Summary

1. Three isomeric crystalline tetra-acetyl-methyl-*d*-mannosides have been prepared and their melting points and specific rotations determined.

2. The isomer designated as γ-tetra-acetyl-methyl-*d*-mannoside exhibited properties not generally characteristic of the acetylated glucosidic derivatives of the sugars. When subjected to alkaline hydrolysis only three of the four acetyl groups were removed and when dissolved in methyl alcohol containing hydrogen chloride it was converted or transformed wholly or partially into other compounds.

3. A small yield of the new crystalline compound designated as β-tetra-acetyl-methyl-*d*-mannoside was obtained from the apparent equilibrium mixture resulting from the solution of γ-tetra-acetyl-methyl-*d*-mannoside in methyl alcohol containing hydrogen chloride.

4. These three crystalline tetra-acetyl-methyl-*d*-mannosides parallel closely the three triacetyl-methyl-*l*-rhamnosides, prepared by Fischer, Bergmann and Rabe, in specific rotation and in behavior upon hydrolysis. This analogy is interesting in view of the similarity in structure of mannose and rhamnose.

DECATUR, ILLINOIS

[CONTRIBUTION FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, LABORATORY OF ORGANIC CHEMISTRY]

COLOR TESTS FOR NITRO DERIVATIVES OF DIPHENYLAMINE[1]

BY TENNEY L. DAVIS AND AVERY A. ASHDOWN

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Means for the identification of the nitro derivatives of diphenylamine are to be desired for the reason that certain of these substances occur in aged smokeless powder. Diphenylamine is incorporated with the nitrocellulose which is used in the manufacture of smokeless powder in order that it may combine with the oxides of nitrogen which arise from the spontaneous decomposition of the nitrocellulose and so may prevent them from encouraging further decomposition. Nitrocellulose decomposes less rapidly when mixed with a little diphenylamine than when exposed to the acid products of its own decomposition. The diphenylamine is converted first into diphenylnitrosamine and later into nitro derivatives. A knowledge of the nitro derivatives of diphenylamine which occur in a sample of old smokeless powder will tell much about the past history of the powder, its present stability, and its fitness for future storage.

Experimentation is now in progress in this Laboratory on the isolation of nitro derivatives of diphenylamine from old smokeless powder. In

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[1] This experimentation was carried out in connection with a contract between the Ordnance Department and the Massachusetts Institute of Technology, and the present paper is published by permission of the Chief of Ordnance.

the present paper we wish merely to report color tests by which the pure nitro derivatives may be identified.

We have prepared all nitro derivatives of diphenylamine which seem likely to be produced during the ageing of smokeless powder, together with certain others which were thought to be of interest, all in a state of great purity, three of them of higher melting point than has been heretofore reported—and have examined the colors which they produce, under reproducible conditions, with alcoholic sodium hydroxide, alcoholic ammonia, alcoholic sodium cyanide, and concd. sulfuric acid. The colors differ greatly, from one end to the other of the visible spectrum.

Color Tests.—Color tests were carried out with the substances which are indicated in Table I. Melting points are corrected temperatures, determined with standard thermometers completely immersed.

TABLE I

COLOR TESTS FOR DIPHENYLAMINE DERIVATIVES

	M. p. °C.	Alcoholic NaOH	Alcoholic NH_3	Alcoholic NaCN	Concd. H_2SO_4
o-Nitro-diphenylamine	75–75.3	Y	Y-GY	Y-GY	none
m-Nitro-diphenylamine	110–112	none	none	none	none
p-Nitro-diphenylamine	131–133	YO-OY	GYT$_1$-GY	GYT$_1$-GY	RVT$_1$
2,4′-Dinitro-diphenylamine	156–156.4	OR	none	YO	YO-OY
2,4′-Dinitro-diphenylamine	220–221.5	R-OR	Y-GYT$_1$	OY	YO
4,4′-Dinitro-diphenylamine	216–216.5	VR	GYT$_1$	YGT$_2$	RO
2,4,6-Trinitro-diphenylamine	179.5–180	O-YO	O-YO	VRT$_2$	O
2,4,4′-Trinitro-diphenylamine	186–186.7	OR	O-OT$_1$	OR	OR
2,4,6,4′-Tetranitro-diphenylamine	220–220.6	YO	O-YO	BT$_2$	OY
2,4,2′,4′-Tetranitro-diphenylamine	201–201.5	ROT$_1$	ROT$_2$-ROT$_1$	ORT$_1$-ROT$_1$	OY
Diphenyl-nitrosamine	66– 67	none	none	none	B-BS$_1$

Tests were made (*a*) with a 1% solution of sodium hydroxide in alcohol previously purified by distillation from sodium hydroxide, (*b*) with 1% alcoholic ammonia, (*c*) with a saturated alcoholic solution of sodium cyanide, (*d*) with concd. sulfuric acid, and (*e*) with 1% alcoholic α-naphthylamine solution. Alcoholic solutions of the diphenylamine derivatives were made of such concentration that 0.2 cc. contained 0.1 mg. of the substance. In the case of three substances which were less soluble, namely, 2,4′-dinitro-diphenylamine, 2,4,4′-trinitro-diphenylamine, and 2,4,6,4′-tetranitro-diphenylamine, solutions of half this strength were prepared. Except in the test with concd. sulfuric acid, the tests were carried out by adding to 5 cc. of the reagent in a 75mm. test-tube an amount of the solution of the diphenylamine derivative equivalent to 0.1 mg. With sulfuric acid about 0.1 mg. of the dry substance was used. After the tubes had stood for five minutes their colors were compared, through the depth of the liquid, with the standard color chart in Vol. I of Mulliken's book on "The Identification of Pure Organic Compounds." The colors are reported by the letters which Mulliken uses in connection with that chart.

Diphenyl-nitrosamine was the only one of our substances which showed any color with the α-naphthylamine solution. In the cold it gave no color, but in hot solution an orange (O) color.

Preparation of Materials.—The three mononitro-diphenylamines were prepared according to the method described by Goldberg,[2] by refluxing bromobenzene with the corresponding nitro-aniline in the presence of anhydrous potassium carbonate and a trace of cuprous iodide. We have also used iodobenzene for the preparation of the *ortho* compound, and have prepared all three substances by refluxing bromobenzene with the corresponding nitro-acetanilide in the presence of anhydrous potassium carbonate and a trace of cuprous iodide, subsequently hydrolyzing the acetylnitro-diphenylamine by warming it with concd. hydrochloric acid solution. The products were purified by recrystallization from alcohol; the *o*-nitro compound gave orange-red leaflets, m. p. 75–75.3°; the *m*-, reddish-brown needles, m. p. 110–112°, and the *p*-, yellow leaflets, m. p. 131–133°.

2,4-Dinitro-diphenylamine was prepared by a slight modification of the method of Hoffman and Dame,[3] by warming aniline and 2,4-dinitro-chlorobenzene together until the reaction started, and recrystallizing the product from alcohol; reddish-brown needles were obtained; m. p., 156–156.5°.

2,4′-Dinitro-diphenylamine and 4,4′-dinitro-diphenylamine were prepared by the method which Gnehm and Werdenberg[4] had used for the preparation of the 4,4′- compound, namely, by the nitration of acetyl-diphenylamine. The crude acetyldinitro-diphenylamine was hydrolyzed by warming it with 40% sulfuric acid and the 2,4′- and 4,4′-derivatives were separated from each other by means of cold toluene in which only the first is soluble. The two substances were also prepared by refluxing *p*-nitro-acetanilide in nitrobenzene solution with *o*-nitro-bromobenzene and with *p*-nitro-bromobenzene in the presence of anhydrous potassium carbonate and a trace of cuprous iodide, followed by hydrolysis of the products by 40% sulfuric acid. They were finally prepared directly from *p*-nitro-aniline in nitrobenzene solution by the method which has been outlined.

When the attempt was made to prepare *o*- and *p*-nitrodiphenyl-nitrosamine by the nitration of diphenyl-nitrosamine according to the procedure of Juillard,[5] the product was found to consist of a mixture of 2,4′- and 4,4′-dinitro-diphenylamine with a certain amount of *p*-nitro-diphenylamine. We give a full report of the experiment, for it shows that nitric acid in glacial acetic acid solution causes diphenyl-nitrosamine to undergo the Fischer-Hepp rearrangement to yield *p*-nitroso-diphenylamine, which is further oxidized and nitrated to yield nitro-diphenylamines with at least one of the nitro groups in the *para* position.

A solution of 150 g. of diphenyl-nitrosamine (prepared according to Fischer,[6] and recrystallized from petroleum ether, m. p., 66–67°) in 1500 g. of glacial acetic acid was cooled in ice to a temperature of about 12°. A large crop of crystals precipitated. A solution of 75 g. (1 equivalent) of nitric acid (d., 1.38) in 100 g. of glacial acetic acid was run in slowly during an hour while the mixture was stirred and the temperature was kept below 15°. The crystals which had first separated dissolved during the nitration and were replaced by a very large crop of nearly white ones. When this white material was collected on a filter, rinsed with cold acetic acid, and exposed to the air for a few days to dry, it became yellow-brown like ocher. At this point in his experiment Juillard

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[2] Goldberg, *Ber.*, **40**, 4541 (1907).

[3] Hoffman and Dame, THIS JOURNAL, **41,** 1013 (1919).

[4] Gnehm and Werdenberg, *Z. angew. Chem.*, **1899,** 1051.

[5] Juillard, *Bull. soc. chim.*, [3] **33,** 1172 (1905).

[6] Fischer, *Ann.*, **190**, 174 (1878).

had obtained 119 g. of white material. We obtained 110 g. of colored material which melted at 128–132° and above. An alcohol solution of the material gave with alcoholic sodium hydroxide the red color which is characteristic of mixtures of 2,4′- and 4,4′-dinitro-diphenylamine and with concd. sulfuric acid the usual violet color of *p*-nitro-diphenylamine in that solvent. The entire product was extracted with cold toluene which dissolves 2,4′-dinitro-diphenylamine and *p*-nitro-diphenylamine but not 4,4′-dinitro-diphenylamine. The residue from the toluene extraction, fractionally recrystallized from alcohol, yielded 7 g. of pure 4,4′- dinitro-diphenylamine, as amber-colored needles with a steel-blue reflection; m. p., 216–216.5°, higher than has been reported heretofore for this substance. The toluene extract on evaporation yielded a residue which was recrystallized from alcohol to yield a high-melting fraction and a low-melting fraction. The high-melting fraction, worked up from a mixture of 9 parts of ethyl acetate and 1 part of alcohol, yielded about 20 g. of pure 2,4′-dinitro-diphenylamine, as orange-red needles melting at 220–221.5°, a higher temperature than has been reported heretofore for this substance. The low-melting fraction, worked up from alcohol, yielded about 3 g. of material melting at 128–131° which was identified as *p*-nitro-diphenylamine and which was not purified further. The "tailings" from this experiment were considerable, but, as there was no evidence that they contained anything except the substances which had already been isolated, they were not worked up.

2,4,6-Trinitro-diphenylamine was prepared by a modification of the original method of Clemm,[7] by the interaction of picryl chloride and aniline in hot alcohol solution, as bright, orange-red, short needles from ethyl acetate; m. p., 179.5–180°.

2,4,4′-Trinitro-diphenylamine was prepared by heating for 16 hours at 100° a mixture of 4 g. of 2,4-dinitro-chlorobenzene, 3.6 g. of *p*-nitro-aniline, 25 cc. of nitrobenzene, 2 g. of anhydrous potassium carbonate, and a trace of cuprous iodide. The nitrobenzene was removed by steam distillation, the excess of *p*-nitro-aniline by treatment with hydrochloric acid, and the solid residue recrystallized from alcohol, yielding a lemon-yellow, felt-like mass of small crystals; m. p., 186–186.7°.

2,4,2′,4′-Tetranitro-diphenylamine was prepared by the nitration of 2,4-dinitro-diphenylamine according to the method of Hoffman and Dame.[3] The crude product amounted to 94% of that calculated and softened at 170°, melting completely at 182–185°. It was sparingly soluble in the usual solvents and such as went into solution dissolved slowly. It was purified by fractional extraction, by heating it under a reflux condenser at least half an hour each time with repeated portions of fresh solvent. By this process the low-melting portions were removed by seven extractions with alcohol, and the high-melting portion (about 57%) by eleven extractions with ethyl acetate. These eleven fractions, combined and recrystallized from ethyl acetate (in which the material is more soluble than in alcohol) yielded beautiful, clear, lustrous, chlorine-green crystals; m. p., 201–201.5°. This melting point is 2° higher than that previously reported by Juillard.

Summary

We have prepared a number of nitro derivatives of diphenylamine in a state of great purity, three of them of higher melting point than has been hitherto reported.

The nitration of diphenyl-nitrosamine in glacial acetic acid at 15° has been studied.

Color reactions have been developed by which diphenyl-nitrosamine and ten nitro derivatives of diphenylamine may be distinguished.

CAMBRIDGE A, MASSACHUSETTS

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[7] Clemm. *J. prakt. Chem.*, [2] **1,** 145 (1870).