(22) R. Baker and L. K. Dyall, *J. Chem. Soc. B*, 1971 (1952).
(23) P. v. R. Schleyer, D. S. Trifan, and R. Bacskai, *J. Amer. Chem. Soc.*, **80**, 6691 (1968).
(24) H. C. Brown, W. J. Hammar, J. H. Kawakami, I. Rothberg, and D. L. Vander Jagt, *J. Amer. Chem. Soc.*, **89**, 6381 (1967).
(25) S. J. Cristol, W. K. Seifert, and S. B. Soloway, *J. Amer. Chem. Soc.*, **82**, 2351 (1960).
(26) H. C. Brown, I. Rothberg, and D. L. Vander Jagt, *J. Org. Chem.*, **37**, 4098 (1972).
(27) K. Alder and G. Stein, *Justus Liebigs Ann. Chem.*, **485**, 223 (1931).
(28) (a) H. C. Brown, J. H. Kawakami, and K. T. Liu, *J. Amer. Chem. Soc.*, **95**, 2209 (1973); (b) M. A. Muhs and F. T. Weiss, *ibid.*, **84**, 4697 (1962).
(29) (a) J. Meinwald, J. Crandall, and W. E. Hymans, *Org. Syn.*, **45**, 77 (1965); (b) R. G. Curtis, I. Heilbron, E. R. H. Jones, and G. F. Woods, *J. Chem. Soc.*, 457 (1953).
(30) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).
(31) C. H. Depuy and B. W. Ponder, *J. Amer. Chem. Soc.*, **81**, 4629 (1959).

Chlorocarbonium Ions. I. Synthesis of Decachlorobicyclo[3.3.0]octa-2,6-diene and Its Chemistry

Kousuke Kusuda, Masaki Endo, Robert West,* and V. N. Mallikarjuna Rao

The Research Institute of Atomic Energy, Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka, Japan, and the Department of Chemistry, University of Wisconsin, Madison 53706

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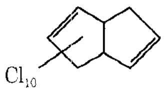
The reaction of hexachlorocyclopentadiene with 1,1,2,3,3-pentachloropropene in the presence of anhydrous aluminum chloride furnished decachlorobicyclo[3.3.0]octa-2,6-diene (**1**) in 75% yield. Evidence for the structure of **1** was obtained from its ^{13}C nmr spectrum, nuclear quadrupole resonance spectrum, elemental analysis, and hydrogenolysis. Hydrolysis of **1** with sulfuric acid afforded diketones **2** and **3** and the hydroxy diketone **4**. A part of **1** rearranged to **6** at 250–270°. The reaction of **1** with 2 equiv of potassium hydroxide in methanol afforded the monomethoxy derivative **7** in good yield, whereas a large excess of potassium hydroxide in methanol furnished small yields of **10** and **11**. Upon treatment with anhydrous aluminum chloride **7** furnished **8** and/or **9** while **10** gave **9**. Similarly, **11** furnished **12**. Treatment of **9** with sulfuric acid produced **12**.

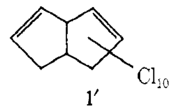
The well-known Prins reaction involves alkylation of a polyhalo olefin with a chlorocarbonium ion, derived from a halocarbon and a Lewis acid such as aluminum chloride.[1] We have extended this reaction to the synthesis of new conjugated cyclic chlorocarbons, a subject in which we have been actively interested,[2] by investigating the reaction between polyhalogenated carbocations and polyhalogenated cyclopentadienes.

Although pentachloropropenium cation[3] failed to react with hexachlorocyclopentadiene at 75–80°, 1,1,2,3-tetrachloropropenium cation[4] prepared from 1,1,2,3,3-pentachloropropene[5] and anhydrous aluminum chloride in the absence of any added solvent reacted with hexachlorocyclopentadiene at 75–80° to yield decachlorobicyclo[3.3.0]octa-2,6-diene (**1**), mp 146–147°, in 75% yield with small amounts of Prins dimer.[6] No other products could be isolated in this reaction except unreacted starting materials.

The infrared spectrum of **1** showed a single olefinic absorption at 1612 cm^{-1} and a strong absorption at 1185 cm^{-1} suggestive of a polychlorinated ring breathing mode.[7] The ultraviolet spectrum in *n*-hexane showed only end absorption with a shoulder at 230 nm, while high-pressure hydrogenation afforded *cis*-bicyclo[3.3.0]octane.[8] These observations suggested two structures, **1** or **1′**, each having two nonconjugated double bonds with cis-fused rings for this chlorocarbon.[12]



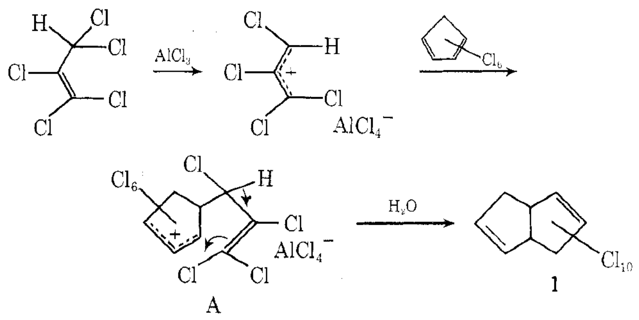
1



1′

An unambiguous choice between the two isomers was made from the ^{13}C nmr spectrum in deuteriochloroform, which showed only four different resonances in approximately equal intensities at 136.7, 132.8, 92.7, and 88.5 ppm downfield from external tetramethylsilane.[13] In addition the nqr spectrum at room temperature showed only five absorptions of equal intensities at 37.34, 38.06, 38.57, 38.94, and 39.13 MHz, indicating the presence of five different symmetry-equivalent pairs of chlorine. Structure **1** is fully consistent with these observations.[14a]

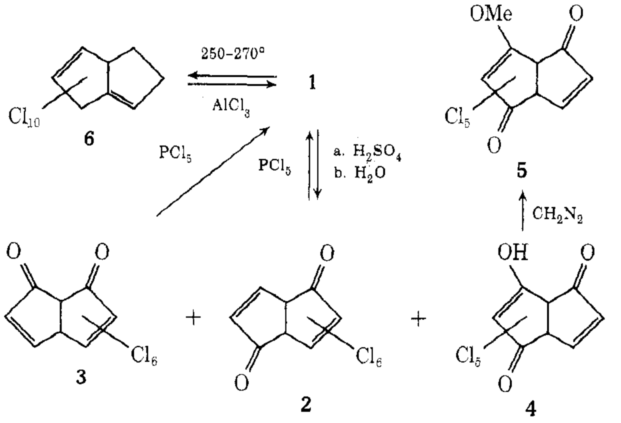
A likely mechanism for the formation of **1** involves the initial abstraction of an allylic chlorine from the propene to yield the 1,1,2,3-tetrachloropropenium cation, which is attacked by hexachlorocyclopentadiene to furnish the intermediate A. Ring closure followed by loss of a proton would furnish **1**.[14b]



When **1** was heated with concentrated sulfuric acid and then treated with water, a 60:40 mixture of two colorless dicarbonyl compounds was obtained. They were separated by repeated fractional crystallization or by glpc. On treatment with excess PCl_5 at 185–190°, both these compounds furnished **1**. Their infrared spectra as mulls in Nujol were also very similar. These observations suggested that the two dicarbonyl compounds had the basic bicyclo[3.3.0] ring skeleton[16] and differed only with respect to the position of the carbonyl groups.

Structure **2** was assigned to the 40% component on the basis of its ^{13}C nmr spectrum, which showed only four resonances at 181.5, 156.7, 131.5, and 72.4 ppm. The resonance at 181.5 ppm is easily assigned to the carbonyl carbon by analogy with cycloalkanones.[17,18] In a similar fashion the absorption at 156.7 ppm is assigned to the olefinic carbon β to the carbonyl group and that at 131.5 ppm to the α carbon.[19] The remaining absorption at 72.4 ppm is assigned to the bridgehead carbon. The 60% com-

Scheme I



ponent (Scheme I) showed five absorptions at 179.8, 158.2, 132.5, 75.4, and 70.1 ppm. Structure **3** is assigned to this diketone. While the carbonyl and olefinic carbon resonances can be assigned similar to **2**, the bridgehead carbon assignments are not certain. However, by analogy with other model chlorocarbon ketones,[13] the absorption at 70.1 ppm may be assigned to the bridgehead carbon which is α to both carbonyl groups and that at 75.1 ppm to the remaining bridgehead carbon. Compound **3** should be more polar than **2**, and dipole moment measurements[15] (μ = 1.12 D for **2** and 3.42 D for **3**) are consistent with the assigned structures.

The ultraviolet spectra of **2** and **3** are shown in Figure 1. It is interesting that, whereas **2** shows distinct fine structure in the long-wavelength region, **3**, which has the larger dipole moment and two parallel enone dipoles, shows very little. Such fine structure, although not a general rule, has been observed for other polychlorinated cyclopentenones.[20] The infrared spectrum of **2** in carbon tetrachloride shows a single strong carbonyl band at 1775 cm^{-1} while **3** shows a rather complicated carbonyl absorption at 1774 and 1745 cm^{-1}.

After removal of the diketones, the aqueous acidic solution was extracted with ether to afford small amounts of hydroxy diketone **4**, which was methylated with diazomethane to afford the monomethoxy diketone **5**. Spectroscopic evidence and elemental analyses support the assigned structures **4** and **5**. Attempts to obtain a dihydroxy diketone from **1** under drastic hydrolysis conditions were unsuccessful.

Compound **1** is quite stable at ordinary temperatures and was unchanged after heating at 200° for 1 hr. However, when **1** was heated to 250-270° for 9-10 hr in a sealed tube it partly isomerized to **6**, which was separated by glpc. The latter chlorocarbon reverts to **1** almost quantitatively upon treatment with anhydrous aluminum chloride in dichloromethane. The infrared spectrum of **6** showed two olefinic absorptions at 1670 and 1580 cm^{-1}. The 1670-cm^{-1} absorption is attributed to the exocyclic double bond in **6**, shifted to higher frequency by ring strain.[21-23] The effect of such a strain reduces the frequency in endocyclic >C=C< bonds.[21] The ultraviolet spectrum did not reveal any conjugation [λ_{max} 226 nm (log ϵ 4.27)] and the ^{13}C nmr spectrum, which showed eight different absorptions (Table I), is consistent with the assigned structure.[14a,24,25] Reaction of **1** with 2 equiv of antimony pentachloride followed by quenching of the reaction mixture with water afforded **1**, **2**, **3**, and **4**. The formation of these products is consistent with the formation of dication B in solution.[26] Attempts to isolate the dication were unsuccessful.[27]

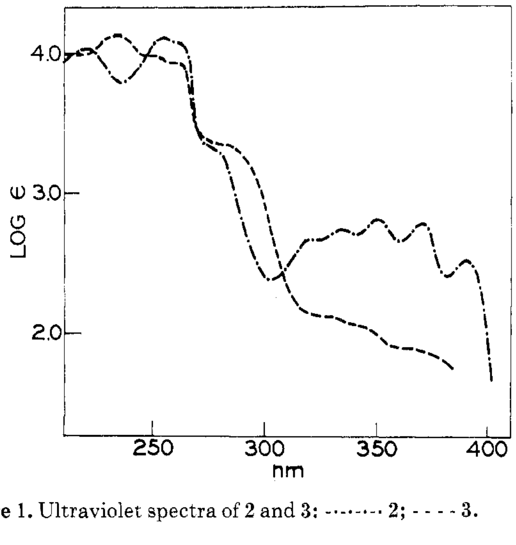
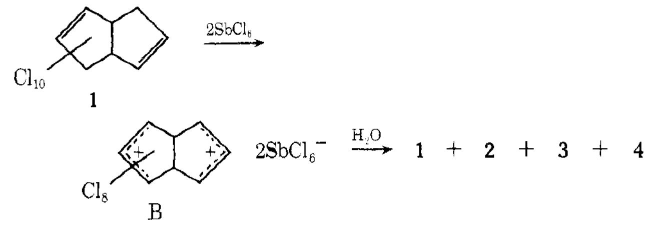
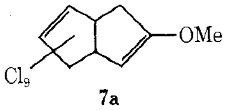


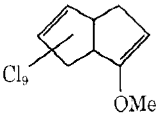
Figure 1. Ultraviolet spectra of 2 and 3: ·········· 2; - - - - 3.



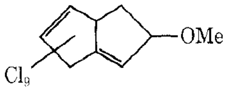
When **1** was allowed to react with 2 equiv of potassium hydroxide in methanol, a 72% yield of a colorless, crystalline compound was obtained, for which structures **7**[14a] and **7a-d** will be considered. The infrared spectrum of this material exhibited carbon-carbon double-bond stretching absorptions at 1675 and 1590 cm^{-1}. The low-frequency olefinic band might be due to methoxy substitution on the double bond[28] as in **7a** or **7b**, which could arise by an addition-elimination mechanism.[29] However, we believe that the more likely explanation is ring strain due to the exocyclic double bond in structure **7**. Similar low-frequency shifts of olefinic frequencies are found for **6**, **8**, and **10**, all of which have a structure analogous to **7** (Table II). Structures **7c** and **7d** would not be expected to show shifted olefinic infrared frequencies and so can be eliminated.[30]



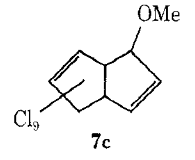
7a



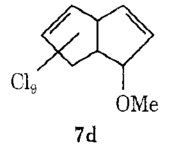
7b



7



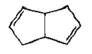
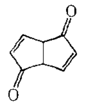
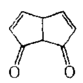
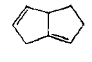
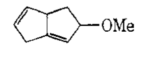
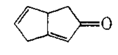
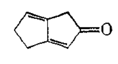
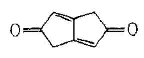
7c



7d

Additional support for structure **7** comes from the ^{13}C nmr spectrum. The proton-decoupled spectrum showed nine different resonances at 137.6, 136.6, 135.1, 133.9, 118.5, 93.4, 80.6, 78.3, and 44.1 ppm. The undecoupled spectrum, however, showed a quartet, J = 146.8 Hz, for the methyl carbon resonance of 44.1 ppm and a second small quartet, J = 4.5 Hz, for the resonance at 118.5 ppm due to secondary splitting[13,31] through the C-O-C link.[32] These two resonances showed a substantial Overhauser enhancement on proton decoupling, while the remaining seven resonances were of comparable intensity.[25] The narrow range of the four olefinic resonances (137.6-133.9 ppm) further suggests that the -OMe group is not attached to a vinylic carbon since such substitution is

Table I
^{13}C Data of Selected Compounds[a,b]

Compd	No.	>C=O	>C=C<	Saturated C
	**1**		136.7 132.8	92.7 88.5
	**2**	181.5	156.7 131.5	72.4
	**3**	179.8	158.2 132.5	75.4 70.1
	**6**		138.0 136.8 136.4 134.5	97.9 96.0 81.2 78.9
	**7**		137.6 136.6 135.1 133.9	118.5 93.4 80.6 78.3 44.1
	**8**	183.2	159.3 138.3 132.5 129.8	84.0 78.1 78.0
	**9**	185.4	158.6 134.8 134.3 124.3	98.8 85.3 68.8
	**12**	183.3	162.0 127.0	68.0

[a] All positions substituted by chlorine unless indicated. [b] Spectra were run in $CDCl_3$ and the data reported in parts per million downfield from external TMS converted from $CDCl_3$ internal standard using δ ($CDCl_3$) 76.9 (ref 31, p 23); accuracy ±0.1 ppm.

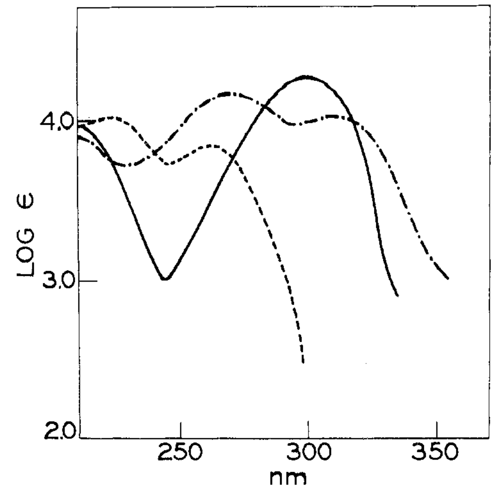


Figure 2. Ultraviolet spectra of 8, 9, and 12: - - - - - 8; -·-·-·-· 9; ———— 12.

known[33] to impart a substantial paramagnetic (downfield) shift to the carbon to which it is attached. This shift is evident on the saturated carbon resonance of 118.5 ppm to which the -OMe group is attached. The other three saturated carbon resonances are significantly higher and have not been assigned.

The monomethoxy derivative **7** upon treatment with 0.5 equiv of anhydrous aluminum chloride in dichloromethane, followed by hydrolysis, afforded a white monoketone **8**.[14a] Further treatment of **8** with excess anhydrous aluminum chloride in dichloromethane, or treatment of **7** with 1 equiv of anhydrous aluminum chloride, afforded yet another monoketone **9**. Treatment of **8** with PCl_5 gave **6** along with **1**. The ^{13}C spectra of **8** and **9** have been reported in Table I. The carbonyl carbon resonances for both **8** and **9** are easily assigned, being farthest downfield. For **8** the resonance at 159.3 ppm is assigned to C-1 and that at 129.8 ppm to C-2.[19] The pair of olefinic carbon resonances at 138.3 and 132.5 ppm are jointly assigned to C-6 and C-7 for lack of suitable chlorocarbon models. Similarly, the pair of resonances at 78.1 and 78.0 ppm are jointly assigned to C-4 and C-5 and that at 84.0 ppm to C-8. In **9** a similar trend is observed with the added effect of conjugation. The resonances at 158.6 ppm is assigned to C-6 and that at 124.3 ppm tentatively to C-2. The presence of a carbonyl group causes an upfield shift[13] on C-4, which absorbs at 68.8 ppm. The remaining two saturated carbon resonances have not been assigned.

The ultraviolet spectra of **8** and **9** are reproduced in Figure 2. The spectra indicate that **9** has a more extended conjugated system than **8**. In addition, whereas the olefinic absorptions in the infrared occur at 1655 and 1580 cm^{-1} for **8** suggesting an endocyclic and an exocyclic double bond,[21] those for **9** occur at 1655 and 1620 cm^{-1}. Additional evidence for the structure of **9** comes from its facile conversion to **12** upon treatment with concentrated sulfuric acid. The structure of **12** itself follows from spectro-

Scheme II

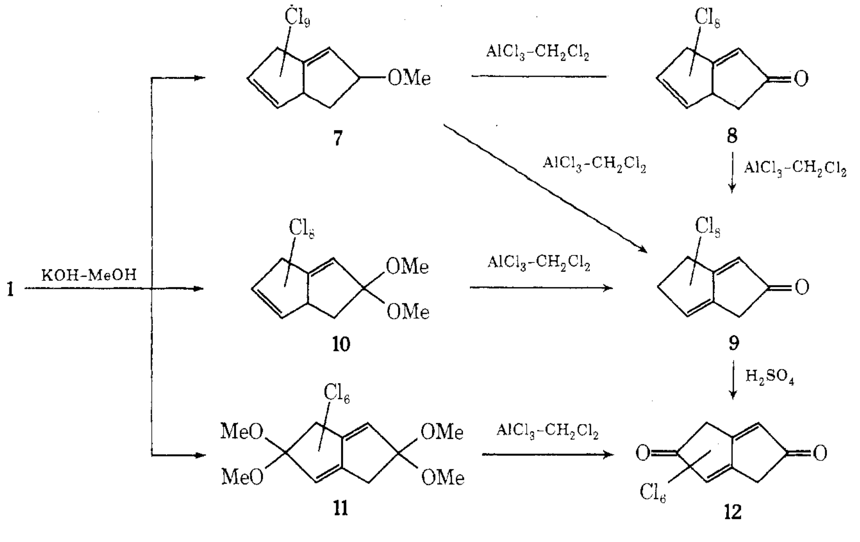


Table II
Infrared Absorptions Due to >C=C< Stretching Mode in Polychlorinated [3.3.0] Ring Systems[a]

Compd	Exocyclic type, cm^{-1}	Endocyclic type, cm^{-1}
1		1612
2		1580
		1588 (soln)
3		1585, 1575
		1592, 1582 (soln)
5		1600, 1580
6	1670	1580
7	1675	1590
8	1655	1580
9	1655, 1620	
10	1675	1585
11	1655	
12	1630	

[a] All spectra were taken as mulls in Nujol between KBr disks except as noted. Solution spectra were taken in CCl_4 using matched 0.5-mm KBr cells. Accuracy ±6.0 cm^{-1}.

scopic data, especially the ^{13}C nmr spectrum, which like **2** shows only four different absorptions.

When **1** was allowed to react with a large excess of potassium hydroxide in methanol, a dimethoxy derivative **10** and a tetramethoxy derivative **11** were isolated in small yields from the reaction mixture by column chromatography (Scheme II). The infrared and ultraviolet spectra of **10** show the presence of isolated double bonds, whereas **11** shows conjugation and only one type of olefinic absorption in the infrared, suggesting that both double bonds are exocyclic (Table II). Treatment of **10** with anhydrous aluminum chloride gave **9**. Additional confirmation for the structures of **10** and **11** is given by their proton nmr spectra. For **10** two different resonances of equal intensity are found at δ 3.55 and 3.67, whereas for **11**, which has C_{2h} symmetry, only a single resonance is observed.

Experimental Section

General. Melting points are uncorrected. Elemental analyses were performed by Chemalytics Inc., Tempe, Ariz., or Mr. J. Goda of Osaka City University, Japan. Chlorine analyses, when required, were carried out according to the combustion method using a modified flask.[34] Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer as mulls in Nujol between KBr disks or as solutions in carbon tetrachloride. Only significant absorptions are reported. Ultraviolet spectra were recorded on a Hitachi EPS-20 spectrophotometer as solutions in *n*-hexane. Nuclear quadrupole resonance spectra were recorded on a Wilks NQR-1A spectrometer at room temperature. Proton nmr spectra were recorded as 10% solutions in carbon tetrachloride on a Varian A-60 spectrometer using tetramethylsilane as an internal standard. ^{13}C nmr spectra were recorded as solutions in $CDCl_3$ on a Varian XL-100-15 spectrometer provided with a Fourier transform accessory. Gas chromatographic analyses were performed on a Varian A90-P gas chromatograph at 210° using a 7 ft 10% SE-30 column with a helium flow of 200 ml/min or a 15 ft 10% SE-30 column at 130° with a helium flow of 80 ml/min. Benzene and dichloromethane were dried prior to use and stored over molecular sieves. Other commercial chemicals were used without further purification.

Decachlorobicyclo[3.3.0]octa-2,6-diene (1). In a dry 1-l. three-necked flask provided with a mechanical stirrer, addition funnel, condenser, and nitrogen inlet was placed 15.0 g (0.11 mol) of anhydrous aluminum chloride and 207 g (0.76 mol) of hexachlorocyclopentadiene. The slurry was stirred while the temperature was gradually raised to 70°. To the stirred slurry was added 204 g (1.1 mol) of 1,1,2,3,3-pentachloropropene.[5] slowly over a period of 2.5 hr. The temperature of the reaction mixture was maintained between 70 and 75° during addition.[35] After completion of addition of the propene, a further 10 g of anhydrous aluminum chloride was added to the reaction mixture. The temperature of the reaction mixture was raised to 75–78° and maintained at this temperature for 5 hr. The dark green reaction mixture was cooled to room temperature and cautiously poured into 1 l. of cracked ice. The precipitated brownish solid was filtered, washed with two 150-ml portions of cold methanol, and dried, yield 257 g (75%). An analytical sample was prepared by recrystallization from ethyl acetate as colorless rhombs: mp 146–147°; ir (mull) >C=C<, 1612 cm^{-1}; uv 230 nm (sh).

Anal. Calcd for C_8Cl_{10}: C, 21.32; Cl, 78.68. Found: C, 21.33; Cl, 78.76.

Total Hydrogenolysis of 1. A mixture of 4.0 g of **1**, 4.0 g of 10% Pd/C, 2.0 g of anhydrous sodium acetate, and 100 ml of absolute ethanol was placed in a steel bomb and hydrogenated using high-pressure equipment for 4 days with constant agitation at 1200 psi. At the end of this period the bomb was opened and the slurry was filtered. The ethanolic solution was diluted with 200 ml of water and extracted with four 100-ml portions of *n*-pentane. The pentane extracts were combined, washed with two 50-ml portions of water and saturated sodium chloride solution, and dried ($MgSO_4$). Removal of solvent by distillation afforded 0.7 g of a pale yellow liquid residue. Analysis of this liquid on a 15 ft SE-30 column indicated the presence of only one major component, which was identified as *cis*-bicyclo[3.3.0]octane by comparison of its spectral properties with those of an authentic sample.[8]

Reaction of 1 with Sulfuric Acid to Give 2 and 3. In a dry 100-ml flask provided with a magnetic stirrer and nitrogen inlet was placed 10.0 g (22.2 mmol) of **1** and 50 ml of concentrated sulfuric acid. The mixture was stirred while the temperature was gradually increased to 100–110° at which it was maintained for 1 hr. The sulfuric acid solution was cooled to room temperature and poured onto 1 l. of cracked ice to precipitate 6.0 g (80%) of an off-white solid which was found to be a mixture of 40% **2** and 60% **3** by gas chromatography. Recrystallization of this mixture from ethyl acetate furnished as the first fraction a mixture of 95% **3** and 5% **2**. A second recrystallization of this fraction afforded pure **3**: mp 120–122°; ir (mull) 1765 (s), 1725 (s), 1585 (s) and 1575 cm^{-1} (s); ir (CCl_4) 1774 (s), 1745 (m), 1592 (s), and 1582 cm^{-1}; uv λ_{max} (log ϵ) 229 (4.114), 235 (4.133), 252 (3.999), 262 (3.951), 330 sh (2.130), and 345 nm sh (2.05).[36]

Anal. Calcd for $C_8Cl_6O_2$: C, 28.20; Cl, 62.42. Found: C, 28.20; Cl, 62.70.

The mother liquor after removal of the first fraction was evaporated to dryness and recrystallized from *n*-hexane to furnish a fraction enriched in **2**. Two further recrystallizations of this fraction from *n*-hexane afforded pure **2**: mp 146–147°; ir (mull) 1755 (s), 1740 (s), and 1580 cm^{-1} (s); ir (CCl_4) 1775 (s) and 1588 cm^{-1} (s); uv λ_{max} (log ϵ) 219 (4.043), 254 (4.101), 260 (4.075), 280 sh (3.313), 310 sh (2.542), 321 (2.669), 334 (2.774), 351 (2.827), 371 (2.810), and 389 nm (2.587).

Anal. Calcd for $C_8Cl_6O_2$: C, 28.20; Cl, 62.42. Found: C, 28.10; Cl, 62.33.

The fractions after removal of most of pure **2** and **3** were combined, evaporated to dryness, dissolved in a small volume of carbon tetrachloride, and placed on top of a column (10 × 50 mm) packed with silica gel in carbon tetrachloride and eluted with carbon tetrachloride. The earlier fraction consisted of pure **2** followed by mixtures and then **3**. Some decomposition was also noticed on the column.

Reaction of 1 with Sulfuric Acid to Give 2, 3, and 4. In a 100-ml flask provided with a magnetic stirrer and nitrogen inlet was placed 5.0 g of well-powdered **1** and 25 ml of a 50:50 mixture of fuming sulfuric acid and concentrated sulfuric acid. The slurry was stirred and heated at 130–140° for 6 hr, cooled to room temperature, and filtered through a sintered glass funnel to remove 0.47 g (7.9%) of a solid identified as Prins dimer.[37] The sulfuric acid solution was cautiously poured onto 250 g of cracked ice. The precipitated tan-colored solid was filtered and recrystallized from methanol to give 1.0 g of **2** as the first crop of crystals. The mother liquor deposited 1.4 g of crystals on cooling to 5°, which was an equimolar mixture of **2** and **3** as shown by glpc.

The aqueous sulfuric acid solution after removal of the diketones was extracted with four 20-ml portions of ether and the organic extracts were combined, washed with water followed by saturated sodium chloride solution, and dried ($MgSO_4$). Removal of ether under reduced pressure afforded 0.39 g of **4** as a light yellow, syrupy liquid which dissolved in a solution of sodium bicarbonate with the evolution of carbon dioxide. Both ferric chloride and 2,4-dinitrophenylhydrazine tests on this oil were positive.[38]

Conversion of 4 to 5. A solution of 380 mg of **4** in 10 ml of dry ether was treated with an excess of diazomethane at 10° and kept at this temperature for 1 hr. After the excess diazomethane was decomposed with acetic acid, the ether solution was washed with water, sodium bicarbonate, and saturated sodium chloride solutions and dried ($MgSO_4$). Removal of ether under reduced pressure afforded an oily residue which was dissolved in carbon tetrachloride. Purification by column chromatography on silica gel using carbon tetrachloride as eluent afforded 300 mg of colorless crystals of **5**: mp 142–144°; ir (mull) 1750 (s), 1720 (s), 1600 (s), and 1580 cm^{-1} (s); uv λ_{max} (log ϵ) 220 sh (4.056), 248 (4.258), and 263 nm sh (4.064); nmr (CCl_4) δ 4.54 (s).

Anal. Calcd for $C_9H_3Cl_5O_3$: C, 32.12; H, 0.90. Found: C, 32.12; H, 0.91.

Reaction of 1 with Fuming Nitric Acid. In a 100-ml round-bottom flask provided with a magnetic stirrer were placed 5.0 g (11.0 mmol) of **1** and 50 ml of 90% nitric acid. The temperature of the stirred slurry was gradually raised to 60°, at which point slow gas evolution was observed. The temperature was raised to 85–90° and maintained at this temperature for 3 hr. A clear yellow-orange solution was obtained. The nitric acid solution was cooled to room temperature and poured onto 250 g of cracked ice. A white, oily solid precipitated. The aqueous slurry was extracted with five 50-ml portions of chloroform. The chloroform solution was washed with two 50-ml portions of water and dried ($CaCl_2$). Removal of chloroform under reduced pressure afforded 3.3 g of a yellow, viscous oil which was triturated with 10 ml of cold *n*-pentane to furnish 2.8 g (74%) of a white solid. This was found to be a 45:55 mixture of **2** and **3** by glpc analysis.

Chlorination of 2 and 3 to Give 1. In a small glass tube of 0.5-g sample of **2** was sealed with 0.6 g of PCl_5 and the tube was heated at 185–190° for 8 hr. The tube was cooled and opened and the contents were treated with water. The oily organic product was extracted with two 5-ml portions of chloroform and the organic extract was dried ($MgSO_4$). Removal of chloroform under reduced pressure afforded 0.6 g of an oily solid which solidified on standing at room temperature. It was identified as **1** by comparison of its ir spectrum with that of an authentic sample. No other product could be detected.

Thermal Isomerization of 1 to 6. In a small glass tube 0.5 g of **1** was sealed and heated to 270° for 10 hr. The tube was cooled and opened, and the contents were dissolved in 5 ml of chloroform. Glpc analysis indicated that the product was a mixture of two components in the ratio 90:10. The 90% component was identified as **1** by comparison of its spectral properties with those of an authentic sample. The 10% component was separated by glpc and recrystallized from acetone, mp 82–84°, and identified as **6**: ir (mull) >C=C<, 1670 and 1580 cm^{-1}; uv λ_{max} (log ϵ) 226 nm (4.27).

Anal. Calcd for C_8Cl_{10}: C, 21.32; Cl, 78.68. Found: C, 21.44; Cl, 78.78.

Isomerization of 6 to 1. A 100-mg sample of **6** was dissolved in 5 ml of dry dichloromethane. An equal weight of anhydrous aluminum chloride was added and the slurry was gently refluxed with stirring for 3 hr under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and the greenish complex was decomposed with ice water. The organic layer was separated and dried (Na_2SO_4). Removal of solvent afforded 89 mg of a buff-colored solid which was recrystallized from acetone, mp 145–147°. It was shown to be **1** by comparison of spectral properties with those of an authentic sample.

Nonachloro-3-methoxybicyclo[3.3.0]octa-1,6-diene (7). A solution of 5.0 g (11.1 mmol) of **1** in 35 ml of benzene was added to a stirred solution of 1.5 g (27.0 mmol) of potassium hydroxide in 40 ml of absolute methanol at room temperature. The mixture was refluxed for 6 hr and filtered to remove sodium chloride. The methanol–benzene filtrate was diluted with 150 ml of water to separate the benzene layer, which was removed. The aqueous methanol layer was extracted with two 50-ml portions of benzene. The benzene extracts were combined, washed successively with two 50-ml portions of water and saturated sodium chloride solution, and dried ($CaCl_2$). Removal of the solvent under reduced pressure afforded 4.5 g of crude **7**. Recrystallization from methanol afforded 3.5 g (72%) of pure **7**: mp 91–92°; ir (mull) 1675 (m), 1590 (m), 1228 (m), 1195 (s), 1145 (m), 890 (m), 800 (m), and 735 cm^{-1} (m); uv λ_{max} (log ϵ) 224 nm (4.286); nmr (CCl_4) δ 3.82 (s).

Anal. Calcd for $C_9H_3Cl_9O$: C, 24.23; H, 0.68; Cl, 71.51. Found: C, 24.53; H, 0.78; Cl, 71.68.

Synthesis of 10 and 11 from 1. A mixture of 20.0 g of **1**, 20 ml of benzene, and 14.8 g of potassium hydroxide in 170 ml of anhydrous methanol was refluxed with stirring for 36 hr. The mixture was cooled, diluted with 200 ml of water, and filtered. The filtrate was extracted with three 50-ml portions of benzene. The benzene extracts were combined, washed successively with water and saturated NaCl solution, and dried ($CaCl_2$). The solvent was removed under reduced pressure to afford 4.5 g of a reddish oil. The oil was taken up in 20 ml of *n*-hexane, placed on top of a column (30 × 50 mm) of Florisil, and eluted with *n*-hexane. The first cut yielded, after removal of solvent, 0.9 g of **10** which was recrystallized from methanol: mp 133–135°; ir (mull) 1675 (m), 1585 (m), 1232 (m), 1222 (w), 1183 (s), 1153 (s), 1108 (m), and 1085 cm^{-1} (s); uv λ_{max} (log ϵ) 223 nm (4.331); nmr (CCl_4) δ 3.67 (s, 1) and 3.55 (s, 1).

Anal. Calcd for $C_{10}H_6Cl_8O_2$: C, 27.19; H, 1.37; Cl, 64.20. Found: C, 27.21; H, 1.48; Cl, 63.87.

Further cuts were evaporated to dryness and examined by infrared spectroscopy. While cuts 2 and 3 were mixtures, cuts 4 and 5 were different from **10**. These cuts were combined and recrystallized from aqueous methanol to afford 140 mg of **11**: mp 148–150°; ir (mull) 1655 (m), 1237 (m), 1189 (m), 1150 (m), 1080 (s), and 808 cm^{-1} (s); uv λ_{max} (log ϵ) 263 nm (4.319); nmr (CCl_4) δ 3.53 (s).

Anal. Calcd for $C_{12}H_{12}Cl_6O_4$: C, 33.23; H, 2.79; Cl, 49.13. Found: C, 33.05; H, 2.84; Cl, 48.97.

Octachlorobicyclo[3.3.0]octa-1,6-dien-3-one (8). To a solution of 6.2 g (13.8 mmol) of **7** in 20 ml of dry dichloromethane was added 1.0 g (7.5 mmol) of anhydrous aluminum chloride. The mixture was stirred and gently refluxed under a nitrogen atmosphere for 2 hr. The purple-brown slurry was cooled to room temperature and poured into ice water. The dichloromethane layer was separated and the aqueous layer was extracted with two 50-ml portions of chloroform. The organic extracts were combined, washed with water, and dried ($MgSO_4$). The solvent was removed under reduced pressure to afford 3.64 g (92%) of **8** as a buff-colored solid. Recrystallization from aqueous ethanol furnished an analytical sample as colorless crystals: mp 97–99°; ir (mull) 1770 (s), 1655 (m), 1580 (m), 1310 (m), 1230 (m), 1135 (m), and 805 cm^{-1} (s); uv λ_{max} (log ϵ) 223 (4.065) and 262.5 nm (3.889).

Octachlorobicyclo[3.3.0]octa-1,5-dien-3-one (9). To a solution of 2.23 g (5.0 mmol) of **7** in 15 ml of dry dichloromethane was added 0.67 g (5.0 mmol) of anhydrous aluminum chloride. The slurry was stirred and gently refluxed for 5 hr. The dark green reaction mixture was cooled to room temperature and poured into 20 ml of ice water. The organic layer was separated and the aqueous layer was extracted with two 50-ml portions of chloroform. The organic extracts were combined, washed with water, and dried ($MgSO_4$). Removal of the solvent afforded 1.8 g (95%) of **9** as a light brown oil that solidified on standing. An analytical sample was prepared by recrystallization from aqueous ethanol: mp 59–60°; ir (mull) 1770 (s), 1655 (m), and 1620 cm^{-1} (m); uv λ_{max} (log ϵ) 271 (4.208) and 312 nm (4.064).

Anal. Calcd for C_8Cl_8O: C, 24.28; Cl, 71.68. Found: C, 24.26; Cl, 72.00.

Under similar conditions **10** furnished **9** in 80% yield.

Isomerization of 8 by Anhydrous Aluminum Chloride to 9. To a solution of 94.7 mg of **8** in 5 ml of dry dichloromethane was added 400 mg of anhydrous aluminum chloride and the slurry was heated at gentle reflux for 6 hr. The brownish reaction mixture was quenched with water. Work-up as usual afforded 83.0 mg of **9**, mp 59–60°.

Chlorination of 8 with Phosphorus Pentachloride. A mixture of 0.4 g of **8** and 1.4 g of phosphorus pentachloride was sealed in a glass tube and heated at 160° for 9 hr. The tube was cooled, opened, and treated with water to decompose the phosphorus halides. The organic products were taken up in 10 ml of carbon tetrachloride. The extract was dried (Na_2SO_4) and concentrated to one-third of its original volume. Glpc analysis indicated the presence of **1** and **6** in the ratio 1:2.5.

Hexachlorobicyclo[3.3.0]octa-1,5-diene-3,7-dione (12). To a 1.0-g sample of **9** was added 10 ml of concentrated sulfuric acid and the slurry was stirred at 70–80° for 2 hr under a nitrogen atmosphere. The clear red-brown solution was cooled to room temperature and poured onto 200 g of cracked ice. The precipitated solid (0.85 g, 99%) was removed, dried, and recrystallized from *n*-hexane to afford colorless crystals of **12**: mp 182–184°; ir (mull) 1764 (s) and 1630 cm^{-1} (m); uv λ_{max} (log ϵ) 300 nm (4.282).

Anal. Calcd for $C_8Cl_6O_2$: C, 28.20; Cl, 62.42. Found: C, 27.73; Cl, 62.70.

In an alternate synthesis of **12** a 16-mg sample of **11** in 3 ml of dry dichloromethane was treated with a catalytic amount of anhydrous aluminum chloride. The mixture was gently refluxed for 2 hr, cooled, treated with a few drops of water to decompose the complex, and worked up as usual to give **12** in about 85% yield.

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Registry No.—**1**, 50558-31-1; **2**, 51075-66-2; **3**, 51075-67-3; **4**, 51075-68-4; **5**, 51075-69-5; **6**, 50558-34-4; **7**, 50558-36-6; **8**, 50558-37-7; **9**, 51075-70-8; **10**, 51075-71-9; **11**, 51075-72-0; **12**, 51075-73-1; hexachlorocyclopentadiene, 77-47-4; 1,1,2,3,3-pentachloropropene, 1600-37-9.

References and Notes

(1) R. Stroh, "Methoden der Organischen Chemie," Band 5/3, E. Mueller, Ed., Georg Thieme Verlag, Stuttgart, 1962, pp 960–978; L. Schmerling, "Friedel-Crafts and Related Reactions," Vol. 2, G. A. Olah, Ed., Interscience, New York, N. Y., pp 1133–1174; C. A. Buehler and D. E. Pearson, "Survey of Organic Synthesis," Wiley-Interscience, New York, N. Y., 1970, pp 356–375.

(2) R. West, *Accounts Chem. Res.*, **3**, 130 (1970); R. West, *Pure Appl. Chem.*, **28**, 379 (1971).

(3) (a) R. West and P. T. Kwitowski, *J. Amer. Chem. Soc.*, **88**, 5280 (1966); (b) K. Kirchoff, F. Boberg, and D. Friedmann, *Tetrahedron Lett.*, 2935 (1968).

(4) Hexachloropropene[3a] and 1,2,3,3-tetrachloropropene[3b] yield the corresponding propenium ion on reaction with anhydrous aluminum chloride. It is reasonable to assume that 1,1,2,3,3-pentachloropropene would behave in a similar fashion.

(5) H. J. Prins, *Recl. Trav. Chim. Pays-Bas*, **65**, 460 (1946).

(6) H. J. Prins, *Recl. Trav. Chim. Pays-Bas*, **65**, 455 (1946).

(7) V. Mark and E. D. Weil, *J. Org. Chem.*, **36**, 676 (1971).

(8) J. D. Roberts and W. F. Gorham, *J. Amer. Chem. Soc.*, **74**, 2278 (1952). American Petroleum Institute Project 44, ir spectrum 1251. Attempts to remove all chlorines present in **1** by reduction with Na-*t*-BuOH-THF[9] or Li-*t*-BuOH-THF[10] under a variety of conditions to give the parent unsaturated hydrocarbon[11] failed, and only tarry products were obtained.

(9) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964); P. G. Gassman and J. L. Marshall, *Org. Syn.*, **48**, 68 (1968).

(10) P. Bruck, *Tetrahedron Lett.*, 449 (1962); E. T. McBee, W. L. Dilling, and H. P. Braendlin, *J. Org. Chem.*, **28**, 2255 (1963); W. L. Dilling, H. P. Braendlin, and E. T. McBee, *Tetrahedron*, **23**, 1211 (1967).

(11) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(12) Stereochemical considerations using appropriate molecular models indicate that **1** is preferable over **1′** since there is considerable crowding between the allylic chlorines facing each other in **1′** but no such interactions in **1**.

(13) G. E. Hawkes, R. A. Smith, and J. D. Roberts, *J. Org. Chem.*, in press. We thank Professor Roberts for informing us of his results prior to publication. Structural assignment for **1** on the basis of its ^{13}C spectrum has been discussed in this paper.

(14) (a) After this manuscript was submitted for publication, a paper appeared giving independent preparations and structural evidence for compounds **1**, **6**, **7** and **8**: A. Roedig, G. Bonse, and R. Helm, *Chem. Ber.*, **106**, 2156 (1973). Our physical data and structural assignments agree with those of Roedig, *et al.* (b) Attack at C-2 of hexachlorocyclopentadiene would furnish a cation with no allylic stabilization. In addition attack at the carbon bearing the dichloromethyl group in the propenyl cation would lead to an intermediate from which the formation of **1** is not easily visualized.

(15) We are most grateful to Mr. Yoshio Toshiyasu of the Science Education Institute of Osaka Prefecture for carrying out the dipole moment measurements.

(16) The reaction of aliphatic ketones with PCl_5 can lead to rearranged or ring-opened products. Elimination products have also been reported in aliphatic systems. See A. G. Giumanini, *Boll. Chim. Farm.*, **106**, 230 (1967); M. S. Newman, *J. Org. Chem.*, **34**, 741 (1969).

(17) J. B. Grutzner, M. Jautelat, J. B. Dence, J. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 7107 (1970); F. J. Weigert and J. D. Roberts, *ibid.*, **92**, 1347 (1970).

(18) The presence of α,β unsaturation or α substitution by halogen results in an upfield shift of carbonyl carbon resonances. See, for instance, E. Lippmaa, T. Pehk, J. Paasivirta, N. Belikova, and A. Plate, *Org. Magn. Resonance*, **2**, 581 (1970); J. B. Stothers and P. C. Lauterbur, *Can. J. Chem.*, **42**, 1563 (1964).

(19) D. H. Marr and J. B. Strothers, *Can. J. Chem.*, **43**, 596 (1965).

(20) E. T. McBee, D. K. Smith, and H. E. Ungnade, *J. Amer. Chem. Soc.*, **77**, 559 (1955).

(21) L. T. Bellamy, "Advances in Infrared Group Frequencies," Metheun, London, 1968, pp 22–26.

(22) N. B. Colthup, *J. Chem. Educ.*, **38**, 394 (1961).

(23) Examples of exocyclic type double bonds which absorb at higher frequencies are plentiful in steroid chemistry. For example, see G. R. Pettit, L. E. Houghton, J. C. Knight, and F. Bruschweiler, *J. Org. Chem.*, **35**, 2895 (1970).

(24) The structural assignment for **6** based on its ^{13}C nmr spectrum and other model compounds is presented in ref 13. Our observations on the chemistry of **6** are consistent with this assignment.

(25) The absence of Overhauser enhancement on spin decoupling owing to lack of protons and the resultant absence of spin-spin splitting information make detection and interpretation of ^{13}C resonances of chlorocarbons much harder than that of hydrocarbons of similar structures. In addition substantial deviations from expected intensities occur owing to long relaxation times. For this reason, definite assignments have not been presented in Table I, but have been discussed in the text for some of the compounds which are more easily interpreted on the basis of models. See ref 13.

(26) J. M. Bollinger and G. A. Olah have shown the existence of octamethylbicyclo[3.3.0]octadienyl dication in strong acid [*J. Amer. Chem. Soc.*, **91**, 3380 (1969)]. An alternate structure which involves one of two possible forms of octamethylcyclooctatrienyl dication has been considered unlikely.

(27) The dication of perchloropentalene has, however, been isolated and characterized: K. Kusuda and N. Osaka, *J. Chem. Soc., Chem. Commun.*, 508 (1972).

(28) Vinyl ethers are frequently known to give >C=C< absorption bands as a doublet with band centers near 1612 and 1635 cm^{-1}. See ref 21, p 32, for leading references.

(29) E. T. McBee, D. L. Crain, R. D. Crain, L. R. Belohlav, and H. P. Braendlin, *J. Amer. Chem. Soc.*, **84**, 3557 (1962); D. J. Burton and H. C. Krutzsch, *J. Org. Chem.*, **36**, 2351 (1971); G. Modena, *Accounts Chem. Res.*, **4**, 73 (1971).

(30) The olefinic absorptions of the hydrocarbons corresponding to **1** and **1′** do not resemble those of **7**. It is reasonable to expect that structures **7c** and **7d** would have olefinic absorptions similar to the parent unsubstituted hydrocarbons. See ref 11.

(31) Secondary splittings are not uncommon. See G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972, p 57.

(32) A. M. Ihrig and J. L. Marshall, *J. Amer. Chem. Soc.*, **94**, 1756 (1972); J. A. Schwarcz and A. S. Perlin, *Can. J. Chem.*, **50**, 3667 (1972).

(33) Reference 31, pp 62–63.

(34) S. Oota, *Bunsekikagaku*, **15**, 689 (1966); **17**, 1322 (1968); **18**, 1257 (1969).

(35) The temperature must be kept below 80°, above which the dimerization of hexachlorocyclopentadiene takes place exothermally and the reaction becomes difficult to control.

(36) The intensities were determined on the chart.

(37) The origin of Prins dimer at higher reaction temperatures is unclear. It is likely that hexachlorocyclopentadiene was generated from **1** which dimerized under the reaction conditions. The three carbon fragments perhaps were hydrolyzed further to water-soluble products.

(38) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Interscience, New York, N. Y., 1957, pp 228 and 264.