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Synthesis of Decachloro-4-allylidenecyclopentene and Its Chemistry[1]

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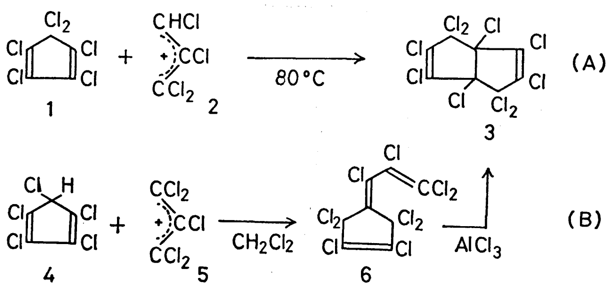
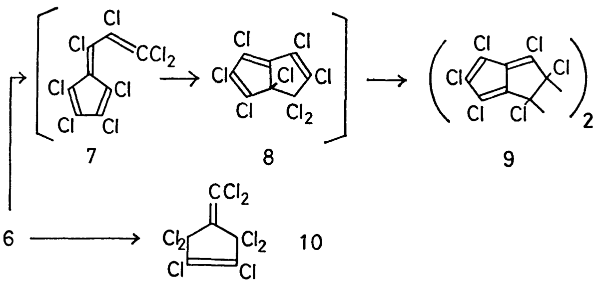
Decachloro-4-allylidenecyclopentene (**6**) was synthesized by the reaction of pentachlorocyclopentadiene with hexachloropropene in the presence of anhydrous aluminium chloride. Hexachloro-2-allylidene-4-cyclopentene-1,3-dione (**11**), prepared from **6** by treatment with concd nitric acid, cyclized to hexachloro-2,5-dihydrocyclopenta[*b*]pyran-5-one (**14**) on heating. In a solvent such as acetone and acetonitrile, **14** rearranged to hexachloro-2,5-dihydrocyclopenta[*b*]pyran-2-one (**18**) at room temperature. The mechanism of this rearrangement is discussed. Hydrolysis of **14** by 90% sulfuric acid afforded tetrachloro-2,5-dihydrocyclopenta[*b*]pyran-2,5-dione (**15**), which was obtained directly from **6** by treatment with sulfuric acid. The reactions of **11** with anhydrous methanol, and of **15** with diazomethane were investigated.

As a part of our study to synthesize new cyclic conjugated chlorocarbons, we have investigated the reaction of 1,1,2,3-tetrachloropropenium cation (**2**) with hexachlorocyclopentadiene (**1**) at 80 °C, obtaining decachlorobicyclo[3.3.0]octa-2,6-diene (**3**).[2] The reaction of pentachloropropenium cation (**5**)[3] with 1,2,3,4,5-pentachlorocyclopentadiene (**4**) has similarly attracted our interest.



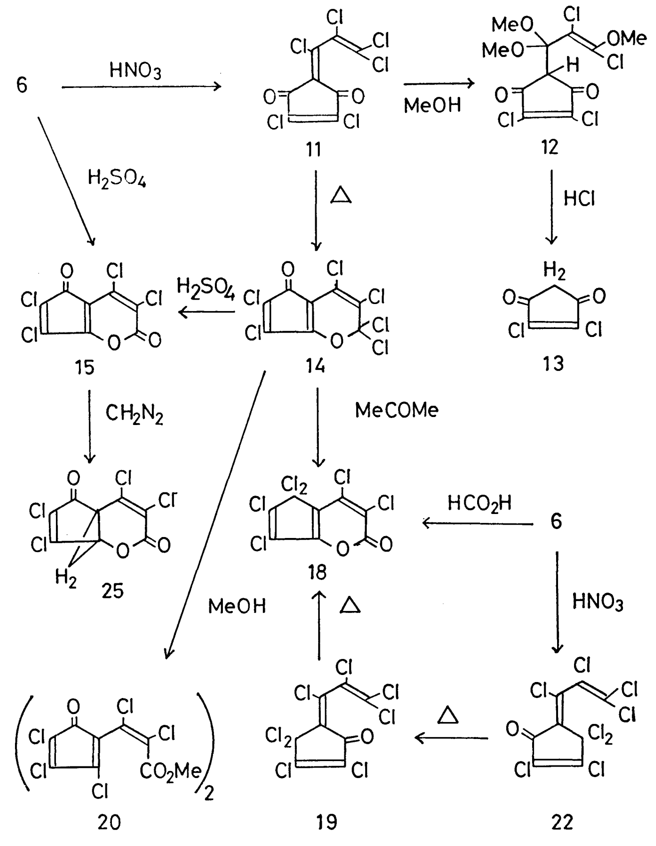
The reaction of **4** with **5** at 80 °C gave a mixture of **3** and a small amount of white crystals of unknown structure (**6**). When the reaction was carried out in refluxing dichloromethane, **6** was obtained in a 87% yield. Treatment of **6** with a catalytic amount of anhydrous aluminium chloride in refluxing carbon tetrachloride afforded **3** quantitatively. This cyclization suggests that **6** is a stable intermediate of reaction B. The mechanism of reaction A seemed to differ from that of B, because **6** could not be detected in the products of reaction A carried out in refluxing dichloromethane. The infrared spectrum of **6** shows three absorptions in the double bond region. Two peaks at 1207 and 1195 cm^{-1} are suggestive of polychlorinated five membered ring, and a peak at 810 cm^{-1} is seemingly due to a double allylic dichloromethylene.[5] The UV spectrum of **6** (Fig. 1) shows that the three double bonds are not fully conjugated. The ^{13}C NMR spectrum of **6** (Table 1) shows the presence of six sp^2 carbons and two doubly allylic dichloromethylene carbons,[6] both of which are under similar circumstances in the molecule.

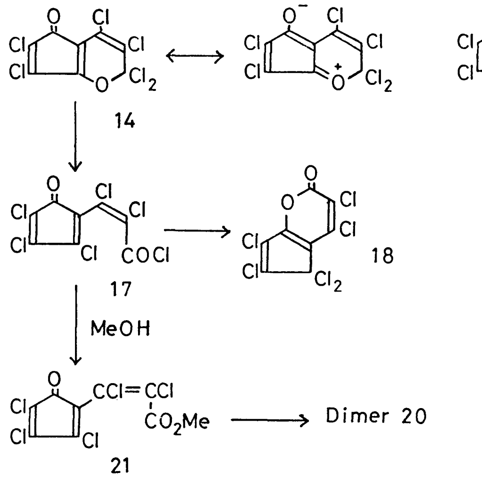
Although chlorination of **6** in carbon tetrachloride was uncuccessful, treatment in liquid chlorine with irradiation by sunlight gave octachloro-4-methylenecyclopentene (**10**).[7] Dechlorination of **6** with copper powder gave brownish red crystals of (**9**), which was identified with an authentic sample of the dimer of hexachloropentalene[3a,8] by their IR spectra. This transformation is well interpreted by assuming intermediary formation of octachloro-6-vinylfulvene (**7**) followed by ring closure and dechlorinative dimerization. Structure **6** is fully consistent with the beforementioned spectral data and its chemical transformations.



When 1,2,3,4-tetrachlorocyclopentadiene was allowed to react with **5** in refluxing dichloromethane, a small amount of octachlorobicyclo[3.3.0]octa-1,4,6-triene[4] was the only product isolated.

Treatment of **6** with 20% fuming nitric acid gave pale yellow crystals. Assignment of the structure (**11**) to the product follows from the elemental analysis, spectroscopic data, and the analogous reaction of **10** to give tetrachloro-2-methylene-4-cyclopentene-1,3-dione.[7] In the reaction of this 1,3-dione with ethanol, an exocyclic dichloromethylene group is eliminated to give (**13**).[9] Therefore, a similar reaction could be expected for **11**, which also has carbonyl groups on both sides of the exocyclic group. By heating 2 h in refluxing methanol, **11** was converted to the compound $C_{11}H_{10}Cl_4O_5$, the spectral data of which point to a monoketalized triketone (**12**) as shown. An attempted hydrolysis of the ketal group with hydrochloric acid in refluxing methanol gave a cyclopentenedione **13**.[10] Identification of the product with an authentic sample was carried out by measurement of the mixed melting point and comparison of their IR spectra. The results suggests intermediary formation of an unstable triketone. When **11** was heated in refluxing carbon tetrachloride under anhydrous conditions, deep red crystals of (**14**) were formed in high yield. Assignment of the structure **14** was based on its IR, UV, and ^{13}C NMR spectra as well as on its formation from **11** and the conversion to (**15**) by 90% sulfuric acid.





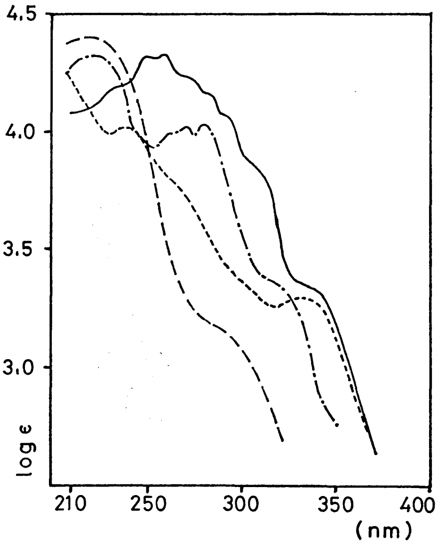


Fig. 1. Ultraviolet spectra of **6**, **11**, **19**, and **22** : — — — **6**; —— **11**; ------ **19**; —·—·— **22**.

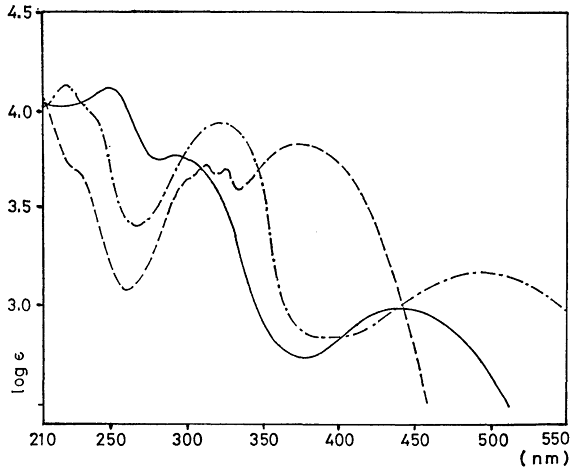


Fig. 2. Ultraviolet spectra of **14**, **15**, and **18** : —— **14**; —·—·— **15**; — — — **18**.

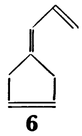
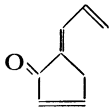
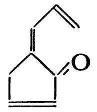
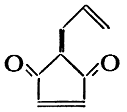
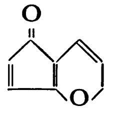
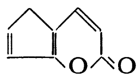
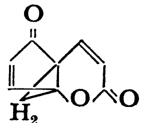
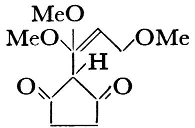
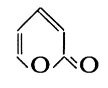
The formation of **14** is significant in view of the mechanism of 1,5-pentadiene-oxygen rearrangements.[12] Because the pyran **14** is stabilized by mesomerism,[1] 1,5-sigmatropic chlorine shift followed by ring opening of the second pyran intermediate (**16**) to an acyl chloride (**17**) is not so favored.

Crystalline **14** decomposed slowly in the air with evolution of hydrogen chloride; however, the solution of **14** in a nonpolar solvent was stable in a dark place. In a polar solvent such as acetone, ethyl acetate, and acetonitrile, an unexpected rearrangement occurred leading to (**18**) at room temperature. Figure 2 shows UV spectra of these compounds. The longest wavelength maxima of both **14** and **15** seem to be due to a cyclopentadienone chromophore.[13] The broad maximum of **18** at 380 nm is due to polychlorinated α-pyrone.[14] Cyclization of (**19**) under mild conditions, resulting in the formation of **18**, and the spectral data indicated the double bond location and the presence of α-pyrone ring in **18**.

When anhydrous methanol was added to **14**, a moderate exothermal reaction took place to afford white crystals, $C_{18}H_6Cl_{10}O_6$ (**20**). Although the structure is unknown, the high resolution mass spectrum of **20** indicates that it is a dimer of (**21**), $C_9H_3Cl_5O_3$, which corresponds to the base peak of the mass spectrum. Plausible mechanisms for the formation of **18** and **20** could be outlined as follows. In a polar solvent, a chlorine migration followed by ring opening takes place, giving an acid chloride **17**, which either reacts with methanol and dimerizes to **20** or, without any reactive materials in the reaction medium, cyclizes to **18**.

On the other hand, the reaction of **6** with dilute nitric acid yielded a pale yellow monoketone (**22**). The transformation is similar to that of **10** with nitric

TABLE 1. ^{13}C DATA OF SELECTED COMPOUNDS[a,b)]

Compound No.	>C=O	>=<	Saturated
 **6**	c)	139.8 137.8 135.5 135.3 128.1 122.1	80.9 82.0
 **22**	d) 174.4	158.5 141.6 137.6 135.4 126.8 123.4	80.7
 **19**	e) 162.0	138.9 137.6 134.2 132.4 128.9 128.0	83.0
 **11**	c) 180.2 179.3	153.7 151.4 140.7 128.2 127.3 124.6	
 **14**	f) 180.3	163.4 149.3 143.8 131.6 130.8 122.6	121.7
 **18**	c) 156.9	155.5 144.2 143.8 126.9 121.1 119.5	80.4
 **25**	g) 185.0 155.3	144.4 129.6 123.7	70.0 43.9 34.4
 **12**	h) 179.5 164.6	156.1 143.3 137.6 128.9	103.4 77.2 54.5 53.7 51.8
 **11**	i) 153.3	146.6 144.8 120.2 112.4	

a) All positions are substituted by chlorine unless indicated. b) Spectra were run in the solvent cited and the data reported in ppm downfield from external TMS converted from the solvent internal standand using (CD_3COCD_3) methyl carbon 29.7, (dioxane) 67.4, (CCl_4) 94.0, $(CDCl_3)$ 76.9, (CH_3COCH_3) methyl carbon 30.4, $(CHCl_3)$ 77.2, (C_6D_6) 128.0 (Ref. 25, p. 23); accuracy ±0.1 ppm. c) CD_3COCD_3. d) Neat sample; dioxane was used as an external standard. e) CCl_4. f) $CDCl_3$. g) CH_3COCH_3. h) $CHCl_3$. i) C_6D_6.

acid or sulfuric acid.[7)] Although **22** was stable at room temperature or during the chromatographic separation, vacuum distillation at 180 °C or heating in refluxing carbon tetrachloride promoted an (*E*)-(*Z*) rearrangement to **19**. In contrast to the (*E*)-ketone **22**, **19** cyclized to **18** during chromatographic separation on silica gel or in the air with the gradual liberation of hydrogen chloride. These chemical behavior as well as the IR, UV, and ^{13}C NMR spectra of both monoketones support the proposed structures. Reaction of **6** with fuming sulfuric acid yielded **15** and two kinds of dimers $C_{16}Cl_8O_6$, (**23**) and (**24**) of unknown structure, which could be distinguished by the IR spectra. It is interesting that **15** gave **23** in ether, while it gave **24** in acetone-d_6 at room temperature.

Since the 1,3-dipolar cycloaddition of diazomethane to tetraphenylcyclopentadienone has been reported,[16)] we wanted to compare the reactivity of the two double bonds in the cyclopentadienone moiety of **15**. The structure (**25**) was assigned on the basis of its high resolution mass, IR, ^{1}H NMR, ^{13}C NMR, and UV spectra. The latter shows one absorption maximum at 257 nm, indicating the existence of α,β-unsaturated carbonyl chromophore. Addition of diazomethane[17)] preferentially at the middle double bond of **15** may be explained in terms of the cationic quasi-aromatic character of the α-pyrone moiety.

Experimental

General. The melting points were determined on a Yanagimoto micro melting point apparatus and were uncorrected. Elemental analyses of carbon, hydrogen, and nitrogen 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.[18)] IR spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer as mulls in Nujol betweeen NaCl disks or as a solution of carbon tetrachloride. Only significant absorptions are reported. UV spectra were recorded on a Hitachi EPS-20 spectrophotometer as solutions in hexane. Nuclear quadrupole resonance spectra were recorded on a Decca Radar NQR spectrometer at 77 K. Both proton and ^{13}C NMR spectra were recorded on a JEOL FX-60 Fourier transform NMR spectrometer. Gas chromatographic analyses were performed on a Nikki Model G-77 gas chromatograph using a 2 m 10% SE-30 column with helium flow. Mass spectra were recorded on a JEOL JMS-D 300 high resolution mass spectrometer.

Decachloro-4-allylidenecyclopentane (6). To a solution of 50.3 g(0.211 mol) of hexachloropropene[20)] in 50 ml of dried dichloromethane was added 2.0 g of powdered anhydrous aluminium chloride,[21)] and the mixture was stirred at room temperature. Owing to an exothermal reaction, the mixture began to reflux after several minutes with the evolution of hydrogen chloride.[22)] After the exothermal reaction had come to an end, the mixture was heated to reflux for 2 h with mechanical stirring . After having been kept at room temperature over night, the reaction mixture was poured into ice-water to decompose the complex. The organic layer was separated and the water solution was extracted with carbon tetrachloride. The combined solution was dried over anhydrous sodium sulfate and filtered, and evaporation of the solvent under reduced pressure afforded sludge. Crystals precipitated from the sludge by the addition of ethanol were collected by vacuum filtration. Yield: 71.1 g. After the mother solution was evaporated under reduced pressure, the residue was distilled at 150 °C under 30—36 mmHg to collect a mixture of the starting materials (44.7 g). Crude **6**(13.4 g) was obtained from the crystalline residue by washing with ethyl alcohol. Total yield was 84.5 g(89%). Recrystallization from ethyl acetate gave an analytical sample. Mp 108 °C;[23] IR: 1648, 1620, 1565(–C=C–); UV: λ_{max} (nm, log ε) 221(4.41), 285(3.09); NQR: (MHz) (77 K) 37.220, 37.607. 37.618, 38.026, 38.100, 38.262, 38.520, 38.733, 38.854, 38.975; (Found: C, 21.47; Cl, 78.45%).

*Chlorination of **6** in Liquid Chlorine.* In an annealed glass tube (wall thickness: 4 mm, outside diameter: 19 mm × 180 mm), 10.0 g(2.22×10^{-2} mol) of **6** and about 10 ml of liquid chlorine were sealed at −70 °C. The mixture was exposed to the sunlight for two weeks at Osaka in May, giving a transparent liquid chlorine solution. Having been chilled in a Dry Ice–acetone bath, the tube was opened. The chlorine was allowed to evaporate at room temperature under atmospheric pressure and finally under reduced pressure by using an aspirator, and the light yellow residue was distilled at 150 °C(bath)/0.5 mmHg. The crystals which appeared in the distillate on standing at room temperature were collected by filtration, and washed with a small amount of ethanol. Yield : 3.9 g. The product was identified as octachloro-4-methylenecyclopentene by comparison of the IR spectrum with that of an authentic sample.[7]

*Dechlorination of **6** with Copper Powder.* A mixture of 5.0 g(8.0×10^{-2} g·atom) of copper powder and 9.0 g(2.0×10^{-2} mol) of **6** in petroleum ether (bp: 30—50 °C) was heated to gentle refluxing with brisk mechanical stirring for 4 days. Insoluble materials were removed by filtration and washed with hot petroleum benzine (bp : 100—140 °C). The solvent was evaporated under vacuum and the residue was triturated with a mixture of petroleum benzine and ethyl alcohol, giving 4.6 g of brown powder. The crude product was dissolved in chloroform and then the small amount of insoluble materials was removed by filtration. After the red solution had been concentrated, petroleum ether was added to precipitate orange crystals. The mother solution was cooled in an ice-bath, and the crystals which precipitated from the solution were collected by filtration. The product was identified as a dimer of hexachloropentalene by means of its IR spectra.

*Isomerization of **6**.* To a solution of 3.22 g(1.6×10^{-2} mol) of **6** in 10 ml of carbon tetrachloride was added a catalytic amount of anhydrous aluminium chloride. The greenish color of a complex appeared immediately. The mixture was heated to gentle reflux with mechanical stirring for 6 h. The reaction mixture was treated in the usual way, giving 3.60 g of light brown crystals of **3**, from which a pure sample was obtained by washing with methanol.

*(E)-Octachloro-5-allylidene-2-cyclopenten-1-one (**22**).* A mixture of 5.0 g(11 mmol) of **6** and 15.0 mol of the nitric acid solution prepared by mixing 50 ml of fuming nitric acid (d=1.52) and 10 ml of nitric acid (d=1.38) was stirred for 40 min at room temperature(19 °C). The reaction mixture was poured into ice–water and the organic products were extracted with carbon tetrachloride. The solution was dried over sodium sulfate and evaporated under reduced pressure, giving 5.2 g of a yellow oily product. Addition of petroleum ether to the product precipitated 1.8 g of **6**, which was removed by means of vacuum filtration. The mother solution was chromatographed on a 22 mm × 35 cm column of silica gel (Mallinckrodt, 100 mesh) by use of petroleum ether at the beginning, followed by 5% acetone in petroleum benzine as an eluent. Unreacted **6** (0.52 g) was obtained from the first band. The second fraction, containing **6** and **22** was followed by a band containing 2.2 g of pure **22**. Evaporation of the solvent under reduced pressure at room temperature gave an analytical sample. IR: 1735 (>CO), 1640, 1590, 1570 (–C=C–), 1240, 1190, 800, 720, 710; UV: λ_{max} 224(4.30), 262 sh(3.91), 272(3.98), 281(3.99), 290sh(3.86), 310sh(3.39), 322sh(3.30); ^{13}C NMR : see Table 1. Found: C, 23.92; H, 0.16%. Calcd for C_8Cl_8O: C, 24.28%.

*(Z)-Octachloro-5-allylidene-2-cyclopentene-1-one (**19**).* 518 mg of **22** that had been purified by column chromatography on silica gel was sealed in a small glass tube. The tube was heated to 100 °C for 6 h in a water bath. The ampoule was opened and the oily product was taken up in petroleum ether. This solution was chromatographed on a column (13 mm × 10 cm) of silica gel by use of 50 ml of petroleum ether and then 40 ml of 3% acetone in petroleum ether as eluent. Pure **22** (180 mg) was recovered by evaporation of the first yellow eluate (25 ml). The second (20 ml) and the third(25 ml) fractions afforded small amounts of oily materials. A subsequent fraction, obtained from the deep yellow band, afforded 318 mg of **19**. Monoketone **22** isomerized to **19** on distillation at 170—180 °C(bath) under a pressure of 2 mmHg. IR: 1760(>CO), 1630, 1590, 1545 (–C=C–), 1230, 1155, 1105, 800, 710; UV: λ_{max} 240(4.00), 330(3.30); ^{13}C NMR: see Table 1. Found: C, 24.76; H, 0.12; Cl, 71.89%. Calcd for C_8Cl_8O: C, 24.28; Cl, 71.68%.

*Reaction of **22** with Anhydrous Aluminium Chloride.* A mixture of 50 mg of **22** and 50 mg of anhydrous aluminium chloride in 5 ml of dried carbon tetrachloride was refluxed for 4.5 h. The reaction complex was quenched by pouring into ice-water. The product, isolated by conventional extraction procedures, was crude **18**, which was purified by recrystallization from petroleum ether.

*Reaction of **6** with 89% Formic Acid; Hexachloro-2,5-dihydrocyclopenta*[b]*pyran-2-one (**18**).* A mixture of 5.0 g (1.1×10^{-2} mol) of **6** and 20 ml of commercially available formic acid(98%) was heated to gentle reflux with stirring for 3 h. The deep yellow reaction mixture was cooled to room temperature, precipitating black materials. The oily black mateirals separated from the formic acid solution by decantation, were triturated in a small amount of methanol to give 1.1 g of slightly gray crystals of **3**. The formic acid solution was diluted with 150 ml of water, and extracted 4 times with chloroform. The extract(50 ml) was washed with water, dried over anhydrous sodium sulfate, and evaporated *in vacuo*. The oily residue (1.77 g) solidified on standing at room temperature. The water layer was further extracted twice with ether, and the solvent was evaporated to yield 0.67 g of **18**. The combined crystals were recrystallized twice from a mixture of benzene and petroleum ether and once from benzene ; mp 117 °C. The mother solution containing crude product was chromatographed on a silica gel column by using chloroform as an eluent. The crystals obtained from the first fraction were recrystallized from petroleum ether to give an analytical sample, mp 118—120 °C. IR: 1745 broad(CO), 1610, 1560, 1500(–C=C–), 1405, 1360, 1188, 1178, 1132, 895, 883, 805; UV: λ_{max} 230 sh(3.75), 305sh(3.66), 317(3.74), 330(3.71), 380(3.85); ^{13}C NMR: see Table 1. Found: C, 28.30; H, 0.07%. Calcd for $C_8Cl_6O_2$: C, 28.20%.

*Reaction of **6** with Fuming Nitric Acid; Hexachloro-2-allylidene-4-cyclopentene-1,3-dione (**11**).* A mixture of 10 g (2.2×10^{-2} mol) of **6** and 30 ml of fuming nitric acid(d=1.53) was placed in a 100 ml Erlenmeyer flask equipped with a magnetic stirring bar and a thermometer. The stirred mixture was heated on a hot plate. The temperature went up to 55 °C after 5 min, and the nitric acid began to reflux after 10 min. The homogeneous reaction mixture obtained by heating for 12 min was poured onto ice–water to precipitate a light yellow oily product. The organic materials were taken up in carbon tetrachloride and dried over sodium sulfate, and the solvent was evaporated on a rotary evaporator at room temperature. The residue (7.1 g) crystallized on standing at room temperature. Washing twice with methanol gave an analytical sample. Mp 88—92 °C; IR: 1710 (>CO), 1630, 1590 (-C=C-); UV: λ_{max} 230sh (4.16), 248(4.32), 255.5(4.32), 267sh(4.21), 277sh(4.16), 288sh(4.05), 300sh(3.84), 330sh(3.33); ^{13}C NMR: see Table 1. Found: C, 27.93; Cl, 61.66%. Calcd for $C_8Cl_6O_2$: C, 28.20; Cl, 62.42%.

*Reaction of **11** with Methanol.* A mixture of 4.03 g (1.18×10^{-2} mol) of **11** and 15.0 ml of anhydrous methanol was heated to gentle reflux for 2 h. The solution was concentrated under vacuum, affording a mixture of sticky oily substance and crystals. Washing the mixture with methanol yielded 0.82 g of white crystals of **12**. Recrystallization twice from petroleum benzine gave an analytical sample. Mp 110—111.5 °C; IR; 1740, 1710(>CO), 1640, 1595(-C=C-), 1450, 1310, 1250; UV: λ_{max} 218—220 (4.13), 285(4.06); ^{13}C NMR: see Table 1. Found: C, 36.55; H, 2.75%. Calcd for $C_{11}H_{10}Cl_4O_5$: C, 36.30; H, 2.70%.

*Reaction of **12** with Methanolic Hydrochloric Acid.* A mixture of 3 ml of methanol, 3 ml of concd hydrochloric acid, and 0.264 g (7.95×10^{-4} mol) of **12** was heated to reflux with stirring for 2 h. The reaction mixture was allowed to stand at room temperature, giving colorless needles, which were collected by filtration. Sublimation under reduced pressure gave 81 mg of a pure sample of **13**, mp 167—168 °C, which was identified as the authentic sample by means of infrared spectra.

*Thermal Reaction of **11** : Hexachloro-2,5-dihydrocyclopenta*[b]*pyran-5-one (**14**).* A solution of 2.5 g (7.3×10^{-3} mol) of **11** in 25 ml of carbon tetrachloride was heated to reflux for 1.25 h, to give a deep red solution. Evaporation of the solvent and recrystallization of the residue from petroleum benzine afforded an analytical sample. Mp 96.5—100 °C; IR: 1745(>CO), 1620, 1575, 1510(-C=C-), 1250, 1180, 1145, 1100; UV: λ_{max} 254 (4.11), 302 (3.76), 445 (2.97); ^{13}C NMR: see Table 1. Found: C, 28.51; H, 0.15; Cl, 62.40%. Calcd for $C_8Cl_6O_2$: C, 28.20; Cl, 62.42%.

*Reaction of **12** with Anhydrous Methanol.* When 10 ml of absolute methanol was added to 2.053 g of **12**, an exothermal reaction took place immediately, giving a yellow precipitate. The crude product (0.20 g) was separated by filtration and recrystallized from ethyl acetate. Mp 245—246 °C; IR : 1755, 1730, 1725 sh (>CO), 1645, 1575 (-C=C-), 1445, 1390, 1290, 1270; Mass: *m/e* 667.7243 (M^+, 31.4), 333.8522 (100); Found: C, 32.13; H, 0.92%. Calcd for $C_9H_3Cl_5O_3$: C, 32.14; H, 0.90%.

*Reaction of **14** with Concd Sulfuric Acid.* To a solution of 100 mg (2.93×10^{-4} mol) of **14** in 1 ml of carbon tetrachloride was added 4 ml of 90% sulfuric acid, and the mixture was vigorously stirred with a magnetic stirrer for 6 h at room temperature. After the addition of water, the organic product was separated and extracted with carbon tetrachloride. The combined solution was washed with water and dried over sodium sulfate. Evaporation of the solvent left 96 mg of crude **15**, which gave 45 mg of pure **15** by washing with a small amount of petroleum ether.

*Reaction of **6** with Sulfuric Acid ; Hexachloro-2,5-dihydrocyclopenta*[b]*pyran-2,5-dione (**15**).* To a mixture of 20 ml of 98% sulfuric acid and 90 g of 20% fuming sulfuric acid was added 32.0 g (7.1×10^{-2} mol) of powdered **6**, whereupon a mild exothermal reaction took place and the mixture changed from dark green to brownish red during 3 h stirring. The mixture was stirred for an additional 45 h at room temperature, and poured onto ice. The precipitated brown solid was isolated by vacuum filtration and washed with water. After being dried overnight, the crude product was 25.5 g in weight. Carbon tetrachloride (200 ml) was added to the powdered product and the suspension was heated to reflux for a short time. Insoluble white crystals were separated by vacuum filtration, and the mother solution was concentrated. The addition of petroleum ether to the solution afforded dark reddish-brown crystals of **15**. Compound **15** dimerizes at approximately 180 °C without melting. IR : 1750 sh, 1730 (>CO), 1625, 1570, 1510 (-C=C-), 1390, 1340, 1160, 1130; UV: λ_{max} 228 (4.16), 332 (3.93), 240 sh (4.04), 488 (2.72); Mass: *m/e* 284 (M^+, 16.2), 256 (19.9), 221 (18.0), 200 (3.9), 193 (4.5), 165 (20.6), 87 (54.4), 43 (100); Found: C, 33.33; H, 0.23; Cl, 49.12%. Calcd for $C_8Cl_4O_3$: C, 33.61; Cl, 49.60%.

The product, which was insoluble in hot carbon tetrachloride, was extracted with 300 ml of benzene by the use of Soxhlet apparatus. The crystals which appeared in the benzene extract were removed by filtration and separated into two parts, powdery crystals **23** and rather big crystals **24**, according to their crystal shape. Compound **23**; mp 337 °C dec; IR: 1788, 1735, 1612, 1535, 1380, 1312, 1195; Found: C, 33.69; H, 0.37; Cl, 50.48%. Calcd for $C_8Cl_4O_3$: C, 33.61; Cl, 49.60%. Compound **24**; 335 °C dec; IR: 1790, 1750, 1617, 1532, 1380, 1310, 1195; Found: C, 33.04; H, 0.22; Cl, 49.60%. Calcd for $C_8Cl_4O_3$: C, 33.61; Cl, 49.60%. Mass: *m/e* 568 (M^+, 5.3), 533 (5.3), 505 (8.6), 371 (18.0), 343 (18.4), 284 (100), 256 (15.8).

Thermal decomposition of **23** was carried out under vacuum in a sublimation apparatus, and reddish brown crystals of **15** were collected on the cold finger condenser. Recrystallization of the product from a mixture of chloroform and petroleum benzine gave a mixture of **23** and **15**.

*Reaction of **15** with Diazomethane: 4,5,8,9-Tetrachloro-2-oxatricyclo[4.3.1.0^{1,6}]deca-4,8-diene-3,7-dione (**25**).* The ether solution of diazomethane, which had been prepared from 5.0 g of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide according to the conventional method,[24] was added to a suspension of 0.5 g (1.75×10^{-4} mol) of **15** in 5 ml of ether until the red solution became orange. About 1/3 of the diazomethane solution was needed. Excess diazomethane was decomposed with acetic acid, and the reaction mixture was worked up in the usual way. Evaporation of the solvent left a sticky light brown material, which was taken up in 3 ml of benzene, and the solution was chromatographed on a column (12 mm × 12 cm) of silica gel by using benzene. The benzene of the eluate was evaporated under vacuum, and the residue was recrystallized twice from a benzene-petroleum ether mixture. Yield: 0.22 g; IR: 3085 ($-CH_2-$), 1760, 1730(>CO), 1610, 1590(-C=C-), 1360, 1310, 1030; UV: λ_{max} 257 (4.08); ^{13}C NMR: see Table 1. ^{1}H NMR: ($CDCl_3$) 2.23 (d), 2.70 (d), $|J_{AB}| = 6.1$ Hz. Mass: *m/e* 297.8749 (M^+, 34.0), 269.8806 ($M^+ - CO$, 32.5), 262.9078 ($M^+ - Cl$, 49.3), 51 (100); Found: C, 35.83; H, 0.90%. Calcd for $C_9H_2Cl_4O_3$: C, 36.04; H, 0.67%.

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References

1) A preliminary report of this work was presented at the 26th IUPAC Congress, Tokyo, 1977; Abstracts of Papers, Sections 4 and 5, p. 1001; see also K. Kusuda, A. Roedig, and G. Bonse, *Chem. Lett.*, **1977**, 819.

2) K. Kusuda, M. Endo, R. West, and V. N. M. Rao, *J. Org. Chem.*, **39**, 1641 (1974).

3) R. West and P. T. Kwitowski, *J. Am. Chem. Soc.*, **88**, 5280 (1966).

4) a) A. Roedig, G. Bonse, and R. Helm, *Chem. Ber.*, **106**, 2156 (1973); b) K. Kusuda and N. Osaka, *J. Chem. Soc., Chem. Commun.*, **1972**, 508.

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

6) R. C. Griffith, D. M. Grant, and J. D. Roberts, *J. Org. Chem.*, **40**, 3726 (1975).

7) A. Roedig, *Ann.*, **569**, 161 (1950); E. T. McBee, H. E. Ungnade, H. Rakoff, and K. Dinbergs, *J. Am. Chem. Soc.*, **77**, 4379 (1955).

8) K. Kusuda and M. Endo, unpublished work.

9) E. T. McBee, C. W. Roberts, and K. Dinbergs, *J. Am. Chem. Soc.*, **78**, 491 (1956).

10) T. Zinke and A. Rhode, *Ann.*, **299**, 371 (1897); A. Roedig and L. Hörnig, *Chem. Ber.*, **88**, 2003 (1955).

11) A. Roedig and G. Märkl, *Ann.*, **636**, 1 (1960); A. Roedig and G. Märkl, *Chem. Ber.*, **95**, 2852 (1962).

12) A. Roedig, H. Göpfert, and A. A. Renk, *Chem. Ber.*, **111**, 860 (1978); and the references cited therein.

13) E. W. Garbish, Jr., and R. F. Sprecher, *J. Am. Chem. Soc.*, **91**, 6785 (1969).

14) A. Roedig, G. Märkl, and V. Schaal, *Chem. Ber.*, **95**, 2844 (1962); A. Roedig, G. Märkl, and H. Schaller, *Chem. Ber.*, **103**, 1101 (1970).

15) X-Ray crystallographical structural determination of **18** was unsuccessful because the crystal surface quickly became clouded after the crystals were separated from the mother solution. The authors express their sincere thanks to Dr. Tai-ichi Higuchi for the X-ray crystallographic study.

16) B. Eistert and A. Langbein, *Ann.*, **678**, 78 (1964).

17) R. Huisgen, *Angew. Chem.*, **75**, 604 (1963).

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

19) Freshly distilled pentachlorocyclopentadiene should be used; otherwise a dimer of pentachlorocyclopentadiene will contaminate the product.

20) When an equimolar amount of hexachloropropene was used, the yield of the product was decreased, but the method of purification was simpler. Washing the crude product with a 1 : 1 mixture of ethyl acetate and methanol was enough for the synthesis. The yield was 78%.

21) The reaction catalyzed by antimony pentachloride under similar conditions yielded much unreacted materials.

22) For a large scale reaction, it is recommended that the pentachlorocyclopentadiene be introduced into the mixture of hexachloropropene and anhydrous aluminium chloride at a slow speed so as to maintain gentle refluxing of dichloromethane.

23) Compound **6** is identical with the substance of unknown structure (mp 108 °C), which was obtained by the reaction between perchlorocyclopentadiene and perchlorocyclopropene at 180 °C in low yield : D. C. F. Low and S. W. Tobey, *J. Am. Chem. Soc.*, **90**, 2376 (1968). We wish to thank Dr. Tobey for supplying us with the IR and UV spectra of the sample.

24) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John & Wiley Sons, Inc., New York (1967), p. 191.

25) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York (1972).