quency difference between the two B bands is hard to estimate. Finally, it is our hope that our contribution will help in shedding some light on the analytical role of B terms and their close relationship with other spectroscopic data.

Acknowledgments. We are grateful to Professors A. Moscowitz (University of Minnesota), W. A. Little (Stanford University), and E. Heilbronner (Eidgenössische Technische Hochschule, Zürich) for stimulating discussions, and to Professor P. J. Stephens (University of Southern Califonia, Los Angeles) for especially useful comments on the final draft. We are also indebted to Mr. G. H. Scott for technical assistance and to Mr. A. M. Babcock for preparation of the figures.

Reactions of Hexabromocyclopentadiene and the Synthesis of Octabromofulvalene[1]

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Abstract: Hexabromocyclopentadiene (**2**) is conveniently synthesized from hexachlorocyclopentadiene (**1**) and BBr_3 in the presence of catalytic $AlBr_3$. **2** dimerizes in the presence of larger amounts of $AlBr_3$ to form the cage compound, dodecabromopentacyclo[5.2.1.0^{2,6}.0^{3,9}.0^{5,8}]decane, $C_{10}Br_{12}$ (**3b**). Mixtures of cage compounds $C_{10}Br_nCl_{12-n}$ (**3c**) containing both bromine and chlorine were synthesized by partial halogen exchange and dimerization, starting either with **1** or **2** or mixtures of **1** and **2**. Reductive coupling of **2** with copper or CuBr gives low yields of a decabromobicyclopentadienyl, $C_{10}Br_{10}$ (**6**), which can also be obtained from the corresponding decachloro compound **4** by halogen exchange. Octabromofulvalene (**8**), a dark blue crystalline solid, is obtained from **2** by reaction with CuBr in 9:1 dimethoxyethane–water at 0°.

R ecently, it was found that complete halogen exchange takes place between tetrachlorocyclopropene and boron tribromide to give, conveniently and in one step, tetrabromocyclopropene.[2] This
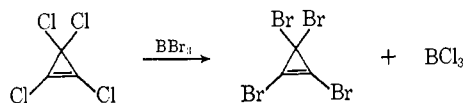
reaction is thought to occur *via* intermediate formation of aromatic trihalocyclopropenium ions.[3] For the vinylogous cyclic chlorocarbon, hexachlorocyclopentadiene (**1**), aromatic stabilization of the pentahalocyclopentadienium ions does not take place,[4] and the corresponding halogen exchange might be predicted to be more difficult. In fact, **1** is inert to boron tribromide alone, even when heated. However, a trace of aluminum tribromide serves to catalyze complete halogen exchange between **1** and BBr_3, giving hexabromocyclopentadiene (**2**). Compound **2** crystallizes
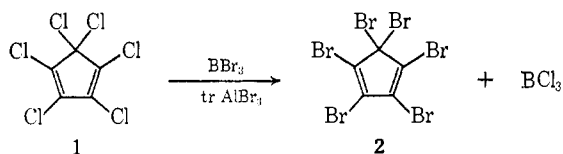
as beautiful amber-colored needles from alkanes. It has been prepared by other methods,[5] but the synthesis from **1** is quite convenient for laboratory use. This

paper describes the dimerization and dehalogenation of **2**, both of which lead to products having unusual structures.

Dimerization. A famous reaction of **1** is its dimerization in the presence of aluminum chloride or other powerful Lewis acids to the "Prins dimer," dodecachloropentacyclo[5.2.1.0^{2,6}.0^{3,9}.0^{5,8}]decane (**3a**).[6] With
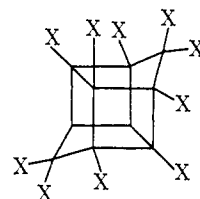
3a, $C_{10}Cl_{12}$ (X = Cl)
b, $C_{10}Br_{12}$ (X = Br)
c, $C_{10}Br_nCl_{12-n}$ (X = Br, Cl)

aluminum tribromide, **2** reacts in an analogous fashion at 100° to give the perbromo Prins dimer, **3b**.[7] **3b** is a colorless crystalline solid, which closely resembles **3a** in its physical properties. The melting point of **3b** is above 350°, and it is nearly insoluble in most organic solvents (recrystallization was effected from dibromomethane). The infrared spectrum of **3b** closely resembles that of **3a**. Each principal band in the spectrum of **3a** finds a counterpart at slightly longer wavelength in the spectrum of **3b**, as shown in Table I.

When a 1:1 mixture of **1** and **2** was treated with $AlCl_3$, a cage dimer (**3c**) containing both halogens is

(1) Abstracted from the Ph.D. thesis of P. T. Kwitowski, University of Wisconsin, 1966.
(2) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **88**, 2481 (1966).
(3) R. West, A. Sadô, and S. W. Tobey, *ibid.*, **88**, 2488 (1966).
(4) R. Breslow, R. Hill, and E. Wasserman, *ibid.*, **86**, 5349 (1964).
(5) F. Straus, L. Kollek, and W. Heyn, *Ber.*, **63B**, 1868 (1930).

(6) H. J. Prins, *Rec. Trav. Chim.*, **65**, 465 (1946).
(7) The use of **3b** as an X-ray opaque agent is described in a patent: C. W. Roberts and M. B. Chenoweth, U. S. Patent 3,212,973 (Oct 19, 1965). The preparation of **3b** is described in the Ph.D. thesis of R. H. Earle, Purdue University, 1957.

produced. The molar proportion of bromine in the "mixed" cage dimer samples is variable, but generally less than the proportion of chlorine, typical analyses showing $C_{10}Br_{3-4}Cl_{8-9}$. The infrared spectrum of **3c** corresponds exactly to those of **3a** and **3b**, with the same number and relative intensity of bands, or groups of bands, appearing at intermediate frequencies and slightly broadened (Table I). We were unsuccessful in attempts to separate discrete compounds from these reactions; it seems probable that extensive solid solutions are formed, not only between isomers but also between compounds containing different numbers of chlorine and bromine atoms.

Table I. Infrared Spectra of Halogenated Prins Dimers[a]

| $C_{10}Cl_{12}$	$C_{10}Br_{3.7}Cl_{8.6}$	$C_{10}Br_{12}$
	1190 (vw)	1170 (w)
1146 (s)	1130 (s)	1085/1075 (s) doublet
1131 (s)		1055 (w)
1056 (vs)	1050/1020 (vs)	1000/990 (vs) doublet
962 (m)	950 (m)	925 (w)
886 (w)	875 (w)	840 (w)
	820 (w)	
820 (s)	810 (m)	740 (s)
	785 (m)	
630 (s)	645 (m)	530/520 (s) doublet
	630 (m)	
	615 (m)	
	600 (m)	

[a] Values given in reciprocal centimeters.

Halogen exchange between aluminum and carbon is expected to take place only in the direction Al–Br + C–Cl → Al–Cl + C–Br.[8] Consistent with this expectation, when **1** is treated with $AlBr_3$, chlorine–bromine exchange does take place as written above. The product is again **3c**, containing about 3 atoms of bromine per molecule.

$$C_5Cl_6 + AlBr_3 \longrightarrow C_{10}Br_nCl_{12-n}$$

**1**   **3c**

$$n = 3\text{-}4$$
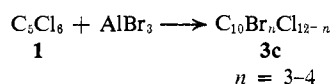
On the other hand, when **2** is treated with $AlCl_3$, **3b** is produced containing only traces of chlorine.

When **2** and $AlBr_3$ are heated in dichloromethane, similar mixed dimers (**3c**) are produced, containing chlorine in excess. In this reaction dichloromethane is the only source of chlorine, showing that halogen exchange involving the solvent can also occur.

$$C_5Br_6 + AlBr_3 \xrightarrow{CH_2Cl_2} C_{10}Br_nCl_{12-n}$$

2   **3c**

$$n = 3\text{-}4$$
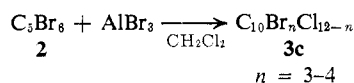
Coupling and Dehalogenation. Hexachlorocyclopentadiene (**1**) can be coupled with copper(I) chloride or with copper to decachlorobi(2,4-cyclopentadien-1-yl)
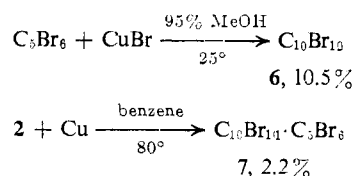
$$C_5Cl_6 \xrightarrow[\text{or CuCl–EtOH}]{\text{Cu–ligroin}}$$

4
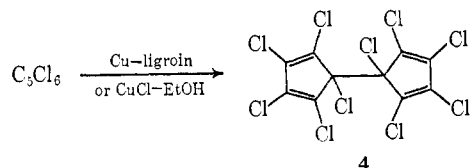
(8) Bond energies are given as follows in kilocalories/mole: C–Cl, 81; C–Br, 65; Al–Cl, 118; Al–Br, 99: T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Academic Press Inc., New York, N. Y., 1958.

(**4**).[9] In 1961, Mark prepared octachlorofulvalene (**5**) as dark blue crystals by reaction of **4** with triethyl phosphite.[10] **5** has also been obtained by gas-phase

$$C_{10}Cl_{10} \xrightarrow{(EtO)_3P}$$

5
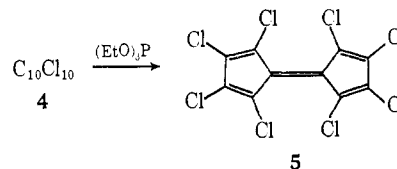
dechlorination of **1** at high temperature[11] and by reaction of **4** with tin(II) chloride dihydrate in acetone.[12]

Many reactions between **2** and metals or metal halides were carried out in order to obtain a decabromo analog of **4**. Coupling agents tried included (a) CuBr in various polar solvents at various temperatures, and (b) various metals (Al, Zn, Cu, Mg) in nonpolar solvents. Results are summarized in Table III. The major products in every case were tars, but small amounts of decabromobicyclopentadienyl (**6**) were formed in many reactions, often along with traces of another compound (**7**), apparently a 1:1 crystalline complex of **2** and **6**. Using copper(I) bromide, the best results were obtained in methanol–water (95:5), while for metals, powdered copper in benzene proved best.

$$C_5Br_6 + CuBr \xrightarrow[25°]{95\% \text{ MeOH}} C_{10}Br_{10}$$

6, 10.5%

$$2 + Cu \xrightarrow[80°]{\text{benzene}} C_{10}Br_{10} \cdot C_5Br_6$$

7, 2.2%

Bromine–chlorine exchange starting with **4** proved to be a better method for the preparation of **6**, though still affording rather low yields.

$$C_{10}Cl_{10} \xrightarrow{BBr_3, \text{ tr } AlBr_3} C_{10}Br_{10}$$

4   **6**, 21%
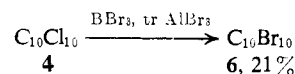
Attempted debromination of **6** to octabromofulvalene with ethyl phosphite or stannous chloride in acetone led only to brown tarry residues. However, in attempts to purify **6** by column chromatography on acid-washed alumina, a dark blue band was observed to develop. Elution of the dark band with petroleum ether gave a green solution, from which octabromofulvalene (**8**) was isolated as metallic blue crystals, in very low yield. The formation of **8** from **6** suggests that **6** is decabromobi(2,4-cyclopentadien-1-yl) (**6a**) bromine analog of **4**. However, isomers of **4** are known to be produced with Lewis acids such as aluminum halides,[13a] and the possibility cannot be ruled out that **6** is an isomer with different position of the double bonds, such as **6b**; rearrangement during the chromatography could account for the formation of **8** from **6b**.
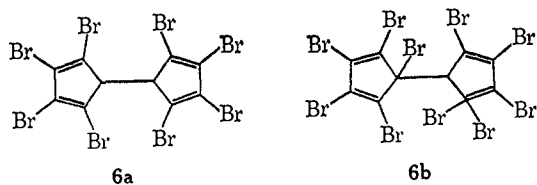
(9) E. T. McBee, J. D. Idol, Jr., and C. W. Roberts, J. Am. Chem. Soc., 77, 4375 (1955).

(10) V. Mark, Tetrahedron Letters, 333 (1961).

(11) A. E. Ginsberg, R. Paatz, and F. Korte, ibid., 779 (1962).

(12) R. West and D. C. F. Law, unpublished work; D. C. F. Law, Ph.D. Thesis, University of Wisconsin, 1966.

(13) (a) E. D. Weil, U. S. Patent 3,219,710 (Nov 23, 1965); Chem. Abstr., 64, 3377 (1964). We thank the referee for calling our attention to this patent. (b) In cosolvents, 8 reacts rapidly with water to give high molecular weight products of unknown structure, whose infrared spectra suggest the presence of a carbonyl group. A small amount of water appears to be essential in the medium in order for formation of 8 to take place.

Figure 1. Infrared spectra of octachlorofulvalene (5) and octabromofulvalene (8). Spectra taken as mulls in purified petroleum oil between KBr plates. Bands due to oil have been eliminated.

Formation of a transient blue or green color early in the reaction was also noted in some attempts to couple 2 with copper(I) bromide. This observation suggested that octabromofulvalene was present at this stage, and led to development of a method for preparing 8 directly from 2. Copper(I) bromide and 2 are allowed to react in 9:1 (v:v) 1,2-dimethoxyethane–water at 0° *for only 3 to 5 min.* The blue precipitate which forms is filtered off immediately and purified chromatographically to give 8, as dark blue crystals, in 5–7% yield.

The difficulty in obtaining 6 by reaction of 2 with copper(I) bromide in polar solvents is probably due to the ease with which further dehalogenation takes place. 6 is probably the first product formed, but under the reaction conditions it is rapidly converted almost completely to 8. However, 8 is also a transient material, undergoing side reactions to give tarry decomposition products.[13b] If the reaction mixture is allowed to stand, 8 disappears completely within less than 1 hr. Formation of 8 accounts for the fact that even when equivalent amounts of 2 and CuBr are used, and all of the CuBr is consumed, substantial amounts of the starting material 2 are recovered unchanged.

Octabromofulvalene.[14] Compound 8 closely resembles its chloro analog 5 in physical properties. The infrared spectra are very similar (Figure 1, Table II). In the region above 800 cm⁻¹, every band for 5 has a counterpart at slightly lower frequency in the spectrum of 8. These absorptions probably result from modes of the carbon skeleton, influenced only slightly by the mass of the halogen substituent. In both compounds, the highest observable infrared frequency appears as a doublet, at 1525 and 1540 cm⁻¹ in 5 and at 1490 and 1505 cm⁻¹ in 8. These bands are ascribed to C=C stretching modes, occurring at unusually low frequency in the fulvalenes. In the region below 800 cm⁻¹ significant differences are found in the spectra of the two compounds, as expected if C–X stretching is involved.

both compounds give greenish blue solutions in solvents such as chlorinated hydrocarbons. The electronic spectra are shown in Figure 2. Each compound shows three absorption maxima, all of which are shifted to slightly lower energy in the bromo compound.

The octahalofulvalenes absorb at much longer wavelength than other simple (nonfused ring) fulvalenes. Other than 5 and 8, the only simple fulvalenes known are 2,3,4,5-tetraphenylbicyclopentadienylidene[15,16] and 2,2',3,3',4,4'-hexaphenylbicyclopentadienylidene[16,17] and fulvalene itself;[18] all three show their lowest energy electronic transition near 24,000 cm⁻¹ (412–416 mμ). The transitions near 16,000 cm⁻¹ (6000 mμ) for 5 and 8 (Figure 2) may reflect in part contributions from nonbonded electrons on halogen, but are probably due principally to twisting of the central C–C double bond joining the rings. A two-dimensional X-ray study of 5 has indicated a dihedral angle of 41° between the two rings,[19] which are twisted out of the preferred planar configuration by steric repulsions of the chlorine atoms at the 2, 2', 5, and 5' positions.[20] Nonplanarity of the fulvalene rings has previously been associated with bathochromic shifts of electronic transitions in fused-ring fulvalenes.[21] The molecular structure of 8 is not yet known, but the steric interactions should be even greater than in 5, so the inter-ring angle will be of considerable interest.

Table II. Infrared Spectrum of Octahalofulvalenes

C₁₀Cl₈, cm⁻¹	C₁₀Br₈, cm⁻¹
1540 (m)	1505 (m–s)
1525 (s)	1490 (m–s)
1257 (s)	1211 (s)
1232 (vs)	1192 (vs)
1158 (m)	1150/1130 (m)
765 (m)	700 (w)
700 (m)	690 (m)
690 (s)	601 (s)
670 (w)	567 (w)
620 (m)	511 (w)
571 (s)	500 (w)
560 (w)	460 (m)

As crystals, both 5 and 8 appear dark blue or purple by reflected light, but reddish by transmitted light, and

(14) The synthesis of 8 was previously described in a communication: P. T. Kwitowski and R. West, *J. Am. Chem. Soc.*, **88**, 4541 (1966).
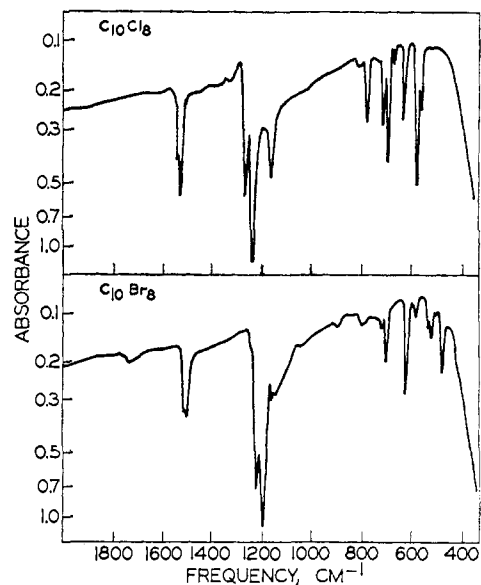
(15) E. C. Schreiber and E. I. Becker, *ibid.*, **76**, 3354, 6125 (1954).

(16) Following current practice we have named these substituted fulvalenes as derivatives of bicyclopentadienyl. The names octachlorofulvalene and octabromofulvalene have been retained for 5 and 8, which would otherwise be designated as 2,2',3,3',4,4',5,5'-octahalobicyclopentadienylidenes.

(17) P. L. Pauson and B. J. Williams, *J. Chem. Soc.*, 4153 (1961).

(18) W. B. DeMore, H. O. Pritchard, and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5874 (1959); K. V. Scherer, *ibid.*, **85**, 1550 (1963); W. von E. Doering, "Theoretical Organic Chemistry—The Kekulé Symposium," Butterworth & Co. (Publishers) Ltd., London, 1959, p 45.

(19) P. J. Wheatley, *J. Chem. Soc.*, 4936 (1961).

(20) A preliminary MO calculation on 5 supports this assignment: R. M. Smith and R. West, unpublished.

(21) E. D. Bergmann, G. Berthier, A. Pullman, and M. B. Pullman, *Bull. Soc. Chim. France*, 1079 (1950).
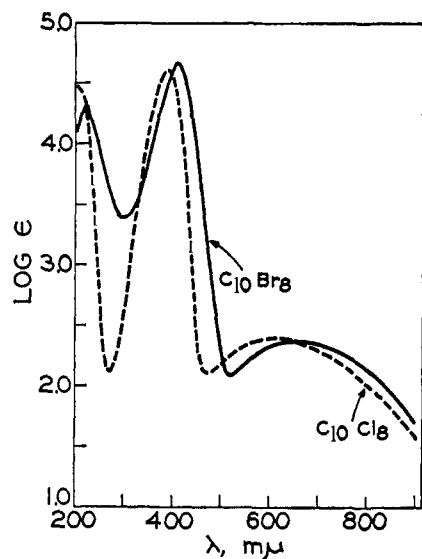
Figure 2.

Chemically, **8** is distinctly more reactive than **5**. The reactions of both compounds are under investigation, and the results will be reported in a later publication.

Experimental Section

Hexabromocyclopentadiene (2). In a 1-l. flask fitted with a dropping funnel, a stirrer, and a gas outlet to a −80° trap was placed 240 g (0.88 mol) of hexachlorocyclopentadiene (**1**). The flask was cooled in an ice bath. The system was purged with nitrogen and 450 g (1.79 mol) of boron tribromide was added slowly with stirring. Next, 0.2 g of anhydrous aluminum bromide was added to the reaction mixture. The ice bath was removed and the reaction was allowed to warm to room temperature. After 18 hr, the reaction mixture was again cooled in an ice bath and an ice-water mixture was slowly added to hydrolyze any excess boron halides present. The reaction mixture was extracted with dichloromethane, and the organic layer was separated and dried with anhydrous magnesium sulfate. The dichloromethane solution was evaporated under reduced pressure to remove solvent. The residual amber-colored oil solidified upon standing to yield bright yellow crude hexabromocyclopentadiene. The crude product was recrystallized from *n*-pentane to yield 409 g (86%) of pure hexabromocyclopentadiene, mp 82–83° (lit.[5] 86–87°).

Anal. Calcd for C_5Br_6: C, 11.1; H, 0.00; Br, 88.9. Found: C, 11.6; H, 0.16; Br, 88.7.

Hexabromocyclopentadiene shows ultraviolet absorption maxima at 3490 Å (log ε 3.09) and 2470 (3.896). The infrared spectrum is very similar to that of **1**; the same number of bands are observed above 500 cm⁻¹, usually shifted to longer wavelength in the spectrum of **2**. For **2**, observed band maxima (in cm⁻¹) are 1570 (s, C=C), 1540 (w), 1190 (s), 1150 (m), 1090 (m), 980 (w), 910 (w), 810 (w), 740/710 (s, doublet), 580 (s), and 550 (s).

Dodecabromopentacyclo[5.2.1.0²,⁶.0³,⁹.0⁵,⁸]decane (3b). Anhydrous aluminum bromide (5.35 g, 0.02 mol) was added to 10.80 g (0.02 mol) of **2**. The mixture was heated, and the aluminum bromide was pulverized with a glass rod. As **2** melted, a green paste formed, and soon a violently exothermic reaction took place. The reaction mixture was cooled, and the reddish mass was added to 100 ml of an ice-water mixture, whereupon a white precipitate formed. Dichloromethane was added, and the water layer was separated. The white precipitate remaining in the dichloromethane layer was separated, and the dichloromethane was evaporated to give a reddish residue. This was treated with ether which dissolved the red by-product leaving behind a white residue. The white solids were combined, washed several times with ether, and recrystallized from hot dibromomethane to give 7.2 g (70%) of **3b** as colorless octahedra, mp 350° dec.

Anal. Calcd for $C_{10}Br_{12}$: C, 11.1; H, 0.00; Cl, 0.00; Br, 88.9. Found: C, 11.2; H, 0.07; Cl, 0.16; Br, 88.9.

"Mixed Prins Dimers," 3c. In 100 ml of dichloromethane was dissolved 5.40 g (0.01 mol) of **2** and 2.73 g (0.01 mol) of **1**. With stirring, 2.70 g (0.02 mol) of anhydrous aluminum chloride was

added, and the resulting mixture was refluxed for 18 hr. The reaction mixture was then added to 100 ml of ice-water mixture, extracted with dichloromethane, and worked up as in the synthesis of **3b** to give a colorless solid product. Recrystallization from chloroform yielded 5.77 g (71%) of colorless octahedra, mp 320° dec.

Anal. Found: C, 16.58; H, 0.00; Cl, 42.35; Br, 40.9; total, 99.8. Corresponding atom ratio: $C_{10}Br_{3.7}Cl_{8.6}$.

Under the same conditions, but using only **1** instead of a mixture of **1** and **2**, and with aluminum tribromide as catalyst, a very similar product was obtained, colorless octahedra, mp 320° dec.

Anal. Found: C, 17.25; H, 0.06; Cl, 43.40; Br, 39.2; total, 99.9. Corresponding atom ratio: $C_{10}Br_{3.4}Cl_{8.6}$.

Reaction of equivalent amounts of **1** and **2** with $AlBr_3$ in the absence of solvent led to a similar product, but in somewhat lower yield, accompanied by a by-product showing olefinic absorption in the infrared spectrum. Essentially identical results were obtained using only **1** with aluminum bromide without solvent.

Decabromobicyclopentadienyl (6). A. By Halogen Exchange from 4. Boron tribromide (6.0 g, 0.024 mol) was mixed with 3.2 g (0.0067 mol) of **4**, and 0.2 g of anhydrous aluminum bromide was added producing a deep blue color. The mixture was stirred for 12 hr and then hydrolyzed with 100 ml of ice-water mixture to give a reddish tarry residue, which was extracted with dichloromethane. The solution was dried and evaporated, and the residue was dissolved in 10 ml of hexane and chromatographed on silicic acid. Elution with hexane gave a trace of **4** followed by fractions yielding an orange-yellow solid which was recrystallized from hexane to give 1.3 g (21%) of **6**, mp 139–140°. The infrared spectrum (mull) showed the following bands (in cm⁻¹): 1620 (m), 1575 (m), 1545 (w), 1285 (m), 1180 (s), 1148 (s), 1095 (s), 997 (m), 845 (w), 735 (vs), 700 (s, doublet), 585 (w), 560 (s), 550 (w), 425 (m), and *ca.* 300 (vs,b).

Anal. Calcd for $C_{10}Br_{10}$: C, 13.1; H, 0.00; Br, 86.9. Found: C, 13.5; H, 0.00; Br, 86.1.

B. By Reaction of 2 with Copper(I) Bromide. In a typical reaction 10.8 g (0.020 mol) of **2** was dissolved in the chosen solvent mixture, and 2.87 g (0.020 mol) of CuBr was added (some reactions were also run on 0.10-mol scale). The mixture was stirred with or without heating for the time selected (Table III) and then water was added to precipitate organic materials. The organic products were extracted with dichloromethane; the solution was dried with $MgSO_4$ and then evaporated. The residue was dissolved in hexane[22] and separated by chromatography on silicic acid or silica gel, using the solvent sequence hexane–benzene–ether or hexane–carbon tetrachloride–ether. The first fractions containing recovered **2** were followed by small amounts of **6**, identical with samples obtained by method A. Results of experiments are summarized in Table III.

Table III. Reaction of C_5Br_6 with Metals and with CuBr

Reactant	Solvent	Time, hr	Temp, °C	Recovered 2, %	Yield 6, %
Cu powd	Heptane	18	95	43	0
Zn powd	Heptane	18	95	57	0
Zn–Cu couple	Heptane	18	95	61	1.3[a]
Mg powd	Heptane	18	95	50	1.3[a]
Mg ribbon	Ether	24	35	59	0.3[a]
Cu powd	Benzene	24	80	36	2.2[a]
Cu powd	CH_3CN	2	25	36	0
Cu powd	DMF	[b]	25	[c]	[c]
CuBr	95% CH_3OH	10	30	41	10.5
CuBr	90% glyme	10	25	21	1.8
CuBr	90% glyme	2	10	47	1.6
CuBr	90% glyme	0.5	0	49	6.5
CuBr	83% diglyme	10	25	25	None
CuBr	85% C_2H_5OH	2	25	37	3.7
CuBr	CH_3CN	2	25	36	0
CuBr	Ether	24	25	93	0
CuBr	Glyme	36	25	77	0
CuBr	DMF	[b]	25	[c]	[c]

[a] Isolated as 1:1 complex, **7**. [b] Instantaneous reaction. [c] No product isolated.

(22) Undissolved suspended matter was sometimes present at this point; if so, the entire suspension was added to the chromatographic column.

Traces of blue solid, probably octabromofulvalene, were observed in some of the above reactions. When solutions of **6** in hexane were chromatographed on acid-washed alumina, a blue band was observed to form. Elution gave green solutions containing small amounts of **8**, mp 170° dec, identical with the material described below.

Reductive Coupling of Hexabromocyclopentadiene by Metals. The 1:1 Complex of 2 and 6 (7). In a typical reaction, 10.8 g (0.020 mol) of **2** was dissolved in 200 ml of solvent (benzene, ether, or petroleum ether (bp 30–60°)). An equivalent amount of metallic copper, zinc, magnesium, or zinc–copper couple was added, and the mixtures were refluxed for periods ranging from 6 to 18 hr. After this period, the organic solutions were separated from the inorganic material by filtration, evaporated to a volume of 15 to 20 ml, and chromatographed on columns packed with silicic acid or silica gel. The solvent sequence hexane–carbon tetrachloride–ether was used for all separations. The results are summarized in Table III. In several reactions, after recovered starting material was eluted, fractions were obtained which gave orange crystals of the 1:1 complex **7**. This material had mp 108–109° and was not separated into its components by fractional crystallization. The infrared spectrum showed all of the bands found for **2** and **6**.

Anal. Calcd for $C_{15}Br_{16}$: C, 12.35; Br, 87.6. Found: C, 12.50; Br, 86.5.

The same 1:1 crystalline complex, mp 110–111°, was obtained by crystallizing solutions of equivalent amounts of **2** and **6** from hexane.

Octabromofulvalene (8). In 25 ml of 1,2-dimethoxyethane was dissolved 10.8 g (0.020 mol) of **2**. Water (2 ml) was added, and the mixture was cooled to −80° with stirring, then 5.75 g (0.040 mol) of copper(I) bromide was introduced. The mixture was allowed to warm slowly. Near 0° the water melted and the mixture turned dark green. The CuBr dissolved in 3–5 min at 0°, and a purple precipitate formed. The mixture was immediately filtered, and the purple solid was purified by chromatography on silicic acid in a 1:1 hexane–chloroform solution, yield 0.50 g (6.6%) of **8** as dark blue crystals, mp 170° dec.

Anal. Calcd for $C_{10}Br_8$: C, 15.8; H, 0.00; Cl, 0.00; Br, 84.2. Found: C, 15.95; H, 0.00; Cl, 0.00; Br, 82.9.

The infrared spectrum of **8** is given in Table II and Figure 1. The electronic spectrum is shown in Figure 2; ν_{max}, cm^{-1} (log ϵ): 45,240 (4.32); 24,150 (4.67); and 15,690 (2.37).

Ethynylsilanes. IV. The Effect of Temperature on the Diels–Alder Addition of Acetylenic Dienophiles to 1-Trimethylsilylcyclopentadiene

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Abstract: Dimethyl acetylenedicarboxylate was treated with 1-trimethylsilylcyclopentadiene to yield a mixture of 7-trimethylsilyl- and 5-trimethylsilyl-2,3-bis(methylcarboxylato)bicyclo[2.2.1]heptadienes. Thermal isomerization of the 7-trimethylsilyl derivative to the 5-trimethylsilyl isomer was shown not to occur. Reactions between $(CH_3)_3SiC\equiv CR$, where R is H, $COCH_3$, or $CO_2C_2H_5$, and 1-trimethylsilylcyclopentadiene were carried out at 180–260°, and only vinyl-substituted derivatives were obtained. It is suggested that 1-trimethylsilylcyclopentadiene undergoes temperature-dependent tautomerism, which may be viewed as a 1,3-proton shift, to form 3-trimethylsilylcyclopentadiene. The reactions between the various dienophiles and this tautomeric form of the diene would be expected to yield the products observed at the high temperature.

We have shown that 2-organosilylnorbornadienes may be obtained from the cycloaddition of alkynylsilanes to cyclopentadiene.[1] In a continuance of our studies on organometallic acetylenes and bicyclo systems we wished to synthesize some 7-organosilyl- and 2,7-bis(organosilyl)bicyclo[2.2.1]heptadienes. 1-Trimethylsilylcyclopentadiene seemed to be an ideal diene for these reactions. However, when the Diels–Alder reactions between 1-trimethylsilylcyclopentadiene and several acetylenes and alkynylsilanes were carried out, the products were found to be 2-organosilylbicyclo-[2.2.1]heptadienes and mixtures of 2,5- and 2,6-bis-(organosilyl)bicyclo[2.2.1]heptadienes. The results of these reactions and a possible mechanism whereby these unexpected products arise are discussed in this paper.

Experimental Section

General. The preparations of the alkynylsilanes employed in the following experiments have been reported elsewhere.[1] The

(1) C. S. Kraihanzel and M. L. Losee, *J. Org. Chem.*, **33**, 1983 (1968).

high-temperature Diels–Alder reactions were carried out in a 150-ml stainless steel bomb purchased from the Matheson Company, East Rutherford, N. J.

Infrared spectra were recorded as 5–10% solutions in carbon tetrachloride on a Perkin-Elmer Model 21 spectrophotometer. Proton magnetic resonance spectra (nmr) were recorded on 30% solutions in carbon tetrachloride on a Varian A-60 spectrophotometer. Tetramethylsilane was used as an internal standard.

An Aerograph Model 221 gas chromatograph was employed for both analytical and preparative purposes (glpc). A stainless steel column (5 ft; 1/4 in. in diameter) packed with 20% SF-96 silicone oil on Chromosorb P was employed. Separations were effected on an aluminum column (5 ft; 3/8 in. in diameter) filled with the same material. The carrier gas was helium. Approximate instrument temperatures for analyses and separation were as follows: column, 225°; injector, 280°; detector, 300°. The maximum sample size used in the preparative work was 0.5 ml. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

1-Trimethylsilylcyclopentadiene. Freshly distilled cyclopentadiene (33 g; 0.50 mol) was added dropwise during 0.5 hr to a stirred mixture of 12 g (0.50 mol) of sodium sand in 150 ml of THF. The reaction mixture was allowed to stir for 3 hr at room temperature. After this time, 54 g (0.50 mol) of trimethylchlorosilane was added dropwise over 1 hr and stirring was continued for 3 hr. The reaction mixture was poured into 150 ml of cold, distilled water and the