solved in 95% alcohol and to this mixture was added $^1/_{10}$ of its volume of conc. hydrochloric acid. On standing the diurethane separated in 90% yield. It forms fine, white crystals from alcohol, is nearly insoluble in hot water and melts at 190°.

Calc. for $C_{13}H_{17}O_6N_3$: N, 13.50. Found: 13.66, 13.41.

The introduction of the negative nitro group was found to have no effect, the urethane does not give an amide either with ammonia or with aniline, at temperatures up to 200°.

It is interesting to note in this connection that substituted urethanes, $R_2NCOOC_2H_5$, exhibit the same stability towards aniline on heating. For instance, phenyl-methyl-urethane[1] and diphenyl-urethane[2] failed to react with this amine when heated at 180–200°.

Summary.

(1) Carbonyl-diurethane and ammonia yield carbethoxy-biuret, allophanic ester, biuret and cyanuric acid.

(2) Aniline and substituted amines at varying temperatures give substituted carbethoxy-biurets, diureas, biurets and mono- and diureas.

(3) Carbethoxy-biurets or substituted carbethoxy-biurets are soluble in alkalies, but on acidifying, ring closure occurs with the formation of cyanuric acid or of mono-substituted-isocyanuric acids.

(4) Methylene-diurethane, phenyl and *o*-nitro-phenyl-methylene-diurethane show no tendency to react with ammonia or aniline, even when heated.

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[CONTRIBUTION FROM THE EXPLOSIVES CHEMICAL LABORATORY OF THE PITTSBURGH EXPERIMENT STATION, BUREAU OF MINES.]

THE PREPARATION OF HEXANITRO-DIPHENYLAMINE FROM CHLOROBENZENE.[3]

BY E. J. HOFFMAN AND PERRY A. DAME.

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The investigation of hexanitro-diphenylamine was undertaken by the Bureau of Mines at the suggestion of Dr. C. E. Munroe, Chairman, Committee on Explosives Investigations, because of interest in the subject on the part of the Army and Navy Ordnance Departments. The experimental part of this paper is confined to the presentation of experiments made by the authors on the preparation of this explosive substance, in 4 successive steps, from chlorobenzene.

Among the earlier investigators of hexanitro-diphenylamine were

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[1] *Ber.*, 17, 3043 (1884).

[2] *Ibid.*, 5, 284 (1872).

[3] Published by permission of the Director, U. S. Bureau of Mines.

Austen,[1] who prepared it by treatment of 2,4,6-picryl-*m*-nitraniline with nitric sulfuric acid; Gnehm,[2] who obtained it by the action of nitric acid alone on methyl-diphenylamine, and Mertens,[3] who prepared it by the action of fuming nitric acid on diphenylamine in conc. sulfuric acid solution.

According to Alexandroff,[4] hexanitro-diphenylamine is a typical example of a pseudo-acid. He describes a number of salts and esters of this pseudo-acid. A similar investigation is that of Hantzsch and Opolski,[5] in which 4 tautomeric forms of hexanitro-diphenylamine are indicated.

Very meagre information is to be found in the literature regarding the explosive properties of hexanitro-diphenylamine or its use as an explosive. Häussermann[6] states the result of a comparison of its explosive power with that of trinitro-toluene, and in a patent granted to Otto Freiherr von Schroetter[7] is described an explosive consisting of 80 parts hexanitro-diphenylamine and 20 parts dinitrotoluene.

In 1910 we find the first published[8] description of a method for the preparation of this explosive on the large scale. Briefly, this method consists in the nitration of diphenylamine in conc. sulfuric acid solution with fuming nitric acid, precipitation in water and purification of the product by washing with water. By this method 100 parts of diphenylamine yield about 170 parts of the explosive.

The method of Carter[9] for the manufacture of hexanitro-diphenylamine from dinitro-diphenylamine, formed by the combination of 1,2,4-chloro-dinitro-benzene and aniline, is the basis of some of the experiments in this paper.

The nitration of the dinitro-diphenylamine is effected in two stages. Tetranitro-diphenylamine is first prepared, using 36° Bé. nitric acid, and this is then converted into the hexanitro-diphenylamine with 48° Bé. acid.

The hexanitro-diphenylamine is a powder of pure yellow color, finely crystalline, needle-form, which melts with decomposition at 240–250°. It is insoluble in ether, benzene and alcohol; is very difficultly soluble in

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[1] P. T. Austen, "Ueber einige neue Nitrodiphenylamine," *Ber.*, 7, 1249 (1874).

[2] R. Gnehm, "Ueber Derivate des Methyl-diphenylamins," *Ibid.*, 7, 1399 (1874).

[3] K. H. Mertens, "Ueber einige neue Doppelverbindungen des Pikramids," *Ibid.*, 11, 843 (1878).

[4] D. K. Alexandroff, *J. Russ. Phys.-Chem Soc.*, 39, 1391 (1907); "Salts and Ethers of Hexanitrodiphenylamine," *J. Chem. Soc.*, Abs., I, 83 (1908).

[5] A. Hantzsch and St. Opolski, "Über einen violetten aci-Äther des Hexanitrodiphenylamins," *Ber.*, 41, 1745 (1908).

[6] C. Häussermann, "Über die explosiven Eigenschaften des Trinitrotoluols," *Z. angew. Chem.*, 17, 510 (1891).

[7] *U. S. Patent* 934,020, Sept. 14, 1909.

[8] "Fabrikation des Hexanitrodiphenylamins," *Z. ges. Schiess-Sprengs.*, 5, 16 (1910).

[9] Thomas Carter, "Ueber die Fabrikation des Hexanitrodiphenylamins," *Z. ges. Schiess-Sprengs.*, 8, 205, 251 (1913).

acetone. The best solvent is 48° Bé. nitric acid from which it separates after a long time as large crystals. Direct sunlight changes its color to brown. It is a very brisant explosive, scarcely suitable for explosive purposes except when mixed with other substances.

Hexanitro-diphenylamine is much more poisonous than nitroglycerin. It causes severe blisters, resembling burns, when it comes in contact with the skin. The fine dust especially affects destructively the mucous membranes of the mouth, nose and lungs.

Experimental.

The procedure followed in the preparation of hexanitro-diphenylamine from chlorobenzene involved the following steps: (1) Dinitro-chlorobenzene from chlorobenzene, $C_6H_5Cl + 2HNO_3 \longrightarrow C_6H_3(NO_2)_2Cl$; (2) dinitro-diphenylamine from dinitro-chlorobenzene, $C_6H_3(NO_2)_2Cl + C_6H_5NH_2 \longrightarrow C_6H_3(NO_2)_2.NHC_6H_5$; (3) tetranitro-diphenylamine from dinitro-diphenylamine, $C_6H_3(NO_2)_2.NHC_6H_5 + 2HNO_3 \longrightarrow C_6H_3(NO_2)_2.NHC_6H_3(NO_2)_2$; (4) hexanitro-diphenylamine from tetranitro-diphenylamine, $C_6H_3(NO_2)_2.NHC_6H_3(NO_2)_2 + 2HNO_3 \longrightarrow C_6H_2(NO_2)_3.NHC_6H_2$-$NO_2)_3$.

Dinitro-chlorobenzene.

Experiment 1.—The mixed acid used for the nitration of the chlorbenzene had the following composition:

		%
H_2SO_4	—	67.26
HNO_3	—	30.06
HNO_2	—	0.16
H_2O	—	2.52
		100.00

The chlorobenzene (101.7 g.), which boiled at 131–132°, was added gradually over a period of two hours to 507 g. of the mixed acid at an initial temperature 23°. The reaction caused a gradual rise of temperature to a maximum of 55°. When the last of the chlorobenzene had been added the temperature was 44°. By means of hot water passing through copper coils immersed in the white mineral oil used as bath for the nitration vessel, a deep liter beaker, the temperature of the reaction mixture was slowly raised to 95° and kept at that temperature for two hours longer.

The formation of dinitro-chlorobenzene was indicated by the separation of a supernatant layer of light yellow liquid, which on cooling solidified as a cake. The spent acid was drained off as much as possible, and the solid was treated with cold water, under which it was crushed. After filtration, the treatment with cold water was repeated several times. The product was then several times washed in the molten condition under hot water, after which it was again treated with cold water, crushed, and dried as much as possible on a Büchner filter. This product, dried at 35°, is designated as (*a*).

From the spent acid, by drowning in a large volume of ice water, filtering, washing and drying, a second lot (*b*) was obtained.

Yield: (*a*) 154.5 g., m. p. 45°; (*b*) 23.3 g., m. p. 47.7°; total, 177.8 g., or 97.12% of theoretical amount.

The reaction and the entire operation was controlled with remarkable ease. The vapors from the products of reaction were observed to cause severe smarting on the face and hands of the operator, but no serious inconvenience resulted. The product was very slightly yellow in color.

Experiment 2.—This experiment was conducted in practically the same manner as Expt. 1, using 118.5 g. of chlorobenzene and 590.6 g. of the mixed acid.

Yield: (*a*) 83.11%, m. p. 46.6°; (*b*) from acids, 13.26%, m. p. 47.7°; total yield. 96.37% of theoretical amount.

To purify further, a sample of (*a*) was washed several times with alcohol, then with water, and dried. The purified sample melted sharply at 50.06°. No further change in melting point was caused by repeating this treatment.

Experiment 3.—This experiment was conducted exactly as the two preceding experiments, except that the mixed acid had only approximately the composition of that previously used. It was prepared by mixing equal parts by weight of nitric acid (92.8%), sulfuric acid (93.3%) and oleum containing 14.2% of sulfur trioxide. Of this acid, 775 g. was taken to nitrate 150 g. of chlorobenzene.

Yield: (*a*) 248 g., m. p. 49°; (*b*) 13.2 g., m. p. at 47.7°; total, 261.2 g., or 96.73% of theoretical amount.

The average yield of dinitro-chlorobenzene in the 3 experiments was 96.74% of the theoretical amount. Since 100 g. of chlorobenzene yield theoretically 180.05 g. of dinitro-chlorobenzene, the experimental yield was 174.16 g. per 100 g. of chlorobenzene.

Dinitro-diphenylamine.

Experiment 1.—The dinitro-chlorobenzene, 150 g., was added gradually to 137.7 g. (approximately 2 molecules) of aniline which boiled at 177.5–179° (uncorr.). During the addition of about 100 g. of the dinitro-chlorobenzene (7 minutes) the temperature of the reaction mixture dropped from 22° to 10°. During the subsequent addition of the remainder of the dinitro-chlorobenzene the temperature rose to 15°. Just before the mixing was completed the entire contents of the beaker became a thick, pasty, red mass. The bath was then warmed up, and the stirring was continued for two hours at 18–29°.

The thick, pasty mixture was then dumped into cold water, filtered, and washed several times with dil. hydrochloric acid and afterwards with water. The product, dried at 75–100°, amounted to 181 g., or 94.32% of the theoretical amount. It melted at 154.2–155.5°.

Experiment 2.—The same proportions of dinitro-chlorobenzene (150 g.) and aniline (137.7 g.) were taken for this experiment and the procedure was the same as in Expt. 1. The temperature dropped from 24° to 12° during the mixing, and then toward the end of this operation, which required 8 minutes, it rose to 16°. The stirring was continued a little more than an hour longer, in which time the temperature had risen to 30°.

The yield of dinitro-diphenylamine, m. p. 157°, was 161 g., or 83.90% of the theoretical amount.

The mean yield of dinitro-diphenylamine from 150 g. of dinitro-chlorobenzene was 171 g. or 89.11% of the theoretical amount. This correponds to a yield of 198.54 g. of dinitro-diphenylamine from 174.16 g. of dinitro-chlorobenzene (from 100 g. of chlorobenzene).

Tetranitro-diphenylamine.

Experiment 1.—The procedure followed in the conversion of dinitro-diphenylamine into tetranitro-diphenylamine was that described by Carter (see p. 1014).

840 g. of 36° Bé. nitric acid was heated to 40° in the liter beaker of the nitration apparatus. To this, 100 g. of the finely powdered dinitro-diphenylamine was added in small portions. The temperature of the mixture rose slowly in one hour to 52°, and in order to maintain this or higher temperatures it was necessary to pass hot water through the heating coils. In another hour the temperature reached a maximum of 62°.

As the nitration progressed there was a gradual change from red to yellow in the color of the solid in suspension. Unfortunately the final volume of the mixture in the beaker was too large to permit of thorough mixing, and in consequence nitration was incomplete and some unchanged red dinitro-diphenylamine was included in the product. The product was filtered directly on cooling, washed until free from acid and dried.

Yield: 103 g., m. p. 164–168.5°; or 76.44% of the theoretical amount.

Experiment 2.—In this experiment the acid was heated to 40°, and moderate heating was continued throughout the entire operation. The proportions of reacting materials taken were 420 g. of 36° Bé. nitric acid and 50 g. of the dinitro-diphenylamine. The addition of the amine to the acid required about 2 hours at a maximum temperature of 62°. Afterwards the operation was continued for 3 hours at 62° to 90°.

The yield of clean yellow product was 55.3 g., m. p. 187.4°; or 82.08% of the theoretical amount.

Experiment 3.—This experiment was made with the same quantities and proportions of reacting materials as in Expt. 2, and under practically the same conditions except that the operation was continued only one hour instead of 3 after completion of the mixing.

Yield of tetranitro-diphenylamine was 53.6 g., m. p. 185.2°; or 79.55% of the theoretical amount.

Since in Experiment 1 the yield of impure and incompletely nitrated product was 103 g. from 100 g. of dinitro-diphenylamine, in the same ratio 198.54 g. of dinitro-diphenylamine (from 100 g. of chlorobenzene) would have yielded 204.5 g. of tetranitro-diphenylamine of the same degree of purity.

The mean yield of tetranitro-diphenylamine in Expts. 2 and 3 (80.82% of the theoretical amount) was 108.9 g. per 100 g. of dinitro-diphenylamine. In this ratio 198.54 g. of dinitro-diphenylamine (from 100 g. of chlorobenzene) would yield 216.21 g. of tetranitro-diphenylamine.

Hexanitro-diphenylamine.

Experiment 1.—In this experiment the method of Carter was followed quite closely (p. 1014). 600 g. of 48° Bé. nitric acid and 54.3 g. of the tetranitro-diphenylamine which melted at 187.4° were used. The solid amine was added a little at a time, throughout one hour, to the acid previously warmed to 40°. Moderate external heat was required to bring the temperature of the mixture up to 70°. After the addition of the last portion of the amine the temperature of the mixture was kept between 70 and 90° for 3 hours, with constant stirring. A very copious evolution of oxides of nitrogen was observed, as well as a very considerable volatilization of acid. At the end of the operation the volume of acid remaining was scarcely $^1/_2$ the original volume, and it is very probable that there was also loss of nitrated product by volatilization.

On cooling and standing overnight some light yellow crystals separated. The acid was drained off as much as possible and the crystals were washed well with water. This portion of the product of nitration amounted to 24.3 g., or only 35.58% of theoretical. The crystals melted at about 240°, but decomposition began much below this temperature.

From the spent acid, by precipitation in cold water, a second lot of crystals, 5.2 g., or 7.61% of theoretical, was obtained. This product, which had a dirty brown color, melted with decomposition at about 233°.

Experiment 2.—The procedure here was the same as in Expt. 1. The same quantity of 48° Bé. nitric acid was used, and 53.6 g. of the tetranitro-diphenylamine which melted at 185.2°. A maximum temperature of 85° was attained and approximately this temperature was maintained for 4 hours. At the end of the operation, on cooling to 60°, beautiful, yellow crystals separated. These were washed with water and brought upon the filter. During filtration the hardened filter paper became brown and the wash water was likewise colored brown. The very small precipitate from the spent acid could not be filtered on account of disintegration of the filter paper, producing dark, frothy filtrates.

The yield of yellow crystals was 21.7 g., or only 32.18% of the theoretical amount. These melted at about 243°, but the decomposition set in at as low as 160°.

Experiment 3.—The two experiments just described having proved unsuccessful, a third was made, in which a mixed acid was used instead of nitric acid alone, and a low temperature of nitration was maintained.

The acid used for nitration was made by mixing equal parts by weight of 92% sulfuric acid and 93% nitric acid, and had approximately the following composition: H_2SO_4, 46%; HNO_3, 46.5%; H_2O, 7.5%.

To 500 g. of the mixed acid at 20°, 50 g. of the tetranitro-diphenylamine prepared in Expt. 1, under Tetranitro-diphenylamine, and known to contain some unchanged dinitro-diphenylamine, was added gradually in a little more than an hour. During this operation the maximum temperature reached was 27°. On each addition of the amine there was considerable darkening of material, but the suspended material slowly became bright yellow as the action continued. Afterwards the temperature was allowed to rise to 32° in 1.5 hours, and during the following 3 hours the temperature dropped to 23°.

The entire contents of the nitration vessel were dumped into a large volume of ice water. The yield of purified product was 65.5 g., somewhat in excess of the theoretical yield, which is readily explained, as above suggested, by the previous incomplete nitration of the dinitro-diphenylamine to tetranitro-diphenylamine.

The product, fine, yellow crystals, was completely soluble in cold acetone and in hot glacial acetic acid, fairly soluble in cold and hot alcohol and very slightly soluble in ether. It was insoluble in cold acetic acid and in cold and hot chloroform.

The original product melted at 244.5° with decomposition beginning at 160°. A sample recrystallized from acetone melted at 242.9°, with decomposition observed at 204°. Recrystallized from glacial acetic acid it melted at 240.1°, with decomposition beginning at about 189°.

In Expt. 3, 50 g. of low grade tetranitro-diphenylamine yielded 65.5 g. of hexanitro-diphenylamine. In this proportion, 204.5 g. of the same tetranitro-diphenylamine (from 100 g. of chlorobenzene) would yield 267.9 g. of hexanitro-diphenylamine. Since 100 g. of chlorobenzene yields theoretically 390.4 g. of hexanitro-diphenylamine, the yield of the latter from 100 g. of chlorobenzene obtained experimentally through Expt. 3 was 68.62% of the theoretical amount.

Conclusions.

The results of this brief investigation show that hexanitro-diphenylamine can be prepared with remarkable ease, and in good yields, from chlorobenzene. No one of the successive operations involves the slightest difficulty, provided nitric-sulfuric acid is substituted for the 48° Be. nitric acid of Carter's method for the conversion of tetranitro-diphenylamine into hexanitro-diphenylamine, and a lower temperature of nitration is maintained in that operation.

The very satisfactory results obtained in converting a crude incompletely nitrated tetranitro-diphenylamine product into hexanitro-diphenylamine by the use of nitric-sulfuric acid at a maximum temperature of 32°, suggest the possibility of eliminating altogether the intermediate preparation of tetranitro-diphenylamine and proceeding directly in one operation from dinitro-diphenylamine to hexanitro-diphenylamine. This procedure should result in considerable reduction in time and cost of production.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE CONDENSATION OF β-AMINO-PROPIOPHENONE WITH NITROMALONIC ALDEHYDE.

BY WILLIAM J. HALE AND EDGAR C. BRITTON.

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The formation of a pyrrole derivative by the condensation of nitromalonic aldehyde with an ester of aminoacetic acid has been demonstrated in the work of Hale and Hoyt.[1] One aldehydic group of this aldehyde was herein found to react primarily with the amino group of the ester and result directly in the production of an intermediate compound (I) which immediately rearranges itself into the form (II), α-carbethoxy-β-methylamino-α-nitro-acrolein, a point just recently explained by Hale and Honan.[2] The next step in the condensation—that of involving the second aldehydic group in reaction with the methylenic group of the aliphatic ester substituent in (II), was brought about by mild alkali and resulted in the formation of the pyrrole (III). In the work of Hale and Honan[3] this investigation was extended to a study of the condensation of β-alanine ester with nitromalonic aldehyde. In this instance two methylenic groups are situated between the amino group and the carbethoxyl group. It was anticipated accordingly that here, after the formation of the first step in the reaction to an acrolein derivative, we should have present the possibility for a pyridine synthesis through the condensation of the aldehydic group with the second methylenic group or that one adjacent to the carbethoxyl group itself. Negative results, however, dismissed this expectancy, and indicated quite clearly that the carbethoxyl group is

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[1] THIS JOURNAL, 37, 2538 (1915).

[2] *Ibid.*, 41, 770 (1919).

[3] *Loc. cit.*