a high degree of symmetry which makes it unlikely that either of these compounds has a significant dipole moment. According to X-ray diffraction data on both lead[5] and copper[6] compounds similar to these, both salts have planar configurations.

It would be possible for a planar salt to have a moment if the molecule were of *cis* configuration (both nitrogen atoms on the same side) and indeed, disalicylidenemethylamine copper is known to exist in two crystalline forms. Of these two forms, the green modification (the one used) is the more stable and therefore is probably the *trans*.

It would appear from this discussion that the results might be reasonably interpreted in terms of the presence of abnormally high atomic polarization as has been observed by Finn, Hampson and Sutton[7] for metallic acetylacetonates. The measurements reported here and those of Sutton and co-workers lead to the doubt of the existence of any metallic chelates which do *not* have any abnormally large atomic polarization. This unfortunately obscures the useful application of the technique of dipole moments to the evaluation of charge distribution in these interesting molecules. There does exist a possibility of evaluation of the dipole moment from the atomic polarization if the latter is viewed as arising from molecular oscillation as described by Coop and Sutton.[8] Coop and Sutton propose an equation relating the atomic polarization to the dipole moment of half of the molecule and to the force constant associated with the corresponding bending of the molecule. If the force constant could be evaluated from infrared absorption data, then it should be possible to apply the Coop and Sutton[8] equation to solve the dipole moment of half the chelate molecule. Without a knowledge of the force constants, atomic polarization data could not give more than the qualitative order of the ring to metal moments of a series of salts of a given chelating agent or of a series of chelates of a given metal and this, only if it could be assumed that the force constants were of approximately the same magnitude.

Acknowledgment.—The authors are grateful for the support of the Atomic Energy Commission, under whose grant this work was performed.

[5] E. G. Cox, A. J. Shorter and W. Wardlaw, *Nature*, **139**, 72 (1937).

[6] E. G. Cox, W. Wardlaw and Webster, *J. Chem. Soc.*, 775 (1936).

[7] Finn, Hampson and Sutton, *ibid.*, 1254 (1938).

[8] Coop and Sutton, *ibid.*, 1269 (1938).

PITTSBURGH 13, PENNA. RECEIVED APRIL 27, 1951

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF ETHYL CORPORATION]

The Partial Additive Chlorination of the Benzene Ring. I. Alpha Benzene Tetrachloride

BY GEORGE CALINGAERT,[1] MARGARET E. GRIFFING, E. ROBERT KERR,[2] ALFRED J. KOLKA AND HAROLD D. ORLOFF

Photochlorination of benzene in the presence of iodine results, in part, in the formation of benzene tetrachloride, a new compound. A steric isomer, designated as alpha benzene tetrachloride, has been isolated and a number of its physical and chemical properties have been determined. The chlorination of benzene tetrachloride to benzene hexachloride has been shown to occur *via* a free radical mechanism. From the photochlorination of alpha benzene tetrachloride, the alpha and gamma isomers of benzene hexachloride were obtained. Bromination and oxidation of alpha benzene tetrachloride yielded two new compounds, 1,2-dibromo-3,4,5,6-tetrachlorocyclohexane and 2,3,4,5-tetrachlorohexanedioic acid, respectively. The partial additive chlorination of chlorobenzene to pentachlorocyclohexene indicates that this type of chlorination reaction may be applicable to a variety of aromatic compounds.

Introduction

The di- and tetrachlorides of benzene, $C_6H_6Cl_2$ and $C_6H_6Cl_4$, have been suggested[3,4,5] as possible intermediates in the additive chlorination of benzene to 1,2,3,4,5,6-hexachlorocyclohexane (benzene hexachloride, BHC). However, no reference to the isolation or confirmation of even the transitory existence of either intermediate has been found in the literature.

The photochlorination of benzene has been shown to occur by means of a free radical mechanism[6] and some estimates of chain lengths and quantum efficiencies have been made.[5,7] On the basis of such a mechanism it may be assumed that the following reactions occur in the formation of dichlorocyclohexadiene

$$Cl_2 \xrightarrow{\text{light}} 2Cl\cdot \qquad (1)$$

$$Cl\cdot + C_6H_6 \longrightarrow ClC_6H_6\cdot \qquad (2)$$

$$ClC_6H_6\cdot + Cl_2 \longrightarrow C_6H_6Cl_2 + Cl\cdot \qquad (3)$$

Because of its expected reactivity, it is possible that dichlorocyclohexadiene might chlorinate to tetrachlorocyclohexene *via* a free radical or an ionic mechanism, or both. It is to be expected that tetrachlorocyclohexene would be a less reactive intermediate than dichlorocyclohexadiene, and that there would be more likelihood of its isolation by modifying the addition chlorination of benzene by means of appropriate reagents.

We have isolated a steric isomer of 3,4,5,6-tetrachlorocyclohexene from the product of the photochlorination of benzene in the presence of iodine. Chlorination of this new compound in the dark at room temperature resulted in no detectable reaction, whereas the rate of photochlorination was rapid under comparable conditions, indicating

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[1] Hobart College, Geneva, New York.

[2] Wayne University, Detroit, Michigan.

[3] H. Müller, *J. Chem. Soc.*, **15**, 41 (1862).

[4] A. Slator, *ibid.*, **83**, 729 (1903).

[5] H. P. Smith, W. A. Noyes, Jr., and E. J. Hart, THIS JOURNAL, **55**, 4444 (1933).

[6] R. Luther and E. Goldberg, *Z. physik. Chem.*, **56**, 43 (1906).

[7] H. N. Alyea, THIS JOURNAL, **52**, 2743 (1930); K. Ueda, *Botyu-Kagaku*, **15**, 149 (1950).

that tetrachlorocyclohexene chlorinates by means of a free radical mechanism.

The use of iodine as a catalyst for the substitution chlorination of benzene has been reported.[3] Slator[4,8] found the reaction between chlorine and benzene in the presence of iodine to be very slow in the dark but to proceed rapidly in the presence of light; approximately 70% of the chlorine was converted to chlorobenzenes and hydrogen chloride, while the remainder reacted additively to form benzene hexachloride. Our investigations have shown that the light-catalyzed reaction yields a mixture comprised of three chemical types: (1) substitution chlorination derivatives of benzene; (2) chlorocyclohexenes resulting from the addition of two molecules of chlorine; and (3) benzene hexachloride isomers.

In the 2nd group, in addition to benzene tetrachloride, pentachlorocyclohexene was also isolated from the mixture. Its formation is attributed to the partial additive chlorination of the monochlorobenzene obtained. Confirmation of this interpretation was obtained by the direct additive chlorination of monochlorobenzene, which also yielded pentachlorocyclohexene (*Anal.* Calcd. for $C_6H_5Cl_5$: C, 28.33; H, 1.98; Cl, 69.69. Found: C, 27.96; H, 2.18; Cl, 69.82). The details of the latter investigation, which is in progress, will be communicated in a subsequent paper.

It is indicated that the formation of appreciable quantities of partial addition chlorination products, in the presence of iodine or iodine chloride, is the result of selective inhibition of the chlorination. Other inhibitors of photochlorination, such as oxygen, have been found to have an analogous effect.

The compound isolated from the partial additive chlorination of benzene was proved to be tetrachlorocyclohexene by chemical analysis, molecular weight determination and chemical reactions. The existence of the double bond was confirmed by alkaline dehydrohalogenation, which yielded a mixture of dichlorobenzenes and two equivalents of hydrogen chloride per mole of dichlorobenzene formed, by additive bromination, and by oxidative cleavage. That the compound is the 3,4,5,6-tetrachloro positional isomer was proved by additive chlorination to a mixture of alpha and gamma benzene hexachlorides. This reaction also established the structure of the products of bromination and oxidation to be 1,2-dibromo-3,4,5,6-tetrachlorocyclohexane and 2,3,4,5-tetrachlorohexanedioic acid, respectively. These two compounds have not been previously reported.

The physical properties of the tetrachlorocyclohexene, together with results of repeated crystallization from various solvents and attempted chromatographic separation, quite definitely establish the new compound as a single steric isomer which we designate as alpha benzene tetrachloride. Other isomers of this compound that are separable by the use of chromatography are present in the product obtained by the procedure described. The investigation of the separation and characterization of these isomers is in progress and will be reported in a subsequent paper. The chlorination of the benzene tetrachlorides should provide confirmation of the steric structures reported for the benzene hexachlorides and establish, by chemical means, the steric structures of the benzene tetrachlorides. Also under investigation is the application of the partial additive chlorination reaction to other aromatic compounds.

Experimental and Results

Preparation of Alpha Benzene Tetrachloride.—Iodine (6.25 g.), dissolved in 2200 g. (28.2 moles) of thiophene-free dry benzene, was charged to a water-jacketed Pyrex test-tube reactor (7 × 190 cm.) equipped with a thermometer, fritted-glass chlorine dispenser, water-cooled reflux condenser, followed by a 2 × 20 cm. water-fed scrubbing tower packed with 6 × 6 mm. glass Raschig rings for the absorption of hydrogen chloride and two tared chlorine traps cooled in a Dry Ice–trichloroethylene mixture. Two 250-watt white glass General Electric Co. infrared heat lamps, placed 2.5 cm. from the cooling jacket and 60 and 120 cm., respectively, from the bottom of the reactor, were used as the source of light energy. Chlorine gas (995 g., 13.5 moles) was introduced at 21–30°. At the flow rate employed (3 g./min.), no chlorine condensed in the cold traps. A stream of nitrogen then was passed through the solution to remove the major portion of the dissolved gases. The hydrogen chloride content of the scrubber solution was determined by titration.

Unreacted benzene was removed from the reaction solution in a packed distillation column operated at atmospheric pressure. Subsequent distillation, carried out at reduced pressure (2–5 mm.), was complicated somewhat by liberation of elemental iodine. Removal of the latter was accomplished by diluting the once-distilled material with 25% of hexane and shaking with an aqueous saturated solution of sodium sulfite. The decolorized organic phase was dried with anhydrous sodium sulfate, the hexane was removed under reduced pressure, and the product was rectified *in vacuo*. The mono-, di- and trichlorobenzenes were readily separated by this procedure and identified by their boiling points, infrared spectra and chlorine analyses. No tetrachlorobenzene was detected. At 80° (1.5 mm.) a mixture of chloroölefins, which were later identified as tetra- and pentachlorocyclohexenes, started to distil. The rectification was discontinued at 132° (1.5 mm.) when solid alpha BHC accumulated in the stillhead. The pot residue was a mixture of BHC isomers of which only alpha and gamma could be identified by infrared spectrophotometry. On the basis of the distillation data and analyses, the product distribution was calculated to be

Compound	Material obtd., g.	Yield based on chlorine fed, %
Monochlorobenzene	906	30.1
Dichlorobenzenes	45	2.3
Trichlorobenzenes	7	0.4
Tetrachlorocyclohexene	196	13.3
Pentachlorocyclohexene	138	10.1
Benzene hexachloride	57	4.4
Hydrogen chloride	342	34.8
		95.4

The chlorine (44 g.) not accounted for in the above tabulation is distributed between unreacted chlorine and iodine chlorides in the final reaction solution.

For further separation of the products of partial additive chlorination, a 698-g. composite sample of the material boiling from 80 to 132° at 1.5 mm. was rerectified. During this distillation, an additional trace of free iodine was liberated. Approximately one-half of the distillation charge, b.p. 80–85° at 1.5 mm., had an infrared spectrum characterized by strong absorption bands at 11.99, 12.47 and 14.45 microns. This lower boiling material was again deiodinated and rectified, yielding a colorless distillate. Of this, a fraction of 80 g., b.p. 80° at 1.5 mm., was indicated by infrared spectrophotometry to be a relatively pure sample of a single compound. On standing at room temperature, 39 g. of colorless crystals separated. After being washed with cold ethyl chloride, the crystals melted at 32–34°. Their infrared spectrum

(8) A. Slator, *Z. physik. Chem.*, **45**, 513 (1903).

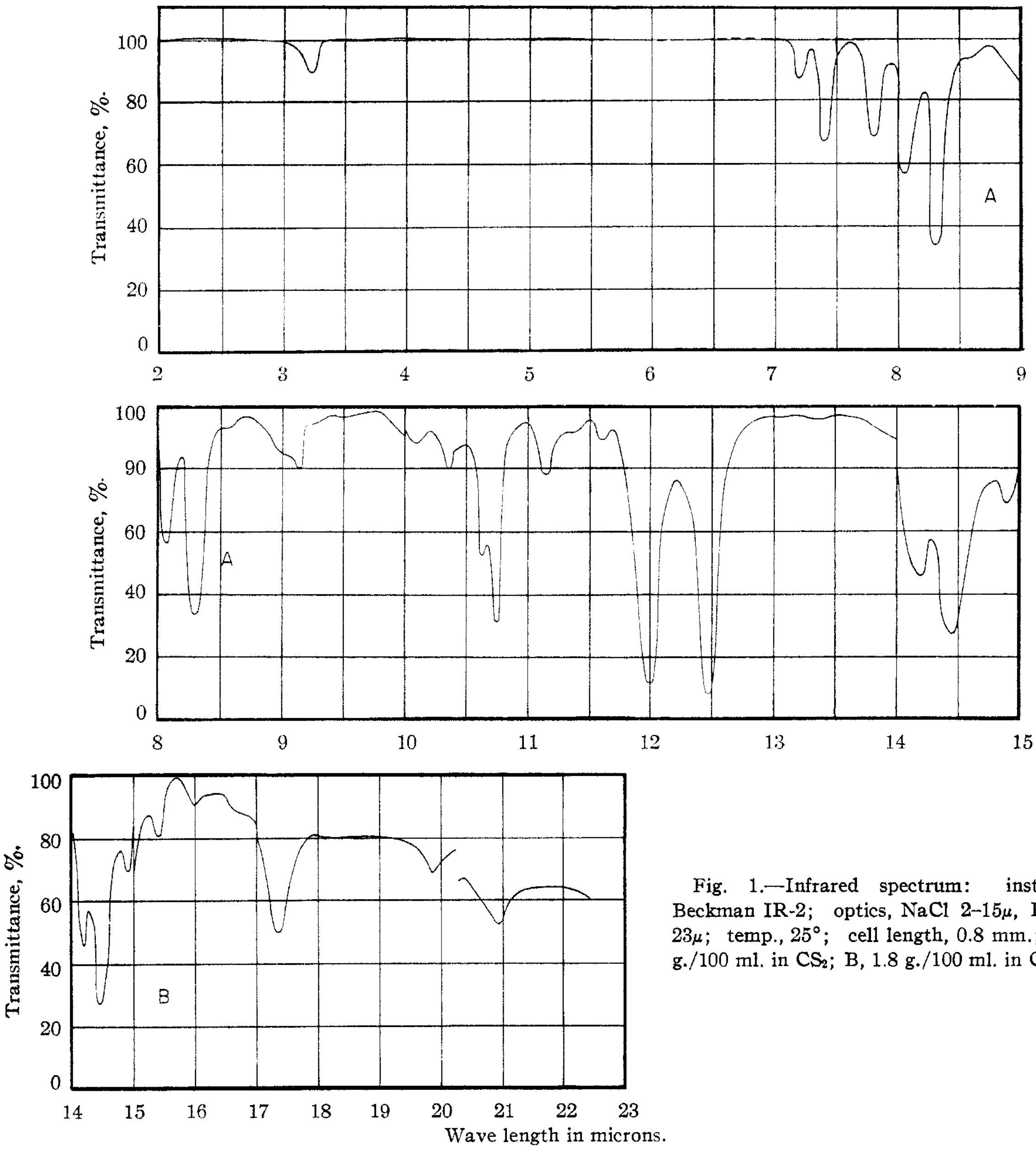

Fig. 1.—Infrared spectrum: instrument, Beckman IR-2; optics, NaCl 2–15μ, KBr 15–23μ; temp., 25°; cell length, 0.8 mm.; A, 1.8 g./100 ml. in CS_2; B, 1.8 g./100 ml. in CCl_4.

was identical with that of the mother liquor. This material has been designated as alpha benzene tetrachloride.

Purification.—Crystalline alpha benzene tetrachloride (751 g.) obtained from a number of runs was combined and recrystallized successively from 95% ethanol, 100% ethanol and isopentane. The resulting crystals (308 g.) were dissolved in 200 g. of hexane at about 35°, and the solution was percolated three times through $^1/_4$-inch thick pads of No. 1 Whatman filter paper to remove adsorbable impurities. The filtered material was recrystallized twice from *n*-hexane, yielding 98 g. of colorless crystals, m.p. 33.2–33.5° (cor.). The melting point was determined with a calibrated thermometer graduated to 0.1° and a temperature rise of 0.1°/min. Infrared spectrophotometric curves recorded for the successive crops of recrystallized material were identical. *Anal.* Calcd. for $C_6H_6Cl_4$: C, 32.76; H, 2.75; Cl, 64.49; mol. wt., 220.0. Found: C, 32.68; H, 2.78; Cl, 64.54; mol. wt. (ebulliometric), 222.7.

Additional proof of purity was obtained by partition chromatography, using a modification of the procedure of Ramsay and Patterson[9] which has been found applicable to the separation of the isomers of tetrachlorocyclohexene. Spectrophotometric examination of the fractions obtained from the chromatography of 4.5 g. of purified alpha benzene tetrachloride on 100 g. of silicic acid in a 3-cm. column indicated the absence of other isomers. The infrared spectra of the fractions collected were identical with each other and with the starting material. Recrystallization of two fractions of the chromatographed materials gave the same melting point as the starting material. These results are strong evidence for the presence of a single isomer of high purity.

Physical Properties.—The data for alpha benzene tetrachloride are recorded in Table I. Boiling points were determined during distillation in a 2.8 × 122 cm. column of low pressure drop packed with $^3/_{32}$-inch multiple-turn glass helices.[10] The boiling points were measured in the stillhead with a calibrated thermometer, and the corresponding stillhead pressures were obtained with a McLeod gage over the range 0.6–15.0 mm. of mercury. The equation

$$\log P_{(\text{mm.})} = 7.8698 - 2383/(t + 230)$$

fits the experimental values to within ±0.5°. This equa-

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[9] L. L. Ramsay and W. I. Patterson, *J. Assoc. Offic. Agr. Chemists*, **29**, 337 (1946).

[10] Obtained through the courtesy of Dr. R. W. Schiessler, Department of Chemistry, Pennsylvania State College.

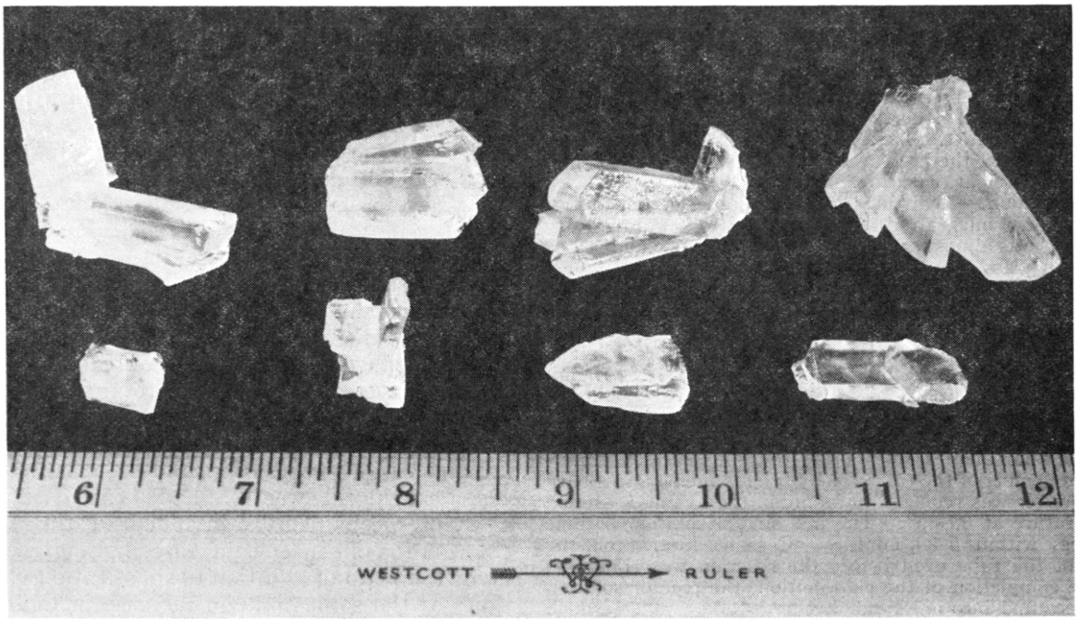

Fig. 2.—Crystals of alpha benzene tetrachloride.

tion is in excellent agreement with a Cox chart estimation using an intersection point for halohydrocarbons based on a variety of compounds[11] and it can probably be extrapolated with but little error to 100 mm.

TABLE I

PHYSICAL PROPERTIES OF ALPHA BENZENE TETRACHLORIDE

Property	Experimental value
Melting point (°C.)	33.2–33.5 (cor.)
Boiling point (°C.)	80.0 (1.5 mm.)
	112.0 (8 mm.)
	126.0 (15 mm.)
	176 (calcd., 100 mm.)
	248 (calcd., 760 mm.)
Density ($d^{35}{}_4$)	1.4852
Refractive index ($n^{35}{}_D$)	1.5425
Solubility (g./100 g. soln.)[a]	
95% ethanol (7°)	14.8
95% ethanol (15°)	20.6
n-hexane (7°)	25.6
n-hexane (15°)	45.7

[a] Temperatures ±0.2°.

The infrared spectrum (Fig. 1) was taken on a Beckman IR-2 spectrophotometer using sodium chloride optics between 2 and 15 μ and potassium bromide optics between 15 and 25 μ. The instrument records the spectrum superimposed on the black body radiation curve. A blank was run on the cell filled with the solvent and the published spectrum was replotted from the calculated values of the recorded spectrum corrected for the blank. The instrument was swept with dry nitrogen to remove atmospheric carbon dioxide and a portion of the water vapor. Some of the water bands persisted and may have distorted the spectrum in the 6–8 μ region. Discontinuities in the spectrum result from changes in slit width and in amplifier gain. The wave length accuracy of the instrument is within 0.04 μ.

The ultraviolet spectrum was obtained on a Beckman quartz spectrophotometer using a hydrogen source. An isoöctane solution containing 0.25 g./l. of alpha benzene tetrachloride was transparent at wave lengths above 240 μ but showed rapidly increasing absorption below 240 μ. This spectrum is consistent with the structure assigned to the compound.

Figure 2 is a photograph of alpha benzene tetrachloride crystals which were grown slowly in a melt of the same material maintained at approximately 25–30°.

Dehydrohalogenation.—To a refluxing solution of 20.00 g. of alpha benzene tetrachloride in 50 ml. of absolute ethanol, 15 g. of potassium hydroxide dissolved in 100 ml. of the same solvent was added dropwise. Almost instantaneous precipitation of potassium chloride occurred. After refluxing for two hours, the reaction solution was cooled and diluted with 500 ml. of distilled water, and the two phases were separated. The organic layer was washed twice with water, dried with anhydrous sodium sulfate and analyzed by infrared spectrophotometry:[12] Only dichlorobenzene isomers were present in the following ratio: ortho 47.8%, meta 50.4%, para 1.8%. The aqueous layer and wash waters were combined and diluted to 1000 ml., and an aliquot was titrated argentimetrically for inorganic chloride. The amount of potassium chloride formed was found to correspond to the elimination of two molecules of hydrogen chloride from $C_6H_6Cl_4$. *Anal.* Calcd. KCl, 13.56 g.; found, KCl, 13.60 g.

Bromination.—Liquid bromine (40.0 g., 0.25 mole) was added to a solution of alpha benzene tetrachloride (55.0 g., 0.25 mole) in 200 ml. of carbon tetrachloride in a 500-ml. round-bottom flask equipped with a reflux condenser and illuminated with a General Electric Co. 275-watt RS Reflector Sunlamp placed two inches from the flask. The reaction was slow; a faint bromine coloration remained after 48 hours. The reaction solution was chilled in ice and 83 g. (87.4% crude yield) of crystalline 1,2-dibromo-3,4,5,6-tetrachlorocyclohexane was removed by filtration. Two recrystallizations from carbon tetrachloride yielded 26 g., m.p. 161.2–161.8° (cor.). *Anal.* Calcd. for $C_6H_6Br_2Cl_4$: Br, 42.10; Cl, 37.36. Found: Br, 42.26; Cl, 37.91.

Oxidation.—To a rapidly agitated suspension of 33.0 g. (0.15 mole) of alpha benzene tetrachloride in 400 ml. of 50% sulfuric acid, in a one-liter, three-neck, round-bottom flask equipped with thermometer, efficient mechanical agitator and reflux condenser, was added 70 g. (0.44 mole) of potassium permanganate in 5-g. portions over a period of three hours. The reaction temperature was maintained below 35° by means of an external cooling bath. The mixture then was heated at 80–90° for 0.5 hr., cooled and treated with a saturated aqueous solution of sodium bisulfite until the reduction of manganese dioxide was complete. The mixture was diluted and the residue was filtered, washed and

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[11] G. W. Thomson in A. Weissberger, "Physical Methods of Organic Chemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1949, pp. 207, 225.

[12] M. E. Griffing and R. L. Hudson, to be published.

dried. The oxidation product, tetrachloroadipic acid (2,3,4,5-tetrachlorohexanedioic acid) (29 g., 68% yield) was dissolved in 10% sodium bicarbonate solution, decolorized with Norit A, acidified and filtered. The precipitate was washed, dried and recrystallized from acetone, yielding 21 g., m.p. 269° (dec.). *Anal.* Calcd. for $C_6H_6Cl_4O_4$: Cl, 49.95. Found: Cl, 49.54. Titration of a sample with standard alkali indicated the presence of two carboxyl groups (milliequivalent weight, calcd. 0.1420, found 0.1423).

Chlorination.—Redistilled reagent grade carbon tetrachloride (200 ml.), after deaeration for two hours with dry nitrogen, was almost saturated with chlorine gas and stored in a ruby-glass Hanus flask. Immediately prior to the actual use of the chlorine solution, a 2-ml. aliquot was titrated iodometrically. A weighed sample of alpha benzene tetrachloride crystals was placed in a 2 × 15 cm. test-tube equipped with a ground glass cap, and a known amount of chlorine in carbon tetrachloride solution was added. Illumination was supplied by a single 15-watt daylight fluorescent lamp mounted two inches from the reactor tube. The reaction was quite exothermic and probably resulted in the loss of a small quantity of chlorine from the solution. Intermittent cooling of the test tube by brief immersion in a bath of ice-water was required to maintain the average reaction temperature at 30–35°. The illuminated solution became colorless within 5–30 minutes. Crystals formed on the walls of the tube even before the reaction was complete. At the completion of the chlorination, the reactor solution was decanted into a 125-ml. beaker. The crystals, which were almost pure alpha BHC, were added to the solution. After evaporation at room temperature in the dark, the combined product was weighed, pulverized and analyzed spectrophotometrically. Three photochlorinations, which differed primarily in the amounts of reactants employed, were carried out. A fourth run, left for 24 hours in the absence of light, did not give addition chlorination to form BHC. The results obtained are listed in Table II.

Table II

Chlorination of Alpha Benzene Tetrachloride

Run	Illumination	Wt. α-$C_6H_6Cl_4$, g.	Moles Cl_2 per mole $C_6H_6Cl_4$	Unconverted $C_6H_6Cl_4$ in product, %	Ratio, BHC isomers formed, α:γ
1	Light	5.00	0.90	7.4	8.6:1
2	Light	5.00	1.00	4.8	7.6:1
3	Light	3.00	1.05	1.2	8.0:1
4	Darkness	5.00	1.00	100	...

Infrared examination of the reaction products indicated the presence of only alpha and gamma BHC, together with small amounts of unconverted benzene tetrachloride. The variation in the alpha:gamma ratio is not considered significant. To concentrate possible trace quantities of other BHC isomers, the products from Runs 1 and 2 (Table II) were combined and extracted with an equal weight of methanol, in which beta BHC has limited solubility and in which the delta BHC solubility is greater than that of any of the other isomers. The filtrate was evaporated to 50% of its volume and the crystals obtained on cooling were removed by filtration. The filtrate from this crystallization was evaporated to dryness. Spectrophotometric curves were obtained of each of the fractions. The bands of beta, delta and epsilon BHC isomers could not be detected in either of the solutes from the methanol extraction. The residual cake from the extraction was alpha BHC with a trace of the gamma isomer.

Discussion of Iodine-photocatalyzed Chlorination

The preparation of benzene tetrachloride was carried out under a variety of conditions and in all cases yielded a mixture of chlorobenzenes, chlorocycloölefins and BHC. Of the variables investigated—including iodine concentration, light source, temperature and dilution with carbon tetrachloride—the most important in controlling the ratio of chlorine addition to chlorine substitution was the concentration of iodine employed; a high concentration of the latter favored a low ratio of addition to substitution products. When 20 g. of iodine per liter of benzene was used, only 10–15% of the chlorine was converted to addition products. With 2.5 g./l., the yield of addition products, based on chlorine, was increased by a factor of two to three. The investigation of smaller quantities of iodine has not been studied quantitatively.

The use of iodine in its elemental state is not essential; partial additive chlorinations of benzene have been carried out with iodine compounds, such as potassium, lead and other metallic iodides. It is believed that any iodine-containing material which will liberate this element on treatment with chlorine will give the same type of reaction.

The iodine-catalyzed chlorination of benzene has been performed satisfactorily in sunlight and with artificial illumination such as a Hanovia mercury arc and various types of incandescent lamps. Benzene tetrachloride was obtained in each case. Since a chain mechanism is involved in the additive chlorination of benzene, increased light intensity will favor the ratio of addition to substitution chlorination; at the same time an increase in the ratio of BHC to benzene tetrachloride may be expected.

The effects of temperature and solvent dilution have not been investigated in detail. Essentially the same reaction takes place at −25 to −40° in benzene diluted with five times its volume of carbon tetrachloride as occurs in benzene at 20–45°.

Two mechanisms whereby iodine might catalyze the partial additive chlorination were considered. The first, involving formation of an unstable intermediate, tetrachlorodiiodocyclohexane, was suggested in part by the behavior of the reaction product, which liberated elemental iodine when heated to remove unreacted benzene from the mixture. Recently, the existence of molecular complexes between iodine or iodine monochloride and aromatic hydrocarbons has been shown.[13] That a tetrachlorocyclohexene–iodine intermediate is not the source of the benzene tetrachloride is indicated by: (1) Refluxing of the iodine-catalyzed reaction solution results in the decomposition of the iodine-containing material, but does not alter the intensities of the infrared spectral bands characteristic of tetrachlorocyclohexene.

(2) The high molar ratio of benzene tetrachloride formed to iodine used, which is of the order of 10:1 to 100:1, indicates that the iodine functions catalytically.

(3) No benzene tetrachloride was present in the product from two experiments in which the characteristic iodine color disappeared during the chlorination. The resulting product contained BHC but no benzene tetrachloride. Presumably, therefore, in order to yield tetrachlorocyclohexene, iodine must be present in its free state or combined with chlorine as iodine chloride. The iodine combined in an organic product was present in both experiments cited, as indicated by the liberation of free iodine on heating, yet in this condition it did not bring about the desired reaction. The nature of the unstable iodine-containing intermediate has not been elucidated.

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(13) H. A. Benesi and J. H. Hildebrand, This Journal, **71**, 2703 (1949); R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 5170 (1950).

The second mechanism, involving selective inhibition by iodine or iodine chloride, appears more likely. Inhibition of chain reactions of the radical type by iodine has been reported by Stevens[14] and others.[15] That an inhibition mechanism is involved in the iodine-catalyzed chlorination of benzene is substantiated by other observations. Although benzene tetrachloride has not been isolated from chlorination reactions other than those catalyzed by iodine, it has been detected by infrared spectrophotometric examination of benzene hexachloride prepared in the presence of oxygen under conditions resulting in poor chlorine conversion, such as low light intensity.

Detroit, Michigan Received February 20, 1951

[14] H. C. Stevens, U. S. Patent 2,415,971, Feb. 18, 1947.

[15] F. Strain, W. E. Bissinger, W. R. Dial, H. Rudoff, B. J. DeWitt, H. C. Stevens and J. H. Langton, This Journal, **72**, 1254 (1950).

[Contribution No. 810 from the Department of Chemistry, University of Pittsburgh and Mellon Institute of Industrial Research]

Electric Moments and Structures of Organosilicon Compounds. I. The Aliphatic Carbon–Silicon Bond

By Henry Freiser, Robert Charles, John Speier and Mary Eagle

The dielectric constants and densities of neopentyl chloride, chloromethyltrimethylsilane, and dichloromethyltrimethylsilane in benzene solution have been determined at 30.0°. The dipole moment values of neopentyl chloride, chloromethyltrimethylsilane and dichloromethyltrimethylsilane have been calculated as 1.93, 2.03 and 2.28 Debye units, respectively. These data permit calculation of the $(CH_3)_3Si-$ group moment as 0.25–0.32 Debye unit. The results are discussed in terms of the large polarizability of the silicon atom.

The interesting properties of organosilicon compounds have merited attention from many investigators. The problem of charge distribution in the organosilicon molecules has been attacked with the hope of shedding light on some of the peculiar behavior of these substances. In this report, there are presented the results of our work with compounds in which silicon is bonded to aliphatic carbon atoms.

Experimental

Chloromethyltrimethylsilane.—This was prepared according to the directions of Whitmore, Sommer and Gold[1] and was purified by fractional distillation through a glass helices packed column, b.p. 97.2°, $n^{25}D$ 1.4148, d^{25}_4 0.8764.

Dichloromethyltrimethylsilane.—This was prepared by the method of Speier and Daubert[2] and was purified by fractional distillation, b.p. 134°, $n^{25}D$ 1.4421, d^{25}_4 1.042.

Neopentyl Chloride.—A sample of purified neopentyl chloride was kindly furnished us by Dr. Leo Sommer of Pennsylvania State College and used without further purification.

Measurements and Calculations.—The procedure used has already been described.[3] The measurements are summarized in Table I where the dielectric constants, ϵ, and the densities, d, of benzene solutions containing mole fraction f_2 of the substance indicated are given along with the molar polarization and molar refraction. The table also includes the polarization obtained by extrapolation to $f_2 = 0$ of the P_2 values and the dipole moment, μ, calculated therefrom in the usual manner.

Table I

Dielectric Constants, Densities, Polarizations and Dipole Moments in Benzene at 30°

f_2	ϵ	d	P_2
Chloromethyltrimethylsilane, MRD = 35.0, μ = 2.03 D			
0.00000	2.2627	0.86823	(118.0)
.00997	2.3136	.86814	117.5
.02434	2.3832	.86800	114.7
.03079	2.4141	.86794	113.9
.05442	2.5294	.86772	112.8
Neopentyl chloride, MRD = 30.1, μ = 1.93 D			
0.00000	2.2627	0.86823	(104.8)
.01145	2.3152	.86796	104.6
.02094	2.3568	.86772	102.9
.03752	2.4291	.86731	101.5
.05257	2.4963	.86691	101.0
Dichloromethyltrimethylsilane, MRD = 40.0, μ = 2.28 D			
0.00000	2.2627	0.86823	(144.4)
.01198	2.3428	.87142	143.7
.02128	2.4071	.87391	144.2
.02989	2.4733	.87633	146.9
.04037	2.5365	.87879	142.7

Discussion of Results

In the organosilicon compounds studied the silicon is bonded to three methyl groups and a fourth, substituted methyl group. In order to study the effect of the silicon atom in the electrical charge distribution of these compounds it was decided to consider the $(CH_3)_3Si-$ group as a unit. Thus the two compounds might be written as RCH_2Cl and $RCHCl_2$ where the R symbolizes the $(CH_3)_3Si-$ group. We have assumed that the moment of RCH_2Cl may be calculated, as is that of a disubstituted methane, as the vector sum of the R–C and C–Cl moments each acting in the direction of the tetrahedral bond angle. The moments of the C–H bonds are not considered in this calculation. In order to obtain as exact correspondence as possible, the value of the C–Cl moment was calculated from the dipole moment of neopentyl chloride assuming that the entire value, 1.93 D, resides in the C–Cl bond. Thus, a comparison of the moments of neopentyl chloride and chloromethyltrimethylsilane permits calculation of the $(CH_3)_3Si-C$ group moment. The value, 0.25 D with the silicon atom assumed to be at the positive end of the dipole, is of the same order of magnitude as that reported by Roberts and coworkers[4] based on measurements of halogen nuclear substituted trimethylsilylbenzenes.

[1] F. C. Whitmore, L. H. Sommer and J. Gold, This Journal, **69**, 1976 (1947).

[2] J. Speier and B. F. Daubert, *ibid.*, **70**, 1400 (1948).

[3] R. K. Keswani and H. Freiser, *ibid.*, **71**, 218 (1949).

[4] J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2294 (1949).