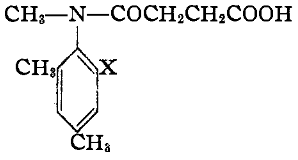
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Restricted Rotation in Substituted Aromatic Amines. V. Derivatives of N,N'-Dimethyldiaminomesitylene

BY ROGER ADAMS AND R. G. CHASE[1]

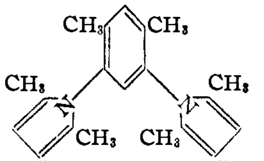
A variety of substituted anilines of the type shown in I and several of their analogs exhibit re-



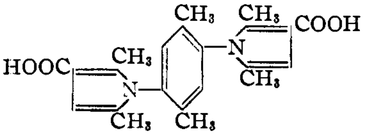
$X = OCH_3, NO_2, Br, I$

I

stricted rotation at the carbon–nitrogen bond and were resolved into their optical antipodes.[2] In certain substituted dipyrrylbenzenes (II and III), two points of restricted rotation are present and



II

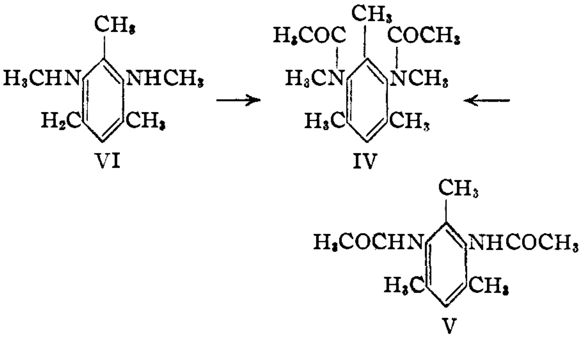


III

cis (meso) and *trans* (racemic) modifications were isolated.[3] The *trans* form of II was resolved into its enantiomorphs.

An attempt has now been made to obtain *cis-trans* isomerism due to two points of restricted rotation in aminobenzene derivatives of a simpler character in which the nitrogen merely has two substituents and is not a member of a aromatic-type ring. N,N'-Diacetyl-N,N'-dimethyldiaminomesitylene (IV) was prepared in two ways, by the alkylation of N,N'-diacetyldiaminomesitylene (V) and by the acetylation of N,N'-dimethyldiaminomesitylene (VI). Both of these methods yielded the same compound and in neither case could an isomer be isolated. In spite of this initial failure, it is likely that with the proper substituents on the nitrogen isomers will be found.

The N,N'-dimethyldiaminomesitylene was prepared by methylation of diaminomesitylene and purified from unmethylated and polymethylated by-products by formation of the dinitroso compound and subsequent reduction. The acetylation of N,N'-dimethyldiaminomesitylene with acetic anhydride in pyridine always gave a pasty mixture from which only a single pure crystalline product was obtained.



Methylation of N,N'-diacetyldiaminomesitylene by methyl iodide and potassium hydroxide, by powdered sodium in xylene and methyl iodide or by potassium hydroxide and dimethyl sulfate, always resulted in a low yield of the dimethyl derivative. The monomethylated compound was found as a by-product.

These results indicate either that the methyl and acetyl groups on the nitrogens do not cause adequate restriction in order that isomers may be formed or that one isomer is formed exclusively.

Experimental

Diaminomesitylene.—Dinitromesitylene was prepared by the method of Küster and Stallberg.[4]

A suspension of 210 g. of dinitromesitylene in 1500 ml. of ethanol was reduced with Raney nickel catalyst and hydrogen under 2000 lb. pressure at 60°. The temperature rose to 100° during the reduction. After filtering the catalyst and evaporating the solvent, the product thus obtained was purified by recrystallization from water and after drying from petroleum ether (b. p. 100–150°). The yield was 126 g. (84%), m. p. 90–90.2°. Fittig[5] reports 90°.

N,N'-Dimethyldiaminomesitylene.—To a mixture of 87.5 g. of diaminomesitylene and 350 ml. of water, 162 g. of dimethyl sulfate was added in small portions with shaking. After standing overnight, the solution was made strongly basic with sodium hydroxide and extracted with ether. The solution was dried over potassium hydroxide, the ether evaporated and the crude dimethyldiamino compound obtained; yield 92.2 g. (89%). It was purified by distillation in vacuum, b. p. 114–116° (3 mm.).

Anal. Calcd. for $C_{11}H_{18}N_2$: C, 74.12; H, 10.16; N, 15.72. Found: C, 74.32; H, 10.37; N, 16.13.

The picrate was formed by adding to a solution of the amine in water acidified to litmus with hydrochloric acid, an aqueous solution of an equivalent amount of picric acid in boiling water. The yellow precipitate which formed was purified by crystallization from ethanol. When pure, it melted at 196.5–196.8° with decomposition.

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(1) An abstract of a thesis submitted in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry.

(2) (a) Adams and Dankert, THIS JOURNAL, **62**, 2191 (1940); (b) Adams and Stewart, *ibid.*, **63**, 2859 (1941); (c) Adams and Albert, *ibid.*, **64**, 1475 (1942); (d) Adams and Sundholm, *ibid.*, **70**, 2667 (1948).

(3) Chang and Adams, *ibid.*, **56**, 2089 (1934).

(4) Küster and Stallberg, *Ann.*, **278**, 213 (1893).

(5) Fittig, *ibid.*, **141**, 135 (1867).

Anal. Calcd. for $C_{23}H_{24}N_8O_{14}$: C, 43.38; H, 3.80. Found: C, 43.73; H, 4.00.

Purification of N,N′-Dimethyldiaminomesitylene through the N,N′-Dinitroso-N,N′-dimethyldiaminomesitylene.—Although analysis indicated that the N,N′-dimethyl derivative was essentially pure as produced from dimethyl sulfate and mesitylene, it was purified further.

A solution of 50 g. of once distilled N,N′-dimethyldiaminomesitylene in 91 ml. of concentrated hydrochloric acid was cooled to 10°. To this was added dropwise with vigorous stirring a solution of 38.5 g. of sodium nitrite in 100 ml. of water. A fine crystalline precipitate of dinitroso compound separated. It was filtered, washed with aqueous sodium hydroxide and then purified by crystallization from petroleum ether (b. p. 70–90°), m. p. 121.5–122°; yield 44 g. (67%).

Anal. Calcd. for $C_{11}H_{16}N_4O_2$: C, 55.91; H, 6.82; N, 23.72. Found: C, 56.31; H, 6.84; N, 23.45.

The filtrate from the crude crystalline dinitroso compound was extracted with ether. From this ether solution was obtained a brown liquid which distilled at 118–120° (8 mm.) with some decomposition; yield 3 g. (4.5%). From the analysis it may be concluded that the product is probably a mixture of mono and dinitroso derivatives. By reduction, pure N,N′-dimethyldiaminomesitylene resulted.

Anal. Calcd. for $C_{11}H_{16}N_4O_2$ (dinitroso derivative): C, 55.91; H, 6.82. Found: C, 58.13; H, 6.32.

The dinitroso derivatives were reduced readily to the N,N′-dimethyldiaminomesitylene. To a solution of 68 g. of stannous chloride in 66 ml. of concentrated hydrochloric acid was added 12 g. of dinitroso compound. After standing overnight, the solution was made strongly alkaline with sodium hydroxide and extracted with ether. The N,N′-dimethyl compound, $n^{20}D$ 1.5549, was distilled in vacuum and had the same boiling point previously mentioned for the crude product. Its picrate was identical in melting point with that reported above for the picrate of the N,N′-dimethyldiaminomesitylene purified merely by distillation.

N,N′-Diacetyl-N,N′-dimethyldiaminomesitylene (Method I).—To a solution of 31.5 g. of N,N′-dimethyldiaminomesitylene in 100 ml. of dry pyridine was added 59.4 g. of acetic anhydride in small portions. After standing overnight, the solvent was distilled under diminished pressure and a gummy residue remained. It was extracted with petroleum ether (b. p. 70–90°) for three days. The first fraction of 6 g. obtained in this way had a m. p. of 141–142° which did not change on recrystallization from petroleum ether (b. p. 30–70°). Successive fractions all melted lower and 5 g. of a partially crystallized oil remained as a final residue. By purification of these low-melting fractions from petroleum ether (b. p. 30–70°) more pure N,N′-diacetyl-N,N′-dimethyldiaminomesitylene resulted. No other solid product could be isolated.

Anal. Calcd. for $C_{15}H_{22}N_2O_2$: C, 68.66; H, 8.46; N, 10.68. Found: C, 68.56; H, 8.54; N, 10.15.

N,N′-Diacetyldiaminomesitylene.—To a solution of 70 g. of diaminomesitylene in 800 ml. of dry pyridine, 210 ml. of acetic anhydride was added in small portions with stirring. Before all the anhydride had been added, the diacetyl derivative began to separate. The mixture was heated a half-hour on the steam-bath then poured into ice-water. The crystalline diacetyl derivative was purified by crystallization from ethanol, m. p. 320–325° with decomposition (Maquenne Block); yield 50 g. (45%).

Anal. Calcd. for $C_{13}H_{18}N_2O_2$: N, 11.97. Found: N, 12.27.

N,N′-Diacetyl-N,N′-dimethyldiaminomesitylene (Method II) and N,N′-Diacetyl-N-methyldiaminomesitylene.—A suspension of 50 g. of N,N′-diacetyldiaminomesitylene in 600 ml. of ethanol was made alkaline with 5 g. of potassium hydroxide. With stirring, 15 ml. of methyl iodide was added. When this had reacted, 10 ml. more of methyl iodide was used and subsequently after standing overnight two additional portions of 10 ml. of methyl iodide and 5 g. of potassium hydroxide. Unchanged N,N′-diacetyldiaminomesitylene was filtered, and amounted to 85% of the total originally employed. The ethanol was distilled and the dry residue taken up in boiling benzene. After filtering from some potassium iodide, the solution was cooled and 5 g. (9.4%) of N,N′-diacetyl-N-methyldiaminomesitylene separated. Upon purification by further crystallizations from benzene, the product melted at 162.5°.

Anal. Calcd. for $C_{14}H_{20}N_2O_2$: C, 67.70; H, 8.12; N, 11.29. Found: C, 68.07; H, 7.97; N, 10.86.

The benzene filtrate from the crude N,N′-diacetyl-N-methyldiaminomesitylene was evaporated to dryness. After several recrystallizations from petroleum ether (b. p. 30–70°) the product was pure and melted at 141–142°. It proved to be identical with the diacetyldimethyldiamino compound previously described.

In the methylation of N,N′-diacetyldiaminomesitylene, powdered sodium in boiling xylene and methyl iodide were used as well as aqueous potassium hydroxide and dimethyl sulfate. The yields in both cases were essentially those reported from potassium hydroxide and methyl iodide.

By the action of powdered sodium and methyl iodide in boiling xylene, the diacetylmonomethyldiamino derivative, m. p. 162.5°, was converted into the diacetyldimethyldiaminomesitylene, m. p. 141–142°.

Diaminobromomesitylene.—To a suspension of 24.5 g. of dinitrobromomesitylene[6] in 100 ml. of 95% ethanol was added 200 ml. of concentrated hydrochloric acid, followed by 4.1 g. of tin. The mixture was heated to reflux and allowed to stand overnight. The unreacted tin was removed by filtration and the solution evaporated to dryness. The residue was taken up in 50 ml. of water. The solution was made alkaline with sodium hydroxide and extracted with ether. The ether solution was evaporated to dryness and the residue extracted repeatedly with hot petroleum ether (b. p. 70–90°). On cooling, 8.5 g. (44%) of crude diaminobromomesitylene crystallized. The product was purified by recrystallization from petroleum ether (b. p. 70–90°), m. p. 141–142°.

Anal. Calcd. for $C_8H_{13}N_2Br$: C, 47.16; H, 5.72; N, 12.22. Found: C, 47.27; H, 5.78; N, 12.16.

N,N′-Diacetyldiaminobromomesitylene.—To a solution containing 6.8 g. of diaminobromomesitylene dissolved in 35 ml. of pyridine was added 18 g. of acetic anhydride in small portions. The mixture was shaken vigorously during the addition and warmed gently for one hour. The precipitated material was filtered and dried; the yield was 7 g. (75%). The compound was purified by recrystallization from ethanol, m. p. 358°.

Anal. Calcd. for $C_{13}H_{17}O_2N_2Br$: C, 49.84; H, 5.47; N, 8.94. Found: C, 49.96; H, 5.59; N, 8.97.

Aminodinitromesitylene and Diaminonitromesitylene.—Trinitromesitylene was prepared according to the method of Blanksma[7] as modified by Lipscomb.[8]

A slow stream of hydrogen sulfide was passed through a refluxing suspension of 30 g. of trinitromesitylene in a mixture of 200 ml. of 95% ethanol and 40 ml. of 20% aqueous sodium hydroxide solution for four hours. At this time all the trinitromesitylene had dissolved leaving a dark red solution. The reaction was stopped and the ethanol partially evaporated on a steam-bath. On cooling the aminodinitromesitylene separated as a solid which after recrystallization from ethanol melted at 194–195°. The yield was 14 g. (53%). This is a superior procedure to that of Fittig[9] who obtained only a very low yield of the same product by the use of aqueous ammonia and hydrogen sulfide. He reported a m. p. 193–194°.

An identical mixture was treated with hydrogen sulfide in the same manner for a total time of ten hours during a three-day period. An additional 20 ml. of 20% aqueous sodium hydroxide solution was added on the second and again on the third day. The product was isolated by crys-

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(6) Fittig and Storer, *Ann.*, **147**, 8 (1868).

(7) Blanksma, *Rec. trav. chim.*, **21**, 336 (1902).

(8) R. D. Lipscomb, private communication.

(9) Fittig, *Ann.*, **141**, 139 (1867).

tallization from the partially evaporated reaction mixture and purified by recrystallization from ethanol. A yield of 15 g. (65%) of diaminonitromesitylene was obtained, m. p. 186–187°. The melting point recorded for this compound is 184°.[9]

N,N'-Dimethyltriaminomesitylene.—To a suspension of 10 g. of diaminonitromesitylene in 60 ml. of water was added 20 g. of dimethyl sulfate and the mixture warmed gently for two hours. A vigorous reaction took place and the diaminonitromesitylene went into solution. After standing overnight, the solution was made alkaline with sodium hydroxide and extracted with ether. The ether solution was dried over potassium hydroxide, filtered, and the ether removed by distillation. The crude mixture of methylated amines was dissolved in 17 ml. of concentrated hydrochloric acid and a solution containing 6.9 g. of sodium nitrite dissolved in 20 ml. of water was added dropwise. The solution was aged for fifteen minutes and the nitroso derivative extracted successively with ether and benzene. The extracts were combined and dried over potassium hydroxide and the solvents removed by distillation. The residue was dissolved in hydrochloric acid and treated with stannous chloride as previously described. The reaction mixture was made alkaline with sodium hydroxide and extracted with ether. After drying over solid potassium hydroxide, the ether was evaporated and the product distilled under reduced pressure, b. p. 139–141° (3 mm.). The yield was 2 g. (20%).

Anal. Calcd. for $C_{11}H_{19}N_3$: C, 68.36; H, 9.89; N, 21.75. Found: C, 68.09; H, 10.07; N, 21.47.

Summary

1. N,N'-Diacetyl-N,N'-dimethyldiaminomesitylene was prepared by methylation of N,N'-diacetyldiaminomesitylene and by acetylation of N,N'-dimethyldiaminomesitylene. Only a single isomer was obtained.

2. It is obvious in these molecules either that the methyl and acetyl groups do not cause adequate restriction between the nitrogen and the ring or that one isomer is formed exclusively in the reactions.

URBANA, ILLINOIS

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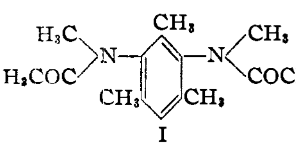
Restricted Rotation in Substituted Aromatic Amines. VI. Stereoisomers of N,N'-Dialkyl-N,N'-dibenzenesulfonyldiaminomesitylene[1]

BY ROGER ADAMS AND J. J. TJEPKEMA

cis and *trans* isomers of N,N'-dimethyl-N,N'-diacetyldiaminomesitylene (I) could not be obtained.[1] This failure may have been due to lack of restricted rotation because of the inadequate size of the methyl and acetyl groups. In this investigation, the influence of larger substituents on the nitrogen atoms was studied. The methyl groups were replaced by larger alkyl radicals and instead of the acetyl groups benzenesulfonyl groups were introduced.

By ethylation of diaminomesitylene, it was possible to obtain either a monoethyl derivative with a single amino group ethylated (II) or a diethyl derivative in which an ethyl group was substituted on each amino group (III). The hindrance to tri- and tetra-alkylation induced by the adjacent ring methyl groups makes possible the isolation of these mono- and dialkyl derivatives in a form essentially free from more highly alkylated products. For the preparation of the dialkyl derivative, one mole excess of ethyl bromide was used and this did not lead to the formation of by-products in appreciable amounts. Upon treatment of either the N-monoethyl (II) or the N,N'-diethyl derivative (III) with excess of benzenesulfonyl chloride in pyridine solution under mild conditions, the same monoethyldibenzenesulfonyl derivative (IV) was formed. An ethyl group from the diethyl derivative (III) is lost and replaced by a benzenesulfonyl group (IV). This unexpected replacement is probably the result of the crowded condition of the atoms. When the reaction of the diethyl derivative (III) with benzenesulfonyl chloride was carried out at more elevated temperatures, a small amount of the N,N'-dibenzenesulfonyldiaminomesitylene (VI) was also isolated. In this case both the ethyl groups were lost. On the other hand, the monoethyldibenzenesulfonyldiaminomesitylene (IV) could be alkylated in alkaline solution with ethyl bromide to the N,N'-diethyl-N,N'-dibenzenesulfonyldiaminomesitylene (V), m. p. 212–212.5°. Only one product was isolated. When N,N'-dibenzenesulfonyldiaminomesitylene (VI) was dialkylated with ethyl bromide under similar conditions, the main reaction product was V but an isomeric by-product was also formed, m. p. 168–169°. Because of the non-identity but great similarity of the infrared spectrum of this compound with that of V it is considered to be the stereoisomer of V. On the basis of the lower melting point and greater solubility it has been assigned the *cis*-form (VII).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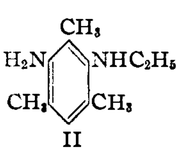
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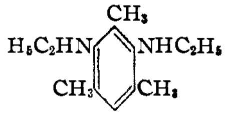
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The N,N'-dibenzenesulfonyldiaminomesitylene (VI) was also treated in alkaline solution with *n*-

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(1) For previous paper in this series, see (a) Adams and Chase, THIS JOURNAL, **70**, 2667 (1948); (b) Adams and Sundholm, *ibid.*, **70**, 2667 (1948).