The inertness of the bridge-head hydroxyl group and chlorine atom may be interpreted as indicating either (1) that a Walden inversion is absolutely necessary in the replacement of these groups, or (2) that in a carbonium ion the central carbon atom and the three atoms forming bonds with it must be coplanar. Certain drawbacks to the former of these interpretations are pointed out.

Cambridge, Massachusetts
Received September 16, 1939

[Contribution from the Department of Chemistry, University of New Hampshire]

Synthesis of α-2-Methoxyphenyl-β,β,β-triphenylethane

By H. A. Iddles, K. S. French and E. F. Mellon

In 1932 Parsons and Porter[1] reported a synthesis of the methyl ether of α-2-hydroxyphenyl-β,β,β-triphenylethane (m. p. 172°) and used the product in establishing the probable structure for the methylation product (m. p. 172°) which they had prepared from Schorigin's[2] so-called "kryptophenol." Schorigin had obtained this rearrangement product as a by-product during the synthesis of triphenylmethyl *o*-tolyl ether and by a direct rearrangement of the ether when it was heated with metallic sodium. He postulated a structure, α-2-hydroxyphenyl-β,β,β-triphenylethane, from a somewhat analogous case in which benzyl *o*-tolyl ether was rearranged to give *o*-hydroxydibenzyl[2] by heating with metallic sodium. Van Alphen[3] also reported results on the preparation and rearrangement of this triphenylmethyl *o*-tolyl ether but gave no proof of structure of the product obtained.

However, the work of Boyd and Hardy[4] has questioned the unusual and special interpretation of Schorigin[2,5,6] which postulates the migration of the triphenylmethyl group to the side chain of *o*-cresol. They distilled the triphenylmethyl rearrangement products from the three cresols and phenol with soda lime, obtaining triphenylmethane in each case, and warmed each product with sulfuric acid, producing triphenylcarbinol. Consequently they conclude there is no evidence for postulating a different constitution for the ortho derivative.

To aid in clarifying these opposing points of view, further syntheses of "kryptophenol" as its methyl ether have been carried out. This seemed particularly desirable since the one direct synthesis of Parsons and Porter[1] has one unusual step in which the hydrolysis of the Grignard addition compound gave a hydrocarbon instead of the expected secondary alcohol.

For use in two separate syntheses, *o*-methoxybenzyl chloride was prepared by methylation of salicylic acid, electrolytic reduction to methoxybenzyl alcohol and treatment of the alcohol with thionyl chloride. In the first method the methoxybenzyl chloride was treated with triphenylmethylsodium in an atmosphere of nitrogen according to the procedure of Schlenk and Marcus,[7] who similarly produced unsymmetrical tetraphenylethane from triphenylmethylsodium and benzyl chloride. The product melted at 142–143°. In a second sequence a Grignard reagent was prepared from the *o*-methoxybenzyl chloride and this was coupled with triphenylchloromethane following an analogous reaction of Gomberg and Cone,[8] who reported an almost quantitative yield of unsymmetrical tetraphenylethane from benzylmagnesium bromide and triphenylchloromethane. The product in this case melted at 140–142° and there was no depression in a mixed melting point of the two synthetic products. However, neither agreed with the m. p. of 172° recorded by Parsons and Porter[1] for their synthetic product and a depression in melting point occurred when each of these synthetic samples was mixed with the methylated rearranged product of m. p. 162–163°.

The non-agreement between these synthetic samples and the methylated rearranged compound supports the interpretation of mechanism of Boyd and Hardy[4] which maintains that the original rearrangement of the triphenylmethyl group involves a ring position instead of the side

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[1] Parsons and Porter, This Journal, **54**, 363 (1932).

[2] Schorigin, *Ber.*, **58**, 2028 (1925); **59**, 2502 (1926).

[3] Van Alphen, *Rec. trav. chim.*, **46**, 287 (1927).

[4] Boyd and Hardy, *J. Chem. Soc.*, 630 (1928).

[5] Porter, "Molecular Rearrangements," Chemical Catalog Co., New York, N. Y., 1928, p. 118.

[6] Houben, "Die Methoden der organischen Chemie," Vol. III, 1930, p. 184.

[7] Schlenk and Marcus, *Ber.*, **47**, 1664 (1914).

[8] Gomberg and Cone, *ibid.*, **39**, 1461 (1906).

chain of *o*-cresol as first postulated by Schorigin.[2] Further work is in progress to determine the actual course of this rearrangement.

Experimental

Preparation of Rearranged Compound from *o*-Cresol.—Approximately the condensation method of Baeyer and Villiger[9] was followed in which 15 g. of triphenylcarbinol, 50 g. of *o*-cresol and 360 g. of glacial acetic acid were mixed and 75 g. of concentrated sulfuric acid was gradually added. After standing for two days or longer, an orange precipitate appeared whereupon the reaction mixture was poured into water. The crystals and oily layer were extracted with ether and this extract repeatedly washed with 10% sodium hydroxide solution. After drying and evaporation of the ether, the residue was taken up in ligroin (b. p. 70–90°) and this solution was extracted with Claisen's solution (equal parts of 50% aqueous potassium hydroxide and methyl alcohol). Upon acidification of the alkaline extract, the product precipitated and was purified by recrystallization from ethyl alcohol. The yields of colorless product (m. p. 182–183°) averaged 70%.

Preparation of Methyl Ether of Rearranged Compound.—Ten grams of the phenolic rearranged compound was suspended in a solution of 250 ml. of 2 *N* sodium hydroxide and 37.5 g. of dimethyl sulfate was added with constant stirring. After stirring for three or four hours, 10 g. of sodium hydroxide was added and the mixture was refluxed for one hour to hydrolyze excess dimethyl sulfate. The reaction mixture was then cooled, neutralized with hydrochloric acid, and the insoluble material filtered from the aqueous solution and dried. The dried solid was dissolved in a mixture of 10% ether and 90% ligroin (70–90°) and the solution extracted with Claisen's solution to remove unchanged phenolic compound. The residue from evaporation of the dried ether layer was recrystallized from alcohol, yielding 3.6 g. of product of m. p. 162–163°. Since 5.2 g. of unchanged phenol was recovered, this was a yield of 73%.

Anal. Calcd. for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found: C, 88.93; H, 6.66.

This product agrees satisfactorily with the product obtained by Boyd and Hardy[4] by two independent syntheses and to which they assign the m. p. 165°. However, there is considerable discrepancy between these two closely agreeing melting point values and that of 172° reported by Parsons and Porter,[1] who methylated by means of methyl iodide and silver oxide.

Preparation of *o*-Methoxybenzoic Acid.—One hundred grams of salicylic acid was methylated according to the directions of Graebe,[10] producing 98.6 g. or a 89.5% yield of methoxybenzoic acid, m. p. 96–98°.

Electrolytic Reduction of *o*-Methoxybenzoic Acid to *o*-Methoxybenzyl Alcohol.—The *o*-methoxybenzoic acid was electrolytically reduced according to the directions of Tafel[11] and Mettler.[12] *o*-Methoxybenzyl alcohol, 49.2 g., was recovered, boiling from 120–122° at 12 mm. pressure, a yield of 54.7%.

Preparation of *o*-Methoxybenzyl Chloride.—*o*-Methoxybenzyl alcohol, 34 g., in 50 ml. of ether was dropped into 50 g. of concentrated hydrochloric acid in 50 ml. of ether according to Quelet and Allard.[13] From the reaction 27.5 g. of product was obtained, boiling at 111–113° at 14 mm. pressure.

Preparation of α-2-Methoxyphenyl-β,β,β-triphenylethane.—A Grignard reagent was prepared by adding 10.7 g. of freshly distilled *o*-methoxybenzyl chloride, dissolved in 300 ml. of anhydrous ether, to 1.58 g. of magnesium turnings. After refluxing and stirring for four hours, the solution was decanted from a trace of unreacted magnesium and a solution of 6 g. of triphenylchloromethane in 50 ml. of dry benzene was added. This mixture was refluxed for two hours, causing the formation of a yellow precipitate.

To prevent subsequent formation of triphenylcarbinol from the hydrolysis of any unreacted triphenylchloromethane with the resulting contamination of the product, 5 g. of zinc dust was added to the reaction mixture to form free triphenylmethyl. After filtering the solution from the zinc, oxygen was passed through the mixture, but no triphenylmethyl peroxide precipitated, indicating complete reaction of the triphenylchloromethane with the Grignard reagent.

The ether–benzene solution was then evaporated to dryness on the steam-bath, leaving a dark oil which was recrystallized from alcohol. Three grams of pure crystals was obtained, m. p. 140–142°. This material was not identical with the methyl ether prepared from the rearranged triphenylmethyl ether of *o*-cresol, m. p. 162–163°.

Anal. Calcd. for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found: C, 88.79; H, 6.68.

Reaction between Triphenylmethylsodium and *o*-Methoxybenzyl Chloride.—The triphenylmethylsodium was prepared by the method of Schlenk and Ochs[14] from 200 g. of 2% sodium amalgam and 10 g. of triphenylchloromethane suspended in ether and protected by an atmosphere of nitrogen. When the triphenylmethylsodium had formed, as evidenced by the deep red color, 5.6 g. of *o*-methoxybenzyl chloride, dissolved in ether, was added. The mixture was allowed to stand until the red color disappeared. It was aerated for several hours with dry air to convert any free triphenylmethyl to the peroxide, then filtered and the ether evaporated. A heavy viscous brown oil remained which, after recrystallization from alcohol, gave 4 g. Several recrystallizations gave 2.2 g. of colorless crystals, m. p. 142–143°. A mixed melting point proved this product was identical with that prepared by the Grignard reaction. It was not identical with the methylated rearranged compound.

Anal. Calcd. for $C_{27}H_{24}O$: C, 88.97; H, 6.64. Found: C, 88.48; H, 6.87.

Summary

1. α-2-Methoxyphenyl-β,β,β-triphenylethane, m. p. 142–143°, has been prepared by two direct syntheses. This compound is not identical with the methylated rearranged compound obtained

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[9] Baeyer and Villiger, *Ber.*, **35**, 3013 (1902).

[10] Graebe, *Ann.*, **139**, 137 (1866).

[11] Tafel, *Ber.*, **33**, 2209 (1900).

[12] Mettler, *ibid.*, **39**, 2933 (1906).

[13] Quelet and Allard, *Bull. soc. chim.*, [v] **4**, 1468 (1937).

[14] Schlenk and Ochs, *Ber.*, **49**, 608 (1916).

from rearrangement of the triphenylmethyl ether of *o*-cresol, m. p. 162–163°.

2. This study supports the evidence of Boyd and Hardy,[4] who conclude the migrating radical has not entered the side chain when triphenylmethyl *o*-tolyl ether undergoes rearrangement.

DURHAM, NEW HAMPSHIRE

RECEIVED SEPTEMBER 28, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Utilization of Aliphatic Nitro Compounds. (I) The Production of Amines and (II) The Production of Oximes[1]

BY KENNETH JOHNSON WITH ED. F. DEGERING

The nitroparaffins were studied by a number of investigators following their first production by Victor Meyer[2] in 1872. The preparation of these compounds, however, was such that not very large amounts were available for experimentation and in many cases the investigators were not very thorough. With the work of Hass, Hodge and Vanderbilt,[3] begun in 1930, a process was perfected whereby the paraffin hydrocarbons were nitrated directly, making the nitroparaffins available at a lower cost and in greater abundance. The possibility of industrial development of this process brought about renewed interest in the study of nitroparaffins and their derivatives and a broad investigation was begun. The work reported here is a part of that much larger work.

I. Reduction of Nitroparaffins to Amines

A number of investigators[3,4] have reported the reduction of nitroparaffins with different reagents and under different experimental conditions, but in every case the yields of isolatable products have been small.

(a) **Reduction with Iron and Hydrochloric Acid.**—After several preliminary experiments the following apparatus and procedure were adopted: a three-necked flask is equipped with a mercury-seal stirrer (motor driven) and a reflux condenser. A trap containing standard hydrochloric acid is arranged to absorb any amines which might pass through the condenser. To 35 g. of 40-mesh iron filings are added 75 ml. of water and 10 ml. of concd. hydrochloric acid. After the evolution of hydrogen has stopped, one-sixth of a mole of the nitroparaffin is added and, with rapid stirring, the mass is heated at 100° for thirteen to fifteen hours. The solution is then made alkaline and the amine distilled out into standard hydrochloric acid. The conversion is calculated from the amount of hydrochloric acid required for neutralization. In another series of experiments, 1 g. of ferric chloride was added to the reaction mixtures.

The reaction mixture was evaporated to dryness, and the hydrochlorides of the amines extracted with butanol. No ammonium chloride remained as a residue. The amine hydrochlorides were further identified by titration with silver nitrate, from which data the molecular weight was calculated, and by a Van Slyke determination of amino nitrogen.

(b) **Catalytic Hydrogenation.**—These nitroparaffins were also reduced with hydrogen to give yields of 92–98% of the theoretical, by dissolving 0.25–0.33 mole of nitroparaffin in 175 ml. of methyl or ethyl alcohol and treating with hydrogen in a Parr bomb under 6–110 atmospheres over 7.5 g. of Raney nickel[5] for two to five hours, at 40–50°, with rocking. The non-formation of ammonia and the identity and yields of the amines were established as in the reductions with iron and hydrochloric acid.

Other catalysts were studied, but the results were unsatisfactory.[6]

The following nitro compounds were reduced in this way: nitromethane, nitroethane, 1- and 2-nitropropane, 1- and 2-nitrobutane, and 1- and 2-nitro-2-methylpropane. Percentage conversions of 82–94% were obtained in the absence of, and 93–97% in the presence of, ferric chloride. The titration gave the calculated molecular weight with an average deviation of only 1% and with an extreme deviation of 2.3%, while the amino nitrogen was found in every case to be either the exact amount required by the formula or within 1% thereof.

II. Reduction of Nitroparaffins to Oximes

The partial reduction of primary and secondary nitroparaffins produces oximes.[7,8] A number of reducing agents were tried, but the procedure adopted is: to 100 ml. of glacial acetic acid and 15 ml. of 1-nitropropane, add 35 g. of zinc dust, stir, and reflux for six hours. Hydrolyze the oxime by adding 25 ml. of water, then 5 ml. of concd. sulfuric acid, and heating. Distil the aldehyde and

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[1] Abstracted from a portion of a Thesis submitted to the Faculty of Purdue University by Kenneth Johnson in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1937. This research project was sponsored by The Commercial Solvents Corporation under the general supervision of Jerome Martin and H. B. Hass. Presented before the Division of Industrial Engineering Chemistry of the American Chemical Society at the Baltimore meeting, April 3–7, 1939.

[2] Victor Meyer, *Ber.*, **5**, 203, 514, 1029, 1034 (1872).

[3] Hass, Hodge and Vanderbilt, *Ind. Eng. Chem.*, **28**, 339 (1936).

[4] Meyer, *Ann.*, **171**, 1 (1874); Kahn and Meyer, *Chem. Abs.*, **21**, 3205 (1927).

[5] Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

[6] Adkins and Connor, *ibid.*, **53**, 1091 (1931).

[7] Konowaloff, *J. Chem. Soc.*, **76**, 733 (1899).

[8] Ponzio, *ibid.*, **82**, 334 (1902).