The picrate of *m*-diethylaminophenetole melted at 132–133° (mixed m.p.).

o-**Bromoanisole and Lithium Piperidide.**—The lithium piperidide was prepared from 0.22 mole of piperidine and 0.2 mole of methyllithium (negative color test I). On the addition of 0.2 mole of *o*-bromoanisole the mixture assumed a reddish tinge. At the end of a 24-hour period of refluxing with stirring almost no precipitate had appeared and the mixture was translucent. The yield of *m*-piperidylanisole was 41%, after allowing for a 34% recovery of *o*-bromoanisole: b.p. 110° (0.2 mm.); $n^{20}{}_D$ 1.5628; $d^{20}{}_4$ 1.059; mol. ref. calcd., 58.9; found, 58.8. The picrate of *m*-piperidylanisole was obtained as yellow needles melting at 159.5–160°.

Anal. Calcd. for $C_{18}H_{20}O_8N_4$: N, 13.3. Found: N, 13.55.

The structure of the reaction product was established by comparison with the picrate of a sample prepared by the reaction of *m*-chloroanisole with lithium piperidide: m.p. and mixed m.p. 159–160°.

o-**Bromoanisole and Lithium Morpholide.**—To lithium morpholide, obtained as a thick white suspension from 0.2 mole of methyllithium and 0.23 mole of freshly distilled morpholine in ether, was added 0.2 mole of *o*-bromoanisole in 50 cc. of ether. The color gradually changed from white to yellowish during a 24-hour period of refluxing with stirring. The initial yield of *m*-morpholylanisole was 8.6%, but after allowing for a recovery of 75% of *o*-bromoanisole the net yield was 35%; b.p. 113° (0.15 mm.); $n^{20}{}_D$ 1.5650. The picrate was obtained as yellow plates melting at 196–197°.

Anal. Calcd. for $C_{17}H_{18}O_9N_4$: N, 13.3. Found: N, 13.5.

The *m*-morpholylanisole was also obtained by reaction of *m*-chloroanisole with lithium morpholide (mixed m.p. of picrates).

p-**Dibromobenzene and Lithium Diethylamide.**—To a suspension of 0.22 mole of lithium diethylamide in 150 cc. of ether was added 0.09 mole of *p*-dibromobenzene in 100 cc. of ether, and the mixture was refluxed for 25 hours. Among the products so far isolated are: 15% of diethylaniline (m.p. and mixed m.p. of picrates 137–138°); and 14% of *p*-bromodiethylaniline (m.p. and mixed m.p. of picrates 165–166°). From another experiment in which 0.1 mole of *p*-dibromobenzene and 0.1 mole of lithium diethylamide were used, there was obtained 23% of *p*-bromodiethylaniline, or a 28% yield when allowance is made for recovered *p*-dibromobenzene.

AMES, IOWA

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

Quinone Imides. XIV. Addition of Hydrogen Chloride to *p*-Quinonedibenzimides and Related Compounds

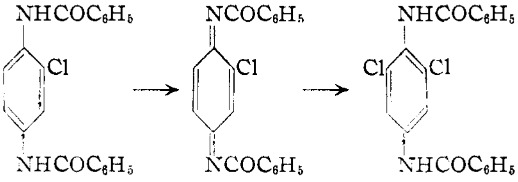
BY ROGER ADAMS AND D. S. ACKER

RECEIVED JANUARY 4, 1952

p-Phenylenedibenzamides may be oxidized to *p*-quinonedibenzimides by means of lead tetraacetate. Hydrogen chloride adds to the imides to give chloro amides. 2-Chloro-*p*-quinonedibenzimide is converted almost exclusively to 2,6-dichloro-*p*-phenylenedibenzamide, the structure of which was proved by an unequivocal synthesis, in contrast to the formation of a mixture of isomeric dichloro derivatives when 2-chloro-*p*-quinonedibenzenesulfonimide reacts under similar conditions. 2,6-Dichloro-*p*-quinonedibenzimide and hydrogen chloride react to give a complicated mixture from which only a small amount of trichloro diamide could be isolated. 2-Chloro-*p*-quinonedicarbethoxyimide adds hydrogen chloride to give a mixture of dichloro diamides from which two were isolated in pure state. 2-Chloro-*p*-quinonedicarbobenzoxyimide is likewise converted to a mixture of dichloro diamides which by oxidation and subsequent addition of hydrogen chloride give a good yield of 2,3,5-trichloro diamide. The substituted *p*-phenylenedibenzylcarbamates are quite readily hydrolyzed to the corresponding diamines by ethanolic hydrochloric acid.

The orientation of the chlorine atom when hydrogen chloride is added to various *p*-quinonedibenzenesulfonimides has been discussed in a previous paper.[1a] A similar study using various acyl and aroyl diimides has now been completed.

2-Chloro-*p*-phenylenedibenzamide (I) is formed when hydrogen chloride is added to *p*-quinonedibenzimide.[1b] This product was oxidized with lead tetraacetate in refluxing benzene or chloroform to 2-chloro-*p*-quinonedibenzimide (II). Subsequent addition of hydrogen chloride gave a good yield of a single product, 2,6-dichloro-*p*-phenylenedibenzamide, with little or no tendency to form isomers. The structure of this product was proved unequivocally by reducing the commercially available 2,6-dichloro-4-nitroaniline to the corresponding diamine and benzoylating. The entrance of the chlorine atom in the 6-position is in contrast to the addition of hydrogen chloride to 2-methyl-*p*-quinonedibenzenesulfonimide which yields exclusively the 2-methyl-5-chloro diamide; addition of hydrogen chloride to 2-chloro-*p*-quinonedibenzenesulfonimide yields primarily the 2,5-dichloro- and 2,3-dichloro diamides.



I II III

When the 2,6-dichloro-*p*-phenylenedibenzamide (III) was oxidized to the corresponding dichloro-*p*-quinonedibenzimide and treated with hydrogen chloride, the reaction was a complicated one, yielding a mixture from which only a small quantity of the expected 2,3,5-trichloro-*p*-phenylenedibenzamide was obtained. The other products were not identified.

2,3,5,6-Tetrachloro-*p*-phenylenedibenzamide was obtained by nitration of 1,2,4,5-tetrachlorobenzene to the dinitro compound, reduction to the corresponding diamine and benzoylation. This diamide was oxidized to the diimide by lead tetraacetate in refluxing benzene somewhat more slowly than the other dibenzamides reported in this paper.

2-Chloro-*p*-phenylenediethylcarbamate[1b] was oxidized by lead tetraacetate in anhydrous ether to

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(1) (a) R. Adams, E. F. Elslager and K. F. Heumann, THIS JOURNAL, **74**, 2608 (1952); (b) R. Adams and J. L. Anderson, *ibid.*, **72**, 5154 (1950).

give 2-chloro-*p*-quinonedicarbethoxyimide. Subsequent addition of hydrogen chloride gave a mixture of dichloro isomers from which two were isolated in a pure state. An attempt to establish the constitution of one of these as 2,6-dichloro-*p*-phenylenediethylcarbamate failed. 2,6-Dichloro-*p*-phenylenediamine was converted by the action of ethyl chlorocarbonate in pyridine to a monoethylcarbamate derivative. *p*-Quinonedicarbomethoxyimide was synthesized from *p*-phenylenedimethylcarbamate but it proved to be less stable on standing than the corresponding ethyl compound and was not studied further.

p-Quinonedicarbobenzoxyimide was prepared from the corresponding diamide by means of lead tetraacetate in hot chloroform. Addition of hydrogen chloride gave 2-chloro-*p*-phenylenedibenzylcarbamate which was oxidized in refluxing chloroform to 2-chloro-*p*-quinonedicarbobenzoxyimide. Treatment of this diimide with hydrogen chloride gave a mixture of dichloro diamide isomers. This mixture was not separated but upon oxidation and subsequent treatment of the solution of the isomeric dichloro-*p*-quinonedicarbobenzoxyimides with hydrogen chloride, a good yield of 2,3,5-trichloro-*p*-phenylenedibenzylcarbamate was obtained. The *p*-quinonedicarbethoxyimide and dicarbobenzoxyimide do not show the abnormal behavior in the reaction with hydrogen chloride noted with the 2,6-dichloro-*p*-quinonedibenzimide.

The ethylcarbamate and benzylcarbamate derivatives were investigated not only to determine whether the addition reactions to the diimides would proceed as readily as in the analogous molecules with benzoyl or benzenesulfonyl groups on the nitrogen atoms, but also to determine whether the diamides from the addition reactions might be hydrolyzed or hydrogenolyzed to the diamines more readily than the benzoyl and benzenesulfonyl derivatives.

Attempts to hydrolyze the dichloro-*p*-phenylenediethylcarbamates with equal parts of concentrated hydrochloric acid and ethanol for extended periods of time failed. On the other hand, *p*-phenylenedibenzylcarbamate, 2,3,5-trichloro-*p*-phenylenedibenzylcarbamate, and 2-chloro-*p*-phenylenedibenzamide, upon similar treatment hydrolyzed to the corresponding diamines.

Catalytic hydrogenolysis of 2-chloro-*p*-phenylenedibenzylcarbamate with Raney nickel or platinum oxide as catalyst was unsuccessful. With palladium chloride-on-carbon (5% of palladium) the benzyl groups were removed, but only small amounts of the catalyst could be used; otherwise the halogen in the ring was also replaced by hydrogen. By using 1% of palladium, 2,3,5-trichloro-*p*-phenylenediamine was prepared in good yield from the corresponding dibenzylcarbamate.

The authors are indebted to Miss Emily Davis, Mrs. Jean Fortney and Mrs. Katherine Pih for the microanalyses and to Miss Elizabeth Petersen and Miss Helen Miklas for the infrared spectra.

Experimental

All melting points below 360° are corrected.

***p*-Phenylenedibenzamide.**—This was prepared as previously described.[1b] However, several recrystallizations from dimethylformamide gave white crystals, m.p. 343–344°, which is higher than that previously reported, m.p. 335–340°.[1b]

Anal. Calcd. for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10. Found: C, 75.80; H, 5.37.

2-Chloro-*p*-phenylenedibenzamide (A).—Dry hydrogen chloride was passed into a solution of 3.1 g. of *p*-quinonedibenzimide[1b] in 50 ml. of dry chloroform for 10 minutes. The red solution had bleached to a light tan. Addition of petroleum ether (b.p. 80–110°) caused the precipitation of 3.1 g. (88%) of the amide which was crystallized from ethyl acetate–petroleum ether and then from benzene, m.p. 243–244° (lit. m.p. 226–228°).[1b]

Anal. Calcd. for $C_{20}H_{15}ClN_2O_2$: C, 68.47; H, 4.31. Found: C, 68.65; H, 4.32.

The discrepancy in the melting point from that previously reported may have been due to the previous use of acetic acid as solvent which has been shown in work to be described in a subsquent communication to add to the diimide. A small impurity of the acetic acid adduct was probably present since heating this crude product with ethanolic alkali served to remove the impurity which depressed the melting point.

2-Chloro-*p*-phenylenedibenzamide was formed also by the reaction of solid *p*-quinonedibenzimide and gaseous hydrogen chloride in 97% yield.

By refluxing 1 g. of 2-chloro-*p*-phenylenedibenzamide in 100 ml. of equal parts of concentrated hydrochloric acid and ethanol for 6 hours, 2-chloro-*p*-phenylenediamine was obtained in 54% yield.

(B).—A convenient procedure for synthesis of the 2-chloro diamide without isolation of the intermediate diimide follows. A suspension of 30 g. of *p*-phenylenedibenzamide and 42.3 g. of lead tetraacetate in one liter of dry, thiophene-free benzene was stirred under reflux for 4 hours. One liter of petroleum ether (b.p. 80–110°) was added and the solution filtered to remove the lead salts and any unreacted amide. Dry hydrogen chloride was passed into the solution for 15 minutes and the product collected by suction filtration. After two crystallizations from ethanol, 20.8 g. (63%) of white crystals were obtained, m.p. 242–244°.

2,6-Dichloro-*p*-phenylenedibenzamide (A).—Dry hydrogen chloride was passed into a solution of 2.1 g. of 2-chloro-*p*-quinonedibenzimide[1b] in 250 ml. of dry, thiophene-free benzene for 15 minutes. The white precipitate weighed 2.1 g. (91%). Recrystallization from ethyl acetate gave pure product, m.p. 262–263°.

Anal. Calcd. for $C_{20}H_{14}Cl_2N_2O_2$: C, 62.35; H, 3.66. Found: C, 62.51; H, 3.64.

(B).—Directions for preparing this compound without isolation of the diimide follow. A suspension of 20.8 g. of 2-chloro-*p*-phenylenedibenzamide and 26.5 g. of lead tetraacetate in one liter of dry, thiophene-free benzene was stirred under reflux for 4 hours. After filtering to remove any lead salts and unreacted amide, dry hydrogen chloride was passed into the solution for 15 minutes. The precipitate of 18.7 g. (82%) of white product melted at 259–262°.

This compound may also be formed by the reaction of solid 2-chloro-*p*-quinonedibenzimide and dry hydrogen chloride.

(C).—This same compound was synthesized by another route. 2,6-Dichloro-*p*-phenylenediamine was prepared by reducing a suspension of 5.0 g. of 2,6-dichloro-4-nitroaniline (Eastman Kodak Co.) in 200 ml. of concentrated hydrochloric acid with 16.5 g. of stannous chloride dihydrate. The reaction was complete after heating for 30 minutes on the steam-bath. The solution was made strongly alkaline with aqueous sodium hydroxide and the free diamine which precipitated was collected by suction filtration and washed with water. The yield was 4.2 g. (98%) of white product, m.p. 122–123° (lit. m.p. 124–125°).[2] A solution of this product in 50 ml. of α-picoline and 6.8 g. of benzoyl chloride was heated under reflux for 2 hours. After cooling, the straw-colored solution was poured into 300 ml. of ice-water containing 50 ml. of concentrated hydrochloric acid. The precipitated 2,6-dichloro-*p*-phenylenedibenzamide was recrystallized from ethanol to give 5.0 g. (55%) of white crystals, m.p. 262–263°.

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[2] N. L. Drake, *et al.*, THIS JOURNAL, **68**, 1602 (1946).

Anal. Calcd. for $C_{20}H_{14}Cl_2N_2O_2$: C, 62.35; H, 3.66. Found: C, 62.55; H, 3.70.

The crystals of this authentic 2,6-dichloro-*p*-phenylenedibenzamide did not depress the melting point of the dichlorodiamide formed by the addition of hydrogen chloride to the 2-chloro-*p*-quinonedibenzimide. Infrared spectra analysis proved that the two compounds were identical.

2,6-Dichloro-*p*-quinonedibenzimide.—A suspension of 1.8 g. of 2,6-dichloro-*p*-phenylenedibenzamide and 2.1 g. of lead tetraacetate in 100 ml. of dry, thiophene-free benzene was stirred under reflux for 6 hours. After filtration to remove the insoluble lead salts, the reddish solution was evaporated *in vacuo* to 10 ml. The precipitated diimide was redissolved by adding boiling petroleum ether (b.p. 80–110°) and the solution filtered while hot. Chilling overnight in the ice-box caused precipitation of 1.4 g. (78%) of yellow crystals which after recrystallization from petroleum ether melted at 138–140°.

Anal. Calcd. for $C_{20}H_{12}Cl_2N_2O_2$: C, 62.68; H, 3.16. Found: C, 62.69; H, 3.38.

2,3,5-Trichloro-*p*-phenylenedibenzamide: Action of Hydrogen Chloride on 2,6-Dichloro-*p*-quinonedibenzimide.—Dry hydrogen chloride was passed into a solution of 1.2 g. of 2,6-dichloro-*p*-quinonedibenzimide in 100 ml. of dry, thiophene-free benzene for 30 minutes. No precipitate was formed but the red solution had bleached to a light yellow. Addition of 200 ml. of petroleum ether (b.p. 80–110°) caused precipitation of 1.3 g. of a crude product which after several recrystallizations from ethyl acetate–petroleum ether and final recrystallizations from ethyl acetate gave a small amount of the pure 2,3,5-trichloro-*p*-phenylenedibenzamide, m.p. 315–316°.

Anal. Calcd. for $C_{20}H_{13}Cl_3N_2O_2$: C, 57.23; H, 3.12; Cl, 25.34. Found: C, 57.62; H, 3.26; Cl, 25.08.

The reaction is obviously complicated by formation of many by-products. Several attempts to prepare the desired 2,3,5-trichloro-*p*-phenylenedibenzamide in good yield using benzene, chloroform or petroleum ether (b.p. 80–110°) as the reaction solvent resulted in essentially the same mixture as encountered above. Attempts to separate the mixture into its components by fractional crystallization from benzene or acetone–water were unsuccessful. The material did not adsorb upon a column of activated alumina from ethyl acetate or acetone–chloroform. The material was adsorbed from benzene solution but the elution did not give sharp fractions.

2,3,5,6-Tetrachloro-*p*-phenylenedibenzamide.—In a modification of the procedure of Berckmans and Holleman,[3] 2,3,5,6-tetrachloro-1,4-dinitrobenzene was prepared by adding dropwise 100 g. of fuming nitric acid (sp. gr. 1.50) to a stirred suspension of 10.8 g. of 1,2,4,5-tetrachlorobenzene (Eastman Kodak Co.) in 100 g. of 30% fuming sulfuric acid. The resulting solution was stirred under reflux for 5 hours and then allowed to cool to room temperature. The crude product was obtained by pouring the reaction mixture into one liter of ice-water. Recrystallization from benzene–ethanol yielded 8.4 g. (55%) of colorless crystals of the dinitro compound, m.p. 233–234° (lit. m.p. 232°).[4] Concentration of the mother liquor yielded 1.4 g. of impure mononitro compound melting at about 100°.

A suspension of 12.0 g. of the 2,3,5,6-tetrachloro-1,4-dinitrobenzene and 70 g. of stannous chloride crystals in 400 ml. of ethanol and 120 ml. of concentrated hydrochloric acid was heated under reflux for 1 hour. The resulting solution was allowed to cool to 60° and then aqueous sodium hydroxide was added in excess to decompose the tin salt. The free amine which precipitated was collected after chilling the solution in an ice-bath. One recrystallization from toluene gave 9.0 g. (93%) of white needles, m.p. 223–224° (lit. m.p. 222–223°).[4]

A solution of 7.9 g. of this amine in 100 ml. of pyridine and 9.1 g. of benzoyl chloride was heated under reflux for 2 hours. The straw-colored solution was allowed to cool to room temperature and then poured into 500 ml. of ice-water. One recrystallization from dimethyl formamide–water gave 13.5 g. (93%) of white crystals. Several recrystallizations from dimethyl formamide–ethanol gave a pure product, m.p. 395–396°.

Anal. Calcd. for $C_{20}H_{12}Cl_4N_2O_2$: C, 52.89; H, 2.66. Found: C, 52.81; H, 2.82.

2,3,5,6-Tetrachloro-*p*-quinonedibenzimide.—A suspension of 2.5 g. of 2,3,5,6-tetrachloro-*p*-phenylenedibenzamide and 2.45 g. of lead tetraacetate in 100 ml. of dry thiophene-free benzene was stirred under reflux for 8 hours. The solution became bright yellow as the oxidation progressed. After cooling, the inorganic salts and unchanged amide were removed by filtration. Addition of 200 ml. of petroleum ether (b.p. 80–110°) and cooling overnight in the ice-box caused precipitation of 2.0 g. (80%) of the yellow diimide. Several recrystallizations from benzene gave a pure product, m.p. 264–265°, after starting to darken slightly at 261°.

Anal. Calcd. for $C_{20}H_{10}Cl_4N_2O_2$: C, 53.13; H, 2.23. Found: C, 53.09; H, 2.28.

When dry hydrogen chloride was passed into a solution of the pure 2,3,5,6-tetrachloro-*p*-quinonedibenzimide in dry, thiophene-free benzene for 15 minutes, the yellow color of the solution was gradually bleached to a light greenish-yellow and a fine white precipitate formed. This was not identified.

2-Chloro-*p*-quinonedicarbethoxyimide.—A suspension of 5.0 g. of 2-chloro-*p*-phenylenediethylcarbamate[1b] and 7.8 g. of lead tetraacetate in 150 ml. of dry ether was stirred vigorously at room temperature for 17 hours. After filtration, the reddish solution was chilled in a Dry Ice–methanol mixture but the crystals which separated could not be collected as they became liquid upon warming to room temperature. The ether was removed *in vacuo* and the red tarry residue, after repeated recrystallization from petroleum ether (b.p. 40–55°), gave light yellow crystals, m.p. 55.5°. The product apparently is formed in reasonably good yield as demonstrated by the results of the next preparation described, but only a very low yield of crystalline material was isolated.

Anal. Calcd. for $C_{12}H_{13}ClN_2O_4$: C, 50.62; H, 4.60; N, 9.84. Found: C, 50.66; H, 4.67; N, 10.04.

2,x-Dichloro-*p*-phenylenediethylcarbamate.—A suspension of 8.1 g. of 2-chloro-*p*-phenylenediethylcarbamate and 12.5 g. of lead tetraacetate in 200 ml. of dry ether was stirred at room temperature for 16 hours. After filtration to remove the unreacted starting material and the inorganic salts, the ether solution was concentrated to 100 ml. and 400 ml. of petroleum ether (b.p. 80–110°) was added. Dry hydrogen chloride was passed into this reddish solution for 10 minutes and a white solid formed. One crystallization of this solid from ethyl acetate gave 6.0 g. (66%) of a mixture of the dichloro isomers. Fractional crystallization from ethyl acetate yielded two compounds, the less soluble, m.p. 183–184°, and the more soluble, m.p. 142–144°.

Anal. Calcd. for $C_{12}H_{14}Cl_2N_2O_4$: C, 44.86; H, 4.39. Found (183–184° isomer): C, 45.16; H, 4.49. Found (142–144° isomer): C, 44.98; H, 4.21.

Attempts to hydrolyze these isomers by refluxing for 24 hours with equal parts of concentrated hydrochloric acid and ethanol failed. About 75% yields of unchanged diamides were recovered.

2,6-Dichloro-*p*-phenylenemonoethylcarbamate Monoamine.—An attempt to prepare 2,6-dichloro-*p*-phenylenediethylcarbamate from the corresponding diamine failed. Only a monourethan resulted. To a solution of 1.77 g. of 2,6-dichloro-*p*-phenylenediamine in 25 ml. of pyridine was added slowly, with stirring and cooling, 2.20 g. of ethyl chlorocarbonate. The solution was allowed to warm to room temperature and then was refluxed for 1.5 hours. After cooling to room temperature, the light brown solution was poured into 500 ml. of ice-water. An oil separated which solidified after standing overnight. Recrystallization from petroleum ether (b.p. 80–110°) gave 1.88 g. of white needles which after recrystallization from the same solvent melted at 106–107°. The analysis indicated a monoethylcarbamate and an infrared spectrum confirmed this.

Anal. Calcd. for $C_9H_{10}Cl_2N_2O_2$: C, 43.39; H, 4.05. Found: C, 43.75; H, 4.29.

***p*-Phenylenedimethylcarbamate.**—To a solution of 20 g. of *p*-phenylenediamine in 200 ml. of pyridine, cooled in an ice-bath, was added with vigorous stirring 29 ml. of methyl

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[3] V. S. F. Berckmans and A. F. Holleman, *Rec. trav. chim.*, **44**, 851 (1925).

[4] A. T. Peters, F. M. Rowe and D. M. Stead, *J. Chem. Soc.*, 233 (1943).

chlorocarbonate over a period of 30 minutes. The solution was stirred for 15 minutes longer at room temperature and then was poured into one liter of ice-water. The crude *p*-phenylenedimethylcarbamate was recrystallized three times from ethanol (Darco) to give 17 g. (41%) of a pure white product, m.p. 216–217°.

Anal. Calcd. for $C_{10}H_{12}N_2O_4$: C, 53.56; H, 5.40. Found: C, 53.41; H, 5.32.

***p*-Quinonedicarbomethoxyimide.**—A suspension of 1.12 g. of *p*-phenylenedimethylcarbamate and 2.22 g. of lead tetraacetate in 100 ml. of dry ether was stirred vigorously at room temperature for 19 hours. After filtration, the yellowish solution was cooled in a Dry Ice–methanol mixture and 0.5 g. (45%) of product separated. Several recrystallizations from petroleum ether (b.p. 45–50°) gave pure yellow crystals of the quinone diimide, m.p. 99–100°. This product is very unstable on standing except when absolutely pure.

Anal. Calcd. for $C_{10}H_{10}N_2O_4$: C, 54.05; H, 4.54. Found: C, 54.04; H, 4.56.

***p*-Phenylenedibenzylcarbamate.**—To a suspension of 10.8 g. of *p*-phenylenediamine in 200 ml. of a 5% solution of sodium hydroxide was added dropwise with mechanical stirring 34.1 g. of carbobenzoxy chloride[5] dissolved in 122 ml. of toluene. After the addition was complete, the suspension was stirred for 2 hours more at room temperature. The product was collected by filtration and recrystallized from acetone to give 28.8 g. (76%) of white crystals, m.p. 231–232° (lit. m.p. 222.5–223°).[6]

By refluxing 1 g. of *p*-phenylenedibenzylcarbamate in 100 ml. of equal parts of concentrated hydrochloric acid and ethanol for 17 hours, an 87% yield of *p*-phenylenediamine dihydrochloride resulted.

A solution of 0.5 g. of *p*-phenylenedibenzylcarbamate in 100 ml. of acetic acid was quantitatively hydrogenolyzed when treated with hydrogen at 10 p.s.i. for 2 hours over 0.5 g. of 5% palladium chloride-on-carbon catalyst.[7] The hydrogenolysis was also accomplished in absolute ethanol containing some acetic acid, but use of ethyl acetate as solvent or platinum oxide or Raney nickel as catalyst gave little or no cleavage.

***p*-Quinonedicarbobenzoxyimide.**—A suspension of 1.5 g. of *p*-phenylenedibenzylcarbamate and 1.8 g. of lead tetraacetate in 50 ml. of dry chloroform was stirred under reflux for 1 hour. After filtration to remove the insoluble material, the red solution was concentrated *in vacuo* to 10 ml. and boiling petroleum ether (b.p. 80–110°) was added to form a solvent pair. Upon cooling 1.1 g. (73%) of the quinone diimide was deposited. Recrystallization from dry diethyl ether gave light yellow prisms, m.p. 99–100°.

Anal. Calcd. for $C_{22}H_{18}N_2O_4$: C, 70.58; H, 4.85. Found: C, 70.54; H, 5.01.

2-Chloro-*p*-phenylenedibenzylcarbamate.—A suspension of 3.0 g. of *p*-phenylenedibenzylcarbamate and 3.6 g. of lead tetraacetate in 100 ml. of dry chloroform was stirred under reflux for one hour. The insoluble material was separated by filtration and washed with 100 ml. of petroleum ether (b.p. 80–110°) to remove any adsorbed diimide. Dry hydrogen chloride was passed into the combined mother liquor and washings for 5 minutes which caused the precipitation of some product and bleaching of the solution. The solvent was removed *in vacuo* and the residue recrystallized from ethyl acetate to give 2.8 g. (85%) of white crystals. Recrystallization from ethyl acetate gave the pure compound, m.p. 176.5–177.5°.

Anal. Calcd. for $C_{22}H_{19}ClN_2O_4$: C, 64.31; H, 4.66. Found: C, 64.52; H, 4.54.

Hydrogenolysis when carried out as described for the halogen-free compound yielded *p*-phenylenediamine. The carbobenzoxy groups were removed and the halogen in the ring was replaced by hydrogen.

2-Chloro-*p*-quinonedicarbobenzoxyimide.—To a suspension of 15.0 g. of 2-chloro-*p*-phenylenedibenzylcarbamate in 300 ml. of refluxing chloroform was added 16.2 g. of lead tetraacetate. The solution became yellow immediately and was stirred under reflux for 3 hours. After cooling to room temperature the insoluble material was removed by filtration and washed with petroleum ether (b.p. 80-110°). The combined filtrate and washings were diluted with more petroleum ether to a volume of 500 ml. and then a 100-ml. portion was evaporated *in vacuo* to 20 ml. and boiling ether added to redissolve the precipitated diimide. Upon cooling, the diimide separated as an oil. Only very slow recrystallization from a dilute solution in absolute diethyl ether gave satisfactory crystals. Two recrystallizations in this way gave 1.15 g. (38%) of fine yellow crystals, m.p. 70–72°.

Anal. Calcd. for $C_{22}H_{17}ClN_2O_4$: C, 64.63; H, 4.19. Found: C, 64.44; H, 4.45.

2,x-Dichloro-*p*-phenylenedibenzylcarbamate.—Dry hydrogen chloride was passed into the remaining 400-ml. portion of the 2-chloro-*p*-quinonedicarbobenzoxyimide for 5 minutes. The yellow solution was bleached to a light tan but no product precipitated. The solvent was removed *in vacuo* and the residue dissolved in boiling ethanol. Upon cooling, 10.1 g. (78%) of the mixture of dichloro isomers precipitated as white needles, m.p. 160–178°. No attempt was made to separate the mixture of isomers. After two more crystallizations from ethyl acetate the crystals were submitted for analysis.

Anal. Calcd. for $C_{22}H_{18}Cl_2N_2O_4$: C, 59.34; H, 4.07. Found: C, 59.53; H, 4.17.

2,3,5-Trichloro-*p*-phenylenedibenzylcarbamate.—To a solution of 8.2 g. of a mixture of 2,x-dichloro-*p*-phenylenedibenzylcarbamates in 200 ml. of refluxing chloroform was added 8.3 g. of lead tetraacetate. The solution became yellow immediately and was stirred under reflux for 1 hour. After cooling to room temperature, the insoluble material was removed by filtration and 200 ml. of petroleum ether (b.p. 80–110°) was added to the mother liquor. Dry hydrogen chloride was passed into the solution for 5 minutes. The color bleached to a light tan but no product precipitated. The solvent was removed *in vacuo* and the residue recrystallized from ethyl acetate–petroleum ether to give 7.49 g. (85%) of white crystals, m.p. 186–187°. Further recrystallization from benzene did not change this melting point.

Anal. Calcd. for $C_{22}H_{17}Cl_3N_2O_4$: C, 55.08; H, 3.57. Found: C, 55.39; H, 3.75.

By refluxing 1 g. of 2,3,5-trichloro-*p*-phenylenedibenzylcarbamate in 100 ml. of equal parts concentrated hydrochloric acid and ethanol for 24 hours, evaporating to dryness, adding aqueous ammonia and recrystallizing the precipitate from chloroform–petroleum ether, 0.33 g. (75%) of the trichloro diamine[8] was obtained which melted at 118–119° after three recrystallizations from methylcyclohexane.

Anal. Calcd. for $C_6H_5Cl_3N_2$: C, 34.07; H, 2.38; N, 13.25. Found: C, 33.95; H, 2.54; N, 13.23.

A hydrogenolysis attempt similar to that previously described for the unsubstituted homolog resulted in extensive chlorine replacement. When 0.50 g. of the trichloro carbamate and 0.10 g. of catalyst in 200 ml. of absolute ethanol containing 5 ml. of acetic acid was treated with hydrogen at 13 p.s.i. for 20 hours, 0.20 g. (91%) of 2,3,5-trichloro-*p*-phenylenediamine[8] was obtained which melted at 118–119° after three recrystallizations from methylcyclohexane. This compound did not depress the melting point of that obtained by hydrolysis.

URBANA, ILLINOIS

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[5] H. E. Carter, R. L. Frank and H. W. Johnston, *Org. Syntheses*, **23**, 13 (1943).

[6] P. Ruggli and H. Dahn, *Helv. Chim. Acta*, **27**, 1116 (1944).

[7] R. Mozingo, *Org. Syntheses*, **26**, 78 (1946).

[8] This compound has been reported by H. A. J. Schoutissen, THIS JOURNAL, **55**, 4535 (1935), as melting at 198°. There was no analysis given.