

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

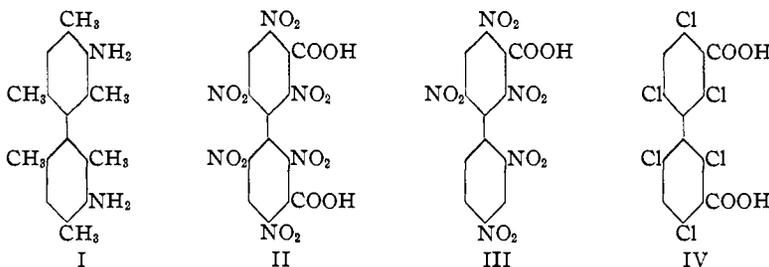
**STEREOCHEMISTRY OF DIPHENYL. XXI.
RESOLUTION OF 2,4,6,2',4',6'-HEXACHLORO-
3,3'-DICARBOXYDIPHENYL^{1,2}**

BY JULIUS WHITE AND ROGER ADAMS

RECEIVED FEBRUARY 11, 1932

PUBLISHED MAY 7, 1932

In previous papers two compounds have been described in which all four groups in the 2,2',6,6' and one compound in which three groups in the 2,2',6 positions in diphenyl have been substituted by the same groups. These are 2,4,6,2',4',6'-hexamethyl-3,3'-diaminodiphenyl (I), 2,4,6,2',4',6'-hexanitro-3,3'-dicarboxydiphenyl (II) and 2,4,6,2',4'-pentanitro-3-carboxydiphenyl (III).³ Since each ring in itself is asymmetrically substituted in these compounds, enantiomorphic forms of each are capable of existence and were actually produced in the laboratory.



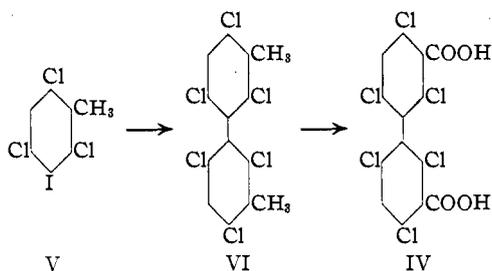
Another example of this type is described in this communication in which the chlorine atom is present in the positions adjacent to the diphenyl linkage. The substance prepared was 2,4,6,2',4',6'-hexachloro-3,3'-dicarboxydiphenyl (IV). It was resolved through the brucine salt. The *d*-active compound was stable to racemization in boiling alcohol, glacial acetic acid and, as the sodium salt, in boiling water.

The compound was synthesized by starting with trichloro-*m*-toluidine and converting it first to 2,4,6-trichloro-3-iodotoluene (V). By means of copper powder 2,4,6,2',4',6'-hexachloro-3,3'-dimethyldiphenyl (VI) was produced. By means of a mixture of potassium permanganate and nitric acid, in a sealed tube at 180°, 2,4,6,2',4',6'-hexachloro-3,3'-dicarboxydiphenyl resulted.

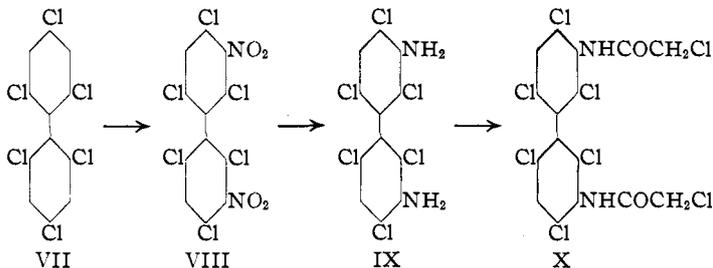
¹ For the last papers in this field see: Woodruff and Adams, *ibid.*, **54**, 1977 (1932); Hill and Adams, *ibid.*, **53**, 3453 (1931); Bock and Adams, *ibid.*, **53**, 3519 (1931).

² This communication is a portion of an abstract of a thesis submitted by Julius White in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

³ Moyer and Adams, *THIS JOURNAL*, **51**, 630 (1929); Bock, Moyer and Adams, *ibid.*, **52**, 2054 (1930); Stearns and Adams, *ibid.*, **52**, 2070 (1930).



Before the above procedure was developed a number of interesting but unsuccessful experiments were performed to obtain compounds containing a properly substituted chlorinated diphenyl with salt-forming groups. In particular 2,4,6,2',4',6'-hexachlorodiphenyl (VII) was readily nitrated to the 3,3'-dinitro-2,4,6,2',4',6'-hexachlorodiphenyl (VIII) and this in turn was reduced to the corresponding diamine (IX).



The diamine, on account of the lack of basicity of the amino group, could not be converted into stable salts. To introduce salt-forming groups the diamine was converted to the di-chloroacetamido compound (X) and then this product was treated with ammonia and amines to replace the halogens. No well-characterized compounds were obtained from the di-chloroacetamido compound.

Experimental

2,4,6-Trichloro-*m*-toluidine.—The general method of Bures and Rubes⁴ was employed. To 90 g. of *m*-toluidine in a 3-liter round-bottomed flask connected with a mechanical stirrer and a reflux condenser was added cautiously 1 liter of acetic anhydride. A continuous stream of chlorine was passed in. The reaction mixture became warm but no external cooling was necessary. At the end of six to eight hours the reaction was complete as indicated by the reaction mixture becoming cold and a portion of the chlorinated product separating out. Water was slowly and carefully added to decompose the excess of acetic anhydride and to precipitate completely the product from solution. It was purified from hot ethyl alcohol and melted at 180–181°. To this acetylated derivative 250 g. of 50% sulfuric acid was added and the trichloro-*m*-toluidine was steam distilled. No recrystallization was necessary, m. p. 77–78°.

1-Iodo-2,4,6-trichloro-3-methylbenzene.—A solution of 65 g. of trichloro-*m*-toluidine⁴ in 400 cc. of concentrated sulfuric acid was cooled to 15–20°, stirred, and

⁴ Bures and Rubes, *Coll. Czechoslov. Chem. Communications*, 1, 648 (1929).

32.5 g. of solid sodium nitrite was slowly added. The mixture was stirred for one hour after addition of the nitrite and then carefully poured into a very large excess of cracked ice. A solution of 65 g. of potassium iodide dissolved in 125 cc. of water was now slowly added with stirring. The solution was warmed to 40° until no more oxides of nitrogen were liberated and the excess of iodine was removed by the addition of sodium bisulfite. The crude iodo product was recrystallized from acetone as white crystals, m. p. 95–97°.

Anal. Calcd. for $C_7H_4Cl_3I$: Cl + I, 72.3. Found: Cl + I, 72.12.

2,4,6,2',4',6'-Hexachloro-3,3-dimethyldiphenyl.—A mixture of 50 g. of the trichloriodotoluene and 50 g. of copper bronze was heated on an oil-bath for three hours at 235–250°. The mixture was cooled and extracted with hot ethyl alcohol several times. Crystals of hexachlorodimethyldiphenyl separated on cooling and could be recrystallized from alcohol as white crystals, m. p. 119–120°.

Anal. Calcd. (Parr Bomb): Cl, 54.75. Found: Cl, 54.92.

2,4,6,2',4',6'-Hexachloro-3,3'-dicarboxydiphenyl.—The hexachlorodimethyldiphenyl was oxidized to the hexachlorodicarboxydiphenyl by means of potassium permanganate and nitric acid (sp. gr. 1.15–1.20). The general method of Rupp⁵ was used. A mixture of 5 g. of hexachlorodimethyldiphenyl, 3.2 g. of solid potassium permanganate, 23 cc. of concentrated nitric acid and 25 cc. of water was placed in a Carius tube and heated on an oil-bath at 175–185° for eight hours. After the tube was cooled, the reaction mixture was treated with water and the precipitate filtered. The acid was dissolved in very dilute sodium hydroxide and reprecipitated with dilute hydrochloric acid. It was further purified by recrystallization from a mixture of ethyl acetate and petroleum ether; white crystals, m. p. 318–320°.

Anal. Calcd. for $C_{14}H_4O_4Cl_6$: C, 38.4; H, 0.89. Found: C, 38.76; H, 0.83.

Resolution of 2,4,6,2',4',6'-Hexachloro-3,3'-dicarboxydiphenyl.—To 450 cc. of anhydrous ethyl acetate containing 5.384 g. (0.0136 mole) of anhydrous *l*-brucine was added 3.0675 g. (0.0068 mole) of hexachlorodicarboxydiphenyl dissolved in 350 cc. of anhydrous ethyl acetate. An immediate precipitate resulted. This was allowed to stand overnight. It was then filtered and washed with a small amount of anhydrous ethyl acetate. The weight of the salt was 3.4 g. melting at 209°.

Rotation. 0.2050 g. made up to 15 cc. with ethyl alcohol (95%) at 25° gave α_D –0.20°; $l = 2$; $[\alpha]_D^{25} = -7.3^\circ$. The salt was purified by washing with boiling ethyl acetate but with no change in melting point or rotation.

Anal. Calcd. for $C_{60}H_{56}Cl_6N_4O_{12}$: C, 56.66; H, 4.53; Cl, 17.08; N, 4.49. Found: C, 56.93; H, 4.68; Cl, 16.79; N, 4.58.

The mother liquor was evaporated to 100 cc. and allowed to stand overnight. More salt separated. It weighed 1.2 g. The mother liquor was further concentrated *in vacuo* to 50 cc. and allowed to stand overnight. The weight of this last fraction of salt was 3.7 g., m. p. 206–210°.

Rotation. 0.2050 g. made up to 15 cc. with ethyl alcohol (95%) at 25° gave α_D –0.49°; $l = 2$; $[\alpha]_D^{25} = -15.5^\circ$. The salt was recrystallized from a mixture of ethyl acetate and petroleum ether, melting again at 206–210° and with no change in rotation.

Anal. Calcd. for $C_{60}H_{56}Cl_6N_4O_{12}$: C, 56.66; H, 4.53. Found: C, 57.13; H, 4.74.

***d*-2,4,6,2',4',6'-Hexachloro-3,3'-dicarboxydiphenyl.**—The pure dibrucine salt was dissolved in chloroform and shaken with dilute hydrochloric acid several times. The chloroform layer was then separated and shaken with dilute sodium hydroxide. The

⁵ Rupp, *Ber.*, 29, 1625 (1896).

sodium hydroxide layer was separated and treated with dilute hydrochloric acid. The acid which precipitated out was filtered off and recrystallized from a mixture of ethyl acetate and petroleum ether. It was found to be brucine-free and melted at 293–294°. Further recrystallization did not change the melting point.

Rotation. 0.4442 g. made up to 15 cc. in ethyl alcohol (95%) at 25° gave $\alpha_D +0.10$; $l = 2$; $[\alpha]_D^{25} +1.7^\circ$. The acid was again recrystallized and the rotation taken. 0.3234 g. made up to 15 cc. in ethyl alcohol (95%) at 25° gave $\alpha_D +0.08^\circ$; $l = 2$; $[\alpha]_D^{25} +1.8$.

Further recrystallization did not alter the rotation.

Anal. Calcd. for $C_{14}H_4O_4Cl_6$: C, 38.4; H, 0.89. Found: C, 38.79; H, 1.08.

l-2,4,6,2',4',6'-Hexachloro-3,3'-dicarboxydiphenyl.—The more soluble salt was hydrolyzed in a manner similar to the less soluble salt. The acid thus obtained was recrystallized from a mixture of ordinary ethyl acetate and petroleum ether, and melted at 292–293°.

Rotation. 0.4425 g. made up to 15 cc. in ethyl alcohol at 25° gave $\alpha_D -0.09^\circ$; $l = 2$; $[\alpha]_D^{25} -1.52^\circ$.

The acid was recrystallized and the rotation again taken.

0.4204 g. made up to 15 cc. in ethyl alcohol (95%) gave $\alpha_D 0.096^\circ$; $l = 2$; $[\alpha]_D^{25} -1.7^\circ$.

Racemization Experiments

1. A sample of the *d*-acid was dissolved in ordinary ethyl alcohol and refluxed in a flask with a ground-glass joint for eight hours. No change in rotation was observed.

Rotation. 0.4464 g. made up to 15 cc. with ethyl alcohol at 25° gave $\alpha_D +0.11$; $l = 2$; $[\alpha]_D^{25} +1.8^\circ$.

2. A second sample of the *d*-acid was dissolved in glacial acetic acid and the rotation taken. 0.4520 g. of acid in 15 cc. of glacial acetic acid at 25° gave $\alpha_D +0.18$; $l = 2$; $[\alpha]_D^{25} +3.01$.

3. After refluxing for periods of two and six hours, respectively, no change in rotation occurred.

4. 0.4005 g. of acid was exactly neutralized with 36.3 cc. of 0.0554 *N* sodium hydroxide and the solution concentrated *in vacuo* to dryness. This was made up with water to 15 cc. of 25° and the rotation taken. $\alpha_D +0.22$; $l = 2$; $[\alpha]_D^{25} +4.01$ based on the sodium salt of 0.4005 g. of acid.

The water solution was then refluxed at intervals of three hours, two hours and nine hours. No change in rotation was observed.

2,4,6,2',4',6'-Hexachloro-3,3'-dinitrodiphenyl.—To 60 g. of fuming nitric acid (sp. gr., 1.50) cooled in an ice-bath was added slowly with rapid stirring 10 g. of hexachlorodiphenyl.⁶ The temperature was maintained at 0° and stirring continued for one hour after all of the hexachlorodiphenyl had been added. The mixture was poured into cracked ice and the precipitate was purified by recrystallization from hot alcohol, m. p. 230–231°.

Anal. Calcd. for $C_{12}H_2Cl_6N_2O_4$ (Parr Bomb): Cl, 47.23. Found: Cl, 47.38.

2,4,6,2',4',6'-Hexachloro-3,3'-diaminodiphenyl.—To a solution of 2 g. of 2,4,6,2',4',6'-hexachloro-3,3'-dinitrodiphenyl in 50 g. of glacial acetic acid and 5 g. of water was added gradually with constant stirring 5 g. of zinc dust. The mixture was allowed to heat up from the heat of reaction (about 80°). It was then heated on a water-bath for fifteen minutes to complete the reaction. The mixture was diluted with water and filtered. The amine was separated from the excess of zinc by several extractions with

⁶ Ullmann, *Ann.*, **332**, 40 (1904).

hot 95% ethyl alcohol. It was purified by recrystallization from hot 60–70° petroleum ether; white crystals, m. p. 167.5–168.5°.

Anal. Calcd. for $C_{12}H_6Cl_6N_2$ (Parr Bomb): Cl, 54.50. Found: Cl, 54.88.

2,4,6,2',4',6'-Hexachloro-3,3'-chloroacetaminodiphenyl.—A mixture of 2 g. of the hexachlorodiaminodiphenyl and an excess of chloroacetyl chloride was refluxed for several hours on a steam cone. The mixture was then cooled and the excess of chloroacetyl chloride was decomposed with cracked ice. The product was recrystallized from 70–80° petroleum ether as white crystals, m. p. 125–126°.

Anal. Calcd. for $C_{16}H_8Cl_6N_2O_2$ (Parr Bomb): Cl, 52.2. Found: Cl, 52.3.

Attempts to condense hexachlorodiaminodiphenyl with *d*-camphorsulfonic acid and oxymethylenecamphor, respectively, proved unsuccessful.

Summary

1. 2,4,6,2',4',6'-Hexachloro-3,3'-dicarboxydiphenyl was prepared by the condensation of 1-iodo-2,4,6-trichloro-3-methylbenzene with copper and oxidation of the product.

2. The product was resolved through the brucine salt. The active forms were stable to ordinary methods of racemization.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE ACTION OF MERCURY ON ORGANIC IODIDES. I. THE FORMATION OF METHYLMERCURIC IODIDE AND BENZYL MERCURIC IODIDE¹

BY J. LEWIS MAYNARD

RECEIVED FEBRUARY 12, 1932

PUBLISHED MAY 7, 1932

Introduction

For over eighty years it has been known that when mercury is allowed to stand in the sunlight with methyl or ethyl iodide, reactions occur with the formation of organomercuric iodides, $RHgI$, and certain gaseous products.² In addition to the instances cited, the direct action of mercury with organic iodides has been noted only in the cases of allyl iodide,³ methylene iodide and iodoform,⁴ and propargyl iodide.⁵ With the higher saturated alkyl iodides it is possible that a very slow reaction with mercury takes place, but no accurate data are available.⁶ Up to the present time,

¹ A part of this material has been presented in a thesis submitted to the University of Minnesota.

² Frankland, *J. Chem. Soc.*, **3**, 322 (1851); *Ann.*, **111**, 59 (1859); Strecker, *ibid.*, **92**, 76 (1854).

³ Zinin, *ibid.*, **96**, 363 (1855).

⁴ Sakurai, *J. Chem. Soc.*, **37**, 658 (1880); **39**, 485 (1881); **41**, 360 (1882).

⁵ Henry, *Ber.*, **17**, 1132 (1884).

⁶ Whitmore, "Organic Compounds of Mercury," A. C. S. Monograph Series, The Chemical Catalog Co., New York, 1921, p. 26.