Pentachloroallyl Cation and Its Salts[1]

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Abstract: The 1:1 complex of hexachloropropene with $AlCl_3$[2] has been shown by infrared spectroscopic studies to be a tetrachloroaluminate salt of the pentachloroallyl cation, $C_3Cl_5^+AlCl_4^-$. The new complexes $C_3Cl_5^+SbCl_6^-$ and $C_3Cl_5^+GaCl_4^-$ have been made from hexachloropropene and the Lewis acids $GaCl_3$ and $SbCl_5$ and shown to have the ionic structures indicated. These salts are partly dissociated into hexachloropropene and free metal chlorides in dichloromethane solution. $C_3Cl_5^+$ appears to be less stable than trichlorocyclopropenium ion, $C_3Cl_3^+$,[3] but more stable than pentachlorocyclopentadienium ion, $C_5Cl_5^+$.[4] The electronic spectra of the three $C_3Cl_5^+$ salts are discussed.

The formation of a bronze-yellow complex from hexachloropropene and $AlCl_3$ was first mentioned by Prins in 1912.[5] In subsequent papers reactions of this material with other chloroolefins were described,[6] and in 1926 Prins reported the isolation and analysis of this compound which proved to be a 1:1 complex (I).[2] However, the structure of the complex has apparently not been investigated.

There are at least three conceivable ways in which hexachloropropene could react with $AlCl_3$ to give different structures for I. (1) A chloride ion could be transferred from C_3Cl_6 to $AlCl_3$, giving a pentachloroallyl tetrachloroaluminate salt, $C_3Cl_5^+AlCl_4^-$. This reaction would be analogous to that of tetrachlorocyclopropene with $AlCl_3$ which yields the stable salt $C_3Cl_3^+AlCl_4^-$.[3] (2) Donor–acceptor bonding from chlorine to aluminum could take place to give a bridged complex, $CCl_2{=}CCl{-}CCl_2\cdots Cl\cdots AlCl_3$. This structure is similar to that proposed for the red complex of hexachlorocyclopentadiene with $AlCl_3$.[7] (3) The Al–Cl bond could undergo addition to the olefinic double bond to give a perchloropropylaluminum compound, CCl_3–CCl_2–CCl_2–$AlCl_2$. Boron trichloride and tin tetrachloride are known to undergo related addition reactions with certain olefins.[8,9]

This paper reports a study of the infrared and electronic spectra of I and of two new hexachloropropene–Lewis acid complexes. Although C_3Cl_6 is unreactive toward many Lewis acids (BCl_3, $SnCl_4$, $FeCl_3$), it forms 1:1 solid complexes with gallium trichloride and antimony pentachloride. C_3Cl_6–$GaCl_3$ was isolated as bronze-yellow crystals resembling those of I, but C_3Cl_6–$SbCl_5$ was obtained as a lemon-yellow powder. All three complexes are intensely reactive, reacting rapidly with alcohols, ethers, olefins, aromatic hydrocarbons, and even saturated hydrocarbons (cyclohexane, mineral oil, polyethylene). They are unreactive toward and insoluble in fully chlorinated or fluorinated solvents. However, the complexes are soluble in dichloromethane, and do not react with this solvent at room temperature.

Infrared Spectra and Structure

Because the hexachloropropene–Lewis acid complexes react rapidly with Nujol, the spectra of the complexes as solids were obtained on mulls made in carbon tetrachloride and in fluorocarbon oil. The infrared spectra of solid I and of pure liquid C_3Cl_6 are shown in Figure 1. Upon formation of the complex I, the C=C stretching band of I at 1550 cm^{-1} disappears and a very strong and broad band centered at 1350 cm^{-1} appears in the spectrum. Another outstanding feature of the spectrum of I is an intense broad adsorption at 480 cm^{-1}.

The infrared spectral frequencies for the solid complexes are listed in Table I. Note that the spectra of all three complexes are essentially *identical* above 500 cm^{-1}, indicating that they must have similar structures. Below 500 cm^{-1}, strong bands are found at 480 cm^{-1} for C_3Cl_6–$AlCl_3$, 405 cm^{-1} for C_3Cl_6–$GaCl_3$, and 345 cm^{-1} for C_2Cl_6–$SbCl_5$. These frequencies are characteristic for the antisymmetric M–Cl stretching frequencies of the corresponding halometal anions, which fall at 480 cm^{-1} for $AlCl_4^-$ in $NaAlCl_4$,[10] 386 cm^{-1} (Raman) for $GaCl_4^-$,[11] and 346 cm^{-1} for $SbCl_6^-$ in $KSbCl_6$. From these results, we conclude that as solids *all three complexes are salts of the pentachloroallyl cation, $C_3Cl_5^+$.*[11a]

Table I. Infrared Bands for Pentachloroallyl Salts

$C_3Cl_5^+$ $AlCl_4^-$	$C_3Cl_5^+$ $SbCl_6^-$	$C_3Cl_5^+$ $GaCl_4^-$	Tentative assignments
3350 (w,b)			O–H stretch
1340 (vs,b)	1320 (vs,b)	1330 (vs,b)	C–C stretch
1140 (m)	1140 (w–m)		Combination
1040 (s)	1040 (s)	1040 (s)	C–C stretch
960 (w–m)	970 (w)		C–Cl stretch?
880 (s)	875 (s)	878 (s)	C–Cl stretch
775 (vs)	760 (vs)	760 (s)	C–Cl stretch
715 (s)	720 (s)	723 (s)	C–Cl stretch
690 (sh)			C–Cl stretch?
480 (vs, b)	345 (vs)	405 (vs)	M–Cl stretch

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[1] Presented before the Organic Chemistry Division, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., April 1966.

[2] H. J. Prins, *Rec. Trav. Chim.*, **51**, 1065 (1932).

[3] (a) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 1459 (1964); (b) R. West, A. Sadô, and S. W. Tobey, *ibid.*, **88**, 2488 (1966).

[4] R. Breslow, R. Hill, and E. Wasserman, *ibid.*, 5349 **86**, (1964).

[5] H. J. Prins, Dissertation, Delft, 1912.

[6] H. J. Prins, *Rec. Trav. Chim.*, 57, 659 (1938).

[7] H. P. Fritz and L. Schafer, *J. Organometal. Chem.* (Amsterdam), **1**, 318 (1964).

[8] F. M. Rabel and R. West, *J. Am. Chem. Soc.*, **84**, 4169 (1962).

[9] F. Joy and F. M. Lappert, *Proc. Chem. Soc.*, 353 (1960).

[10] G. L. Carlson, *Spectrochim. Acta*, **14**, 1291 (1963).

[11] L. A. Woodward and A. A. Nord, *J. Chem. Soc.*, 3721 (1956).

[11a] Note Added in Proof. After this work was completed we learned of the independent observation of pentachloroallyl cation reported by J. O. Turner, Ph.D. Thesis, Pennsylvania State University, 1965.

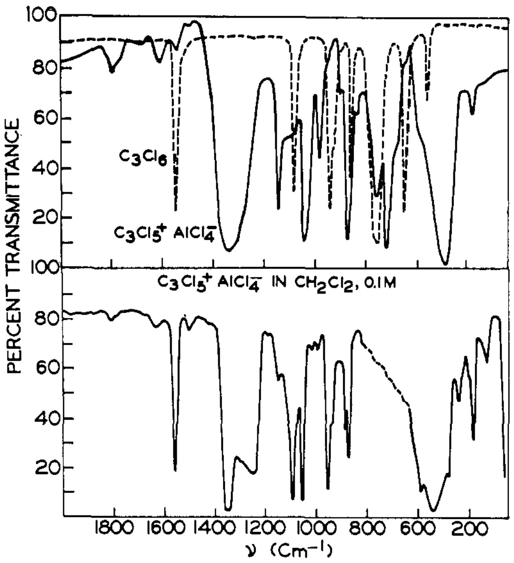
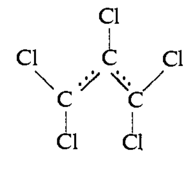


Figure 1. Infrared spectra. Above, – – – –, hexachloropropene, liquid film; ———, $C_3Cl_5{}^+AlCl_4{}^-$, mull in CCl_4 and fluorocarbon oil. Below, $C_3Cl_5{}^+AlCl_4{}^-$ in CH_2Cl_2 solvent.

Eight absorption bands in the region from 300 to 4000 cm^{-1} are found for the pentachloroallyl cation (Table I). This ion should have 18 normal vibrations and, if it is assumed to have the structure pictured below with C_{2v} symmetry, these can be classified as seven of A_1 type, two A_2, three B_1, and six B_2, as shown in Table II. The two A_2 modes are predicted to be Raman active only, but the other 16 modes are active in both the infrared and Raman.[12] However, of these 16, eight modes involve predominantly C–Cl bending and so should lie below 300 cm^{-1}. Thus only eight fundamentals, involving principally C–C and C–Cl stretching and C–C–C bending, are expected to be in the 300–4000-cm^{-1} region.

Table II. Generalized Types of Vibration for C_{2V} Pentachloroallyl Cation

Symmetry type	Activity	No. of modes	Generalized type of vibration
A_1	Raman, infrared	7	1 (C–C) stretch, 1 (C–C–C) bending 3 (C–Cl) stretch, 2 (C–Cl) in plane bending
A_2	Raman	2	2 (C–Cl) out of plane bending
B_1	Raman, infrared	3	3 (C–Cl) out of plane bending
B_2	Raman, infrared	6	3 (C–Cl) in plane bending



Tentative assignments for vibrational bands are given in Table I. The absorptions at 1340 and 1040 cm^{-1} are assigned to asymmetric and symmetric C–C stretching modes, respectively. These frequences are consistent with a C–C bond order of about 1.5 in $C_3Cl_5{}^+$, as expected for an allylcarbonium ion.[13] The frequencies at 715, 755, and 880 cm^{-1} are in the right range for C–Cl stretching and can be assigned to modes involving C–Cl stretching motions. The band at 960 cm^{-1} may be either a C–Cl stretching mode[14] or a combination band; the band of weak-to-moderate intensity at 1140 cm^{-1} is probably a combination.

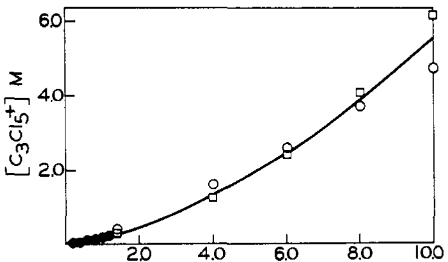


Figure 2. Spectral measurement of actual concentration of $C_3Cl_5{}^+$ *vs.* amount of $C_3Cl_5{}^+AlCl_4{}^-$ added. Data are as follows: ●, ultraviolet, 2290 A; ○, infrared, 950 cm^{-1}; □, infrared, 1090 cm^{-1}.

Although the hexachloropropene complexes are simple ionic salts in the solid phase, dissociation of the salts to their uncharged components appears to take place in dichloromethane.

Figure 1 also shows the spectrum of I in CH_2Cl_2; comparison shows that bands due to *both* I and C_3Cl_6 are present. We interpret this as indicating partial reversion of I to the neutral components, C_3Cl_6 and $AlCl_3$.

$$\underset{\text{I}}{C_3Cl_5{}^+AlCl_4{}^-} \overset{CH_2Cl_2}{\rightleftharpoons} C_3Cl_6 + AlCl_3$$

For I and $C_3Cl_5{}^+GaCl_4{}^-$ dissociation is incomplete and infrared bands due to both $C_3Cl_5{}^+$ and C_3Cl_6 can be observed at moderate concentrations in CH_2Cl_2. However, $C_3Cl_5{}^+SbCl_6{}^-$ apparently dissociates essentially completely under the same conditions, for only the spectra of C_3Cl_6 and $SbCl_5$ are observed when this complex is dissolved in CH_2Cl_2.

$$C_3Cl_5{}^+SbCl_6{}^- \xrightarrow{CH_2Cl_2} C_3Cl_6 + SbCl_5$$

A rough quantitative study of the dissociation reaction was carried out for I in CH_2Cl_2 by measuring the absorbances of the 950- and 1090-cm^{-1} bands of C_3Cl_6 at various concentrations. The measurements were extended to low concentrations by means of ultraviolet spectroscopy, using the absorbance of the hexachloropropene band at 2290 A. Results, shown in Figure 2 and Table III, are compatible with the equilibrium written above. The equilibrium constant for dissociation of the complex ($K = [C_3Cl_6][AlCl_3]/[C_3Cl_5{}^+AlCl_4{}^-]$) has a value of about 0.04 in molar units.

Hydrolysis and Reactions with Chlorocarbons

Prins reported in his original paper that I reacts with water to regenerate hexachloropropene.[2] Our experi-

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(12) The general treatment follows that given in K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

(13) H. Gerding and G. W. A. Rijnders, *Rec. Trav. Chim.*, **66**, 225 (1947).

(14) The frequency is higher than any previously reported for a C–Cl stretching band, but the related cation $C_3Cl_3{}^+$ shows a C–Cl stretching fundamental at 945 cm^{-1} and an unusually high value for the C–Cl stretching force constant.[3b] The positive charge may increase the C–Cl stretching force constant and vibrational frequencies in both species.

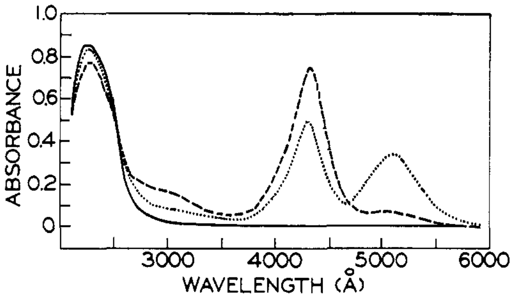


Figure 3. Electronic spectra in dichloromethane solvent. ———, hexachloropropene, 8×10^{-3} *M*; – – – –, $C_3Cl_5{}^+AlCl_4{}^-$, 8×10^{-3} *M*; . . . . ., $C_3Cl_5{}^+AlCl_4{}^-$, 8×10^{-3} *M* and water, 4×10^{-3} *M*.

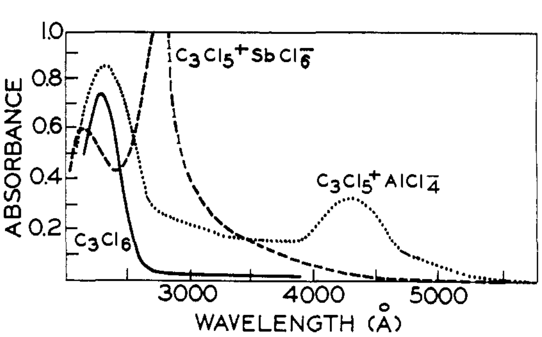


Figure 4. Electronic spectra of pure substances (C_3Cl_6 as liquid film; pentachloroallyl salts as mulls in fluorocarbon oil).

ments confirm this both for the solid salt and for its solution in dichloromethane.

$$C_3Cl_5{}^+AlCl_4{}^- + H_2O \longrightarrow C_3Cl_6 + [AlCl_2OH]$$

This result indicates that chloride ion from $AlCl_4{}^-$ competes very effectively with water in attack on $C_3Cl_5{}^+$. Similar results are obtained for the tetrachloroaluminate salt of trichlorocyclopropenium ion, which gives tetrachlorocyclopropene on treatment with water.[3]

Table III. Dissociation of Pentachloroallyl Tetrachloroaluminate in Dichloromethane

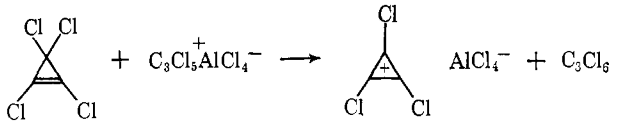
$C_3Cl_5{}^+AlCl_4{}^-$ added, $M \times 10^2$	% reversion to C_3Cl_6	C_3Cl_6, $M \times 10^2$	$K \times 10^2 = \dfrac{[C_3Cl_6][AlCl_3]}{[C_3Cl_5{}^+AlCl_4{}^-]}$
10.0	43	4.3	3.1
8.0	52	4.2	4.5
6.0	58	3.5	4.9
4.0	65	2.6	4.7
1.4	75	1.05	3.1
1.2	81	0.97	4.1
1.00	81	0.81	3.5
0.80	82	0.66	3.1
0.60	84	0.50	2.5
0.40	89	0.36	3.2
0.20	93	0.19	3.6

The results with $C_3Cl_5{}^+GaCl_4{}^-$ and $C_3Cl_5{}^+SbCl_6{}^-$ are quite different. As solids, both compounds undergo hydrolysis with attack on the pentachloroallyl ion to give trichloroacrylic acid as the major product. In

$$CCl_2\cdots CCl\cdots CCl_2{}^+ + 3H_2O \longrightarrow CCl_2{=}CCl{-}COOH + 3HCl$$

dichloromethane, however, in which it undergoes reversion to C_3Cl_6 and $SbCl_5$, the hexachloroantimonate salt produces hexachloropropene upon hydrolysis.

Reaction of I with some other chlorocarbons provides an indication of the relative stability of $C_3Cl_5{}^+$ compared to other perchlorocarbonium ions. I reacts rapidly and completely with tetrachlorocyclopropene, converting it to the $AlCl_4{}^-$ salt of the trichlorocyclopropenium ion. However, no reaction was observed



between II and hexachlorocyclopentadiene. It appears that the allylic ion $C_3Cl_5{}^+$ is less stable than the aromatic trichlorocyclopropenium ion,[3] but more stable than the antiaromatic $C_5Cl_5{}^+$ ion.[4]

Electronic Spectra

The continuous-scan visible and ultraviolet spectra for I and hexachloropropene in dichloromethane solution are shown in Figure 3. C_3Cl_6 shows only a band at 2290 A (ϵ 8700). This band also appears in the spectra of solutions of I in CH_2Cl_2 because these are largely dissociated to C_3Cl_6 and $AlCl_3$ at the low concentrations employed.

In addition, solutions of I show three other electronic spectral features: (1) a weak band at about 3000 A, appearing as a shoulder on the 2290-A hexachloropropene band; (2) a strong absorption at 4350 A; and (3) a weak band at 5080 A, exhibiting variable intensity in different preparations. The 5080-A band appears to be an artifact due to moisture in the system. As seen from Figure 3, purposeful addition of water causes the 5080-A band to increase and the 4350-A band to decrease in intensity. As the solutions stand over a period of several hours, the intensity of the band at 5080 A slowly decreases while those at 4350 and 2290 A both increase somewhat. These observations suggest that the 5080-A band results from an ion pair containing $C_3Cl_5{}^+$ and a partly hydrolyzed anion which might be of the form $AlCl_4(H_2O)^-$ or $AlCl_3OH^-$. With time, irreversible chloride transfer to the $C_3Cl_5{}^+$ cation may take place

$$C_3Cl_5{}^+AlCl_4(OH)_2{}^- \longrightarrow C_3Cl_6 + (AlCl_2OH)_n + HCl$$

The resulting hexachloropropene could enter into the primary equilibrium between I, C_3Cl_6, and $AlCl_3$, accounting for the increase of absorbance due to $C_3Cl_5{}^+$-$AlCl_4{}^-$ at 4350 A. This interpretation further suggests that the 4350-A band is characteristic of the ion pair or ion aggregate $C_3Cl_5{}^+AlCl_4{}^-$, and not of the free $C_3Cl_5{}^+$ ion. The spectrum of $C_3Cl_5{}^+GaCl_4{}^-$ is similar to that of I, but the maximum for the corresponding absorption is shifted to 4380 A.

The spectrum of I as a solid is shown in Figure 4; it is similar to that of I in dichloromethane except that the 5080-A band is not observed. However, no absorption bands in the visible region were observed for solid $C_3Cl_5{}^+SbCl_6{}^-$. The only absorption found for this compound was an extremely strong band near 2700 cm^{-1}, in the same region where $SbCl_5$ absorbs (Figure 4). Tailing of this band into the visible accounts for the pale yellow color of $C_3Cl_5{}^+SbCl_6{}^-$. The great dependence of the transition energy on the nature of the anion is not clearly understood, but suggests that anion–cation excited-state charge transfer may be important in the electronic transition. The maxima for I and $C_3Cl_5^+GaCl_4^-$ occur at the same wavelength in the solid and in dichloromethane solution, so the local environment of the cation must be similar in both phases. (Tight ion pairing between $C_3Cl_5^+$ and anions would be expected in CH_2Cl_2.)

Based on concentration data shown in Table III, and neglecting the concentration of any traces of hydrated species, the molar extinction coefficient corresponding to the absorbance at 4350 A for I is calculated to have a minimum value of 6.5×10^4.

Experimental Section

Materials. Hexachloropropene was obtained from Matheson Scientific Co. and was redistilled before use. Anhydrous aluminum chloride was obtained from Baker and Adamson Co., antimony pentachloride from J. T. Baker Chemical Co., and gallium trichloride from Penn Rare Metals Inc. The dichloromethane used as a solvent was Matheson Scientific spectral grade material; for electronic spectral studies it was redistilled from Linde type 4A Molecular Sieve. Carbon tetrachloride was Mallinckrodt Analytical Grade, used without further purification. The fluorocarbon oil was Hooker Fluorolube, Grade S-30.

Infrared Spectra. Beckman IR-10 and Perkin-Elmer 221 and 112 spectrometers were used in the infrared studies. The spectrometer sample compartment was purged with a continuous flow of dry nitrogen. The solid complexes were studied as mulls made by grinding the solids under dry carbon tetrachloride in a nitrogen atmosphere. Mulls in fluorocarbon oil were also prepared in order to study the region from 750 to 850 cm^{-1} where carbon tetrachloride absorbs strongly.

The spectra of solutions of the complexes were obtained in dichloromethane using sodium chloride cells with path length 0.2 mm, referenced with the pure solvent. At ~0.5 *M* in dichloromethane, $C_3Cl_5^+AlCl_4^-$ and $C_3Cl_5^+GaCl_4^-$ showed bands due both to $C_3Cl_5^+$ and to free hexachloropropene, but $C_3Cl_5^+SbCl_6^-$ showed only bands attributable to hexachloropropene and $SbCl_5$.

Electronic Spectra. Ultraviolet and visible spectra were obtained using a Cary Model 14 spectrophotometer. Solutions in dichloromethane solvent were prepared under nitrogen. To study the electronic spectra of solid salts, these were finely ground under fluorocarbon oil in a nitrogen atmosphere and the resulting mulls were pressed between sodium chloride plates.

Spectral Measurements of Dissociation of I. The concentration dependence of the reversion of I to C_3Cl_6 and $AlCl_3$ of I was studied in the range 0.1–0.01 *M* using a KBr cell with 1.0-mm path length, with matching solvent compensation. Calibration curves were first constructed for the 1090- and 950-cm^{-1} bands of hexachloropropene, and the C_3Cl_6 concentration in the solution of $C_3Cl_5^+$-$AlCl_4^-$ was determined using these.[15] The measurements were extended to lower concentrations by a similar method using the 2290-A band of hexachloropropene in the ultraviolet.

Pentachloroallyl Tetrachloroaluminate (I). Anhydrous aluminum chloride (4.50 g, 0.032 mole) was added to 7.50 g (0.030 mole) of hexachloropropene. The mixture was heated to 55° under nitrogen, whereupon the mass began to solidify and turn an amber yellow color. The mixture was removed from the heat and stirred until soldification was complete. Approximately 30 ml of dichloromethane was added immediately. The resulting dark orange solution was decanted into a new receiver, leaving behind the excess aluminum chloride. The solution was allowed to evaporate slowly under nitrogen. I was obtained as amber-yellow needles; yield 9.60 g (83%). The product was further dried under vacuum, mp 110–111° (in sealed evacuated capillary).

Anal. Calcd for C_3Cl_9Al: C, 9.45; Cl, 83.5; Al, 7.05. Found: C, 9.17; Cl, 82.30; Al, 6.62 (based on Al_2O_3 ash).

Hydrolysis of I. Ice water (40 ml) was added to 6.90 g (0.018 mole) of I. The solid reacted instantly with the formation of an oil and a white precipitate. This mixture was extracted with dichloromethane, the organic portion was dried over anhydrous magnesium sulfate, and the solvent was evaporated, leaving 3.85 g (86%) of a colorless oil. This was identified as pure hexachloropropene by infrared spectroscopy and gas chromatography.

Similar hydrolysis of I dissolved in dichloromethane also produced hexachloropropene, identified similarly and recovered in 93% yield.

Reaction of I with Tetrachlorocyclopropene. I (11.52 g, 0.030 mole) was dissolved in 35 ml of dichloromethane. To the resultant red-orange solution was added a solution of 5.04 g (0.030 mole) of tetrachlorocyclopropene in 15 ml of dichloromethane. Upon addition the orange-red solution was immediately decolorized and a white solid precipitated. The solid was isolated by filtration under reduced pressure and dried under vacuum. The infrared spectrum of the white solid was identical with that of the tetrachloroaluminate salt of the trichlorocyclopropenium ion ($C_3Cl_3^+$-$AlCl_4^-$), ν(C–C) 1345, 1310, ν(C–Cl) 723, and ν(Al–Cl) 480 cm^{-1}.[3]

In a similar experiment a dichloromethane solution containing 0.02 mole of hexachlorocyclopentadiene was added to a dichloromethane solution containing 0.02 mole of I. This time, no decolorization or precipitation took place. After evaporation of the solvent, an upper liquid layer of hexachlorocyclopentadiene was observed along with an amber solid lower layer of unchanged I.

Further Reactions of I. In qualitative tests, I was observed to react rapidly with methanol, ethanol, 2-propanol, diethyl ether, 1-pentene, 1-hexene, 2-hexene, 1-hexyne, fluoro-, chloro-, and bromobenzenes, toluene, anisole, and xylene. Slow reactions were observed with benzene, benzonitrile, cyclohexane, and mineral oil. No attempt was made to identify the products of most of these reactions, but infrared spectra of the products obtained with alcohols and diethyl ether indicated that they were probably trichloroacrylate esters.

Pentachloroallyl Tetrachlorogallate. A sealed vial containing 10 g (0.057 mole) of gallium trichloride was inserted into a rubber stopper. The vial was broken under nitrogen and the stopper was inserted into a nitrogen-purged 250-ml three-necked flask containing 14.2 g (0.057 mole) of hexachloropropene. While the hexachloropropene was stirred by a magnetic stirrer, the vial containing gallium trichloride was heated and the melted gallium chloride dropped from the vial and into the hexachloropropene. The resulting viscous red-orange oil was stirred for 5 min, and then 100 ml of dichloromethane was added to dissolve the oil. The dichloromethane was slowly evaporated under vacuum; when about 30 ml of solvent remained, the product had precipitated as amber-colored needles. These were filtered off under nitrogen, washed with three 10-ml portions of dichloromethane, and dried under vacuum; yield 12.6 g (52%), mp 76° dec (sealed evacuated capillary).

Anal. Calcd for C_3Cl_9Ga: C, 8.54; Cl, 74.9; Ga, 16.5. Found: C, 9.12; Cl, 71.9; Ga, 17.7.

Hydrolysis. $C_3Cl_5^+GaCl_4^-$ (9.3 g, 0.022 mole) was treated with 100 ml of ice-water mixture. The solid reacted immediately to form a milky white aqueous suspension and a pale yellow oil. The mixture was extracted with dichloromethane and the organic layer was dried with anhydrous magnesium sulfate and filtered. Evaporation of the solvent left a yellow-white residue which was sublimed at 73° (15 mm). The white sublimated proved to be trichloroacrylic acid (3.4 g, 88%), mp 75.5°, lit.[16] mp 76°.

Anal. Calcd for C_3HCl_3O: C, 20.6; H, 0.57; Cl, 60.4; O, 18.3. Found: C, 20.2; H, 0.67; Cl, 60.8; O, 18.4.

Pentachloroallyl Hexachloroantimonate. Antimony pentachloride (9.0 g, 0.030 mole) was added to 7.5 g (0.030 mole) of hexachloropropene under nitrogen. When the mixture was stirred and gently heated crystals began to form, and the mixture soldified completely to a lemon-yellow solid within 1 min. The solid was recrystallized from dichloromethane. The resulting lemon-yellow powder was filtered by reduced pressure under nitrogen, washed with three 20-ml portions of cold dichloromethane, and dried under vacuum to yield 15.3 g (93%) of $C_3Cl_5^+SbCl_6^-$, mp 55–58°.

Anal. Calcd for $C_3Cl_{11}Sb$: C, 6.7; H, 0.0; Cl, 71.0; O, 0.0; Sb, 22.1. Found: C, 6.8; H, 0.0; Cl, 70.5; O, 0.0; Sb, 22.0.

Hydrolysis. $C_3Cl_5^+SbCl_6^-$ (6.0 g, 0.011 mole) was gradually added to 50 ml of an ice–water mixture. A white aqueous suspension and a yellow oil formed. The mixture was extracted with two 50-ml portions of dichloromethane. The resulting organic layer was dried over anhydrous magnesium sulfate and filtered. Solvent was removed under vacuum, leaving an off-white residue which was sublimed at 72° (10 mm) to give 1.83 g (96%) of trichloroacrylic acid, mp 75–76°, lit.[16] mp 76°.

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(15) Complete data are given in the doctoral thesis of P. T. Kwitowski, University of Wisconsin, 1966.

(16) J. Boeseken and P. Dujardin, *Rec. Trav. Chim.*, **32**, 98 (1913).

Hydrolysis of a solution of $C_3Cl_5^+SbCl_6^-$ in dichloromethane and similar work-up gave only hexachloropropene in 98% yield.

Potassium Hexachloroantimonate. The procedure of Jander and Swart[17] was followed. Potassium chloride (1.51 g, 0.02 mole) was added to 17 ml of melted antimony(III) chloride and heated gently until the potassium chloride completely dissolved. Antimony(V) chloride (6.10 g, 0.021 mole) was added dropwise and the resulting brown solution was allowed to cool, whereupon solidification took place. The solid mass was ground and washed with three 50-ml portions of carbon disulfide to dissolve the antimony(III) chloride and any excess antimony(V) chloride. The light gray solid residue was dried under vacuum.

Anal. Calcd for $KSbCl_6$: K, 10.5; Sb, 32.6; O, 0.00; Cl, 56.9. Found: K, 10.2; Sb, 32.4; O, 0.00; Cl, 57.0.

A mineral oil mull smeared between CsI plates gave a single infrared absorption band at 346 cm^{-1}.

Acknowledgments. The authors thank the National Science Foundation for a grant in support of this research.

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Conformational Variation in the Electron Spin Resonance Spectra of Some Phenoxy Radicals

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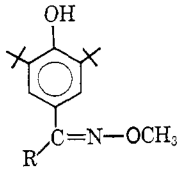
Abstract: We have examined the esr and optical spectra of a series of 4-substituted 2,6-di-*t*-butylphenoxy radicals. The magnitude of the coupling constant of the 4 substituent is shown to depend on the conformation of the radical. The extinction coefficient and position of the ultraviolet maximum are also related to the radical's conformation. The nmr and ultraviolet spectra of the phenols, from which the radicals were made, show that these compounds also exist in different conformations.

Electron spin resonance spectroscopy can be used to obtain information about the conformational identity of organic free radicals. Geske's group has studied a series of nitrobenzene anion radicals, and found that the nitrogen coupling constants increase as the nitro group twists from coplanarity with the aromatic ring.[1] Tetraisopropylnitrobenzene shows two different nitrogen splittings which have been shown to come from two different conformation isomers.[2] The nitrogen splitting in these radicals depends on the angle of twist between the nitro group and the plane of the aromatic ring. Substituents on the aromatic ring affect this angle and change the nitrogen coupling constant.

We have conducted a study to examine how steric hindrance affects the spin distribution in a series of conjugated phenoxy radicals. The odd electron spin was introduced into the phenoxy ring, and the coupling constants of groups of nuclei connected in the *para* position were determined. The radicals which we have studied were derived from phenols of the general structure



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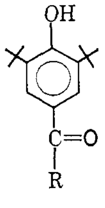

II

+ = *t*-butyl

a, R = H
b, R = CH_3
c, R = *t*-butyl
d, R = phenyl

The radicals were made by removal of the hydroxyl hydrogen atom by oxidation. Conjugation between the phenoxy ring and the *para* substituent depends on the angle, θ, between the plane of the aromatic ring and a plane projected through the RC=R group. If this twist angle is large, conjugation between the two parts of the molecules is reduced.

The coupling constant of the nitrogen, in compounds Ia–d, should depend on the value of the resonance integral of the Ar–C bond (β_{Ar-C}). The magnitude of β_{Ar-C} depends on the twist angle θ[3] and the Ar–C bond length.[4] The variation of β_{Ar-C} with the twist angle, θ, can be written as

$$\beta_{Ar-C} = \beta_0 \cos\theta \tag{1}$$

where β_0 is the normal resonance integral. Bulky substituents on the oximido carbon should increase the twist angle and decrease the value of β_{Ar-C}. This change will be reflected in a decrease of the nitrogen coupling constant if the phenoxy ring has a higher electron affinity than the oxime group.

The radicals with a carbonyl group rather than the oxime group should show the same general behavior. It is interesting to compare the splitting of the R group in the ketones and aldehyde with those of the corresponding groups in the oximes. Some idea of the relative twist angles in the two series of compounds can be obtained by comparison of these splittings.

Experimental Section

A. Magnetic Resonance Measurements. The esr spectra were taken on a Jeolco 3BSX, esr spectrometer with 100-kc field

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