and some external cooling was applied to compensate an initial heat effect and maintain a moderate temperature. After the mixture had stood at room temperature for two hours, 1 lb. (320 cc.) of concentrated nitric acid (sp. gr. 1.5) was added all at once with external cooling and the solution was allowed to stand at room temperature for five hours and then drowned in 1500 cc. of ice and water. The crude, nearly colorless precipitate, when air-dried weighed 126 g. (99%) and melted at 124–129°. For crystallization it was dissolved rapidly in 250 cc. of hot acetone and 1 liter of 95% alcohol was added all at once, whereupon there was deposited 95.3 g. (75%) of the product in the form of colorless, diamond-shaped prisms, m. p. 131.8–132.8°. A sample for analysis was recrystallized by dissolving the material in cold acetone, adding a large volume of alcohol, and chilling the solution in order to promote rapid crystallization and avoid decomposition. The sample melted at 132.2–132.7° and after solidification remelted at the same temperature.

Anal. Calcd. for $C_8H_7O_7N_3$: C, 37.36; H, 2.74. Found: C, 37.68; H, 2.76.

When the mother liquors from this preparation were concentrated on the steam-bath, the solution on cooling deposited 11.8 g. of the known[8] *2,ω-dinitrostyrene* in the form of yellow needles, m. p. 106.2–107.2°; a recrystallized sample melted at 106.5–107.5°. In earlier experiments in which the crude nitrate was crystallized from acetone–alcohol in the ordinary way without avoidance of all unnecessary heating, the recovery of the nitrate was small, for the bulk of the material had been converted into the dinitrostyrene.

α-(2,4-Dinitrophenyl)-β-nitroethanol (V).—Upon the addition of 0.1 cc. of triethylamine to 6 g. of 2,4-dinitrobenzaldehyde in 6 cc. of nitromethane the solution at once acquired a red color and became warm. It was cooled to room temperature and allowed to stand overnight in the cold room, when 3.85 g. (49%) of prisms of the alcohol had separated. The crystallizate was contaminated with a trace of a reddish impurity which was eliminated easily by recrystallization from alcohol containing two drops of hydrochloric acid; this gave 3.22 g. (41%) of slightly yellow prisms, m. p. 123–125°. After three recrystallizations from alcohol (Norit) the substance formed nearly colorless prisms, m. p. 124.5–125.5°.

Anal. Calcd. for $C_8H_7O_7N_3$: C, 37.36; H, 2.74. Found: C, 37.51; H, 3.18.

α-(2,4-Dinitrophenyl)-β-nitroethyl Nitrate (VI).—A solution of 1.55 g. of the above alcohol in 25 cc. of nitric acid (sp. gr. 1.5) was allowed to stand at room temperature for one and one-half hours and drowned in cold water. The precipitate of crude but satisfactory nitrate ester amounted to 1.33 g. (73%), m. p. 108–112°. Two crystallizations made by dissolving the substance in cold acetone and adding alcohol afforded 0.2 g. of colorless, diamond-shaped prisms, m. p. 114.2–114.8°. After solidification, the test sample remelted at the same temperature.

Anal. Calcd. for $C_8H_6O_9N_4$: C, 31.80; H, 2.00. Found: C, 32.22; H, 2.17.

2,4,ω-Trinitrostyrene (VII).—The mother liquors from the crystallization of the above nitrate ester were combined and concentrated and the solution was heated for one hour on the steam-bath to effect complete elimination of nitric acid. On cooling, there was obtained 0.4 g. of prisms, m. p. 103–106°. Three recrystallizations from alcohol afforded light yellow prisms, m. p. 106.2–106.8°.

Anal. Calcd. for $C_8H_5O_6N_3$: C, 40.18; H, 2.11. Found: C, 40.38; H, 2.31.

Summary

A convenient procedure for the preparation of the 2-nitro derivative of α-phenyl-β-nitroethyl nitrate has been found in the condensation of *o*-nitrobenzaldehyde with nitromethane in the presence of triethylamine, and nitration of the total reaction mixture. The 2,4-dinitro derivative has been prepared by a similar process. The nitrate esters probably are too labile to merit consideration as explosives.

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CAMBRIDGE, MASSACHUSETTS
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, HARVARD UNIVERSITY]

Aromatic–Aliphatic Nitro Compounds. II. The Condensation of Nitrophenylnitromethanes with Formaldehyde[1]

BY LOUIS F. FIESER AND MARSHALL GATES

Vanderbilt and Hass[2] have described excellent procedures for the condensation of formaldehyde with nitroparaffins, for example, using calcium hydroxide as the condensing agent without solvent, and for the conversion of the resulting nitro diols into the dinitrate esters. On undertaking to apply this scheme of synthesis to phenylnitromethane derivatives in the hope of obtaining polynitro nitrate esters having the properties of high explosives, we thought it desirable to use a solvent and to employ an organic catalyst. It was found that phenylnitromethane and its nuclear nitro derivatives condense smoothly with two molecules of formaldehyde in aqueous dioxane in the presence of triethylamine at moderate temperatures.

Phenylnitromethane itself afforded in excellent yield the crystalline condensation product VI, 2-nitro-2-phenylpropanediol-1,3. Before investigating the nitration of this compound, we first prepared by independent syntheses the products expected to result from an attack of the nucleus. Holleman[3] found that phenylnitromethane can be converted into the *m*-nitro derivative II by nitration with fuming nitric acid at a low temperature, while Urbanski[4] observed that the further nitration of II with fuming nitric and sulfuric acids results in the formation of 3,5-dinitrophenylnitromethane (III), a substance reported to be as powerful an explosive as 2,4,6-trinitrotoluene, more stable to heat than this substance, but less stable to shock. No data have been given concerning the yields in these reactions. In our

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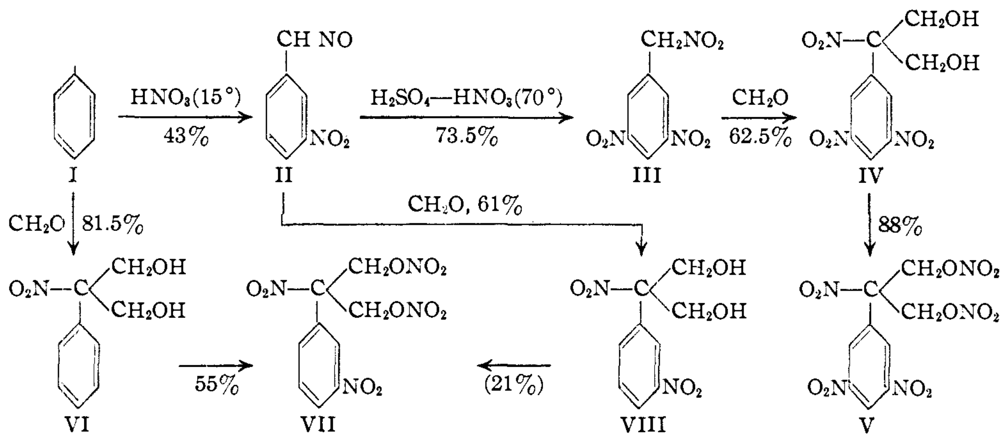
[1] Work conducted in 1940–1941 under Contract No. NDCrc-5 with the Office of Scientific Research and Development.

[2] Vanderbilt and Hass, *Ind. Eng. Chem.*, **32**, 34 (1940).

[3] Holleman, *Rec. trav. chim.*, **14**, 121 (1895).

[4] Urbanski, *Compt. rend.*, **206**, 1122 (1938).



hands the mononitration according to Holleman, conducted in 50-g. lots, gave the *m*-derivative II in 40–43% yield, along with 2–3% of the *p*-isomer, while the further nitration could be conducted on an even larger scale and afforded III in 71–73.5% yield. Both substances condensed smoothly with formaldehyde in dioxane in the presence of triethylamine to give the crystalline diols VIII and IV. The nitration of these diols with fuming nitric acid presented no difficulties, and the dinitrate esters VII and V were obtained as stable crystalline solids which melt without decomposition and give no test for acidity. The former substance, 2-nitro-2-(*m*-nitrophenyl)-propanediol-1,3 dinitrate (VII) was then found to be obtainable more conveniently and in much higher over-all yield by nitration of the product of the condensation of phenylnitromethane with formaldehyde (VI). Attempted further nitration of VII, which might be expected to afford the 3,5-dinitro compound V, either yielded unchanged starting material or resulted in its destructive oxidation. Since the reaction was tried under conditions suitable for conversion of *m*-nitrophenylnitromethane into the 3,5-dinitro .compound III, it appears that the group —$C(NO_2)(CH_2ONO_2)_2$ has a stronger deactivating or meta effect on the aromatic nucleus than the substituent —CH_2NO_2. A similar relationship is manifest in the higher yield of meta isomer in the nitration of VI, as compared with the reaction I → II.

2-Nitro-2-(3′,5′-dinitrophenyl)-propanediol-1,3 dinitrate (V), the most highly nitrated member of the series, melts at 115.2–115.8° and has an almost ideal oxygen balance: $C_9H_7O_{12}N_5 \rightarrow 9\,CO + 5/2\,N_2 + 3\,H_2O + 1/2H_2$.

The explosive properties of the new substances were investigated by the staff of the explosives Research Laboratory of NDRC at Bruceton, Pa., and were reported by Dr. R. McGill of that Laboratory. 2-Nitro-2-(*m*-nitrophenyl)-propanol-1,3 dinitrate (VII) was found slightly less sensitive to impact than TNT, and 2-nitro-2-(3′,5′-dinitrophenyl)-propanol-1,3 dinitrate (V) slightly less sensitive than PETN. Ballistic strengths relative TNT (100), Tetryl (125.5), PETN (145.8), and Cyclonite (150.2) are as follows: 2-nitro-2-(*m*-nitrophenyl)-propanediol-1,3 dinitrate (VII), 114; 2-nitro-2-(3′,5′-dinitrophenyl)-propanediol-1,3 dinitrate (V), 126.

Experimental Part[5]

Preparation of Starting Materials.—***m*-Nitrophenylnitromethane** was prepared satisfactorily by the nitration of phenylnitromethane[6] in 50-g. batches according to Holleman[3] with fuming nitric acid (sp. gr. 1.5, 250 cc.) at 15°. It was found expedient to crystallize the crude product from a rather large volume of glacial acetic acid (120 cc.) in order to avoid contamination of the main product with the *p*-isomer. The yield of satisfactory *m*-isomer, m. p. 92–94°, was 40–43%, and the mother liquors afforded up to 2.7% of ***p*-nitrophenylnitromethane**, m. p. 89–91°; a recrystallized sample formed yellow blades, m. p. 90–91.5° (depression with *m*-isomer).

The preparation of **3,5-dinitrophenylnitromethane** by the nitration of *m*-nitrophenylnitromethane according to Urbanski[4] was carried out with lots as large as 107 g. (added to a chilled mixture of 250 cc. of 25% fuming sulfuric acid and 300 cc. of fuming nitric acid, sp. gr. 1.5, temperature controlled to 65–70°). The crude product was best dissolved by adding a slurry of the material in acetone to 1 liter of alcohol near the boiling point, followed by brief heating to bring it all into solution. The product crystallized in nearly colorless, large flat plates, m. p. 131–132°; yield 71–73.5%.

The Formaldehyde Condensation

2-Nitro-2-phenylpropanediol-1,3 (VI).—A mixture of 52.2 g. of freshly distilled phenylnitromethane, 65 g. of 37% formalin solution, and 90 cc. of purified dioxane was treated with 2.5 cc. of triethylamine, added slowly. The solution warmed rapidly to 60°, at which point the rise was checked by brief cooling under the tap. After standing for one-half hour, the mixture was diluted with water and extracted three times with ether. The ethereal solution was washed with saturated brine, filtered through sodium sulfate, and concentrated, eventually at the vacuum pump. The weakly colored residual oil partially crystallized, and after dilution with ether–petroleum ether and chilling, the solid was collected. This first crop consisted of 33.6 g. of small, colorless prisms, m. p. 94–97°. The filtrate was concentrated until the bulk of the solvent had been removed and the oil was taken up in benzene, whereupon there was obtained two successive crops of colorless prismatic blades, 18.1 g. (95–97°) and 9.4 g. (96–98°); total yield 61.2 g. (81.5%). The use of benzene in place of ether–petroleum ether for the collection of the second and third

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[5] Microanalyses by Eleanor Werble. All melting points are corrected.

[6] We are indebted to Ernst Berliner for the preparation of the bulk of the phenylnitromethane required according to Black and Babers, "Organic Syntheses," 19, 73 (1939), yield 56–60%

crops gives material of superior quality and the recovery is better by about 10%.

The yield recorded was duplicated in other runs, but on one occasion a sample of phenylnitromethane which had been standing for about one month gave only a small amount of material which melted at 65–75° even after repeated crystallization. The remainder of the phenylnitromethane was then washed with saturated bisulfite solution and with bicarbonate solution and redistilled at 0.4 mm., whereupon it afforded a satisfactory condensation product in the yield reported.

The nitro alcohol is very soluble in alcohol or acetone, readily soluble in ether, very slightly soluble in petroleum ether, and rather sparingly soluble in cold benzene. A sample recrystallized twice from ether–petroleum ether melted at 97.5–98.5°.

Anal. Calcd. for $C_9H_{11}O_4N$: C, 54.81; H, 5.62. Found: C, 55.02; H, 5.85.

2-Nitro-2-(*m*-nitrophenyl)-propanediol-1,3 (VIII) — The homogeneous, nearly colorless, solution of 2.00 g. of *m*-nitrophenylnitromethane, 2 cc. of formalin solution, and 6 cc. of dioxane when treated with 0.1 cc. of triethylamine immediately turned bright orange-yellow and warmed to about 45°. The product was recovered as before by drowning and ether extraction (the yellow color remains largely in the water layer) and obtained as an oil which solidified when rubbed under petroleum ether containing a little ether. Crystallization from ether–petroleum ether and recrystallization of the three crops obtained gave a total of 1.63 g. (61%) of product melting in the range 105-107°. On further crystallization the substance formed faintly yellow, flat, hexagonal plates, m. p. 106.1–107.1°. The substance is only moderately soluble in ether, readily soluble in alcohol, and very slightly soluble in petroleum ether.

Anal. Calcd. for $C_9H_{10}O_6N_2$: C, 44.63; H, 4.16. Found: C, 44.73; H, 4.09.

2-Nitro-2-(3,5-dinitrophenyl)-propanediol-1,3 (IV).— The addition of 1 cc. of triethylamine to a mixture of 10.0 g. of 3,5-dinitrophenylnitromethane, 10 cc. of formalin solution, and 40 cc. of dioxane produced an orange color and caused the temperature to rise from 38 to 55°. The solution was warmed to 60° on the steam-bath and then allowed to cool and processed as usual. The mixture was darker than in the above instances, and it was found advantageous to add a little hydrochloric acid to the brine used to wash the ethereal extract in order to discharge a dark brown or purplish color. The oily product collected after removal of the solvent was pumped out overnight to remove traces of dioxane and then taken up in benzene and allowed to crystallize. A first crop of tan needles (7.00 g., 121–124°) when recrystallized from benzene containing a little acetone gave 6.26 g. of satisfactory material, m. p. 124–125°, and a second crop when recrystallized afforded 1.67 g., m. p. 123-125°; total yield, 7.93 g. (62.5%). In another run with 1 g. of starting material the yield was 69%, but when the amount was increased to 170 g. the yield was only 45%.

A sample of the condensation product when recrystallized twice from benzene containing a little acetone formed very nearly colorless needles, m. p. 124.6–125.3°.

Anal. Calcd. for $C_9H_9O_8N_3$: C, 37.64; H, 3.16. Found: C, 38.02, 38.08; H, 3.34, 3.36.

Nitration of the Nitroalcohols

2-Nitro-2-(*m*-nitrophenyl)-propanediol-1,3 Dinitrate (VII). (a) From the Corresponding Diol, VIII.—On adding 200 mg. of 2-nitro-2-(*m*-nitrophenyl)-propanediol to a well-chilled mixture of 0.4 cc. of concentrated sulfuric acid and 0.15 cc. of nitric acid (sp. gr. 1.41, freed from nitrous acid with urea) the solid first became oily and finally went into solution. The mixture was drowned after ten minutes, giving a heavy oil which failed to solidify when rubbed with alcohol (only moderately soluble) or hexane, but which eventually crystallized on standing under alcohol for two weeks. The washed solid (86 mg., 65–70°) when recrystallized from alcohol afforded 59 mg. (21%) of the colorless dinitrate, m. p. 72–73.5°. On a further recrystallization from alcohol the crystals separated as sheaves of acicular prisms, m. p. 72.6–73.6°. A crushed sample gives no test for acidity with moistened litmus paper.

Anal Calcd. for $C_9H_8O_{10}N_4$: C, 32.54; H, 2.43. Found: C, 32.34; H, 2.44.

In another experiment with 200 mg. of the diol, nitric acid alone was used (2 cc., sp. gr. 1.5, room temperature); the yield of product of the same quality from the first crop was again 21%. The yield probably could be improved, but in view of the superiority of the alternate one-step process (b) this was not investigated.

(b) **From 2-Nitro-2-phenylpropanediol-1,3 (VI).**—To 100 cc. of fuming nitric acid (sp. gr. 1.5), which had been chilled to 5°, 10.0 g. of 2-nitro-2-phenylpropanediol-1,3 was added at such a rate that the temperature did not rise above 10°; the solid dissolved at once with a transient orange color and no fuming or gas evolution occurred. When the addition had been completed the mixture was drowned in 500 cc. of ice water and extracted twice with ether. The ethereal layer was washed several times with water and then with brine, filtered through sodium sulfate and concentrated. The residual oil crystallized when manipulated in alcohol containing a little acetone. Probably because of the presence of isomers, the material initially tends to oil out, and it is advantageous to seed the solution and allow it to cool very slowly. The first crop gave, on recrystallization as before, 9.27 g. (55%) of satisfactory material in the form of column-like prisms, m. p. 72.6–73.6°. There was no depression in the melting point on mixing samples prepared by methods (a) and (b). The yield cited was duplicated in 200-mg. runs, and when 70 g. of material was nitrated the yield was 49.5%.

2-Nitro-2-(3′,5′-dinitrophenyl)-propanediol-1,3 Dinitrate (V).—To 130 cc. of fuming nitric acid (sp. gr. 1.5), cooled to 5°, 20.0 g. of 2-nitro-2-(3′,5′-dinitrophenyl)-propanediol was added in several portions. The temperature rose to 10° and after six minutes the material had all gone into solution, and at this point the mixture was drowned in 1.5 liters of ice and water. The precipitated gummy solid soon hardened and, after standing for fifteen minutes, was collected and washed well with water. For purification the crude product was dissolved in acetone (readily soluble) and the solution was filtered and diluted with alcohol (sparingly soluble cold), and allowed to crystallize. The first crop was light tan material weighing 23.0 g. (87.8%) and melting at 114.6–115.5°. The yield was about the same with 0.2–2 g. lots (84–86%), but when 83 g. of material was nitrated by the same procedure, the yield dropped to 67%. The nitration proceeded less satisfactorily with a mixture of nitric acid (sp. gr. 1.5, 1 cc.) and 30% fuming sulfuric acid (2 cc.), for the solid changed to a gummy oil which hardened when manipulated but at no time went completely into solution (yield 52%)

When crystallized for analysis from alcohol containing a little acetone, the dinitrate formed colorless, flat, rectangular plates, m. p. 115.2–115.8° (test for acidity negative). The substance sometimes crystallizes in the form of prisms.

Anal. Calcd. for $C_9H_7O_{12}N_5$: C, 28.66; H, 1.87 Found: C, 28.85; H, 2.19.

All attempts to prepare the dinitrate V starting with 2-nitro-2-(*m*-nitrophenyl)-propanediol (VIII) or its dinitrate (VII) were unsuccessful. Thus when a mixture of 200 mg. of VIII with 1 cc. of 30% fuming sulfuric acid and 1.2 cc. of nitric acid (sp. gr. 1.5) was warmed cautiously at 70–75° for five minutes, the only reaction product was the dinitrate VII (124 mg., m. p. 72.8–73.4°), and when VII was submitted to the same treatment for ten minutes it was recovered unchanged. In another trial the diol (200 mg.) was heated with 2 cc. each of oleum (30%) and nitric acid (sp. gr. 1.5) at 80° for two hours, but when the mixture was drowned in water no product precipitated, indicating that the starting material had been oxidized. An attempt to carry out the nitration at 100–110° in the course of a few minutes resulted in a fume-off.

Summary

The condensation of two molecules of formaldehyde with phenylnitromethane and with its *m*-nitro and 3,5-dinitro derivatives can be accomplished smoothly in dioxane solution in the presence of triethylamine and gives crystalline diols. The first two on nitration afford 2-nitro-2-(*m*-nitrophenyl)-propanediol-1,3 dinitrate, and the third yields 2-nitro-2-(3′,5′-dinitrophenyl)-propanediol-1,3 dinitrate. The first ester is a slightly more powerful explosive than TNT, the second is comparable to Tetryl.

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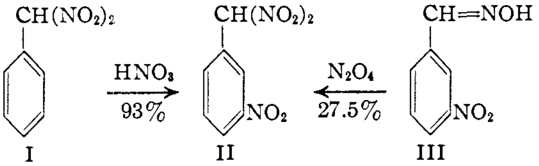
[CONTRIBUTION FROM THE CHEMICAL LABORATORY, HARVARD UNIVERSITY]

Aromatic-Aliphatic Nitro Compounds. III. The Ponzio Reaction; 2,4,6-Trinitrobenzyl Nitrate[1]

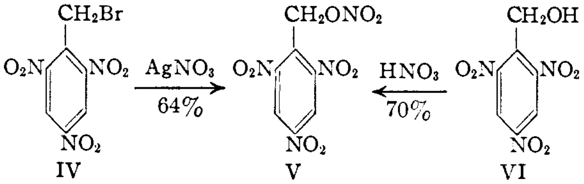
BY LOUIS F. FIESER AND WILLIAM VON E. DOERING

m-Nitrophenyldinitromethane (II) is reported by Milone and Massa[2] to be a more powerful explosive than the isomers TNT and 3,5-dinitrophenylnitromethane.[3] In the preparation of a large quantity of II for further evaluation, some additional observations have been made concerning the interesting reaction discovered by Ponzio[4] in which benzaldoxime is converted into phenyldinitromethane (I) by the action of nitrogen dioxide in ether. When the reagents were merely mixed and allowed to react in the prescribed way a fume-off sometimes occurred, but we found that the controlled addition of the oxime in ether to ethereal nitrogen dioxide under reflux obviated the difficulty. This has the further advantage of maintaining an excess of nitrogen dioxide over oxime, for the reverse situation promotes side reactions producing the insoluble benzaldoxime hyperoxide and benzaldehyde.[2] The main reaction, which proceeds best with 2.5 equivalents of nitrogen dioxide, appears to be: $2C_6H_5CH{=}NOH + 5NO_2 \rightarrow 2C_6H_5CH(NO_2)_2 + 3NO + H_2O$. A pure product is easily isolated in 38% yield by sodium bicarbonate extraction.



The Ponzio reaction was found applicable to the preparation of II by the alternate route from *m*-nitrobenzaldoxime (III), but the yield is poor. Trials with the *o*- and *p*-nitro and 2,4-dinitro derivatives of benzaldoxime gave very little bicarbonate-soluble product. The 3-nitro-4-methoxy derivative gave a bicarbonate-soluble product but this proved to be unstable at room temperature.

In another series of experiments 2,4,6-trinitrobenzyl bromide (IV) was prepared by the bromination of TNT at 160°[5] and converted by treatment with a solution of silver nitrate in acetonitrile into the nitrate, V. The same product was obtained from the alcohol VI, but the preparation of this intermediate from the bromide is a tedious process. The ester V has a favorable melting point (119°), possesses adequate stability, and has a perfect explosive balance: $C_7H_4O_9N_4 \rightarrow 7\,CO + 2\,H_2O + 2N_2$.



Dr. R. McGill's report on the explosive properties (see Paper II) indicate that *m*-nitrophenyldinitromethane (II) is slightly less sensitive to impact than TNT but unsatisfactory with respect to thermal stability; 2,4,6-trinitrobenzyl nitrate is slightly less sensitive to impact than PETN. Ballistic strengths relative to TNT (100), Tetryl (125.5), PETN (145.8), and Cyclonite (150.2) are: *m*-nitrophenyldinitromethane, 100; 2,4,6-trinitrobenzyl nitrate 126.5.

Experimental Part[6]

Phenyldinitromethane.—A solution of 60.5 g. of benzaldoxime in 500 cc. of absolute ether was added from a dropping funnel into a solution of 115 g. of commercial nitrogen dioxide (N_2O_4) in 100 cc. of absolute ether in a 2-l. flask fitted with a condenser at a rate sufficient to maintain vigorous refluxing (forty-five minutes). After one hour, during which time no peroxide precipitated, the clear solution was transferred to a separatory funnel, washed three times with water, and extracted with twenty 100-cc. portions of saturated aqueous sodium bicarbonate solution. The first few extracts removed inorganic acids and a small amount (3.7 g.) of crude phenyldinitromethane contaminated with a yellow impurity and melting below 78°. The subsequent extracts were clear yellow and frequently deposited yellow needles of the sodium salt of the reaction product; acidification of these portions gave in all

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[1] Work conducted in 1940–1941 under Contract No. NDCrc-5 with the Office of Scientific Research and Development.

[2] Milone and Massa, *Gazz. chim. ital.*, **70**, 196 (1940).

[3] Urbanski, *Compt. rend.*, **206**, 1122 (1938).

[4] Ponzio, *J. prakt. chem.*, **73**, 494 (1906); see also Ponzio, *Gazz. chim. ital.*, **36**, II, 287 (1906).

[5] Ganguly, *Ber.*, **58**, 708 (1925).

[6] Microanalyses by Eleanor Werble. All melting points are corrected.