

TABLE IV  
TERTIARY-BUTYL PHENYLACETATE

Nitration number.....	1	2	3
Weight nitrated.....	6.46	6.88	6.56
Weight of nitro compounds obtained.....	7.39	7.55	7.90
Nitration yield, %.....	93	89	98
Molecular weight of nitration product.....	239.3	238.1	237.8
Weight oxidized by KMnO <sub>4</sub> .....	5.13	4.86	4.75
Weight of oxidation products obtained (benzoic and nitrobenzoic acids).....	3.15	3.04	3.10
Oxidation yield, %.....	87	89	93
Weight of benzoic acid sublimed.....	0.038	0.027	0.016
Benzoic acid present in product, %.....	1.2	0.9	0.5
Molecular weight of oxidation products.....	166.9	167.3	167.1
0.2507 <i>N</i> TiCl <sub>3</sub> required to reduce the sample, cc.	32.48	30.81	32.83
Total nitrobenzoic acids present, g.....	0.2267	0.2151	0.2292
Tribromoaniline formed from reduced sample including solubility correction, g.....	0.421	0.400	0.429
<i>o-p</i> -Nitrobenzoic acids present, g.....	0.2133	0.2026	0.2173
Meta compound, %.....	5.9	5.8	5.2

Average percentage of meta compound, 5.6

### Summary

As a continuation in the study of the influences of remote atoms on the residual charge of the key atom in benzene derivatives, the quantitative nitration of the methyl, ethyl and tertiary-butyl esters of phenylacetic acid has been accomplished. The percentages of the meta derivatives formed were 12.1, 10.3 and 5.6, respectively.

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## NITRATION OF META-DIPHENYLBENZENE AND DERIVATIVES OF NITRO-META-DIPHENYLBENZENE<sup>1</sup>

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In the process for the preparation of diphenyl from benzene, considerable amounts of high boiling products are produced. *m*-Diphenylbenzene is one of the constituents of this high boiling material. Since the trinitro compound is the only nitro derivative of *m*-diphenylbenzene which has been recorded, a study of the nitration of this hydrocarbon was undertaken with the object of synthesizing the mono and dinitro compounds and some of their derivatives.

<sup>1</sup> Abstracted from a thesis presented by C. Arthur Wardner to the Graduate School in partial fulfilment of the requirement for the Ph.D. degree.

References to the literature<sup>2</sup> deal mainly with the preparation of *m*-diphenylbenzene from various sources.

The only derivatives which have been recorded for this hydrocarbon are the trinitro, triamino, bromo and tetrabromo compounds.

The writers are indebted to Mr. R. E. Bowman of Wilmington, Delaware, who is investigating the high boiling material furnished by the Swann Corporation, for providing a generous supply of *m*-diphenylbenzene. The *m*-diphenylbenzene thus obtained was recrystallized twice from ethyl alcohol, producing white needle-shaped crystals, m. p. 85°, as reported by Schultz, Schultz and Schmidt, Olgiati, Adam, Möhlun and Berger, Chattaway and Evans.<sup>2</sup> *m*-Diphenylbenzene is described in Beilstein<sup>3</sup> as white needle-shaped crystals. It is soluble in ethyl alcohol, ethyl ether, benzene and acetic acid. It boils at 363° under atmospheric pressure.

Several preliminary experiments were conducted, in which such factors as time, concentration of nitrating agent, temperature and solvent were varied, before the following procedures were adopted.

#### A. Nitration of *m*-Diphenylbenzene

**Nitro-*m*-diphenylbenzene.**—Fifty grams of *m*-diphenylbenzene and 200 cc. of acetic anhydride were mixed thoroughly with a mechanical agitator in a 600-cc. beaker until a uniform suspension was obtained and then cooled to 0°; 17.5 cc. of fuming nitric acid (sp. gr. 1.5) was added drop by drop with continuous stirring in the course of twenty minutes. As the reaction proceeded, the *m*-diphenylbenzene gradually dissolved. The same low temperature was maintained for fifteen minutes after the last drop of fuming nitric acid had been added. The solution was then warmed gradually to a temperature of 25°, which required twenty minutes. To ensure complete nitration, the reaction mixture was heated at 50° for thirty minutes.

The oily nitro compound separated as a distinct layer at the bottom when the nitrating mixture was poured into 500 cc. of ice water. The water layer was decanted and the nitro compound was washed with 500 cc. of warm water (temp. 50°). This was followed by several washings with warm five per cent. sodium carbonate solution. It was then washed with warm water. The oily product was dissolved in 150 cc. of ethyl ether and the resulting solution was dried over calcium chloride for twelve hours. The solution was filtered and the solvent was removed. The residual oil was vacuum distilled and the portion boiling at 197–198° (1 mm.) or 203° (2 mm.) was collected; yield, 36 g.

Attempts to crystallize this nitro compound were futile. Although it could be frozen to a solid with carbon dioxide snow, it acquired the characteristic viscous property when it warmed to room temperature. A portion of the nitro compound was kept in a refrigerator, while another portion was kept in a vacuum desiccator for ten months but there was no crystal formation in either of these samples.

<sup>2</sup> Schultz, *Ann.*, **174**, 228 (1874); Schultz and Schmidt, *ibid.*, **203**, 118 (1880); Olgiati, *Ber.*, **27**, 3385 (1894); Bachmann and Clarke, *This Journal*, **49**, 2089 (1927); Chattaway and Evans, *J. Chem. Soc.*, **69**, 980 (1896); Adam, *Ann. chim. phys.*, [6] **15**, 224 (1888); Möhlun and Berger, *Ber.*, **26**, 1994 (1893); Mannich, *ibid.*, **40**, 159 (1907); Gastaldi and Cherchi, *Gazz. chim. ital.*, **45**, II, 251 (1915).

<sup>3</sup> Beilstein, "Handbuch der organischen Chemie," 4th ed., Vol. V, System No. 450–498, p. 695.

Experiments were also conducted to crystallize the nitro compound from organic solvents. It was dissolved in ethyl ether, benzene, acetic acid and acetone, but these solvents did not affect crystallization, even after the solutions were concentrated and cooled. The nitro compound is insoluble in water.

*Anal.* Calcd. for  $C_{18}H_{18}O_2N$ : C, 78.54; H, 4.72; N, 5.09. Found: C, 78.00, 78.17; H, 4.50, 4.94; N, 5.03, 5.21.

**Dinitro-*m*-diphenylbenzene.**—A mixed acid solution was prepared, consisting of 30 cc. of sulfuric acid (sp. gr. 1.82), 15 cc. of nitric acid (sp. gr. 1.42) and 7.5 cc. of water. This mixture was kept at a constant temperature of 40° and stirred while 20 g. of *m*-diphenylbenzene was added in small portions, over a period of twenty minutes. A yellow oil formed which was insoluble in the nitrating acid. At this stage 10 cc. of nitric acid (sp. gr. 1.42) was added drop by drop. The product became pasty. The formation of this insoluble viscous product made further nitration almost impossible, and since higher temperature in this acid medium is conducive to oxidation, the operation was discontinued. The nitrating acid was decanted and the insoluble material was washed with cold water. The solid material thus obtained was crystallized from acetic acid, washed with water and dried. A yield of 14 g. was obtained, which had a melting point range of 160–190°. The product was crystallized six times from acetic acid, washed with water and dried in an oven at 80°; m. p. 214°; yield, 7. g. This product is soluble in acetic acid, benzene and acetone when heated.

*Anal.* Calcd. for  $C_{18}H_{12}O_4N_2$ : N, 8.75. Found: N, 8.76, 8.85.

The mother liquor from the first acetic acid crystallization was poured into 200 cc. of cold water. The oily material which separated was washed with water, dissolved in ether and the resulting solution was dried over calcium chloride for twelve hours. After filtration and evaporation of the solvent, a small amount of an oily liquid was obtained.

**Trinitro-*m*-diphenylbenzene. 1. From *m*-Diphenylbenzene.**—Five grams of *m*-diphenylbenzene and 25 cc. of acetic acid were mixed thoroughly in a 250-cc. round-bottomed flask; 16 cc. of fuming nitric acid (sp. gr. 1.5) was added in the course of one hour, while stirring and heating at 30°. The reaction mixture was heated for another hour on a boiling water-bath. A red coloration was noted in the solution at this point. Upon cooling, white needle-shaped crystals separated which were filtered by suction, washed with water and recrystallized three times from acetic acid. The resulting product was again washed with water and dried in an oven at 80°; m. p. 204°; yield, 4.5 g.; soluble in hot acetic acid, hot benzene and hot acetone, and slightly soluble in hot ethyl alcohol.

*Anal.* Calcd. for  $C_{18}H_{11}O_6N_3$ : N, 11.50. Found: N, 11.25, 10.96.

**2. From Nitro-*m*-diphenylbenzene.**—Five grams of nitro-*m*-diphenylbenzene was dissolved in 25 cc. of acetic acid in a 250-cc. round-bottomed flask; 16 cc. of fuming nitric acid (sp. gr. 1.5) was added slowly to the solution in the course of one hour, while the temperature was maintained at 25°. The temperature was raised gradually to 96–100°, where it was maintained for four hours. On cooling, white needle-shaped crystals separated, which were filtered and washed with water. These were crystallized three times from acetic acid; m. p. 204°; yield, 1 g.

The filtrate from the reaction mixture was poured into 250 cc. of cold water. A viscous semi-solid material separated, which was washed with water. This material was dissolved in ethyl ether and the solution dried over calcium chloride for twelve hours. One gram of a yellow solid separated. It was filtered but it could not be purified to a constant melting point by crystallization. Upon evaporation of the ether, a yellow oil having the appearance of the original mononitro derivative was obtained.

**Oxidation of Nitro-*m*-diphenylbenzene.**—Five grams of the nitro compound was dissolved in 25 cc. of acetic acid. To this solution while refluxing there was added a solution containing 40 g. of chromic acid in 40 cc. of acetic acid and 25 cc. of water in small quantities. After the last portion had been added, boiling was continued for one and a half hours. The reaction mixture was poured into 500 cc. of ice water, and the yellow precipitate which formed was filtered by suction and washed with water. It was dissolved in a 10% sodium hydroxide solution and reprecipitated with 1:1 hydrochloric acid. The resulting product was recrystallized twice from dilute ethyl alcohol (one part of alcohol to three parts of water). It was filtered by suction and dried in a vacuum desiccator; m. p. 224°. The product sublimed and this gave a melting point of 227°; yield, 0.9 g.

There are several possible oxidation products of nitro-*m*-diphenylbenzene, but only a few of these are recorded in the literature. The ones that are recorded with their respective melting points are as follows: 1-nitrobenzene-2,4-dicarboxylic acid, 245–246°; 1-nitrobenzene-3,5-dicarboxylic acid, 248–249°; 2-nitrobenzene-1,3-dicarboxylic acid, 300°; 2-nitrobenzoic acid, 148°; 3-nitrobenzoic acid, 140–141°; 4-nitrobenzoic acid, 238–240°.

The product obtained in the above oxidation experiment did not correspond with any of the compounds listed above. With the idea that one of these compounds might be obtained, the nitrodiphenylcarboxylic acid was subjected to a chromic acid oxidation for six hours more. However, the original acid was recovered. The product of oxidation is evidently a hitherto unreported nitrodiphenylcarboxylic acid.

*Anal.* Calcd. as nitrodiphenylcarboxylic acid ( $C_{13}H_9O_4N$ ): N, 5.76; mol. wt., 243. Found: N, 5.51, 5.74; mol. wt. by titration of its neutral equivalent, 246.1, 245.9.

**Oxidation of Dinitro-*m*-diphenylbenzene.**—One gram of dinitro-*m*-diphenylbenzene was dissolved in 25 cc. of acetic acid. The procedure from this point was identical with that of the above oxidation experiment, except that the oxidizing agent consisted of 10 g. of chromic acid in 10 cc. of acetic acid and 5 cc. of water. White needle-shaped crystals formed which were recrystallized twice from water and dried in a vacuum desiccator; m. p. 238°; yield, 0.1 g. This melting point corresponds to that of *p*-nitrobenzoic acid. A mixed melting point indicated that the product was *p*-nitrobenzoic acid.

All attempts to oxidize the trinitro compound were futile, which is in accordance with the results of Schultz and Schmidt.<sup>2</sup>

**Discussion of the above Results.**—Theoretically, there are six mono-nitro derivatives of *m*-diphenylbenzene. Since in the nitration of diphenyl the ortho and para derivatives predominate, the mononitro products that would most likely form during the nitration of *m*-diphenylbenzene would be the following: (a) 2-nitro-5'-phenyl-diphenyl, (b) 4-nitro-5'-phenyl-diphenyl, (c) 1,3-diphenyl-2-nitrobenzene, (d) 1,3-diphenyl-4-nitrobenzene. The oxidation of nitro-*m*-diphenylbenzene yielded a hitherto unreported nitrodiphenylcarboxylic acid instead of a nitro-isophthalic acid or a nitrobenzoic acid, as would be expected. *o*-Nitrodiphenyl is not attacked by oxidizing agents while<sup>4</sup> *p*-nitrodiphenyl yields *p*-nitrobenzoic acid. This seems to indicate<sup>5</sup> that a phenyl group adjacent to a nitro group on a benzene nucleus is protected against oxidation. Reasoning by analogy from similar diphenyl type oxidations the formulas designated by (a) and

<sup>4</sup> Schultz, Schmidt and Strasser, *Ann.*, **207**, 348 (1881).

<sup>5</sup> Schultz, *ibid.*, **174**, 201 (1874).

(d) may be regarded as the two possible structures for nitro-*m*-diphenylbenzene, since a nitrodiphenylcarboxylic acid was isolated as an oxidation product.

The fact that *p*-nitrobenzoic acid was isolated as an oxidation product of dinitro-*m*-diphenylbenzene proves that a nitro group is attached in the para position on an end ring.

### B. Derivatives of Nitro-*m*-diphenylbenzene

**Amino-*m*-diphenylbenzene.**—Ten grams of nitro-*m*-diphenylbenzene was dissolved in 30 cc. of ethyl acetate; 0.2 g. of platinum oxide, prepared according to the directions given in "Organic Syntheses,"<sup>6</sup> was used as a catalyst. The reduction was performed in a Parr catalytic hydrogenation machine. One hour was allotted for the completion of the reaction. The resulting solution was filtered to remove the platinum black. The solvent was removed and the resulting product was treated with 25 cc. of 1:5 hydrochloric acid. The white hydrochloride salt was filtered by suction, washed once with dilute hydrochloric acid and twice with 50 cc. of ethyl ether. The hydrochloride was then neutralized with a five per cent. solution of sodium carbonate. A small amount of ether was added to the mixture to dissolve the amine as it was formed. The ether was allowed to evaporate, and the amine separated in the form of a light gray solid. It was filtered and recrystallized three times from ethyl alcohol; m. p. 64°; yield, 6 g.; soluble in ethyl alcohol, ethyl ether, ethyl acetate, benzene and acetone.

*Anal.* Calcd. for C<sub>18</sub>H<sub>15</sub>N: N, 5.71. Found: N, 5.69, 5.81.

This product was also prepared by using the iron reduction method for reducing nitrodiphenyl.<sup>7</sup>

**Amino-*m*-diphenylbenzene Hydrochloride.**—One gram of amino-*m*-diphenylbenzene was dissolved in 20 cc. of ethyl acetate. This solution was agitated with dry hydrogen chloride gas until the amine had been precipitated as the white hydrochloride salt. It was filtered and dried in a vacuum desiccator.

*Anal.* Calcd. for C<sub>18</sub>H<sub>15</sub>NCl: N, 4.97. Found: N, 4.87, 4.80.

**Acetylamino-*m*-diphenylbenzene.**—One gram of amino-*m*-diphenylbenzene was dissolved in 5 cc. of acetic anhydride. The solution was heated for three minutes and then cooled. The addition of 5 cc. of water decomposed the excess acetic anhydride and caused the acetylated derivative to separate as a white solid. It was filtered by suction and recrystallized twice from 50% ethyl alcohol; m. p. 117°; yield, 1 g.

*Anal.* Calcd. for C<sub>20</sub>H<sub>17</sub>ON: N, 4.86. Found: N, 5.11, 4.96.

**Benzoylamino-*m*-diphenylbenzene.**—Two grams of amino-*m*-diphenylbenzene was dissolved in 5 cc. of pyridine. While stirring, three cc. of benzoyl chloride was added drop by drop. The reaction mixture became warm. On cooling, white needle-shaped crystals were deposited which were filtered by suction and washed with 0.5 *N* sulfuric acid. It was recrystallized from ethyl alcohol; m. p. 152°; yield, 2 g.

*Anal.* Calcd. for C<sub>26</sub>H<sub>19</sub>ON: N, 4.01. Found: N, 4.13, 3.78.

***m*-Diphenylbenzene-azo- $\beta$ -naphthol.**—*m*-Diphenylbenzenediazonium chloride was prepared by diazotizing 2 g. of amino-*m*-diphenylbenzene hydrochloride in a solution of 100 cc. of distilled water and 10 cc. of hydrochloric acid (sp. gr. 1.18) at a temperature of 5°. This diazotized solution was poured slowly into a cooled solution containing 1.5

<sup>6</sup> Adams, Voorhees and Shriner, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1928, Vol. VIII, p. 92.

<sup>7</sup> Jenkins, McCullough and Booth, *Ind. Eng. Chem.*, **22**, 31 (1931).

g. of  $\beta$ -naphthol and 5 g. of sodium hydroxide in 100 cc. of water. A red precipitate formed, which was filtered by suction and washed with water. A red crystalline product was obtained after crystallization from acetic acid; yield, 2 g.

*Anal.* Calcd. for  $C_{22}H_{20}ON_2$ : N, 7.00. Found: N, 6.67, 6.86.

Other compounds were also coupled qualitatively with *m*-diphenylbenzenediazonium chloride, *e. g.*: 1,8-dihydroxynaphthalene-3,6-disulfonic acid, red-purple; 1-naphthol-4-sulfonic acid, bright red; 1,8-aminonaphthol-3,6-disulfonic acid, blue-purple; 2-naphthol-7-sulfonic acid, bright red; 1,8-aminonaphthol-2,4-disulfonic acid, purple; 2-naphthol-3,6-disulfonic acid, light purple.

### Summary

1. The mononitro, dinitro and trinitro derivatives of *m*-diphenylbenzene have been prepared.

2. The oxidation of nitro-*m*-diphenylbenzene yielded a nitrodiphenylcarboxylic acid. The oxidation of dinitro-*m*-diphenylbenzene yielded *p*-nitrobenzoic acid. No reaction was observed in the attempted oxidation of trinitro-*m*-diphenylbenzene.

3. The nitro-*m*-diphenylbenzene was reduced to the corresponding amine. The following new derivatives of amino-*m*-diphenylbenzene were prepared: (a) amino-*m*-diphenylbenzene hydrochloride, (b) acetylamino-*m*-diphenylbenzene, (c) benzoylamino-*m*-diphenylbenzene, (d) *m*-diphenylbenzene-azo- $\beta$ -naphthol, and other dyes.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

## PHENYL SUBSTITUTED ALIPHATIC ACIDS

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The mechanism of the oxidation of the fatty acids in the animal body has long been the subject of speculation by chemists interested in metabolism. The most satisfactory theory that has been advanced to account for the oxidation of fatty acids to carbon dioxide and water in the animal was propounded by Knoop<sup>1</sup> in 1904. His theory of beta oxidation has been tested on various omega substituted fatty acids of the type  $C_6H_5-(CH_2)_xCOOH$  where the phenyl group which is not generally oxidized in the animal body acted as a barrier to further oxidation and left an identifiable residue to be eliminated as a waste product from the body. In these studies all of those acids in which  $x$  had an uneven value were found to be burned in the body to phenylacetic acid and those in which  $x$  had an even value were burned to benzoic acid.

Thus far most of the experiments which have been devised to test Knoop's theory of  $\beta$ -oxidation have confirmed it. However, it has been

<sup>1</sup> Knoop, *Beitr. Chem. Physiol. Path.*, **6**, 150 (1905).