Hyperconjugation involving the phenyl group might even exert its effect by loosening the α-hydrogen atoms in phenylacetic acid and promoting direct interaction (I) of the α-hydrogens with the carboxyl group oxygen atoms. Were hyperconjugation involving the phenyl group the dominant factor, a smaller isotope effect on the ionization constant would be expected for α-deuterated acetic acid than for α-deuterated phenylacetic acid. The ratio of the ionization constants of acetic acid and α,α,α-trideuterioacetic acid will be reported later.

Acknowledgments.—Helpful suggestions of John D. Roberts and G. H. Cartledge are acknowledged.

[DEPARTAMENTO DE QUÍMICA ORGÁNICA DE BARCELONA, INSTITUTO DE QUÍMICA "ALONSO BARBA," UNIVERSIDAD DE BARCELONA, SPAIN]

Preparation of Highly Strained Aromatic Chlorocarbons. I. A Powerful Nuclear Chlorinating Agent. Relevant Reactivity Phenomena Traceable to Molecular Strain[1]

BY MANUEL BALLESTER, CARLOS MOLINET AND JUAN CASTAÑER

RECEIVED OCTOBER 6, 1959

The preparation of perchlorotoluene and perchloro-*p*-xylene is effected starting from 2,3,4,5-tetrachloro-1-trichloromethylbenzene and 1,4-bistrichloromethylbenzene, respectively, by means of a powerful nuclear chlorinating agent. 1,3,5-Tristrichloromethylbenzene is inert under the same conditions. Chlorination of 2,4,6-trichloromesitylene with chlorine and white light gives 2,4,6-trichloro-1,3,5-trisdichloromethylbenzene and products of chlorinolysis; no perchloromesitylene is isolated. Under similar conditions perchlorotoluene and perchloro-*p*-xylene readily undergo chlorinolysis. 2,3,5,6-Tetrachloro-1-trichloromethylbenzene, 2,5-dichloro-1,4-bistrichloromethylbenzene and 2,3,5,6-tetrachlorobenzoic acid are also reported for the first time. Some significant results related to the preparation and stability of those chlorocarbons are explained on the basis of steric strain and distortion.

Introduction

A number of exhaustive chlorinations of alkylbenzenes starting either from ring[2–9] or side-chain[2,5,9–12] perchlorinated alkylbenzenes have been described. The chlorination either stopped before replacement of the last (alpha or *ortho*) hydrogen atom or chlorinolysis occurred.

The perchlorinations here reported have been accomplished by means of an extremely powerful yet selective nuclear chlorinating agent. Its composition is similar to the one described by Silberrad,[13] *i.e.*, a solution containing sulfur monochloride and anhydrous aluminum chloride in sulfuryl chloride. Apparently, the essential difference consists in the concentration of the catalysts which in the present case is very high.

Results

2,3,5,6-Tetrachloro-1-trichloromethylbenzene.—Perchlorotoluene (IV) was obtained starting from 2,3,4,5-tetrachloro-1-trichloromethylbenzene (III) In the preparation of the latter, as described previously,[5,11] 2,3,5,6-tetrachloro-1-trichloromethylbenzene (II) occurred as a by-product. It was hydrolyzed (90.9% yield) to 2,3,5,6-tetrachlorobenzoic acid, which was subsequently decarboxylated to 1,2,4,5-tetrachlorobenzene. Neither II nor the acid had been described previously. It appears therefore that the compound melting at 101–102° described as II by Nicodemus[14] was something else.

Perchlorotoluene.[15]—Perchlorotoluene (IV) was obtained from III. Perchlorobenzene (V) was also formed and some starting material was recovered. The yield was about 60%. Under stronger chlorinating conditions an increased amount of perchlorobenzene was formed. It was found that under these conditions IV undergoes chlorinolysis.

Perchlorotoluene was hydrolyzed (98% yield) to pentachlorobenzoic acid, which was subsequently decarboxylated to pentachlorobenzene.

Under photochlorinating conditions with chlorine and white light perchlorotoluene is readily and quantitatively converted into perchlorobenzene.

Perchloro-*p*-xylene.—The preparation of perchloro-*p*-xylene (VIII) was performed starting from *p*-bistrichloromethylbenzene (VI). The yield was 71%; neither perchlorobenzene nor 2,3,5-trichloro-1,4-bistrichloromethylbenzene was detected. 2,5-Dichloro-1,4-bistrichloromethylbenzene (VII) melting at 202–204°, was isolated as a by-product. Shorter reaction times gave greater amounts of the latter. This octachloro-

---

[1] Part of this work has been sponsored by the Air Research and Development Command (European Office), U. S. Air Force, under the Contract AF 61(052)-141.

[2] F. Beilstein and A. Kuhlberg, *Ann.*, **150**, 286 (1869).

[3] P. C. Harvey, F. Smith, M. Stacey and J. C. Tatlow, *J. Appl. Chem.* (*London*), **4**, 319 (1954).

[4] G. Lock, *Ber.*, **66**, 1527 (1933).

[5] M. Ballester, *Mem. real. acad. cienc. y artes Barcelona*, **29**, 271 (1948).

[6] E. T. McBee and R. E. Leech, *Ind. Eng. Chem.*, **39**, 393 (1947).

[7] E. T. McBee, H. B. Hass, P. E. Weimer, W. E. Burt, Z. D. Welch, R. M. Robb and F. Speyer, *ibid.*, **39**, 387 (1947).

[8] L. Cassella and Co., German Patent 360,414 (*Chem. Zentr.*, **94II**, 406 (1923).

[9] E. T. McBee, H. B. Hass, P. E. Weimer, W. E. Burt, Z. D. Welch, R. M. Robb and F. Speyer, *Natl. Nuclear Energy Serv., Div. VIII*, **1**, 235 (1951) (*C. A.*, **46**, 2513 (1952)).

[10] P. G. Harvey, F. Smith, M. Stacey and J. C. Tatlow, *J. Appl. Chem.* (*London*), **4**, 325 (1954).

[11] M. Ballester, *Anales real. soc. españ. fís. y quím.* (*Madrid*), **50B**, 765 (1954).

[12] E. T. McBee, H. B. Hass, G. M. Rothrock, J. S. Newcomer, W. V. Clipp, Z. D. Welch and C. I. Gochenour, *Ind. Eng. Chem.*, **39**, 384 (1947).

[13] O. Silberrad, *J. Chem. Soc.*, **121**, 1015 (1922).

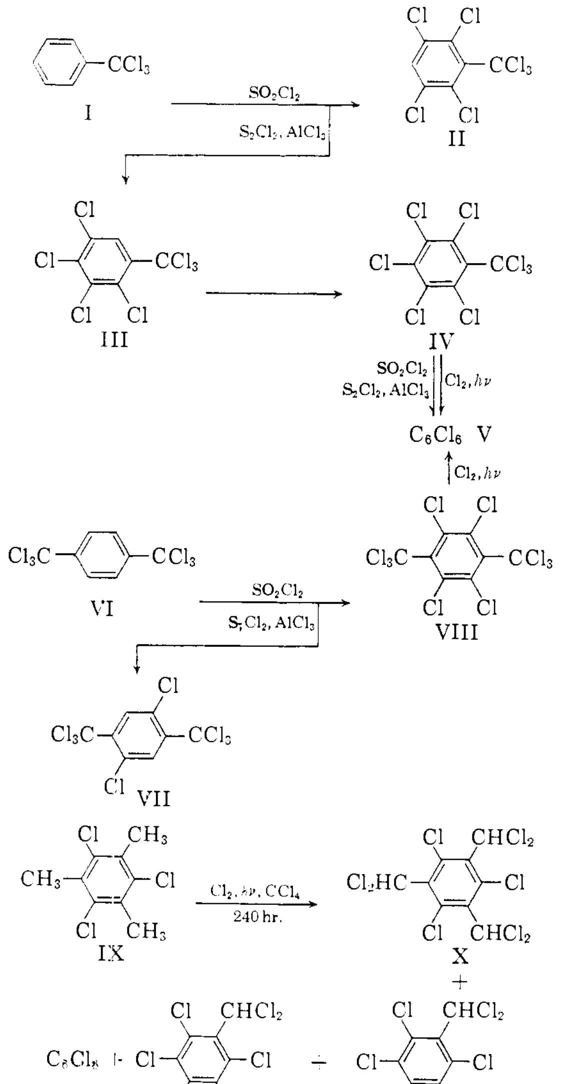
[14] O. Nicodemus, *Chem. Zentr.*, **82I**, 1682 (1911).

[15] A short communication on the isolation of perchlorotoluene has already been published.[16]

[16] M. Ballester and C. Molinet, *Chemistry & Industry*, 1290 (1954).

p-xylene has been described previously.[17,18] However, the melting points reported were considerably lower (193° and 150°). For this reason it was fully analyzed and characterized. Derivatives prepared: 2,5-dichloroterephthalic acid, methyl 2,5-dichloroterephthalate, *p*-dichlorobenzene.

The perchloro-*p*-xylene, greenish-yellow needles, was hydrolyzed to tetrachloroterephthalic acid. The methyl ester was prepared.



Smith and Turton reported[19] spectral data on perchloro-*p*-xylene. However, in the articles on chlorination published by Smith and co-workers during the same period it is stated that its preparation could not be effected.[3,10] Consequently, the ultraviolet spectrum of this compound was recorded.[20] It differs profoundly from that reported by those authors, suggesting that the confusion concerning this compound may be due to a misprint.

Perchloro-*p*-xylene is remarkably stable under the nuclear chlorinating conditions attendant to its preparation. However, it is readily converted into perchlorobenzene by photochlorination with chlorine and white light.

Attempted Preparations of Perchloromesitylene.—McBee and Leech reported the preparation of perchloromesitylene (m.p. 178–179°) by photochlorination of 2,4,6-trichloromesitylene with chlorine and white light.[6] However, under very similar conditions Smith, *et al.*,[3] prepared 2,4,6-trichloro-1,3,5-trisdichloromethylbenzene (m.p. 178.5°). On the other hand, Smith and Turton reported[19] the ultraviolet spectrum of perchloromesitylene, despite their earlier reports and announcement[10] that 1,3,5-tristrichloromethylbenzene was quite inert under nuclear chlorinating conditions.[21]

Because of these contradictory results and for other reasons to be considered later, exhaustive photochlorinations of 2,4,6-trichloromesitylene (IX) under the conditions reported by McBee and Leech, as well as nuclear chlorination of 1,3,5-tristrichloromethylbenzene, were undertaken.

The chlorination of IX (48 hours) gave 2,4,6-trichloro-1,3,5-trisdichloromethylbenzene (X, 68.5% yield, m.p. 178.5–180.5°) and 2,4,5,6-tetrachloro-1,3-bisdichloromethylbenzene (XI, 25.2% yield). Longer reaction times (240 hours) gave the latter as the main product along with substantial amounts of the former, 2,3,4,5,6-pentachloro-1-dichloromethylbenzene (XII) and perchlorobenzene.

1,3,5-Tristrichloromethylbenzene was found to be quite inert *versus* the nuclear chlorinating agent here described.

Experimental

Perchlorinating Agent. General Procedure.—From a dropping funnel, a solution of the substrate (10 g.) and sulfur monochloride (5 g.) in sulfuryl chloride (250 cc.) is added slowly (20 minutes) to a boiling solution of anhydrous aluminum chloride (2.5 g.) in freshly distilled sulfuryl chloride (about 750 cc.) placed in a flask fitted with a reflux condenser and heated in an oil-bath.

The reflux condenser is replaced by a distilling condenser and the solution is concentrated to about 50 cc. and then refluxed for several hours. Occasionally, small amounts of fresh sulfuryl chloride must be added to keep the volume of the solution constant.

If during the concentration a white powder separates the distillation must be stopped and enough sulfuryl chloride added to dissolve it. The concentration is then resumed carefully.

Overheating must be avoided; this can be done by carefully maintaining the level of the oil-bath below that of the reacting solution.

The sulfuryl chloride is then evaporated under reduced pressure at room temperature and the residue treated with water (1 liter). Solid sodium bicarbonate is added gradually until no more gas evolution takes place. The mass is then heated on a steam-bath for one hour and strongly acidified with excess concentrated hydrochloric acid. The solid is collected, dried and recrystallized.

Isolation of 2,3,5,6-Tetrachloro-1-trichloromethylbenzene (II).—The preparation of 2,3,4,5-tetrachloro-1-trichloromethylbenzene (III) was effected as described.[5,11] The solid portion of the product, upon recrystallization from carbon tetrachloride, gave 2,3,4,5-tetrachloro-1-trichloro-

---

[17] P. Ruggli and F. Brand, *Helv. Chim. Acta*, **27**, 274 (1944).

[18] Vereignite Glanzstoff-Fabriken A. G., British Patent 737,626 (*C. A.*, **50**, P 15588a (1956)).

[19] F. Smith and L. M. Turton, *J. Chem. Soc.*, 1350 (1955).

[20] M. Ballester and J. Castañer, THIS JOURNAL, **82**, 4259 (1960).

[21] Professor Smith has kindly informed the senior author that Dr. Tatlow checked some of their early experiments and was unable to prepare either perchloro-*p*-xylene or perchloromesitylene.

methylbenzene, m.p. 122–123°. From the mother liquor, by concentration and multiple recrystallizations. 2,3,5,6-tetrachloro-1-trichloromethylbenzene (II), white leaflets, m.p. 68–69°, was obtained (Found: C, 25.4; H, 0.6; Cl, 74.4. Calcd. for C_7HCl_7: C, 25.2; H, 0.3; Cl, 74.5). The product begins to decompose appreciably at about 200°.

Hydrolysis of 2,3,5,6-Tetrachloro-1-trichloromethylbenzene.—2,3,5,6-Tetrachloro-1-trichloromethylbenzene (II, 0.470 g.) and concentrated sulfuric acid (25 cc.) were heated on a steam-bath (about 2 hours). The mixture was poured into aqueous sodium chloride. The precipitate formed consisted of 2,3,5,6-tetrachlorobenzoic acid (0.333 g.), white needles, m.p. 180–181° (Found: C, 32.6; H, 0.9; Cl, 54.3; neut. equiv., 265. Calcd. for $C_7H_2O_2Cl_4$: C, 32.3; H, 0.8; Cl, 54.6; neut. equiv., 259.9).

Decarboxylation of 2,3,5,6-Tetrachlorobenzoic Acid.—2,3,5,6-Tetrachlorobenzoic acid (0.100 g.) and acetic acid (5 cc.) were heated for 5 hours at 300–310° in a sealed glass tube. The mixture was diluted with water, neutralized and extracted with ether. The ethereal solution gave 1,2,4,5-tetrachlorobenzene (0.060 g.), white needles m.p. 138.5–140.0° (Found: Cl, 65.9. Calcd. for $C_6H_2Cl_4$: Cl, 65.7).

Perchlorotoluene (IV). Isolation.—2,3,4,5-Tetrachloro-1-trichloromethylbenzene (III, 10 g.) was chlorinated as indicated in the general description for 2 hours and 40 minutes. The solid obtained (9.75 g.) by repeated recrystallizations from benzene, petroleum ether and acetic acid, and distillations at 0.01 − 0.1 mm. gave perchlorotoluene (IV, 5.61 g.), white leaflets, m.p. 71.5–72.5° (Found: C, 22.7; H, 0.3; Cl, 77.1; mol. wt., 359. Calcd. for C_7Cl_8: C, 22.9; H, 0.0; Cl, 77.1; mol. wt., 367.7), perchlorobenzene (0.04 g.) and starting material (2.09 g.).

Preparation.—Digestion of the reaction mass with a small amount of ether (20 cc.) left insoluble most of the perchlorobenzene. The soluble part with one recrystallization from acetic acid gave 5.80 g. of perchlorotoluene (52.6% yield).

The compound begins to decompose appreciably at about 200°.

Hydrolysis of Perchlorotoluene.—A mixture of perchlorotoluene (IV, 0.500 g.) and concentrated sulfuric acid (25 cc.) was heated on a steam-bath (48 hours). The resulting solution was cooled and poured into aqueous sodium chloride. The precipitate was pentachlorobenzoic acid (0.392 g.). It was identified by melting point and mixed melting point with an authentic sample prepared from 2,3,4,5,6-pentachlorotoluene.[4,22] The yield was 98%.

Decarboxylation of Pentachlorobenzoic Acid.—Pentachlorobenzoic acid (0.120 g.) and acetic acid (5.5 cc.) were heated at 320–330° in a sealed glass tube for 6.5 hours. The mixture was diluted with water, neutralized with aqueous sodium bicarbonate and extracted with ether. Evaporation of the ethereal solution gave pentachlorobenzene (0.085 g.), white needles (petroleum ether), m.p. 85–86°, 83, 3% yield.

Photochlorination of Perchlorotoluene.—A solution of perchlorotoluene (IV, 0.200 g.) in carbon tetrachloride (7.5 cc.) was placed in a 50-cc. round-bottomed, Pyrex-brand flask equipped with a reflux condenser and an inlet tube.

Through the solution, heated on a steam-bath and illuminated by a 500-watt incandescent lamp at 20 cm. distance from the flask, a slow stream of dry chlorine was passed for 6 hours. Upon evaporation of the solvent a white residue was obtained; it was identified by melting point and mixed melting point as perchlorobenzene. The yield was quantitative.

Chlorination of Perchlorotoluene with Silberrad Chlorinating Agent.—A solution of sulfur monochloride (0.13 g.), anhydrous aluminum chloride (0.13 g.), perchlorotoluene (0.10 g.) and sulfuryl chloride (25 cc.) was heated on a steam-bath for 75 minutes. After distillation of the sulfuryl chloride and treatment with water and aqueous sodium bicarbonate a solid was obtained, which was recrystallized from a mixture of ethanol and benzene. It was identified by melting point and mixed melting point as perchlorobenzene.

Perchloro-*p*-xylene (VIII).—1,4-Bistrichloromethylbenzene (VI, 10 g.) was chlorinated as indicated in the general description (9 hours) to yield 12.4 g. of a solid, which by recrystallizations from petroleum ether was resolved into perchloro-*p*-xylene (VIII), 10.2 g., pale greenish-yellow needles, m.p. 153.0–154.5° (Found: C, 21.5; H, 0.1; Cl, 78.9. Calcd. for C_8Cl_{10}: C, 21.3; H, 0.0; Cl, 78.7), and 2,5-dichloro-1,4-bistrichloromethylbenzene (VII) 1.45 g., colorless cubes, m.p. 202–204° (Found: C, 24.9; H, 0.7; Cl, 74.5. Calcd. for $C_8H_2Cl_8$: C, 25.2; H, 0.5; Cl, 74.3).

A reaction conducted under the same conditions but performed in a shorter reaction time (4 hours) gave 58.7 and 34.5 yields of perchloro-*p*-xylene and VII, respectively. The rest, accounting therefore for 6.8% of the starting material, was a viscous oil which was not investigated.

Hydrolysis of Perchloro-*p*-xylene.—A mixture of perchloro-*p*-xylene (VIII, 0.58 g.) and concentrated sulfuric acid (30 cc.) was heated on a steam-bath for 10 hours. The resulting solution was poured into cracked ice, and the precipitate was filtered. Upon recrystallization from ethyl ether–petroleum ether it gave tetrachloroterephthalic acid, 0.39 g., white needles, m.p. 335° dec. (reported melting points: 343–345° dec.[23] and 330° dec.[24]).

The acid was converted into its dimethyl ester with diazomethane in ether: white needles, m.p. 156–157° (reported[23] m.p. 153–155°).

Both substances gave correct analyses for carbon, hydrogen and chlorine, and the acid had the proper neutralization equivalent

Hydrolysis of 2,5-Dichloro-1,4-bistrichloromethylbenzene.—2,5-Dichloro-1,4-bistrichloromethylbenzene (VII, 0.60 g.) and concentrated sulfuric acid (30 cc.) were heated for 12 hours on a steam-bath. The solution was poured into cracked ice and the precipitate was filtered. Upon recrystallization from ethyl ether–petroleum ether it gave an almost quantitative yield of 2,5-dichloroterephthalic acid, white needles, m.p. 305° (subl.) (reported[25,26] m.p. 305–306° (subl.)).

Treatment with diazomethane in ether the acid yielded the dimethyl ester, white needles, m.p. 138–140° (reported melting points: 131–132°[25] and 137–138°.[26,27]). Both substances gave correct analyses for carbon, hydrogen and chlorine, and the neutralization equivalent checked for the acid.

Decarboxylation of 2,5-Dichloroterephthalic Acid.—A mixture of 2,5-dichloroterephthalic acid (0.114 g.) and acetic acid (5.5 cc.) was heated at about 350° in a sealed glass tube for 5 hours. The reaction solution was diluted with ether, washed with aqueous sodium bicarbonate and evaporated to dryness. The residue consisted of *p*-dichlorobenzene, 0.041 g., white needles, m.p. 52–54.

Photochlorination of Perchloro-*p*-xylene.—A solution of perchloro-*p*-xylene (VIII, 0.215 g.) and carbon tetrachloride (10 cc.) was placed in a 50-cc. round bottomed, Pyrex-brand flask equipped with a reflux condenser and an inlet tube.

Through the solution, heated on a steam-bath and illuminated by a 500-watt incandescent lamp situated at 20 cm. from the flask, a slow stream of dry chlorine was passed for 4 hours. Distillation of the solvent gave a white residue, which by recrystallization from absolute ethanol yielded perchlorobenzene (0.134 g.). From the mother liquor more product (0.008 g.) was obtained. It was identified by melting point and mixed melting point.

Nuclear Chlorination of 1,3,5-Tristrichloromethylbenzene.—1,3,5-Tristrichloromethylbenzene (5.0 g.) was chlorinated as indicated in the general description (12 hours). The starting material was recovered quantitatively.

Preparation of 2,4,6-Trichloromesitylene (IX).—To a gently refluxing mixture of mesitylene (10 g.), sulfur monochloride (0.5 g.) and sulfuryl chloride (25 g.), a solution of anhydrous aluminum chloride (0.5 g.) in sulfuryl chloride (25 g.) was gradually added (10 min.). Near the end of the addition the mass solidified partially. The refluxing was continued (30 min.) and then the mass allowed to cool. Treatment as in the general description yielded a dark-brown solid which when treated with charcoal and re-

---

[22] G. Lock, *Ber.*, **72**, 300 (1939).

[23] N. Rabjohn, THIS JOURNAL, **70**, 3518 (1948).

[24] W. Qvist and N. Holmberg, *Acta Acad. Aboensis Math. et Phys.*, **6**, No. 14, 3 (1932) (*Chem. Zentr.*, **103**, **II**, 2815 (1932).

[25] S. Levy and A. Andreocci, *Ber.*, **21**, 1463, 1959 (1888).

[26] I. G. Farbenind, A. G., French Patent 663,791 (*C. A.*, **24**, 628 (1930)).

[27] A. S. Wheeler and M. Rose, THIS JOURNAL, **46**, 2572 (1924).

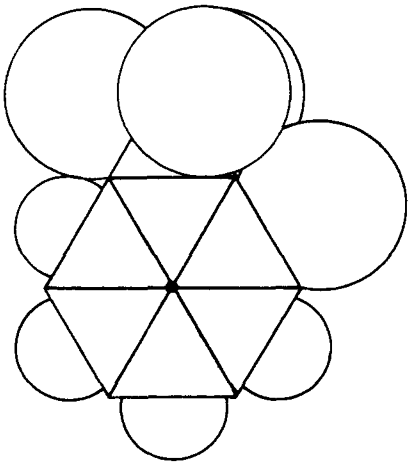


Fig. 1.

crystallized from carbon tetrachloride yielded 2,4,6-trichloromesitylene (IX) 9.7 g., m.p. 206–208° (Found: C, 48.2; H, 4.4. Calcd. for $C_9H_9Cl_3$: C, 48.3; H. 4.1) (reported[6,10] m.p. 204–205°).

Photochlorination of 2,4,6-Trichloromesitylene.—A slow stream of dry chlorine was passed (48 hours) through a gently refluxing solution of 2,4,6-trichloromesitylene (IX, 4.00 g.) in chemically purified, distilled carbon tetrachloride (40 cc.) illuminated by a 500-watt incandescent lamp. The lamp, situated underneath the Pyrex-brand container, also provided the heat.

Elimination of the solvent under vacuum afforded a solid which by repeated recrystallizations from petroleum ether was resolved into 2,4,6-trichloro-1,3,5-trisdichloromethylbenzene (X) 5.24 g., m.p. 178.5–180.5° (Found: C, 25.3; H, 0.9; Cl, 73.9. Calcd. for $C_9H_3Cl_9$: C, 25.1; H, 0.7; Cl, 74.2), and 2,4,5,6-tetrachloro-1,3-bisdichloromethylbenzene (XI) 1.72 g., m.p. 99–101°[3] (Found: C, 25.4; H, 0.8; Cl, 74.4. Calcd. for $C_8H_2Cl_8$: C, 25.2; H, 0.6; Cl, 74.3). The combined yields account for 93.7% of the starting material.

An experiment carried out under the same conditions but for 240 hours yielded 2,4,5,6-tetrachloro-1,3-bisdichloromethylbenzene (XI) as a predominant product, along with substantial amounts of 2,4,6-trichloro-1,3,5-trisdichloromethylbenzene (X) 2,3,4,5,6-pentachloro-1-dichloromethylbenzene (XII) m.p. 118–120°[4,5] (Found: Cl, 74.2. Calcd. for C_7HCl_7: Cl, 74.5), and perchlorobenzene, m.p. 228° (Found: Cl, 74.5. Calcd. for C_6Cl_6: Cl, 74.7). Mixed melting points were also performed, no depression being observed with the authentic samples.

Discussion

Steric Strain and Molecular Distortion.—In 2,3,5,6-tetrachloro-1-trichloromethylbenzene (II) perchlorotoluene (IV) and perchloro-*p*-xylene (VIII) strong steric interactions take place between the trichloromethyl groups and the *ortho* chlorine atoms. This strain is of the type that can be found in 2,6-dimethyl-*t*-butylbenzene and homomorphs.[28,29] Brown and co-workers estimated their strain to be about 24 kcal./mole.[28] Since the sizes of chlorine atom and methyl group are similar the steric strain of 2,3,5,6-tetrachloro-1-trichloromethylbenzene (II) and perchlorotoluene (IV) should be close to this value. On the same basis, that of perchloro-*p*-xylene should be about 48 kcal./mole.

Electron diffraction measurements have shown that even the perchlorobenzene molecule—where

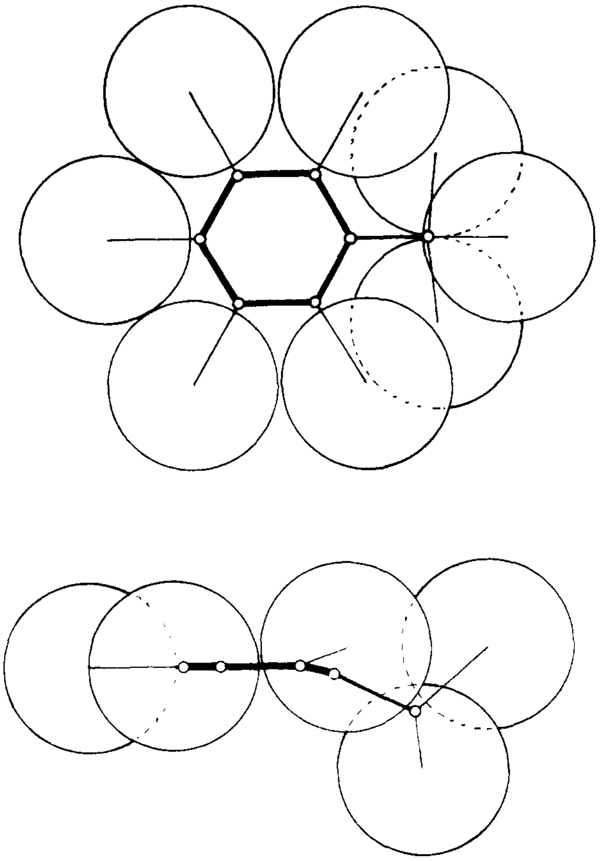


Fig. 2.

only comparatively small steric interactions take place—is distorted, with the chlorine atoms being displaced alternately above and below the mean plane of the benzene ring.[30] It adopts therefore a chair-like conformation.

In a 2-chloro-1-trichloromethylbenzene such as III or VII due to the shape of the trichloromethyl group a low-distortion arrangement is obtained when two α-chlorine atoms are located symmetrically above and below the plane of the benzene ring while the third one lies on it, pointing away from the 2-chlorine atom. Introduction of a chlorine atom in the 6-position can take place only with great distortion (Fig. 1). In this event, minimum strain occurs when two α-chlorine atoms lie below and the third one above the plane of the benzene ring. In Fig. 2, representing perchlorotoluene, it can be noticed that this third chlorine atom interacts very little with the two *ortho* chlorine atoms which along with the trichloromethyl group are forced out of the plane. Spectral evidence for this is given in the forthcoming paper.[20]

Nuclear Chlorinations.—Nuclear exhaustive chlorination of benzotrichloride[10,11] and phenylpentachloroethane[10,12] is either incomplete or gives perchlorobenzene. Although electronic deactivation by the substituents may be partly responsible for these results, the main reason is doubtless the high strain of the corresponding perchloroaralkanes. However, deactivation is almost cer-

---

[28] H. C. Brown, D. Gintis and L. Domash, This Journal, **78**, 5387 (1956).

[29] H. C. Brown and M. Grayson, *ibid.*, **75**, 20 (1953).

[30] O. Bastiansen and O. Hassel, *Acta Chem. Scand.*, **1**, 489 (1947).

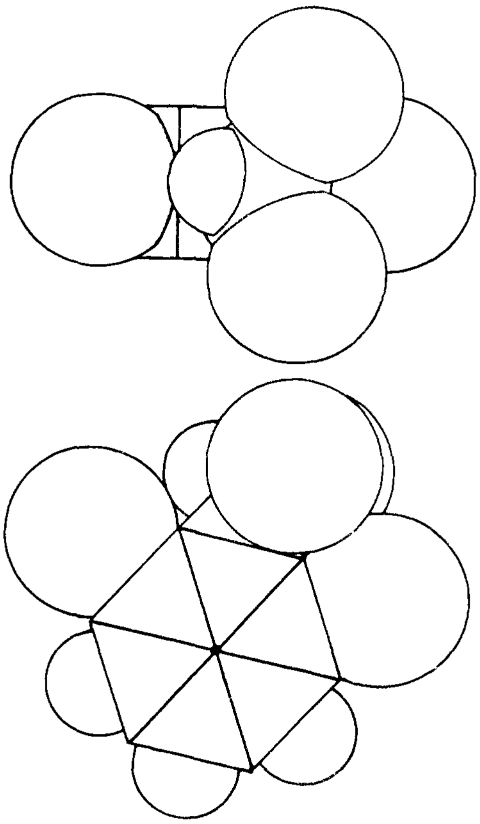


Fig. 3.

tainly the sole reason for the reported[10] inertness of 1,4-bistrichloromethylbenzene because the equivalent positions for the substitution should not have restrictive steric requirements.

The formation of perchloro-*p*-xylene from 1,4-bistrichloromethylbenzene here reported occurs obviously through the intermediate 2,3,5-trichloro-1,4-bistrichloromethylbenzene. However, the fact that the only intermediate that can be isolated in a substantial amount is VII shows that that intermediate must be formed about as quickly as it is converted into perchloro-*p*-xylene. This surprising result could be related either to an increased electron accesion to the 6-position due to the 3-chlorine atom in such an intermediate or to the fact that the 6-position in it is made more vulnerable than the equivalent 3-position of low-distorted VII because of the out-of-plane bond bending of the 5-chlorine atom in the former intermediate.

The remarkable resistance of perchloro-*p*-xylene toward chlorinolysis under nuclear chlorinating conditions may be traced to some bond strengthening due to the symmetrical character of its distortion.

A chlorine atom between two *ortho* trichloromethyl groups buttressed only by hydrogen atoms represents little steric strain. Therefore, the inertness of 1,3,5-tristrichloromethylbenzene is presumably due to electronic deactivation by the trichloromethyl groups.

Side-chain Chlorinations.—Exhaustive side-chain chlorination of alkylbenzenes under normal reproducible conditions—which normally replaces all α-hydrogen atoms— when the alkyl groups are flanked by two *ortho* chlorine atoms either stops just before substitution of the last α-hydrogen atoms or gives chlorinolysis.[3,4,5,31] The results reported here confirm this conclusion. (An exception is the preparation of perchloromesitylene reported by McBee and Leech[6] which we also have so far been unable to reproduce.) The products obtained are almost strain-free. In the case of 2,6-dichloro-1-dichloromethylbenzenes for example a low-strain arrangement is obtained when the α-hydrogen atoms lie in the plane of the benzene ring (Fig. 3).

It is currently accepted that photochlorination of side-chain α-carbon atoms in alkylbenzenes is a chain reaction taking place through benzyl-type radicals.[32] In the case of 2,3,4,5,6-pentachloro-1-dichloromethylbenzene it would be the perchlorobenzyl radical.

$$C_6Cl_5CHCl_2 + Cl \longrightarrow C_6Cl_5CCl_2 + HCl \qquad (a)$$

$$C_6Cl_5CCl_2 + Cl_2 \longrightarrow C_6Cl_5CCl_3 + Cl \qquad (b)$$

This radical is a remarkably stable one, as shown by its tendency to dimerize, even in the presence of an active-methylene compound such as toluene.[33] Also, its reaction with molecular chlorine is an energetically unfavorable one since it would give the energy-rich perchlorotoluene (step b). Furthermore, it is pointed out that in the most favorable conformation of a 2,6-dichloro-1-dichloromethylbenzene the α-hydrogen atom is strongly shielded against attack of chlorine (step a) by the surrounding chlorine atoms (Fig. 3).

Acknowledgments.—The authors wish to acknowledge their indebtedness to Dr. Leonard Spialter, Wright Air Development Center, U. S. Air Force, for his kind interest in the present research and his valuable suggestions; to Dr. Juan Estevan for the analyses; and to Mr. Juan Riera for his assistance.

[31] H. C. Brimelow, R. L. Jones and T. P. Metcalfe, *J. Chem. Soc.*, 1208 (1951).

[32] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 352.

[33] M. Ballester, C. Molinet and J. Rosa, *Tetrahedron*, **6** 109 (1959).