finally precipitated with 5% sodium hydroxide. The free base was crystallized from 35% alcohol and melted at 106–108°. After several recrystallizations it melted at 107–108°.

The Diazotization of Thioaniline by a Modification of the Method of Bass and Johnson.[8]

4,4'-Dihydroxydiphenyl Sulfide.—Thioaniline sulfate (10 g.) was suspended in 75 ml. of glacial acetic acid and 5 ml. of concentrated sulfuric acid in an ice-bath at 0–5°. Isoamyl nitrite (5 g.) was slowly added over a period of thirty minutes with vigorous stirring for thirty minutes longer. A solution of 100 ml. of concentrated sulfuric acid and 80 ml. of water was heated to boiling (160°) and the diazotized solution slowly added, when a dark oil separated. After heating the solution to boiling for about forty-five minutes it was then diluted with water and cooled. The oil was separated and dissolved in 5% sodium hydroxide solution and boiled with Norite. Upon cooling, the solution was neutralized with dilute hydrochloric acid. The straw-colored precipitate was dissolved in 50% alcohol, decolorized with Norite and crystallized; yield, 2.5 g., m. p. 149°.[9]

Action of Sulfur on Benzalaniline.—Benzalaniline (180 g.) and sulfur (32 g.) were heated at 140–150° in the presence of lead oxide (160 g.) for six hours. On working up the reaction mixture after digestion with hydrochloric acid we obtained only benzaldehyde and aniline the hydrolysis products of benzalaniline. No thioaniline was formed.

Action of Sulfur on Dimethylaniline.—Freshly distilled dimethylaniline, b. p. 190–192° (121 g.), was heated with sulfur (32 g.) and lead oxide (160 g.) at 140–150° for six hours. Upon extraction with alcohol and steam distilling, 110 ml. of unused dimethylaniline was recovered. The water solution remaining contained no thiodimethylaniline.

Bis - (4 - monomethylaminophenyl) Sulfide.—Monomethylaniline, b. p. 193–195° (90 g.), sulfur (28 g.) and lead oxide (125 g.) were heated together in the usual manner for six hours at 140–160°. Upon extraction and steam distilling, 25 ml. of unused monomethylaniline was recovered. The remaining material was purified according to the above method. The sulfate did not precipitate completely from the alcohol–ether mixture, so it was evaporated and 25 g. of a gray powder obtained. This was dissolved in hot water, boiled with Norite several times, neutralized with 5% sodium hydroxide, and finally crystallized as a colorless solid from an ether–petroleum ether mixture, m. p. 58–60° (Beilstein, m. p. 60°). The material turned purple upon standing in the air.

Summary

The action of sulfur on certain aromatic amines, namely, aniline, benzalaniline, monomethylaniline and dimethylaniline, has been studied in which it was observed that benzalaniline and dimethylaniline do not react to form the corresponding sulfides. These results together with those for *o*-toluidine and acetanilide, lead the writers to propose a possible mechanism for the explanation of this reaction, involving the intermediate formation of a sulfanilide type of compound through the replacement of a labile hydrogen on the nitrogen atoms with sulfur. This compound under the conditions of the experiment immediately undergoes a rearrangement to the corresponding amino-sulfide. The research will be continued.

An improvement has been noted in the technique for the purification of the products obtained from this reaction.

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(8) Bass and Johnson, THIS JOURNAL, **52**, 1146 (1930).

(9) Tassinari, *Gazz. chim. ital.*, **17**, 83 (1887), (m. p. 150–151°); Krafft, *Ber.*, **7**, 1165 (1874), m. p. 143–144°.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Studies on the Polymethylbenzenes. XI. The Nitration of Pentamethylbenzene and of Hexamethyl- and Hexaethylbenzene[1,2]

BY LEE IRVIN SMITH AND S. ARTHUR HARRIS

The nitration of pentamethylbenzene was investigated in 1887 by Gottschalk,[3] who by adding the hydrocarbon to fuming nitric acid at 0° obtained a small amount of a dinitrotetramethylbenzene, m. p. 178°, together with much oily material. Willstätter and Kubli[4] obtained the same solid product from the hydrocarbon by nitrating it with a mixture of sulfuric acid and fuming nitric acid in the presence of chloroform. Both investigators assigned to this product the ortho dinitro structure, regarding it as dinitroprehnitene.

The work of Barbier[5] and of Alfthan[6] indicates that in those nitrations of benzene derivatives in which a nitro group displaces an alkyl or acyl group, the group displaced is always meta to the first entering nitro group. On this basis, the

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(1) Paper X, THIS JOURNAL, **56**, 2169 (1934).

(2) Abstracted from a thesis by S. Arthur Harris, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Master of Science, July, 1934.

(3) Gottschalk, *Ber.*, **20**, 3287 (1887).

(4) Willstätter and Kubli, *ibid.*, **42**, 4151 (1909).

(5) Barbier, *Helv. Chim. Acta*, **11**, 157 (1928).

(6) Alfthan, *Ber.*, **53**, 78 (1920).

dinitrotetramethylbenzene obtained from pentamethylbenzene should be dinitroisodurene with the two nitro groups in the meta position.

We decided to investigate this reaction, because of the unusual orientation of the two nitro groups, and also because it seemed a very promising method for the preparation of dinitroprehnitene in quantity, since pentamethylbenzene is the most readily available of all the polymethylbenzenes.

Although the product obtained by nitrating prehnitene melts at 177–178°, while the corresponding product obtained from isodurene melts at 180°, the two substances are different. That the former product is an ortho dinitro compound was shown by Smith and Hac[7] by converting it into a diamine and then into tetramethyl-*o*-benzoquinone. The product obtained by nitrating durene is a para dinitro compound, for it can be converted into duroquinone in good yield; hence the third dinitro compound, obtained by nitrating isodurene, must be the meta dinitro compound. This establishes conclusively the orientation of the three dinitrotetramethylbenzenes and ***proves that in the direct nitration of these hydrocarbons no rearrangements are involved.***

We found that pentamethylbenzene could be nitrated to give nearly 75% yield of a dinitrotetramethylbenzene, if the nitration were carried out at 0–10° in the presence of chloroform and with a very great excess of sulfuric acid in the nitrating mixture. The dinitro compound so obtained melts at 176–177° and is dinitroprehnitene as shown by the mixed melting point with an authentic specimen and by its ready conversion into a good yield of 2,4,5,6,7-pentamethylbenzimidazole when reduced with stannous chloride in the presence of hydrochloric and acetic acids.

With regard to the mechanism of this nitration, two theories appear worthy of consideration. The first of these involves a Jacobsen rearrangement, two molecules of pentamethylbenzene giving one each of prehnitene and hexamethylbenzene; nitration of *both* of these hydrocarbons then leads to dinitroprehnitene. This theory was originally proposed by Gottschalk,[3] but he was unable to obtain any dinitroprehnitene by nitrating hexamethylbenzene. Obviously, if hexamethylbenzene cannot be converted to dinitroprehnitene, the maximum yield of this dinitro compound from pentamethylbenzene would be 50% on the basis of Gottschalk's mechanism. When we succeeded in obtaining 75% yields in our nitrations of pentamethylbenzene, we were at first inclined to dismiss Gottschalk's mechanism, especially since Willstätter and Kubli[4] had also failed to obtain any dinitroprehnitene by nitrating hexamethylbenzene, although it is true that Willstätter and Kubli used entirely different conditions from those used by Gottschalk and by us. Nevertheless, we decided to try the nitration of hexamethylbenzene ourselves before eliminating Gottschalk's mechanism.

We found that hexamethylbenzene, nitrated with fuming nitric acid in the presence of chloroform and a large excess of sulfuric acid, gave as much as 22% yield of dinitroprehnitene. This curious nitration has no parallel anywhere; the only other nitration of a hexaalkylbenzene reported in the literature is that of hexaethylbenzene, reported by Galle[8] and by Jannasch and Bartels[9] to give the *para* dinitrotetraethylbenzene. On the basis of our work on the nitration of hexamethylbenzene, we were inclined to doubt that this dinitrotetraethylbenzene could be para and we accordingly repeated the work of Galle and Jannasch and Bartels. Although the yields were poor, there is no question but that the dinitrotetraethylbenzene obtained in this way is a para dinitro compound; we reduced it to the corresponding diamine, and this, on oxidation with ferric chloride, gave a yellow substance, m. p. 58°, with the odor of a para quinone and analyzing for tetraethylquinone.

The second plausible mechanism for the conversion of pentamethylbenzene to dinitroprehnitene involves a preliminary oxidation of the hydrocarbon to prehnitene-carboxylic acid and the nitration of this to dinitroprehnitene with elimination of carbon dioxide. We prepared this acid and nitrated it; the result was a quantitative yield of dinitroprehnitene, as reported by Auwers and Köckritz.[10]

Thus both mechanisms at first glance seem reasonable, for Gottschalk's mechanism in view of our nitration of hexamethylbenzene, can account for a yield of about 70% of dinitroprehnitene from pentamethylbenzene; this is only slightly less than we obtained in our best runs. Nevertheless, there are important arguments against both mechanisms, and we believe that neither mecha-

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[7] Smith and Hac, THIS JOURNAL, **56**, 477 (1934).

[8] Galle, *Ber.*, **16**, 1748 (1883).

[9] Jannasch and Bartels, *ibid.*, **31**, 1717 (1898).

[10] Auwers and Köckritz, *Ann.*, **352**, 320 (1907).

nism can account for more than a small proportion of the total product, at the most. Against Gottschalk's mechanism is the fact that our nitrations were carried out at 0–10°, and the previous studies carried out in this Laboratory on the Jacobsen rearrangement[11] have shown that at these temperatures the amount of pentamethylbenzene rearranged in thirty minutes (the average time of a nitration) would be so small as to be negligible, even if the chloroform were absent. In the presence of chloroform, the rate of the Jacobsen rearrangement would be still less. Moreover, the figure of 70% dinitroprehnitene as the maximum yield by Gottschalk's mechanism assumes a quantitative yield of nitro compound from the prehnitene; the best yield that can be obtained in a direct nitration is about 90%, and usually the yield is somewhat less than this.[7]

Against the second mechanism, in which prehnitene-carboxylic acid is assumed to be an intermediate, is the fact that pentamethylbenzene is converted into the dinitro compound under milder conditions (0–5°) than those necessary to convert it to the carboxylic acid. For the latter, a temperature of 25° is necessary, and when lower temperatures—even 10–15°— are used, no acid at all results, although the dinitro compound is readily obtained at these lower temperatures.

Finally, some recent work in this Laboratory has indicated that there may be several intermediates in this nitration of pentamethylbenzene. We hope to isolate these and to report on their nature in a later paper.

Experimental

Nitration of Pentamethylbenzene.—The yield of dinitro compound depends greatly upon the experimental conditions, particularly upon the amount of sulfuric acid, the kind of fuming nitric acid, and the temperature. The procedure which gave the best yields is as follows: the nitrating mixture consisted of fuming nitric acid, *d* 1.52 (30 g.) and concentrated sulfuric acid (130 g.). This was covered with an equal volume of chloroform, the whole cooled to 5° and vigorously stirred. The finely powdered hydrocarbon (10 g.) was added in small portions, allowing time for the deep red color to fade after each addition before adding another portion, and taking care that the temperature did not exceed 10°. The chloroform layer was washed with water and then with carbonate, and the solvent replaced by alcohol by boiling the solution on the steam-bath, keeping the volume constant by adding alcohol from time to time. Cooling to 0° gave fine white needles, m. p. 176–177°. Five such nitrations gave 70, 65, 73, 70 and 74% yields. The excess of sulfuric acid is important, for if the amount is reduced until it equals that of the nitric acid, the red color developed during the nitration fades very slowly and the yields of product drop to 50% or less.

2,4,5,6,7-Pentamethylbenzimidazole Hydrochloride.—The above nitro compound (10 g.) was dissolved in boiling acetic acid (45 cc.) and to it was added a boiling solution of stannous chloride (100 g.) in concentrated hydrochloric acid (90 cc.). After the vigorous reaction subsided, the mixture was refluxed for five hours, then cooled and the crystalline solid filtered off and washed with water and ether. It weighed 15 g., but was contaminated with tin compounds, which were removed by recrystallizing it several times from 50% alcohol. It was the pentamethylbenzimidazole hydrochloride dihydrate.

Anal.[12] Calcd. for $C_{12}H_{17}N_2Cl\cdot 2H_2O$: H_2O, 13.85. Found: H_2O (loss at 100°), 14.21, 13.92. Calcd. for $C_{12}H_{17}N_2Cl$: C, 64.24; H, 7.59. Found: anhydrous substance C, 64.22; H, 7.80.

The hydrochloride can be titrated with sodium hydroxide, using phenolphthalein as the indicator. Calcd. for $C_{11}H_{17}N_2Cl$: n. e., 224. Found: n. e., 224, 225.

The free benzimidazole was precipitated by adding excess sodium hydroxide to the aqueous alcoholic solution of the hydrochloride. Recrystallized from dilute alcohol it formed white needles, m. p. 264°, readily soluble in ether or alcohol, insoluble in dilute sodium hydroxide.

Anal. Calcd. for $C_{12}H_{16}N_2$: C, 76.59; H, 8.51. Found: C, 76.53, 76.30; H, 8.72, 8.42.

In order to characterize this new benzimidazole more completely, we made several derivatives of it.

Methiodide.—The benzimidazole (2.6 g.) and pure methyl iodide (12 cc.) in benzene (150 cc.) were refluxed for six hours, the product then washed with ether and crystallized from 50% alcohol; white needles, darkening at 310° but still solid at 350°, insoluble in ether and cold water, readily soluble in alcohol. The substance turns yellow on standing in the air. Its solutions react with alcoholic silver nitrate, giving silver iodide, and with chlorine water free iodine is formed.

Anal. Calcd. for $C_{13}H_{19}N_2I$: C, 47.27; H, 5.75. Found: C, 46.74, 46.93; H, 5.73, 5.81.

Methyl Sulfuric Acid Salt.—Refluxing the benzimidazole (1 g.) with excess pure methyl sulfate (2 g.) in dry methyl alcohol (50 cc.) for twenty-four hours, and then adding ether, gave the salt (2 g.). Crystallized by dissolving in alcohol, adding ether to cloudiness and cooling, it formed white needles, darkening at 255°, m. p. 258–261° (dec.); easily soluble in water, and the solution gives the benzimidazole when excess alkali is added.

Anal. Calcd. for $C_{13}H_{20}N_2SO_4$: C, 52.00; H, 6.66; S, 10.64. Found: C, 51.84, 51.82; H, 6.93, 6.61; S, 10.83.

2-Styryl-4,5,6,7-tetramethylbenzimidazole.—Using the method of Bogert and Bender,[13] the benzimidazole (1 g.) was converted into the styryl derivative (0.3 g.) which

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[11] Smith and Lux, THIS JOURNAL, **51**, 2996 (1929); Smith and Cass, *ibid.*, **54**, 1617 (1932); Smith and Moyle, *ibid.*, **55**, 1676 (1933).

[12] This compound, and the derivatives of it, must be mixed with copper oxide in the combustion in order to ensure complete burning.

[13] Bogert and Bender, THIS JOURNAL, **36**, 571 (1914).

was recrystallized from alcohol as light yellow needles, m. p. 279–280°.

Anal. Calcd. for $C_{19}H_{20}N_2$: C, 82.60; H, 7.15. Found: C, 82.48, 82.53; H, 7.25, 7.34.

1,2,4,5,6,7-Hexamethylbenzimidazole.[14]—The benzimidazole (3.4 g.) and methyl sulfate (12 g.) were refluxed in dry methyl alcohol (50 cc.) for half an hour, when the solution became acid to litmus. It was made alkaline with sodium hydroxide, 10 cc. of methyl sulfate added, and the refluxing continued. This process was repeated three times more during the course of one hour. The alcohol was then distilled from the acid solution, alkali added to the residue, and without filtering the white precipitate the mixture was extracted with ether several times. The ethereal extract was dried over solid sodium hydroxide, which removed unchanged benzimidazole as the insoluble sodium salt. The ether was filtered and evaporated, and the residue crystallized first from methyl alcohol and then from ether until the m. p. became constant at 165°. (This requires eight to ten recrystallizations.) The substance can also be sublimed. It is believed that this is the first case in which methyl sulfate has been used to methylate a benzimidazole.

Anal. Calcd. for $C_{13}H_{18}N$: C, 77.2; H, 8.91. Found: C, 77.20, 77.30, 76.70; H, 9.10, 8.70, 9.20.

Nitration of Hexamethylbenzene.—The hydrocarbon (2 g.) was added in small portions to a vigorously stirred mixture of concd. sulfuric acid (50 cc.), fuming nitric acid, *d* 1.52 (15 cc.), and chloroform (50 cc.), at 0–5°, waiting between additions for the red color to fade to yellow. After adding all the hydrocarbon, the reaction mixture immediately was poured onto ice and the product isolated and purified as described under the nitration of pentamethylbenzene; yield 0.6 g. (22%), m. p. and mixed m. p. with an authentic sample, 176°.

Nitration of Hexaethylbenzene. *p*-Dinitrotetraethylbenzene.—The hydrocarbon (2 g.), nitrated at 10° by exactly the same procedure used for hexamethylbenzene, gave 0.3 g. (13%) of white needles, m. p. 143–145°.

Anal. Calcd. for $C_{14}H_{20}O_4N_2$: C, 60.0; H, 7.15. Found: C, 60.00; H, 7.10.

***p*-Diaminotetraethylbenzene.**—The dinitro compound (1.5 g.) in boiling glacial acetic acid (30 cc.) was reduced with stannous chloride (10 g.) and hydrochloric acid (50 cc.). The stannichloride of the diamine formed on cooling and was filtered and washed with hydrochloric acid and ether. A small sample of it was treated with alkali and converted into the diamine, m. p. 92°,[8,9] which rapidly turns brown, then green, on standing in the air.

Tetraethyl-*p*-benzoquinone.—The amine stannichloride (1 g.) was dissolved in excess of warm ferric chloride solution and allowed to stand on the steam-bath for five hours. Steam distillation gave 0.3 to 0.4 g. of a yellow solid, which when recrystallized from alcohol melted at 56–58°.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.36; H, 9.09. Found: C, 75.98, 76.45; H, 9.25, 8.74.

2,3,4,5-Tetramethylbenzoic Acid, Prehnitene-carboxylic Acid.—We were able to obtain only very small yields using either the procedure of Gottschalk[15] or that of Nef[16] but the following procedure gave fair results: pentamethylbenzene (5 g.) was stirred slowly into concd. nitric acid (100 cc.) at 0° until all the lumps were broken up. The cooling bath was then removed, and the stirring continued until a vigorous evolution of oxides of nitrogen occurred (about 25°). At this point the mixture was poured *immediately* into a large volume of ice water. (When the reaction was interrupted at 10–15°, before the vigorous evolution of nitrogen oxides, no acid resulted.) The solid was removed, dissolved in ether, the ether extracted with bicarbonate and the acid precipitated with hydrochloric acid; yield 2 g., m. p. 165°. Crystallized once from ethyl alcohol (the solution must be strongly cooled to get it to crystallize) the product was colorless and melted at 167–168°, the melting point given in the literature.[15a,17]

Anal. Calcd. for $C_{11}H_{13}O_2$: n. e., 178. Found: neutral. equiv., 184.

Amide.—This was obtained by treating the acid with phosphorus pentachloride and pouring the mixture into ammonia; m. p. 220–220.5° as compared with 222° given in the literature.[15a,17]

Nitration of Prehnitene-carboxylic Acid.—The acid, stirred into a mixture of fuming nitric acid, sulfuric acid, and chloroform at 10° for a few minutes, gave a quantitative yield of dinitroprehnitene, m. p. and mixed m. p. 174–176°.

Summary

1. The optimum conditions for the nitration of pentamethylbenzene have been established.

2. The product of this nitration is an ortho dinitro compound, dinitroprehnitene, obtained in 70% yields. It was reduced to the diamine, and this converted to 2,4,5,6,7-pentamethylbenzimidazole, which was characterized by a number of derivatives, including 1,2,4,5,6,7-hexamethylbenzimidazole.

3. Hexamethylbenzene also gives dinitroprehnitene on nitration, but the yield is only 20%.

4. Hexaethylbenzene, however, gives a para dinitro compound on nitration, and the yield is very poor. From this dinitro compound, tetraethyl-*p*-benzoquinone has been made.

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(14) We were unable to alkylate the benzimidazole by Fischer's method [O. Fischer, *Ber.*, **34**, 936 (1901)] and refluxing with excess methyl iodide in xylene gave only the hydriodide, white needles (from alcohol) m. p. >350° (still solid at 350°, the limit of the bath). With alkali, the benzimidazole was precipitated quantitatively. *Anal.* Calcd. for $C_{12}H_{17}N_2I$: C, 45.5; H, 5.37. Found: C, 45.51, 45.07; H, 5.51, 5.43.

(15) (a) Gottschalk, *Ber.*, **20**, 3287 (1887); (b) see also Meyer and Wöhler, *ibid.*, **29**, 2569 (1896).

(16) Nef, *Ann.*, **237**, 7 (1887); Nef made durylic acid and we applied his procedure to the oxidation of pentamethylbenzene.

(17) (a) V. Meyer, *Ber.*, **29**, 2569 (1896); (b) Auwers and Köckritz, *Ann.*, **352**, 320 (1907).