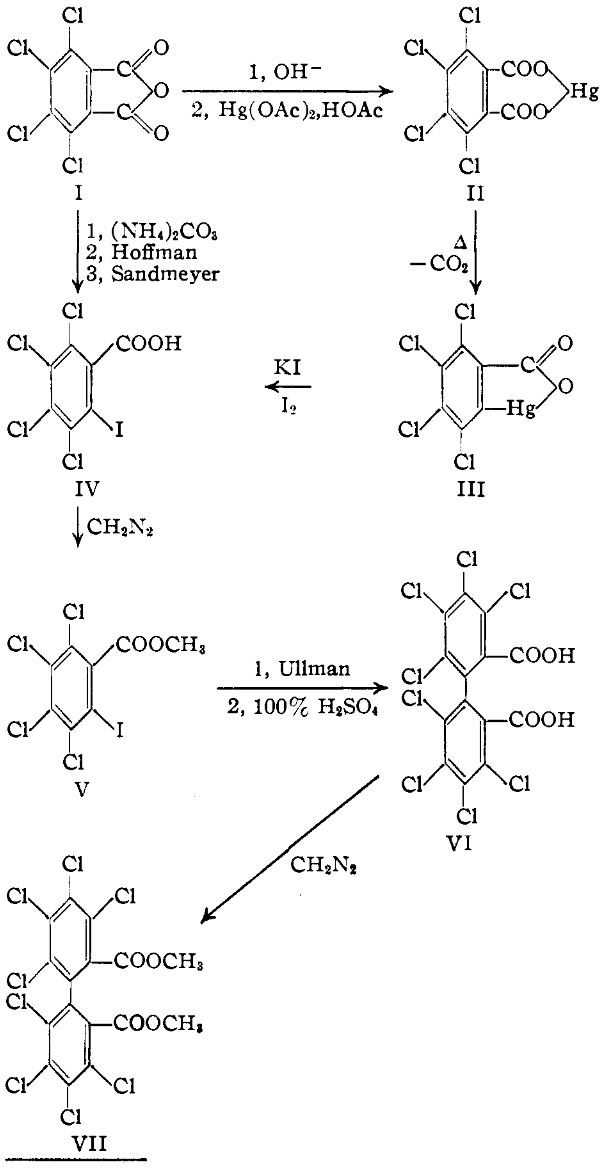
Diphenates. II. Synthesis of 3,3',4,4',5,5',6,6'-Octachloro-2,2'-dicarboxybiphenyl

By William F. O'Connor and Emil J. Moriconi

Of the fifteen theoretically possible symmetrically chlorinated 2,2'-diphenic acids, all four of the dichloro derivatives,[1,2] and only one tetrachloro derivative, 4,4',6,6'-tetrachloro-2,2'-dicarboxybiphenyl,[2] have been prepared, There is no recorded instance of the preparation of any of the symmetrical hexachloro derivatives nor the single octachloro-2,2'-diphenic acid.

In the course of chlorination studies of 2,2'-diphenic acid, it became of necessity to synthesize independently the perchlorinated 2,2'-diphenic acid, 3,3',4,4',5,5',6,6'-octachloro-2,2'-dicarboxybiphenyl (VI).

This note deals with the preparation of VI and its ester (VII) using conventional laboratory methods. Their synthesis is represented by the scheme



Experimental[3]

2-Iodo-3,4,5,6-tetrachlorobenzoic Acid (IV).—A cooled solution of 20.0 g. (0.073 mole) of tetrachloroanthranilic acid[4] dissolved in dilute sodium hydroxide solution containing 17.3 g. (0.025 mole) of sodium nitrite, was dropped slowly into 300 ml. of concd. sulfuric acid maintained below 20° with an ice-bath and vigorously stirred. At the same time, a solution of cuprous iodide was prepared by the procedure of Yuan and Hsu.[5] The diazotized acid[6] was added rapidly with vigorous stirring to the cuprous iodide suspension maintaining the temperature between 10–20° during the addition (one hour). The mixture was brought slowly to room temperature and finally boiled for one-half hour. The excess iodine was destroyed with solid sodium thiosulfate. After cooling, the residue was filtered and dissolved in 400 ml. of 20% sodium hydroxide. Red, hydrated cuprous oxide was filtered, whereupon the solution was treated with charcoal, filtered and acidified with concd. hydrochloric acid. The yield of iodo-acid was 19.7 g. (70%). Recrystallization from alcohol–water gave white needles, m.p. 223–224°.

Anal. Calcd. for $C_7HO_2Cl_4I$: C, 21.79; H, 0.26. Found: C, 21.56; H, 0.50.

2-Bromo-3,4,5,6-tetrachlorobenzoic Acid.—The sulfuric acid suspension of diazotized tetrachloroanthranilic acid, as previously prepared, was added to a cuprous bromide–hydrobromic acid solution as prepared by the method of Buck and Ide[7] or Bigelow.[8] The bromo-acid was obtained in a 73% yield as white needles, m.p. 222–223°, after recrystallization from alcohol–water.

Anal. Calcd. for $C_7HO_2Cl_4Br$: C, 24.81; H, 0.29. Found: C, 24.96; H, 0.61.

Mercuric Salt of 3,4,5,6-Tetrachlorophthalic Acid (II).—To 57.2 g. (0.20 mole) of the anhydride (I)[9] was added 16.0 g. (0.40 mole) of sodium hydroxide in 500 ml. of water and the whole refluxed until solution was effected, To this hot solution was added a solution of mercuric acetate made by dissolving 70.0 g. (0.22 mole) of the acetate in 12 ml. of acetic acid and 500 ml. of boiling water. The white mercuric salt (II) immediately precipitated. It was filtered, washed thoroughly with hot water, dried and pulverized. The yield was 77.0 g. (77%).

Anhydro-2-hydroxymercuri-3,4,5,6-tetrachlorobenzoic Acid (III).—Forty grams (0.080 mole) of the dry, finely powdered mercuric salt (II) was placed in a round-bottomed flask heated by a Glas-col mantle. Stirring intermittently, CO_2 evolution commenced at 250° and proceeded slowly for 8–10 hours. The heating and stirring were continued until a sample of the powder showed a negative test for inorganic mercury.[10] The mercuration product (III) was obtained as a gray powder in a 30.9 g. (84%) yield. To purify for analysis, several grams of III was alternately washed with dilute sodium hydroxide solution and dilute hydrochloric acid, finally boiling for five minutes with 50 ml. of glacial acetic acid. The material undissolved by this treatment were filtered, dried and analyzed.

Anal. Calcd. for $C_7O_2Cl_4Hg$: C, 18.32. Found: C, 18.10.

Iodination of the Anhydro-2-hydroxymercuri-acid (III).[11]—To 5.0 g. (0.011 mole) of III suspended in 150 ml. of water were added 8.3 g. (0.033 mole) of iodine and 1.8 g. (0.011

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[1] Christie, James and Kenner, *J. Chem. Soc.*, **123**, 1948 (1923).

[2] Atkinson, Morgan, Warren and Manning, This Journal, **67**, 1513 (1945).

[3] All melting points were determined in the Fisher–Johns apparatus and are uncorrected. Microanalyses were done by Mr. A. A. Sirotenko of the Fordham Microchemical Laboratory.

[4] Graebe and Rostowzev, *Ber.*, **35**, 2747 (1902); Villiger and Blangey, *ibid.*, **42**, 3549 (1909).

[5] Yuan and Hsu, *J. Chinese Chem. Soc.*, **3**, 206 (1935).

[6] Diazotized tetrachloroanthranilic acid has been successfully utilized by Orndorff and Nichols, *Am. Chem. J.*, **48**, 473 (1912), and Lesser and Weiss, *Ber.*, **46**, 3929 (1913), to prepare coupled products.

[7] Buck and Ide, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 132.

[8] Bigelow, *ibid.*, Coll. Vol. I, 2nd Edit., John Wiley and Sons, Inc., New York, N. Y., 1946, p. 136.

[9] Research sample of 1 (Niagathal W, m.p. 254–255°) supplied by Niagara Alkali Co., Niagara Falls, N. Y.

[10] Whitmore and Carnahan, This Journal, **51**, 856 (1929).

[11] This method of preparing the iodo-acid (IV) involves a process analogous to that of Whitmore and co-workers, *ibid.*, **51**, 602, 2785 (1929).

mole) of potassium iodide. The whole reaction mass was heated to 50–60° and stirred for 24 hours. At the end of the reaction time, it was brought to a boil and the excess iodine was destroyed with solid sodium thiosulfate. On cooling, the solution was acidified and filtered. The residue was digested with boiling sodium hydroxide solution, filtered, and the filtrate was treated with charcoal. Upon filtration and acidification, the iodo-acid (IV) was obtained in a 0.5 g. (12%) yield as a white powder which when recrystallized from alcohol–water gave white needles, m.p. 223–224°.

A mixed melting point of the iodo-acid prepared in this manner and by the Sandmeyer reaction on diazotized tetrachloroanthranilic acid showed no depression.

A sealed-tube iodination of III (8 hr., 210–220°) gave approximately the same yields of IV.

Bromination of the Anhydro-2-hydroxymercuri-acid (III). —In a similar manner, 15.0 g. (0.033 mole) of III suspended in 250 ml. of water when treated with 6.8 g. (0.066 mole) of sodium bromide and 10.6 g. (0.066 mole) of bromine gave a 2.0 g. (18%) yield of the bromo-acid. Recrystallization from alcohol–water gave white needles, m.p. 222–223°.

A mixed melting point of the bromo-acid prepared in this manner and by the Sandmeyer reaction on diazotized tetrachloroanthranilic acid showed no depression.

A sealed-tube bromination of III (8 hr., 210–220°) gave lower yields of IV.

Methyl 2-Iodo-3,4,5,6-tetrachlorobenzoate (V).—The iodo-acid (IV) was quantitatively converted to the methyl ester (V) by adding the solid acid to an ethereal solution of diazomethane. After evaporation of the ether on a steam-bath, the crude product was recrystallized from alcohol to yield white fluffy needles, m.p. 103–103.5°.

Anal. Calcd. for $C_8H_3O_2Cl_4I$: C, 24.03; H, 0.76. Found: C, 24.36; H, 0.95.

Methyl 2-Bromo-3,4,5,6-tetrachlorobenzoate.—The bromo-ester was prepared from the bromo-acid in the same manner as the iodo-ester (V). The white needles melted at 111–112°.

Anal. Calcd. for $C_8H_3O_2Cl_4Br$: C, 27.23; H, 0.85. Found: C, 27.00; H, 0.97.

3,3',4,4',5,5',6,6'-Octachloro-2,2'-dicarboxybiphenyl (VI).[12]—To 15.0 g. (0.0375 mole) of molten iodo-ester (V) maintained at 240–260° in a silicone oil-bath, was added, in small portions and with constant stirring, 15.0 g. (0.24 mole) of Baker precipitated copper. At the end of the addition, the reaction mass was heated to 290° for one-half hour. On cooling, the solid mass was thoroughly extracted with hot alcohol and filtered. The alcohol was removed by distillation and the dark brown residue was taken up in 30 ml. of 100% sulfuric acid, according to Newman's[13] rigorous procedure. After remaining overnight at room temperature, the acidic solution was poured into 500 ml. of ice-water and neutralized with solid sodium carbonate. Any insoluble tar was filtered, and the filtrate was treated with charcoal, reacidified and filtered. The light brown powder was then extracted with 150 ml. of boiling benzene to remove unreacted iodo-acid (IV) and the benzene-insoluble portion redissolved in alkali solution, treated with charcoal, filtered and reacidified. After several such treatments, the perchlorinated 2,2'-diphenic acid (VI) was obtained in a 2.9 g. (15%) yield as a tan powder which melts with decomposition to a brown viscous liquid, 265–275°.

Anal. Calcd. for $C_{14}H_2O_4Cl_8$: C, 32.47; H, 0.39; neut. equiv., 258.9. Found: C, 32.70; H, 0.80; neut. equiv., 258.7.

3,3',4,4',5,5',6,6'-Octachloro-2,2'-dicarbomethoxybiphenyl (VII).—The dimethyl ester (VII) was obtained quantitatively from the dicarboxylic acid (VI) *via* the diazomethane technique. Recrystallization from alcohol–water gave white fluffy needles, m.p. 152–152.5°.

Anal. Calcd. for $C_{16}H_6O_4Cl_8$: C, 35.20; H, 1.11; Cl, 51.95. Found: C, 34.95; H, 1.26; Cl, 51.80.

ORGANIC PROCESS LABORATORY
FORDHAM UNIVERSITY
BRONX 58, NEW YORK

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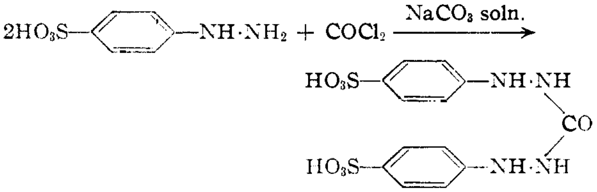
Synthesis of 1,5-Bis-(1-phenyl-4-sulfonic Acid) Carbohydrazide (Sodium Salt)[1]

BY JAMES S. PARSONS[2] AND JOHN H. YOE

1,5-Bis-(1-phenyl-4-sulfonic acid)-carbohydrazide (sodium salt) has been recently recommended[3] as a good indicator in the mercurimetric determination of chloride. At the end-point the indicator gives a water-soluble deep violet complex with mercuric ions.

The indicator was synthesized by condensing phenylhydrazine *p*-sulfonic acid with phosgene in sodium carbonate solution as indicated



Bucherer and Schmidt[4] employed this type of reaction to prepare 1,5-bis-(1-naphthyl-4-sulfonic acid) carbohydrazide. The product was easily isolated as the sodium salt. We were unable to obtain 1,5-bis-(1-phenyl-4-sulfonic acid) carbohydrazide in a pure form by crystallization. However, using a simple chromatographic adsorption separation a product of satisfactory purity was easily obtained. The sodium and barium salts were prepared; both are highly soluble in water.

Experimental

Dissolve 0.3 mole of phenylhydrazine-*p*-sulfonic acid (sodium salt) and 15 g. of sodium carbonate in 400 ml. of distilled water. Transfer to a gas saturation apparatus provided with a fine fritted glass tube so that efficient saturation is obtained. Heat the solution to 50° and lead phosgene in slowly for 3 to 4 hours. The reaction mixture usually becomes acid in this time. Adjust the solution to about *p*H 1 with hydrochloric acid; filter off and discard any precipitate that forms. Pour the mixture through a column (diameter 3 cm., length 75 cm.) which has been carefully packed with about 200 g. of adsorption grade alumina (80–200 mesh). The column should be prewashed with water and then with 0.5 *N* hydrochloric acid. Care should be taken to avoid sucking air through the column and to prevent air bubbles lodging at the top surface of the alumina. Using either suction or air pressure the reaction mixture is allowed to flow through the column at about 5 ml. per minute. The 1,5-bis-(1-phenyl-4-sulfonic acid) carbohydrazide is adsorbed, giving a colorless band. A narrow brown band may be seen at the top of the column if any carbazone is present. Follow by pouring through distilled water until the filtrate gives a negative test for chloride or shows a leveling off of chloride traces. The water tends to develop or to spread the band which becomes slightly yellowish, apparently due to a slight oxidation of carbazide to carbazone. The distilled water is followed by pouring through 0.25 *M* sodium hydroxide. After a few minutes the top of the column begins to turn red and the band below turns darker

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(12) A direct synthesis of this symmetrical biaryl from the amino-acid,[4] using the procedures of Atkinson and co-workers, THIS JOURNAL, **62**, 1704 (1940); **63**, 730 (1941); **65**, 476 (1943), was unsuccessful. Our diazotization step occurred only in a large volume of a concentrated acid medium, whereas Atkinson's reductive coupling procedures invariably required ammoniacal solutions of the reducing agents. When a solution of cuprous chloride in concentrated hydrochloric acid was used as the coupling agent, no biaryl was isolated, as was expected from Atkinson's work.

(13) Newman, *ibid.*, **63**, 2431 (1941).

(1) From the Ph.D. dissertation of James S. Parsons, University of Virginia, 1950.

(2) American Cyanamid Company, Bound Brook, New Jersey.

(3) J. S. Parsons and J. H. Yoe, *Anal. Chim. Acta.*, in press.

(4) H. T. Bucherer and M. Schmidt, *J. prakt. Chem.*, **79**, 408 (1909).