

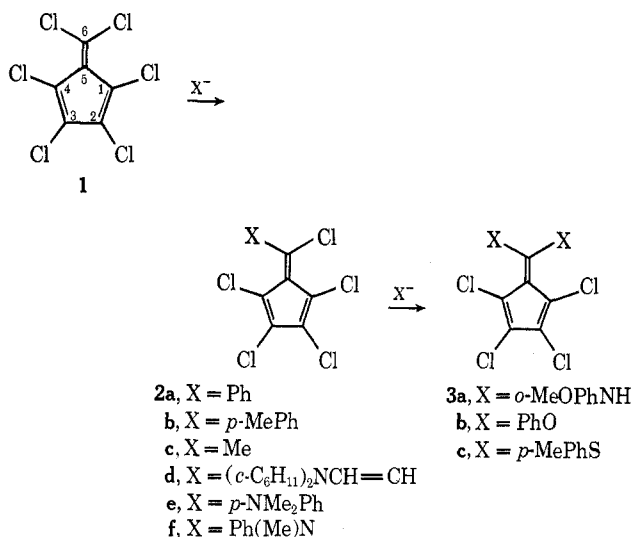
## Hexachlorofulvene. II. Reactions under Ionic Conditions

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Hexachlorofulvene (1) has been subjected to a number of nucleophiles of varying reactivity. The products resulted from displacement of one or both of the chlorine atoms in the dichloromethylene group. Their structures were assigned by spectral analysis and by analogy with that of 2a, which was confirmed in three different ways. Fulvene products were also obtained by displacement of the ring chlorines in 1 under Friedel-Crafts conditions. Treatment of 1 with concentrated sulfuric acid gave products arising from initial protonation at the 1 position and subsequent destruction of the fulvene system.

The first paper<sup>3</sup> in this series reported a new method for the preparation of hexachlorofulvene (1) and a study of its behavior under Diels-Alder conditions. The reactivity of 1 under ionic conditions is considered in this paper. Thus, we have subjected 1 to a representative set of nucleophiles and to a number of Brønsted and Lewis acids.



## Results and Discussion

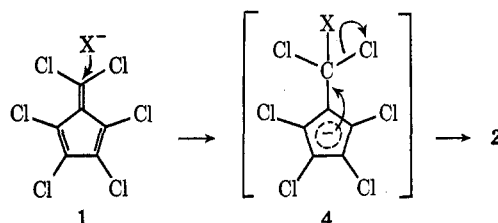
## Reaction of Hexachlorofulvene (1) with Nucleophiles.

—Previously, Roedig<sup>4</sup> showed that two of the chlorine atoms in 1 were labile to aromatic amines (aniline, *p*-toluidine, and *o*-phenylenediamine), but the products were not further identified. We have shown that the nucleophilic reagents given in Table I react with 1 to give monosubstituted (2) or disubstituted (3) products.

Evidence that nucleophilic substitution occurred exclusively at the 6 position is given later. Representative nucleophiles were chosen so that the products obtained had a variety of atoms bonded to the 6 position. The reaction conditions used were relatively mild, and product mixtures were not encountered. In all of the reactions with 1, the nucleophile was present in excess amounts. Interestingly, those products having a carbon linked directly to the 6 position (2a–e) were monosubstituted, whereas, except for 2f, the products with a heteroatom attached to the 6 position were di-

substituted. Compound 2a was recovered unchanged after an attempted further reaction with phenylmagnesium bromide, thus indicating the decreased reactivity of the remaining 6-chlorine atom relative to those in 1.

The exclusive replacement of the 6-chlorine atom by nucleophiles may be attributed to the extra stabilization in intermediate 4 provided by the delocalization of



the electrons into a six- $\pi$ -electron aromatic system. Hydrocarbon fulvenes also undergo nucleophilic attack at the 6 position. However, because they lack suitable leaving groups, the products<sup>5</sup> are not substituted fulvenes, since the intermediate carbanions analogous to 4 undergo secondary reactions such as autooxidation, hydrolysis, or ferrocene formation.

Elucidation of the structures of 2 and 3 was based on the following arguments. Elemental analysis and mass spectroscopy gave the molecular formulas, which together with (1) the color of the products, (2) ir absorptions in the carbon-carbon double-bond stretching frequency region (6.20–6.47  $\mu$ ) and at 7.75–8.00  $\mu$ ,<sup>5,6</sup> and (3) the strong uv absorption at long wavelengths [314–425 nm (log  $\epsilon$  4.14–4.36)<sup>7</sup>] provided reliable evidence for fulvene structures. That substitution of the fulvene occurred at the 6 position was established by analogy to the formation of 2a, whose structure was proven in the following way. First 2a was prepared by an alternate synthesis. Benzotrichloride and 1,2,3,4,5-pentachlorocyclopentadiene (5)<sup>8</sup> formed an addition compound, 6, which was converted by base to the diene 7. Dechlorination of 7 with triethylphosphite yielded a deep red solid with an ir spectrum identical with that of 2a prepared previously from 1. Secondly, 2a was treated with morpholine and gave a product, 9, whose ir and melting point were identical with those of a sample prepared from the sodium salt of 1,2,3,4-tetrachlorocyclopentadiene (8)<sup>9,10</sup> and *S*-methylthiobenzoyl-

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) Supported by the Purdue Research Foundation.

(3) E. T. McBee, E. P. Wesseler, D. L. Crain, R. Hurnaus, and T. Hodgins, *J. Org. Chem.*, **37**, 683 (1972).

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

(5) P. Yates, *Advan. Alicycl. Chem.*, **2**, 59 (1968).

(6) J. C. Wood, R. M. Eloffson, and D. M. Saunders, *Anal. Chem.*, **30**, 1339 (1958).

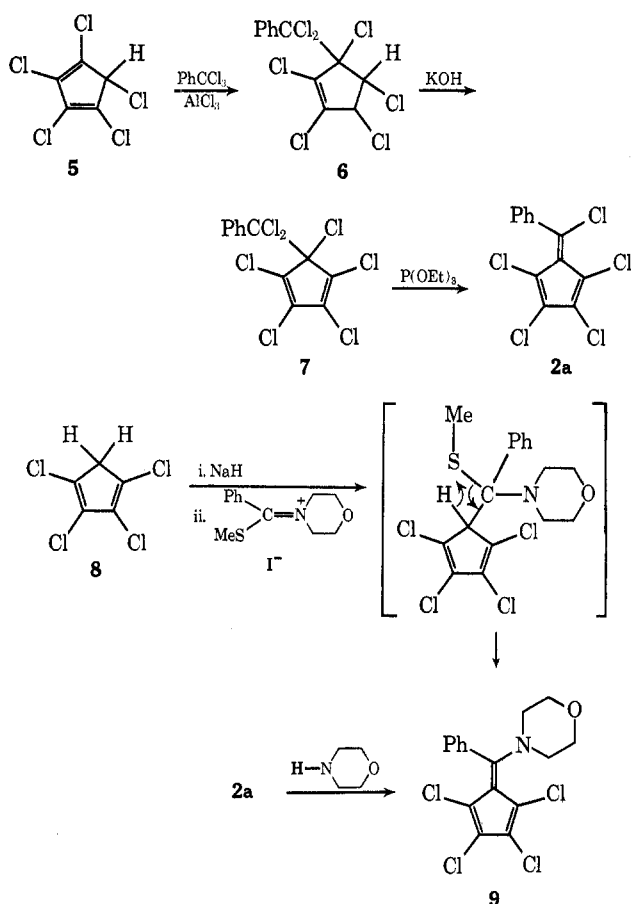
(7) Shifts to even longer wavelengths (see Table I) occurred when the 6 substituent had a resonance donor group in conjugation with the fulvene moiety.

(8) E. T. McBee and D. K. Smith, *J. Amer. Chem. Soc.*, **77**, 389 (1955).

TABLE I  
 NUCLEOPHILIC REACTIONS OF 1

Nucleophilic reagent	Product	% yield	Mp, °C	$\lambda_{\max}$ (C <sub>6</sub> H <sub>6</sub> ), nm (log $\epsilon$ )
PhMgBr	2a	49 <sup>a</sup>	75.5-76	334 <sup>b</sup> (4.16)
<i>p</i> -MePhMgBr	2b	56	113-115	350.5 (4.2)
MeMgI	2c	73.5 <sup>c</sup>	160-162	299 <sup>d</sup> (4.14)
( <i>o</i> -C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> NCH=CH <sub>2</sub>	2d	83.5	154.5-155.5	467 (4.74)
PhNMe <sub>2</sub>	2e	78.5	149-150.5	488 (4.45)
PhNHMe	2f	82.5	86-88	393 (4.31)
<i>o</i> -MeOPhNH <sub>2</sub>	3a	32.5 <sup>e</sup>	176.5-177.5 dec	384.5 (4.43)
PhONa	3b	55	133-135	314.5 (4.45)
<i>p</i> -MePhSH <sup>f</sup>	3c	75	172-173	425 (4.34)

<sup>a</sup> Conversion of 1 was 57%. <sup>b</sup> 95% ethanol was used as the solvent. <sup>c</sup> A trace amount of material (possibly 3c) was also formed. <sup>d</sup> Also 416 nm ( $\epsilon$  2.63). <sup>e</sup> Acetylation gave the *N,N'*-diacetyl derivative. <sup>f</sup> Reaction was performed in the presence of triethylamine.



morpholinium iodide.<sup>11</sup> Spectral data for 9 (nmr, ir, and uv) were totally consistent with its structure. The third method, which indicated the accuracy of the structure assigned to 2a, involved the use of <sup>13</sup>C nmr and is discussed later.

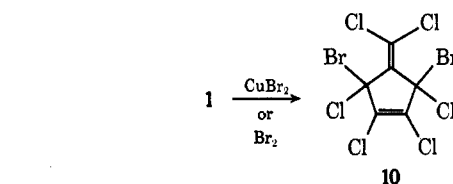
In addition to the nucleophiles listed in Table I, several others were studied. Both sodium bromide and calcium bromide in refluxing acetone were unreactive toward 1. However, 1,4 addition of bromine to 1 occurred to a limited extent in a reaction with cupric bromide. Adduct 10 was identified by ir comparison with that of a sample prepared by an alternate method.<sup>4</sup>

Sodium cyanide, potassium thiocyanate, sodium methoxide, and metal hydrides (LiAlH<sub>4</sub> and NaBH<sub>4</sub>) were extremely reactive with 1, yielding dark amorphous solids or intractable tars from which products

(9) E. T. McBee, R. K. Meyers, and C. F. Baranauckas, *J. Amer. Chem. Soc.*, **77**, 86 (1955).

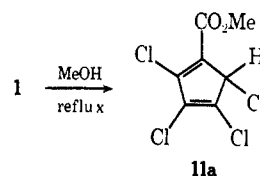
(10) A. S. Kende, P. T. Izzo, and P. T. MacGregor, *ibid.*, **88**, 3359 (1966).

(11) (a) F. H. McMillan, *ibid.*, **70**, 868 (1948); (b) L. Maier, *Angew. Chem., Int. Ed. Engl.*, **8**, 141 (1969).

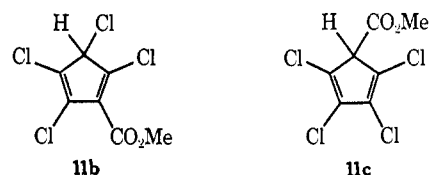


were not isolable. Sodium ethoxide and 1 gave a violet solution which similarly decomposed to a black tar on evaporation of the solvent.

Roedig has reported<sup>4</sup> that 1 also decomposed slowly when heated in alcohol. We have confirmed this fact and find that an ester is formed as the principal product. For example, after refluxing in methanol until the red color disappeared, distillation of the reaction mixture afforded a trace amount of 8 and a 55% yield of 11a.



The dichloromethylene group of 2-dichloromethylene-cyclopentanone has similarly been converted to a carbomethoxy group with sodium methoxide.<sup>12</sup> The structure of 11a was assigned from spectral data. The mass spectrum of the ester had ions with the predicted isotopic pattern corresponding to the molecular ion (M), M - 59, and 59 (COOMe). The ir spectrum of 11a had absorptions typical of an ester,<sup>13</sup> and its nmr spectrum had singlets at  $\delta$  3.85 (3 H, COOMe) and 5.18 (1 H). The latter resonance distinguishes 11a from other reasonable isomers since  $\delta$  5.18 is low for a vinylic hydrogen.<sup>14</sup> In addition, the proton in 5 absorbs at  $\delta$  4.71. Isomer 11b would be expected to



have a very similar chemical shift, while the proton in 11c should be more shielded since carbomethoxy substituents deshield  $\alpha$  protons less than chlorine sub-

(12) J. Wolinsky and R. Kasubick, *J. Org. Chem.*, **35**, 1211 (1970).

(13) R. Silverstein and G. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1967, p 91.

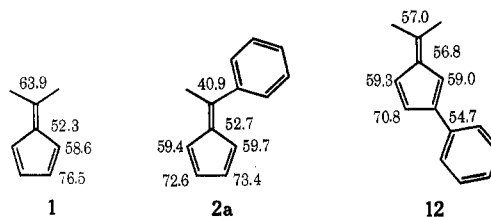
(14) D. W. Mathieson, "Nuclear Magnetic Resonance for Organic Chemists," Academic Press, New York, N. Y., 1967, p 183.

stituents.<sup>15</sup> Presumably the extended conjugation in **11a** makes it the most thermodynamically stable product. Absolute ethanol also gave an analogous ester. Since **1** was completely unreactive in refluxing glacial acetic acid, the reaction most likely proceeds by nucleophilic attack of alcohol on the 6 position of **1**.

**Reaction of Hexachlorofulvene Under Acidic Conditions.**—While nucleophilic substitution allows the 6 chlorines of **1** to be replaced with a large number of substituents, Lewis acids allow replacement of the ring chlorines. One example of the latter type was given in an earlier paper,<sup>3</sup> where **1** in the presence of a small amount of aluminum chloride yielded a difulvene. However, when a 1:1 molar ratio of **1** to aluminum chloride (instead of 2:1 or higher) was used, **1** was recovered unchanged after hydrolysis. Apparently a complex is formed which cannot react further to give the difulvene under these circumstances. However, if a substrate such as benzene is present, the electrophilic complex reacts with the subsequent replacement of the ring chlorines. The number and position of the chlorines replaced can be controlled to some degree as shown in Table II. At room temperature, 2-phenylpenta-

slightly shorter wavelength in the uv as was observed. In addition, **12** is the only isomer without any appreciable steric hindrance to planarity. Slight crowding is known to result only in a hypochromic shift<sup>16</sup> which would account for the lower extinction coefficients of **2a** and **13**. This same steric hindrance may explain why these two isomers appeared as singlets in the nmr while **12** was a multiplet.

The final evidence for the structural assignment given was provided by <sup>13</sup>C nmr data.<sup>17</sup> Unfortunately, the amount of **13** necessary for <sup>13</sup>C nmr could not be isolated. The chemical shifts measured for the other two isomers and **1** are shown in Chart I. The assign-

CHART I<sup>a</sup>

<sup>a</sup> Chemical shifts (given in parts per million upfield from CS<sub>2</sub>) were obtained from the <sup>13</sup>C nmr spectra of **1**, **2a**, and **12**. For simplicity the chlorine atoms are omitted.

TABLE II  
REACTION OF **1** AND BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE UNDER VARIOUS CONDITIONS

Temp, °C	Molar ratio of <b>1</b> :benzene	Position of phenyl substitution	Yield, %
5	1:1 (in CS <sub>2</sub> )	1 and 2	46
25	1:1 (in CS <sub>2</sub> )	2	45
25	Benzene as solvent	2,3 and 1,2,3	41 and 10
80	Benzene as solvent	1,2,3	46.5

chlorofulvene (**12**) was the only product isolated when a 1:1 molar ratio of **1** to benzene reacted in the presence of aluminum chloride. Lowering the reaction temperature to 5° resulted in a mixture (approximately 1:1) of **12** and 1-phenylpentachlorofulvene (**13**). In Table III is listed some of the data of the three possible

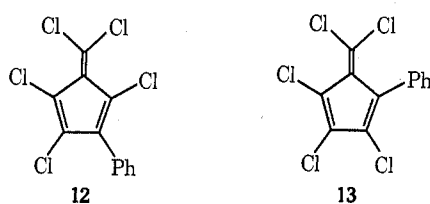


TABLE III  
COMPARISON OF THE THREE ISOMERIC PHENYLPENTACHLOROFULVENES

	<b>2a</b>	<b>12</b>	<b>13</b>
Mp, °C	75.5-76	72-73	94-95
UV λ <sub>max</sub> (log ε)	334 (4.16)	296 (4.21)	317 (4.11)
Nmr, δ	7.40 (s)	7.30 (m)	7.38 (s)
Color	Very deep red	Orange	Deep red

monophenylated fulvenes. Proof for structure **2a** has already been given. Identification of **12** and **13** is not nearly so rigorous, but all the information suggests that the assigned structures are correct. Both **2a** and **13** have extended conjugated systems while **12** is cross conjugated and would therefore be expected to absorb at

ments were based on substituent effects. All the values above 70 ppm were assigned to the 2,3 positions of the fulvenes because the same positions of 6,6-dimethylfulvene were found to absorb at 71.9 ppm.<sup>18</sup> The fact that **12** contains only one absorption above 70 ppm immediately suggests that the phenyl group is in the 2 position and is lowering the absorption of this carbon below 70 ppm. In fact, the lowest absorption observed (40.9 ppm) must be assigned to the carbon bearing the phenyl group in **2a**. This is a decrease or α shift of 23.0 ppm from **1**. A similar shift of 21.8 ppm is observed in **12**. The remaining chemical shifts in Chart I are only tentatively assigned owing to the lack of suitable models.

2,3-Diphenyltetrachlorofulvene and 1,2,3-triphenyltrichlorofulvene have also been prepared. As shown in Table II the use of benzene as the solvent at room temperature yields predominantly the former compound, while at 80° only the latter compound was isolated. No attempt was made to prove rigorously the structures of these two compounds, but the isomers given are the most reasonable based on an analogy to the monophenylated products. Attempts to replace more than three chlorines in this reaction were unsuccessful. Apparently steric factors inhibit the replacement of the last ring chlorine.

Weaker Lewis acids, such as ferric chloride, cannot be used in place of aluminum chloride as they are unreactive. Aluminum bromide, on the other hand, gave partial exchange of the chlorines with bromines in addition to the reactions previously discussed.<sup>3</sup> Attempts to achieve complete exchange were unsuccessful.

We had previously hydrolyzed several chlorocarbons

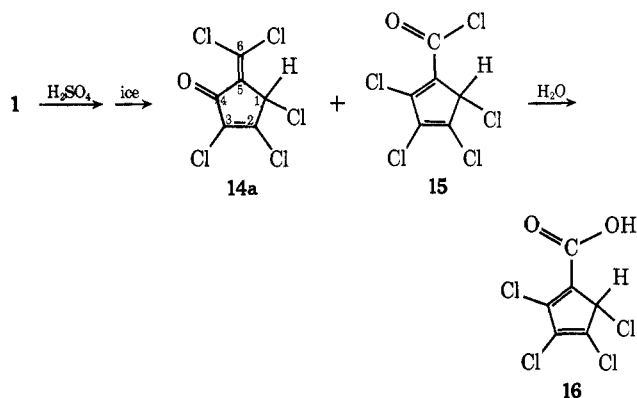
(15) Reference 13, p 137.

(16) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 384.

(17) We are indebted to Dr. J. Grutzner for determining the <sup>13</sup>C nmr spectra and for his help in analyzing them.

(18) J. B. Grutzner, unpublished results.

with concentrated sulfuric acid,<sup>19</sup> and we were consequently interested in the hydrolysis of 1 with this acid.<sup>20</sup> The reaction was carried out by heating 1 in concentrated sulfuric acid until a green solution resulted. When this solution was poured over ice a tan solid consisting of 14 and 15 precipitated. Two singlets were

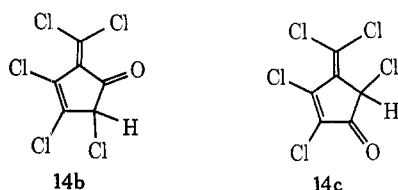


present in the nmr of the crude product at  $\delta$  5.43 and 4.88 in a ratio of 6:1. The larger singlet corresponded to the ketone 14a as shown by the nmr spectrum of a pure sample. The structure of 14a was determined mainly by the <sup>13</sup>C nmr data given in Table IV. The

TABLE IV  
<sup>13</sup>C NMR DATA FOR COMPOUND 14a

Position	Shift upfield from CS <sub>2</sub> , ppm	Coupling, Hz
1	5.5	2.8
2	54.4	3.7
3	29.8	7.1
4	128.5	174.4
5	47.3	4.5
6	49.6	3.2

carbonyl carbon (position 1) was readily assigned the absorption at 5.5 ppm since carbonyl carbons are known to absorb at very low field.<sup>21</sup> The tetrahedral carbon (position 4) is also easily assigned for it is observed at very high field (128.5 ppm) and it has the largest <sup>13</sup>C-H coupling constant (174.4 Hz).<sup>22</sup> Since the carbonyl carbon is observed to have the *smallest* <sup>13</sup>C-H coupling constant, which generally decreases with increasing number of intervening bonds,<sup>23</sup> the alternative structures (14b and 14c) having the carbonyl and tetra-



(19) (a) J. S. Newcomer and E. T. McBee, *J. Amer. Chem. Soc.*, **71**, 946 (1949); (b) D. L. Crain, Ph.D. Thesis, Purdue University, 1956.

(20) After completion of this work the same hydrolysis was reported by V. D. Simonov, R. T. Gazizov, and M. I. Kollegova, *J. Org. Chem. USSR*, **6**, 1613 (1970). We report our study here because these workers did not report a minor product which we found, and also we have further confirmation that the structure of the major product reported is correct.

(21) J. B. Stothers, *Quart. Rev., Chem. Soc.*, **19**, 144 (1965).

(22) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 235.

(23) The authors are aware that there are a number of exceptions to the simple relationship between the magnitude of the coupling constant and the number of intervening bonds; however, in the alternate structures the carbonyl carbon is not likely to have the *smallest* coupling constant.

hedral carbons adjacent are not so likely as structure 14a.

Roeding has reported,<sup>4</sup> and we have confirmed, that 1 is oxidized to 2,3,4-trichloro-5-(dichloromethylene)-cyclopentene-1,4-dione by heating with fuming nitric acid. Under the same conditions 14a is totally unreactive and consequently does not appear to be an intermediate in the oxidation reaction.

The minor product (15), although shown to be present in the crude reaction mixture by nmr and mass spectroscopy, was isolated only as the corresponding carboxylic acid (16). The structure of 16 was determined mainly from mass spectroscopy, ir, and nmr data. Mass spectroscopy, as well as elemental analysis, indicated that the molecular formula was C<sub>6</sub>H<sub>2</sub>Cl<sub>4</sub>O<sub>2</sub>. The ir spectrum of 16 had broad absorption between 3.6 and 4.0  $\mu$  characteristic of an acid. In addition, this compound was soluble in sodium bicarbonate, and its nmr spectrum (in acetonitrile) contained two singlets at  $\delta$  5.30 and 8.56. The singlet at 5.30 is close to that observed for the analogous ester 11a, and, by the same reasoning used to deduce the structure of this ester, structure 16 was assigned to the acid. Because of the instability of these compounds, several attempts to interconvert 11a and 16 were not successful.

## Experimental Section

**Procedures and Equipment.**—Melting points were determined with a Mel-Temp apparatus in sealed tubes and are uncorrected. Proton nmr spectra were obtained on a Varian Associates A-60A spectrometer; carbon tetrachloride was used as a solvent with tetramethylsilane as an internal standard. <sup>13</sup>C nmr spectra were determined by J. Grutzner using a Varian XL 100 nmr spectrometer operating at 25.2 MHz. Infrared spectra were determined as KBr pellets using a Perkin-Elmer 221 ir 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.

**6-Phenylpentachlorofulvene (2a).**—A Grignard solution was prepared from 10.5 ml (0.10 mol) of bromobenzene and 2.4 g (0.10 g-atom) of magnesium turnings in 400 ml of anhydrous ether. This solution was filtered and allowed to drop slowly into a solution of 14.1 g (0.05 mol) of 1 in 150 ml of THF at 10°. After 5 hr, dilute HCl was added; the organic layer was separated, dried, and evaporated to a dark solid. Column chromatography (silica gel, hexane) gave 6 g of 1 as the first fraction and 4 g (49% yield) of 2a as the second red fraction. After recrystallization of 2a from methanol, crystals were obtained which were so deep red that they appeared black unless examined closely: ir (KBr) 6.28 (s), 6.45 (m), 6.90 (w), 7.87 (s), 7.97 (m), 10.27 (w), 10.77 (w), 10.98 (w), 13.14 (s), 14.06 (w), 14.47 (m), 14.79  $\mu$  (m).

*Anal.* Calcd for C<sub>12</sub>H<sub>5</sub>Cl<sub>5</sub>: C, 44.13; H, 1.54; Cl, 54.33. Found: C, 44.12; H, 1.75; Cl, 54.20.

**6-p-Tolylpentachlorofulvene (2b).**—A Grignard solution, prepared from 3.44 g (20 mmol) of *p*-bromotoluene and 0.50 g (20 mg-atoms) of magnesium in 100 ml of dry ether, was added dropwise to a solution of 2.85 g (10 mmol) of 1 in 100 ml of ether. After the mixture was stirred for 60 hr, dilute HCl was added. The organic layer was separated, washed with a NaHCO<sub>3</sub> solution, and dried, and the solvent was removed. Recrystallization of the residue from acetonitrile gave deep red crystals of 2b: ir (KBr) 6.30 (s), 6.44 (s), 7.32 (s), 7.95 (s), 8.43 (m), 9.05 (w), 10.23 (w), 10.84 (w), 12.25 (s), 14.23  $\mu$  (s).

*Anal.* Calcd for C<sub>13</sub>H<sub>7</sub>Cl<sub>5</sub>: C, 45.86; H, 2.07; Cl, 52.07. Found: C, 46.02; H, 1.94; Cl, 52.06.

**6-Methylpentachlorofulvene (2c).**—A Grignard solution was prepared from 1 g (0.4 g-atom) of magnesium and 6 g (0.4 mol) of methyl iodide in 100 ml of dry ether. Then 3.00 g (0.105 mol)

of 1 in 100 ml of ether was added dropwise to the stirred ice-cold Grignard solution. After an additional 30-min stirring, the product was isolated as in the previous example and recrystallized from hot acetonitrile to give reddish orange needles of **2c**: ir (KBr) 6.23 (m), 6.42 (m), 7.83 (s), 7.95 (w), 8.11  $\mu$  (w).

*Anal.* Calcd for  $C_7H_3Cl_2$ : C, 31.78; H, 1.14; Cl, 67.07. Found: C, 31.95; H, 1.36; Cl, 67.09.

**Synthesis of 6-[2-(*N,N*-Dicyclohexylamino)-1-vinyl]pentachlorofulvene (2d).**—A mixture of 4.4 g (0.10 mol) of acetaldehyde, 17.5 g (0.096 mol) of *N,N*-dicyclohexylamine, and 5 g (0.04 mol) of magnesium sulfate in 70 ml of dry benzene was stirred for 30 min. Then 1.0 g (3.5 mmol) of 1 in benzene (20 ml) was added dropwise, and the reaction was stirred for 3 hr at room temperature. The addition of dilute HCl caused a white precipitate to form which was filtered off and washed with ethyl acetate. The solid residue from evaporation of the filtrate was recrystallized from petroleum ether yielding 1.50 g of **2d** as deep red crystals: ir (KBr) 2.90 (w), 3.40 (w), 3.49 (w), 6.27 (s), 6.56 (s), 6.88 (m), 6.95 (m), 7.75–7.90 (s), 8.06 (s), 8.68 (w), 9.02 (w), 9.16 (w), 9.87 (w), 11.31  $\mu$  (w).

*Anal.* Calcd for  $C_{20}H_{22}NCl_5$ : C, 52.71; H, 5.31; N, 3.07; Cl, 38.90. Found: C, 52.89; H, 5.31; N, 3.03; Cl, 39.19.

**Synthesis of 6-(*p*-Dimethylaminophenyl)pentachlorofulvene (2e).**—To 1.0 g (3.5 mmol) of 1 in 20 ml of tetrahydrofuran was added 5 ml (40 mmol) of *N,N*-dimethylaniline. After the mixture was stirred for 24 hr at room temperature, dilute HCl was added. The product was isolated by extraction with ethyl acetate and evaporation of the solvent. Recrystallization from hot petroleum ether gave greenish blue prisms of **2e**: ir (KBr) 6.20 (s), 6.44 (m), 6.59 (s), 6.91 (w), 7.28 (m), 7.81 (s), 8.17 (w), 8.37 (m), 9.19 (m), 12.25 (w), 14.35  $\mu$  (w).

*Anal.* Calcd for  $C_{15}H_{10}NCl_5$ : C, 45.51; H, 2.73; N, 3.79; Cl, 47.98. Found: C, 45.81; H, 2.90; N, 3.76; Cl, 48.06.

**Synthesis of 6-*N*-Methylanilinopentachlorofulvene (2f).**—For 2 hr 1.0 g (3.5 mmol) of 1 and 5 ml (46 mmol) of *N*-methylaniline were stirred in an ice bath. The product was then isolated as in the previous example and recrystallized from petroleum ether. Dark red prisms of **2f** were obtained: ir (KBr) 6.46 (s), 6.70 (m), 6.84 (m), 6.89 (m), 7.05 (s), 7.20 (m), 7.76 (s), 8.10 (w), 9.04 (s), 9.74 (m), 10.04 (w), 11.06 (m), 12.42 (w), 13.0–13.2 (m), 14.05 (w), 14.47  $\mu$  (m).

*Anal.* Calcd for  $C_{13}H_8NCl_5$ : C, 43.92; H, 2.27; N, 3.94; Cl, 49.87. Found: C, 43.92; H, 2.28; N, 3.80; Cl, 49.74.

**6,6-Di(*o*-anisidino)tetrachlorofulvene (3a).**—A solution containing 2.0 g (7 mmol) of 1 in 25 ml of tetrahydrofuran was treated under cooling and stirring with 5.0 ml (45 mmol) of *o*-anisidine. After 30 min the solution was poured onto crushed ice, dilute HCl was added, and the resulting yellow precipitate was sucked off. Chartreuse needles of **3a** were obtained after recrystallization from carbon tetrachloride: ir (KBr) 2.95 (w), 6.19 (s), 6.32 (s), 6.60 (m), 6.88 (s), 6.97 (m), 7.62 (s), 8.00 (s), 8.20 (w), 8.30 (w), 8.50 (m), 8.92 (m), 8.97 (m), 9.74 (m), 13.38  $\mu$  (s).

*Anal.* Calcd for  $C_{20}H_{16}N_2Cl_4O_2$ : C, 52.43; H, 3.52; N, 6.12; Cl, 30.95. Found: C, 52.45; H, 3.40; N, 6.26; Cl, 30.82.

**6,6-Di(*N*-acetyl-*o*-anisidino)tetrachlorofulvene (17).**—A solution containing 2 g (7 mmol) of 1 in 25 ml of tetrahydrofuran was treated as above with 5 ml of *o*-anisidine. The crude **3a** was dried and dissolved in tetrahydrofuran. Then 2.5 ml (35 mmol) of acetyl chloride was added dropwise followed by 8.0 ml (58 mmol) of triethylamine. After the mixture was stirred for 1 hr, ethyl acetate was added followed by dilute HCl and  $NaHCO_3$  solutions. The product was then isolated as usual, and, after recrystallization from acetonitrile, 1.51 g (38.5% yield) of **17** as red needles was obtained: mp 202–203° dec; ir (KBr) 2.89 (w), 5.76 (s), 6.24 (m), 6.35 (s), 6.64 (m), 7.67 (m), 7.82 (s), 7.96 (m), 8.18 (w), 8.41 (m), 8.59 (m), 8.94 (m), 9.74 (w), 13.31  $\mu$  (w); uv max (benzene) 393.5 nm (log  $\epsilon$  4.36); mass spectrum (75 eV)  $m/e$  (rel intensity) 540 (54), 498 (40), 425 (19), 390 (13), 333 (100).

*Anal.* Calcd for  $C_{24}H_{20}N_2O_4Cl_4$ : C, 53.16; H, 3.72; N, 5.17; Cl, 26.15. Found: C, 52.90; H, 3.75; N, 4.89; Cl, 26.21.

**6,6-Diphenoxytetrachlorofulvene (3b).**—To 2.85 g (10 mmol) of 1 in 50 ml of acetone was added 3.32 g (20 mmol) of sodium phenoxide. The mixture was stirred in an ice bath for 1 hr, poured over crushed ice, and extracted with ethyl acetate. After evaporation of the solvent, the residue was recrystallized from acetonitrile yielding golden needles of **3b**: ir (KBr) 6.06 (s),

6.28 (s), 6.46 (w), 6.72 (s), 7.58 (m), 7.66 (w), 7.78 (s), 8.02 (s), 8.53 (m), 8.67 (s), 9.75 (w), 9.88 (m), 10.03 (m), 11.98 (w), 13.09 (m), 14.33 (w), 14.67  $\mu$  (w).

*Anal.* Calcd for  $C_{18}H_{10}O_2Cl_4$ : C, 54.05; H, 2.52; Cl, 35.46. Found: C, 53.88; H, 2.41; Cl, 35.70.

**6,6-Bis(*p*-thiocresyl)tetrachlorofulvene (3c).**—To an ice-cold solution containing 5 g (17.5 mmol) of 1 in 200 ml of dry benzene was added dropwise a solution of 5.0 g (40 mmol) of *p*-thiocresole and 7.5 ml (54 mmol) of triethylamine in 100 ml of benzene. After 4 hr of stirring, the reaction mixture was washed with dilute HCl and a  $NaHCO_3$  solution. The solution was then dried and evaporated. The residue after recrystallization from hot petroleum ether yielded deep red needles of **3c**: ir (KBr) 6.80 (s), 7.73 (s), 8.09 (w), 8.99 (w), 11.88 (w), 12.42  $\mu$  (m).

*Anal.* Calcd for  $C_{20}H_{14}S_2Cl_4$ : C, 52.19; H, 3.07; S, 13.93; Cl, 30.81. Found: C, 52.32; H, 3.36; S, 14.04; Cl, 30.93.

**1,2,3,4,5,5-Hexachloro-3-phenyldichloromethylcyclopentene (6).**—To 23 g (97 mmol) of **5** and 100 ml (0.7 mol) of benzotrichloride was added 2.0 g (15 mmol) of aluminum chloride. The mixture was stirred and heated on a water bath for 3 hr and then stirred overnight at room temperature. Water was added, and the organic layer separated. Unreacted benzotrichloride was removed by vacuum distillation. The residue after recrystallization from hexane yielded 29 g (67% yield) of **6**: mp 142–143°; ir (KBr) 6.17 (m), 6.67 (w), 6.88 (m), 7.57 (w), 7.81 (m), 8.04 (w), 8.39 (s), 9.72 (m), 12.13 (m), 12.90 (s), 13.04 (w), 13.91 (m), 14.48 (s), 14.53  $\mu$  (m); nmr ( $CCl_4$ )  $\delta$  7.3–8.0 (m, 5, Ar H), 5.05 (s, 1).<sup>24</sup>

*Anal.* Calcd for  $C_{12}H_6Cl_6$ : C, 33.21; H, 1.39; Cl, 65.43. Found: C, 33.29; H, 1.46; Cl, 65.36.

**Conversion of 6 to 6-Phenylpentachlorofulvene (2a).**—To a solution of 5.0 g (11.6 mmol) of **6** in 100 ml of absolute ethanol was added 0.65 g (11.6 mmol) of KOH. After the mixture was stirred at room temperature for 2.5 hr, water was added and the product was extracted with hexane. The residue after evaporation of the hexane was chromatographed on a silica gel column, and 4.2 g of clear crystals of **7** was obtained: mp 72.5–73°; ir (KBr) 6.23 (s), 6.37 (w), 6.67 (w), 6.88 (m), 8.00 (s), 8.62 (m), 8.94 (m), 12.58 (s), 13.80 (s), 14.20 (s), 14.52  $\mu$  (s); mass spectrum (75 eV)  $m/e$  (rel intensity) 394 (0.8), 324 (3.1), 289 (10), 254 (35), 159 (100).

A solution of 4.2 g (10.5 mmol) of **7** was cooled in an ice bath, and then 0.2 g (12 mmol) of triethylphosphite in 25 ml of hexane was added slowly. The solution gradually turned red and 1 hr after the addition tlc indicated that the dechlorination was proceeding very slowly. After 18 hr the solvent was removed, the residue was chromatographed on a silica gel column, and 0.4 g (13% conversion) of **2a** was isolated, as shown by tlc and ir.

**Preparation of 6-Phenyl-6-morpholinotetrachlorofulvene (9).**  
**Method A.**—A solution containing 2.04 g (10.0 mmol) of **8** in 20 ml of diglyme was cooled to –20° and treated carefully with 500 mg (10.4 mmol, 50% in paraffin oil) of sodium hydride. When a clear dark blue solution was obtained, 3.40 g (9.7 mmol) of the salt, prepared from phenylmorpholino thioketone and methyl iodide in acetone, was added in small portions. After the mixture was stirred for 1 hr, ethyl acetate, dilute HCl, and  $NaHCO_3$  were successively added. The organic layer was separated, dried, and then evaporated. The residue was recrystallized from methanol and then from cyclohexane from which was obtained 0.5 g (13.4% yield) of orange crystals of **9**: mp 199.5–200°; uv max (benzene) 403.5 nm (log  $\epsilon$  4.18); ir (KBr) 6.52 (s), 6.82 (m), 6.97 (m), 7.54 (s), 7.75 (s), 7.96 (m), 8.98 (m), 9.20 (m), 9.78 (m), 13.02 (m), 13.87 (w), 14.4 (w), 14.77  $\mu$  (w).

**Method B.**—An ice bath was used to cool a solution of 0.5 g (1.5 mmol) of **2a** in 50 ml of anhydrous ether. Then 0.68 g (3.7 mmol) of morpholine was added all at once. The reaction mixture was stirred for 2.5 hr. From this reaction was obtained 0.56 g (99% yield) of **9** as shown by ir spectroscopy.

*Anal.* Calcd for  $C_{16}H_{12}NOCl_4$ : C, 50.96; H, 3.47; N, 3.71; Cl, 37.61. Found: C, 51.05; H, 3.53; N, 3.82; Cl, 37.65.

**3,5-Dibromo-1,2,3,5-tetrachloro-4-(dichloromethylene)cyclopentene (10).**—After 2.2 g (10 mmol) of cupric bromide and 2.8 g (10 mmol) of 1 were refluxed for 4 hr in acetonitrile, 0.17 g (5% conversion) of a clear crystalline material was found in addition to unreacted 1. This compound decomposed to a red melt between 177 and 187° and had an ir spectrum identical with that

(24) On heating, compound **6** gradually isomerized to an isomer with a singlet at  $\delta$  5.27.

of 10 prepared by an alternate route:<sup>4</sup> ir (KBr) 6.11 (s), 6.25 (m), 8.28 (m), 8.60 (s), 10.77 (w), 12.75–12.95  $\mu$  (s).

**Methyl 2,3,4,5-Tetrachlorocyclopentadiene-1-carboxylate (11a).**—A dark solution was obtained after refluxing 8.5 g (30 mmol) of 1 in 75 ml of dry methanol for 24 hr. The methanol was removed, and the dark residue was vacuum distilled [90° (0.08 mm)]. The distillation yielded 4 g (51% yield) of 11a as a yellow liquid and also a small amount of 8 (identified by mass spectroscopy, nmr, and melting point).<sup>9</sup> The yellow distillate decomposed on attempted purification by gas and column chromatography; however, after about 1 month in a refrigerator, it suddenly crystallized. It was then recrystallized from hexane: mp 59.5–60.5°; ir (KBr) 5.90 (s), 6.25 (w), 6.45 (m), 6.96 (m), 7.49 (m), 7.68 (m), 8.19 (s), 8.41 (m), 8.96 (m), 12.71 (m), 13.57  $\mu$  (m); uv max (95% EtOH) 216 nm (log  $\epsilon$  4.03), 298 (3.94); mass spectrum (75 eV) *m/e* (rel intensity) 260 (11), 200 (31), 59 (100).

*Anal.* Calcd for C<sub>7</sub>H<sub>4</sub>Cl<sub>4</sub>O<sub>2</sub>: C, 32.10; H, 1.54; Cl, 54.11. Found: C, 32.01; H, 1.73; Cl, 54.01.

#### Aluminum Chloride Catalyzed Reactions of 1 with Benzene.

**Method A. Monophenylation at 23°.**—To a solution containing 5.68 g (20 mmol) of 1 and 1.56 g (20 mmol) of benzene in 75 ml of CS<sub>2</sub> was added 2.66 g (20 mmol) of AlCl<sub>3</sub> at room temperature. After the mixture was stirred for 1 hr, dilute HCl was added and the organic material was isolated. Column chromatography (silica gel–hexane) gave 0.7 g of 1 and 2.6 g of 12 (45% yield). Orange-red needles of 12 were obtained from methanol: ir (KBr) 6.38 (s), 6.71 (m), 6.91 (w), 7.96 (s), 8.45 (m), 9.74 (w), 10.33 (m), 10.82 (s), 10.94 (m), 11.26 (w), 13.03 (m), 13.67 (m), 14.38  $\mu$  (s); mass spectrum (75 eV) *m/e* (rel intensity) 324 (24.6), 289 (42.6), 254 (100), 184 (27.8).

*Anal.* Calcd for C<sub>12</sub>H<sub>5</sub>Cl<sub>5</sub>: C, 44.13; H, 1.55; Cl, 54.32. Found: C, 44.19; H, 1.55; Cl, 53.90.

**Method B. Monophenylation at 5°.**—A solution containing 5.68 g (20 mmol) of 1 and 1.56 g (20 mmol) of benzene in 50 ml of CS<sub>2</sub> was cooled by means of an ice bath to 5° before 2.66 g (20 mmol) of AlCl<sub>3</sub> was added. The reaction mixture was stirred at this temperature for 3 hr, then dilute HCl was added, and the reaction was worked up as in the previous example. About 1.9 g of 1 and 2.0 g (46% yield) of a mixture of 12 and 13 were obtained. A small amount of 13 was isolated as dark red needles by careful recrystallizations from methanol: ir (KBr) 6.37 (s), 6.72 (w), 6.90 (w), 7.71 (m), 8.16 (m), 8.71 (m), 10.52 (w), 10.82 (w), 11.28 (w), 13.07 (m), 13.92 (m), 14.48 (s), 14.93  $\mu$  (m); mass spectrum (75 eV) *m/e* (rel intensity) 324 (100), 289 (4.2), 254 (65.5), 184 (31.9). More data on 12 and 13 are given in Table III.

*Anal.* Calcd for C<sub>12</sub>H<sub>5</sub>Cl<sub>5</sub>: C, 44.13; H, 1.55; Cl, 54.32. Found: C, 43.89; H, 2.04; Cl, 53.87.

**Method C. Diphenylation at 23°.**—A solution containing 5.68 g (20 mmol) of 1 in 125 ml of benzene was stirred while 5.33 g (40 mmol) of AlCl<sub>3</sub> was added. After 2 hr at room temperature,

the reaction was worked up as usual. Column chromatography (silica gel, 10:1 hexane–benzene) gave 3.0 g (41% yield) of diphenyltetrachlorofulvene and 0.8 g (10% yield) of triphenyltrichlorofulvene (see method D). The former product was a red oil and all attempts to crystallize it failed: ir (neat) 6.42 (s), 6.91 (m), 8.72 (w), 10.94 (m), 11.30 (w), 13.60 (m), 14.37 (s), 14.77  $\mu$  (m); mass spectrum (75 eV) *m/e* (rel intensity) 366 (42), 331 (86), 296 (100), 260 (45), 224 (41); nmr (CCl<sub>4</sub>)  $\delta$  7.2 (br m).

**Method D. Triphenylation.**—A mixture of 1.42 g (5 mmol) of 1, 3.0 g (22 mmol) of AlCl<sub>3</sub>, and 50 ml of benzene was refluxed for 6 hr. The organic material was isolated as usual. From column chromatography (silica gel, 8:1 hexane–chloroform) was obtained 1.4 g of brown needles. After recrystallization from methanol, 0.95 g (46.5% yield) of triphenyltrichlorofulvene was obtained: mp 126–128°; ir (KBr) 6.45 (m), 6.71 (w), 6.94 (m), 7.75  $\mu$  (w); uv max (benzene) 312 nm, sh at 420 nm (log  $\epsilon$  4.20).

*Anal.* Calcd for C<sub>24</sub>H<sub>15</sub>Cl<sub>3</sub>: C, 70.35; H, 3.69; Cl, 25.96. Found: C, 70.44; H, 3.83; Cl, 26.01.

**Hydrolysis of 1 with Concentrated Sulfuric Acid.**—A mixture of 2.84 g (10 mmol) of 1 and 40 ml of concentrated H<sub>2</sub>SO<sub>4</sub> was stirred and heated on a steam bath for 3 hr. The dark green solution was then cooled and poured over ice. A tan solid formed which was filtered off and washed with water. Recrystallization from ethanol yielded 1.7 g (64% yield) of 2,3,4-trichloro-5-(dichloromethylene)cyclopent-2-en-1-one (14a): mp 100–100.5°.

*Anal.* Calcd for C<sub>6</sub>HCl<sub>5</sub>O: C, 27.04; H, 0.38; Cl, 66.56. Found: C, 27.10; H, 0.34; Cl, 66.75.

A minor product was also isolated in 8% yield by adding the crude product to a NaHCO<sub>3</sub> solution. Insoluble material was filtered off and the filtrate was acidified. The amorphous light tan solid that precipitated was identified as 2,3,4,5-tetrachlorocyclopentadiene-1-carboxylic acid 16: mp 202–204° dec; ir (Nujol) 3.6–4.0 (m), 5.89 (m), 6.15 (s), 6.48 (s), 6.83 (s), 8.58 (m), 10.83 (m), 13.95 (s), 14.17  $\mu$  (s); mass spectrum (75 eV) *m/e* (rel intensity) 246 (63), 211 (100), 183 (65); uv max (CCl<sub>4</sub>) 286 nm (log  $\epsilon$  3.93).

*Anal.* Calcd for C<sub>6</sub>H<sub>2</sub>Cl<sub>4</sub>O<sub>2</sub>: C, 29.06; H, 0.81; Cl, 57.23. Found: C, 29.08; H, 1.07; Cl, 57.51.

**Registry No.**—1, 6317-25-5; 2a, 33834-97-8; 2b, 33834-98-9; 2c, 33834-99-0; 2d, 33835-00-6; 2e, 33835-01-7; 2f, 33835-02-8; 3a, 33835-03-9; 3b, 33835-04-0; 3c, 33835-05-1; 6, 33835-06-2; 7, 33835-07-3; 9, 33835-08-4; 10, 33835-09-5; 11a, 33835-10-8; 12, 33835-11-9; 13, 33835-12-0; 14a, 29897-40-3; 16, 33835-14-2; diphenyltetrachlorofulvene, 33825-85-3; triphenyltrichlorofulvene, 33825-86-4.