[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Studies on the Structure and Oxidation Products of 1-Methyl-3-phenylindane, a Dimer of Styrene[1]

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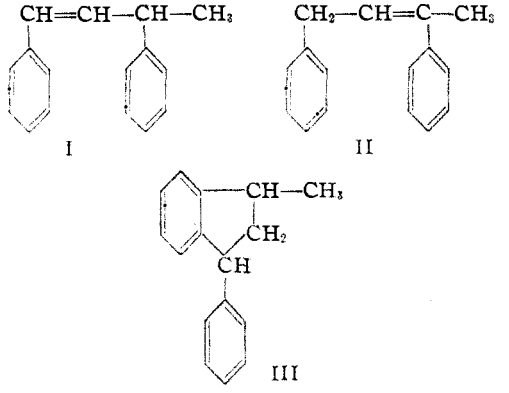
In the course of an investigation on the sulfonation of dimers of styrene, it became necessary to obtain further information on the exact nature of the products obtained upon dimerizing monomeric styrene. Risi and Gauvin[3] have dimerized monomeric styrene by refluxing it with aqueous sulfuric acid. They have shown their product to be a mixture of two isomeric dimers, identical with a product previously prepared by Fittig and Erdmann[4] from cinnamic acid and aqueous sulfuric acid. Stoermer and Kootz,[5] upon investigation of the product obtained by Fittig and Erdmann, had concluded that it consisted mainly of 1,3-diphenylbutene-1 (I) together with some 1,3-diphenylbutene-2 (II). Risi and Gauvin, however, while accepting the 1,3-diphenylbutene-1 structure for the isomer present in greater amount, postulated that the other isomer present was 1-methyl-3-phenylindane (III), and not 1,3-diphenylbutene-2, since it did not add bromine and



was not polymerized by stannic chloride. The results of our investigation confirm the 1-methyl-3-phenylindane structure postulated for this isomer.

Our conclusions are based on data from two sources: oxidation studies and ultraviolet absorption curves. In order to obtain a pure sample of the 1-methyl-3-phenylindane isomer, monomeric styrene was first dimerized by refluxing it with 5:4 (wt.) sulfuric acid, using a variation of the method of Risi and Gauvin, and then the resulting mixture of isomers was converted completely to the 1-methyl-3-phenylindane isomer by refluxing it with 1:1 (vol.) sulfuric acid, using a modification of the method first described by Stoermer and Kootz. By this method, the over-all yield of 1-methyl-3-phenylindane, based on the starting amount of monomeric styrene, was 67%.

Upon oxidation of this material with chromic acid in glacial acetic acid, only two products were obtained in any significant amounts: a major yield of *o*-benzoylbenzoic acid (34%) and a small yield of anthraquinone (3.7%). Only a trace (<0.15%) of benzoic acid was obtained. The absence of any significant amount of benzoic acid among the oxidation products indicated that 1,3-diphenylbutene-2 could not be a possible structure for this isomer. The presence of *o*-benzoylbenzoic acid, on the other hand, was evidence for the 1-methyl-3-phenylindane structure of this material.

Further evidence for the 1-methyl-3-phenylindane structure of this dimer was obtained from its ultraviolet absorption spectrum. Figure 1 shows the striking similarity between the ultraviolet absorption spectrum of this hydrocarbon and that of indane.[6]

An explanation for the presence of anthraquinone as an oxidation product of 1-methyl-3-phenylindane was sought. The presence of the anthraquinone could be explained by (1) cyclodehydration of *o*-benzoylbenzoic acid under the conditions of the oxidation, (2) the oxidation of some contaminant such as dihydrodimethylanthracene, an isomer of 1-methyl-3-phenylindane, or (3) condensation of an oxidation product of 1-methyl-3-phenylindane to an anthracene derivative with subsequent oxidation to anthraquinone. This mechanism has been used by Muller[7,8] to explain the formation of 2,3,6,7-tetramethoxyanthraquinone from 1-veratryl-2-methyl-3-ethyl-5,6-dimethoxyindane (diisohomogenol).

The first possibility was ruled out when it was found that pure *o*-benzoylbenzoic acid gave no anthraquinone under the conditions of our oxidation. Moreover, oxidation of 1-methyl-3-phenylindane with chromic acid in anhydrous acetic acid did not increase the yield of anthraquinone.

The second suggestion proved unlikely when we observed that 1,3-diphenylbutene-1, purified *via* the dibromide, yielded only benzoic acid on oxidation. When the compound was cyclized to 1-methyl-3-phenylindane and the resulting product was oxidized with chromic acid, no benzoic acid was isolated, but the usual small amount of anthraquinone (3.4%) was again

(1) From a dissertation submitted by Milton J. Rosen to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1949.

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(3) Risi and Gauvin, *Can. J. Research*, **B14**, 255 (1936).

(4) Fittig and Erdmann, *Ann.*, **216**, 179 (1883).

(5) Stoermer and Kootz, *Ber.*, **61**, 2330 (1928).

(6) Morton and DeGoveia, *J. Chem. Soc.*, 911 (1934).

(7) Muller, *Ber.*, **77**, 159 (1944).

(8) Muller, *J. Org. Chem.*, **12**, 815 (1947).

present in addition to a major yield (40%) of *o*-benzoylbenzoic acid. These results force us to conclude that the anthraquinone present is formed by the oxidation of 1-methyl-3-phenylindane itself, possibly by a condensation mechanism similar to those suggested by Muller for the oxidation of diisohomogenol to tetramethoxyanthraquinone.

Experimental

Dimerization of Monomeric Styrene.—The method was that of Risi and Gauvin,[3] but, since this is a heterogeneous reaction, the addition of a mechanical stirring device caused a considerable increase in the yield of product. The yield of dimeric styrenes, b. p. 172–178° (cor. 177–183°) (14 mm.), $n^{20}D$ 1.5900, was 80%. The yield reported by Risi and Gauvin, without use of a mechanical stirring device, was 65%.

1-Methyl-3-phenylindane from Dimeric Styrene.—The method used was that of Stoermer and Kootz,[5] but the addition of a mechanical stirring device caused a considerable increase in the yield of product. The yield of 1-methyl-3-phenylindane, b. p. 146–148° (cor. 148.5–150.5°) (6.5 mm.), $n^{20}D$ 1.5797, d^{20}_4 1.024, was 84%. The previously reported yield,[3] without use of a mechanical stirring device, was 63%.

1,3-Diphenylbutene-1.—In a 1-l. round-bottomed 3-necked flask equipped with a dropping funnel, a ground glass sealed stirrer, and a reflux condenser, were placed 83.2 g. (0.4 mole) of dimeric styrene and 250 ml. of carbon tetrachloride. The reaction mixture was stirred and cooled in an ice-water-bath at a temperature of approximately 10° while 96 g. (0.6 mole) of bromine was added dropwise. After addition had been completed, stirring was continued for one-half hour, while the temperature was maintained at 10°.

The reaction mixture was then warmed gently on a steam-bath, while air was blown through it to remove excess bromine. Gentle heating and air blowing were continued until the volume of the reaction mixture was reduced to 150–200 ml. Two hundred ml. of isopropyl alcohol was then added, the mixture was warmed on the steam-bath to dissolve any precipitated material, and the solution allowed to crystallize in the refrigerator.

The yellow crystals were removed by filtration and recrystallized twice from 400 ml. of isopropyl alcohol. The yield of crude **1,2-dibromo-1,3-diphenylbutane**, m. p. 95–98°, was 61 g. (41%).

During nine more recrystallizations from isopropyl alcohol, the melting point of the product slowly rose until a constant value of 100.7–101.7° (cor. 101.5–102.5°) was reached. The yield of this purified 1,2-dibromo-1,3-diphenylbutane was 42.5 g. (29%).

The purified 1,2-dibromo-1,3-diphenylbutane was converted to **1,3-diphenylbutene-1** by refluxing it with zinc in absolute alcohol, after the method of Stoermer and Kootz.[5] The 1,3-diphenylbutene-1 boiled at 163° (cor. 166.8°) (9 mm.), $n^{20}D$ 1.5930, d^{20}_4 1.002. The yield, based on 1,2-dibromo-1,3-diphenylbutane, was 89%.

1-Methyl-3-phenylindane from 1,3-Diphenylbutene-1.—The procedure used was the same as that used above for preparing 1-methyl-3-phenylindane from dimeric styrene. The product, $n^{20}D$ 1.5805, d^{20}_4 1.027, boiled at 152° (cor. 155.2°) (8 mm.).

Oxidation of 1-Methyl-3-phenylindane, Prepared from Dimeric Styrene.—Three grams (0.0144 mole) of 1-methyl-2-phenylindane, $n^{20}D$ 1.5797, and 60 ml. of glacial acetic acid were placed in a 250-ml. round-bottomed flask equipped with a reflux condenser. The solution was heated to 140° and a solution of 15 g. (0.15 mole) of chromic acid in 30 ml. of glacial acetic acid and 30 ml. of water was added, in small portions. The mixture was allowed to reflux at 140° for one hour, then cooled, and most of the solvents (about 70 ml.) removed by distillation under reduced pressure. The residue was taken up in 200 ml. of water, and extracted with benzene. The benzene extracts were combined and extracted with sodium hydroxide solution.

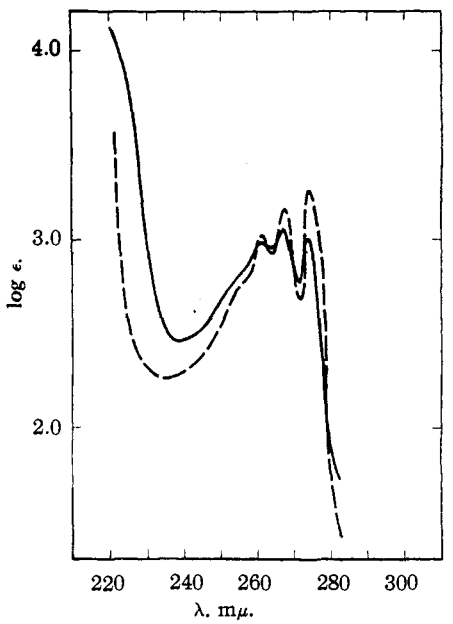

Fig. 1.—Ultraviolet absorption curves: ——, 1-methyl-3-phenylindane (in isopropyl alcohol), prepared from 1,3-diphenylbutene-1; — — —, indane (in hexane)[6].

The alkali-extracted benzene layer was washed free of alkali with water, and evaporated to dryness. The residue, pale yellow needles, weighed 110 mg. (3.7%), and gave the oxanthranol reaction for anthraquinone.[9] After two recrystallizations from isopropyl alcohol, the material melted at 285–286° (cor.) and showed no depression of m. p. when mixed with an authentic sample of anthraquinone.

The alkali extracts were acidified with dilute sulfuric acid, made alkaline with ammonia water, heated to boiling, cooled, and any precipitated chromic hydroxide removed by filtration. The clear filtrate was acidified to congo red with dilute sulfuric acid, and steam distilled. Less than 5 mg. of steam distillable material (benzoic acid) was obtained (< 0.15%).

The residue was cooled and extracted with benzene. The combined benzene extracts were evaporated to a volume of 25 ml., and 50 ml. of petroleum ether (30–75°) and 3 drops of water were added. Crystallization was promoted by chilling and scratching the sides of the beaker. After one day in the ice-chest, the pure white crystals were removed by filtration and washed well with petroleum ether.

The yield of product (*o*-benzoylbenzoic acid), m. p. 124–125° (cor. 126–127°), after drying *in vacuo* over phosphorus pentoxide, was 1.1 g. (34%). Upon heating 0.2 g. of this product and 5 ml. of 25% oleum at 150° for about ten minutes, and then pouring the cooled mixture into water, a yellow solid was obtained which, upon recrystallization from isopropyl alcohol, yielded pale yellow needles, m. p. 285–286° (cor.), identical with anthraquinone.

Treatment of *o*-Benzoylbenzoic Acid with Aqueous Chromic Acid Solution.—Two grams of *o*-benzoylbenzoic acid was suspended in 60 ml. of glacial acetic acid and treated with a solution of 15 g. of chromic acid in 30 ml. of glacial and 30 ml. of water, according to the procedure described above. The reaction mixture was worked up as described in that same procedure. The only product ob-

(9) Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 625.

tained was 0.9 g. of recovered *o*-benzoylbenzoic acid (45% of the starting amount).

Oxidation of Dimeric Styrene.—Three grams of dimeric styrene, $n^{20}D$ 1.5900 was oxidized, and the oxidation products isolated, in accordance with the usual procedure. The products obtained were: benzoic acid, 1.8 g. (51%), *o*-benzoylbenzoic acid, 0.2 g. (7%), and anthraquinone, 70 mg. (2.3%).

Oxidation of 1,3-Diphenylbutene-1.—Three grams of 1,3-diphenylbutene-1 was oxidized and the products isolated by the usual procedure.

The only oxidation product obtained was benzoic acid, 1.8 g. (51%).

Oxidation of 1-Methyl-3-phenylindane, Prepared from 1,3-Diphenylbutene-1.—Three grams of 1-methyl-3-phenylindane, $n^{20}D$ 1.5805, was oxidized and the products isolated by the usual procedure. The oxidation products obtained were: *o*-benzoylbenzoic acid, 1.3 g. (40%) and anthraquinone, 102 mg. (3.4%).

Oxidation of 1-Methyl-3-phenylindane, Prepared from Dimeric Styrene, in Anhydrous Medium.—The oxidation procedure and product separation scheme was the same as usual, but the chromic acid used was dissolved, without the use of water, in fifteen times its weight of glacial acetic acid, and the reaction mixture was protected from moisture by means of a calcium chloride drying tube placed on top of the reflux condenser. Under these conditions, the products obtained were: *o*-benzoylbenzoic acid (34%), anthraquinone (3.4%), and benzoic acid, 6 mg. (0.18%).

Ultraviolet Absorption of 1-Methyl-3-phenylindane.—A solution of 1-methyl-3-phenylindane, $n^{20}D$ 1.5805, in isopropyl alcohol, containing 0.1375 g. of 1-methyl-3-phenylindane per 100 ml. of solution, was diluted 1:9 with isopropyl alcohol and the ultraviolet absorption of the resulting solution measured with a Beckman quartz spectrophotometer.

Summary

Evidence has been obtained from a study of oxidation products and ultraviolet absorption which confirms the 1-methyl-3-phenylindane structure postulated for one of the dimers of styrene.

The presence of anthraquinone among the oxidation products of this hydrocarbon is not due to cyclodehydration of the *o*-benzoylbenzoic acid formed or to an impurity present, but is formed during the oxidation of the hydrocarbon itself.

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Migrations of Acyl Groups in Aminoethanols. II.[1] Analogy with Mixed Diacyl *o*-Aminophenols

BY ARTHUR P. PHILLIPS AND ALLISON MAGGIOLO

Numerous examples of acyl migrations between oxygen and nitrogen have been reported for derivatives of *o*-aminophenols.[2,3,4,5]

Very recently careful work by LeRosen and Smith[6] has demonstrated that, in contrast with some of the earlier findings, in the introduction of a second, different acyl group into an *o*-acylaminophenol a mixture, in varying proportions, of the two isomers results regardless of the order of introducing the groups. They also showed that half hydrolysis of *either* of the purified isomeric diacyl *o*-aminophenols gave not a single product but a mixture of the two possible N-acylaminophenols in nearly constant proportions, independent of which isomer was hydrolyzed.

This earlier work showed that acyl migrations in *o*-aminophenols occur very frequently both during the formation as well as during the half hydrolyses of mixed diacyl compounds. These facts as well as the facile rearrangements known to occur with monoacylethanolamines[1] warranted the anticipation of similar acyl shifts during the preparation and hydrolysis of the mixed diacyl ethanolamines described below.

The two isomers, 2-acetamidoethyl *p*-nitrobenzoate (I) and 2-(*p*-nitrobenzamido)-ethyl acetate (II) were obtained by appropriate acylation of the ethanolamides.

Compounds I and II had different melting points and mixtures of the two showed marked depressions of the melting temperature. Hydrolysis of I with dilute aqueous alkali gave a quantitative amount of *p*-nitrobenzoic acid while II gave the calculated quantity of *p*-nitrobenzoic acid ethanolamide as the readily isolable hydrolysis product.

Compound I was treated under a variety of conditions thought likely to favor acyl wandering: (1) refluxing several hours with sodium in xylene; (2) heating two hours at 70° in pyridine solution; (3) heating two hours at 70° in pyridine solution containing one mole of hydrogen chloride; (4) heating for two hours at 70° in alcoholic hydrogen chloride. In every case a nearly theoretical recovery of unchanged I was obtained. Samples of I and II refluxed separately for five hours in triethylamine gave back all of the unchanged starting compound.

Surprisingly, these seem to represent examples in which no acyl migrations occurred either in the formation or hydrolysis of I and II, nor could I or II be induced to rearrange under various "forced conditions."

This difference in migration aptitude may be attributable to a less favorable steric configuration in the open chain ethanolamine derivatives.

(1) Paper I of this series. Phillips and Baltzly, THIS JOURNAL, **69**, 200 (1947).

(2) Böttcher, *Ber.*, **16**, 629 (1883).

(3) Raiford, THIS JOURNAL, **41**, 2068 (1919).

(4) Bell, *J. Chem. Soc.*, 2962 (1931).

(5) Raiford and LeRosen, THIS JOURNAL, **67**, 2163 (1945).

(6) LeRosen and Smith, *ibid.*, **71**, 2815 (1949); **70**, 2705 (1948).