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]

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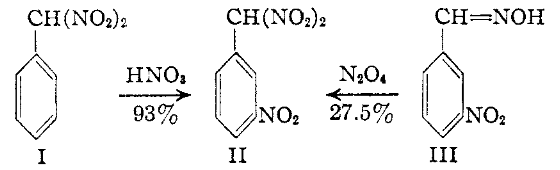
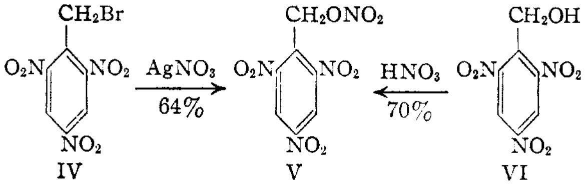
m-Nitrophenyldinitromethane (II) is reported by Milone and Massa[2] to be a more powerful explosive than the isomers TNT and 3,5-dinitrophenylnitromethane.[3] In the preparation of a large quantity of II for further evaluation, some additional observations have been made concerning the interesting reaction 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.

34.8 g. (38%) of nearly colorless material of high purity, m. p. 78–80°, and suitable for use in the nitration.

***m*-Nitrophenyldinitromethane.** (a) **By Nitration.**[2]—Three hundred and fifty cc. of fuming nitric acid (sp. gr. 1.5) was cooled to −15° and poured onto 34.8 g. of phenyldinitromethane, when the temperature rose to 13°. The solution was allowed to stand at room temperature for one hour and poured into 1400 cc. of cold water. The precipitated material, when washed thoroughly with water and dried, consisted of 43.0 g. of fine needles melting at 96–98° (hydrate or polymorph). One crystallization from methanol gave 40.5 g. (93.3%) of large yellow prisms, m. p. 125–126°. The yellow impurity has no noticeable effect on the melting point and is not easily removed by Norit in methanol without loss of material; thus the above sample afforded only 27.6 g. of nearly colorless prims, m. p. 125–126° (M. and M.,[2] 124–125°). It was found, however, that even very crude material can be purified easily through the sodium salt. Thus the dark red product resulting from the nitration of the crude residues of phenyldinitromethane was dissolved in the minimum amount of hot, saturated sodium bicarbonate solution and the solution was clarified with Norit, filtered hot and set aside for crystallization. The resulting yellow needles, when recrystallized from water, afforded beautiful yellow prismatic needles and on acidification of a solution of the salt and crystallization of the precipitate from methanol there resulted colorless prisms of *m*-nitrophenyldinitromethane, m. p. 128–130°.

(b) **By the Ponzio Reaction.**—A solution of 9.55 g. of *m*-nitrobenzaldoxime in 75 cc. of absolute ether was added dropwise to a solution of 21.5 g. of nitrogen dioxide in 25 cc. of absolute ether under reflux. At the conclusion of the reaction the solution was extracted with three 50-cc. portions of water and then with eight 50-cc. portions of saturated sodium bicarbonate solution. Acidification gave a total of 3.56 g. (27.5%) of material melting in the range 117–125°. A crystallized sample of *m*-nitrophenyldinitromethane melted at 125–126° alone or mixed with (a).

Other Trials of the Ponzio Reaction.—In the following experiments the reaction with nitrogen dioxide was conducted as described above. The bicarbonate extract of the reaction mixture from **2,4-dinitrobenzaldoxime** (8.09 g.) gave a glassy product on acidification, and when this was collected in ether and then rubbed with a small amount of this solvent, it afforded a small amount of crystalline material (0.5 g.) that appeared to be the desired dinitrophenyldinitromethane. When heated in a capillary tube it exploded at 133°, and the substance could be detonated by rubbing it on a porous plate with a wire. It was very sparingly soluble in ether or acetone, rather soluble in alcohol, and readily soluble in water. Attempted crystallization from alcohol led to the transformation of the material into a decomposition product that no longer exploded.

The acidic fraction from ***o*-nitrobenzaldoxime** consisted of a dark resin from which no solid material could be obtained. Extraction of the neutral fraction with ether–petroleum ether gave a yellow solid that after repeated crystallization from benzene formed needles, m. p. 155–157° (Found: C, 60.25; H, 4.52). From ***p*-nitrobenzaldoxime** (16.6 g.) there was obtained 4.2 g. of solid acidic material that proved to be a mixture. Fractional crystallization from methanol afforded a small crop of yellow needles, m. p. 240–243° (Found: C, 54.86; H, 2.90) and 0.5 g. of small yellow prisms, m. p. 72–73°. In a trial with **phenylacetaldoxime**, the acidic fraction was an oil from which no crystalline product could be isolated with the use of solvents or by nitration. From **3-nitro-4-methoxybenzaldoxime** (10 g.) there was obtained by sodium bicarbonate extraction and acidification 7.0 g. of solid product, which when crystallized from methanol afforded 5.17 g. (39.5%) of large clear prisms, m. p. 88–89.5°. This had the properties of an aryldinitromethane but the dried crystals on brief storage lost the characteristic luster and gave off nitrogen dioxide. In a repetition of the experiment the partially soda-washed ethereal solution fumed off with such suddenness and force as to blow the contents of the funnel across the room.

2,4,6-Trinitrobenzyl Nitrate.—The required **2,4,6-trinitrobenzyl bromide** was prepared[5] by sealing a mixture of 34.0 g. of trinitrotoluene, 12.6 g. of magnesium carbonate and 17 cc. of bromine in a 150-cc. Pyrex bomb tube and heating it at 160° for eighteen hours. The reaction mixture was removed from the tube with ether and water, enough sodium bisulfite was added to decolorize the excess bromine and dissolve the unchanged magnesium carbonate, and the ethereal solution was washed twice with water and once with brine, filtered through sodium sulfate and concentrated to a volume of 200 cc. for crystallization. The first crop amounted to 24.2 g. of product, m. p. 63–65°; total yield 72%. In six runs the yield varied from 61.3 to 77.6% and averaged 70.7%.

(a) **From the Bromide.**—A solution of 90.0 g. of trinitrobenzyl bromide and 55 g. of silver nitrate in 300 cc. of acetonitrile was stirred at 3° for twenty-four hours, when the silver bromide that had precipitated was collected and found to weigh 47.5 g. (86%). The filtrate, on standing at room temperature for one hour, deposited 1.0 g. more of silver bromide, and after this had been removed the solution was drowned in 1.5 liters of water. The dark red precipitate was dried and pulverized to pass through a 40-mesh sieve and the powdered product (80.5 g.) placed on a Büchner funnel and washed with two 300-cc. portions of ether; this removed the red color and left 60.1 g. of undissolved product. The material was then extracted in a Soxhlet apparatus with ether, in which it is but sparingly soluble. The first crop consisted of pure, colorless material, m. p. 118–120°, yield 43.8 g. (52%), and the mother liquors afforded 7.3 g. (8.5%) of less pure product, m. p. 102–106°. A sample crystallized for analysis from methanol formed colorless prismatic needles, m. p. 118.5–119.5°. The substance appears to be stable on storage and gives no test for acidity when rubbed with water. A semimicrocombustion for the determination of carbon and hydrogen resulted in a destructive explosion.

Anal. Calcd. for $C_7H_4O_9N_4$: N, 19.45. Found: (Kjeldahl) N, 18.84.

In another experiment the crude precipitated product (27.7 g.) from 30.6 g. of trinitrobenzyl bromide was dissolved in 50 cc. of acetone and the filtered solution was diluted with 200 cc. of ether and set aside to crystallize. Three crops of material were obtained totalling 22.2 g., and recrystallization from methanol afforded 13.3 g. (46%) of light yellow nitrate, m. p. 118–120°, and 5.2 g. (18%), m. p. 112–116°. When the reaction was conducted at 25–45° the product was darker and the yield lower. When the crude trinitrobenzyl bromide was used directly without purification from ether the yield was very low.

(b) **From the Alcohol.**—2,4,6-Trinitrobenzyl alcohol was prepared[5] by refluxing the bromide (15 g.) with water; the yield of total crude material (m. p. 70–80°) was 10.4 g. (87%). When 7.8 g. of the crude alcohol was added to 70 cc. of fuming nitric acid (sp. gr. 1.5) that had been chilled to −15°, the temperature soon rose to 13°. The mixture was drowned in ice and water and the dried precipitate (8.8 g.) was dissolved in 180 cc. of methanol. A reddish color gave place to yellow on Norit treatment, and on cooling the solution deposited 5.7 g. (62%) of light yellow prisms, m. p. 118–120°; no depression with (a). A second crop was obtained from the mother liquor and when recrystallized gave 0.75 g. (8%) of material, m. p. 117–119°.

Summary

Some improvements have been made in the preparation of phenyldinitromethane from benzaldoxime and nitrogen dioxide (Ponzio reaction) and in its conversion to *m*-phenyldinitromethane by nitration.

2,4,6-Trinitrobenzyl nitrate has been prepared by reaction of the corresponding bromide with silver nitrate in acetonitrile solution; it has favorable properties as an explosive.

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