Tetrachlorocyclopentadienylidene and Thermal Rearrangements of Its Cyclopropyl Adducts[1]

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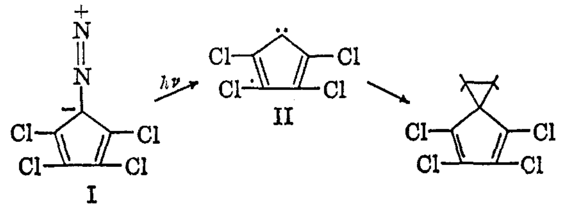
Tetrachlorocyclopentadienylidene, generated by the photolysis of tetrachlorodiazocyclopentadiene, has been shown to undergo carbon–hydrogen insertion in cyclohexane, carbon–chlorine insertion in carbon tetrachloride, and to add to olefins to give cyclopropyl compounds. The addition to *cis*-2-butene was nonstereospecific. The reaction with 2-methyl-2-butene gave 1,2,3,4-tetrachloro-6,6,7-trimethylspiro[2.4]hepta-1,3-diene, which isomerized on pyrolysis to give 2,3,4,5-tetrachloro-6-methyl-6-isopropylfulvene, but 1,2,3,4-tetrachloro-6,6,7,7-tetramethylspiro[2.4]hepta-1,3-diene gave 2′-(3′,3′-dimethyl-1′-butenyl)tetrachlorocyclopentadiene isomers *via* a fulvene intermediate. Other spiro compounds prepared did not give fulvenes on pyrolysis, but those with alkyl groups oriented *cis* were converted into their respective *trans* isomers at 435–460°.

Two previous reports have given the preparation of tetrachlorodiazocyclopentadiene (I).[2,3] Both have involved the preparation of 2,3,4,5-tetrachlorocyclopentadienone hydrazone[4] which was then oxidized by either mercuric oxide[2] or sodium hypochlorite[3] to give I. We now report the preparation of I, in 78% yield from the hydrazone using silver oxide, and its photolysis to generate tetrachlorocyclopentadienylidene (II).

The diazo compound I is an orange solid of surprising stability and can be stored under nitrogen in the dark for several months without decomposition. It is not shock sensitive and is stable in solutions below 80°, but heating for 16 hr at 120° caused complete destruction. No appreciable decomposition of the solid occurred before its sharp melting point.

Solutions of I in eight olefins were irradiated at 16° by ultraviolet light to give cyclopropyl compounds as shown in eq 1. The possibility that these reactions proceed *via* an intermediary pyrazoline in preference to a carbene cannot be rigorously excluded. However, it is known[5] that pyrazoline formation is hindered, as in this case, where nonconjugated olefins are used and when the diazo compound has the negative charge on its α-carbon atom dispersed.



(1)

The existence of a carbene under these conditions was indicated by a carbon–hydrogen insertion reaction in which irradiation of I in cyclohexane gave a 49% yield of cyclohexyltetrachlorocyclopentadiene isomers. This compares with a 57% yield of the insertion product obtained from diazocyclopentadiene and cyclohexane.[6] Carbon–chlorine insertion was also effected by photolysis of I in carbon tetrachloride to give the known octachloro-5-methylcyclopentadiene,[7] probably by a radical abstraction–recombination mechanism.

The cyclopropyl compounds, with the exception of 1,2,3,4-tetrachloro-6,6,7,7-tetramethylspiro[2.4]hepta-1,3-diene (III), all displayed absorption in the infrared characteristic of a cyclopropane ring (9.88–10.00 μ).[8] The ultraviolet spectra of all the adducts showed peaks at 241–254 and 283–292 mμ; the higher absorptions for both bands corresponded to the more highly alkylated cyclopropanes.

All the adducts were light- and oxygen-sensitive and, except for III and those from *cis*-2-butene and cyclohexene, all were liquids, which were purified by distillation *in vacuo* and by vapor phase chromatography.

The photolysis of I in cyclohexene gave norcarane-7-spiro-5′-(1′,2′,3′,4′-tetrachlorocyclopenta-1′,3′-diene) (IV), a white solid. There was no evidence of any insertion products as the nmr spectrum[9] displayed only a broad envelope between 1.0 and 2.5 ppm. There were no peaks indicative of vinyl protons in this spectrum or in those obtained from the first and last chromatographic fractions containing IV, even at maximum sensitivity. As chlorinated cyclopentadienes are very weakly adsorbed on acid-washed alumina and are quickly eluted with hexane, any carbon-hydrogen insertion product would have been eluted with IV.

The reaction with 1-hexene gave 1,2,3,4-tetrachloro-6-*n*-butylspiro[2.4]hepta-1,3-diene (V), but 2-hexene (84% *cis*, 16% *trans*) gave a mixture of two isomers of 1,2,3,4-tetrachloro-6-methyl-7-*n*-propylspiro[2.4]hepta-1,3-diene, VI and VII, in the ratio 77:23, which were separated by vpc. The larger component was assigned the *cis* structure as the mixture was converted to 25:75 ratio by a pyrolysis at 460°. The *cis* isomer is expected to be less stable than the *trans* because of steric interactions between the *n*-propyl and the methyl groups.

A pair of isomers was also obtained from the photolysis of I in *cis*-2-pentene (95%) and preparative vapor phase chromatography separated 75% *cis*-

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[1] From a thesis submitted by J. A. Bosoms to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] F. Klages and K. Bott, *Chem. Ber.*, **97**, 735 (1964).

[3] H. Disselnkotter, *Angew. Chem. Intern. Ed. Engl.*, **3**, 735 (1964).

[4] E. T. McBee, U. S. Patent, 3,141,043 (July 14, 1964), *Chem. Abstr.*, **61**, 8205*f* (1965).

[5] R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 563 (1963).

[6] W. Kirmse, L. Horner, and H. Hoffman, *Ann.*, **614**, 19 (1958).

[7] J. Newcomer and E. T. McBee, *J. Am. Chem. Soc.*, **71**, 946 (1949).

[8] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 29. This characteristic is sometimes unreliable: *e.g.*, see G. E. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960).

[9] Proton nmr spectra were obtained using a Varian A-60 spectrometer and measurements are given in parts per million downfield relative to tetramethylsilane used as internal reference. Carbon tetrachloride was used as solvent unless otherwise indicated.

(VIII) and 22% *trans*- (IX) 1,2,3,4-tetrachloro-6-methyl-7-ethylspiro[2.4]hepta-1,3-diene. The nmr spectrum of each isomer displayed a multiplet at 2.0 (cyclopropyl protons and $-CH_2-$ of the ethyl group), a triplet at 0.98 (CH_3- of the ethyl group), and a doublet at 1.49 ppm (CH_3- on the cyclopropane ring). The structures were assigned according to the argument advanced earlier as a 75:22 mixture of VIII and IX isomerized to a 25:75 mixture on pyrolysis at 435°.

The photolysis of 2-methyl-2-butene and I gave 1,2,3,4-tetrachloro-6,6,7-trimethylspiro[2.4]hepta-1,3-diene (X) whose structure was supported by the nmr spectrum (in $CDCl_3$) which showed a doublet at 1.49 (J = 12 cps) (CH_3- on the cyclopropane ring), a singlet at 1.60 (protons of the *gem*-dimethyl group), and a quartet centered at 2.43 ppm (cyclopropyl proton); the area ratio was 3.0:6.0:1.1. 2,3-Dimethyl-2-butene gave 1,2,3,4-tetrachloro-6,6,7,7-tetramethylspiro[2.4]hepta-1,3-diene (III), a white solid whose nmr spectrum showed a single peak at 1.67 ppm.

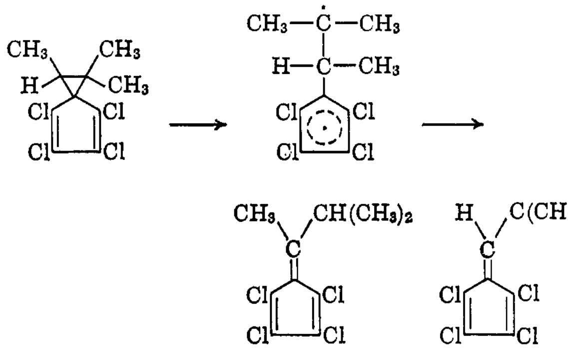
Photolysis of I in pure *cis*-2-butene gave both *cis*- (XI) and *trans*- (XII) 1,2,3,4-tetrachloro-6,7-dimethylspiro[2.4]hepta-1,3-diene, and pure *trans*-2-butene gave mainly XII and only a trace of XI. The nmr of each (in $CDCl_3$) showed a doublet at 1.43 (J = 10 cps) and a multiplet at 2.3 ppm; the relative areas were 3.0:1.0. *cis*-2-Butene and I were also photolyzed using a filter[10] and the ratio of XI:XII was approximately 90:10.

The possibility that the nonstereospecificity was caused by I or some intermediate (perchlorofulvalene, for example) acting as a photosensitizer was eliminated when the irradiation of I with XI in a 1:1 ratio did not produce any XII.[10]

Thus it appears that the carbene II is responsible for the nonstereospecific additions. It is not possible to correlate this precisely with the electronic state of II as, although Skell's postulate[12] that stereospecific addition indicates a singlet state is generally accepted,[13] the corollary that nonstereospecific addition indicates a triplet state is disputed.[14]

The thermal properties of the spiro compounds were also investigated. When X was heated at 190° for 12 min, a red solid, 2,3,4,5-tetrachloro-6-methyl-6-isopropylfulvene (XIII), was obtained in 45% yield. The fulvene structure of the compound, suspected from its color and elemental analysis, was confirmed spectroscopically. Its ultraviolet spectrum showed a broad band with maxima at 290 and 297 mμ, similar to hexachlorofulvene which displays a broad band with peaks at 297 and 308 mμ.[15] The infrared spectrum showed the presence of an isopropyl group and nmr data showed a singlet at 2.40 (CH_3-), a doublet at 1.17 (CH_3- of the isopropyl group), and a multiplet at 4.38 ppm (proton of the isopropyl group); the area ratio was 3.0:6.0:1.1.

The mechanism proposed for this rearrangement is based on that discussed by Breslow[16] for the pyrolysis of cyclopropane. The initial breaking of the cyclopropane ring results in the formation of a trimethylene diradical, in which one terminal position is occupied by a tetrachlorocyclopentadiene radical and the other by a tertiary radical, as shown in eq 2. This stabilized intermediate may be responsible for the low reaction temperature (pyrolysis of cyclopropane requires 500°). Any other cleavage would involve less stable secondary radicals. The second and rate-determining step is the migration of a hydrogen atom in preference to a methyl radical giving the fulvene XIIIa and not XIIIb.


XIIIa XIIIb (2)

The pyrolysis of III gave different results. When III was heated at 210° for 10 min, a transient red color appeared but the final product was a yellow liquid which was shown to be an inseparable mixture of 2′-(3′,3′-dimethyl-1′-butenyl)-tetrachlorocyclopentadiene isomers (XIV).

These isomers are presumably formed by the migration of a proton around the diene ring, as shown in Scheme I. This property of alkylcyclopentadienes has been investigated by several workers.[17-19] Isomerization by chlorine migration has been shown to be less favored.[20]

The ultraviolet spectrum of the isomeric mixture XIV showed a broad maximum at 298–307 mμ (ε 2200).[21] This compares with the maximum for cyclohexyltetrachlorocyclopentadiene at 299 mμ (ε 1880) and 1,2,3,5,5-pentachlorocyclopentadiene at 310 mμ (ε 1000).[23] There were no peaks at longer wavelengths. The nmr spectrum displayed large peaks at 1.11 and 1.13 (CH_3- of the *t*-butyl group), and smaller peaks at 4.56, 4.79, 4.87, 4.93 and 5.34 ppm (terminal methylene protons and the proton on the ring); the area ratio of the two large peaks to the five smaller ones was 3.0:1.0. Peaks due to terminal

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[10] Complete absorption of ultraviolet radiation below 322 mμ was achieved with a filtering solution (0.1 *M*, 1 cm thick) of naphthalene[11] in decalin. Under these conditions, isomerization of XI to XII was prevented.

[11] M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).

[12] P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956).

[13] P. P. Gaspar and G. S. Hammond, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 261.

[14] Reference 13, p 270.

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

[16] R. Breslow in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 233.

[17] V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963).

[18] V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Proc. Acad. Sci. USSR, Chem. Sect.*, 1467 (1963).

[19] S. McLean and P. Haynes, *Tetrahedron Letters*, 2385 (1964).

[20] E. T. McBee, R. A. Halling, and C. J. Morton, unpublished results.

[21] Molecular models indicate that in XIVb the side chain is distorted out of the plane of the ring, such that linear conjugation[22] cannot occur. The magnitude of the distortion in XIVc is not as great and cross-conjugation[22] may occur. In this case, it is assumed that the longer wavelength absorption would correspond to the chlorinated cyclopentadiene ring. As a result, the ultraviolet spectra of XIVb and XIVc would be similar in this region.

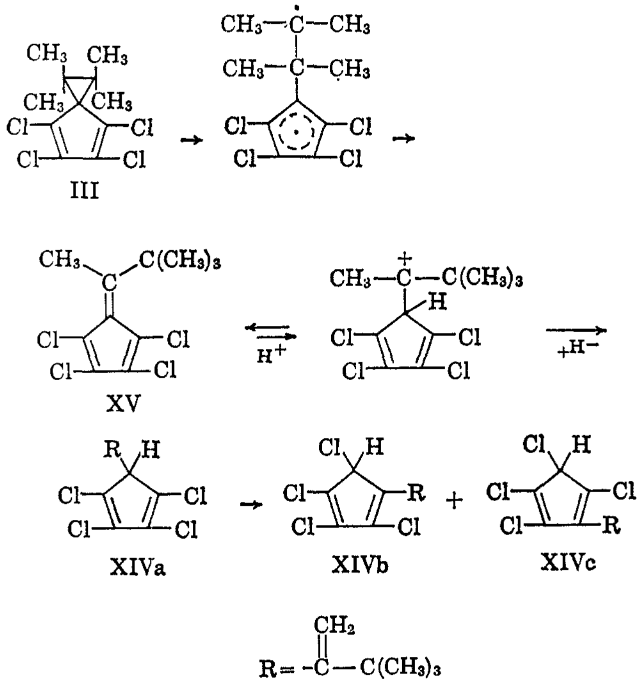
[22] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons Inc., New York, N. Y., 1962, p 204.

[23] R. D. Crain, Ph.D. Thesis, Purdue University, 1958.

methylene protons usually appear[24] at 4.56 ppm, but the tetrachlorocyclopentadiene system could shift these, especially when the ethylenic group is bonded to the vinyl positions of the ring. Infrared absorption in the 3.35-μ region and at 7.09 μ and weaker absorption at 5.40 and 5.55 μ supported an asymmetric disubstituted olefin structure and peaks at 7.18 and 7.33 μ were attributed to the *t*-butyl group.[25]

The most probable initial isomer is XIVa, some of which isomerized to XIVb and XIVc.

Scheme I



The appearance of the red color suggested a fulvene intermediate, so the pyrolysis of III was performed under milder conditions (180° for 21.5 min). The red oil obtained could not be purified by distillation, elution, or vapor phase chromatography, or by crystallization from methanol. All these techniques resulted in XIV.

However, the nmr spectrum of the oil indicated the presence of III (16%), XIV (12%), and the isomeric 2,3,4,5-tetrachloro-6-methyl-6-*t*-butylfulvene (XV, 72%). Proton resonances for XV occurred at 2.43 (CH_3-) similar to that for XIII, and at 1.43 ppm (CH_3- of the *t*-butyl group); the area ratio was 0.9:3.0. The ultraviolet spectrum showed two bands: the smaller one at 254–256 mμ was attributed to III and the other at 308–314 mμ (ε 19,500 calculated for 100% XV) was assigned to the fulvene by comparison with that for XIII. Further evidence for the *t*-butyl group was obtained from the infrared spectrum.

The only difference between the fulvenes XV and XIII is that the *t*-butyl group on the 6-position of XV is replaced by an isopropyl group, yet the two have widely differing properties. Molecular models indicate that there is steric strain caused by the interactions of two of the methyl groups of the *t*-butyl group with the chlorine atom on the same side of the ring, and this makes the fulvene structure XV unstable. The mechanism for the conversion of XV into XIV is not proved but in the cases of isomerization on acid-washed alumina and Chromosorb P, an ionic process can be invoked. Protonation of any of the five positions of the cyclopentadiene ring should lead to a structure with a positive charge on the 6-position of the fulvene. This carbonium ion can then lose either an allylic proton giving XIV or a ring proton forming XV. For steric reasons, XIV is favored.

It is not clear whether an alternative mechanism, conceivably a radical mechanism, operates in those reactions at high temperatures. It has been noticed, however, that some of the tars produced in all the photolyses slowly evolved acidic gases (HCl?) and these may have catalyzed the isomerization.

The adducts IV, V, and the isomeric mixture of VI and VII were unchanged after heating near 190° for 1 to 3 hr. In each case, the expected intermediary trimethylene diradical would have a terminal secondary radical. The resultant decrease in the stabilization of the transition state compared with that for III or X is apparently large enough to prevent diradical formation under these conditions. However, such intermediates were formed in the pyrolysis of the isomeric mixtures VI, VII and VIII, IX. Hence, at 435–460°, the predominant *cis* isomer was converted in high proportion to the corresponding *trans* compound. Under these conditions, fulvene formation was not observed.

Experimental Section[26]

Cyclohexene was Eastman Organic Chemicals Reagent and was distilled immediately before use. *cis*-2-Pentene was Phillips 66 Technical Grade (95%) and the other olefins were Phillips 66 Pure Grade compounds. Each was used without further purification. Cyclohexane was purified by distillation and carbon tetrachloride was Baker Analyzed Reagent Spectrophotometric Grade. **2,3,4,5-Tetrachlorocyclopentadienone hydrazone** was prepared by the method of McBee.[4]

Tetrachlorodiazocyclopentadiene (I).—2,3,4,5-Tetrachlorocyclopentadienone hydrazone (11.8 g. 0.051 mole), silver oxide (15.5 g. 0.125 mole), anhydrous sodium sulfate (2 g), and anhydrous ether (125 ml) were shaken mechanically in a bottle wrapped with a wet towel. After 9.5 hr the reaction mixture was filtered and the solvent was evaporated. The residue was chromatographed on acid-washed alumina. Hexane eluted 9.2 g (78%) of I: mp 105–106° (lit.[2] mp 108°); λ_{max}^{Nujol} 4.58 (m), 4.72 (s), 6.54 (s), 7.85 (s), and 13.61 (s) μ; λ_{max}^{EtOH} 307 mμ (log ε 4.40).

Anal. Calcd for $C_5Cl_4N_2$: C, 26.10; Cl, 61.68; N, 12.18; mol wt, 229.9. Found: C, 26.30; Cl, 61.80; N, 12.23; mol wt, 235.2.

Photochemical Decomposition of Tetrachlorodiazocyclopentadiene. Procedure A.—Solutions were irradiated in a cylindrical flask of Pyrex (length 50 cm, diameter 7 cm) and cooled by cold water passing through an internal spiral condenser. An inlet diffusion tube extended from the upper portion of the flask to within 1 cm of its bottom, and dry nitrogen was thus passed through the system from 1 hr before the photolysis. The light source was a 400-w General Electric H400 A 33-1 mercury lamp

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[24] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Macmillan Co., New York, N. Y., 1959, p 61.

[25] Reference 8, p 24.

[26] All melting points are uncorrected. Analyses and molecular weights (measured by vapor pressure osmometry and run in $CHCl_3$ unless otherwise stated) were determined by Dr. C. S. Yeh, Purdue University. Infrared spectra were obtained using a Perkin-Elmer 137B Infracord spectrophotometer or a Beckman IR8 infrared spectrophotometer. Ultraviolet spectra were obtained on a Bausch and Lomb Spectronic 505 spectrometer. Vapor phase chromatograms were obtained using either a Perkin-Elmer Model 154 Vapor Fractometer and a 4-ft adiponitrile on Chromosorb W column, or an Aerograph Model A-700 Autoprep and a 3% GE-SF-96 on 60–80 mesh acid-washed Chromosorb P column (10 ft × 0.5 in.). The latter was used for all the chlorinated compounds.

and power was supplied to it from a Jefferson 237-421 mercury lamp ballast transformer.

Decomposition of Tetrachlorodiazocyclopentadiene in Cyclohexane.—A solution of I (11.3 g. 0.0491 mole) in cyclohexane (200 ml) was irradiated for 1 week according to procedure A. Excess cyclohexane was then evaporated and the residue was chromatographed on acid-washed alumina. Hexane eluted 6.93 g (49%) of crude cyclohexyltetrachlorocyclopentadiene isomers as a yellow liquid, purified by distillation: $\lambda_{\max}^{\text{neat}}$ 3.44 (s), 6.26 (s), 6.91 (s), 12.97 (s), and 13.20 (s) μ; $\lambda_{\max}^{\text{EtOH}}$ 299 mμ (log ϵ 3.25). The nmr spectrum displayed a broad band from 0.5 to 3.0, a doublet at 3.08, and singlets at 4.48, 4.62, 6.07, and 6.18 ppm.

Anal. Calcd for $C_{11}H_{12}Cl_4$: C, 46.19; H, 4.20; Cl, 49.62. Found: C, 46.01; H, 4.05; Cl. 49.88.

Decomposition of Tetrachlorodiazocyclopentadiene in Carbon Tetrachloride. Procedure B.—Material was irradiated in a 500-ml creased flask equipped with stirrer and two gas-inlet tubes and cooled by cold water. The light source was as in procedure A. Tetrachlorodiazocyclopentadiene (5 g, 0.0260 mole) and carbon tetrachloride (150 ml) were irradiated for 46 hr. Excess carbon tetrachloride was then evaporated and the residue was chromatographed on acid-washed alumina. Hexane eluted 5.2 g (56%) of octachloro-5-methylcyclopentadiene, and two recrystallizations from methanol gave a white solid, mp 93–93.5° (lit.[3] mp 93–94°), with infrared spectrum identical with that of authentic material.

Photochemical Decomposition of Tetrachlorodiazocyclopentadiene in Olefins. Cyclohexene.—A solution of I (21.6 g, 0.0940 mole) and cyclohexene (250 ml) was irradiated using procedure A. After 78 hr, the solvent was evaporated and the residue was chromatographed on acid-washed alumina. Hexane eluted 23.7 g (89%) of crude norcarane-7-spiro-5′-(tetrachlorocyclopenta-1′,3′-diene) (IV), and 1.37 g of tars was eluted with benzene, chloroform, and methanol. Two recrystallizations of IV from methanol gave a white solid: mp 104–104.5°; $\lambda_{\max}^{\text{CCl}_4}$ 6.3 (s), 9.88 (m), and 14.55 (s) μ; $\lambda_{\max}^{\text{EtOH}}$ 247 mμ (log ϵ 4.03) and 289 mμ (log ϵ 3.60). The nmr spectrum only displayed a broad band from 1.0 to 2.5 ppm.

Anal. Calcd for $C_{11}H_{10}Cl_4$: C, 46.51; H, 3.52; Cl. 49.97; mol wt, 283.8. Found: C, 46.59; H, 3.39; Cl, 49.84; mol wt, 285.9.

1-Hexene.—A solution of I (14.7 g, 0.0639 mole) in 1-hexene (250 ml) was irradiated using procedure A. After 72 hr, excess olefin was evaporated and the residue was chromatographed on acid-washed alumina. Hexane eluted crude 1,2,3,4-tetrachloro-6-butylspiro[2.4]hepta-1,3-diene (V). Distillation gave 9.86 g (54%) of pure V: bp 108° (0.85 mm); n^{19}D 1.5474; $\lambda_{\max}^{\text{neat}}$ 6.37 (s), 6.80 (s), 9.82 (m), and 14.58 (s) μ; $\lambda_{\max}^{\text{EtOH}}$ 241 mμ (log ϵ 3.90) and 285–288 mμ (log ϵ 3.53). The nmr spectrum was very complex between 0.6 and 2.2 ppm.

Anal. Calcd for $C_{11}H_{12}Cl_4$: C, 46.19; H, 4.20; Cl, 49.62. Found: C, 46.50; H, 4.42; Cl, 50.00.

2-Hexene.—A solution of I (17.7 g, 0.0769 mole) in 2-hexene (250 ml, 84% *cis*) was irradiated according to procedure A. After 81.5 hr, excess olefin was evaporated and the residue was chromatographed on acid-washed alumina. Hexane eluted 19.05 g (87%) of a mixture of *cis*- and *trans*-1,2,3,4-tetrachloro-6-methyl-7-propylspiro[2,4]hepta-1,3-diene (VI and VII), which was distilled, bp 89–91° (0.14 mm). Vapor phase chromatography (column temperature 160°, injector temperature 240°, He flow rate 300 cc/min) of the distillate indicated two peaks, VII at 12 min and VI at 14 min retention time, in a ratio of 23:77. Neither compound was isomerized by passage through the column under the conditions used. Spectral data for the *cis* isomer were $\lambda_{\max}^{\text{neat}}$ 6.33 (s), 9.88 (m), and 14.50 (s) μ; $\lambda_{\max}^{\text{EtOH}}$ 244 mμ (log ϵ 4.06) and 285 mμ (log ϵ 3.64).

Anal. Calcd for $C_{11}H_{12}Cl_4$: C, 46.19; H, 4.20; Cl, 49.62. Found: C, 46.40; H, 4.07; Cl, 49.30.

Spectral data for the *trans* isomer were $\lambda_{\max}^{\text{neat}}$ 6.36 (s), 9.85 (m), and 14.23 (s) μ; $\lambda_{\max}^{\text{EtOH}}$ 245 mμ (log ϵ 3.97) and 284–288 mμ (log ϵ 3.57).

Anal. Calcd for $C_{11}H_{12}Cl_4$: C, 46.19; H, 4.20; Cl, 49.62. Found: C, 46.35; H, 4.35; Cl, 49.21.

2-Methyl-2-butene.—A solution of I (20.6 g, 0.0896 mole) in 2-methyl-2-butene (250 ml) was irradiated according to procedure A. After 76 hr, excess olefin was evaporated and the residue was chromatographed on acid-washed alumina. Hexane eluted 21.15 g (87%) of crude 1,2,3,4-tetrachloro-6,6,7-trimethylspiro-[2.4]hepta-1,3-diene (X) purified by vpc: n^{22}D 1.5620; $\lambda_{\max}^{\text{neat}}$ 6.34 (s), 9.86 (m), 13.13 (s), and 13.95 (m) μ; $\lambda_{\max}^{\text{EtOH}}$ 250 mμ (log ϵ 3.94) and 292 mμ (log ϵ 3.59).

Anal. Calcd for $C_{10}H_{10}Cl_4$: C, 44.15; H, 3.68; Cl, 52.17. Found: C, 44.25; H, 4.01; Cl, 52.40.

2,3-Dimethyl-2-butene.—A solution of I (15.9 g, 0.0691 mole in 2,3-dimethyl-2-butene (200 ml) was irradiated according to procedure A. After 109.5 hr, excess solvent was evaporated and the residue was chromatographed on acid-washed alumina. Hexane eluted 15.74 g (80%) of crude 1,2,3,4-tetrachloro-6,6,7,7-tetramethylspiro[2.4]hepta-1.3-diene (III), and two recrystallizations from ethanol gave a white solid, mp 122–123°. Spectral data for III were $\lambda_{\max}^{\text{CCl}_4}$ 6.42 (s) and 14.21 (s) μ; $\lambda_{\max}^{\text{EtOH}}$ 254 mμ (log ϵ 4.03) and 296 mμ (log ϵ 3.24).

Anal. Calcd for $C_{11}H_{12}Cl_4$: C, 46.19; H, 4.20; Cl, 49.62. Found: C, 46.10; H, 4.43; Cl, 49.36.

***cis*-2-Pentene.**—A solution of I (15.28 g, 0.664 mole) in *cis*-2-pentene (200 ml) was irradiated according to procedure A. After 110 hr, excess olefin was evaporated and the residue was chromatographed on acid-washed alumina. Hexane eluted 14.58 g (81%) of a crude mixture of *cis*- and *trans*-1,2,3,4-tetrachloro-6-methyl-7-ethylspiro[2.4]hepta-1,3-diene (VIII and IX), which was distilled to give a liquid, bp 90° (1.6 mm). This was analyzed by vpc (column temperature 160°, injector temperature 230°, He flow rate 300 cc/min) and gave three components: (a) 2.75 min, not identified (3%) (b) 8 min, *trans* isomer (22%); and (c) 10 min, *cis* isomer (75%), n^{22}D 1.5640. Spectra of the *cis* isomer showed peaks at $\lambda_{\max}^{\text{neat}}$ 6.42 (s), 9.97 (s), 12.92 (s), and 14.59 (s) μ; $\lambda_{\max}^{\text{EtOH}}$ 245 mμ (log ϵ 3.95) and 287 mμ (log ϵ 3.54).

Anal. Calcd for $C_{10}H_{10}Cl_4$: C, 44.15; H, 3.68; Cl, 52.17. Found: C, 44.08; H, 3.98; Cl, 52.09.

Spectral data for the *trans* isomer were $\lambda_{\max}^{\text{neat}}$ 6.38 (s) and 14.18 (s) μ; $\lambda_{\max}^{\text{EtOH}}$ 254 mμ (log ϵ 3.88) and 284–289 mμ (log ϵ 3.48).

Anal. Calcd for $C_{10}H_{10}Cl_4$: C, 44.15; H, 3.68; Cl, 52.17. Found: C, 44.19; H, 3.85; Cl, 52.02.

Photolysis of Tetrachlorodiazocyclopentadiene in *cis*-2-Butene. Procedure C.—A 4-oz Pyrex ampoule containing tetrachlorodiazocyclopentadiene (1.64 g, 0.0057 mole) was cooled in a Dry Ice bath, and *cis*-2-butene (25 ml) was condensed into it. The ampoule was frozen in liquid nitrogen, evacuated, sealed, and then warmed to room temperature and irradiated. After 93 hr, the ampoule was frozen in liquid nitrogen and opened, and the excess olefin was boiled away. The residue was chromatographed on acid-washed alumina. Hexane eluted 1.26 g (83.5%) of a mixture of crude *cis*- and *trans*-1,2,3,4-tetrachloro-6,7-dimethylspiro[2.4]hepta-1,3-diene (XI and XII) and sublimation at 90° (1.6 mm) gave a yellow solid, mp 64–76°. Vapor phase chromatography of the solid in cyclohexane solution (column temperature 158°, injector temperature 230°, He flow rate 300 cc/min) indicated two components in the ratio 79:21. The crude product was recrystallized three times from methanol to give XI, a white solid, mp 83.5–84.5°, which had the same retention time as the larger peak. Spectra of this solid displayed maxima $\lambda_{\max}^{\text{CCl}_4}$ 9.90 (s) and 14.49 (s) μ; $\lambda_{\max}^{\text{EtOH}}$ 245 mμ (log ϵ 3.98) and 287 mμ (log ϵ 3.70).

Anal. Calcd for $C_9H_8Cl_4$: C, 41.89; H, 3.10; Cl, 55.00. Found: C, 41.56; H, 2.92; Cl, 54.55.

Photolysis in *trans*-2-Butene.—A solution of I (1.52 g, 0.006 mole) in *trans*-2-butene (40 ml) was irradiated according to procedure C. After 113 hr, the ampoule was opened, the olefin was evaporated, and the residue was chromatographed on acid-washed alumina. Hexane eluted 1.26 g (68%) of crude *trans*-1,2,3,4-tetrachloro-6,7-dimethylspiro[2.4]hepta-1,3-diene (XII). Distillation gave a yellow liquid, bp 81° (1.5 mm), with the same vpc retention time as the smaller of the two peaks obtained from the reaction with *cis*-2-butene. A barely detectable peak owing to the *cis* isomer was present. The main product was purified by vpc and showed maxima at $\lambda_{\max}^{\text{neat}}$ 6.39 (s), 9.99 (w), 15.46 (m), and 15.75 (m) μ; $\lambda_{\max}^{\text{EtOH}}$ 244 mμ (log ϵ 3.84) and 283–288 mμ (log ϵ 3.44).

Anal. Calcd for $C_9H_9Cl_4$: C, 41.89; H, 3.10; Cl, 55.00. Found: C, 41.89; H, 3.10; Cl, 54.72.

Rearrangement of *cis*-1,2,3,4-Tetrachloro-6,7-dimethylspiro-[2.4]hepta-1,3-diene.—A solution of pure XII (0.147 g, 0.00057 mole) and 2,3-dimethyl-2-butene (25 ml) was irradiated according to procedure C. After 71.5 hr, the ampoule was opened and the excess olefin was evaporated. Analysis by vpc indicated two components, XII and XI, in the ratio of 47:53. The first peak had the same retention time as the *trans* isomer and the second peak had the same retention time as the *cis* isomer.

Photolyses Using a Filtering Solution. Procedure D.—The solution to be irradiated was placed in a 20-ml ampoule, cooled in a Dry Ice bath, evacuated, and frozen in liquid nitrogen. The ampoule was then sealed, warmed to room temperature, and immersed in the stirred filtering solution[10] contained in a 1-l. beaker. The edge of the ampoule was placed 1.1 to 1.2 cm from the edge of the beaker and the solution was irradiated. After photolysis, the ampoule was frozen in liquid nitrogen and opened. The ampoule was warmed to room temperature, the reaction mixture was removed from it, and the residue was washed with chloroform. The solutions were combined, solvent and excess olefin were evaporated, and the residue was washed with chloroform.

Photolysis in *cis*-2-Butene.—Pure I (0.054 g. 0.0023 mole) and *cis*-2-butene (8 ml) were irradiated according to procedure D. After 52 min, the mixture was worked up and analyzed by vpc (column temperature 161°, injector temperature 240°, He flow rate 300 cc/min). The *trans* peak appeared at 16.5 min and the *cis* at 21 min. The areas of the peaks were measured with a planimeter. The ratio of the isomers was obtained from calibration curves whch indicated that approximately 10% of the *trans* isomer was formed.

Photolysis in *trans*-2-Butene.—A solution of I (0.041 g. 00017 mole) and *trans*-2-butene (11 ml) were irradiated according to procedure D. After 52 min, the mixture was worked up and analyzed by vpc. There was only one component, corresponding to the *trans* isomer.

Photolysis of Tetrachlorodiazocyclopentadiene in the Presence of XI.—A solution of I (0.052 g, 0.00023 mole), pure XI (0.058 g, 0.00023 mole), and spectral grade isooctane (8 ml) was irradiated according to procedure D. The products were analyzed by vpc (column temperature 153°, injector temperature 240°, He flow rate 300 cc/min). No peak for the *trans* isomer could be detected.

Thermal Rearrangement of 1,2,3,4-Tetrachlorospiro[2.4]hepta-1,3-dienes at 180–210°. Procedure E.—Material was placed in a 50-ml round-bottomed flask which had one neck and a side arm and was fitted with a reflux condenser. The system was flushed with dry nitrogen and the flask was completely immersed in an oil bath at 180–210°.

2,3,4,5-Tetrachloro-6-methyl-6-isopropylfulvene (XIII).—1,2,3,4-Tetrachloro-6,6,7-trimethylspiro[2.4]hepta-1,3-diene (X) (1.39 g, 0.00511 mole) was heated at 190° for 20 min according to procedure E. On cooling, the mixture was chromatographed on acid-washed alumina, and hexane eluted 0.91 g of a mixture of X and XIII. Distillation gave a red oil, bp 90° (1 mm), which crystallized on standing in an icebox. Recrystallization from methanol gave 0.63 g (45%) of a red solid: mp 59–60°; $\lambda_{max}^{CCl_4}$ 6.28 (s), 6.45 (s), 13.75 (s), and 14.35 (s) μ.

Anal. Calcd for $C_{10}H_{10}Cl_4$: C, 44.15; H, 3.68; Cl, 52.17. Found: C, 44.19; H, 3.88; Cl, 52.30.

2′-(3′,3′-Dimethyl-1′-butenyl)tetrachlorocyclopentadiene (XIV).—1,2,3,4-Tetrachloro-6,6,7,7-tetramethylspiro[2.4]hepta-1,3-diene (III) (2.0 g, 0.0070 mole) was heated for 10 min at 210° according to procedure E. Distillation of the product gave 1.02 g (52%) of yellow liquid: bp 90° (0.1 mm); λ_{max}^{neat} 6.24 (s), 6.34 (m), 7.18 (m), 7.33 (s), 13.12 (s), 13.65 (s), 14.35 (m), and 15.06 (m) μ.

Anal. Calcd for $C_{11}H_{12}Cl_4$: C, 46.19; H, 4.20; Cl, 49.62; mol wt, 286. Found: C, 46.28; H, 4.48; Cl, 50.00; mol wt, 290 (in benzene).

2,3,4,5-Tetrachloro-6-methyl-6-*t*-butylfulvene (XV).—A portion of III (5.42 g, 0.0190 mole) was heated for 21.5 min at 186° according to procedure E. Distillation of the product gave a red oil, bp 90° (0.07 mm), which could not be crystallized or further purified despite many varied attempts. Spectral data for the fulvene were λ_{max}^{neat} 6.43 (s), 6.51 (s), 7.17 (m), 7.31 (s), 13.92 (s), and 15.10 (s) μ.

Procedure for Rearrangements at 435–460°. Procedure F.—The reactions were carried out in a vertical glass column packed with glass helices and heated by an electrical furnace. Material was dropped onto the column from an addition funnel attached to the top and collected in a Dry Ice cooled trap fitted with side arm. The temperature of the furnace was measured with a thermocouple. The system was flushed with nitrogen for 1 hr before the reaction *via* a three-way tap attached to the top of the addition funnel, and then was evacuated to 2.5 mm. Material was then allowed to drop on to the column over a 30-min period, the pressure difference being maintained by a small flow of nitrogen from a balloon also attached to the addition funnel.

When reaction was complete, the column was cooled, the helices were washed with chloroform, and the washings were added to the material in the trap. The chloroform was evaporated and the residue was chromatographed on acid-washed alumina.

Thermal Rearrangement of 1,2,3,4-Tetrachloro-6-methyl-7-*n*-propylspiro[2.4]hepta-1,3-diene.—The mixture of VI and VII isomers (1.67 g, 0.00588 mole), present in the *cis*:*trans* ratio of 77:23, was dropped on to the column at 460° according to procedure F. Hexane eluted 1.30 g (78%) of crude product, which was distilled and analyzed by vpc (column temperature 170°, injector temperature 245°, He flow rate 300 cc/min). The *cis*:*trans* isomer distribution was shown to be 25:75 as determined by chromatographic peak areas.

Thermal Rearrangement of 1,2,3,4-Tetrachloro-6-methyl-7-ethylspiro[2.4]hepta-1,3-diene.—The mixture of isomers of VIII and IX (2.23 g, 0.00820 mole), present in the *cis*:*trans* ratio of 80:20, was dropped onto the column at 435° according to procedure F. Hexane eluted 2.01 g (90%) of crude product, which was distilled and analyzed by vpc (column temperature 160°, injector temperature 240°, He flow rate 300 cc/min). The *cis*:*trans* isomer distribution was shown to be 25:75.

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Synthesis of Some Alkylidenecyclopropanes from Allenes[1]

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2,2-Dibromoalkylidenecyclopropanes have been prepared by the addition of dibromocarbene to allenes. The dibromo derivatives have been reduced successively to the monobromides and the hydrocarbons. Infrared and proton magnetic spectra of the adducts and their dehalogenation products are discussed.

Alkylidenecyclopropanes comprise a group of compounds which are of particular interest in the study of angle strain on chemical and physical properties. Early attempts to prepare the parent compound of the series, methylenecyclopropane,[4–6] met with little success. Boord and co-workers[7] obtained the compound in 17% yield by the dechlorination of 3-chloro-(2-chloromethyl)-1-propene with magnesium in dry tetrahydro-

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