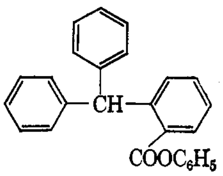
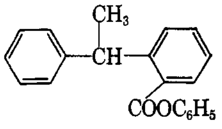


III

hydrylbenzoate (III) is treated with molecular chlorine or bromine under conditions which lead to the reaction of the methyl ester.[1] The carbophenoxy group must constitute a formidable steric barrier to tertiary hydrogen atom extraction. It is interesting to note that 1-phenyl-1-(*o*-carbophenoxyphenyl)ethane (IV) is much less easily photochlorinated than is the corresponding methyl ester.[2]



IV

The *o*-carbophenoxy group also screens the tertiary carbon of triphenylmethane against attack by an oxidizing agent. Under conditions which promote the reaction of tri-*p*-nitrophenylmethane with chromium trioxide in acetic acid to form the corresponding carbinol,[3] III is unreactive. The methyl ester (I) reacts under these same conditions to produce a mixture of products in which 3,3-diphenylphthalide again appears to be the major component.

Experimental

The Methyl (I) and Phenyl (III) Esters of *o*-Benzhydrylbenzoic Acid.—A sample of *o*-benzhydrylbenzoic acid was prepared by the aluminum chloride-catalyzed reaction of 3-phenylphthalide and benzene.[4] The acid was converted to the acid chloride by refluxing in carbon tetrachloride, with an equimolar quantity of phosphorus pentachloride. When the reaction was complete, the solvent was removed and the residue was refluxed with methanol for several hours. The methyl ester, m.p. 94–96° (lit.[5] m.p. 98°), was isolated in 52% yield from the methanol solution. The phenyl ester was prepared by refluxing a mixture of crude samples of the acid chloride, phenol, and pyridine (in equimolar amounts) in carbon tetrachloride for 2 hr. The product was isolated in 71% yield (9.0 g. from 10.0 g. of starting acid), m.p. 89–90.5°, after recrystallization from petroleum ether (b.p. 30–60°).

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.60; H, 5.55. Found: C, 85.90; H, 5.26.

Photochlorination. A. Triphenylmethane.—A solution of 4.0 g. (0.016 mole) of triphenylmethane in 150 ml. of carbon tetrachloride was irradiated with a tungsten lamp as it was treated dropwise with a solution of 1.2 g. (0.015 mole) of chlorine in 100 ml. of the same solvent. After the reaction was complete, the solvent was removed and the crude trityl chloride was recrystallized from petroleum ether to provide 3.0 g. (67% yield) of pure material, m.p. 111–112° (lit.[6] m.p. 112°).

B. Methyl *o*-Benzhydrylbenzoate.—A 2.0-g. sample of this ester was photochlorinated with an equimolar quantity of chlorine by essentially the same procedure as was used for the reaction of triphenylmethane. From the product a sample of 3,3-diphenylphthalide was obtained. This was crystallized from petroleum ether to provide 1.0 g. (56% yield) of pure material of m.p. 115° (lit.[7] m.p. 116°) and equiv. wt., 284 (calcd. for $C_{20}H_{14}O_2$, 286).

C. Phenyl *o*-Benzhydrylbenzoate.—A 1.0-g. (0.004 mole) sample of this ester was treated with 3.0 g. (0.04 mole) of chlorine, again by essentially the same procedure as has been described for the preparation of trityl chloride. The crude product was crystallized from petroleum ether to provide 0.8 g. of a solid of m.p. 88–90°. The melting point of this material was not depressed by mixing with a sample of the starting ester.

Photobrominations. A. Methyl *o*-Benzhydrylbenzoate.—A 5.0-g. sample of this ester was photobrominated by the general procedure described previously.[1] From the reaction product 3.0 g. (62%) of 3,3-diphenylphthalide, m.p. 116–118°, was isolated. This material had an infrared spectrum identical with that of the product of photochlorination of the starting ester.

B. Phenyl *o*-Benzhydrylbenzoate.—A 10.0-g. sample of the phenyl ester was treated with an equimolar amount of bromine in carbon tetrachloride and irradiated under the same conditions, which lead to rapid photobromination of diphenylmethane derivatives and also of methyl *o*-benzhydrylbenzoate.[1] After 1 hr. the reaction mixture still had an intense bromine color. The solvent and unchanged bromine were removed by evaporation. In this fashion 9.5 g. (crystallized from petroleum ether) of unchanged phenyl *o*-benzhydrylbenzoate was obtained, m.p. 87–90°. The melting point of this material was not depressed by mixing with a sample of the starting ester.

Oxidation of the Esters.—A 1.0-g. sample of methyl *o*-benzhydrylbenzoate was oxidized by refluxing for 3 hr. in a solution of 0.2 g. of chromium trioxide in 50 ml. of acetic acid. The solution turned green during this period. The crude product was isolated by the procedure reported by Fischer and Fischer.[3] This was an oil (0.6 g.) which could not be induced to crystallize. On the basis of its infrared spectrum it was concluded that this material was predominantly 3,3-diphenylphthalide.

An attempt was made to oxidize a 1.0-g. sample of phenyl *o*-benzhydrylbenzoate by the same procedure used in oxidizing the corresponding methyl ester. After it was refluxed for 3 hr., the reaction mixture was still purple. From the acetic acid solution 0.8 g. (after crystallization from petroleum ether) of the starting phenyl ester, m.p. 85–87°, was obtained. The infrared spectrum of this material was identical with that of phenyl *o*-benzhydrylbenzoate.

Acknowledgment.—The authors are indebted to the National Science Foundation for a grant in support of this research.

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[1] In an earlier investigation [A. Singh, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **84**, 1179 (1962)], it was found that methyl *o*-benzylbenzoate also underwent photobromination to yield a lactone, 3-phenylphthalide. The corresponding phenyl ester, however, reacts with bromine under irradiation to provide *o*-carbophenoxybenzhydryl bromide in excellent yield.

[2] Unpublished results of E. A. Jeffery, L. J. Andrews, and R. M. Keefer.

[3] E. Fischer and O. Fischer, *Ann.*, **194**, 242 (1878).

[4] E. J. King, *J. Am. Chem. Soc.*, **49**, 562 (1927).

[5] A. Haller and A. Guyot, *Bull. soc. chim. France*, **31**, 979 (1904).

[6] M. Gomberg, *Ber.*, **33**, 3144 (1900).

[7] C. Graebe and M. Leonhardt, *Ann.*, **290**, 217 (1896).

The Preparation of N,N,N'N'-Tetramethyl-*p*-phenylenediamine[1]

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The N-methylation of *p*-phenylenediamine by heating its dihydrochloride with methanol in a sealed tube was first described by R. Meyer.[2] Although this procedure gives low yields and purification of the

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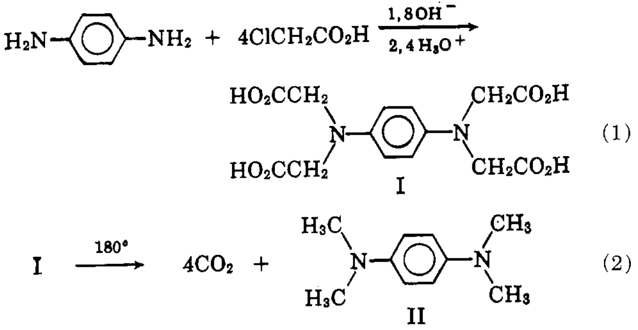
[2] R. Meyer, *Ber.*, **36**, 2979 (1903).

product is tedious, it is apparently the most satisfactory synthesis of N,N,N'N'-tetramethyl-p-phenylenediamine (II) yet reported. Application of the Eschweiler-Clark modification of the Leuckart Reaction[3] to p-phenylenediamine fails, apparently due to condensation of formaldehyde with the activated ring.[4] Although the decarboxylation of phenyliminodiacetic acid to N,N-dimethylaniline has been reported,[5] this type of reaction seems not to have been applied very frequently to the methylation of anilines. We wish to report a facile example of this reaction (eq. 2), which affords a ready synthesis of II.



Although the mechanism of the decarboxylation is presently unknown, the reported catalysis by ferric ion[5b] and the induction period occasionally observed in the present work are suggestive of a homolytic process.

Experimental

p-Phenylenediiminotetraacetic Acid (I).—p-Phenylenediamine, 10.8 g. (0.1 mole), chloroacetic acid, 37.8 g. (0.4 mole), sodium hydroxide, 32.0 g. (0.8 mole), and potassium iodide, 5.0 g. (0.03 mole), were dissolved in 500 ml. of water and boiled under reflux for 1 hr. To the hot solution there was added cautiously 40 ml. of concentrated hydrochloric acid. The precipitate which formed upon cooling the solution in ice was filtered with suction and dried under vacuum at room temperature. The nearly colorless crystals melted at 165° with decomposition (lit.[6] m.p. 165° dec.) and weighed 18.9 g. (55%).

Decarboxylation of I to N,N,N',N'-Tetramethyl-p-phenylenediamine (II).—I (17.0 g., 0.05 mole) was placed in a large vacuum sublimation apparatus which was then evacuated by means of an aspirator to approximately 20 mm. A Wood's Metal bath which had been preheated to 180° was cautiously applied to the sublimer. Melting of the solid was accompanied by evolution of gas, and the product sublimed on the cold finger.

In order to remove colored impurities the product was dissolved in petroleum ether (b.p. 30–60°) and passed through a short column of basic activated alumina. Evaporation of the solvent, followed by one additional vacuum sublimation, afforded colorless crystals (4.3 g., 52%), m.p. 51–52° (lit.[2] m.p. 51°). Recrystallization from petroleum ether afforded glistening platelets of the same melting point. The visible absorption spectrum of the radical cation, "Wurster's Blue," formed on oxidation of the amine was in quantitative agreement with that reported.[7] Several samples of the purified amine have remained colorless in contact with air, but with exclusion of light and moisture, for periods of up to 3 years.

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[3] M. L. Moore, *Org. Reactions*, **5**, 301 (1949); H. T. Clarke, H. B. Gillespie, and S. Z. Weisshaus, *J. Am. Chem. Soc.*, **55**, 4571 (1933).

[4] J. R. Cox, Jr., unpublished results.

[5] (a) A. Hausdörfer, *Ber.*, **22**, 1798 (1889); (b) Kalle and Co., German Patent 375463, abstracted in P. Friedländer, *Fortsch. Teerfarbenfabrik.*, **14**, 400 (1926).

[6] L. Michaelis and M. P. Schubert, *J. Biol. Chem.*, **106**, 331 (1934).

[7] L. Michaelis, M. P. Schubert, and S. Granick, *J. Am. Chem. Soc.*, **61**, 1981 (1939).

Arylation Reactions of Anthraquinones. The Preparation of 1-Aryl-4-aminoanthraquinones

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Nesmeyanow and co-workers[1] have studied the decomposition of the simpler diazonium fluoroborates in organic solvents; low yields of arylated products are always obtained.[2] In intramolecular arylations (Pschorr synthesis), fluoroborates are good sources of radicals; for example, benzofluorenone is obtained in 66% yield.[3] The thermal decomposition of a number of anthraquinone diazonium fluoroborates, for example, anthraquinone-1-diazonium fluoroborate and -1,5-bisdiazonium fluoroborate, in aromatic solvents gives the corresponding fluorinated anthraquinones[4] in high yield; however, the diazonium fluoroborates derived from 1-amino-4-chloro- and 1-amino-4-nitroanthraquinone under similar conditions proved to be effective sources of anthraquinyl radicals. These compounds, when decomposed by heating a suspension in an aromatic solvent, form 1-aryl-4-chloro- and 1-aryl-4-nitroanthraquinones in yields of 40–65%.

The yields reported in Table I were calculated by analysis of the crude reaction product. The melting points refer to products purified by several recrystallizations.

Table I

Anthraquinone-1-chloro-4-	Yield, %	M.p., °C.
o-Dichlorophenyl-	61	267–268
Nitrophenyl-	44	273–274
α-Chloronaphthyl-	48	274–275
α-Bromonaphthyl-	43	260–264
Anthraquinone-1-nitro-4-		
o-Dichlorophenyl-	43	261–264
Bromophenyl-	39	295–298

It has been suggested that arylations by thermal decomposition of diazonium fluoroborates involve cationoid radical intermediates. Phenyl diazonium fluoroborate decomposed in methyl benzoate gives m-phenyl benzoate but little of the *para* isomer.[5] In the Pschorr synthesis the operation of two distinct mechanisms, ionic and radical, has been suggested.[6] In the present work there is also evidence of a cationoid intermediate in that only with electron-attracting substituents can arylation (a) compete with the Schiemann reaction (b). (See p. 490 col. 1.)

The 1-aryl-4-chloroanthraquinones when treated with p-toluenesulfonamide[7] form 1-aryl-4-p-toluenesulphonamidoanthraquinones which on hydrolysis in sulfuric

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[1] O. A. Reutow, *Angew. Chem.*, **72**, 198 (1960).

[2] L. G. Makarova and M. K. Matveeva, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1974 (1960); *Chem. Abstr.*, **54**, 1403 (1960).

[3] R. Huisgen and W. D. Zahler, *Ber.*, **96**, 736 (1963).

[4] G. Valkanas and H. Hopff, *J. Org. Chem.*, **27**, 3680 (1962).

[5] L. G. Makarova and E. A. Gribtchenko, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 693 (1958); *Chem. Abstr.*, **52**, 20,002 (1958).

[6] R. Huisgen and W. D. Zahler, *Ber.*, **96**, 747 (1963).

[7] G. Valkanas and H. Hopff, *J. Chem. Soc.*, 1923 (1963).