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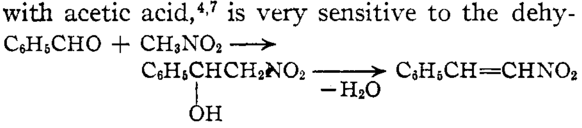
Aromatic–Aliphatic Nitro Compounds. I. The Condensation of Nitrobenzaldehydes with Nitromethane[1]

BY LOUIS F. FIESER AND WILLIAM H. DAUDT

It is well known that the condensation of benzaldehyde with nitromethane can be brought about under the influence of various organic and inorganic bases and that the initially formed α-phenyl-β-nitroethanol (I) is a labile substance that loses water very readily to give ω-nitrostyrene (II).[2-9] The nitro alcohol, which has been prepared in an impure condition by conducting the condensation at 0° and acidifying the mixture with acetic acid,[4,7] is very sensitive to the dehydrating action of traces of mineral acids and loses water readily even under the influence of the basic condensing agents[6,7,8] unless a low temperature is maintained.[2] When a primary amine is used to effect the condensation, the nitrostyrene is produced even at room temperature.[5,7]

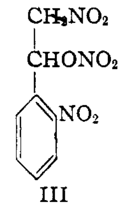


$$C_6H_5CHO + CH_3NO_2 \longrightarrow \underset{\text{OH}}{C_6H_5CH}CH_2NO_2 \xrightarrow[-H_2O]{} C_6H_5CH{=}CHNO_2$$

I II

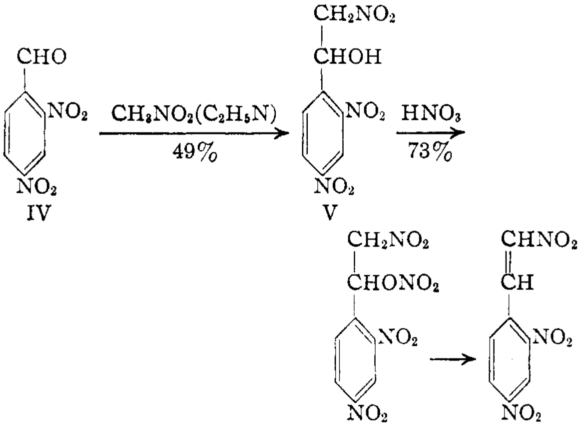
From these observations it would seem rather unpromising to attempt the conversion of the labile nitro alcohols into nitrate esters as a route to possible explosives. Two citations in the literature, however, indicate that an ortho nitro group has a marked stabilizing influence. Thiele[6] obtained nitrostyrenes on the condensation of nitromethane with *m*- and *p*-nitrobenzaldehyde in the presence of methyl alcoholic potassium hydroxide, followed by acidification of the cold solution, but found that under the same conditions the ortho isomer yielded the potassium derivative of the nitro alcohol and that the oil liberated on acidification could be acetylated. Bouveault and Wahl[2] observed further that α-(*o*-nitrophenyl)-β-nitroethanol is so unusually stable as to be resistant to the dehydrating action of zinc chloride.

Of the basic condensing agents previously employed (KOH–ROH,[6,8] NaOR–ROH,[2,3] RNH_2,[5,7] R_2NH,[7] R_3N[7,9]), tertiary amines seemed most promising for the present purpose, and indeed it was found that a very smooth condensation occurs on adding a trace of triethylamine to a solution of *o*-nitrobenzaldehyde in excess nitromethane. For the preparation of the nitrate it is not necessary to isolate the resulting nitroalcohol, for when the total reaction mixture is treated at room temperature with concentrated nitric acid it affords in nearly quantitative over-all yield crystalline α-(2-nitrophenyl)-β-nitroethyl nitrate (III) of good quality. Analytically pure material melting without decomposition at 132.2–132.7° can be obtained with fair recovery by rapid crystallization from acetone–alcohol with avoidance of undue heating, but when the solutions are warmed even moderately the substance readily loses nitric acid and affords 2,ω-dinitrostyrene, previously isolated along with the para isomer as a product of the nitration of ω-nitrostyrene.[10]



III

When 2,4-dinitrobenzaldehyde was condensed with nitromethane by the same procedure the nitroalcohol V was isolated in moderate yield as a crystalline solid, and by nitration of V the ester VI could be obtained in 73% yield. α-(2,4-Dinitrophenyl)-β-nitroethyl nitrate (VI) when purified by careful crystallization melts without decomposition at 114.2–114.8°, but moderate warming of the solution results in its conversion into the trinitrostyrene VII. Although the ester VI contains a fairly favorable proportion of oxygen and nitrogen and displays some explosibility, the tendency to lose nitric acid in contact with neutral solvents probably militates against any practical application of this type of ester in the field of explosives. Attempts to condense 2,4,6-trinitrobenzaldehyde with nitromethane in the presence of triethylamine were unsuccessful.



IV V VI VII

Experimental[11]

α-(2-Nitrophenyl)-β-nitroethyl Nitrate.—A solution of 75 g. of *o*-nitrobenzaldehyde in 75 cc. of nitromethane at room temperature was treated with 0.5 cc. of triethylamine

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

[2] Bouveault and Wahl, *Compt. rend.*, **135**, 41 (1902).

[3] Holleman, *Rec. trav. chim.*, **23**, 283 (1904).

[4] Holleman, *ibid.*, **23**, 298 (1904).

[5] Knoevenagel and Walter, *Ber.*, **37**, 4502 (1904).

[6] Thiele, *ibid.*, **32**, 1293 (1899).

[7] Worrall, THIS JOURNAL, **56**, 1556 (1934).

[8] Worrall, "Organic Syntheses," **1**, 413 (1941).

[9] Worrall and Wolosinski, *ibid.*, **62**, 2449 (1940).

[10] Priebs, *Ann.*, **225**, 350 (1884).

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

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[3] *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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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).