fore condensation, the condensate was shaken with cold water and distilled. The wet distillate was dried over calcium chloride and refractionated. The isopropyl chloride obtained in this manner weighed 92 g., which is equivalent to a yield of 62% from phthalyl chloride. The low yield of chloride is explained by the fact that isopropyl chloride readily undergoes decomposition to propylene and hydrochloric acid.

Summary

The chlorides of high boiling monocarboxylic acids react with ethyl ether in the presence of traces of zinc chloride. With benzoyl chloride, ethyl chloride and the ester are obtained in good yield.

Equimolecular amounts of *o*-phthalyl chloride and ethyl ether react to give phthalic anhydride and approximately two molecules of ethyl chloride.

o-Phthalyl chloride and isopropyl ether react similarly to give phthalic anhydride and isopropyl chloride, but in this case larger amounts of propylene are formed as a by-product.

ST. LOUIS, MISSOURI

RECEIVED SEPTEMBER 21, 1932
PUBLISHED MARCH 7, 1933

[CONTRIBUTION FROM THE KNIGHT CHEMICAL LABORATORY, UNIVERSITY OF AKRON]

The Halogenation of Meta-Diphenylbenzene. I. The Monochloro and Monobromo Derivatives

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In the commercial manufacture of biphenyl from benzene, considerable quantities of the meta and para isomeric diphenylbenzenes are formed as by-products, the meta isomer predominating. Very little is reported in the literature on derivatives of the latter hydrocarbon. Olgiati[1] described the monobromo and tetrabromo derivatives and others the trinitro and triamino derivatives.[2] Recently, Wardner and Lowy[3] reported the synthesis of the mononitro, the dinitro and related compounds. In no case, however, has sufficient experimental proof been advanced to establish completely the structures of the above-mentioned derivatives.

This paper is limited to an account of the monochloro and monobromo derivatives, their oxidation products, and their proof of structure. A later publication will describe the preparation and properties of the polychloro and polybromo derivatives. Further study of the applications of the monohalogen derivatives to the Grignard reaction and the synthesis of metallo organo compounds, including the mercury and arsenic types, has been planned, and work in that direction is being pursued in this Laboratory.

The authors acknowledge their great indebtedness to Mr. R. E. Bowman of Wilmington, Delaware, for the generous supply of purified *m*-diphenyl-

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(1) Olgiati, *Ber.*, **27**, 3385 (1894).

(2) Schultz and Schmidt, *Ann.*, **203**, 118 (1880).

(3) Wardner and Lowy, THIS JOURNAL, **54**, 2510 (1932).

benzene, and for the frequent suggestions and aid given during the course of this investigation.

Experimental Part

Chlorination of *m*-Diphenylbenzene

4-Chloro-1,3-diphenylbenzene.—Fifty-four grams of *m*-diphenylbenzene and several nails freshly cleaned with hydrochloric acid were placed in a 250-cc. distilling flask and heated on a water-bath. After the material had liquefied, a slow stream of chlorine gas was introduced. Reaction occurred rather slowly and the introduction of gas was continued until the weight of the reaction mixture had increased to 20% excess over the theoretical quantity. The flask and contents were then set aside for several hours to ensure completion of the reaction, and the increase in weight of the contents of the flask again determined so as to ensure the required excess indicated above. The mixture was then dissolved in petroleum ether (30–60°) to remove a small quantity of insoluble material which had formed. After filtration and removal of solvent, a thick yellow oil remained. This on fractionation yielded 52.6 g. (84.2%) of a viscous almost colorless and odorless oil with a boiling range of 214–216° (4 mm.). Specific gravity, 25/25°, 1.1903; refractive index (n^{25}_{D}), 1.6564.[4]

Anal. Calcd. for $C_{18}H_{13}Cl$: Cl, 13.40. Found: Cl, 13.63.

Oxidation of Monochloro-*m*-diphenylbenzene.—Seven grams of the above oil was dissolved in sufficient glacial acetic acid so that none separated when cooled to room temperature. To this was added in small portions with frequent cooling of the reaction mixture, an 85% excess of CrO_3 over the theoretical quantity required for the oxidation of a phenyl group. It was allowed to stand for several hours at room temperature and poured into a large volume of cold water, whereupon a voluminous precipitate of the acid appeared. The pale yellow color of the resulting product was due to a small quantity of the unoxidized monochloro derivative contaminating the acid. A product of higher purity was obtained when a greater excess of CrO_3 was employed, but the yield was much lower than in the previous instance. Oxidation with potassium permanganate in acetic acid also gave a purer product but lower yield. Hence the contaminated product was dissolved in concentrated ammonium hydroxide and treated with a solution of manganous acid freshly prepared from manganese sulfate, potassium chlorate and nitric acid. On filtration, the flocculated manganese dioxide adsorbed the small quantity of oily monochlorodiphenylbenzene and the filtrate on acidifying with sulfuric acid yielded a voluminous white precipitate of the acid. The acid was removed by filtration, then redissolved in ammonium hydroxide, filtered and reprecipitated by the addition of sulfuric acid. The yield of the pure product was 3.5 g. (30%). Ordinary methods of purification of the contaminated acid by the use of solvents in place of the treatment with manganese dioxide require several recrystallizations with far less satisfactory yields due largely to increased mechanical losses. The melting point of the purified product was 208–209°.

Anal. Calcd. for $C_{13}H_9O_2Cl$: Cl, 15.25. Found: Cl, 15.18.

Silver Salt of the above Chlorophenylbenzoic Acid.—Two grams of the above acid was suspended in water and neutralized with 6 *N* ammonia. On addition of an equivalent of silver nitrate (aqueous solution), a heavy white precipitate formed. This was filtered on a Buchner funnel and then transferred to an amber desiccator; yield, 2.8 g. (theoretical, 2.9 g.). The moist silver salt turns pink on exposure to light and is soluble both in ammonium hydroxide and acids.

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(4) Crude *m*-diphenylbenzene can be chlorinated in the same way and the monochloro derivative obtained by a similar method of purification.

Methyl Ester of the above Chlorophenylbenzoic Acid.—One gram of the above silver salt was suspended in ether and treated with an equivalent of methyl iodide. After standing for several days in the dark the silver iodide was removed by filtration and the filtrate warmed to remove the solvent; yield, 0.5 g. of a yellow pungent oil; refractive index (n^{30}_{D}), 1.5952.

Anal. Calcd. for $C_{14}H_{11}O_2Cl$: Cl, 14.38. Found: Cl, 14.47.

Benzyl Ester of the above Chlorophenylbenzoic Acid.—One and eight-tenths grams of the silver salt and an equivalent of benzyl chloride dissolved in 40 cc. of ether were allowed to stand in the dark for one week. After it was apparent that no reaction had occurred, the ether was removed by warming the mixture, and 40 cc. of chloroform added. After refluxing this mixture for sixty hours, the silver chloride was removed by filtration, and the filtrate heated cautiously to expel solvent; 1.6 g. of a thick yellow oil remained and this solidified in a short time on standing When recrystallized from alcohol and water a mass of lustrous plates formed; m. p. 90°.

Anal. Calcd. for $C_{20}H_{15}O_2Cl$: Cl, 10.99. Found: Cl, 11.13.

Proof of Structure of Monochloro-*m*-diphenylbenzene

Synthesis of 3-Nitro-4-chlorotoluene.—This derivative was prepared from 3-nitro-4-aminotoluene (Eastman grade) according to the procedure of Gattermann and Kaiser,[5] with the modification that the diazotization was carried out at 0° in the presence of sulfuric acid, and the resulting diazonium solution then added to the boiling CuCl–HCl mixture; yield, 44.6%.

Synthesis of 3-Amino-4-chlorotoluene.—The above mentioned workers and also Goldschmidt and Hönig[6] prepared the amine by reduction of the nitro derivative with tin and hydrochloric acid. Iron powder and sulfuric acid was used in our work in order to avoid the formation of a dichlorotoluidine, which occurs when tin and hydrochloric acid are employed. The details of the reduction are the same as described later for the synthesis of 3-amino-4-bromotoluene; yield 88.2%. Identification of our product was established through its acetyl derivative; melting point observed, 97°. The value given in the literature is 96°.

Synthesis of 2-Chloro-5-methylbiphenyl.—The method of Gomberg and Bachmann[7] for the synthesis of unsymmetrical biaryls was employed. From 75 g. of 3-amino-4-chlorotoluene, 16.3 g. of a brownish yellow oil boiling at 294–304° (735 mm.) was obtained; yield, 15%; specific gravity 25/25°, 1.139; refractive index (n^{25}_{D}), 1.5977.

Anal. Calcd. for $C_{13}H_{11}Cl$: Cl, 17.51. Found: Cl, 17.61.

Oxidation of 2-Chloro-5-methylbiphenyl.—Two grams of 2-chloro-5-methylbiphenyl was dissolved in glacial acetic acid and cooled to room temperature; 3.1 g. of powdered potassium permanganate was added in small portions with occasional stirring of the mixture. After standing for two hours, the mixture was made ammoniacal and filtered. The filtrate on acidifying with sulfuric acid yielded a white flocculent precipitate of 3-phenyl-4-chlorobenzoic acid. After separation of the precipitate, it was redissolved in ammonium hydroxide, filtered and reprecipitated with sulfuric acid; yield of purified product 0.5 g. (21.7%); melting point, 208–209°.

Anal. Calcd. for $C_{13}H_9O_2Cl$: Cl, 15.25. Found: Cl, 15.20.

A mixed melting point of this product and the acid obtained from the oxidation of monochloro-*m*-diphenylbenzene indicated that these substances were identical. From the above, it follows that the chlorination of *m*-diphenylbenzene produced 4-chloro-1,3-diphenylbenzene and the oxidation product of the latter was 3-phenyl-4-chlorobenzoic acid.

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(5) Gattermann and Kaiser, *Ber.*, **18**, 2600 (1885).

(6) Goldschmidt and Hönig, *ibid.*, **19**, 2442 (1886).

(7) Gomberg and Bachmann, THIS JOURNAL, **46**, 2339 (1924).

Bromination of *m*-Diphenylbenzene

4-Bromo-1,3-diphenylbenzene.—Fifty grams of *m*-diphenylbenzene and several iron nails (freshly cleaned with hydrochloric acid) were placed in a short-necked 500-cc. round-bottomed flask to which was attached a dropping funnel and a reflux condenser. The flask was heated in a water-bath to melt the hydrocarbon and then 14 cc. of bromine (25% excess) was added very slowly from the dropping funnel, with vigorous agitation after each addition of several drops in order to minimize the quantity of higher brominated products formed. The time required for the complete addition of halogen was four to five hours. After the evolution of hydrogen bromide had ceased the reaction mixture was heated on a sand-bath to 200° to expel remaining traces of bromine and then allowed to cool to room temperature. Petroleum ether (30–60°) was then added to precipitate solid contaminants, and the reaction mixture filtered. The solvent was expelled from the filtrate by cautious heating and the residual oil fractionated under diminished pressure. Forty-two and four-tenths grams of a pale yellow viscous oil boiling at 208–213° (1 mm.) was obtained; theoretical yield, 67.1 g.; specific gravity 25/25°, 1.355; refractive index (n^{25}_{D}) 1.6720, (n^{39}_{D}) 1.6653.

Anal. Calcd. for $C_{18}H_{13}Br$: Br, 25.88. Found: Br, 25.97.[8]

Olgiati prepared this derivative by allowing equivalent quantities of *m*-diphenylbenzene and bromine in the presence of carbon disulfide to stand at room temperature for three days and then warming under a reflux condenser until the reaction was complete.[9] On solution of the reaction product (after removal of solvent and unreacted bromine) in a dilute alcohol-water mixture and spontaneous evaporation at low temperatures, he obtained a crystalline product melting at 31°. Numerous attempts to solidify our product were futile; even after standing several weeks in a refrigerator, the product remained an oil. Olgiati assumed the structure of this derivative from the fact that on oxidation a bromo-diphenylcarboxylic acid was obtained, and from the fact that the tetrabromo-*m*-diphenylbenzene (synthesized from the monobromo derivative) on oxidation yielded *p*-bromobenzoic acid and 3,4-dibromobenzoic acid. From the above he assumed that the position occupied by the fourth bromine atom was probably position 4 of the inner ring of *m*-diphenylbenzene. Proof for the latter conclusion was not completely established.

Oxidation of 4-Bromo-1,3-diphenylbenzene.—Six grams of 4-bromo-1,3-diphenylbenzene on oxidation with 30 g. of CrO_3 in glacial acetic acid yielded after several recrystallizations from alcohol and water 0.9 g. of pure bromophenylbenzoic acid (16.6%); melting point 242–243°. This agrees with the value reported by Olgiati for the acid.[10]

Proof of Structure of Monobromo-*m*-diphenylbenzene

Synthesis of 3-Nitro-4-bromotoluene.—The procedure described for the preparation of *p*-bromotoluene[11] was adopted for this preparation, except for the minor changes referred to below.

From 152 g. of 3-nitro-4-aminotoluene (Eastman grade), 170 g. of crude 3-nitro-4-bromotoluene was obtained by steam distillation. This was dissolved in ether and the ether layer washed with two separate 25-cc. portions of cold normal sodium hydroxide and then with water. After drying the ether layer with calcium chloride, and evaporating the solvent 153 g. of oily product remained; yield, 70.9%.

Synthesis of 3-Amino-4-bromotoluene.—To 153 g. of 3-nitro-4-bromotoluene and

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[8] In several successive runs, traces of white solid appeared in the pure fraction on standing. In such cases, the treatment with petroleum ether was repeated and the oil again fractionated after removal of solvent.

[9] Ref. 1, pp. 3386–3387.

[10] Ref. 1, p. 3388.

[11] "Organic Syntheses," John Wiley and Sons, N. Y., 1925, Vol. V, p. 21.

150 cc. of water in a 3-liter flask with reflux condenser attached, 130 g. of powdered iron and 350 cc. of 18 *N* sulfuric acid were added alternately in small portions, shaking vigorously after each addition and with occasional cooling of the reaction mixture. After the last portions of iron and acid had been added, the mixture was refluxed on a water-bath for eight hours. It was then cooled, made basic with concd. sodium hydroxide and steam distilled. The distillate was extracted with ether, the ether layer dried with calcium chloride and solvent removed by distillation. A dark red oil weighing 118 g. remained; theoretical yield, 124 g. This product was purified by preparation of its acetyl derivative in the usual way, recrystallization of the latter from alcohol and water, and saponification with alcoholic potash; melting point of the acetyl derivative, 120–121°. Nevile and Winther[12] reported a value of 113.7–114.6° and Claus, 164°.[13]

Anal. Calcd. for $C_9H_{10}ONBr$: N, 6.14; Br, 35.07. Found: N, 6.18; Br, 35.43.

The purified amine is a pale yellow oil with a characteristic odor; b. p. 129–130° (16 mm.); sp. gr. 25/25° 1.474; refractive index (n^{25}_{D}) 1.5990. This oil gave no indication of crystallization even after standing for several months at ordinary temperatures.

Anal. Calcd. for C_7H_8NBr: N, 7.53; Br, 42.97. Found: N, 7.32; Br, 42.61.

Wroblewsky[14] prepared the base by reduction of 3-nitro-4-bromotoluene (liquid −20°) with tin and hydrochloric acid; m. p. of amine, 67°. Hübner and Roos[15] described the nitro compound with a melting point 31–32°, and its corresponding amino derivative melting at 75°. Claus[13] prepared the amine by saponification of its acetyl derivative and reported a melting point of 35°. His acyl derivative in turn was obtained by rearrangement of the oxime of 6-bromo-3-methyl-acetophenone in the presence of sulfuric acid and the latter compound was prepared from *p*-bromotoluene, acetyl chloride and aluminum chloride. Nevile and Winther[12] reported the melting point of the amine as 30.6–32°. Recently, Huston and Hutchinson,[16] following the procedure of Nevile and Winther, obtained an amine melting at 32–33°, and boiling at 115–118° (16 mm.).

We attempted the reduction of 3-nitro-4-bromotoluene employing tin and hydrochloric acid and obtained a product melting at 30–32°, but this substance after recrystallization gave qualitative tests for both chlorine and bromine. Moreover, this compound and benzene, by the Gomberg–Bachmann procedure, gave a chlorobromomethylbiphenyl, which was not investigated further. It is apparent that some of the earlier workers were nitrating mixtures of para and ortho bromotoluene without separating the desired nitro body from the mixture, while others presumably were unaware of a partial substitution of halogen in the ring when tin and hydrochloric acid were used in the reduction of the nitro derivative. Furthermore, analytical data to substantiate the purity of the particular compounds described by the above mentioned investigators is notably absent. Hence, it is very probable that Nevile and Winther were describing a chlorobromotoluidine, or a mixture of this and the expected bromotoluidine, the separation and purification of which was only partially possible under the conditions employed in their work.

In order to characterize further our 3-amino-4-bromotoluene, the benzoyl derivative was prepared. After recrystallization from alcohol and water it melted at 107.5–108.5°.

Anal. Calcd. for $C_{14}H_{12}ONBr$: N, 4.92; Br, 27.55. Found: N, 4.66. Br, 27.84.

Synthesis of 2-Bromo-5-methylbiphenyl.—From 45 g. of 3-amino-4-bromotoluene,

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(12) Nevile and Winther, *Ber.*, **13**, 972 (1880).

(13) Claus, *J. prakt. Chem.*, [2] **46**, 25 (1892).

(14) Wroblewsky, *Ann.*, **168**, 177 (1873).

(15) Hübner and Roos, *Ber.*, **6**, 800 (1873).

(16) Huston and Hutchinson, THIS JOURNAL, **54**, 1504 (1932).

diazotized and coupled with benzene as described for the preparation of 2-chloro-5-methylbiphenyl, 9.5 g. (16%) of an aromatic yellow oil boiling at 304–308° (740 mm.) was obtained; density 25/25°, 1.358; refractive index (n^{25}_D), 1.6150.

Anal. Calcd. for $C_{13}H_{11}Br$: Br, 32.35. Found: Br, 32.45.

Oxidation of 2-Bromo-5-methylbiphenyl.—From 1 g. of the derivative just described, and 1.5 g. of powdered potassium permanganate in glacial acetic acid, there was obtained, after following the method employed for the oxidation of 2-chloro-5-methylbiphenyl, 0.3 g. of 3-phenyl-4-bromobenzoic acid; yield 27%; m. p. 242–243°.

Anal. Calcd. for $C_{13}H_9O_2Br$: Br, 28.85. Found: Br, 28.81.

A mixed melting point of this product and that obtained from the oxidation of 4-bromo-1,3-diphenylbenzene indicated that the two acids were identical. Therefore, the structure assumed by Olgiati for the monobromo derivative of *m*-diphenylbenzene is confirmed by the above results. Moreover, the salts and the methyl and ethyl esters derived from the bromo-diphenylcarboxylic acid described by Olgiati, are those of 3-phenyl-4-bromobenzoic acid.

In the course of the experimental proof of structure of 4-bromo-1,3-diphenylbenzene, the synthesis of 2-bromo-5-phenylbenzoic acid was also attempted, since this was the only other bromo-diphenylcarboxylic acid theoretically possible from the oxidation of 4-bromo-1,3-diphenylbenzene. The general steps taken to accomplish this end are represented schematically as follows: *m*-toluidine ⟶ *m*-acetotoluide ⟶ 3-acetamino-6-bromotoluene ⟶ 3-amino-6-bromotoluene ⟶ 3-methyl-4-bromobiphenyl ⟶ 2-bromo-5-phenylbenzoic acid. Since the first three stages in the synthesis are described elsewhere in the literature, it will suffice to report only the preparation of 3-methyl-4-bromobiphenyl. This derivative was obtained from 6-bromo-3-aminotoluene according to the method described previously for 2-chloro-5-methylbiphenyl; b. p. 318–323° (760 mm.); refractive index (n^{25}_D), 1.6358.

Anal. Calcd. for $C_{13}H_{11}Br$: Br, 32.35. Found: Br, 32.27.

All attempts to oxidize 3-methyl-4-bromobiphenyl by the methods already described in the preceding were unsuccessful, the desired product being destroyed by the oxidation. In view of this observation, it is very probable that the oxidation of 4-bromo-1,3-diphenylbenzene proceeded simultaneously with the formation of both isomeric acids, 3-phenyl-4-bromobenzoic acid and 2-bromo-5-phenylbenzoic acid, but the latter compound was destroyed and thus only the former acid was isolated.

Summary

1. The preparation and proof of structure of 4-bromo-1,3-diphenylbenzene and 4-chloro-1,3-diphenylbenzene are reported.

2. Several new unsymmetrical biaryl derivatives have been prepared and their properties determined.

3. The structure of the bromobiphenylcarboxylic acid and its methyl and ethyl esters first prepared by Olgiati, has been established.

4. An explanation of the discordant data in the literature and also the corrected physical constants for 3-amino-4-bromotoluene and its acetyl derivative are given.

5. An improved method for the purification of acids obtained on oxidation of liquid halogenated aromatic hydrocarbons with CrO_3 and glacial acetic acid has been suggested.

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RECEIVED SEPTEMBER 22, 1932
PUBLISHED MARCH 7, 1933