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Hexachlorofulvene. I. Synthesis and Reactions under Diels–Alder Conditions[1]

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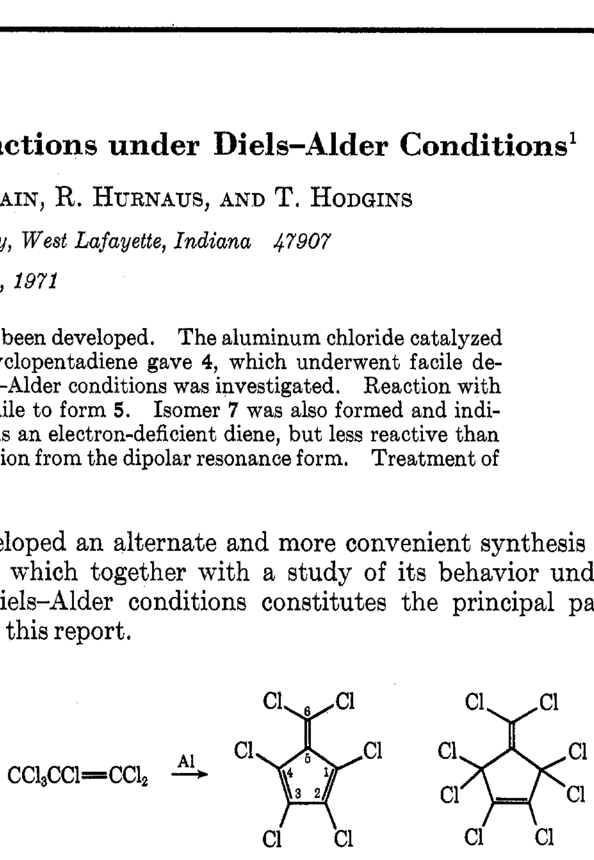
A new method for the preparation of hexachlorofulvene has been developed. The aluminum chloride catalyzed reaction of carbon tetrachloride and 1,2,3,4,5-pentachlorocyclopentadiene gave **4**, which underwent facile dechlorination to the desired **1**. The behavior of **1** under Diels–Alder conditions was investigated. Reaction with cyclopentadiene showed that **1** acts primarily as the dienophile to form **5**. Isomer **7** was also formed and indicated that **1** may also react as a diene. Hexachlorofulvene is an electron-deficient diene, but less reactive than hexachlorocyclopentadiene, possibly reflecting some stabilization from the dipolar resonance form. Treatment of **1** with $AlCl_3$ gave a dimer and a difulvene.

We have reported previously that the condensation between 1,2,3,4-tetrachlorocyclopentadiene and aromatic aldehydes[2] yields the corresponding 6-aryl-1,2,3,4-tetrachlorofulvenes. Another entry into this tetrachlorofulvene system, developed from tetrachlorodiazocyclopentadiene,[5,6] appears to have only limited applicability.

Substituent chlorine atoms modify the chemical behavior of these fulvenes, and enable reactions to be performed other than those to which hydrocarbon fulvenes[7] are normally susceptible. In order to clarify the extent of the similarities and differences between the two systems, we have subjected the parent chlorocarbon, hexachlorofulvene (**1**), to a representative set of reactions, described in this and subsequent papers. The results are also pertinent to work done in the area of alicyclic chlorocarbon chemistry.[8]

Roedig[9] reported the first preparation of hexachlorofulvene from the reaction of hexachloropropene and aluminum; a co-product of this reaction was octachloro-4-methylenecyclopentene (**2**). We have developed an alternate and more convenient synthesis of **1**, which together with a study of its behavior under Diels–Alder conditions constitutes the principal part of this report.



Results and Discussion

The aluminum chloride catalyzed reaction between carbon tetrachloride and 1,2,3,4,5-pentachlorocyclopentadiene (**3**)[10] gave octachloro-5-methylcyclopentadiene (**4**)[5,11] (Scheme I). The mechanism of this unusual reaction is not known, since both **3** and CCl_4 are capable of interacting with this Lewis acid.[13,14]

Dechlorination of **4** gave **1** in a yield of 94%. The reagent of choice was triethyl phosphite, although sodium iodide and stannous chloride were also effective. Using this procedure, 100-g quantities of **1** were made routinely. The fulvene formed deep red needles (hexane), mp 153–154°, appeared to be indefinitely stable in air, and was identical with a sample prepared

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[1] Taken in part from the Ph.D. Thesis of D. L. Crain, Purdue University, 1958, and the Ph.D. Thesis of E. P. Wesseler, Purdue University, 1971. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[2] E. T. McBee, R. K. Meyers, and C. F. Baranauckas, *J. Amer. Chem. Soc.*, **77**, 86 (1955). This procedure has been extended to give analogous fulvenes[3] and related derivatives.[4]

[3] J. S. Meek and P. Argabright, *J. Org. Chem.*, **22**, 1708 (1957).

[4] Y. Kitahara, I. Murata, M. Ueno, K. Sato, and H. Watanabe, *Chem. Commun.*, 180 (1966), and references cited therein.

[5] E. T. McBee, J. A. Bosoms, and C. J. Morton, *J. Org. Chem.*, **31**, 768 (1966).

[6] D. Bretches, Ph.D. Thesis, Purdue University, 1970.

[7] For a recent review on fulvenes, see P. Yates, *Advan. Alicycl. Chem.*, **2**, 59 (1968).

[8] R. West, *Accounts Chem. Res.*, **3**, 130 (1970).

[9] A. Roedig, *Justus Liebigs Ann. Chem.*, **569**, 161 (1950). Yields of **1**, mp 153°, were *ca.* 10%. The addition of chlorine to **1** gave **2**. This important result is mentioned here to exemplify the behavior of **1** under free radical conditions.

[10] E. T. McBee and D. K. Smith, *J. Amer. Chem. Soc.*, **77**, 389 (1955). An improved procedure gave **3** from the commercially available hexachlorocyclopentadiene in higher yields (Experimental Section).

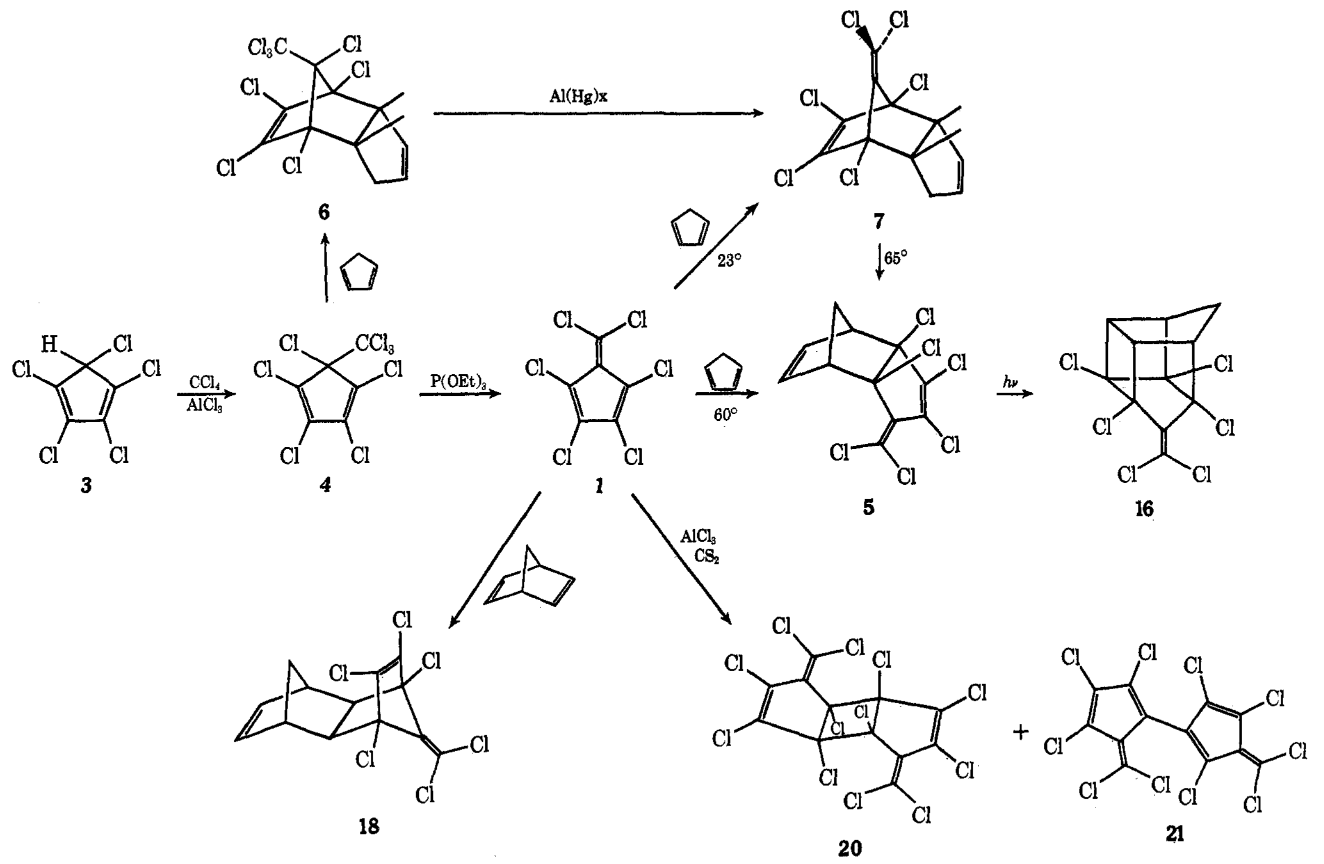
[11] This compound was prepared differently by H. J. Prins [*Recl. Trav. Chim. Pays-Bas*, **72**, 253 (1953)] and correctly identified later by spectral examination.[12]

[12] E. Ziegler, *Z. Anal. Chem.*, **213**, 9 (1965), and references cited therein.

[13] C. H. Wallace and J. E. Willard, *J. Amer. Chem. Soc.*, **72**, 5275 (1950).

[14] For example, see H. P. Fritz and L. Schäfer, *J. Organometal. Chem.* **1**, 318 (1964).

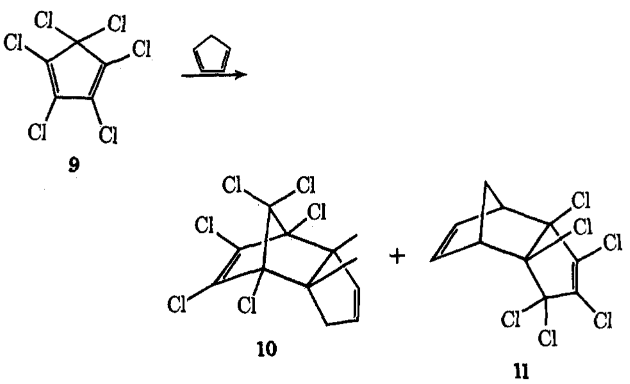
Scheme I



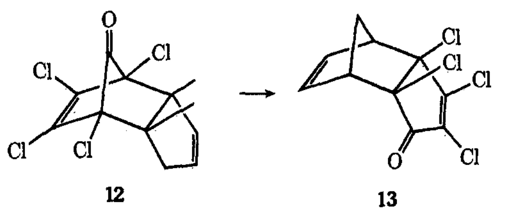
according to Roedig's procedure.[9,15,16] The ir double-bond stretching frequency of 1 was at 6.35 μ[17] and its uv absorption was at λ_{max} 296 and 307 nm (log ϵ 4.24 and 4.21, respectively).[18]

Diels-Alder Reaction.—Hydrocarbon fulvenes participate readily in this reaction,[7] although extensive studies have not been undertaken. In this work, we sought reactions which would demonstrate behavior of 1 both as a diene and as a dienophile.

In benzene at 60°, 1 and cyclopentadiene gave adduct 5 exclusively. The isomeric adduct 7 was synthesized by an alternative procedure, and was shown to isomerize quantitatively to 5 at this temperature. Repetition of this Diels-Alder reaction at 23° gave 5 and 7 in an approximate ratio of 4:1, together with some *endo*-dicyclopentadiene (8), as shown by nmr analysis. The adduct 7 was stable under these conditions. In addition, a sample of 1 in benzene at room temperature or at 60° was also recovered unchanged after 4 days (tlc); no evidence for Diels-Alder dimerization was found. In a related system, hexachlorocyclopentadiene (9) and cyclopentadiene are known[19,20] to yield the two adducts, 10 and 11, in a 5:1 ratio; this reaction was repeated in order to determine the nmr parameters of these products. This data also verified the accuracy of the previous structural assignments.[19]



The rearrangement of 7 and 5 is of interest. Generally, analogous behavior has been observed in Diels-Alder adducts containing the *endo*-dicyclopentadiene skeletal structure. For example, the isomerization of 11 to 10 and of 12 to 13 have been reported.[19,21] Re-



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(15) 1 has been obtained in small quantities both by A. E. Kulikova, N. M. Pinchuk, and E. N. Zil'berman [*Zh. Org. Khim.*, **3**, 1388 (1967)] and G. W. Calundann [Ph.D. Thesis, Purdue University, 1967].

(16) The attempted conversion of **2** to **1** with triethyl phosphite at room temperature failed.

(17) Compare the similar absorptions at 6.05 and 6.20 μ for **2**, and 6.22 μ for perchlorocyclopentene.

(18) (a) Fulvenes also possess a longer wavelength band of much lower intensity which extends into the visible region, accounting for the color of fulvenes.[7] This broad band reportedly[9] possesses a maximum at 450 nm for **1**. (b) The mass spectrum of **1** has been recorded by S. Meyerson and E. K. Fields [*J. Chem. Soc. B*, 1001 (1966)].

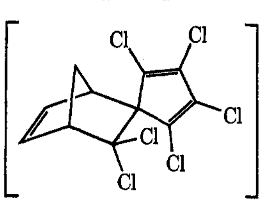
(19) M. Livař, P. Klucho, and M. Paldan, *Tetrahedron Lett.*, 141 (1963).

(20) (a) R. Riemschneider, *Monatsh. Chem.*, **83**, 802 (1952); (b) R. Riemschneider, *Botyu Kagaku*, **28**, 83 (1963).

(21) P. Yates and P. Eaton, *Tetrahedron*, **12**, 13 (1961).

arrangements of this type are generally held to be intramolecular,[22] and the unusually low temperature (60°) required for the isomerization of **7** to **5** supports this contention. It may also be noted that the strain due to the exo chlorines in **11** is relieved somewhat in **10**, but apparently with **5** and **13** the increased conjugation and the release of strain in the sp^2 carbon is of more importance.

The structure of **5** was elucidated by comparison of its nmr spectrum with those of **11** and other norbornene derivatives.[23] In particular, the broadened methine proton signals and the 0.15 ppm coupling constant between the methylene protons, which appear as the upfield AB quartet, are features normally diagnostic of such systems. Apparently, dienophilic fulvenes undergo reaction at one of the endocyclic rather than the exocyclic double bond.[24] That the behavior of **1** was consistent with this precept, and did not yield **14**, was supported by the following information. First, the uv spectrum of **5** contained absorptions at 267, 274, and 284 nm (log ε 4.26, 4.37, and 4.26, respectively); these extinction coefficients are about an order of magnitude larger than the values for chlorinated cyclopentadienes.[5,25] Second, a model was constructed[28] whereby the chemical shifts shown were estimated for compound **15**. Agreement with the corresponding values for **5** (and also **11**) was reasonable except for the C-7 proton, which, as would be expected, is influenced strongly by the chlorine substituents. Lastly, the photocyclization of **5**, a reaction for which there is considerable precedent,[30] gave **16** together with some unidentified products. The mass spectrum of **16** contained the molecular ion with the correct isotopic pattern. In addition, the nmr spectrum of **16** was similar to that of **17**, and the ir spectra of these two compounds were nearly identical between 6.9 and 8.4 μ. There was also a strong double-bond stretching absorption for **16** at 5.98 μ.[17] Compound **17**[31] was prepared by irradiation of **10**. This product, identified primarily from the method of preparation, gave an nmr spectrum which contained a single resonance (4 H) for the methine protons and an upfield AB quartet for the methylene bridge (2 H).



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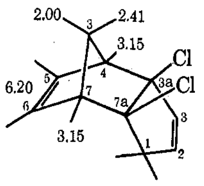

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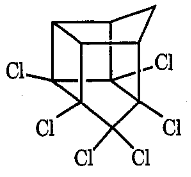

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The isolation and subsequent dechlorination of **6**, obtained from **4** and cyclopentadiene (Scheme I), provided the first important chemical evidence supporting the structure assigned[12] to **4**, which was shown to be stable to the Diels-Alder conditions. Compound **6** was identified by the extremely close similarity of its nmr spectrum with that of **10**. Differences in the chemical shifts between corresponding protons were less than 0.17 ppm. For this reason, the C-8 chlorine substituent was assigned the position anti to the chlorinated double bond. None of the isomeric *syn*-chloro analog of **6** was isolated. The factors that control the stereochemistry in this type of reaction are not understood. In probably the only systematic study of consequence, Williamson and coworkers[32] examined the reaction of **3** with a series of dienophiles and established that the appropriate products contained isomers, which differed according to whether the chloro substituent on the bridging methylene group occupied a syn or anti position. These results were rationalized[32] in terms of the steric effects, electrostatic interactions, and substituent polarizabilities operating in the reactant complex.[33] The structure of **6** is consistent with these concepts,[32,33] particularly in that the bulky trichloromethyl substituent occupies the less sterically demanding syn position.

The structure of **7** followed from the methods of preparation and from spectral data. Thus, the nmr

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[22] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[23] (a) K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuju, and H. Tanida, *Tetrahedron Lett.*, 9 (1966); (b) P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964); (c) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).

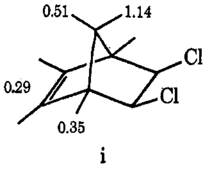
[24] See ref 7, p 142.

[25] The following are uv data: **9**, 322 nm (log ε 3.17);[26] **4**, 326 nm (log ε 3.23); and 5-methylpentachlorocyclopentadiene,[27] 308 nm (log ε 3.025).

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

[27] R. A. Halling, Ph.D. Thesis, Purdue University, 1965.

[28] Examination of the literature data[23] on the nmr chemical shifts of halo- and dihalonorbornenes gave the approximate *incremental* values (parts per million), relative to norbornene, for the protons in the unknown *exo-cis*-5,6-dichloronorbornene (i). These values were added subsequently to the corresponding ones in *endo*-dicyclopentadiene[29] to obtain the results for **15**. The incremental values shown in i resulted necessarily from personal judgments and should be treated accordingly.



i

[29] T. Hodgins, unpublished results.

[30] W. L. Dilling, H. P. Braendlin, and E. T. McBee, *Tetrahedron*, **23**, 1211 (1967), and references cited therein.

[31] (a) L. Vollner, W. Klein, and F. Korte, *Tetrahedron Lett.*, 2967 (1969); (b) F. Korte, W. Klein, and B. Drefahl, *Naturwiss. Rundsch.*, **23**, 445 (1970).

[32] (a) K. L. Williamson, Y-F. L. Hsu, R. Lacko, and C. H. Youn, *J. Amer. Chem. Soc.*, **91**, 6129 (1969); (b) K. L. Williamson and Y-F. L. Hsu, *ibid.*, **92**, 7385 (1970).

[33] Bulky 5 substituents in cyclopentadienes, lying between the parallel planes which define the reactant complex, tend to hinder product formation. In principle, the least hindrance occurs in the limiting case, when the 5-carbon atom in the cyclopentadiene has sp^2 hybridization; a situation that could result with a good leaving group at the 5 position. In such circumstances, a developing carbonium ion at this position would be better stabilized when the transition stage resembles the product with the leaving group in an anti position.[34]

[34] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 599.

spectrum of **7** was very similar to those of **10** and **6**. The compound exhibited ir double-bond stretching absorptions at 5.98 and 6.1 μ, comparable to the corresponding ones[17] found in **2**. Also, the uv data (λ_{max} 205 nm, log ϵ 4.26)[35] confirmed that **7** did not contain a conjugated double-bond system.

The formation of **7** from **1** and cyclopentadiene demonstrated the ability of **1** to act as the diene under Diels–Alder conditions. Another example was found in the reaction of **1** with norbornadiene. Product **18** (Scheme I) was identified readily by comparison[36] of its nmr spectrum (Table I) with that of aldrin (**19**).

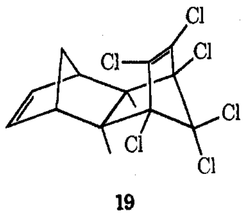


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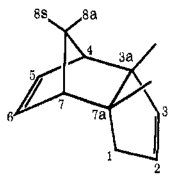
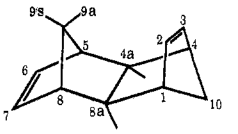
Table I

Nuclear Magnetic Resonance Data[a]





	4^b	5 and 6^c	7^b	8 syn^d	8 anti
5	3.27	6.10	3.81	2.00	2.50
11	3.18	6.24	3.46	2.05	2.58
	1	2	3	3a	7a
6^e	2.38	5.60	5.85	3.98	3.60
7^e	2.43	5.61	5.83	3.70	3.21
10^e	2.42	5.65	5.8.	3.83	3.43
	4a and 8a^f	5 and 8^b	6 and 7^c	9 syn^g	9 anti
18	2.57	2.90	6.32	1.35	1.52
19	2.73	2.90	6.32	1.32	1.61

[a] Chemical shifts (δ) in parts per million downfield from TMS. [b] Singlet with fine structure. [c] Vinylic signal centered at this position. [d] J_{8s-8a} = 9.5 Hz. [e] All signals were complex multiplets and errors may be present in the estimated chemical shifts. [f] Singlet. [g] J_{9s-9a} = 11.0 Hz.

On the other hand, **1** and 6-phenyltetrachlorofulvene are reported[3,9] to be unreactive toward maleic anhydride, even under more extreme conditions.[37,38] Thus, the behavior of **1** as a diene parallels that of **9**, which also reacts faster with cyclopentadiene than with maleic anhydride.[40] This order of reactivity appears to be characteristic of electron-deficient dienes.

The early stages of a competition reaction between **1** and **9** with norbornadiene (an electron-rich dienophile) were monitored by nmr. The results showed that **9** was 1.7 times more reactive.[41] The lower reactivity of **1** compared to **9** with both norbornadiene and maleic anhydride depends in part on the intrinsic reactivity of the dienes, which is unrelated to the nature of the dienophile. For example, benzene is normally unreactive as a diene under Diels–Alder conditions. Hence, the reactivity of **1** may merely reflect its partial aromatic character.[43]

In concluding this section, the preferred dienophilic reaction of **1** with cyclopentadiene is emphasized.[44] This study demonstrated that **1** can participate in the Diels–Alder reaction both as a diene and a dienophile, and that the substituent chlorine atoms exert an important but not overriding influence.

Dimerization.—Although **1** was found to be stable at 105° as shown by tlc, decomposition[45] occurred at 196°. In the latter case, no evidence for thermal dimerization was obtained. Instead, the major product was found to be **2**. Some red, oily material was also isolated, but not identified. Dimerization was observed when **1** was treated with approximately a 0.5 mole ratio of aluminum chloride. The product mixture included some **2** and a difulvene. Both the dimer and the difulvene appeared to be homogeneous (tlc, melting point) and were tentatively assigned structures **20** and **21**, respectively (Scheme I). The molecular formulas of these compounds were established from elemental analyses and mass spectra, but their precise structure would not be proven rigorously because of numerous isomeric possibilities. Thus **20**, which reverted to **1** on heating, had a uv absorption at λ_{max} 272 nm (log ϵ 4.62); this wavelength is very similar to that of **5**, though the relative extinction coefficients are different by the significant factor of 1.78. This data eliminated the possibility of a norbornenyl system in **20** and suggested the presence of two identical but noninteracting chromophores as shown in the given structure. There are three other isomers of this type, with the cyclopentene systems on the same side of the cyclobutane ring or with the dichloromethylene substituents aligned. The choice of the centrosymmetric **20** was made by comparison of infrared data with that for a similar dimer derived in principle from tetrachlorocyclopentadienone.[46] The ir spectrum of **20** contained about the same number of absorption bands as in the model[46] and four of them occurred at similar wavelengths.

The isolation of **21** from the reaction mixture was unexpected since Lewis acid promoted dechlorinations are rare.[47] The red color of this product suggested a fulvene moiety and evidence for a difulvene structure was derived from spectral comparisons. Thus, the uv absorption of **21** was at 302 nm (log ϵ 5.53). The

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(35) Octachlorocyclopentene[26] has λ_{max} 230 nm (log ϵ 4.00).

(36) (a) A. P. Marchand and J. E. Rose, *J. Amer. Chem. Soc.*, **90**, 3724 (1968); (b) Sadtler Standard Spectra, No. 6239.

(37) We have confirmed this result for **1**.

(38) Failure of **1** and maleic anhydride to react may be an equilibrium rather than a kinetic effect.[39]

(39) D. Craig, J. J. Shipman, J. Kiehl, F. Widmer, R. Fowler, and A. Hawthorne, *J. Amer. Chem. Soc.*, **76**, 4573 (1954). These authors observed facile dissociation of the Diels–Alder adduct from 6,6-dimethylfulvene and maleic anhydride. They noted the conversion of the adduct to a more stable isomer and suggested that this rearrangement proceeded *via* an intramolecular process.[21]

(40) (a) J. Sauer, D. Lang, and A. Mielert, *Angew. Chem., Int. Ed. Engl.*, **1**, 268 (1962); (b) J. Sauer and H. Wiest, *ibid.*, **1**, 269 (1962).

(41) The reaction conditions employed here are much less severe than those apparently needed for the reaction of cyclopentadiene and norbornadiene,[42] as would be predicted.[40]

(42) J. K. Stille and D. A. Frey, *J. Amer. Chem. Soc.*, **81**, 4273 (1959).

(43) A. discussion on this point is given by K. Hafner, *et al.*, *Angew. Chem., Int. Ed. Engl.*, **2**, 123 (1963).

(44) The ratio of **5** to **8** was >10:1 (nmr) in this reaction.

(45) Rearrangement of **1** to hexachlorobenzene was observed at 250–300° when bromine was present.[9]

(46) R. M. Scribner, *J. Org. Chem.*, **30**, 3657 (1965). This paper illustrates the difficulties encountered in differentiating complex chlorocarbon isomers. The tetrachlorocyclopentadienone dimer analog of **20** has ir absorptions at 5.71 (C=O), 6.33, 8.06–8.13, 8.34, 9.35, 9.75, 10.87, 12.84, and 13.89 μ.

(47) E. N. Zilberman, A. E. Kulikova, and E. G. Pomerantseva, *J. Org. Chem., USSR.*, **3**, 1158 (1967).

spectrum is similar to that of **1** except that the extinction coefficient is greater by a factor of 2.0. The ir spectrum of **21** is also very similar to that of **1**. Molecular models show that in the 2,2′-linked isomer there is a lack of steric distortion which would allow coplanarity of the fulvene rings and hence this isomer would be expected to have a bathochromic shift in the uv relative to **1**. The tentative choice of a 1,2′ linkage in **21** was made from the evidence (developed in a subsequent paper) that **1** is susceptible to attack by electrophiles at the 1 position, whereas the $AlCl_3$–**1** complex is electrophilic at the 2 position. The structure of **21** is consistent with this idea.

The formation of **2** and **21** is an interesting example of an aluminum chloride catalyzed redox process, although the exact mechanistic details are not known.

Experimental Section

Procedures and Equipment.—Melting points were determined with a Mel-Temp apparatus in sealed tubes and are uncorrected. Proton nmr spectra (Table I) were obtained on a Varian Associates A-60A spectrometer; carbon tetrachloride was used as a solvent with tetramethylsilane as an internal standard. Infrared spectra were determined on the compounds as KBr pellets using a Perkin-Elmer 221 or Beckman IR-8 infrared spectrophotometer. Ultraviolet spectra were determined in 95% ethanol on a Bausch and Lomb Spectronic 505 spectrophotometer. Thin layer chromatography (tlc) was carried out on glass plates coated with silica gel HF-254, E. Merck AG. Mass spectra were recorded on a Hitachi Perkin-Elmer HU-6D high-resolution mass spectrometer. Elemental analyses were performed by Dr. C. S. Yeh and her staff at Purdue University.

1,2,3,4,5-Pentachlorocyclopentadiene (3).—A solution containing 136.5 g (0.5 mol) of **9** in 50 ml of acetone was cooled with an external ice bath while 113 g (0.5 mol) of stannous chloride dihydrate in 200 ml of acetone was added at such a rate as to keep the temperature near 45°. The ice bath was then removed and the solution was stirred an additional 30 min. The solution was poured into 300 ml of water and the organic material was then extracted with CCl_4. After removing the solvent from the dried extract, the product was distilled (52–53° at 0.25 mm) rapidly to prevent dimerization, giving 95 g of monomeric **3** (80% yield).

Octachloro-5-methylcyclopentadiene (4).—A mixture of 95 g (0.4 mol) of **3**, 400 ml of CCl_4, and 10 g (0.075 mol) of $AlCl_3$ was stirred and heated on a water bath at 75° for 2 hr. After cooling, 300 ml of water was added and the organic material was extracted with CCl_4. This yielded 128 g of a brown solid, which was then dissolved in hot acetone to which decolorizing charcoal was added. After filtering, the acetone solution yielded 118 g (83%) of slightly yellow **4**. Further purification by recrystallization from CCl_4 gave colorless crystals: mp 93.5–94°; ir (KBr) 6.24 (s), 6.38 (w), 7.98 (s), 8.56 (m), 8.62 (m), 8.92 (w), 9.93 (m), 10.42 (m), 11.94 (s), 12.29 (s), and 14.16 μ (s).

Anal. Calcd for C_6Cl_8: C, 20.25; H, 0.00; Cl, 79.75. Found: C, 20.34; H, 0.00; Cl, 79.49.

A solution of **4** in benzene was refluxed for 65 hr. A 98% recovery of **4** was realized.

Hexachlorofulvene (1).—A solution of 118 g (0.33 mol) of **4** in 500 ml of hexane was cooled in an ice bath while 46 g (0.36 mol) of triethyl phosphite in 50 ml of hexane was added dropwise. After 15 min following the addition, the solvent was distilled off. The residue was recrystallized from CCl_4 and yielded 88 g (94%) of deep red needles: mp 153–154°; ir (KBr) 6.35 (s), 7.81 (s), 7.95 (s), 8.16 (m), 10.75 (m), 14.16 μ (m).

A solution of **4** in acetone, when treated with stannous chloride dihydrate or sodium iodide at room temperature, gave **1** in 63 and 98.2% yield, respectively. The latter conversion, however, was *ca.* 67%.

Synthesis of *endo*-2,3,3a,7a-Tetrachloro-1-dichloromethylene-3a,4,7,7a-tetrahydro-4,7-methanoindene (5). A. At 60°.—Hexachlorofulvene (10.0 g, 0.035 mol), cyclopentadiene (2.6 g, 0.04 mol), and benzene (30 ml) were sealed in a Carius tube and heated to 60° for 12 hr. The product was chromatographed on a 30 × 1.5 in. column packed with 200 mesh silica gel. Hexane was used as an eluent. The first fraction was 5.9 g of **1**. The second contained 4.7 g (41% conversion, 95% yield) of **5** as colorless crystals: mp 121–122°; ir (KBr) 6.24 (s), 6.34 (s), 6.86 (w), 7.53 (m), 8.00 (s), 8.07 (s), 8.17 (s), 10.26 (m), 10.61 (m), 10.79 (m), 10.90 (s), 11.53 (m), 12.77 (m), 13.07 (s), 13.82 (m), 14.14 (m), 14.64 μ (s).

Anal. Calcd for $C_{11}H_6Cl_6$: C, 37.65; H, 1.72; Cl, 60.63. Found: C, 37.30; H, 1.60; Cl, 61.00.

B. At 23°.—A solution containing 14.2 g (0.05 mol) of **1**, 10 g (0.15 mol) of cyclopentadiene, and 70 ml of benzene was stirred on a water bath (23°) for 71 hr. An aliquot removed at this time and one at 27 hr were analyzed by nmr, which indicated that the ratio of **5**:**7**:**8** was approximately 4:1:1 The product was chromatographed on a silica gel column which was eluted with hexane. Only 0.1 g of **1** was recovered as the first fraction. A later fraction yielded 13.1 g (77%) of adducts **5** and **7**.

Preparation of *endo*-4,5,6,7,8-*anti*-Pentachloro-8-*syn*-trichloromethyl-3a,4,7,7a-tetrahydro-4,7-methanoindene (6).—A solution of 13.2 g (0.037 mol) of **4**, 7 ml (0.086 mol) of cyclopentadiene, and 30 ml of benzene was heated to 83° for 2 days in a sealed ampule. The product was chromatographed on a silica gel column. Elution with hexane gave 7.8 g of **4** and later 4.0 g (62% yield) of **6** was isolated: mp 157–160° dec; uv max (95% EtOH) 214 nm (log ϵ 3.66); ir (KBr) 6.15 (s), 6.90 (m), 7.37 (m), 7.93 (s), 8.40 (s), 8.61 (m), 9.58 (s), 9.95 (s), 12.23 (s), 12.66 (s), 12.84 (s), 13.32 (s), 14.07 (m), 14.40 (s), 14.94 μ (s).

Anal. Calcd for $C_{11}H_6Cl_8$: C, 31.32; H, 1.53; Cl, 67.25. Found: C, 31.04; H, 1.33; Cl, 67.40.

***endo*-4,5,6,7-Tetrachloro-8-dichloromethylene-3a,4,7a-tetrahydro-4,7-methanoindene (7).**—Aluminum shot (1.0 g) was washed with 30 ml of 5% sodium hydroxide for 3 min, three times with water, and twice with ethanol and then amalgamated with a saturated solution of mercuric chloride (50 ml). The amalgam was washed with water, ethanol, and pentane. A solution of 1.38 g (0.0033 mol) of **6** in 20 ml of pentane and 20 ml of ethanol was added to the amalgam. After 3 hr with occasional agitation, the mixture was filtered. The product **7**, 1.12 g (98% crude yield), was isolated. After recrystallization from pentane a colorless solid was obtained: mp 108–109°; ir (KBr) 5.98 (s), 6.17 (s), 6.88 (s), 7.38 (m), 7.69 (w), 7.97 (s), 8.24 (w), 8.50 (m), 8.73 (m), 8.90 (s), 9.53 (s), 9.68 (m), 9.95 (s), 10.51 (m), 10.62 (m), 11.21 (s), 12.40 (s), 12.86 (s), 13.75 (s), 14.11 (s), 14.73 μ (s).

Anal. Calcd for $C_{11}H_6Cl_6$: C, 37.65; H, 1.72; Cl, 60.63; mol wt, 351. Found: C, 37.65; H, 1.88; Cl, 60.43; mol wt, 346.

A sample of **7** was heated in benzene at 60° for 18 hr. Nmr analysis showed that quantitative conversion to **5** occurred. A similar experiment at 23° left **7** unchanged.

1,7,8,9-Tetrachloro-10-dichloromethylenepentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{5,8}$]decane (16).—An irradiation flask, equipped with a Pyrex filter and 450 W Hanovia type L lamp, was filled with a solution of 2.8 g (0.008 mol) of **5** in 375 ml of spectral grade acetone. The progress of the reaction was followed by tlc, and after 6 days the reaction was terminated. A chromatographic column of *deactivated* silica gel was eluted with CCl_4 to separate the numerous products. Fraction three was a white solid: mp 128.5–129°; mass spectrum (75 eV) *m/e* 348 (M). The nmr spectrum of crude **16** contained a broad singlet at δ 3.23 (4 H) and 2.98 (impurity), and doublets at 1.73 (1 H) and 2.15 (1 H, J = 12.0 cps).

By comparison, the nmr of **17**, which was prepared similarly, exhibited a broad singlet at δ 3.30 (4 H) and doublets at 1.65 (1 H) and 2.40 (1 H, J = 12.5 cps).

1,2,3,4-Tetrachloro-10-dichloromethylene-1,4,4a,5,8,8a-hexahydro-1,4:5,8-*endo-exo*-dimethanonapththalene (18).—A solution of 2.0 g (0.007 mol) of **1** in 30 ml of norbornadiene was heated with an oil bath at 100° for 48 hr. The addition of acetone gave a solid material which, after recrystallization from ethanol, yielded 1.4 g (53%) of colorless crystals: mp 138–139°; uv max (95% EtOH) 215 nm (log ϵ 3.96); ir (KBr) 6.24 (s), 6.34 (s), 6.86 (w), 7.53 (m), 8.00 (s), 8.07 (s), 8.17 (s), 10.26 (m), 10.61 (m), 10.79 (s), 10.91 (s), 11.03 (m), 12.78 (m), 13.08 (s), 13.31 (m), 14.14 (m), 14.65 μ (s).

Anal. Calcd for $C_{13}H_8Cl_6$: C, 41.42; H, 2.14; Cl, 56.44. Found: C, 41.28; H, 2.24; Cl, 56.12.

Thermolysis of 1.—Hexachlorofulvene (1.0 g) was heated to 196° for 18 hr in a sealed tube under N_2. Column chromatography using silica gel separated the products on elution with hexane. Approximately 0.4 g of **2** was isolated and identified by ir and melting point comparison with an authentic sample.[26] A red oil was also obtained, but not identified.

Dimerization of 1 with Aluminum Chloride.—To a solution of 2.84 g (0.01 mol) of **1** in 20 ml of carbon disulfide at 23° was added 0.67 g (0.005 mol)[48] of $AlCl_3$. After stirring for 24 hr, distilled water was added, and the product was extracted with CCl_4. The crude product was chromatographed on a 40-cm column of silica gel. Elution with hexane gave as the first fraction a small amount of **1** and approximately 0.4 g of **2**. A second larger red band consisted of a mixture of **20** and **21** (0.9 g, 46% yield). The latter two compounds were separated by recrystallization from ethyl acetate. Compound **20** was a colorless solid: mp 262° dec; ir (KBr) 6.29 (s), 8.07 (s), 8.34 (w), 9.66 (m), 10.70 (w), 10.97 (s), 12.02 (w), 12.81 (m), 13.52 μ (s).

Anal. Calcd for $C_{12}Cl_{12}$: C, 25.30; Cl, 74.70. Found: C, 25.14; Cl, 75.00.

Compound **21** is a stable red solid: mp 185–186°; ir (KBr) 6.36 (s), 6.44 (s), 7.85 (s), 7.93 (s), 8.22 (m), 10.33 (m), 10.82 (s), 11.53 (m), 13.92 μ (w); mass spectrum (75 eV) *m/e* 494 (M), 459 (M − Cl), 424 (M − Cl_2, base ion), 354 (M − Cl_4), 282 (M − Cl_6).

Anal. Calcd for $C_{12}Cl_{10}$: C, 28.90; Cl, 71.10. Found: C, 28.65; Cl, 71.40.

Registry No.—**1**, 6317-25-5; **3**, 25329-35-5; **4**, 6928-57-0; **5**, 33065-95-1; **6**, 33065-96-2; **7**, 33122-14-4; **10**, 33065-97-3; **11**, 33065-98-4; **16**, 33061-05-1; **18**, 33065-99-5; **19**, 309-00-2; **20**, 33066-00-1; **21**, 33061-04-0.

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[48] Larger ratios of **1** to $AlCl_3$ yield larger amounts of **21** and **2** at the expense of **20**.

Protonation and Deuteration of the Isopropenylcyclopentadienyl Anion. Trapping of the Isomeric Product Mixture[1]

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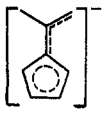
Protonation of the isopropenylcyclopentadienyl anion (**1**) gave a mixture of 15 ± 3% dimethylfulvene (**2**), 58 ± 3% 1-isopropenyl-1,3-cyclopentadiene (**3**), and 25 ± 2% 2-isopropenyl-1,3-cyclopentadiene (**4**). Deuteration of **1** afforded a mixture of 10 ± 4% **2**, 64 ± 3% **3**, and 26 ± 2% **4**. Mass spectral evidence indicates that a lower limit of 97% of the total product mixture was derived from reactions of **1**, while 3% of the product mixture was residual, un-ionized **2**. Chemical trapping of the isomeric product mixture as Diels–Alder adducts of tetracyanoethylene was accomplished. Isomers **2**, **3**, and **4** gave on treatment with tetracyanoethylene adducts 7-isopropylidene-5,5,6,6-tetracyanonorbornene (**6**), 3a,4,5,6,6-pentahydro-4,4,5,5-tetracyano-7-methylindene (**7**), and 2-isopropenyl-5,5,6,6-tetracyanonorbornene (**8**), respectively. The relative amounts of **6**, **7**, and **8** were within experimental error of the relative amounts of **2**, **3**, and **4**, in the mixtures from which the adducts were derived.

Hine and Knight[3] recently reported a study of the protonation of the isopropenylcyclopentadienyl anion (**1**) derived from the treatment of 6,6-dimethylfulvene



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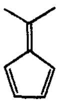
(**2**) with base. Kinetic control of the protonation was hoped for but was not conclusively demonstrated, largely because they did not show whether or not the dimethylfulvene present in the product mixture composed of **2**, 1-isopropenyl-1,3-cyclopentadine (**3**), and 2-isopropenyl-1,3-cyclopentadiene (**4**) was derived from **1** or was **2** that never was ionized.



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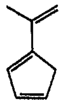

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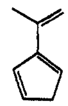

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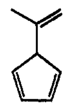

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We have repeated part of this work and in addition report here a detailed study of the deuteration of **1**. Also we succeeded in chemically trapping the thermally unstable (due to Diels–Alder addition) mixture of **2**, **3**, and **4** as Diels–Alder adducts of tetracyanoethylene (TCNE).

Results and Discussion

Several repetitions of the isomerization of dimethylfulvene *via* protonation of anion **1** gave product mixtures in which the relative amounts of **2**, **3**, and **4** were in good agreement with previous work.[3] Table I summarizes the results of seven experiments in which anion **1** was deuterated.

TABLE I

DEUTERATION OF ISOPROPENYLCYCLOPENTADIENYL ANION 1[a]

Run	**2**, %	**3**, %	**4**, %
1	7	63	30
2	8	64	28
3	20	57	23
4	10	64	26
5	9	66	25
6	9	67	24
7	10	65	25
	10 ± 4	64 ± 3	26 ± 2

[a] Equivalent amounts of **2** and potassium *tert*-butoxide in bis(2-methoxyethyl) ether (diglyme) were mixed at room temperature. The homogeneous solution containing anion **1** was added to deuterium acetate in deuterium oxide. Products **2**, **3**, and **4** were quickly extracted into CCl_4 or light petroleum ether and stored at −78° until analyzed. No evidence for the formation of 5-isopropenyl-1,3-cyclopentadiene (**5**) was found.

Relative amounts of **2**, **3**, and **4** in the deuteration–isomerization experiment were determined primarily by nuclear magnetic resonance (nmr) and by gas–liquid partition chromatography (glpc).[4] Deuterium uptake into **3** and **4** should occur at the ring methylene positions

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[2] (a) Abstracted in part from the M.S. Thesis of R. L. H., University of North Carolina at Greensboro, 1971. (b) National Science Foundation Undergraduate Research Participant, summer, 1970.

[3] J. Hine and D. B. Knight, *J. Org. Chem.*, **35**, 3946 (1970).

[4] Details of the nmr spectra of **2**, **3**, and **4** are described in ref 3.