leaflets, mp 208.5–209.5°. *Anal.* Calcd for $C_{11}H_{17}N_3O$: C, 63.77; H, 8.21. Found: C, 63.40; H, 8.33.

The isomeric olefins **22** and **23** were identified by the spectral properties of the mixture [ir (film) 1712 and 3070 cm^{-1}; nmr (CCl_4) τ 4.5 (1.3 H, m)].

A solution of the 2-acetyl-6-acetoxybicyclo[3.3.0]octane isomers (**17**, 36 g) in chloroform (200 ml) was treated with *m*-chloroperbenzoic acid (85%, 45 g) and was refluxed gently for 16 hr. Hexane was added to the warm solution and the mixture was chilled in the refrigerator. The crystalline mass of *m*-chlorobenzoic acid was filtered and washed twice with 9:1 hexane–chloroform. The combined filtrates were evaporated to give a colorless, faintly cloudy oil whose infrared spectrum [ν_{max} (film) 1729 cm^{-1}] indicated it to be the desired diacetate, **18**. Distillation gave a colorless oil, bp 84–88° (0.2 mm). The diacetate thus obtained (32 g) was hydrolyzed by stirring overnight at 5–15° with 100 ml of 10% aqueous sodium hydroxide. The reaction mixture was extracted continuously with ether for 30 hr; the ether extracts were washed with saturated sodium chloride solution and concentrated under reduced pressure. The residue was distilled to give a mixture of stereoisomers of bicyclo-[3.3.0]octane-2,6-diol (**19**) as a colorless, extremely viscous syrup: bp 90–96° (0.3 mm) (11.4 g, 81% from **17**); ir (film) 3500 (broad) and 1050–1100 cm^{-1}. Analysis on a 20 ft × $^1/_8$ in. SE-30 column showed two components in a ratio 63:37, of respective retention times 10.8 and 11.6 min at 215°. Treatment of a sample with phenyl isocyanate at 80–100° without solvent for 0.5 hr and fractional crystallization of the reaction mixture from ethyl acetate–benzene gave two bis(phenylurethanes). The major, less soluble, isomer had mp 190–192°, whereas the minor isomer melted at 136–137°.

The diol mixture was oxidized by treatment of a solution in reagent grade acetone (10 g in 100 ml) with Jones reagent[16] (20 ml, 8 *N* in oxygen) and stirring at 20–30° for 6 hr. Most of the acetone was removed by evaporation under reduced pressure and the residue was treated with water (100 ml). The resulting mixture was extracted continuously with ether overnight; the ether extract was washed with saturated sodium chloride solution, dried, and concentrated under reduced pressure. The oil thus obtained (6.4 g) showed two peaks on column B at 200°, in a ratio of 80:20. The major component, collected from a 5 ft × $^3/_8$ in. Carbowax column, was identical (infrared spectrum and mixture melting point) with an authentic sample of bicyclo-[3.3.0]octane-2,6-dione. The minor component appeared to be a mixture of the epimers of 6-hydroxybicyclo[3.3.0]octan-2-one.

Registry No.—*cis*-Cyclooctene, 931-87-3; 1,3-cyclooctadiene, 1700-10-3; 1,5-cyclooctadiene, 111-78-4; **9**, 26908-76-9; **9** semicarbazone, 26908-77-0; **10**, 26908-78-1; **10** semicarbazone, 26963-84-8; **14**, 26908-79-2; **21**, 26908-80-5; **21** semicarbazone, 26908-81-6.

Acknowledgments.—The authors are grateful to the Robert A. Welch Foundation for partial support of this work. We also thank Mr. Richard Gandour for performing the nmr double resonance experiment.

[16] See L. F. Fieser and M. Fieser, "Reagents in Organic Synthesis," Wiley, New York, N. Y., 1967, pp 142–144.

The Isomerization and Chlorination of Decachlorobi-2,4-cyclopentadien-1-yl

VICTOR MARK* AND EDWARD D. WEIL

Research Department, Hooker Chemical Corporation, Niagara Falls, New York 14302

Received November 3, 1969

Decachlorobi-2,4-cyclopentadien-1-yl, $C_{10}Cl_{10}$, mp 125° (1), yielded on heating above its melting point or on contacting with aluminum chloride a mixture of isomeric chlorocarbons with extended conjugation (linear and cross). Structural assignments are given to the three major constituents of the equilibrium mixture, which is obtainable also from each of the pure isomers. A new structure is offered for the major photochlorination product of 1, $C_{10}Cl_{12}$, mp 221–223° (7), replacing the methanoindene structure ("Diels–Alder dimer" of C_5Cl_6) previously assigned to this derivative. Two novel $C_{10}Cl_{12}$ compounds, obtained from the chlorination of 1, were shown to be the endo and exo isomers of the true methanoindene chlorocarbons. A new structure is assigned to the known $C_{10}Cl_{14}$ chlorocarbon, mp 169°. ^{13}C nmr, ^{35}Cl nqr, ultraviolet, infrared, and mass spectral data as well as mechanistic rationalizations are given in support of the new structures and of the chemistry involved.

In the course of a study of the thermal stability of decachlorobi-2,4-cyclopentadien-1-yl, $C_{10}Cl_{10}$, mp 125° (**1**), a commercial acaricide, it was observed that the heating of **1** above its melting point, but below 240°, brought about complete isomerization.[1] When the isomerization was carried out to the point where the infrared spectrum of the mixture remained constant, none of the characteristic bands of **1** was detectable.

By elution chromatography over alumina or by suitable crystallization from acetic acid, the reaction mixture was separated into two pale-yellow (nearly colorless) $C_{10}Cl_{10}$ isomers of melting point 111° (**3**) and 82° (**4**) and one bright yellow isomer of melting point 114° (**5**). By heating each of these isomers under the original isomerization conditions, a mixture of all three was produced.

The ease of equilibration suggested that the three isomers differed from **1** only in regard to the position of the double bonds. That **3**, **4**, and **5** have the same carbon skeleton as the starting material **1** was confirmed by their catalytic hydrogenation to bicyclopentyl, $C_{10}H_{18}$, and by their photochemical chlorination to the known chlorocarbon $C_{10}Cl_{14}$, mp 169° (**6**), which also has been shown to yield bicyclopentyl on catalytic hydrogenation.[2]

Eight double bond position isomers of the $C_{10}Cl_{10}$ chlorocarbons with the bicyclopentyl skeleton are possible (excluding strained cumulene structures). Of these structures A was assigned[2] to the isomer with mp 125° (**1**) and confirmed by its ready dechlorination to perchlorofulvalene under mild reaction conditions.[3–5]

In the selection of structures for **3**, **4**, and **5** from the remaining seven alternatives (B to H), two with the

---

[1] E. D. Weil, U. S. Patent 3,219,710 (1965); *Chem. Abstr.*, **64**, 3377*c* (1965).

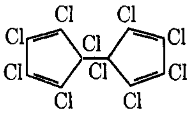
[2] E. T. McBee, J. D. Idol, and C. W. Roberts, *J. Amer. Chem. Soc.*, **77**, 4375 (1955).

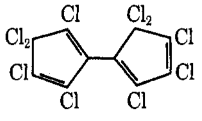
[3] V. Mark, *Tetrahedron Lett.*, 333 (1961); *Org. Syn.*, **46**, 93 (1966).

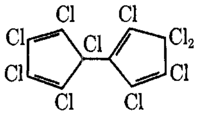
[4] (a) None of the new $C_{10}Cl_{10}$ isomers, **3–5**, yield perchlorofulvalene under the conditions reported. Instead they undergo an alkylation reaction, similar to that described for polyhalocyclopentadienes[4b] which will be the subject of a separate publication. (b) V. Mark, *Tetrahedron Lett.*, 296 (1961).

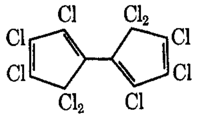
[5] D. C. F. Law, Ph.D. Thesis, The University of Wisconsin, 1966.

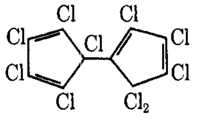
fulvenoid features (G and H) can be excluded on the basis of the absence of intense absorption in the visible region.[6]

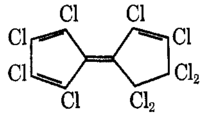

A

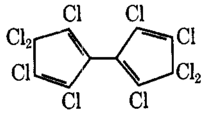

E

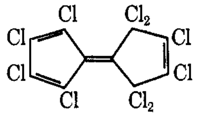

B


F


C


G


D


H

On the basis of converging evidence to be discussed below, structures D, E, and F are suggested for **3**, **4**, and **5**, respectively.

Ultraviolet Spectra.—These were as follows (λ_{max} isooctane, ε in parentheses): **3**, 207 mμ (16,500), 274 (5800), and 327 (2400); **4**, 205 (12,600), 228 (shoulder), and 319 (4200); **5**, 204 (18,100), 233 (6900), and 352 (4650). The long wavelength maximum of **5**, which tails into the visible region accounting for its yellow color, represents a marked bathochromic shift relative to analogs with two conjugated bonds[8] and suggests a more extended conjugation, thus excluding structures B and C for **5**.[9]

Infrared Spectra.—The infrared maxima of **3**, **4**, and **5** are abstracted in Table I. Inspection and analysis of the data yield the following interpretation. (a) All three isomers contain very strong maxima in the 807–812 cm^{-1} region. A maximum in this region is characteristic of the CCl$_2$ group between two double bonds in chlorinated five-membered cyclic systems and may be ascribed to the asymmetric C–Cl stretch.[12] The somewhat weaker absorptions in the 665–710 cm^{-1} regions might be the symmetric stretching of the CCl$_2$ group and the C–Cl bending modes.[12] Compound **1**, which lacks this feature, has no comparable strong absorption at 807–812 cm^{-1} but shows three maxima between 645 and 705 cm^{-1}, ascribable to C–Cl bending and to the tertiary C–Cl stretching modes. (b) A second region of very strong absorption common in all three isomers is between 1209 and 1235 cm^{-1}; the corresponding maxima in hexachlorocyclopentadiene (**2**) and **1** are at 1230 and 1250 cm^{-1} and are assigned as ring-breathing vibrations.[13] (c) The third area of high maxima is due to the C=C stretching vibrations. Hexachlorocyclopentadiene (**2**) and compounds **1** and **5** have only one very strong and one medium intensity peaks,

TABLE I

INFRARED PARAMETERS OF CHLOROCARBONS **3**–**5**[a]

3	**4**	**5**
1640 m	1650 m	
1610 s		
1600 s	1600 vs	
1580 m	1585 s	1590 vs
	1550 m	1540 s
1306 m	1299 m	1282 w
	1235 vs	1230 vs
1209 s		
1190 m	1193 s	
1180 s	1177 s	1173 m
1140 s	1144 s	1153 s
	1125 m	
1035 m		
	1009 w	
		992 w
	970 m	962 m
896 s	900 s	903 s
808 vs	812 vs	807 vs
755 s		
	737 m	
729 s		728 w
		699 m
676 s	668 s	665 s
	553 m	
550 w	547 m	550 s
537 s	533 m	533 w

[a] Absorption peaks, cm^{-1}; vs, very strong; s, strong; m, medium; w, weak.

---

(6) (a) Perchlorofulvalene has maxima at 277 mμ (ε 9850), 288 (16,100), 298 (22,300), 309 (21,600), 322 (11,500), and 444 (320) in cyclohexane[12] (at 450 mμ in benzene[7]), and perchlorofulvalene has maxima at 386 mμ (ε 36,000) and 590 (500) in isooctane.[3-5] (b) Very recently the preparation of H [λ_{max} 512 mμ (ε 230), 302 (18,600), and 227 (sh)] and of C [324 mμ (ε 3720) and 228 (sh)] by the chlorination of perchlorofulvalene under mild conditions was reported.[6c] (c) R. West and R. M. Smith, *J. Org. Chem.*, **35**, 2681 (1970).

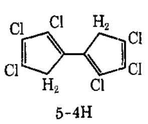
(7) A. Roedig, *Justus Liebigs Ann. Chem.*, **569**, 161 (1950).

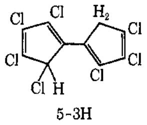
(8) Under identical analytical conditions **1** has maxima at 280 mμ (ε 2060) and 330 (2800), and hexachlorocyclopentadiene (**2**), at 324 mμ (ε 1670).

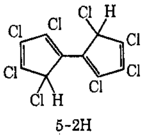
(9) No appropriate chlorocarbon model could be located for the ultraviolet spectra of cross-conjugated systems (D and E). It is probable that no definite conclusion could be obtained from the ultraviolet parameters of hydrocarbon models even if they were available, since steric interactions due to the presence of chlorine may drastically affect the planarity and hence the electronic spectrum of the system.[10,11]

(10) The X-ray analysis of perchlorofulvalene shows, for instance, that the cyclopentadiene rings are twisted through an angle of 41° due presumably to nonbonding chlorine–chlorine repulsion: P. J. Wheatley, *J. Chem. Soc.*, 4936 (1961).

(11) Steric repulsion and resultant enhanced deviation from coplanarity are probably the cause of the hypsochromic shift in **5** (for which structure F is assigned; *vide infra*) relative to its orange-colored hexa-, hepta- and octachloro analogs, which have the longest wavelength maxima at 370–380 mμ and for which structures **5**-4H, **5**-3H, and **5**-2H, respectively, have been proposed.[5]


5-4H


5-3H


5-2H

(12) V. Mark, unpublished correlations. As representative examples, the following compounds can be cited: hexachlorocyclopentadiene 804 (vs), 680 (s); octachloro-4-methylene-1-cyclopentene (mp 183°) 806 (vs), 665 (s); octachloroindene 805 (s), 650 cm^{-1} (s); chlorocyclopentadienes with no CCl$_2$ function (*e.g.*, 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene, perchlorofulvalene) have no strong absorption in the 800–815 cm^{-1} region. When the dichloromethylene group becomes adjacent to one double bond only in the polychlorocycloolefin ring strong maxima occur in the 750–785 cm^{-1} region (*e.g.*, tetrachlorocyclopropene 750, hexachlorocyclobutene 783, octachlorocyclopentene 755, octachloro-1,2-dimethylenecyclobutane 780, decachloroindan 752 cm^{-1}).

(13) (a) H. Gerding, H. J. Prins, and H. van Brederode, *Recl. Trav. Chim. Pays-Bas*, **65**, 168 (1946); (b) J. C. Wood, R. M. Elofson, and D. M. Saunders, *Anal. Chem.*, **30**, 1341 (1958).

whereas **3** and **4** have four peaks each in this region (1540–1650 cm^{-1}).

An interesting feature emerges from the comparison of the infrared spectra of these isomers: most of the bands present in the spectrum of **4** are either a reproduction of the maxima present in both **3** and **5**, or they are single bands at an intermediate position. This observation, in conjunction with the conclusion derived from the ultraviolet spectra, suggests the assignment of the symmetrical structures D and F to the isomers with the simpler spectra, **3** and **5**, respectively, and the assignment of the unsymmetrical structure E to the isomer **4** with the hybrid spectrum.

Best support for the structures of compounds **3–5** is provided by their ^{13}C nmr (cmr) spectra. These, together with the spectra of **1** and **2**, are abstracted in Table II. As is the case in the nonchlorinated hydrocarbon analogs, there is a clear and wide spread separation in the resonances of the sp^2 and sp^3 carbons, the latter occurring at higher field.[14] It is evident that the various structures (A–H) considered above require the following numbers of nonequivalent carbons: A, 3; B and C, 8 each; D and F, 5 each; H, 6; E and G, 10 each. Since compounds **3**, **4**, and **5** have 5, 10, and 5 resonance peaks of equal intensities, respectively, and thus the same numbers of magnetically different carbons, it is apparent that on the basis of the cmr spectra alone all structures except those of D–G can be excluded from further consideration. Since the electronic spectrum already eliminated G as a possible structure, the presence of ten different carbons in the cmr spectrum identifies **4** definitely with structure E. With further help from uv (*vide supra*) of the two remaining structures, F is assigned to **5** and D to **3**. The good match of the ten chemical shifts of the hybrid structure **4** with those of the two pure constituent compounds, **3** and **5**, possessing five resonance peaks each is noteworthy. As expected, compounds **3**, **4**, and **5** had peaks of about equal intensities, whereas **1** and **2** showed the correct 2:2:1 ratios for the sp^2:sp^2:sp^3 carbons.

TABLE II

^{13}C NMR PARAMETERS OF CHLOROCARBONS **1–6**, **9**, **10**, **12**[a]

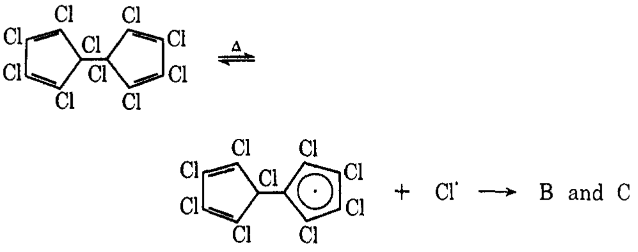
Compd	sp^2 carbons	sp^3 carbons
1	60.8, 61.8	119.7
2	59.2, 63.8	110.6
3	51.8, 61.1, 64.3, 67.0	110.5
4	49.6, 54.9, 55.9, 59.4, 61.9, 62.9, 64.5, 66.5	109.7, 110.4
5	54.3, 54.5, 60.4, 64.7	109.4
9	51.5, 54.1, 57.4, 60.9	94.9, 99.5, 104.0, 106.1, 109.0, 109.5
10	57.8, 59.3, 61.4, 63.7	88.2, 98.4, 104.6, 106.3, 107.9, 109.5
6	48.3, 61.8	91.6, 99.7, 100.7
12	57.6	93.4, 99.9

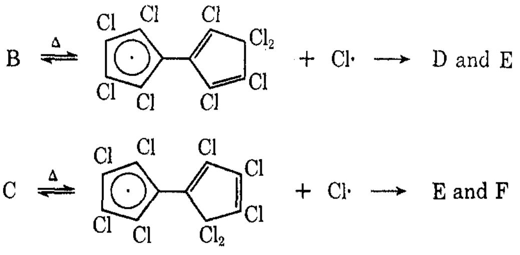
[a] δ, ppm, upfield from CS$_2$ (0.0 ppm).

On the basis of these data and interpretation, we propose structures D, E, and F for the bicyclic C$_{10}$Cl$_{10}$ chlorocarbons **3**, **4**, and **5**, respectively.[15]

The only previous reference in the literature to an isomer of **1** is found in a paper by Rabovskaya and Kogan, who obtained a C$_{10}$Cl$_{10}$ compound, mp 110.1–110.3°, from the γ-ray irradiation of **2** and to which they have assigned structure B or C.[16] On the basis of the data presented above, we propose the reassignment of the structure for their chlorocarbon, mp 110.1–110.3° (whose published infrared spectrum is identical with that of our compound **3**), to D.

The probable mechanism of the thermal isomerization of **1** to **3**, **4**, and **5** involves a homolytic C–Cl bond rupture on the doubly allylic sp^3 carbon.[17] Recombination of Cl with the organic radical would yield A, B, or C. Since the tertiary sp^3 carbon in B and C is triply allylic, an even more facile cleavage of the carbon–chlorine bond to the corresponding stabilized radicals is expected.[6b,c] These, on recombination with Cl would yield D, E, and F.[18]





The fact that pure **1**, **3**, **4**, and **5** on thermolysis yield exactly identical reaction mixtures indicates a thermodynamic control and the relative abundance of D (**3**) and E (**4**) over F (**5**) suggests that steric influences outweigh conjugation effects.

The isomerization of **1** was also effected under mild conditions by aluminum chloride yielding essentially the same equilibrium mixture that results from the thermal reaction.[20] A mechanism similar to that outlined above is proposed, except that Cl· is replaced by

---

[14] J. B. Stothers, *Quart. Rev., Chem. Soc.*, **19**, 144 (1965).

[15] The assigned structures are also consistent with the relative chromatographic elution rates (**1** > **3** > **4** > **5**) over alumina. The low melting point of **4** is again more compatible with the hybrid structure E than with those having elements of symmetry and thus, very likely, better packing in the crystal lattice.

[16] N. S. Rabovskaya and L. M. Kogan, *Proc. Acad. Sci. USSR*, **165**, 1094 (1965). *Dokl. Akad. Nauk SSSR*, **165**, 337 (1965); *Chem. Abstr.*, **64**, 4899 (1966).

[17] The equally feasible homolytic rupture of the C–C bond connecting the two rings probably also takes place. Recombination of the two pentachlorocyclopentadienyl radicals, however, would result in the formation of unisomerized **1** only.

[18] Present data do not indicate the detailed mode of the chlorine migration. In a study of the thermal isomerization of protio cyclopentadienes, rearrangement involving an intramolecular 1,2 hydrogen shift was proposed.[19]

[19] S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965).

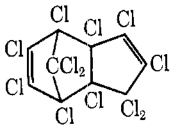
[20] We observed that the use of more than catalytic amounts of AlCl$_3$ resulted in the formation of an additional C$_{10}$Cl$_{10}$ isomer, mp 173–174°. The structure determination and chemistry of this novel chlorocarbon, which structurally is not directly related to **3–5**, are the topics of a separate publication.[21]

[21] R. M. Smith, R. West, and V. Mark, *J. Amer. Chem. Soc.*, in press.

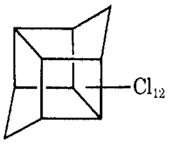
$AlCl_4^-$ and the cyclopentadienyl radicals are replaced by the corresponding cyclopentadienyl cations.[22]

The energy relationships of the proposed mechanism outlined above for the formation of **3**, **4**, and **5** from **1** also support structures D, E, and F for these isomers and militate against B and C.

In contradistinction to **1**, isomers **3**, **4**, and **5** yield on chlorination the known bicyclic chlorocarbon $C_{10}Cl_{14}$ (**6**), mp 169°, for which the bicyclopentyl skeleton basis was demonstrated.[2] The chlorination of **1**, however, was reported to yield $C_{10}Cl_{12}$, mp 221–223° (**7**), for which a structure (J) with a rearranged carbon skeleton (4,7-methanoindene) of undefined stereochemistry was proposed.[2] This earlier assignment of structure J to **7** was based on the following information: elemental analyses, ir and uv spectra [λ_{max} 232 mμ (ε 19,500) in either hexane, cyclohexane, or ethanol], its conversion to the cage structure [K, $C_{10}Cl_{12}$, mp 485° (**8**)] by $AlCl_3$ and SbF_3–$SbCl_5$, and its thermolysis at 340° to hexachlorocyclopentadiene (**2**).[2]



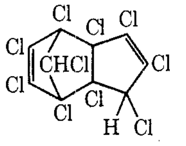
J



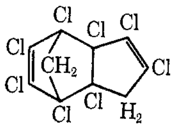
K

On the basis of the following data we would like to suggest an alternate structure for the $C_{10}Cl_{12}$ chlorocarbon **7**, mp 221–223°.

(a) The infrared spectrum of **7** shows a very sharp and narrow band at 1600 cm^{-1}, suggesting the presence of only one kind of double bond in the molecule. Chlorocarbons with the established carbon skeleton of J, *e.g.*, L and M,[25] have two C=C stretching modes in their spectra (at 1625–1630 and at about 1605 cm^{-1}, respectively) corresponding to the two kinds of double bond in the molecule. It would be anticipated that a compound possessing structure J would also display two different double bond stretching vibrations.



L

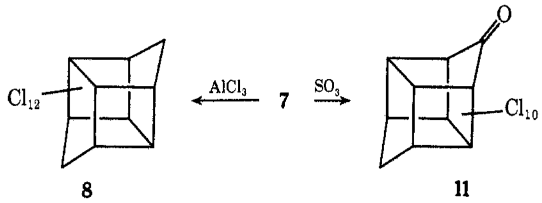


M

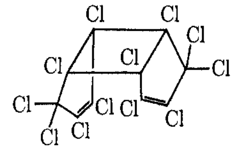
(b) When the chlorination of **1** was repeated photochemically under conditions similar to those specified, (method A) and compound **7** was separated by crystallization, infrared analysis of the mother liquor fractions revealed the presence of several additional compounds. These included small amounts of unreacted starting material **1**, the cage $C_{10}Cl_{12}$ chlorocarbon (**8**), and the bands of what were subsequently found to be two new $C_{10}Cl_{12}$ isomers, **9**, mp 186–187°, and **10**, mp 237–239°. Both **9** and **10** displayed in their infrared spectra two strong C=C stretching modes each (**9** at 1615 and 1630, and **10** at 1600 and 1630 cm^{-1}) and were assigned the exo and endo 4,7-methanoindene structures, respectively (*vide infra*).

(c) Under mild reaction conditions (room temperature), **7** was transformed by aluminum chloride quantitatively into the known isomeric cage chlorocarbon **8**.[2]

(d) Under similar mild conditions **7** yielded on contacting with sulfur trioxide in high conversion the known cage ketone, $C_{10}Cl_{10}O$ (**11**), in the form of its hydrate.[26] On the basis of these data and of the argument presented below, we propose the novel structure N (dodecachloro-1,3a,3b,4,6a,6b-hexahydro-*syn*-cyclobuta[1,2:3,4]dicyclopentane) for chlorocarbon $C_{10}Cl_{12}$, mp 221–223° (**7**), which is to replace the 4,7-methanoindene structure previously assigned to this compound.[2]



8 **11**



N

Analysis of structure N requires several stereochemical considerations.

(a) The first was the mode of fusion of the five-membered and four-membered rings. It is assumed that the fusion of the rings is cis. Although examples of trans-fused 5–4 bicyclic rings are known, their only known method of preparation involves the creation of the cyclopentane rings from a preformed trans-1,2-substituted cyclobutane.[27] No examples were found of trans-fused 5–4 rings from cyclization of monosubstituted cyclobutenes or cyclopentenes. It seems highly unlikely that the mild reaction conditions employed in the chlorination of **1** would allow the exclusive formation of trans-fused 5–4 rings in view of the inherent strain of this system, which is further augmented by the bulky chlorine substituents and by the double fusion.[28]

(b) The second was the syn *vs.* anti relationship of the two cis-fused cyclopentene rings. Evidence favoring the syn structure rests on the facile and essentially quantitative cyclization of **7** to **8** and to **11**, a process which requires a syn relationship of the five-membered rings. Although a multistep carbonium ion mechanism could be devised for the isomerization of an anti-fused cis,cis-5–4–5 ring system to the corresponding syn

---

[22] The facile formation at room temperature of pentachlorocyclopentadienyl radical and cation (a ground-state triplet) from hexachlorocyclopentadiene and Lewis acids has been reported.[23] A red 1:1 adduct of **2** and $AlCl_3$ has also been isolated and its magnetic and spectral properties accounted for on the basis of a partially ionic cyclopentadienyl cation.[24]

[23] R. Breslow., R. Hill, and E. Wasserman, *J. Amer. Chem. Soc.*, **86**, 5349 (1964).

[24] H. P. Fritz and L. Schafer, *J. Organometal. Chem.*, **1**, 318 (1964).

[25] H. E. Ungnade and E. T. McBee, *Chem. Rev.*, **58**, 249 (1958).

[26] (a) E. T. McBee, C. W. Roberts, J. D. Idol, and R. H. Earle, *J. Amer. Chem. Soc.*, **78**, 1511 (1956); (b) D. H. Zijp and H. Gerding, *Recl. Trav. Chim. Pays-Bas*, **77**, 682 (1958); (c) P. Eaton, E. Carlson, P. Lombardo, and P. Yates, *J. Org. Chem.*, **25**, 1225 (1960).

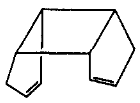
[27] (a) N. L. Allinger, M. Nakazaki, and V. Zalkow, *J. Amer. Chem. Soc.*, **81**, 4074 (1959); (b) J. Meinwald, J. Tufariello, and J. Hurst, *J. Org. Chem.*, **29**, 2914 (1964).

[28] Were only one of the five-membered rings fused trans to a cis-5–4 system, the effect of dissimilar strains would result in the presence of two different double bond stretching vibrations. It is characteristic for **7** the very sharp single band at 1600 cm^{-1} corresponding to this mode.

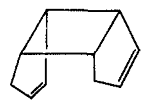
isomer, such a process seems energetically unfavorable.[29] Superimposed on the unfavorable energy relationship is the added steric influence of the bulky chlorine substituents which renders the syn,cis,cis-5–4–5 chlorocarbon even less favored in a hypothetical equilibrium reaction. Strong support for this reasoning comes from experiments in which **9** and **10** were exposed to aluminum chloride under the same mild conditions that resulted in the quantitative cyclization of **7** to **8**. The exo isomer **9** remained completely unaffected, while the endo isomer **10** underwent complete isomerization to the cage compound **8** (*vide infra*). The all-exclusive cyclization reaction of **7** to **8** is favored probably by the presence of already one cylcobutane ring in the molecule, which not only reduces the energy requirement of the overall cyclization process, but establishes a better bonding relationship (shorter distances) between the pertinent protons of the reaction intermediates. Even when both cyclobutane rings need be formed, as in **10** → **8**, no other products (*e.g.*, **9**) were detected in the reaction mixture.

These results indicate that under the mild conditions employed the ring fusions are not severed; the substrates either undergo quantitative cyclization (**7**, **10**) or they are recovered unaltered (**9**), but in both cases the original ring fusions are apparently completely preserved.

(c) The final step in the assignment of structure to chlorocarbon **7** concerns the position of the two double bonds. The cyclization experiments, resulting in the formation of **8** and **11**, and the infrared spectrum of **7** clearly indicate that the double bonds cannot be part of or attached to the cyclobutane ring, leaving structures N and O as the only alternatives. A rather unambiguous choice between the two isomers can be made with the aid of appropriate molecular models, which indicate a prohibitive crowding of two of the allylic chlorines facing each other in O but do accommodate them in N.[30]



N



O

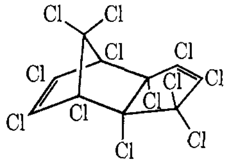
Although the low solubility of **7** at room temperature in all solvents tried precluded the determination of its cmr parameters by natural abundance ^{13}C nmr spectroscopy, additional support for the proposed structure was provided by its ^{35}Cl nuclear quadrupole resonance (nqr) spectrum. This showed the presence of three types of chlorines: two vinylic chlorines having the lowest frequency resonances (37.2 and 37.8 MHz), two geminal chlorines (38.0 and 38.3 MHz), and two bridgehead chlorines (at 39.5 and 40.0 MHz).[31] Considerably more resonance peaks were observed in the nqr spectrum of one of the methanoindene chlorocarbon isomers (*vide infra*).

Having determined the structure of the major product **7** of the light-catalyzed chlorination of **1** as being N,[32] we turned next to the analysis of the two novel chlorocarbons **9** and **10**.

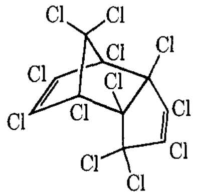
The two strong C═C stretching bands present in the infrared spectra of **9** (at 1616 and 1630 cm^{-1}) and **10** (at 1600 and 1630 cm^{-1}) suggest the presence of two different kinds of double bond in the molecule. Doublets at similar frequencies occur in the spectra of both L and M, further suggesting that the four compounds might have similar or the same carbon skeletons and that, indeed, **9** and **10** might be the exo and endo isomer pair of the chlorocarbon represented by the planar structure J. To ascertain this, both **9** and **10** were treated, under mild and identical reaction conditions, with aluminum chloride. Decomposition of the dark methylene chloride solutions by water led to the essentially quantitative recovery of **9**, whereas **10** yielded exclusively the cyclized cage isomer **8**.

The ultraviolet spectra of **9** and **10** displayed no maxima above 220 mμ thus indicating the absence of *de facto* conjugation of double bonds. While no nqr spectrum of **10** could be obtained at room and at liquid nitrogen temperature,[31c] isomer **9** showed four vinylic chlorines (between 36.91 and 37.51 MHz), four geminal chlorines (between 38.30 and 38.67 MHz), and four chlorines on tertiary carbons (between 39.13 and 39.60 MHz), thus indicating the presence of twelve distinct, nonequivalent chlorine substituents in the molecule.[31]

The analytical, spectroscopic, and isomerization data thus suggest that **9** and **10** do indeed possess the structure represented by the planar formula J and that **9** is the exo and **10** is the endo isomer.[34]



$C_{10}Cl_{12}$, mp 186–187°
9, J (*exo*)



$C_{10}Cl_{12}$, mp 237–239°
10, J (*endo*)

Convincing proof for the proposed structures was again provided by the cmr spectra of the chlorocarbons.

---

(29) The prevalence or the exclusive formation of the anti (trans) isomers in ring-fused or tetrasubstituted cyclobutanes is apparent from the several pertinent examples of [2 + 2] cycloaddition products illustrated in a review article by R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, pp 779–798.

(30) All efforts (*e.g.*, *via* thermolysis) to obtain the isomer of **7** corresponding to O resulted only in partial isomerization to **8** or reversion to the bicyclic ring system or in degradation and disproportionation yielding a variety of C_5, C_{10}, C_{15}, and indene chlorocarbons.

(31) (a) Nqr spectra of related pertinent chlorocarbons,[6c] including those of **2**,[31b] have been analyzed. (b) M. Hayek, D. Gill, I. Agranat, and M. Rabinovitz, *J. Chem. Phys.*, **47**, 3680 (1967), and references listed. (c) Being run on samples in solid state the nqr spectra are strongly dependent on the crystal structure(s) of the compound; for instance, merely freezing a liquid sample often results in no nqr spectrum at all.[31b]

(32) The photochemical bromination of **1** was reported to yield a dibromodecachloro analog (**7**-Br) ($C_{10}Br_2Cl_{10}$, mp 147°) of **7**, for which a structure analogous to J was proposed.[33] Based on the very close similarity between the infrared spectra of **7**-Br and **7**, we wish to suggest the N framework for **7**-Br as well, in which the two bromines occupy one of the allylic carbons each. As anticipated from its structure, **7**-Br was readily cyclized in high yield by $AlBr_3$ to a double bond-free dibromodecachloro analog of **8**.

(33) R. D. Crain, Thesis, Purdue University, 1958.

(34) A compound, $C_{10}Cl_{12}$, mp 328–329°, with the J (*exo*) structure has been reported in the literature.[35] The structure assignment was based on chlorine analysis and dipole moment. Due to the lack of additional and more meaningful structural data (*e.g.*, ultraviolet and infrared spectra, molecular weight), to the ambiguous nature and notoriously poor performance of dipole moment interpretation as a means of structural assignment,[36] to the drastic conditions (250–260°, 60 hr), and to the poor yield (5%), a reinvestigation of the structure of the above chlorocarbon seems desirable.

(35) B. A. Arbuzov and A. N. Vereshchagin, *Bull. Acad. Sci. USSR*, 586 (1965); *Chem. Abstr.*, **63**, 4142*d* (1965).

(36) A critical analysis of some of the difficulties encountered in the application of dipole moment data to structural assignments is given by J. G. Tillett, *Quart. Rep. Sulfur Chem.*, **2**, 227 (1967); for an example in a different area, see A. T. Blomquist and A. G. Cook, *Chem. Ind.* (*London*), 873 (1960).

TABLE III

MASS SPECTRAL PARAMETERS OF THE $C_{10}Cl_{12}$ ISOMERS **7**, **9**, AND **10**

m/e	540	505	470	435	400	388	365	353	330	318	306	295	283	270
	Relative intensities of the higher fragments[a]													
Compd	$C_{10}Cl_{12}^+$	$C_{10}Cl_{11}^+$	$C_{10}Cl_{10}^+$	$C_{10}Cl_9^+$	$C_{10}Cl_8^+$	$C_9Cl_8^+$	$C_{10}Cl_7^+$	$C_9Cl_7^+$	$C_{10}Cl_6^+$	$C_9Cl_6^+$	$C_8Cl_6^+$	$C_{10}Cl_5^+$	$C_9Cl_5^+$	$C_5Cl_6^+$
7	0.1	0.4	8.7	1.7	100	2.1	12.4	2.2	99.7	0.5	5.3	6.8	2.1	28.1
9	0.07	0.5	4.8	37.0	100	0.09	5.2	11.3	31.6	2.4	5.0	19.2	7.3	24.6
10	0.4	0.4	6.6	58.0	100	1.6	6.6	14.7	49.5	2.8	8.8	3.8	9.3	57.7
13					77.7	0	20.2	1.5	100	0	7.4	19.9	0	0

[a] Relative intensities, in per cent, refer to the lowest mass peak in each cluster. The spectra did not contain metastable peaks to determine the fragmentations leading to the C_9 and C_8 series of ions.

These, obtained with samples containing ^{13}C in its natural abundance (1.1%), are abstracted in Table II. Both **9** and **10** displayed ten peaks each of equal intensities and in three distinct regions. The frequencies farthest downfield, between 51.5 and 63.7 ppm, belong to the olefinic carbons, and the presence of four separate peaks in each isomer indicates the four nonequivalent sp^2 carbons required by the nonsymmetrical structures **9** and **10**. The second region, between 88.2 and 99.5 ppm, comprises the dichloromethylene carbons, represented by two peaks in each isomer. Frequencies belonging to the third region, between 104.0 and 109.5 ppm, are those of the four tertiary (bridgehead) carbons.

Further confirmation of the structures proposed for **9** and **10** was obtained from their mass spectra which, together with those of **7** and perchlorofulvalene, **13** (reference compound), are abstracted in Table III. Although all three $C_{10}Cl_{12}$ compounds showed the correct, but very weak, molecular ions and yielded $C_{10}Cl_8^+$ ions as the most abundant component, there was a discernible difference in the subsequent fragmentation patterns. Thus while the $C_{10}Cl_8^+$ fragment originating from **7** yielded an equally abundant $C_{10}Cl_6^+$ species, thus closely resembling the pattern of **13**, those obtained from **9** and **10** yielded less abundant $C_{10}Cl_6^+$ descendants. Unfortunately, the spectra did not contain diffuse peaks corresponding to metastable ions leading to, and revealing, skeletal fragmentation patterns; they rather indicated the gradual and extensive stripping of chlorines from the carbon framework.[37] A noteworthy difference, however was found at *m/e* 270, corresponding to $C_5Cl_6^+$; the endo $C_{10}Cl_{12}$ isomer, **10**, produced twice as abundant peaks of this species as did its exo isomer **9** and compound **7**. This indicates that **10** undergoes, expectedly, a more facile retro-Diels–Alder reaction than does its stereomer[38] and that both **9** and **7** yield fair amounts of C_5Cl_6 cleavage products, the latter presumably by a retro [2 + 2] addition. When the chlorination of **1** was carried out under conditions favorable to an ionic mechanism (in the dark and catalyzed by aluminum chloride), **9** and **10** became the major products.[40]

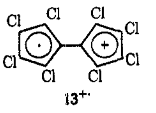
Much of the difference in the product distribution of the chlorination of **1** by the photochemical or by the aluminum chloride catalyzed routes can be interpreted by the probable mechanism underlying the reactions. Assuming that the light-catalyzed process involves a chlorine radical initiator which adds to the conjugated system to yield preferentially the allylic radical **1A** (Scheme I) and that the aluminum chloride catalyzed reaction involves the sequence initiated by a chloronium ion to yield preferentially **1B**, the evolvement of both reactions can be illustrated by the flow diagram outlined in Scheme I.

The major product of the photochlorination of **1** is **7**, which is best derived from the allylic radical involving both termini of one of the unsaturated systems, *i.e.*, **1A** (the "1,4 adduct").[41a,b] Ring closure with the other cyclopentadiene moiety, which, assuming the principle of least motion,[44] is gauche (and not trans)[45] oriented, is followed by the uptake of a second chlorine atom resulting in the formation of **7**. The change occurring on the second cyclopentadiene ring corresponds to a 1,2 addition[41a] and is probably the result of a steric effect which prevents the analogous chlorine terminated 1,4 addition[41a] to take place (*vide supra*). That addition of the latter kind, albeit not terminated directly by chlorine, can still take place is evidenced by the formation of **8**; the radical species formed on the second cyclopentadiene ring *via* a 1,4 addition,[41a] not being able to abstract or to take up chlorine, undergoes two additional cyclization steps and yields the fully saturated bishomocubane chlorocarbon.

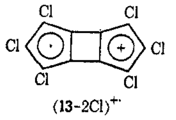
A second possible (but unlikely) mode of cyclization of **1A** is addition of the cyclopentenyl radical to one of

---

[37] The similarity between **7** and **13** (which incidentally yielded, as expected, a very abundant molecular ion) in their mass spectral behavior could tentatively be rationalized by the occurrence in the $C_{10}Cl_8^+$ and $C_{10}Cl_6^+$ fragments of considerable amounts of ions $\mathbf{13}\cdot^+$ and $(\mathbf{13}\text{-}2Cl)\cdot^+$, presumed to be common to both compounds. Ions with the same mass numbers originating from **9** and **10** might contain tricyclic and bicyclic species other than or in addition to those shown above (*e.g.*, ions with the methanoindene and methyleneindene skeletons).



$13^{+\cdot}$



$(13\text{-}2Cl)^{+\cdot}$

[38] A recent, thorough analysis of the mass spectral fragmentation patterns of a variety of highly chlorinated bridged-ring compounds indicated the ready occurrence of retro-Diels–Alder fragmentation in appropriate precursors.[39]

[39] R. Binks, K. Mackenzie, and D. L. Williams-Smith, *J. Chem. Soc. C*, 1528 (1969).

[40] To avoid isomerization, a solution of **1** in methylene chloride was first saturated with chlorine in the dark and only then was aluminum chloride introduced.

[41] (a) The numbering 1,4 and 1,2 is intended to show only the relative positions of the carbon atoms directly affected in the particular steps or in the overall reaction. (b) Examples for 1,4 addition in the photochlorination of polychlorocyclopentadiene substrates are provided by 1,2,3,4-tetrachlorocyclopentadiene,[42] 5,5-dimethoxytetrachlorocyclopentadiene,[43] and perchlorofulvalene.[7]

[42] A. Roedig and L. Hornig, *Chem. Ber.*, **88**, 2003 (1955).

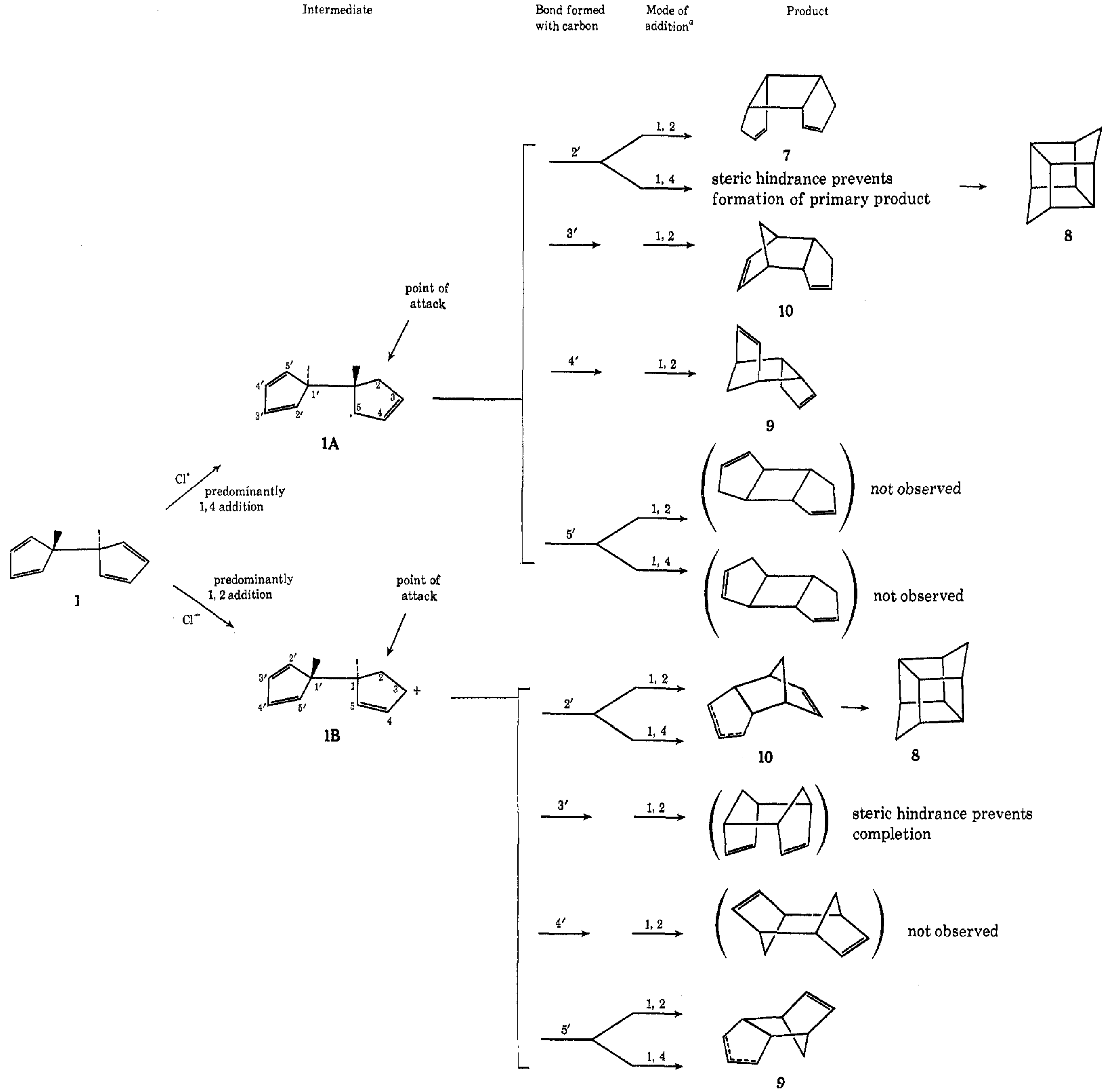
[43] E. T. McBee, D. L. Crain, R. D. Crain, L. R. Belohlav, and H. P. Braendlin, *J. Amer. Chem. Soc.*, **84**, 3557 (1962).

[44] F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938); *ibid.*, **7**, 199 (1939); J. Hine, *J. Org. Chem.*, **31**, 1236 (1966); J. Hine, *J. Amer. Chem. Soc.*, **88**, 5525 (1966); S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 185 (1968); O. S. Tee, *J. Amer. Chem. Soc.*, **91**, 7144 (1969).

[45] Were the cyclopentadiene rings oriented in a predominantly anti fashion to each other, cyclization would have resulted, applying the principle, in cis, anti,cis products, none of which was detected in the reaction mixture.

SCHEME I

MECHANISTIC SCHEME FOR THE CHLORINATION OF 1 (CHLORINE SUBSTITUENTS ARE OMITTED FROM STRUCTURES)



[a] 1,2 and 1,4 indicate the positions of attachment of the second chlorine reactant species (Cl^+ or Cl^-) on the second cyclopentadiene ring relative to the newly formed C–C bond.

the center carbons (3', 4') of the adjacent cyclopentadienyl ring to form the minor products **9** and **10**. These, however, arise more likely from the 1,2 addition of Cl· to **1**, followed by cyclization of the allylic radical with the termini of unsaturation (reaction path corresponding to that of **1B**).

The relative proportions of products **7** *vs.* **9**, **10** are reversed when the chlorination of **1** is carried out in the dark and in the presence of aluminum chloride. As before, the initiation step seems to be attack on one of the termini of unsaturation, but this time by Cl^+. In contrast to **1A**, however, the carbonium ion species seems to be localized on the carbon adjacent to the point of attack, due probably to the involvement of a cyclic chloronium ion intermediate.[46,47] The major products are thus derivable from the cyclization of ion **1B** of Scheme I, involving each of the termini of unsaturation on the adjacent ring and leading thus to the formation of **9** and **10**, *viz.* **8**. No products are feasible or were observed

---

(46) The occurrence of a chloronium ion could localize the electron deficiencies on carbons 2 and 3 of Scheme I. The reaction sequence initiated by carbonium ion 3 is depicted by the sequence starting with intermediate **1B** of Scheme I. The products derived from carbonium ion 2 are the same as those originating from the free radical on carbon 5 in intermediate **1A**.

(47) A similar reasoning could account also for the chlorination of the basic prototype, butadiene, which was shown to yield predominantly (3.5:1) 1,4 adducts by the radical pathway and more (1.2:1) 1,2 adducts by the polar pathway.[48] It has been suggested that a chloronium species can coordinate with only one double bond of butadiene at a time and not with both simultaneously.[49]

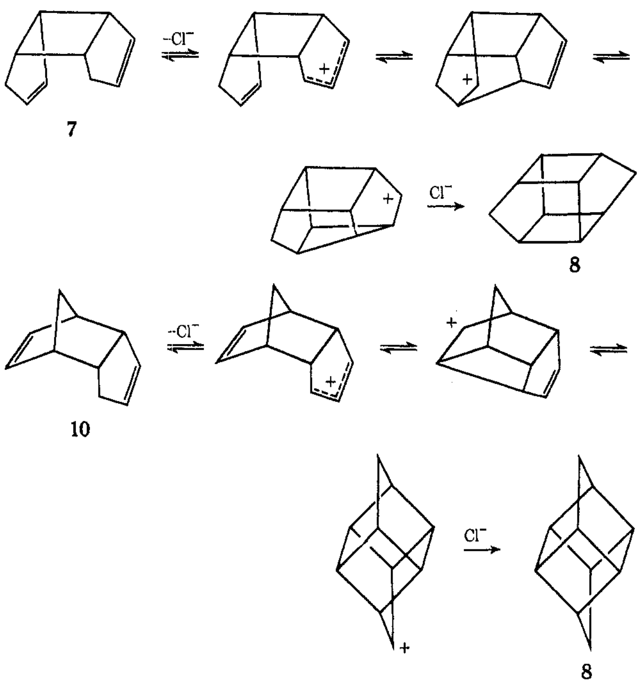
(48) M. L. Poutsma, *J. Org. Chem.*, **31**, 4167 (1966); M. L. Poutsma, *Science*, **157**, 997 (1967).

(49) K. Mislow and H. M. Hellman, *J. Amer. Chem. Soc.*, **73**, 244 (1951).

from cyclization steps involving any of the center carbons (3′, 4′) of the conjugated system.[50]

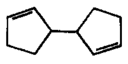
The mechanism outlined in Scheme I considers the formation of **7**, **9**, and **10** from **1** as being the result of kinetic control. The possibility of the formation of **9** and **10** from **7** in the ionic pathway due to isomerization by aluminum chloride can be excluded on the basis of control experiments, in which it was found that **9** was completely unaffected by the catalyst and that **10** yielded, under identical conditions, exclusively **8**. The total absence of **9** and the quantitative formation of **8** in the aluminum chloride catalyzed isomerization of **7** thus indicate that neither **9** nor **10** can originate from **7** in a secondary reaction. Thus kinetics seem to control not only the free-radical but the ionic chlorination mechanisms reported in this paper.

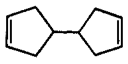
Plausible mechanisms for the cyclization of **7** and **10** to the cage structure under aluminum chloride catalysis can be outlined as follows (for clarity chlorines are omitted from structures).

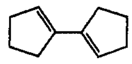


The light-catalyzed chlorination of **3**, **4**, and **5** yielded the noncyclized chlorocarbon $C_{10}Cl_{14}$ (**6**), mp 169°, as the major product. In contrast to **1**, in isomers **3**, **4**, and **5** the cyclopentadiene rings are connected through two sp^2 carbons. The geometry of the resultant linear (or planar) molecules is such that by no radical or ionic intermediates are the two rings within easy bonding distance. Hence the chlorination mechanism works on the two cyclopentadiene moieties independently and forms on each ring an analog of octachlorocyclopentene, which is known to be the end product of the chlorination of hexachlorocyclopentadiene.[52]

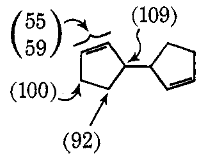
Although known for some time, no definite structure has so far been assigned to **6**.[2,53,54] Based on its hydrogenation under mild conditions to bicyclopentyl and on its uv spectrum [λ_{max} 224–230 mμ (ϵ 15,800–16,900)], it was concluded that this $C_{10}Cl_{14}$ chlorocarbon is a bi(cyclopentenyl) possessing one of the six possible structures with two nonconjugated double bonds, preferably P and Q.[2,53,54] As before, cmr was again definite in indicating a specific structure. Compound **6** exhibited five cmr peaks of equal intensities (Table II) thus indicating that the molecule is symmetrical and that of the three symmetrical structures, P, Q, and R, only P and R need to be considered.


P

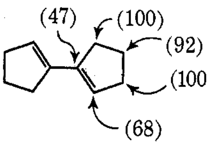

Q


R

With the help of appropriate models, including octachlorocyclopentene (**12**) and the other compounds already included in Table II, the following chemical shifts can be predicted for P and R.



P



R

The very good match between the predicted and the experimental chemical shifts (Table II) indicates rather convincingly that **6** possesses the novel structure R. The latter has not previously been considered based on the interpretation of its uv spectrum.[2,53,54] This, however, indicates only that there is no effective interaction between the two olefinic chromophores, a condition that requires coplanarity between two adjacent double bonds, as, *e.g.*, in cyclopentadiene. Two double bonds can still be adjacent and electronically nonconjugated if they are noncoplanar, especially orthogonal (type II steric effect).[55] We thus suggest that the uv datum does not conflict with the cmr evidence and that **6** has structure R in which the two cyclopentene rings are not coplanar.[10,11,56] The new structure accommodates also the chemical behavior reported[2,53,54] for **6**; its resistance to chlorination is analogous to the similar behavior of **12**,[52] and its preferential or exclusive formation under drastic, presumably thermodynamic, conditions (175–200°, liquid chlorine, sealed tube) is better accounted for by the highest branched olefinic structure R than by any of the other alternatives.[58]

---

(50) Since the electron density is significantly higher at the terminal carbons of a 1,3-butadiene system than at the central carbons,[51] any electrophilic reagent seeks out and reacts with carbons at the former positions.

(51) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 51.

(52) J. A. Krinitsky and R. W. Bost, *J. Amer. Chem. Soc.*, **69**, 1918 (1947).

(53) E. T. McBee, C. W. Roberts, and J. D. Idol, *ibid.*, **78**, 996 (1956).

(54) J. D. Idol, Thesis, Purdue University, 1955.

(55) (a) W. F. Forbes and R. Shilton, *J. Amer. Chem. Soc.*, **81**, 786 (1959), and references cited; (b) W. F. Forbes, R. Shilton, and A. Balasubramanian, *J. Org. Chem.*, **29**, 3527 (1964); (c) H. Wynberg, A. DeGroot, and D. W. Davies, *Tetrahedron Lett.*, 1083 (1963); (d) G. Vogel, *Chem. Ind.* (*London*), 1954 (1964).

(56) It is becoming increasingly evident, especially with the aid of nmr spectroscopy, that even in solution multiply substituted aliphatic compounds are often present in fixed conformational states.[57]

(57) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966, p 683.

(58) It is well documented that in thermodynamic equilibria the most branched olefins (*i.e.*, those substituted with the most alkyl, vinyl, phenyl, etc., groups) are favored.[59]

(59) See, *inter alia*, P. B. D. de la Mare, "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, pp 34–42.

Experimental Section

Decachloro-1,1-dihydrofulvalene (**1**),[60] mp 125°, was obtained by recrystallization of the commercially available material (Pentac, Hooker Chemical Corp.). Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer in tetrachloroethylene and carbon disulfide solution. Ultraviolet spectra were obtained in a Cary Model 14 spectrophotometer as solutions in cyclohexane. Nuclear quadrupole resonance spectra were recorded by Dr. R. M. Smith of the University of Wisconsin on a Wilks NQR-1A commercial spectrometer and some of the low temperature spectra were obtained by Drs. J. A. S. Smith and A. Royston of the University of Warwick on a Decca Radar spectrometer with superregenerative oscillating detector and side-band suppressor. Mass spectra were determined on a GEC-AEI MS1201B spectrometer using the direct insertion probe, at a source temperature of 150–170° and electron beam energy of 70 eV. Elution chromatography was carried out on 1-in. diameter columns, using neutral alumina (507-C, Camag-A. H. Thomas Co.). Elemental analyses and molecular weights on a Mechrolab vapor pressure osmometer were carried out by Galbraith Laboratories, Knoxville, Tenn.

Thermal Isomerization of Decachloro-1,1′-dihydrofulvalene (1).—A 450.0-g sample of **1** was placed in a 500-ml round-bottomed flask, which then was evacuated to 1 mm of pressure, closed by a stopcock, and placed into an oil bath kept at 145° for 24 hr. After removal and cooling of the flask to room temperature, its contents (a red-brown viscous syrup) was dissolved in 1250 ml of glacial acetic acid and chilled, depositing 210 g of crystalline solid. This was removed by filtration and recrystallization from hot glacial acetic acid to obtain pale yellow platelets of decachloro-3,3′-dihydrofulvalene (**3**), structure D, mp 110–111°: infrared maxima are abstracted in Table I; uv (isooctane) max 274 mμ (ϵ 5800) and 327 (2400); cmr chemical shifts are shown in Table II.

Anal. Calcd for $C_{10}Cl_{10}$: Cl, 74.7; mol wt, 475. Found: Cl, 74.3; mol wt, 473.

The original mother liquor deposited, on standing or when it was treated with water to the point of incipient oiling-out, oily crystals, which were isolated by suction filtration. After several recrystallizations from acetic acid, pure crystalline decachloro-2,3′-dihydrofulvalene (**4**), structure E, mp 82°, was obtained:[61] infrared parameters, see Table I; uv (isooctane) max 228 mμ (shoulder) (ϵ 6400) and 319 (4200); cmr parameters are given in Table II.

Anal. Calcd for $C_{10}Cl_{10}$: Cl, 74.7; mol wt, 475. Found: Cl, 74.3; mol wt, 468.

The third novel $C_{10}Cl_{10}$ isomer, decachloro-2,2′-dihydrofulvalene (**5**), structure F, was isolated conveniently by elution chromatography over alumina. When a 20.0-g sample of the original mother liquor in pentane was passed over about 450–500 g of alumina and was eluted continuously with pentane, the first three 100-ml cuts of the total twenty cuts taken yielded, after stripping of the solvent, pure **3** (about 2–3 g). Subsequent cuts contained mixtures of **3** and increasing amounts of **4**, followed by cuts containing further diminishing amounts of **3** and increasing amounts of **5**, and the last 8–10 fractions, which had a yellow color, contained pure **5**, mp 114–115°: major infrared peaks of this compound are listed in Table I; uv (isooctane) max 233 mμ (ϵ 6900) and 352 (4650); for cmr data see Table II.

Anal. Calcd for $C_{10}Cl_{10}$: Cl, 74.7; mol wt, 475. Found: Cl, 74.5; mol wt, 466.

The spectral parameters of the parent $C_{10}Cl_{10}$ isomer **1** are as follows: ir (C_2Cl_4) 1594 vs, 1555 cm^{-1} m; ir (CS_2) 1282 w, 1252 vs, 1230 w, 1180 s, 1162 s, 1118 m, 1008 m, broad, 970 s, 952 s, 904 m, 812 s, 702 vs, 678 vs, 648 vs, 640 s, 610 s, and 502 w cm^{-1}; uv (isooctane) 235 mμ (sh) (ϵ 6100), 282 (2000), and 333 (2900); for cmr data see Table II.

The reference chlorocarbon, and progenitor of all of the compounds discussed in this article, hexachlorocyclopentadiene (**2**), had the following spectral data: ir (film) 1602 vs, 1570 m, 1230 vs, 1210 w, 1188 m, 1162 w, 1140 vs, 1024 w, 975 w, 962 w, 938 w, 802 vs, 708 s, 681 s, and 548 w cm^{-1}; uv (isooctane) 324 mμ (ϵ 1670); cmr data are shown in Table II.

Thermal Isomerization of Decachloro-1,1′-, -3,3′-, -2,3′-, and 2,2′-dihydrofulvalenes (1,3,4, and 5).—Approximately 0.2-g samples of **1**, **3**, **4**, and **5** were sealed in about 5-mm o.d. glass tubes, which then were placed and kept in an oil bath at 145° for 14 hr. Analysis of the resultant melts by ir indicated that they had exactly identical spectra, containing **3**, **4**, and **5** (but no **1**), in identical proportions (about 50–55% **3**, 30–35% **4**, and 10–15% **5**).

In order to determine the time needed for equilibration, 0.2-g samples of **1** were sealed in glass tubes and placed in an oil bath kept at 145°. The extent of isomerization was followed by removing tubes at hourly intervals and analyzing them by ir. It was found that the sample heated for 5 hr had already attained the equilibrium composition, whereas the tube kept in the oil bath for 4 hr contained, except for traces of **1**, nearly the final reaction mixture.

Isomerization of 1, 3, 4, and 5 by Aluminum Chloride.—To a solution of 25 g of **1** in 100 ml of methylene chloride there was added 5 g of aluminum chloride, and the resultant slurry was stirred for a period of 20 hr. The color of the slurry changed from yellow to brownish-green to deep purple. Decomposition of the reaction mixture by water yielded a yellow syrup, whose ir was identical, both qualitatively and quantitatively, with that resulting from the thermal isomerization experiment. Under similar conditions **3**, **4**, and **5** (0.3 g each) yielded reaction mixtures identical with each other and with that of the isomerization of **1**.

Chlorination of 1 Catalyzed by Light.—The procedure of McBee, Idol, and Roberts[2] was followed (method A), except that the reaction was carried out in a Pyrex flask in refluxing carbon tetrachloride solution, and heated and irradiated by a bright heating lamp (150 W). The chlorination of 10.0 g of **1** yielded 11.25 g of product, which, after trituration with pentane, left behind 7.5 g (66% of the theory) of pure **7**, mp 221–222° (lit.[2] mp 221–223°). The spectral data were as follows: ir (C_2Cl_4) 1600 cm^{-1}; ir (CS_2) 1205 s, 1182 s, 1138 w, 1122 m, 1068 m, 1040 sh, 1020 s, 957 w, 905 sh, 892 m, 884 m, 852 s, 794 w, 764 w, 709 s, 697 s, 664 s, 630 w, 605 s, 582 s, and 546 m cm^{-1}; uv, same as reported;[2] the compound was too insoluble for natural abundance cmr characterization; its nqr frequencies were of equal intensities at 37.2, 37.8, 38.0, 38.3, 39.5, and 40.0 ± 0.1 MHz; for mass spectral data see Table III.

Analysis by infrared of the residue, left behind after evaporation of pentane of the mother liquor, indicated the presence of many new bands. The mixture was redissolved in pentane and chromatographed over alumina. The earliest elution cuts contained traces of **1** followed, in order of emergence, by the cage chlorocarbon K, $C_{10}Cl_{12}$, mp 485° (**8**),[2] and the novel $C_{10}Cl_{12}$ chlorocarbons **10**, mp 237–239°, and **9**, mp 186–187°.

A second chromatography of fractions of similar composition and recrystallization led to the isolation of the pure chlorocarbons **9** and **10**.

When recrystallized from hexane, **9** had mp 186–187° and the following spectral data: ir (C_2Cl_4) 1630 s, 1615 s cm^{-1}; ir (CS_2) 1202 s, 1165 s, 1138 m, 1090 m, 1062 m, 1052 m, 1030 w, 997 m, 960 w, 922 w, 905 m, 890 s, 848 m, 805 w, 761 m, 734 w, 698 w, 674 s, 649 s, 624 m, 607 s, 580 m, 542 w cm^{-1}; uv (cyclohexane) no maximum higher than 220 mμ; for cmr and mass spectral parameters, see Tables II and III, respectively; nqr frequencies were found at 36.91 (1), 37.09 (1), 37.41 (1), 37.51 (1) 38.30 (2), 38.56 (1), 38.67 (1), 39.13 (1), 39.38 (2), and 39.60 (1) ± 0.1 MHz; numbers in parentheses indicate relative intensities.

Anal. Calcd for $C_{10}Cl_{12}$: C, 22.02; Cl, 77.98; mol wt, 545.6. Found: C, 22.2; Cl, 78.0; mol wt, 549.

The recrystallization of **10** from hexane yielded white crystals, mp 237–239°, with the following spectral parameters: ir (C_2Cl_4) 1630 s, 1600 s, cm^{-1}; ir (CS_2) 1197 s, 1174 s, 1161 s, 1088 m, 1034 s (broad), 997 s (broad), 908 s, 878 w, 836 s, 746 s, 719 m, 672 s, 662 s, 640 s, 620 w, 602 s, 568 s, 540 w, 468 w, cm^{-1}; uv showed no maximum higher than 210 mμ; for cmr and mass spectral parameters, see Tables II and III; no nqr spectrum could be secured at room or at liquid nitrogen temperature.

Anal. Calcd for $C_{10}Cl_{12}$: C, 22.02; Cl, 77.98; mol wt, 545.6. Found: C, 22.0; Cl, 78.2; mol wt, 557.

The cage chlorocarbon K, $C_{10}Cl_{12}$, mp 485° (**8**),[2] had the following infrared maxima: (CS_2) 1152 s, 1134 s, 1160 s, 968 m, 891 m, 818 s, 666 m, 655 s, and 521 s cm^{-1}; no nqr spectrum could be obtained at room or at liquid nitrogen temperature.

Chlorination of 1 Catalyzed by Aluminum Chloride.—In order to avoid the isomerization of **1** by aluminum chloride, a solution of 25.4 g of **1** in 175 ml of methylene chloride was saturated with

---

[60] We are adopting the nomenclature proposed[6c] for the various $C_{10}Cl_{10}$ isomers since it is simpler and easier to visualize than the corresponding IUPAC name.

[61] Neither **3** or **4** had miticidal activity comparable to that of **1**.

Cl_2 while being protected from light by aluminum foil, and only after chlorine was bubbling through was 1.0 g of aluminum chloride added to the solution. After standing at room temperature for 24 hr, during which period a slow stream of chlorine gas was introduced, the reaction mixture was added to water, and the organic layer was stripped of solvent on a rotating evaporator. Work-up of the pale yellow slush by trituration with hexane and filtration yielded 9.1 g of rather pure **9** as the insoluble component. Elution chromatography of the remainder of the mixture (23.5 g) resulted in the isolation of a small amount of **8**, followed (in order of emergence) by **10** (amounting to about a total of 10–12 g), **7**, and small amounts of **9**.

Light-Catalyzed Bromination of 1.—A solution of 40.6 g of **1** in 173 g of bromine was both irradiated and refluxed with the aid of a 100-W uv lamp (General Electric H100 A-4) for 16 hr. The excess bromine, which acted also as a solvent, was evaporated on steam bath in a well-vented hood, and the resultant crystal mass was triturated with methylene chloride and filtered by suction. The insoluble portion, 27.5 g, mp 162.0–163.5°, after recrystallization from cyclohexane, matched the properties of the $C_{10}Br_2Cl_{10}$ halocarbon, mp 147°, obtained by R. D. Crain by a similar procedure.[32] The infrared pattern of this compound (1595 s, 1205 s, 1182 s, 1138 m, 1121 m, 1069 m, 1022 s, 958 w, 892 m, 875 m, 839 m, 778 w, 742 w, 689 s, 659 w, 655 w, 604 m, 589 w, 582 w, 561 m, 552 m, and 540 m cm^{-1}) resembles very closely that of **7**, thus suggesting that the bromine adduct of **1** has the same structure as its chlorine adduct, *i.e.*, N.

Anal. Calcd for $C_{10}Br_2Cl_{10}$: C, 18.93; Br, 25.19; Cl, 55.88. Found: C, 19.0; Br, 25.4; Cl, 55.5.

Light-Catalyzed Chlorination of 3, 4, and 5.—The same procedure, which transformed **1** into the further cyclized products **7**, **9**, **10**, and **8**, resulted in the formation of the bicyclic $C_{10}Cl_{14}$ adduct **6**, mp 169°,[2] when applied to **3**, **4**, and **5**.

Cyclization of 7 to the Cage Chlorocarbon 8.—To a solution of 1.0 g of **7** in 20 ml of methylene chloride there was added 0.6 g of anhydrous aluminum chloride and the resultant mixture was stirred for 20 hr at room temperature. Work-up by treatment with water and stripping of the solvent resulted in 1.0 g of off-white crystalline product, shown by ir to be pure **8** by comparison with the spectrum of an authentic sample.[2]

Cyclization of 7-Br to the Cage Halocarbons 8-Br.—A slurry of 3.62 g of **7**-Br in 35 ml of methylene chloride, to which 0.5 g of anhydrous aluminum bromide was added, was stirred at room temperature for 23 hr. The resultant deep-purple reaction mixture was poured into water, the organic layer was separated and washed, and finally the solvent was stripped in a rotary evaporator. The resultant off-white solid, 3.60 g, was analyzed by ir, which indicated the complete absence of starting material or of any species with a double bond and which showed a pattern closely resembling that of **8**. Elution chromatography over alumina indicated the presence of a small amount of **8**, which was eluted first followed by several species of bromochlorocarbons.

Cyclization of 7 to 11 by Sulfur Trioxide.—A solution of 20.0 g of **7** in 200 g of liquid sulfur trioxide was kept at room temperature for 2 hr, during which period the originally deep-purple solution acquired a strong maroon color. Distillation of most of the sulfur trioxide and pouring the residue onto ice gave a white precipitate, which after washing and air-drying (18.5 g) was found by ir to be the pure hydrate of **11**.[62]

Effect of Aluminum Chloride on *endo*-Dodecachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (10).—To a solution of 1.4 g of **10** in 10 ml of methylene chloride there was added 0.5 g of aluminum chloride, and the resultant dark greenish-gray slurry was stirred for 24 hr. Quenching by water, extraction by methylene chloride, and stripping of the solvent in a rotating vacuum evaporator resulted in the formation of a crystalline mass, the ir spectrum of which indicated it to be pure **8**. No starting material or its isomer **9** was detectable by ir.

Effect of Aluminum Chloride on *exo*-Dodecachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (9).—When carried out with **9**, the preceding procedure resulted in the quantitative recovery of the starting material.

Registry No.—**1**, 2227-17-0; **2**, 27425-39-4; **3**, 27425-40-7; **4**, 27425-41-8; **5**, 27425-42-9; **6**, 27396-27-6; **7**, 27396-29-8; **8**, 2385-85-5; **9**, 2626-29-1; **10**, 27425-43-0; **12**, 706-78-5; bromine adduct of **1**, 27396-30-1.

Acknowledgments.—We express our appreciation with thanks to Professor J. D. Roberts and Dr. R. Smith of the California Institute of Technology for determining the ^{13}C nmr parameters of our chlorocarbons and of a large number of model compounds and to Professor R. West and Dr. R. Martin Smith of the University of Wisconsin for informing us of their results and for the subsequent discussions, as well as for determining the nqr spectra of several of our compounds. We also thank Dr. M. P. Williamson of our Research Center for obtaining and discussing the mass spectra of several chlorocarbons and Dr. K. L. Loening of the Chemical Abstracts Service for his advice on nomenclature.

(62) E. E. Gilbert, U. S. Reissue Patent Re 24,397 (1957).