

tioned above was added dropwise to a 300-ml. ether solution of phenyllithium, which had been made from 110 g. (0.70 mole) of bromobenzene and an excess of lithium metal. After refluxing for one hour, this reaction mixture was poured onto cracked ice and dilute sulfuric acid to destroy the excess phenyllithium. The ether was then removed by evaporation, leaving a white solid, which was collected and dried. This solid was placed in a Soxhlet extractor and extracted for one hour with 20–40° petroleum ether to dissolve the methyltriphenylsilane (derived from the methylphenylsilane). The yield of this compound was 7.9 g. (0.03 mole), m.p. 65–66°. The remaining solid was extracted with toluene for 12 hours to give 33.0 g. (0.10 mole) of tetraphenylsilane (derived from phenylsilane), m.p. 232–233°.

Cleavage of *sym*-Diphenyldisiloxane by Ethylmagnesium Bromide.—A 46-g. (0.20 mole) sample of *sym*-diphenyldisiloxane in 50 ml. of ether was added dropwise to a 200-ml. solution of ethylmagnesium bromide, which had been made from 70 g. (0.50 mole) of ethyl bromide and 12 g. (0.50 g. atom) of magnesium turnings. The reaction mixture was held at the reflux temperature for one hour, then hydrolyzed and worked up as described in the above experiment. The phenylsilane and ethylphenylsilane obtained were converted to tetraphenylsilane and ethyltriphenylsilane, respectively. The yield of tetraphenylsilane was 24.6 g. (0.073 mole), m.p. 232–233°; that of triphenylethylsilane was 7.0 g. (0.024 mole), m.p. 73–73°. The liquid remaining after the separation of the phenylsilane and ethylphenylsilane was distilled under reduced pressure, giving 12.0 g. of crude *sym*-diethyldiphenyldisiloxane, (C₆H₅)₂SiH(C₂H₅)₂O, distilling at 140–200° (0.05 mm.). The crude product was redistilled at 107° (0.03 mm.) to obtain a sample for analysis and physical properties. The infrared spectrum of the compound was identical with that of an authentic sample of *sym*-diethyldiphenyldisiloxane, μ 1.523.

Anal. Calcd. for C₁₈H₂₀OSi₂: C, 67.2; H, 7.75; mol. wt., 286. Found: C, 67.0; H, 7.90; mol. wt., 282.

Cleavage of *sym*-Diphenyldisiloxane by Phenylmagnesium Bromide.—A 23-g. (0.10 mole) sample of *sym*-diphenyldisiloxane in 20 ml. of ether was added dropwise to a 200-ml. ether solution of phenylmagnesium bromide, which had been made from 63 g. (0.40 mole) of bromobenzene and 4.8 g. (0.40 g. atom) of magnesium turnings. The reaction mixture was held at the reflux temperature for one hour, then hydrolyzed and worked up in the usual way. The ether was removed, and the residual liquid fractionated. A 3.0-g. (0.03 mole) fraction composed of phenylsilane distilled at 118–120°. This compound was identified by its infrared spectrum¹⁴ and its boiling point. The residual liquid was distilled under reduced pressure, giving 11.7 g. (0.064 mole) of diphenylsilane, which distilled at 60° (0.6 mm.). The diphenylsilane was identified by its infrared spectrum.¹⁵ A fraction consisting of 5.0 g. (0.014 mole) of 2,4,6-triphenylcyclotrisiloxane, (C₆H₅SiH)₃, distilled at 168° (0.02 mm.), μ 1.566; calcd. mol. wt. 366, found 352. The infrared spectrum of this compound was identical

with that of the sample of the trimer obtained by the hydrolysis of phenylbromosilane.

Anal. Calcd. for C₁₈H₁₈OSi₃: C, 59.0; H, 4.96. Found: C, 59.9; H, 5.20.

Cleavage of *sym*-Diphenyldisiloxane by Benzylmagnesium Chloride.—A 23-g. (0.10 mole) sample of *sym*-diphenyldisiloxane in 25 ml. of ether was added dropwise to a 200-ml. ether solution of benzylmagnesium chloride, which had been made from 63 g. (0.50 mole) of benzyl chloride and 12 g. (0.5 g. atom) of magnesium turnings. The reaction started immediately and refluxing of the solvent resulted. The reaction mixture was held at the reflux temperature for one hour, then hydrolyzed and worked up in the usual manner. The ether was distilled off and a 19-g. mixture of phenylsilane and toluene distilled at 120°, leaving a residue which was distilled later. The mixture of phenylsilane and toluene was treated with phenyllithium, which had been made from 94 g. (0.60 mole) of bromobenzene and an excess of lithium metal. The yield of tetraphenylsilane was 7.0 g. (0.03 mole), m.p. 232–233°. The residual liquid was distilled under vacuum, giving a 24-g. mixture of 1,2-diphenylethane and benzylphenylsilane, which distilled at 100–160° (0.43 mm.). This mixture was treated with an ether solution of phenyllithium, which had been made from 63 g. (0.40 mole) of bromobenzene and an excess of lithium metal. The reaction mixture was hydrolyzed and worked up in the usual manner. The ether was evaporated, and the residual liquid distilled under reduced pressure to remove the 1,2-diphenylethane. The residue was treated with 20–40° petroleum ether, which caused benzyltriphenylsilane to precipitate. This compound was recrystallized twice from 95% ethanol; yield 16 g. (0.04 mole), m.p. 96–97°.

Cleavage of *sym*-Diphenyldisiloxane by Lithium Aluminum Hydride.—A 4.0-g. (0.03 mole) sample of *sym*-diphenyldisiloxane was added dropwise to 2.0 g. (0.7 mole) of lithium aluminum hydride in 250 ml. of ether. Slight refluxing of the solvent resulted, and a heavy white precipitate formed. The reaction mixture was allowed to stand for two hours and then it was poured onto a mixture of cracked ice and dilute hydrochloric acid. The ether layer was separated, washed first with dilute hydrochloric acid and then with water, and dried over Drierite. The ether was distilled off and the product (2.1 g., 50%) distilled at 119° (740.3 mm.). The product was identified as phenylsilane by its boiling point and infrared spectrum.¹⁶

Acknowledgments.—Analyses were by Miss J. Dickey of the Indiana University Microanalytical Laboratory. This paper is based upon work performed under contract Nonr-90802 NR 358-321 (Office of Naval Research).

(16) C. Haack and C. Hamner, *Trans. Journal*, 74, 1844 (1957).

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Halogen Derivatives of Dibenzo-*p*-dioxin

BY HENRY GILMAN AND JOSEPH J. DIETRICH

RECEIVED OCTOBER 16, 1956

Direct preparations for 2-chloro- (II), 2,7-dichloro- (III), 2,7-dibromo- (VI) and 2,3,7,8-tetrabromo-dibenzo-*p*-dioxin (VII) from dibenzo-*p*-dioxin (I) are reported. The 1-bromo-dibenzo-*p*-dioxin (IV) and the 2-iodo-dibenzo-*p*-dioxin (IX) are obtained by indirect methods. II, IV, VI, VIII and IX are new compounds. Structure proofs for these and 2,8-dibromo-dibenzo-*p*-dioxin (VII) are included along with a brief theoretical discussion dealing with VI, VII and VIII. Brief instructions are given for the preparation of 2-bromo-dibenzo-*p*-dioxin (V) and of VII. I is formed from inexpensive *o*-chlorophenol in low yield.

Studies on the orientation of entering groups on the dibenzo-*p*-dioxin (I) nucleus have led to the

preparation of a number of halogen derivatives and confirmation of their structures.

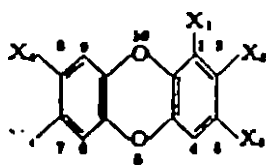


Fig. 1.

- I. $X_1, X_2, X_3, X_4, X_5, X_6 = H$
 II. $X_2 = Cl; X_1, X_3, X_4, X_5, X_6 = H$
 III. $X_3 = Cl; X_1, X_2, X_4, X_5, X_6 = H$
 IV. $X_1 = Br; X_2, X_3, X_4, X_5, X_6 = H$
 V. $X_2 = Br; X_1, X_3, X_4, X_5, X_6 = H$
 VI. $X_3 = Br; X_1, X_2, X_4, X_5, X_6 = H$
 VII. $X_4 = Br; X_1, X_2, X_3, X_5, X_6 = H$
 VIII. $X_5 = Br; X_1, X_2, X_3, X_4, X_6 = H$
 IX. $X_6 = I; X_1, X_2, X_3, X_4, X_5 = H$
 X. $X_2, X_4, X_6 = NH_2; X_1, X_3, X_5 = H$
 XI. $X_2 = NH_2; X_1, X_3, X_4, X_5, X_6 = H$
 XII. $X_2, X_4 = COOCH_3; X_1, X_3, X_5 = H$

These consist of the 2-chloro-dibenzo-*p*-dioxin (II), 2,7-dichloro-dibenzo-*p*-dioxin (III), 1-bromo-dibenzo-*p*-dioxin (IV), 2-bromo-dibenzo-*p*-dioxin (V), 2,7-dibromo-dibenzo-*p*-dioxin (VI), 2,8-dibromo-dibenzo-*p*-dioxin (VII), 2,8,7,8-tetrabromo-dibenzo-*p*-dioxin (VIII) and the 2-iodo-dibenzo-*p*-dioxin (IX). Only 2,7-dichloro-dibenzo-*p*-dioxin, 2-bromodibenzo-*p*-dioxin and an unnamed dibromodibenzo-*p*-dioxin have been reported in the literature to date. 2,7-Dichloro-dibenzo-*p*-dioxin was obtained from 2,7-diamino-dibenzo-*p*-dioxin (X) by a Sandmeyer reaction.¹ Later, Julia and Bailarge² prepared the same compound by ring closure of 2,4-dichlorophenol. A Sandmeyer reaction was also used in the preparation of 2-bromo-dibenzo-*p*-dioxin from 2-amino-dibenzo-*p*-dioxin (XI).³ The identification of the unnamed dibromo compound⁴ was accomplished in the course of these studies.

Direct chlorination of dibenzo-*p*-dioxin in glacial acetic acid at room temperature gave 2-chloro-dibenzo-*p*-dioxin and a small amount of 2,7-dichloro-dibenzo-*p*-dioxin. Attempts to increase the yield of the 2,7-compound by use of ultraviolet light and elevated temperatures were only partially successful. 2-Chloro-dibenzo-*p*-dioxin was also formed when a Sandmeyer reaction was run on 2-amino-dibenzo-*p*-dioxin.

Metalation of dibenzo-*p*-dioxin with phenylthium followed by addition to a bromine-ether mixture produced a monobromo compound differing from 2-bromo-dibenzo-*p*-dioxin and must therefore be 1-bromo-dibenzo-*p*-dioxin, the only other possible isomer.

With the constitution of 2-bromo-dibenzo-*p*-dioxin known, the structure proofs of the two dibromo-dibenzo-*p*-dioxin derivatives were undertaken. 2,8-Dibromo-dibenzo-*p*-dioxin, being the easier to obtain, was converted to the di-Grignard, carbonated and finally treated with thionyl chloride followed by absolute methyl alcohol to give the dimethyl ester of 2,8-dibenzo-*p*-dioxin-dicarboxylic acid (XII), a known compound.⁵ The other dibromo-dibenzo-*p*-dioxin was thus considered to be 2,7-dibromo-dibenzo-*p*-dioxin on the

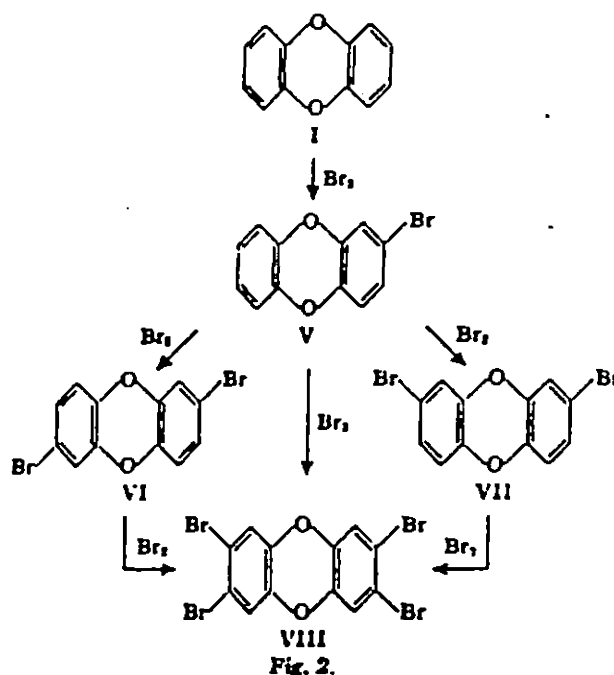


Fig. 2.

basis of infrared spectra comparisons. Both compounds gave the same infrared spectra which would only be true if the second bromine atom were in the 7-position. The positions occupied by the bromine atoms in the tetrabromo-dibenzo-*p*-dioxin must be 2,3,7,8, since exhaustive bromination of a mixture of 2-bromo-, 2,7-dibromo- and 2,8-dibromo-dibenzo-*p*-dioxin gave only one tetrabromo derivative as shown in Fig. 2.

A Sandmeyer reaction carried out on 2-amino-dibenzo-*p*-dioxin gave 2-iodo-dibenzo-*p*-dioxin. Attempts to make the compound directly by a method developed for the iodination of a closely related compound in this Laboratory failed.⁶

It has been found that 2,8-dibromo-dibenzo-*p*-dioxin can be made in 22% yield whereas 2,7-dibromo-dibenzo-*p*-dioxin can be formed in only 7% yield using forced conditions. These results can be explained satisfactorily by consideration of Fig. 3.

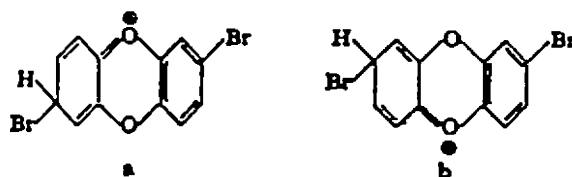


Fig. 3.

In Fig. 3(a), the oxonium ion formed in the intermediate stage received no assistance from the bromine atom in the 2-position. However, in Fig. 3(b), the oxonium ion is para to the initial bromine atom and can therefore receive a certain amount of resonance stabilization. The evidence for a quinoid-type intermediate is enhanced by the formation of 2,3,7,8-tetrabromo-dibenzo-*p*-dioxin, where the third and fourth entering bromine atoms, despite steric hindrance, enter *ortho* to the bromine, although a completely unhindered position *ortho* to the oxygen is available.

(1) S. Ueo, *Bull. Chem. Soc. Japan*, **36**, 177 (1961).

(2) M. Julia and M. Bailarge, *Bull. soc. chim. France*, 640 (1953).

(3) French Patent 790,627 (June 16, 1936).

(4) Swiss Patent 238,627 (July 31, 1945).

(5) M. Tomita, *J. Pharm. Soc. Japan*, **86**, 906 (1936).

(6) H. Gilman, O. Brown, W. Bywater and W. Kirkpatrick, *THE JOURNAL*, **86**, 2473 (1934).

Experimental

Dibenzo-*p*-dioxin (I).—Using the method developed by Tomita⁸ but substituting *a*-chlorophenol for *a*-bromophenol, it is possible to obtain yields ranging from 10–20%, using this inexpensive starting material. Under the conditions and with the equipment used below, it has been found that increasing the size of the preparation apparently decreases the yield.

a-Chlorophenol (410 g., 3.16 moles), 230 g. (1.6 moles) of anhydrous potassium carbonate and 34 g. of copper powder were heated for 6 hr. in an oil-bath at 170–180°. The tarry mixture was further refluxed with aqueous potassium hydroxide, allowed to cool and finally extracted with ether. Washing the ether layer with concentrated potassium hydroxide dispelled the dark color. The ether was evaporated, the residue dissolved in benzene and chromatographed on alumina. Best results were obtained by evaporation of the effluent and recrystallization of the residue from hot ethanol to white plates or needles, m.p. 120–122° (reported⁸ m.p. 119°).

2-Chloro-dibenzo-*p*-dioxin (II).—Chlorine gas was slowly bubbled into a stirred solution of 4.6 g. (0.025 mole) of dibenzo-*p*-dioxin in 125 ml. of glacial acetic acid over a period of 2 hr. at room temperature. At that time, a yellow color was evident in the clear solution. Aqueous sodium bisulfite was used to dilute the reaction mixture and destroy the excess chlorine. Filtration gave 5 g. of crude material melting over the range 65–85°. Vacuum distillation of this produced 2.4 g. of material, b.p. 93–94° (0.25 mm.). Five recrystallizations from ethanol–water yielded 1 g. (18%) of white needles, m.p. 87–90°. A 0.05 mole preparation run at 75° did not result in a higher yield.

Anal. Calcd. for $C_{12}H_8O_2Cl$: Cl, 16.34. Found: Cl, 15.81, 15.86.

2,7-Dichloro-dibenzo-*p*-dioxin (III).—An identical procedure was employed for this reaction as in the preceding experiment except for irradiation of the flask with ultraviolet light for 4.5 hr. giving a crude yield of 5.8 g., melting over the range 93–106°. Two recrystallizations from methyl alcohol and a final recrystallization from petroleum ether (b.p. 60–70°) produced 0.3 g. (3%) of white needles, m.p. 201–203° (reported¹³ m.p. 207°, 201–202°).

This same reaction gave only a trace of product when run at room temperature in the absence of ultraviolet light. A Pyrex flask was used in all of the preparations.

1-Bromo-dibenzo-*p*-dioxin (IV).—A 0.05-mole preparation of phenyllithium was added to a solution of 0.05 mole of dibenzo-*p*-dioxin in anhydrous ether under an atmosphere of dry, oxygen-free nitrogen. Due to the ease of di-metalation, an excess of metalating agent was avoided. Di-metalation did not occur when methylolithium was used, but the yield of mono-metalated product was significantly lower.

A 0.05-mole preparation of phenyllithium was added to 9.2 g. (0.05 mole) of dibenzo-*p*-dioxin in 50 ml. of ether and refluxed with stirring for 5 hr. The resulting mixture was added to a stirred mixture of 10 g. (0.05 mole) of bromine in 150 ml. of ether at ice-bath temperature over a period of 15 min. It was allowed to warm to room temperature, stirred for 3 hr. and then washed with aqueous sodium bisulfite. The ether layer, after drying over anhydrous sodium sulfate, was evaporated and the residue vacuum distilled at 131–136° (0.1 mm.) to give 1.5 g. of crude product. Two recrystallizations from methyl alcohol resulted in 1 g. (8%) of white needles, m.p. 104–106°.

Anal. Calcd. for $C_{12}H_7O_2Br$: Br, 30.40. Found: Br, 29.51, 29.52.

2-Bromo-dibenzo-*p*-dioxin (V).—Several 0.05- to 0.1-mole preparations were carried out using potassium bromide-bromate in refluxing acetic acid as the brominating agent. The crude product was purified by vacuum distillation and a final recrystallization from ethanol–water, m.p. 93–94.5°. Yields of 40% were obtained consistently. Earlier workers⁹ prepared this compound by direct bromination in carbon disulfide reporting a melting point of 90–92° but making no mention of percentage yield.

2,7-Dibromo-dibenzo-*p*-dioxin (VI).—In 100 ml. of glacial acetic acid were dissolved 4.6 g. (0.025 mole) of dibenzo-*p*-dioxin and 12.8 g. (0.08 mole) of bromine and the resulting solution stirred and refluxed for 5.5 hr. Dilution with aqueous sodium bisulfite and filtration gave 11 g. of crude material melting over the range 110–130°. Five recrystallizations of this material from glacial acetic acid yielded 0.6 g. (7%) of white needles, m.p. 174–176°.

Anal. Calcd. for $C_{12}H_6O_2Br_2$: Br, 46.75. Found: Br, 46.91, 46.73.

2,8-Dibromo-dibenzo-*p*-dioxin (VII).—This compound was prepared in 22% yield using the theoretical amount of potassium bromide-bromate in refluxing acetic acid. The crude material was purified by repeated recrystallizations from ethanol to a constant melting point of 149.5–151°. It had been prepared previously by direct bromination of dibenzo-*p*-dioxin in nitrobenzene at room temperature with a reported melting range of 145–150° and in unspecified yield.⁶

The dimethyl ester obtained via the Grignard reagent and subsequent carbonation and esterification of this dibromo compound melted at 168–171°. A melting point of 167° has been reported⁶ earlier for the dimethyl ester of 2,8-dibenzo-*p*-dioxin-dicarboxylic acid.

2,3,7,8-Tetrabromo-dibenzo-*p*-dioxin (VIII).—A solution of 9.3 g. (0.05 mole) of dibenzo-*p*-dioxin, 64 g. (0.4 mole) of bromine and 200 ml. of glacial acetic acid was stirred and refluxed for 6 hr. Dilution with aqueous sodium bisulfite followed by filtration produced 18.2 g. of crude material melting over the range 297–330°. Due to the insolubility of this material in all common solvents, only a small portion was purified by three recrystallizations from hot pyridine to yield a white, granular product, m.p. 334–336°.

Anal. Calcd. for $C_{12}H_2O_2Br_4$: Br, 62.00. Found: Br, 62.49, 62.64.

2-Iodo-dibenzo-*p*-dioxin (IX).—Nitrosylsulfuric acid was made by dissolving 0.8 g. (0.015 mole) of sodium nitrite in 8 ml. of concentrated sulfuric acid and then slowly warming it to 70°. This was cooled to 15° in an ice-bath and 2 g. (0.01 mole) of 2-amino-dibenzo-*p*-dioxin in 25 ml. of glacial acetic acid was added slowly with vigorous stirring.⁹ After addition, it was stirred 15 min. before being added rapidly to a cold solution of 2.5 g. (0.015 mole) of potassium iodide in dilute sulfuric acid. The now brown mixture was heated to boiling to destroy the complex, diluted and filtered. Recrystallization of the crude material from ethanol–water (Norit A) gave 1 g. of product, m.p. 92–94.5°. Two more recrystallizations from ethanol–water (Norit A) resulted in 0.4 g. of fine, white needles, m.p. 95–97°.

Anal. Calcd. for $C_{12}H_7O_2I$: I, 40.96. Found: I, 40.64, 40.40.

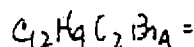
Acknowledgment.—The authors are indebted to R. McCord of the Institute of Atomic Research, Ames, Iowa, for infrared spectra.

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(7) All melting points are uncorrected.

(8) M. Tomita, *J. Pharm. Soc. Japan*, **82**, 66 (1932).

(9) This procedure was adapted from K. R. Saunders, "The Aromatic Dioxin Compounds," Edward Arnold and Co., London, 1949, p. 13.



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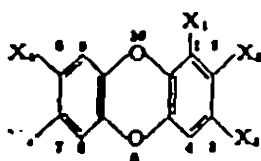


Fig. 1.

1. $X_1, X_2, X_3, X_4 = H$
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 75. $X_1 = Br; X_2, X_3, X_4 = H$
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 78. $X_1 = Br; X_2, X_3, X_4 = H$
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 92. $X_1 = Br; X_2, X_3, X_4 = H$
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 96. $X_1 = Br; X_2, X_3, X_4 = H$
 97. $X_1 = Br; X_2, X_3, X_4 = H$
 98. $X_1 = Br; X_2, X_3, X_4 = H$
 99. $X_1 = Br; X_2, X_3, X_4 = H$
 100. $X_1 = Br; X_2, X_3, X_4 = H$

consist of the 2-chloro-dibenzo-*p*-dioxin (II), 2,7-dichloro-dibenzo-*p*-dioxin (III), 1-bromo-dibenzo-*p*-dioxin (IV), 2-bromo-dibenzo-*p*-dioxin (V), 2,7-dibromo-dibenzo-*p*-dioxin (VI), 2,8-dibromo-dibenzo-*p*-dioxin (VII), 2,3,7,8-tetrabromo-dibenzo-*p*-dioxin (VIII) and the 2-iodo-dibenzo-*p*-dioxin (IX). Only 2,7-dichloro-dibenzo-*p*-dioxin, 2-bromo-*p*-dioxin and an unnamed dibromo-*p*-dioxin have been reported in the literature to date. 2,7-Dichloro-dibenzo-*p*-dioxin was obtained from 2,7-diamino-dibenzo-*p*-dioxin (X) and Meyer reaction.¹ Later, Julia and Bail prepared the same compound by ring closure of dichlorophenol. A Sandmeyer reaction was used in the preparation of 2-bromo-dibenzo-*p*-dioxin from 2-amino-dibenzo-*p*-dioxin (XI).² The isolation of the unnamed dibromo compound was accomplished in the course of these

studies. Chlorination of dibenzo-*p*-dioxin in glacial acetic acid at room temperature gave 2-chloro-dibenzo-*p*-dioxin and a small amount of 2,7-dichloro-dibenzo-*p*-dioxin. Attempts to increase the yield of the 2,7-compound by use of ultraviolet light and elevated temperatures were only partially successful. 2-Chloro-dibenzo-*p*-dioxin was also obtained when a Sandmeyer reaction was run on 2-iodo-dibenzo-*p*-dioxin.

Chlorination of dibenzo-*p*-dioxin with phenylmagnesium bromide followed by addition of a bromine-ether reagent produced a monobromo compound different from 2-bromo-dibenzo-*p*-dioxin and must therefore be 1-bromo-dibenzo-*p*-dioxin, the only other isomer.

In the constitution of 2-bromo-dibenzo-*p*-dioxin, the structure proofs of the two dibromo-dibenzo-*p*-dioxin derivatives were under investigation. 2,8-Dibromo-dibenzo-*p*-dioxin, being the most difficult to obtain, was converted to the di-Grignard, isolated and finally treated with thionyl chloride followed by absolute methyl alcohol to give the methyl ester of 2,8-dibenzo-*p*-dioxin-dicarboxylic acid (XII), a known compound.³ The dibromo-dibenzo-*p*-dioxin was thus considered to be 2,7-dibromo-dibenzo-*p*-dioxin on the

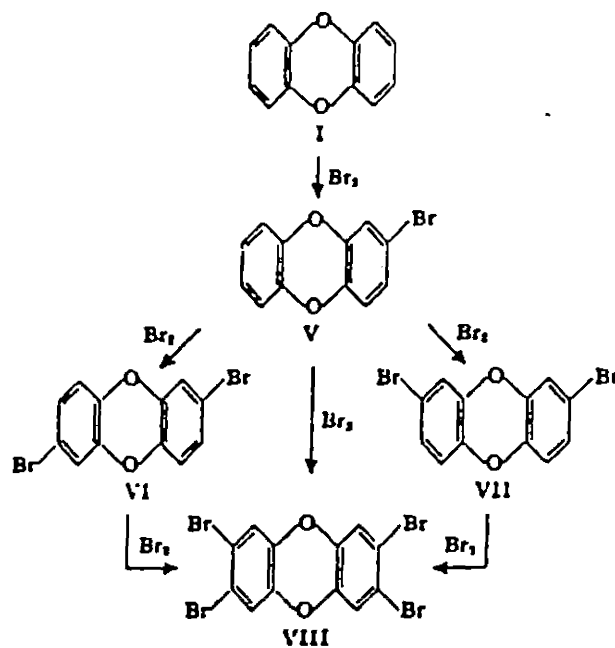


Fig. 2.

basis of infrared spectra comparisons. Both compounds gave the same infrared spectra which would only be true if the second bromine atom were in the 7-position. The positions occupied by the bromine atoms in the tetrabromo-dibenzo-*p*-dioxin must be 2,3,7,8, since exhaustive bromination of a mixture of 2-bromo-, 2,7-dibromo- and 2,8-dibromo-dibenzo-*p*-dioxin gave only one tetrabromo derivative as shown in Fig. 2.

A Sandmeyer reaction carried out on 2-amino-dibenzo-*p*-dioxin gave 2-iodo-dibenzo-*p*-dioxin. Attempts to make the compound directly by a method developed for the iodination of a closely related compound in this Laboratory failed.⁴

It has been found that 2,8-dibromo-dibenzo-*p*-dioxin can be made in 22% yield whereas 2,7-dibromo-dibenzo-*p*-dioxin can be formed in only 7% yield using forced conditions. These results can be explained satisfactorily by consideration of Fig. 3.

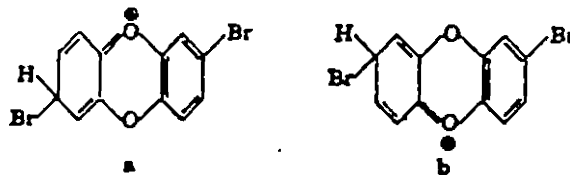


Fig. 3.

In Fig. 3(a), the oxonium ion formed in the intermediate stage received no assistance from the bromine atom in the 2-position. However, in Fig. 3(b), the oxonium ion is *para* to the initial bromine atom and can therefore receive a certain amount of resonance stabilization. The evidence for a quinoid-type intermediate is enhanced by the formation of 2,3,7,8-tetrabromo-dibenzo-*p*-dioxin, where the third and fourth entering bromine atoms, despite steric hindrance, enter *ortho* to the bromine, although a completely unhindered position *ortho* to the oxygen is available.

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