Synthesis of Octachlorobicyclo[3.3.0]octa-1,4,6-triene and Lewis Acid Catalyzed Isomerization of Hexachlorobicyclo[3.3.0]octa-3,5,8-trien-2-one*

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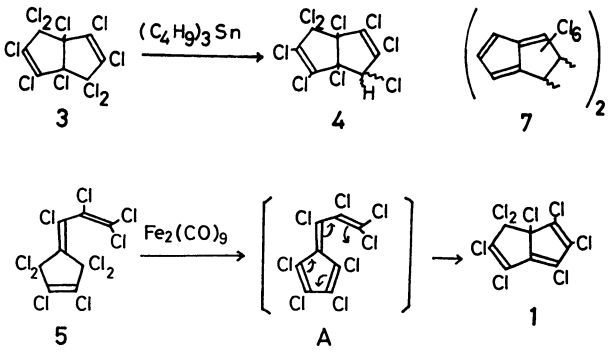
Treatment of decachloro(4-allylidenecyclopentene) with enneacarbonyldiiron(0) gave octachlorobicyclo-[3.3.0]octa-1,3,7-triene (δ-C_8Cl_8) in 40% yield. Dechlorination of decachlorobicyclo[3.3.0]octa-2,6-diene with powdered selenium, sulfur, phosphorus, or titanium in the presence of anhydrous aluminium chloride without any adde d solvent at 90—100 °C afforded octachlorobicyclo[3.3.0]octa-1,4,6-triene (**2**) (ε-C_8Cl_8) in good yield. Hexachlorobicyclo[3.3.0]octa-3,5,8-trien-2-one obtained from **2** was chlorinated by a concentrated solution of antimony(V) chloride in refluxing dichloromethane to give octachlorobicyclo[3.3.0]octa-3,6(or 7)-dien-2-one, but in a dilute solution (less than 0.1 g of antimony(V) chloride/cm^3 of dichloromethane) hexachlorobicyclo[3.3.0]octa-4,6,8-trien-2-one (**14**) was obtained. Mechanism of the isomerization is discussed in terms of antiaromaticity of cyclopentadienyl cation. Reaction of **14** with methanol afforded pentachloro-4-methoxybicyclo[3.3.0]octa-3,5,7-trien-2-one. Ethanol or 2-propanol reacted with **14** similarly giving pentachloro-4-ethoxybicyclo[3.3.0]octa-3,5,7-trien-2 -one or pentachloro-4-isopropoxybicyclo[3.3.0]octa-3,5,7-trien-2-one, respectively.

In a series of continuing studies on the chemistry of cyclic conjugated chlorocarbons,[1] the author reported on reactions of δ-C_8Cl_8 (**1**) and ε-C_8Cl_8 (**2**) with antimony(V) chloride or anhydrous aluminium chloride to give dicationic complexes.[2] In the report, octachlorobicyclo[3.3.0]octa-1,3,7-triene and octachlorobicyclo-[3.3.0]octa-1,4,6-triene were assigned to the structure of **1** and **2**, respectively, which were confirmed later by X-ray crystallographic analyses.[3]

The objective of the present work was to extend the investigation on these chlorocarbons toward development of a new synthetic method for **2** and elucidation of Lewis acid-catalyzed isomerization of a perchlorinated ketone obtained from **2**. Since the reported syntheses of **1** and **2**[4] seemed to be unsuitable for a large-scale preparation, it has been desired to develop a convenient synthetic method for **1** or **2**.

Treatment of decachlorobicyclo[3.3.0]octa-2,6-diene (**3**)[5] with tributylstannane[6] at around 50 °C gave a mixture, from which a small amount of 1,2,3,4,4,5,6,7,8-nonachlorobicyclo[3.3.0]octa-2,6-diene (**4**), C_8HCl_9, mp 134 °C, was separated by column chromatography on silica gel eluted by petroleum ether. Dehydrochlorination of **4** with methanolic sodium hydroxide at room temperature gave yellow crystals of **1**. Dechlorination of decachloro(4-allylidenecyclopentene) (**5**)[7] with enneacarbonyldiiron(0) at room temperature afforded **1** in 37% yield. A reasonable pathway for the formation of **1** could involve transformation of **5** to reactive octachlorovinylfulvene (**A**) followed by cyclization, as is similar to the mechanism postulated for the formation of dihydropentalene derivatives.[8] Attempted isolations of intermediate **A** and its iron carbonyl complex[9] were unsuccessful.

As the foregoing preparations of **1** were unsatisfactory for a large-scale preparation, synthesis of **2** was investigated. When a mixture of **3** and anhydrous aluminium chloride was heated at 220—240 °C for 2.5 h, the reaction mixture changed into a reddish brown mass and sublimed white crystals, from which octachlorocyclopentene and hexachlorobenzene were separated by making use of solubility in methanol. Treatment of the dark solid on the bottom of flask with a mixture of water and carbon tetrachloride afforded **2** and hexachlorobicyclo[3.3.0]octa-3,5,8-trien-2-one (**6**), C_8Cl_6O, mp 82 °C, in yields of 35 and 28%, respectively. Structural assignment of **6** rested on its IR, UV, and ^{13}C NMR spectra. Dechlorinations of **3** with powdered copper in petroleum benzine, tin(II) chloride in aq acetone, or aluminium amalgam in diethyl ether[10] gave a dimer of hexachloropentalene (**7**).[4a] It seemed difficult to obtain an octachlorodihydropentalene from **3** by regulating conditions of the usual dechlorination. However, it was expected that Lewis acid metal halide in the reaction mixture should react with an octachlorodihydropentalene produced by dechlorination of **3**, thus preventing further dechlorination, since known perchlorinated dihydropentalenes, **1** and **2**, easily react with Lewis acid metal halide affording stable complexes. Most of the popular dehalogenating reagents[11] are inadequate because they react with anhyd aluminium chloride and/or because they are usually used in some solvent which is reactive to anhyd aluminium chloride. With these restrictions taken into account, powdered selenium was chosen for the dechlorination. A mixture of **3**, selenium, and two equivalents of anhyd aluminium chloride was heated at 90 °C for 1 h and then quenched with 2 M (1 M=1 mol dm^{-3}) hydrochloric acid. The crude product was purified by the conventional isolation procedure including chromatography on silica gel to

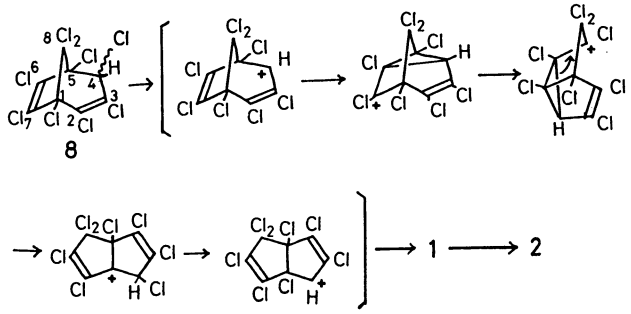


3 4 7

5 A 1

* Dedicated to Emeritus Professor Takeo Sakan on his 70th Anniversary.

give **2** in 98% yield. Under similar conditions, sulfur, red phosphorus, or titanium gave **2** in yield of 91, 52, or 64%, respectively, but powdered aluminium, tin, silicon, and zinc were ineffective for the dechlorination. A mixture of selenium or sulfur and antimony(V) chloride did not react with **3** at 100 °C. When a mixture of **3** and sulfur was heated at 180 °C, **7** was the only product identified. These findings indicate that anhyd aluminium chloride activates selenium and sulfur in the dechlorination of **3**. Dechlorinations of hexachlorocyclopropane,[12] octachloro(4-methylenecyclopentene),[13] and octachloro(1,2-dimethylenecyclobutane)[14] with selenium–anhyd aluminium chloride were unsuccessful. Treatment of 1,2,3,4,5,6,7,8,8-nonachlorobicyclo[3.3.0]octa-2,6-diene (**8**)[15] with two equivalents of anhyd aluminium chloride at 150 °C gave a black solid, which gave **2** in 69% yield upon quenching with concd hydrochloric acid. The reaction probably proceeds similarly to the rearrangement of homonorbornadienyl cation:[16]



^{35}Cl nuclear quadrupole resonance (NQR) spectra of **2** (Table 1) furnish useful information on the chemical structure. There are six resonance lines indicating the presence of six kinds of chlorine atoms, hence the planarity of the molecule. Each signal in MHz at 78 K shifts downward at higher temperatures. Four lines between 37.056 and 37.372 MHz are in the proper region for vinylic chlorines, whereas two lines at 38.898 and 39.053 MHz suggest two equivalent chlorine atoms on a carbon.[17]

Treatment of **2** with formic acid or sulfuric acid afforded **6** in 65—72% yield.[4d] In order to hydrolyze a dichloromethylene group of **2**, excess fuming nitric acid was added to powdered **2** at room temperature, causing an exothermic reaction immediately. From the reaction mixture **6** and tetrachloro-2,5-cyclopentadiene-1,2-dicarboxylic acid (**9**), $C_7H_2Cl_4O_4$, mp 208 °C, were isolated. The structure of **9** was speculated on the basis of the elemental analysis and IR and UV spectra. Refluxing a mixture of **6** and powdered potassium carbonate in abs methanol afforded pentachloro-4-methoxybicyclo[3.3.0]octa-3,5,8-trien-2-one (**10**), $C_9H_3Cl_5O_2$, mp 96 °C. The transformation is similar to that of **2** with secondary amines.[4d]

Table 1. NQR signals of **2** (MHz)[a]

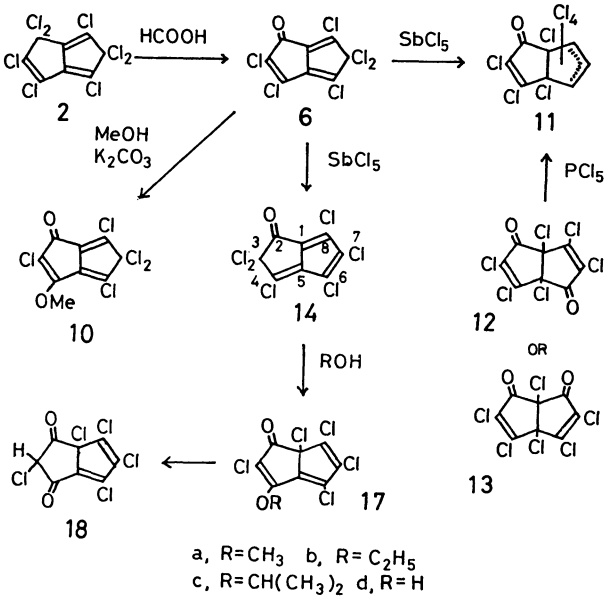
Temp/K	78	200	296
	39.053	38.722	38.392
	38.898	38.577	38.245
	37.372	37.089	36.826
	37.348	37.074	36.785
	37.268	36.976	36.637
	37.056	36.809	36.493

a) Accuracy: ±0.003 MHz.

When a mixture of **6** and excess antimony(V) chloride in dichloromethane was refluxed for 5 h, a deep red color developed during the reaction, but a colorless oily material, octachlorobicyclo[3.3.0]octa-3,6(or 7)-dien-2-one (**11**), C_8Cl_8O, was the product, which was obtained also by chlorination of hexachlorobicyclo[3.3.0]octa-3,7-diene-2,6-dione (**12**) or hexachlorobicyclo[3.3.0]-octa-3,6-diene-2,8-dione (**13**)[5] with phosphorous(V) chloride. The complete structure of **11** remains to be determined. However, diluted antimony(V) chloride (less than 0.1 g/cm^3 of dichloromethane) does not chlorinate **6** but catalyzes a rearrangement, affording quantitatively deep red crystals of hexachlorobicyclo-[3.3.0]octa-4,6,8-trien-2-one (**14**), C_8Cl_6O, mp 70 °C. Treatment of **6** with anhyd aluminium chloride under similar conditions yielded a mixture of **6** and **14** in approximately 1 : 1 ratio (*vide infra*). Reaction of **14** with concd antimony(V) chloride in the same solvent furnished **11**.[18]

The ^{13}C NMR spectrum of **14** shows a peak due to a chlorinated sp^3 carbon at 85.1 ppm and no alkenic carbon peak characteristic of α,β-unsaturated ketone.[19] It can be assumed that the UV spectrum of **14** (Fig. 1) consists of two groups of higher intensities, one between 220 and 300 nm and the other between 300 and 350 nm, and one broad peak of lower intensity. The maxima in the region 300—450 nm are similar to that of hexachlorofulvene (**15**)[20] and quite different from that of cyclopentadienone derivative.[21] These spectral data were all compatible with the assigned structure, which was further confirmed by the following chemical reaction indicating absence of cyclopentadienone moiety. Neither maleic anhydride nor furan reacted with **14** in refluxing benzene. Chlorination of **14** with liquid chlorine in a sealed tube at room temperature afforded white crystals of decachlorobicyclo[3.3.0]oct-6(or 7)-en-2-one (**16**), $C_8Cl_{10}O$, mp 130 °C, which was stable to treatment with anhyd aluminium chloride in boiling dichloromethane. The structure of **16** was assigned on the basis of elemental analysis and IR and UV spectra. Ethereal diazomethane apparently reacted with **14** with evolution of nitrogen gas and with its red color fading, but isolation of a pure product was unsuccessful.

When methanol was added to **14**, a moderate exothermic reaction furnished yellow crystals of pentachloro-4-methoxybicyclo[3.3.0]octa-3,5,7-trien-2-one (**17a**), $C_9H_3Cl_5O_2$, mp 152 °C. Similarly, ethoxy derivative (**17b**), $C_{10}H_5Cl_5O_2$, mp 186 °C, or 2-propoxy derivative (**17c**), $C_{11}H_7Cl_5O_2$, mp 149 °C, was obtained by the reaction with ethanol or 2-propanol, respectively, but 2-methyl-2-propanol did not react with **14** under similar conditions. Methanolic solution of **14a** yielded 1,3,6,7,8-pentachlorobicyclo[3.3.0]octa-5,7-diene-2,4-dione(**18**)[4d] on standing at room temperature for 2 d. Comparison of the UV spectra of **1** and **17a—d** makes it clear that these chlorocarbons have a similar double bond



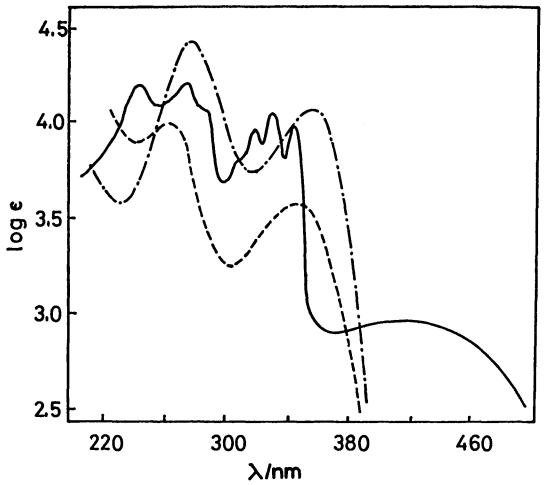
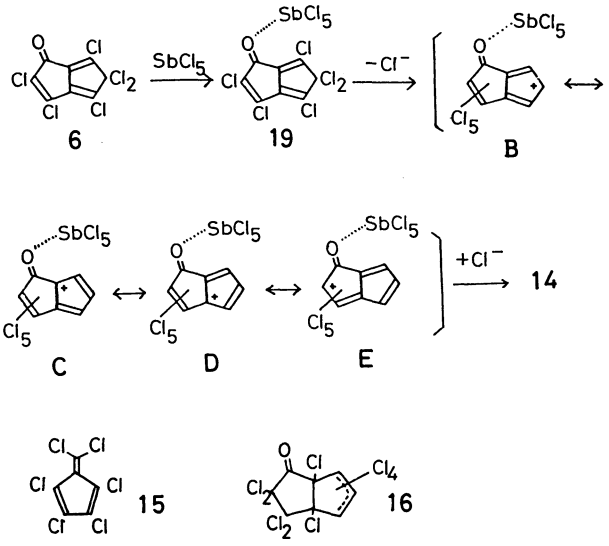


Fig. 1. Ultraviolet and visible absorption spectra of **1**, **14** and **17a**.
------: **1** (in dichloromethane), ——: **14** (in hexane), -·-·-: **17a** (in hexane).

system (Fig. 1 and Experimental section). ^{13}C NMR and IR spectra as well as these findings support the proposed structures **17a—d**.

In view of the generalization that nucleophilic substitution on a polychlorinated double bond proceeds through the addition-elimination mechanism,[22] the formation of **17a—c** seemed to be abnormal. Although a mechanism composed of catalyzed isomerization of the double bonds of **14** followed by substitution of an alkoxyl group can be written, isomerization of the double bonds is probably not the initial step since **14** cannot be isomerized by hydrochloric acid or acetic acid. On the other hand, it has been known that nucleophiles will initially attack on C(6) of **15**, then allowing the addition-elimination reaction to occur.[23] It is considered that the reactions of alcohols with **14** take place on C(4) similarly with **15**, then allowing the isomerization of the double bonds and 1,7-rearrangement of a chlorine atom to proceed.

Addition of excess antimony(V) chloride to a concd solution of **6** in dichloromethane immediately precipitated a yellow complex (**19**), IR spectrum of which is quite similar to that of **6** in the region 1500—500 cm^{-1}. On the other hand, a large difference was found in the carbonyl and C=C double bond regions, indicating that the complex was formed by coordination of antimony(V) chloride to the carbonyl group. Quenching **19** with 6 M hydrochloric acid afforded **6** quantitatively. The isomerization of **6** to **14** presumably takes place through cationic species (B—E) produced by the attack of antimony(V) chloride on **19**. Monocationic B—D are considered unstable because of the contribution of antiaromatic cyclopentadienylium cation,[24] whereas E is free from such destabilization and contains stable polychlorinated fulvene moiety and hence contribution of E seems to be predominant.[25] Recombination of chloride anion with E completes the rearrangement.



Experimental

General. The melting points were determined on a Yanagimoto micro melting point apparatus and were uncorrected. Elemental analyses of carbon and hydrogen were performed by Mr. J. Goda of Osaka City University. Chlorine analyses, when required, were carried out according to the combustion method by use of a modified flask.[26] IR spectra were recorded on a Perkin-Elemer Model 337 spectrophotometer as mulls in Nujol between KBr disks unless otherwise mentioned. Significant absorptions are reported. UV spectra werer ecorded on a Hitachi Model 200-10 spectrophotometer in solution. Nuclear quadrupole resonance spectra were recorded on a Decca Radar NQR spectrometer and summarized in Table 1. Both ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-60 F-T NMR spectrometer. Mass spectra were recorded on a JEOL JMS-01SG-2 double focus mass spectrometer at 80 eV ionizing potential. Petroleum ether and petroleum benzine used are hydrocarbon mixtures boiling in the ranges 48—66 and 68—69 °C, respectively.

1,2,3,4,4,5,6,7,8-Nonachlorobicyclo[3.3.0]octa-2,6-diene (4). A mixture of 4.5 g (10 mmol) of **3** and 5.8 g (20 mmol) of tributylstannane in 30 cm^3 of benzene was heated at around

50 °C under a nitrogen atmosphere with stirring for 33 h. After removal of the solvent under reduced pressure, the reaction mixture was chromatographed on silica gel (3 cm × 60 cm) with petroleum ether as eluent. The crude product obtained from a slightly yellow band was washed with ethanol and crystallized from ethanol to give 48 mg of **4**: mp 133—134 °C; IR 1630, 1610, 1235, 1205, 1175, 1030, 1022, 832, and 755 cm^{-1}; ^1H NMR (CCl_4) δ=5.07. Found: C, 23.29; H, 0.45; Cl, 76.58%. Calcd for C_8HCl_7: C, 23.09; H, 0.24; Cl, 76.67%.

Octachlorobicyclo[3.3.0]octa-1,3,7-triene (1) (δ-C_8Cl_8). a) From 4: To an ethereal solution (1 cm^3) of **4** (35 mg, 0.048 mmol) was added 5 drops of 20% methanolic potassium hydroxide solution and the mixture was stirred for 30 min at room temperature, whereupon the solution turned light yellow. Water was added and the organic materials were extracted with diethyl ether. The combined ethereal solution was washed with water and dried over sodium sulfate. The solvent was evaporated under vacuum to give 30 mg of yellow crystals of **1**. Identification was made by comparison of the IR and UV spectra with those of authentic sample synthesized by the reported method: IR 1615, 1545, 1535, 1267, 1215, 1130, and 765 cm^{-1}; UV λ_{max}^{hexane} 260 (3.99) and 352 (3.67).

b) From 5: A mixture of 1.73 g (3.84 mmol) of **5** and 1.40 g (3.84 mmol) of enneacarbonyldiiron(0) in 15 cm^3 of petroleum benzine was stirred for 3 h at 35 °C and was kept at room temperature overnight. The reaction mixture was filtered and the solvent was evaporated to dryness to give 0.546 g (37%) of crude **1**. Column chromatography on silica gel eluted by petroleum benzine gave a pure sample.

A Dimer of Hexachloropentalene (7). Powdered sulfur (0.50 g) was mixed with 1.32 g (2.93 mmol) of **3** and the mixture was heated at 150—180 °C for 1.5 h. The organic products were extracted with carbon tetrachloride by use of a Soxhlet extractor. The crystals obtained by evaporation of the solvent were sublimed at 135 °C/3 mmHg (1 mmHg= 133.3 Pa) to remove a volatile yellow solid. The residue was 244 mg (27%) of bright deep red crystals of the dimer of hexachloropentalene: mp 315 °C; IR 1638, 1604, 1500, 1232, and 1155 cm^{-1}; UV $\lambda_{max}^{dichloromethane}$ 250 (3.57), 290 sh (3.86), 300 (3.96), 390—460 (2.64). Found: C, 31.15; H, 0.14; Cl, 68.34%. Calcd for $C_{16}Cl_{12}$: C, 31.12; Cl, 68.88%. Identification was made by comparison of mp and IR and UV spectra with those of the authentic sample.

Octachlorobicyclo[3.3.0]octa-1,4,6-triene (2). (ε-C_8Cl_8) a): A mixture of 5.00 g (11.1 mmol) of **3**, 1.05 g (13.29 mg atom) of selenium, and 2.96 g (22.17 mmol) of powdered anhyd aluminium chloride was heated in an oil bath at around 90 °C with stirring for 1 h. The reaction mixture melted and turned dark brown. After being cooled to room temperature, the reaction mixture was quenched with a mixture of 2 M hydrochloric acid and chloroform under ice cooling. A small amount of insoluble materials was removed by filtration and the chloroform solution was separated. The water layer was extracted twice with a small amount of chloroform. The combined solution was dried over sodium sulfate. The crude product obtained by evaporation of the solvent was chromatographed on silica gel (12 mm × 7 cm) with petroleum benzine as eluent. Evaporation of the solvent gave 4.14 g (98.2%) of pure **2**: mp 111—112 °C; IR 1685, 1640, 1530, and 800 cm^{-1}; UV λ_{max}^{hexane} 262 (4.01) and 325 (3.38); MS *m/e* (%) 376 (3.1), 341 (33.8), 306 (100), 271 (30.8), 236 (24.6), 201 (13.8), and 153 (29.2).

Dechlorinations of **3** by use of sulfur, red phosphorus and titanium are summarized in Table 2.

e): A mixture of powdered anhyd aluminium chloride (0.60 g, 4.5 mmol) and 0.82 g (2.2 mmol) of **8** was heated at 150 °C for 1.25 h. A dark brown reaction mixture was solidified on standing at room temperature. The reaction mixture was quenched by a mixture of ice and concd hydrochloric acid. Extraction with carbon tetrachloride, drying over sodium sulfate, and evaporation of the solvent gave 0.56 g (69%) of **2**.

Table 2. Dechlorinations of **3**

Dechlorinating reagent(g)	**3**(g)	$AlCl_3$ (g)	Temp/°C	Time/h	Yield of **2**/g(%)
b) S: 0.33	4.60	6.90	80—85	3	3.25(91)
c) Red P: 0.10	1.80	1.21	100	2	0.79(52)
d) Ti: 0.12	1.80	1.21	98—100	2	0.98(64)

f): A mixture of 5.0 g (11.1 mmol) of **3** and 5.0 g (37.5 mmol) of powdered anhyd aluminium chloride in a 50 cm^3 flask was heated at 220—240 °C in an oil bath for 2.5 h. White powders sublimed were collected and treated with water. The mixture was separated by making use of solubility in methanol. The white crystal (20 mg) insoluble in methanol was hexachlorobenzene and the crystal (700 mg) obtained by evaporation of the methanol was octachlorocyclopentene. The reddish-brown reaction mixture on the bottom of the flask was decomposed with a mixture of water and carbon tetrachloride and the organic layer was separated. Evaporation of the solvent gave 3.98 g of mixture. Column chromatography on silica gel (2.2 cm × 13 cm) eluted with petroleum benzine gave 1.48 g (35%) of **2** and 1.02 g (28%) of **6** successively. Both the oily material (0.14 g) from the third and the yellow crystals (0.26 g) from the fourth fraction were not identified.

Hexachlorobicyclo[3.3.0]octa-3,5,8-trien-2-one (6) and Tetrachloro-2,5-cyclopentadiene-1,2-dicarboxylic Acid (9). Fuming nitric acid (d=1.535) was added to 15.0 g (39.5 mmol) of powdered **2**, whereupon a moderate exothermic reaction took place. After having been stirred for 15 min at room temperature, the reaction mixture was diluted with water and the organic materials were extracted with chloroform. Concentration of the organic solution and addition of petroleum benzine afforded 3.46 g of **6**. Recrystallization from petroleum benzine gave an analytical sample of **6**, mp 80—82 °C. Identification was made by comparison of mp and IR spectrum with reported data:[4d] IR (hexane) 1730, 1665, 1630, and 1505 cm^{-1}; UV λ_{max}^{hexane} 260 (4.32) and 270 (4.34); ^{13}C NMR ($CHCl_3$) δ=171.2, 146.1, 142.4, 134.0, 128.9, 127.6, 125.6, and 89.8. Evaporation of the mother solution afforded 11.1 g of an oily product, which was chromatographed on silica gel (18 mm × 14 cm) with petroleum benzine as eluent. The first light yellow band and the second light brown band gave 4.27 g of **6** and the third brown band gave 2.01 g of an oily mixture of **6** and nitro compounds. The upper black part of column was separated and extracted with ethyl acetate. Evaporation of the solvent gave 1.46 g of crude **9**, which was crystallized from a mixed solvent of chloroform and ethyl acetate (4 : 1) to give an analytical sample: mp 204—208 °C; IR 1710 and 1575 cm^{-1}; UV λ_{max}^{hexane} 328 (3.30). Found: C, 28.88; H, 0.69; Cl, 48.69%. Calcd for $C_6H_2Cl_4O_4$: C, 28.80; H, 0.68; Cl, 48.58%.

Pentachloro-4-methoxybicyclo[3.3.0]octa-3,5,8-trien-2-one (10). A mixture of 1.00 g (3.08 mmol) of **6**, half of 0.426 g (3.08 mmol) of potassium carbonate, and 10 cm^3 of abs methanol was stirred at room temperature for 30 min, then the rest of the potassium carbonate was added and heated to reflux for 1 h. The reaction mixture was diluted with water and the organic materials were extracted with chloroform. Drying over sodium sulfate and evaporation of the solvent afforded 0.84 g of crystals. Recrystallization from petroleum ether gave an

analytical sample of **10**: mp 92—96 °C; IR 1700, 1660, 1630, 1550, 1350, and 800 cm^{-1}. Found: C, 33.49; H, 0.93%. Calcd for $C_9H_3Cl_5O_2$: C, 33.53; H, 0.99%.

*Hexachlorobicyclo[3.3.0]octa-4,6,8-trien-2-one (**14**).* To a suspension of 1.5 g (4.6 mmol) of **6** in 5 cm^3 of dichloromethane was added a solution of 4.10 g (13.7 mmol) of antimony(V) chloride in 40 cm^3 of dichloromethane and the solution was heated to reflux for 3 h. Chloroform (20 cm^3) was added to the deep red reaction mixture and the antimony(V) chloride was decomposed with concd hydrochloric acid. The organic phase was separated and washed twice with water. The solution was dried over sodium sulfate and the solvent was evaporated to dryness. Chromatography of silica gel with petroleum ether gave **14** quantitatively: mp 68—70 °C; IR 1750, 1615, 1560, 1455, 830, and 765 cm^{-1}; UV λ_{max}^{hexane} 245 (4.17), 274 (4.21), 285 sh (4.11), 318 (3.94), 331 (4.06), 346 (3.97), and 410—420 (2.97); ^{13}C NMR ($CHCl_3$) δ=171.6, 144.2, 142.5, 136.8, 130.8, 120.7, 119.8, and 85.1. Found: C, 29.86; H, 0.15%. Calcd for C_8Cl_6O: C, 29.58%.

*Reaction of **6** with Anhydrous Aluminium Chloride.* To 0.92 g (2.83 mmol) of **6** dissolved in 15 cm^3 of dried dichloromethane was added 1.0 g (7.5 mmol) of anhyd aluminium chloride and the mixture was heated under reflux for 7 h and quenched by hydrochloric acid. The organic solution was separated and dried over sodium sulfate and the solvent was evaporated under reduced pressure to give 0.91 g of brown solid, whose IR spectrum showed it was an approximately 1 : 1 mixture of **6** and **14**.

*Decachlorobicyclo[3.3.0]oct-6(or 7)-en-2-one (**16**).* *a) Chlorination of **14** in Liquid Chlorine*: A mixture of 0.377 g (1.16 mmol) of **14** dissolved in 10 cm^3 of carbon tetrachloride and about 10 cm^3 of liquid chlorine was sealed in a thick wall glass tube and kept under sunlight for one week. The tube was chilled in a Dry Ice–acetone bath and opened. Excess chlorine was removed by evaporation and the residue was chromatographed on silica gel (13 mm × 10 cm) with petroleum ether as eluent. The product was eluted as a light brown band. Evaporation of the solvent and recrystallization from a mixture of methanol and ethanol afforded white crystals of **16**: mp 126—130 °C; IR 1795, 1760, 1620, and 1585 cm^{-1}; UV λ_{max}^{hexane} 230 (3.98). Foun d: C, 20.85; H, 0.10; Cl, 75.97%. Calcd for $C_8Cl_{10}O$: C, 20.59; Cl, 75.98%.

b) Chlorination with Phosphorus(V) Chloride: Phosphorus(V) chloride (0.55 g) was mixed with 0.566 g (1.74 mmol) of **14** in a sealed tube and the mixture was heated at 170—200 °C for 4 h. The crude product was purified by column chromatography on silica gel eluted with petroleum benzine. Yield: 0.208 g (26.0%).

*Pentachloro-4-methoxybicyclo[3.3.0]octa-3,5,7-trien-2-one (**17a**).* Abs methanol (5 cm^3) was mixed with with 1.821 g (5.61 mmol) of **14** at room temperature and stirred for 5 min to precipitate yellow crystals. Then, 2 cm^3 of petroleum ether was added and the crystals were separated by filtration. Recrystallization three times from petroleum ether gave 0.365 g of an analytical sample of **17a**: mp 152 °C; IR 1740, 1730, 1595, 1550, and 1290 cm^{-1}; UV λ_{max}^{hexane} 220 (3.70), 277 (4.44), and 355 (4.13); ^{13}C NMR ($CHCl_3$) δ=174.4, 165.4, 140.7, 125.3, 124.6, 117.1 (d),[27] 81.6, and 65.1. Found: C, 33.67; H, 0.92; Cl, 55.60%. Calcd for $C_9H_3Cl_5O_2$: C, 33.74; H, 0.94; Cl, 55.34%.

*Pentachloro-4-ethoxybicyclo[3.3.0]octa-3,5,7-trien-2-one (**17b**).* Into a mixture of ethanol (4.7 cm^3) and chloroform (9.3 cm^3) was dissolved 1.624 g of **14** and the solution was stirred for 5 h at room temperature to precipitate yellow crystals. The solvent was evaporated under reduced pressure to give yellow crystal sludge. The crystals were separated by filtration and washed with a small amount of acetic acid. Crystallization from 7 cm^3 of chloroform afforded 0.67 g of **17b**: mp 186 °C; IR 1740, 1730, 1600, and 1550 cm^{-1}; UV λ_{max}^{hexane} 220 (3.65), 276 (4.50), and 357 (4.19); ^{13}C NMR ($CHCl_3$) δ=174.4, 165.0, 140.6, 125.0, 116.0, 117.1, 82.1, 74.9, and 14.7.[28] Found: C, 35.77; H, 1.50; Cl, 53.25%. Calcd for $C_{10}H_5Cl_5O_2$: C, 35.92; H, 1.50; Cl, 53.01%.

*Pentachloro-4-isopropoxybicyclo[3.3.0]octa-3,5,7-trien-2-one(**17b**).* A mixture of 2-propanol (10 cm^3), chloroform (5 cm^3) and 0.913 g of **14** was stirred for 1 h and kept at room temperature overnight. The yellow crystals obtained by evaporation of the solvent under reduced pressure were separated by filtration and crystallized from carbon tetrachloride: mp 149 °C dec; IR 1740, 1730, 1590, and 1540 cm^{-1}; UV λ_{max}^{hexane} 220 (3.68), 277 (4.27), and 355 (4.16); ^{13}C NMR ($CHCl_3$) δ=174.5, 164.5, 140.1, 124.9, 124.4, 116.6, 115.9, 83.0, and 22.0. Found: C, 37.51; H, 1.97; Cl, 50.88%. Calcd for $C_{11}H_7Cl_5O_2$: C, 37.92; H, 2.02; Cl, 50.88%.

*Pentachloro-4-hydroxybicyclo[3.3.0]octa-3,5,7-trien-2-one (**17d**).* Methanol (10 cm^3) was added to 1.038 g of **14** and refluxed gently for 10 min. The solution turned strongly acidic and dark greenish brown. Evaporation of the solvent left greenish yellow crystals, which were crystallized from a mixture of benzene (5 cm^3) and petroleum ether (3 cm^3) to give 0.837 g of yellow crystals of **17d**: mp 178 °C decomp; IR 3600, 3375, 1715, 1645, 1265, and 1130 cm^{-1}; UV λ_{max}^{hexane} 220 (3.62), 276 (4.56), and 357 (4.23). Found: C, 30.69; H, 0.67%. Calcd for $C_8HCl_5O_2 \cdot 1/2\ H_2O$: C, 30.43; H, 0.64%.[29]

*Chlorination of **6** with Antimony(V) Chloride. Formation of **11**:* A mixture of 5.5 g (16.9 mmol) of **6**, 6.13 g (20.5 mmol) of antimony(V) chloride, and 40 cm^3 of dry dichloromethane was refluxed for 4 h. After quenching the red reaction mixture with 50 cm^3 of concd hydrochloric acid, organic products were extracted with carbon tetrachloride. The organic solution was washed with water and dried over sodium sulfate. Evaporation of the solvent left 3.30 g of crude product. Distillation at 180—190 °C/2 mmHg gave a pure sample which showed single peak on gas chromatography (Nikki Model G-77) column: 20% SE-30 on Celite 545, mesh 60—80, and 2 m, He flow: 16.4 cm^3/min; column temperature: 250 °C: IR 1757, 1616, and 1590 cm^{-1}; UV λ_{max}^{hexane} 248 (3.90). Found: C, 24.80; H, 0.06%. Calcd for C_8Cl_8O: C, 24.28%.

*Chlorination of **12** with Phosphorus(V) Chloride.* In a thick wall glass tube, 1.126 g (3.3 mmol) of **12** and 0.894 g (4.3 mmol) of phosphorus(V) chloride was sealed and heated at 140—150 °C in an oil bath for 8 h, and allowed to cool to room temperature. The reaction mixture was treated with water and the products were taken up in carbon tetrachloride. The crude product was chromatographed on silica gel with petroleum benzine as eluent. A fraction eluted as a light yellow band was collected and evaporation of the solvent afforded 479 mg of **11**. Found: C, 24.38; H, 0.16; Cl, 71.83%. Calcd for C_8Cl_8O: C, 24.28; Cl, 71.68%.

*Chlorination of **13** with Phosphorus(V) Chloride.* Phosphorus(V) chloride (896 mg) was allowed to react with 467 mg of **13** under the same conditions as mentioned for the preceding reaction and 560 mg of **11** was obtained by the conventional isolation procedure.

*3,6,7,7,8-Pentachlorobicyclo[3.3.0]octa-5,8-diene-2,4-dione (**18**).* A methanolic solution of 1.325 g of **17a** was kept at room temperature for 2 d. Evaporation of the solvent afforded a brown oily product, which crystallized on trituration with petroleum ether. The product was chromatographed on silica gel (13 mm × 11 cm) with chloroform as eluent. The first yellowish brown band yield, after being stripped of the solvent, 0.3 g of **18**. Recrystallization from petroleum ether gave an analytical sample, mp 118—119 °C. Identification

was made by comparison of the IR spectrum with that of authentic sample prepared from **1** by the reported method.[4d]

*A Complex of **6** with Antimony(V) Chloride. Formation of **19**:* To a saturated solution of 0.488 g of **6** in dry dichloromethane (2.0 cm^3) were added 4 drops of antimony(V) chloride to precipitate an orange-brown crystalline material immediately, which was washed with a small amount of dichloromethane: IR (suspension in dichloromethane) 1690, 1640, 1500, 1305, 1245, 1195, 1100, 1033, 860, 805, 765, 745, and 580 cm^{-1}.

*Quantitative Analysis of **19**.* To a solution of **6** (0.40 g) in 1 cm^3 of carbon tetrachloride in a dry centrifuge tube (20 mm × 9 cm) sealed with a rubber cup was added 0.75 g of antimony(V) chloride in 1 cm^3 carbon tetrachloride. Precipitated yellow crystals were washed with two portions of carbon tetrachloride (2 cm^3) and the residual solvent was evaporated under reduced pressure on phophorus pentaoxide to give 0.595 g of **19**. The complex was decomposed with 40 cm^3 of 6 M hydrochloric acid to give yellow crystals, which were separated by filtration and washed with a small amount of distilled water. Yield: 0.298 g (96.2%) of **6**. To the aq mother solution was added 0.90 g sodium sulfite and the solution was kept at room temperature for 17 h and then refluxed gently for 1.5 h to remove excess sulfite ion (potassium periodate–starch test paper). The filtrate (50.479 g) was divided into three portions and 20 cm^3 of distilled water was added to each portion, which was titrated with 0.02 M potassium permanganate solution. The average volume of permanganate solution corresponding to the whole filtrate was 19.52 ± 0.29 cm^3 (1.1% in excess of the value calcd for $C_8Cl_6O \cdot SbCl_5$).

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