mixture of C₁₀Cl₁₀ isomers.

**Aluminum Chloride Catalyzed Rearrangement of 7 at Short Reaction Times.**—0.4 g (0.8 mmol) of decachloro-1,2'-dihydrofulvalene (7) was dissolved in 5 ml chloroform, and 0.2 g (1.4 mmol) of anhydrous aluminum chloride was added. After stirring this suspension vigorously for 4–6 min at room temperature, the color became dark yellow, then green. Hydrolytic work-up, as before, led to an oil whose infrared spectrum showed mainly bands due to the starting material. Also present, however, were new bands at 1543, 1277, 992 and 699 cm$^{-1}$; these bands are unique for 5 and were superimposable upon the corresponding peaks in the infrared spectrum of pure 5. Noticeably less intense, on the other hand, were bands at 1645–1640, 1303–1299 and 1030 cm$^{-1}$, which are unique for 3 and 4.

**Registry No.**—1, 24807-57-6; 2, 24807-58-7; 3, 24807-59-8; 4, 24807-60-1; 5, 24807-61-2; 6, 24807-05-4; 7, 24807-06-5; 10, 24807-07-6; 11, 24854-63-5; 14, 24807-08-7; 15, 559-40-0; 16, 24807-10-1; 17, 24807-11-2; hexachlorocyclopentadiene, 77-47-4.

(24) In working up the reaction solution small amounts of a new chlorocarbon (mp ~125°, presumably a C₁₀Cl₁₄) were found. These results were not reproducible, but do emphasize the lack of structural relationship between 11 and 10.

(25) We wish to thank Dr. Mark for a sample of 4 and for experimental details for isolating 4 from the isomer mixture.

(26) The rearrangement of 2 must be carried out in refluxing chloroform.