and room temperature in a standard Hershberg apparatus; 1.71 and 1.72 moles of hydrogen per $C_{19}H_{36}$ were consumed, respectively.

Maleic Anhydride Addition.—The distillate (2.5 g.) was refluxed for 5 hr. with maleic anhydride (3.0 g.) in xylene (10 ml.). After cooling, petroleum ether was added and the mixture extracted with water to remove unchanged maleic anhydride. The residue after removal of solvent (3.08 g.) was refluxed with sodium hydroxide (2.0 g.) in methanol (25 ml.) overnight. Water was added and the alkaline solution extracted with petroleum ether to yield an oil (0.9 g.) representing 36% of the distillate used in the experiment.

In a second run, the distillate (2.18 g.) was refluxed with maleic anhydride (2.00 g.) in xylene (10 ml.) overnight. Petroleum ether was added and the unchanged maleic anhydride extracted with water. Evaporation of the solvent left an oil (2.66 g.) which was distilled. A product (0.77 g., 35% of starting material) was obtained at 107° (0.05 mm.) whose infrared spectrum was the same as the neutral fraction obtained from the first run.

Ozonolysis.—The distillate (33.0 g.) of isomerized sterculene in dry methylene chloride (250 ml.) was cooled to −50° and ozone (3.36 g./hr.) was passed through the solution for 7 hr. The solution was allowed to warm to room temperature and was added to a suspension of zinc dust (16.0 g.) in 50% aqueous acetic acid (150 ml.) in a 1-l. flask fitted with stirrer, dropping funnel, and Vigreux condenser. Considerable heat was evolved during the addition, enough to distil most of the methylene chloride. The mixture was stirred overnight, refluxed an hour, filtered, and extracted three times with petroleum ether.

A portion of the aqueous layer was added to a solution of 10% dimedone in ethanol. White crystals were obtained, m.p. 190–191°, unchanged on admixture with an authentic sample of the dimedone derivative of formaldehyde, lit.[10] m.p. 187°.

The petroleum ether solution was extracted twice with 5% aqueous sodium hydroxide, dried over sodium sulfate, and evaporated to leave the neutral oxidation products (16.2 g.). G.l.c. showed four peaks and three of them corresponded to enanthaldehyde, caprylaldehyde, and 2-decanone. The aqueous solution was acidified and extracted to yield the acidic oxidation products (11.5 g.). These were esterified with a solution (80 ml.) of 7% boron trifluoride in methanol. G.l.c. showed three peaks corresponding to methyl enanthate, caprylate, and pelargonate. The neutral fraction was distilled. Four fractions were obtained: N-1, 5.50 g., b.p. 90–120° (45 mm.); N-2, 1.85 g., b.p. 60–100° (0.10 mm.); N-3, 2.62 g., b.p. 100–148° (0.10 mm.); N-4, residue, 6.20 g.

The methyl esters of the acidic fraction were distilled to yield three fractions: A-1, 8.45 g., b.p. 110–124° (45 mm.); A-2, 1.00 g., b.p. 60° (0.05 mm.); A-3, residue, 2.00 g.

Identification of Neutral Constituents.—A sample (0.6 g.) of N-1 was treated with 2,4-dinitrophenylhydrazine (0.4 g.) in ethanol (20 ml.). Yellow crystals were obtained, m.p. 104–105°, unchanged upon admixture with an authentic sample of caprylaldehyde 2,4-dinitrophenylhydrazone, lit.[11] m.p. 106°.

Fraction N-2 on similar treatment yielded the 2,4-dinitrophenylhydrazone of 2-decanone, m.p. and m.m.p. 73–74°, lit.[12] m.p. 73–74°.

Fraction N-3 on g.l.c. showed a small peak corresponding to 2-decanone and a large peak of long retention time, similar to that observed for 9,11-nonadecadione obtained by ozonolysis of sterculene (see below). It did not yield any crystalline carbonyl derivatives or a chelate with cupric acetate. It is presumed to be a dicarbonyl compound arising from structure V.

9,11-Nonadecadione.—I (10.0 g.) was ozonized as were the rearrangement products above and worked up in the same way. The product was distilled, b.p. 130–140° (0.10 mm.), to give 7.9 g. (70% of I) of a pale yellow sirup.

Anal. Calcd. for $C_{19}H_{36}O_2$: C, 76.97; H, 12.24. Found: C, 76.85; H, 12.39.

A sample of this compound yielded readily a bluish precipitate, m.p. 104–105°, on treatment with cupric acetate in ethanol.

Anal. Calcd. for $Cu(C_{19}H_{35}O_2)_2$: C, 69.74; H, 10.78. Found: C, 69.83; H, 11.05.

Identification of Acidic Constituents.—Fraction A-1 showed peaks on g.l.c. corresponding to the methyl esters of enanthic, caprylic, and pelargonic acid. Fraction A-2 contained only methyl pelargonate. Fraction A-1 was separated on a preparative g.l.c. column into its constituents.

Each was saponified and the *p*-toluidides of the acids prepared by the method given in Shriner and Fuson.[13] In this way, the *p*-toluidides of enanthic acid (m.p. 79–80°, lit.[13] m.p. 80°), caprylic acid (m.p. 69°, lit.[13] m.p. 70°), and pelargonic acid (m.p. 82°, lit.[13] m.p. 84°) were obtained. The melting points of the derivatives were not depressed upon admixture with authentic samples.

Ozonolysis of Ethyl Vinyl Ketone (VI).—A solution of ketone VI (10.5 g.) in methylene chloride (200 ml.) was cooled to −50° and ozone (2.88 g./hr.) was passed through it for 5.5 hr. The solution was allowed to warm to room temperature and added to zinc dust (11 g.) in 50% acetic acid (60 ml.).

The mixture was extracted with petroleum ether to yield an acid that was esterified with the 7% boron trifluoride in methanol reagent (70 ml.). Methylene chloride was added to the esterification medium and the solution washed several times with water, dried, and distilled. When about 30 ml. of material were left in the distillation flask, 20 ml. of bromobenzene were added and the distillation resumed. A fraction was collected, b.p. 75–78° (3.5 g.). It was saponified and its *p*-toluidide prepared. The melting point of the derivative, 123°, was unchanged on admixture with the *p*-toluidide of propionic acid, lit.[13] m.p. 124°.

The dimedone derivative of formaldehyde was obtained from the aqueous layer as before, m.p. and m.m.p. 190–191°, lit.[10] m.p. 187°.

(10) W. Weinberger, *Ind. Eng. Chem., Anal. Ed.*, **3**, 365 (1931).
(11) C. F. H. Allen, *J. Am. Chem. Soc.*, **52**, 2955 (1930).
(12) C. Jutz, *Ber.*, **91**, 1867 (1958).
(13) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 200, 276.

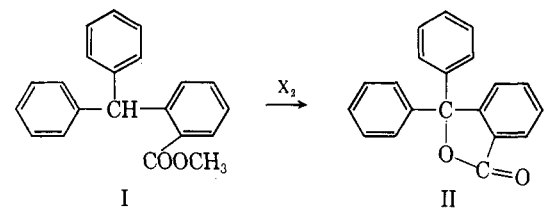
Steric Hindrance to Halogenation and Oxidation at the Tertiary Carbon of *o*-Carbophenoxytriphenylmethane

R. E. LOVINS AND L. J. ANDREWS

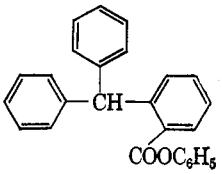
Department of Chemistry, University of California, Davis, California

Received September 3, 1963

In connection with another investigation, various substituted trityl halides have been prepared by free-radical halogenation of the corresponding triphenylmethanes. An interesting example of the steric protection of the tertiary position of the triphenylmethane molecule by a bulky *ortho* substituent has been encountered in the course of this synthetic work. Generally, trityl halides can be prepared in good quantity from the corresponding triphenylmethanes by photochemical methods or by reaction with N-bromosuccinimide. For example, a pure sample of trityl chloride itself has been obtained in 67% yield through photochlorination of triphenylmethane. Methyl *o*-benzhydrylbenzoate readily undergoes radical-type halogenation to give 3,3-diphenylphthalide (eq. 1). Presumably the tertiary halide derived from the ester is highly unstable with respect to lactone formation. No reaction occurs, however, when phenyl *o*-benz-

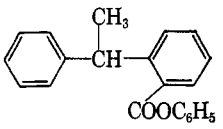


I II (1)



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.

(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]

JAMES R. COX, JR., AND BENJAMIN D. SMITH

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Received July 8, 1963

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

(1) This work was supported by a grant, NSF-G18894, from the National Science Foundation.

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