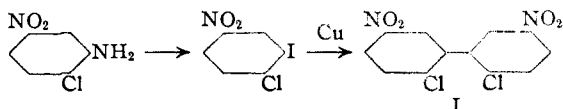


[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF TEMPLE UNIVERSITY]

The Nitration of Certain Halobiphenyls. II. Di- and Tetra-nitro Derivatives of 2,2'-Dichlorobiphenyl

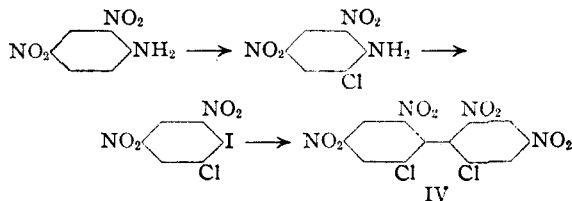
BY FRANCIS H. CASE AND RICHARD U. SCHOCK, JR.

According to Mascarelli and co-workers,¹ the nitration of 2,2'-dichlorobiphenyl in a sulfuric-nitric acid mixture yields a dinitro dichlorobiphenyl I (m. p. 205°). Its structure was not further investigated. We have repeated the directions of these authors and have isolated, in addition to I, a second isomer II (m. p. 128-129°). We have established the structure of I by synthesizing it by the following series of reactions



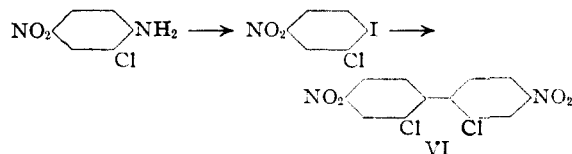
The structure of II, due to the small amount obtainable, and difficulties in preparation, is still in doubt.

According to Van Alphen,² the nitration of 2,2'-dichlorobiphenyl under more drastic conditions produces a tetranitrodichlorobiphenyl III, which he regarded as 2,2'-dichloro-4,4',6,6'-tetranitrobiphenyl, largely on the basis that the chlorine atoms were inactive toward such reagents as sodium ethylate, sodium hydroxide and dimethylamine in alcohol solution. We have now synthesized a compound IV of the structure assumed by Van Alphen for III and found it to be different from III. This synthesis involves the following series of reactions

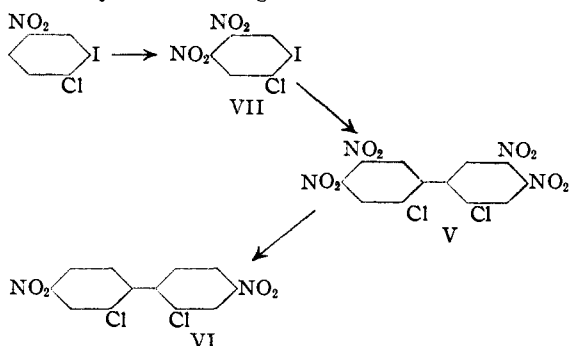


Further proof of the incorrectness of Van Alphen's formula for III is seen in the fact that both I and II, the former containing nitro groups situated in the 5 and 5' positions relative to chlorine, yield III on further nitration.

Another possibility featuring inactive chlorine would be 2,2'-dichloro-4,4',5,5'-tetranitrobiphenyl (V). If this were the structure for III, the structure for II might be 2,2'-dichloro-4,4'-dinitrobiphenyl (VI), the preparation of which has been accomplished as follows



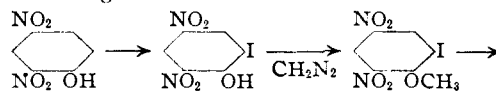
Compound VI has however been found to be quite different from II, melting at a much lower temperature. The synthesis of V has been effected by the following series of reactions.

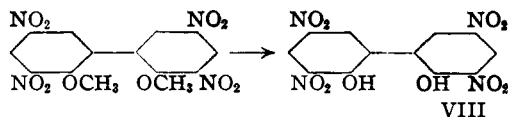


The existence of nitro groups in V *meta* to chlorine is proved by its synthesis from VI, and of nitro groups *para* to chlorine, by its synthesis from 2-chloro-5-nitroiodobenzene. The position taken by the second nitro group in VII, hitherto undescribed, follows from its conversion to V. Compound V has been shown to be different from III, the result of the nitration of 2,2'-dichlorobiphenyl.

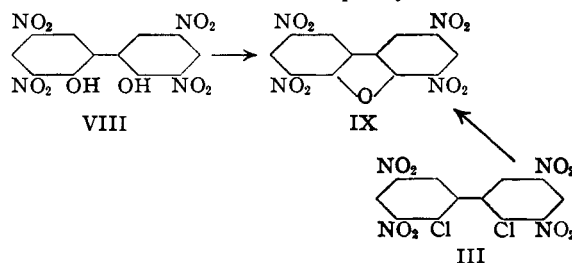
A re-investigation of the activity of the chlorine in III shows that, contrary to the results of Van Alphen, the chlorine may be removed entirely by hydrolysis in a 50% aqueous dioxane solution of sodium nitrite. The resulting compound is, however, non-phenolic. This fact makes it likely that the correct structure for III is 2,2'-dichloro-3,3',5,5'-tetranitrobiphenyl. The synthesis of this compound by Ullmann's reaction from the appropriate iodo derivatives would not be likely to be successful, since the chlorine would be activated by the adjacent nitro group. An attempt to prepare it by first nitrating 5,5'-dinitro-2,2'-diacetaminobiphenyl³ failed, since no tetranitration was observed.

The synthesis of 3,3',5,5'-tetranitro-2,2'-diphenol (VIII) by nitration of 2,2'-diphenol has already been reported.⁴ Its structure rests upon the fact that it can be obtained by the nitration of either 3,3'-dinitro-2,2'-diphenol,⁴ or of 5,5'-dinitro-2,2'-diphenol.⁵ Since the proof of structure of neither of these dinitro diphenols is entirely clear-cut, we have synthesized VIII by the following direct method

(1) Mascarelli and Gatti, *Gazz. chim. ital.*, **63**, 654 (1933).(2) Van Alphen, *Rec. trav. chim.*, **51**, 453 (1932).(3) Sako, *Mem. Coll. Eng. Kyushu Imp. Univ.*, **6**, 327-351 (1932)(4) Diels and Biebergeil, *Ber.*, **35**, 302 (1901).(5) Borsche and Scholten, *ibid.*, **50**, 596 (1917).



It was found by Borsche and Scholten⁵ that when VIII is treated with *p*-toluenesulfonyl chloride the resulting product is not the expected dichloro-tetranitro derivative, but a tetranitrobiphenylene oxide IX. We have repeated this work and found IX to be identical with the product obtained from the hydrolysis of III. This demonstrates quite clearly, therefore, that the structure of III is 2,2'-dichloro-3,3',5,5'-tetranitrobiphenyl.



The structure of II, while most probably 2,2'-dichloro-3,3'-dinitrobiphenyl, might also be that of the unsymmetrical product, 2,2'-dichloro-3,5'-dinitrobiphenyl.

Experimental

Dinitration of 2,2'-Dichlorobiphenyl.—To a mixture of 14 g. of concd. nitric acid and 21 g. of concd. sulfuric acid, 15 g. of 2,2'-dichlorobiphenyl was added slowly with stirring, keeping the temperature below 40°. The reaction was completed by heating at 100° for one hour. The reaction mixture was poured on ice, and the product washed and dried. It was then extracted with ether. The insoluble part, after crystallization from acetone, yielded 8.7 g. of I (m. p. 202–203°).

Anal. Calcd. for $C_{12}H_8O_4N_2Cl_2$: Cl, 22.65. Found: Cl, 22.74.

An analytical sample melted at 203–204°. By evaporation of the ether solution and repeated crystallization from methanol, 0.5 g. of II (m. p. 128–129°) was obtained.

Anal. Calcd. for $C_{12}H_8O_4N_2Cl_2$: N, 8.95. Found: N, 9.10.

2,2'-Dichloro-5,5'-dinitrobiphenyl.—This was prepared from 2-chloro-5-nitroiodobenzene by Ullmann's reaction. The melting point (203–204°) was unchanged by admixture with I.

Tetranitration of 2,2'-Dichlorobiphenyl.—The procedure was essentially that of Van Alphen.² Five grams of 2,2'-dichlorobiphenyl was heated on the steam-bath with 25 cc. of fuming nitric acid (sp. gr. 1.6) and 100 cc. of concd. sulfuric acid for two hours. The product III obtained by pouring the nitrating mixture onto ice was extracted with boiling ether and then recrystallized from dioxane; yield, 3.4 g. (m. p. 304–305°).

Anal. Calcd. for $C_{12}H_4O_8N_4Cl_2$: Cl, 17.59. Found: Cl, 17.58.

The pure compound melts at 307–308° (Van Alphen reports two dimorphic forms, melting at 308 and 316°). The nitration of either I or II produced compounds which melted unchanged on admixture with III.

2-Chloro-4,6-dinitroiodobenzene.—This was prepared from 2-chloro-4,6-dinitroaniline by the method of Hodgson and Walker.⁶ After crystallization from ethanol, it melts at 117–118°.

Anal. Calcd. for $C_6H_3O_2N_2ClI$: I, 38.64; Cl, 10.79. Found: I, 38.02; Cl, 10.98.

2,2'-Dichloro-4,4',6,6'-tetranitrobiphenyl (IV).—This was prepared from 2-chloro-4,6-dinitroiodobenzene by Ullmann's reaction. From 25.5 g. of iodo compound and 10 g. of copper heated at 240° for forty-five minutes, was obtained 7.2 g. of IV (m. p. 159–160°).

Anal. Calcd. for $C_{12}H_4O_8N_4Cl_2$: Cl, 17.59. Found: Cl, 17.44.

2,2'-Dichloro-4,4'-dinitrobiphenyl (VI).—This was prepared from 2-chloro-4-nitroiodobenzene by Ullmann's reaction. After crystallization from methanol, it melts at 107–108°.

Anal. Calcd. for $C_{12}H_6O_2N_2Cl_2$: Cl, 22.65. Found: Cl, 22.67.

On nitration, using Van Alphen's method, a tetranitro derivative V was obtained (m. p. 201–202°). It was crystallized from acetone-alcohol.

Anal. Calcd. for $C_{12}H_4O_8N_4Cl_2$: Cl, 17.59. Found: Cl, 17.52.

2-Chloro-4,5-dinitroiodobenzene (VII).—2-Chloro-5-nitroiodobenzene (24.9 g.) was heated for two hours with 200 cc. of concd. sulfuric acid and 100 cc. of fuming nitric acid (s. g. 1.6) on the steam-bath. After pouring on ice the precipitate was crystallized from methanol; yield, 14.2 g. (m. p. 98–99°).

Anal. Calcd. for $C_6H_3O_2N_2ClI$: I, 38.64; Cl, 10.79. Found: I, 38.59; Cl, 11.00.

2,2'-Dichloro-4,4',5,5'-tetranitrobiphenyl.—Copper powder (5 g.) was added to a refluxing solution of 10 g. of the above iodo compound in 15 cc. of nitrobenzene. After refluxing for one hour, the mixture was allowed to cool and then extracted with boiling acetone. The residue from the acetone extract after concentration was taken up in 50 cc. of benzene; 200 cc. of petroleum ether was added and the mixture allowed to cool in the ice chest. The precipitate was recrystallized from acetone-alcohol; yield, 2.5 g. (m. p. 201–202°). Admixture with the product resulting from the nitration of 4,4'-dinitro-2,2'-dichlorobiphenyl (V) did not change the melting point.

2,4-Dinitro-6-iodoanisole.—This was prepared by the action of diazomethane on the corresponding phenol.⁷ After crystallization from ethanol, it melts at 69–70°.

Anal. Calcd. for $C_7H_5O_3N_2I$: I, 39.17. Found: I, 39.39.

2,2'-Dimethoxy-3,3',5,5'-tetranitrobiphenyl.—This was prepared from the above iodo compound by a method similar to that for 2,2'-dichloro-4,4',5,5'-tetranitrobiphenyl. From 7 g. of the iodoanisole was obtained, after three recrystallizations from glacial acetic acid, 0.5 g. of a solid (m. p. 186–187°), identical with the product resulting from the tetranitration of 2,2'-dimethoxybiphenyl.⁵ Hydrolysis, employing the method of Raudnitz,⁸ yielded the diphenol (VIII) (m. p. 245–246°). (He reports m. p. 249–250°.)

Hydrolysis of Tetranitration Product of 2,2'-Dichlorobiphenyl.—Sodium nitrite (10 g.) dissolved in 50 cc. of water was added to a refluxing solution of 3 g. of III in 50 cc. of dioxane. After refluxing three hours the resulting solution was diluted with water. The precipitate was filtered off and crystallized twice from glacial acetic acid; yield, 1.2 g. (m. p. 249–250°). The product was identical with 3,3',5,5'-tetranitrobiphenylene oxide (IX) prepared from VIII according to the directions of Borsche and Scholten.⁵

Summary

1. The structure of Mascarelli's dinitro-2,2'-dichlorobiphenyl has been shown to be 5,5'-dinitro-2,2'-dichlorobiphenyl.

2. The structure of Van Alphen's tetranitro-2,2'-dichlorobiphenyl has been shown to be 2,2'-

(7) Armstrong, *Ber.*, **6**, 651 (1873).

(8) Raudnitz, *ibid.*, **60**, 742 (1927).

(6) Hodgson and Walker, *J. Chem. Soc.*, 1620 (1933).

dichloro-3,3',5,5'-tetranitrobiphenyl and not 2,2'-dichloro-4,4',6,6'-tetranitrobiphenyl as he assumed.

3. The latter compound has been synthesized.

PHILADELPHIA, PA.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Studies on Some *t*-Butyl Homologs of Naphthalene¹

BY FRANK C. WHITMORE AND WILLIAM HOLDEN JAMES

In view of the recent report by Bromby, Peters and Rowe,² we wish to present, from an investigation terminated by circumstances beyond our control, results obtained in preliminary experiments on the mono-*t*-butylnaphthalenes.

The Friedel-Crafts reaction between naphthalene and *t*-butyl chloride in carbon disulfide solution at 0–5° gave a 45% yield of monoalkylated product. The data, when collated with those recorded in the literature, indicate that the reaction leading to the di-*t*-butylnaphthalenes is much more accelerated by an increase in temperature so that dialkylation outstrips monoalkylation at higher temperatures.

The mono-*t*-butylnaphthalene obtained, b. p. 145° (15 mm.), 115° (6 mm.); n_D^{20} 1.5795; m. p. –4°, like the 2-*t*-butylnaphthalene synthesized by Bromby, Peters and Rowe, gave a picrate, m. p. 100–101°, and a quinone, m. p. 76–77°. The observation of these authors that no naphthoic acid could be obtained by oxidative degradation was substantiated. Treatment with bromine or phosphorus pentachloride gave halogenated products of unknown structure.

The preparation of *t*-butylnaphthalene by the dehydrogenation of *t*-butyltetralin, or by the reaction between isobutylene and naphthalene, gave lower yields and lacked the simplicity of the direct Friedel-Crafts reaction employing *t*-butyl chloride and naphthalene.

The preparation of 1-*t*-butylnaphthalene by the reaction between 1-naphthylmagnesium bromide and *t*-butyl chloride, or by the Wurtz-Fittig reaction between 1-naphthyl bromide and *t*-butyl chloride, was unsatisfactory because of the very poor yield of product.

Experimental

1. **The Reaction between *t*-Butyl Chloride and Naphthalene.**—The apparatus consisted of a five-liter, three-necked, round-bottomed flask equipped with a thermometer, a 50-cc. container for the aluminum chloride consisting of a small flask attached to one of the side-necks by a piece of large rubber tubing, and a trident adapter bearing a one-liter dropping funnel, a mercury-sealed mechanical stirrer and an ice-cooled spiral condenser connected through a trap containing distilled water for collecting the evolved hydrogen chloride, to a second trap containing a solution of bromine in carbon tetrachloride for detecting any gase-

ous olefins. In the reaction flask was placed about 50 cc. of a solution prepared by dissolving 896 g. (7 moles) of naphthalene in a mixture of 647.5 g. (7 moles) of *t*-butyl chloride, b. p. 50° (732 mm.), n_D^{20} 1.3848, and 1875 g. (1.5 liters) of carbon disulfide. The reaction was initiated at room temperature by adding about 1 g. of anhydrous aluminum chloride from a quantity previously weighed in the container. The reaction flask was then cooled in an ice-salt bath which maintained the temperature of the reaction mixture at 0°. With stirring, the 3 liters of carbon disulfide solution was added dropwise from the funnel over a period of five and one-half hours. During this time a steady evolution of hydrogen chloride was maintained by adding aluminum chloride in 1-g. portions from time to time; a total of 25.9 g. (0.194 mole) of aluminum chloride was used. After all the carbon disulfide solution had been added, the reaction mixture was stirred for forty minutes; then 750 cc. of water at 0° was added. The red-brown reaction mixture became colorless. It was allowed to stand for one hour. The carbon disulfide layer was separated. It was washed with 800 cc. of a 12% sodium carbonate solution and was dried, first for thirty hours over 100 g. of anhydrous calcium chloride, then for twenty-four hours over 30 g. of anhydrous potassium carbonate. The liquid was decanted and filtered from the drying agent. The carbon disulfide was removed by distillation at atmospheric pressure on the steam-bath. The residue was then distilled under reduced pressure through a 3.3 × 88 cm. packed, electrically heated, total condensation, adjustable take-off column.³ Three fractions were collected: (1) 225 g., b. p. 99° (18 mm.); (2) 583 g., b. p. 115° (6 mm.), n_D^{20} 1.5795, m. p. –4°; (3) residue, 351 g. Fraction (1) solidified immediately when cooled to room temperature and presumably was unchanged naphthalene; the amount, 225 g., (1.75 moles), represented a recovery of 25% of the starting hydrocarbon. Fraction (2) was a colorless liquid; calculated as mono-*t*-butylnaphthalene, it corresponded to a yield of 45% based on the *t*-butyl chloride used. The residue was a white crystalline solid; calculated as di-*t*-butylnaphthalene, it corresponded to a yield of 41% based on the *t*-butyl chloride used.

A small portion of fraction (2) was treated with a solution of picric acid in 95% ethyl alcohol. A yellow, wax-like solid, m. p. 100–101°, was obtained.⁴

Oxidation of fraction (2) by boiling 50% nitric acid for forty-eight hours or 10% nitric acid for 240 hours or by 20% nitric acid at 180–200° for eight hours yielded no naphthoic acid.

A portion of the crystalline residue was distilled at atmospheric pressure. A fraction, b. p. 310–312° (730 mm.), 181° (15 mm.), when treated with a solution of picric acid in 95% ethyl alcohol gave golden yellow leaflets, m. p. 155–156°.⁵

(3) Whitmore and Lux, *THIS JOURNAL*, **54**, 3451 (1932).

(4) For other values of the m. p. of the picrate, see: Wegscheider, *Monatsh.*, **8**, 236 (1884); Baur, *Ber.*, **27**, 1623 (1894); Barbot, *Bull. soc. chim.*, (4) **47**, 1314 (1930); Fieser and Price, *THIS JOURNAL*, **58**, 1838 (1936); Price and Ciskowski, *ibid.*, **62**, 2499 (1938); Tsukervanik and Terentjeva, *J. Gen. Chem.* (U. S. S. R.), **7**, 637 (1937); and Pavelkina, *J. Applied Chem.* (U. S. S. R.), **12**, 1422 (1939).

(5) The composition of this picrate has been elucidated by Price, Shafer, Huber and Berstein, *J. Org. Chem.*, **7**, 517 (1942), who re-

(1) The experimental data in this paper are taken from a thesis submitted by William Holden James in partial fulfillment of the requirements for the Ph.D. degree at the Pennsylvania State College.

(2) Bromby, Peters and Rowe, *J. Chem. Soc.*, 144 (1943).