Octachlorocycloheptatriene and Related Compounds[1]

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Received September 19, 1970

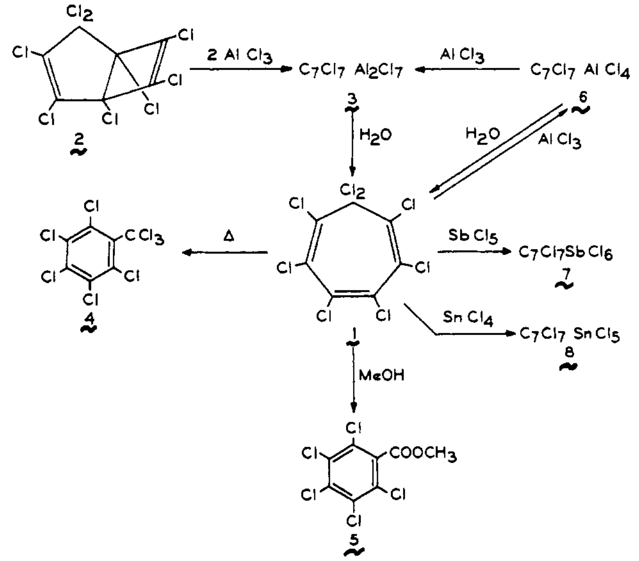
Abstract: Thermal ring expansion of octachlorobicyclo[3.2.0]hepta-2,6-diene (**2**) in the presence of 2 mol of anhydrous aluminum chloride gave heptachlorotropylium heptachlorodialuminate (**3**) which yielded octachlorocycloheptatriene (**1**) upon quenching with water. Evidence for the structure of **1** was obtained from its nuclear quadrupole resonance (nqr) spectrum, mass, ir, uv, and cmr spectra, thermal rearrangement to octachlorotoluene (**4**), methanolysis to methyl pentachlorobenzoate (**5**), and hydrolysis to hexachlorotropone (**9**). Reaction of **1** with other Lewis acids furnished the corresponding heptachlorotropylium cation complexes. Hexabromotropone (**10**) was obtained in good yield from **9** by bromination with boron tribromide. The thermolyses of **9** and **10** were studied by differential scanning calorimetry.

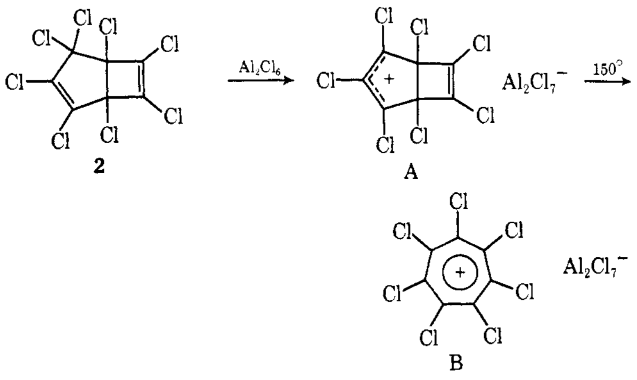
Cyclic conjugated chlorocarbons have recently been the subject of active research.[2] The three-membered ring trichlorocyclopropenium ion, first prepared in 1964,[3] has been of considerable interest both as a very simple aromatic species and as an intermediate for synthesis of other three-membered ring compounds.[2] The corresponding seven-membered ring, heptachlorotropenium ion, was expected to have an equally interesting chemistry.[4] As a starting material for the synthesis of $C_7Cl_7^+$, we have investigated the chemistry of octachlorocycloheptatriene (**1**).

When the known C_7Cl_8 species, octachlorobicyclo[3.2.0]hepta-2,6-diene[5] (**2**), was treated with 1 equiv of aluminum chloride in refluxing dichloromethane, no reaction took place. However, when **2** was heated to 150–155° with 2 equiv of aluminum chloride in the absence of any added solvent, the aluminum chloride dissolved in molten **2**, forming a dark green complex. Careful decomposition of this complex with ice water afforded colorless **1**. For purification, the product was continuously extracted with carbon tetrachloride in a Soxhlet extractor to remove insoluble aluminum salts; evaporation and recrystallization afforded pure **1** in 80% yield.

The mechanism of formation of **1** from **2** apparently involves the abstraction of an allylic chloride ion from **2** by dimeric aluminum chloride[6] to produce cation A.[7] At 150°, the bond joining the bridgehead atoms in A breaks to yield the heptachlorotropylium cation B. The neutral compound **2** does not undergo thermal ring opening below its decomposition temperature; probably the development of aromatic stabilization in the transition state facilitates ring opening in the cation.[8]

Scheme I





Octachlorocycloheptatriene is a stable colorless solid crystallizing in the orthorhombic system.[10] It is freely

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[1] For a preliminary report of this work see R. West and K. Kusuda, *J. Amer. Chem. Soc.*, **90**, 7354 (1968).

[2] R. West, *Accounts Chem. Res.*, **3**, 130 (1970).

[3] S. W. Tobey and R. West, *J. Amer. Chem. Soc.*, **86**, 1459 (1964); R. West, A. Sado, and S. W. Tobey, *ibid.*, **88**, 2488 (1966); R. West and S. W. Tobey, *ibid.*, **88**, 2481 (1966).

[4] W. von E. Doering in "Theoretical Organic Chemistry (Kekule Symposium)," Butterworth, London, 1958, pp 35–48.

[5] A. Roedig and L. Hornig, *Justus Liebigs Ann. Chem.*, **598**, 219 (1956).

[6] The group III halides dissolve readily in many nonpolar solvents in which they are dimeric. See, for example, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Wiley, 1967, p 441.

[7] Allylic chlorines of hexachloropropene and 1,1,2,3,3-pentachloropropene are reactive toward aluminum chloride: (a) R. West and P. T. Kwitowski, *J. Amer. Chem. Soc.*, **88**, 5280 (1966); (b) K. Kirchoff, F. Boberg, and D. Freedman, *Tetrahedron Lett.*, 2935 (1968). However, octachlorocyclopentene and hexachlorocyclobutene were unreactive toward anhydrous aluminum chloride under conditions where the halopropenes afforded the halopropenium ions: R. West and K. Kusuda, unpublished work.

[8] The ring opening of A to B is, however, much slower than the corresponding reaction in the hydrogen series: H. L. Dryden, *J. Amer. Chem. Soc.*, **76**, 2841 (1954). Thermal ring opening of both cyclopentenium cation and cyclobutene are allowed conrotatory processes for hydrocarbons,[9] but polychloro compounds may not follow orbital symmetry rules precisely.

[9] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1969).

[10] We thank Dr. Y. Kushi of Osaka City University, Osaka, Japan, for providing us the crystallographic data for **1**: *a*, 13.0 ± 0.2 Å; *b*, 12.3 ± 0.2 Å; *c*, 7.2 ± 0.2 Å.

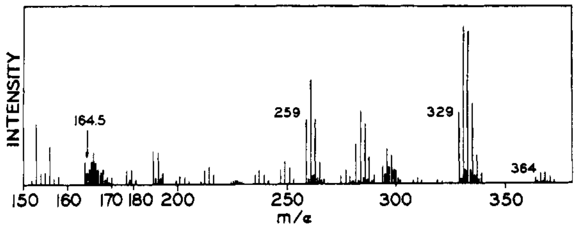


Figure 1. Partial mass spectrum of **1**.

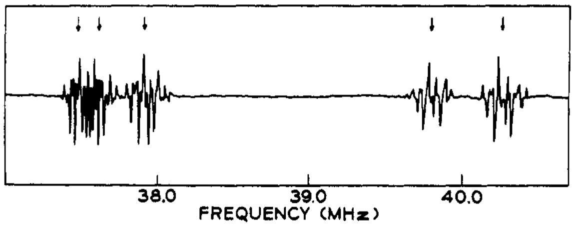


Figure 2. Nuclear quadrupole resonance spectrum of **1** at room temperature.

soluble in most organic solvents, but is insoluble in water. It shows a positive silver nitrate test in ethanol and is unreactive toward bromine in chloroform.

The formula of C_7Cl_8 for **1** is confirmed by elemental analysis and by the mass spectrum (Figure 1), which shows a parent molecular ion at *m/e* 364, base peaks beginning from *m/e* 329 corresponding to $C_7Cl_7^+$, and doubly charged peaks beginning from *m/e* 164.5.[11]

The structural assignment for **1** is strongly supported both by its nqr spectrum (Figure 2) and its ^{13}C nmr spectrum (Table I). The nqr spectrum of **1** at room temperature showed resonances at 37.35, 37.44, 37.78, 39.78, and 40.35 MHz, in an approximate ratio of 2:2:2:1:1. The lines at 37.35–37.78 are in the proper region for vinylic chlorines[12] whereas the lines at 39.78 and 40.35 MHz suggest two nonequivalent chlorine atoms in a CCl_2 group, as might be expected for the nonplanar molecule **1a**. The spectrum, as well as the chemistry of **1**, is clearly incompatible with structure **1b** which would exhibit an abnormally low-field ionic chlorine or the norcaradiene structure **1c** which should show only four vinylic chlorine resonances and four resonances for chlorine atoms attached to saturated carbons.

Table I. ^{13}C Nuclear Magnetic Resonance Spectral Data of **1** and Cycloheptatriene

Carbon	C_7Cl_8 (**1**)[a]	C_7H_8[a]	Δ
C(7)	106.5	163.7	−57.3
C(1,6)	61.8	71.3	−9.5
C(2,5)	56.9	65.1	−8.2
C(3,4)	56.5	60.9	−4.4

[a] Parts per million upfield from CS_2.

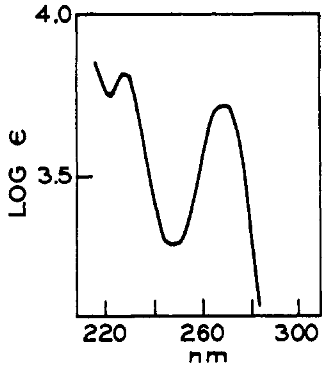
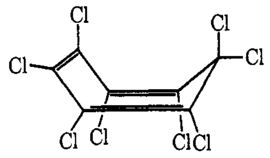
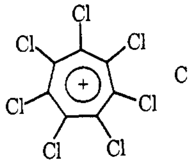


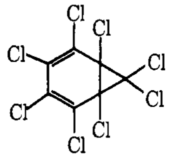
Figure 3. Uv spectrum of **1** in *n*-hexane.



1a



1b



1c

The cmr spectrum of **1** in carbon disulfide shows four resonances at 56.5, 56.9, 61.8, and 106.4 ppm upfield from carbon disulfide in the approximate ratio of 2:2:2:1. The data are quite consistent with structure **1**, which has three equivalent pairs of olefinic carbons and one aliphatic carbon. Comparison of the cmr spectra of **1** and cycloheptatriene shows that the ^{13}C resonant frequency shifts downfield with chlorine substitution (Table I).

In the ultraviolet, **1** shows two bands, as usually found for cycloheptatrienes, at 227 (log ε 3.81) and 268 nm (log ε 3.71). Cycloheptatriene itself exhibits two absorptions at 199 and 261 nm in *n*-heptane;[13] the perhalogenation introduces a small bathochromic shift (Figure 3).

Like most cycloheptatrienes, **1** undergoes ring contraction to afford a benzene derivative. Differential thermal analysis of **1** in an open aluminum capsule showed an endothermic peak at 92° (mp), an exothermic broad peak at 161°, and three other exothermic peaks at 231, 250, and 300°. The exothermic peak at 161° was confirmed as due to the rearrangement of **1** to octachlorotoluene[14] by carrying out the thermolysis on a preparative scale. The other absorptions in the thermogram perhaps originate by the reaction of octachlorotoluene with the aluminum capsule[15] and were not investigated further.

Perhaps the most significant property of **1** is its reaction with metal halides which are strong Lewis acids, to

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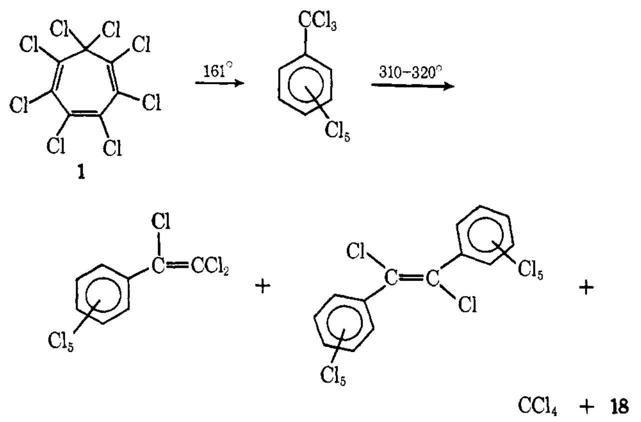
(11) Due to the natural abundance of ^{35}Cl and ^{37}Cl isotopes, there are always peaks higher than the parent ion in the mass spectrum. An isotopically pure peak such as *m/e* 364 does identify the formula as C_7Cl_8 although this peak is not always the highest one. See, for example, J. H. Benon, "Mass Spectrometry and its Application to Organic Chemistry," Elsevier, Amsterdam, 1960, p 298.

(12) A. Roedig, R. Helm, R. West, and R. M. Smith, *Tetrahedron Lett.*, 2137 (1969); R. M. Smith and R. West, *ibid.*, 2141 (1969). The megahertz values reported in ref 1 are slightly in error due to a faulty frequency calibration.

(13) "UV Spectra of Organic Compounds," Butterworths, London, 1968, spectrum No. A 15/4.

(14) M. Ballester and C. Molinet, *Chem. Ind. (London)*, 1290 (1957); M. Ballester, C. Molinet, and J. Castaner, *J. Amer. Chem. Soc.*, **82**, 4254 (1960).

(15) Octachlorotoluene gives perchlorostyrene, hexachlorobenzene, carbon tetrachloride, *trans*-perchlorostilbene, and traces of the cis isomer when heated to 310–320° under a nitrogen atmosphere: M. Ballester, C. Molinet, and J. Rosa, *Chem. Abstr.*, **56**, 8599d (1962).



form salts of the stable heptachlorotropylium cation B. When 1 was mixed with 1 equiv of anhydrous aluminum chloride in dry dichloromethane, precipitation of an insoluble powder began at room temperature. The mixture was heated to reflux for 1 hr to complete the reaction and cooled, and the resulting $C_7Cl_7^+AlCl_4^-$ was isolated by filtration under a nitrogen atmosphere in essentially quantitative yield as a pale yellow powder. Similar 1:1 complexes are formed when 1 is treated with antimony pentachloride or tin tetrachloride.[16] A 1:2 complex of 1 and aluminum chloride was also formed as greenish crystals soluble in dichloromethane when 1 was treated with 2 equiv of anhydrous aluminum chloride in refluxing dichloromethane or when 6 was treated with 1 equiv of anhydrous aluminum chloride. All these salts regenerate 1 in nearly quantitative yield upon quenching with water.[17]

The salts of 1 exhibit essentially identical infrared spectra above 600 cm^{-1}, consisting of just four bands at 1252 (w), 1180 (s), 750 (vw), and 700 (s) cm^{-1}. This extreme similarity clearly indicates the presence of the same type of cationic species in all these salts (Figure 4). At the lower frequency region, absorption bands characteristic of chlorometallate anions are observed.

In addition to its ability to form ionic salts, 1 also exhibits a wide variety of other interesting reactions. Treatment of 1 with excess boron tribromide gave, upon aqueous work-up, the monochloroheptabromo compound 12 as stable brown crystals. The remaining chlorine is most likely in the geminal position and resists replacement for steric reasons. However, if the reaction was carried out with just $^1/_3$ equiv of boron tribromide, a good yield of 7-bromoheptachlorocycloheptatriene (11) was obtained. Compound 11 is a lachrymatory solid which undergoes further bromination to afford 12 and reacts with methanol to yield 5. Exchange of chlorine for bromine in chlorocarbons upon treatment with BBr_3 has been discussed earlier.[3] The reaction appears to take place through a chlorocarbon–tetrahaloborate ion pair, so for 1 the initial intermediate is probably $C_7Cl_7^+BBr_3Cl^-$.

Each important band in the infrared spectrum of 11 finds a counterpart at a slightly shorter wavelength in the spectrum of 1. Although an elemental analysis could not be obtained for 11 because of its instability, the great similarity in the infrared spectrum of 1 and 11 and the conversion of 11 to hexachlorotropone with H_2SO_4 clearly indicate the proposed structure.

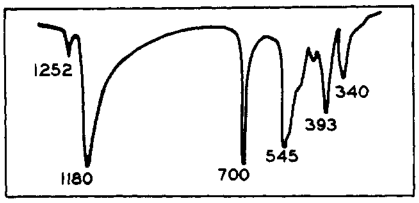
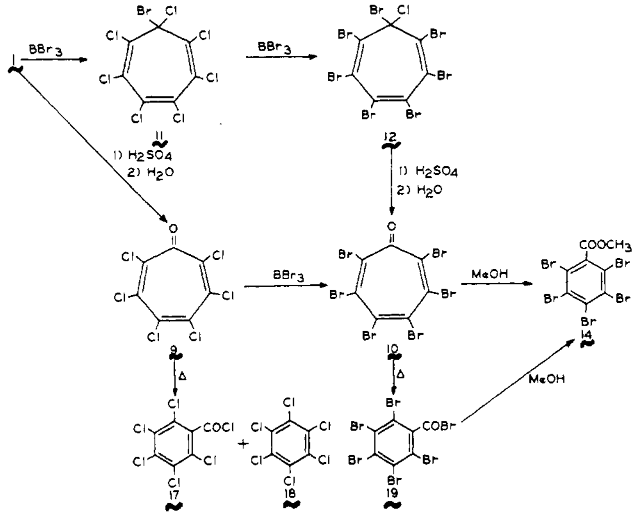
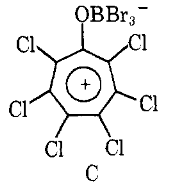


Figure 4. Infrared spectrum of $C_7Cl_7^+Al_2Cl_7^-$ (3).

Scheme II



There is no direct evidence for the structure of 12, but its ultraviolet spectrum and its facile conversion to 10 upon hydrolysis with concentrated sulfuric acid and water rule out a norcaradiene skeleton. Compound 1 gave hexachlorotropone (9)[18] in good yield on treatment with concentrated sulfuric acid, which in turn gave exclusively 10 upon treatment with excess boron tribromide, thus lending support to the structure of 12. Bromination of 9 probably takes place through formation of an intermediate C, in which the C_7 ring bears a substantial positive charge so that halogens are easily exchanged.



C

The structure of 10 follows from a comparison of its ultraviolet spectrum with other known bromotropones[19] (Table II). In addition, 10 reacts with methanol to give a single product, identified as methyl pentabromobenzoate (14), by an independent synthesis from pentabromobenzoic acid[20] and also from pentabromobenzoyl bromide (19), obtained by thermolysis of 10.

The facile rearrangement of troponoids to benzenoid derivatives during pyrolysis has recently been demonstrated.[21] Depending upon the substituent, these sys-

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(16) Attempts to observe an nqr spectrum for salts of 1 or its partially brominated derivatives have so far been unsuccessful. Whether this is due to crystal disorder, poor crystallinity, or other causes is not yet clear.

(17) Regeneration of a chlorocarbon from its aluminum chloride adduct on hydrolysis is frequently observed; see ref 2.

(18) K. Scherer, Jr., *J. Amer. Chem. Soc.*, **90**, 7352 (1968).

(19) T. Nozoe, "Nonbenzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience, New York, N. Y., 1959, p 371.

(20) D. J. Berry and B. J. Wakefield, *J. Chem. Soc. C*, 2342 (1969).

(21) T. Mukai, T. Nakazawa, and T. Shishido, *Tetrahedron Lett.*, 2465 (1967).

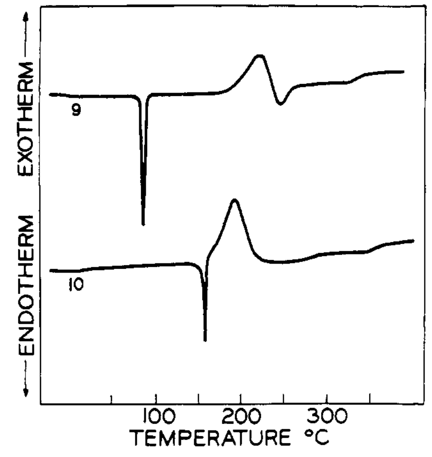


Figure 5. DSC thermograms of **9** and **10**.

Table II. Ultraviolet Spectra of Tropones

Compd	Solvent	λ_{max}, nm (log ϵ)
Tropone[a]	Cyclohexane	225 (4.33), 297 (3.74), 310 (3.67)
2-Bromotropone[b]	Isooctane	243 (4.3), 313 (3.9)
2,4,7-Tribromotropone[c]	Ethanol	270 (4.3), 349 (3.9), 380 (3.5)
Perbromotropone	*n*-Hexane	238 (4.61), 277 (4.54), 345 (3.13), 380 (3.20)

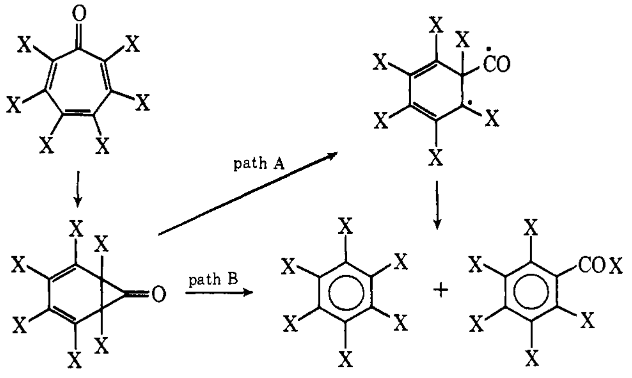
[a] T. Nozoe, T. Mukai, K. Takase, and T. Nagase, *Proc. Jap. Acad.*, **28**, 477 (1952). [b] W. von E. Doering and C. F. Hiskey, *J. Amer. Chem. Soc.*, **77**, 5688 (1952). [c] M. Tsuboi, *Bull. Chem. Soc. Jap.*, **25**, 369 (1952).

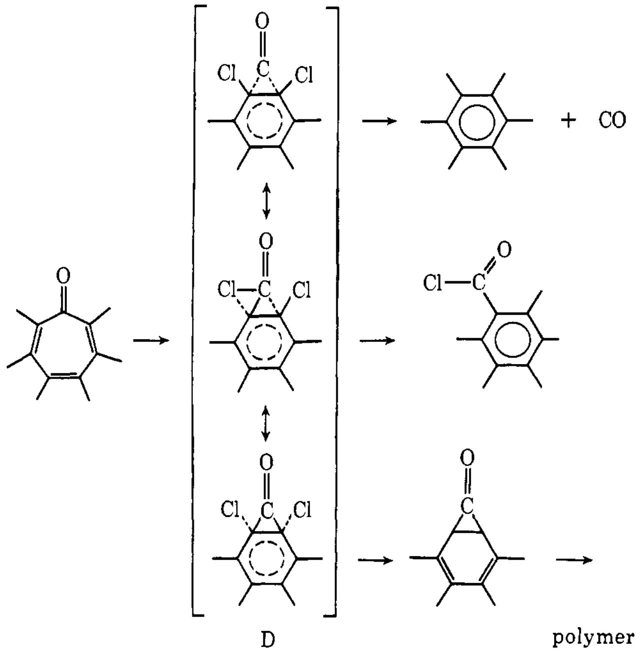
tems have been shown to undergo either decarbonylation or rearrangement or both simultaneously.[22] Hexachlorotropone and hexabromotropone should also behave similarly, and with this in mind, the differential scanning calorimetry of **9** and **10** have been studied. Figure 5 shows the DSC thermograms obtained from **9** and **10**. The rate of heating was arbitrarily selected as 10°/min although reproducible thermograms were obtained at higher heating rates.

The endothermic peaks at 84° (center of the peak) for **9** and 158° (center of the peak) for **10** correspond to their melting points. It is, however, of interest to note that the latent heat of fusion of the two compounds are almost identical (ΔH_f = 2.41 kcal/mol for **9** and 2.39 kcal/mol for **10**). The first exothermic peak in the thermogram of **9** starts at 175° and the reaction is essentially complete at 240°, followed by an unidentified endothermic absorption between 240 and 260°. Similarly in the case of **10**, the first exothermic peak starts at 163°. For **9** the first exothermic peak was established as being due to rearrangement concomitant with fragmentation to a mixture of pentachlorobenzoyl chloride and hexachlorobenzene. Similarly, for **10** the principal rearrangement product was identified as **19**, both reactions being repeated on a preparative scale.

Thermal reaction of 2-halotropones in the temperature range 400–600° shows a decrease in the ratio of benzene–benzoyl halide if the 2 substituent was bromine. The results that we have obtained seem to follow this general trend.

A mechanism has been suggested by Mukai[22] for the thermolysis of 2-substituted tropolones, involving formation of a norcaradienone intermediate which can decompose either to form a diradical (path A) or directly (path B). However, the DSC thermograms of **9** and **10** provide no evidence that the norcaradienone is an intermediate. An alternate possibility is that thermolysis takes place with formation of a bond between the 2 and 7 carbons to give a transition state D in which there is already considerable aromatic stabilization. Decomposition of D could take place to give various products as indicated.





Experimental Section

General. Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded on a Perkin-Elmer Model 237 or 437 recording spectrophotometers as mulls in Nujol or fluorolube between NaCl, KBr, or CsI disks. Ultraviolet spectra were determined on a Cary Model 14 spectrophotometer as solutions in *n*-hexane using 0.5-mm quartz cells. Mass spectra were recorded on a CEC Model 21-103C mass spectrometer equipped with a heated inlet and an AEI MS-902 high-resolution mass spectrometer. Nuclear quadrupole resonance spectra were obtained on a Wilks NQR-1A spectrometer, using a Northeastern Model 14-21C electronic counter to measure frequencies or a Decca Radar Commerical spectrometer. In the Wilks instrument, wherever the center of the envelope due to a single peak was obvious, the frequency at that point was measured with an accuracy of 0.1 MHz. In cases where the center was not obvious, due to overlapping absorptions, the approximate center of the group of absorptions was measured to the same degree of accuracy.

Octachlorocycloheptatriene (1). A mixture of 7.36 g (20 mmol) of **2** and 5.40 g (40.6 mmol) of freshly sublimed, powdered, an-

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(22) T. Mukai, T. Nakazawa, and K. Okayama, *Tetrahedron Lett.*, 1695 (1968).

hydrous aluminum chloride was heated with stirring to a temperature of 150–155° under an atmosphere of nitrogen. The dark green complex that was formed was kept at this temperature for a further 15 min to complete the reaction. The reaction mixture was cooled to room temperature and cautiously added to ice water to precipitate a crude gray solid. The solid was filtered, washed with ice water, pressed dry, and extracted with carbon tetrachloride using a Soxhlet extractor. The CCl_4 extract was dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under reduced pressure. The residue was recrystallized from *n*-hexane to furnish 5.90 g (80%) of colorless orthorhombic crystals of **1**: mp 86°; uv λ_{max} (*n*-hexane) 227 (log ϵ 3.81) and 268 nm (log ϵ 3.71); ir (mull) 1545 (w), 1230 (s), 1148 (s), 1105 (s), 1052 (w), 970 (w), 788 (w), 745 (s), 680 (s), 667 (s), 650 (s), and 615 (w) cm^{-1}. The mass spectrum of **1** (Figure 1) showed a weak molecular ion at *m/e* 364 with a cluster of peaks above it due to the natural abundance of the two chlorine isotopes, and a strong cluster of peaks beginning with a base peak of *m/e* 329 ($C_7Cl_7^+$). The nqr spectrum of **1** (Figure 2) showed resonances at 37.35, 37.44, 37.78, 39.78, and 40.35 MHz in an approximate ratio of 2:2:2:1:1 at room temperature and at 38.00, 38.17, 38.48, 40.39, and 40.90 MHz in approximately the same ratio at 77°K.

Anal. Calcd for C_7Cl_8: C, 22.83; Cl, 77.17. Found: C, 22.94; Cl, 77.07.

Thermal Rearrangement of 1 to Octachlorotoluene (4). An 0.8-g sample of **1** was heated in an evacuated glass tube at 185–190° for 6 hr. The tube was cooled and opened and the contents extracted with pentane. Removal of solvent afforded 0.42 g of a crude oily residue which was recrystallized from ethyl acetate to give 0.28 g of colorless crystals, mp 68–71.5°, whose spectral properties were identical with those of an authentic sample of **4** (lit.[14] mp 71–72°).

Reaction of 1 with Methanol. A mixture of 10 ml of anhydrous methanol and 3.0 g (8.4 mmol) of **1** was refluxed with stirring for 4 hr. The reaction mixture was cooled to 0° and the precipitated solid removed by filtration, washed with cold methanol, and dried under vacuum. The yield of methyl pentachlorobenzoate (**5**), mp 98–100° (lit.[23] mp 97°), was 2.3 g (85.5%).

Heptachlorotropylium Tetrachloroaluminate (6). To a stirred solution of 1.80 g (4.89 mmol) of **1** in 6 ml of dry dichloromethane was added 0.62 g (4.66 mmol) of freshly sublimed, powdered anhydrous aluminum chloride. The slurry was stirred under nitrogen when a white amorphous powder started to separate. After a few minutes at room temperature, the slurry was refluxed gently for 1 hr to complete the reaction. The mixture was then allowed to come to room temperature, and the insoluble pale yellow **6** was filtered under a nitrogen atmosphere, washed with dry dichloromethane, and dried over phosphorus pentoxide under vacuum. The yield was quantitative: ir (mull) 1250 (s, broad), 745 (w), 700 (s), and 495 (s) cm^{-1}.

Anal. Calcd for C_7AlCl_{11}: C, 16.78; Cl, 77.83. Found: C, 16.79; Cl, 78.54.

Heptachlorotropylium Heptachlorodialuminate (3). A mixture of 4.28 g (32.1 mmol) of freshly sublimed, anhydrous aluminum chloride and 5.80 g (15.75 mmol) of **1** in 10 ml of dry dichloromethane was gently refluxed under a nitrogen atmosphere for 30 hr. The pale yellow **6** formed during the initial stages of the reaction redissolved in the dichloromethane to afford a green-brown solution. At the end of the reaction, the solution was filtered under an atmosphere of nitrogen and the solvent was removed under vacuum to yield 9.8 g of crude **3** which was recrystallized from dry dichloromethane and dried over phosphorus pentoxide under vacuum. The infrared spectrum (Figure 4) of **3** as a mull in fluorolube between CsI disks showed absorptions at 1252 (w), 1180 (s, broad), 700 (s), 545 (s), 445 (w), 393 (m), and 340 (m) cm^{-1}.

Anal. Calcd for $C_7Al_2Cl_{14}$: C, 13.25; Cl, 78.24. Found: C, 13.56; Cl, 78.56.

Heptachlorotropylium Hexachloroantimonate (7). To a stirred solution of 2.18 g (7.3 mmol) of antimony pentachloride in 6 ml of dry dichloromethane was added slowly, under a nitrogen atmosphere, a solution of 2.68 g (7.3 mmol) of **1** in 30 ml of dry dichloromethane. The reaction was mildly exothermic and no attempt was made to cool the reaction during addition (15 min). After addition of **1**, the reaction mixture was stirred at room temperature for 1 hr. The precipitated white amorphous **7** (4.66 g) was removed by filtration under a nitrogen atmosphere, washed with dry dichloromethane, and dried under vacuum over phosphorus pentoxide: ir (mull) 1250 (w), 1200 (s), 1185 (s), 700 (s), and 342 (s) cm^{-1}.

Heptachlorotropylium Pentachlorostannate (8). A solution of 3.68 g (10 mmol) of **1** in 10 ml of dry dichloromethane was slowly added, under a nitrogen atmosphere, to a stirred solution of 3.05 g (11.4 mmol) of tin tetrachloride in 5 ml of dry dichloromethane during a period of 10 min. After addition, the solution was gently heated for 10 min when pale yellow **8** was precipitated in essentially quantitative yield. The reaction mixture was cooled, filtered in a drybox, washed with cold dry CCl_4, and dried over phosphorus pentoxide under vacuum: ir (mull) 1250 (w), 1180 (s), 790 (vw), 700 (s), 410 (w), 360 (s), and 300 (s) cm^{-1}.

7-Bromoheptachlorocycloheptatriene (11). To 5.0 g (13.6 mmol) of finely powdered **1** in a 50-ml round-bottomed flask provided with a magnetic stirrer, nitrogen inlet, and dropping funnel was added a solution of 4.0 g (16 mmol) of boron tribromide in 30 ml of dry dichloromethane during 10 min. The mixture was stirred at room temperature for a further 5 min and poured cautiously into 100 g of cracked ice to decompose the boron halides present. The organic layer was separated, and the aqueous layer extracted with two 20-ml portions of chloroform. The combined organic extracts were dried over sodium sulfate and filtered and the solvent was removed under reduced pressure to afford 5.0 g of pale yellow lachrymatory **11**, which was recrystallized from *n*-hexane: mp 93–95°; ir (mull) 1550 (m), 1228 (m), 1144 (s), 1100 (m), 1043 (m), 960 (m), 800 (w), 766 (m), 730 (w), 710 (s), 659 (s), and 630 (s) cm^{-1}.

The mass spectrum of **11** at 20 eV showed only a very weak molecular ion peak. However, a moderately strong cluster was observed starting at *m/e* 373; calcd intensities[11] for $C_7Cl_6Br^+$, M + 2, 293%; M + 4, 351; M + 6, 226%; M + 8, 85%; M + 10, 19%; obsd, M + 2, 290%; M + 4, 350%; M + 6, 220%; M + 8, 85%; M + 10, 20%; A very strong cluster of peaks was observed starting at *m/e* 329; calcd intensities for $C_7Cl_7^+$, M + 2, 228%; M + 4, 223%; M + 6, 121%; M + 8, 40%; found, M + 2, 230%; M + 4, 225%; M + 6, 120%; M + 8, 40%.

7-Chloroheptabromocycloheptatriene (12). Finely powdered **1**, 3.0 g (8.15 mmol), was added cautiously to 12.5 g (50 mmol) of boron tribromide contained in a 50-ml round-bottomed flask under an atmosphere of nitrogen. A moderate exothermic reaction resulted and brownish crystals were formed almost immediately. After addition of **1** (15 min), the reaction mixture was gently refluxed for 10 min, cooled, and cautiously poured into 100 g of cracked ice. A pasty mass, slowly solidifying to a dark yellow-brown solid, was obtained. A single recrystallization from a 25:75 mixture of benzene–*n*-heptane afforded 2.75 g (50%) of **12**: mp 129–132°; ir (mull) 1500 (w), 1190 (m), 1060 (m), 990 (w), and 720 (w) cm^{-1}; uv λ_{max} (*n*-heptane) 226 with a shoulder at 245 nm (log ϵ 4.683 and 4.445).

Anal. Calcd for C_7ClBr_7: C, 12.37; halogen, 87.63. Found: C, 12.27; halogen, 87.63.

Hexachlorotropone (9). A mixture of 10.0 g (27.2 mmol) of finely powdered **1** and 10.0 g of 99% sulfuric acid was stirred at room temperature for 2 hr. The initial greenish yellow suspension that was formed went into solution giving a clear solution attended by gaseous evolution. The temperature of the stirred reaction mixture was raised to 55° for 5 min and the mixture was then cooled to room temperature and carefully poured into cracked ice. The sticky solid that separated was taken up in about 200 ml of ether, washed with water, and dried over sodium sulfate. Removal of the ether under reduced pressure afforded 8.4 g of a bright yellow oil which solidified slowly upon standing. The yield of **9** was almost quantitative. An analytical sample was prepared by recrystallization from pentane, mp 82.5–83.5°. A mixture melting point of this material with an authentic sample of **9**[18] showed no depression in the melting point.

Hexabromotropone (10). In a 50-ml round-bottomed flask provided with a nitrogen inlet, magnetic stirrer, and condenser was placed 1.0 g (3.19 mmol) of **9** and 6.74 g (26.7 mmol) of boron tribromide. The mixture was heated to gentle reflux for 15 min, cooled to room temperature, and cautiously poured into 100 g of cracked ice to decompose the excess boron halides. The aqueous slurry was extracted with about 100 ml of chloroform and the chloroform solution was dried by passing through a column of sodium sulfate. Removal of the chloroform under reduced pressure furnished 1.75 g of **10** as lemon yellow crystals. An analytical sample was prepared by recrystallization from benzene: mp 156–158°; ir (mull) 1700 (s), 1530 (m), 1210 (m), 1080 (m), 960 (m), 825 (w), 710 (w), and 645 (s) cm^{-1}; uv λ_{max} (*n*-heptane) 238

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(log ε 4.613), 277 (log ε 4.536), 345 (log ε 3.126), and 380 (log ε 3.195) nm.

Anal. Calcd for C_7Br_6O: C, 14.50; Br, 82.73. Found: C, 14.59; Br, 82.79.

Pentabromobenzoic Acid from 10. A mixture of 0.5 g of **10** and 5 ml of 95% sulfuric acid was heated at 130–140° for 30 min, cooled to room temperature, and cautiously poured on cracked ice when a brownish solid was precipitated. The crystals were isolated by filtration, dissolved in hot saturated sodium bicarbonate solution, boiled for 10 min with Norit, and filtered and the aqueous filtrate was acidified to give 0.26 g of colorless pentabromobenzoic acid which was recrystallized from aqueous methanol, mp 261–262° (lit.[20] mp 252°). The spectral properties of this material were identical with those of an authentic sample prepared by an independent method.[20]

Hydrolysis of 12 with Sulfuric Acid. A 0.53-g sample of **12** was mixed with 5 ml of 99% sulfuric acid and heated to 50° for 5 min. The resulting intense red solution was filtered through a sintered crucible and poured cautiously into cracked ice. The organic material was taken up in carbon tetrachloride, washed with sodium bicarbonate solution, and dried by passing through a short column packed with anhydrous sodium sulfate. Removal of solvent under reduced pressure afforded 70 mg of a sticky solid which was recrystallized from benzene and whose spectral properties were identical with those of an authentic sample of **10**.

Methanolysis of Hexachlorotropone (9). Methanol (2 ml) was added to 0.33 g of **9** and the mixture was refluxed for 4 hr with stirring. Upon cooling to room temperature, a buff-colored solid precipitated. It was filtered and recrystallized from methanol to give 0.15 g of methyl pentachlorobenzoate, mp 98–101° (lit.[23] mp 97°).

Methanolysis of Hexabromotropone (10). A mixture of 0.4 g of **10** and 7 ml of anhydrous methanol was refluxed for 30 min and filtered while still hot, and the methanol was removed under reduced pressure to afford 0.35 g of white needles of methyl pentabromobenzoate (**14**). An analytical sample was prepared by recrystallization from *n*-hexane, mp 134–136°. A sample of **14** was also independently prepared by the esterification of pentabromobenzoic acid with methanol. The infrared spectra of the two samples were identical.

Anal. Calcd for $C_8H_3O_2Br_5$: C, 18.11; H, 0.57. Found: C, 18.50; H, 0.70.

Thermolysis of 9. A 1.01-g sample of **9** was heated to 200° in an evacuated tube for 5 min, cooled to room temperature, and opened, and the contents were extracted with pentane. The pentane-insoluble material still left in the tube (0.240 g) was extracted with hot benzene and recrystallized from the same solvent to yield fine colorless needles, mp 232–234°, identified as hexachlorobenzene, by comparison of its spectral properties with those of an authentic sample.

The pentane solution on evaporation furnished 0.76 g of crude pentachlorobenzoyl chloride (**17**), whose infrared spectrum was identical with that of an authentic sample of **17** prepared from pentachlorobenzoic acid and phosphorus pentachloride.

Thermolysis of 10. A 1.0-g sample of **10** was placed in a 25-ml flask provided with a calcium chloride guard tube, heated to 180° for 15 min, and cooled, and the residue was taken up in about 10 ml of benzene and diluted with an equal volume of *n*-hexane. The small amount of solid that separated was discarded and the hexane–benzene filtrate was concentrated under reduced pressure to give 0.9 g of a crude sample which was identified as pentabromobenzoyl bromide. It was recrystallized from the same solvent mixture, mp 148–150°. An authentic sample of pentabromobenzoyl bromide was prepared from pentabromobenzoic acid.

Differential Scanning Calorimetry of 9 and 10. Equipment was a Rigaku Denki DSC Model 8001 differential scanning calorimeter. Two methods were employed. (a) A finely powdered 12.0-mg sample of **9** was placed in a flat-bottomed open platinum crucible (diameter 4.8 mm; height, 2.45 mm) and covered with 6.3 mg of calorimeter standard alumina and the thermogram run under air with 19.2 mg of alumina as reference material in a separate capsule at a heating rate of 10°/min.

(b) The experiment was performed as in (a) above, but with 13.6 mg of **10** covered with 7.2 mg of standard alumina. The DSC thermograms have been reproduced in Figure 5. The instrument was standardized on the heat of fusion of standard indium (mp 156.8°, $\Delta H = 0.78$ kcal/mol) in an open aluminum capsule. Total thermicities were measured by integration of the peaks on the thermogram.

Acknowledgments. The authors thank the Public Health Service, National Institutes of Health, for a grant in support of this work. We are also grateful to Professor John D. Roberts and Dr. Robert Smith of the California Institute of Technology for determining the ^{13}C nmr spectrum of **1** and a number of other model compounds.