sity in large scale operation of recovering the excess acetic and nitric acids, and (*c*) the potential hazard since tetranitromethane is formed from the reaction of nitric acid and acetic anhydride.[3]

Using essentially the same procedure as employed by Chute *et al.*,[2] that is, the simultaneous addition of iminodipropionitrile, nitric acid, and hydrochloric acid to acetic anhydride, a systematic study of this nitration was undertaken to determine the conditions and reactant ratios for optimum yields. Using one mole of iminodipropionitrile and varying the molar quantities of nitric acid, acetic anhydride, and hydrochloric acid, it was found that an optimum yield of 73.1% was obtained with 1.1 moles of nitric acid, 1.4 moles of acetic anhydride, and 0.05 mole of hydrochloric acid. Several more runs were made with these quantities and consistent yields of 70–73% were obtained. On scaling the nitration up to a 15.0 mole batch, it was found that the yield decreased to 43.2%. This was substantiated in subsequent runs. In the larger run the addition of amine, nitric acid, and hydrochloric acid was carried out over a greater length of time than in the smaller run. Thus the amine was exposed to a large excess of acetic anhydride for a greater length of time in the larger run; this resulted in a reduced yield apparently owing to acetylation of the amine. In order to keep the concentration of the acetic anhydride at a minimum, the addition procedure was reversed. The amine was added to the nitric acid followed by the addition of acetic anhydride and hydrochloric acid. A yield of 77% of the nitramine was then obtained on a 15.0 mole batch. Subsequent runs substantiated this yield.

This procedure was then applied to improve the synthesis of *N*-methyl-3-nitraminopropionitrile, which was previously prepared by isolating the nitric acid salt of *N*-methyl-3-aminopropionitrile and then dehydrating the salt with an excess of nitric acid and acetic anhydride; the over-all yield was 50.7%.[1] Using a modification of the improved procedure, the direct nitration of *N*-methyl-3-aminopropionitrile gave *N*-methyl-3-nitraminopropionitrile in yields of 87–89%. This modification consisted in using methylene chloride as a solvent for the nitration reaction. In the preparation of nitriminodipropionitrile, the product precipitated when the reaction mixture was quenched with water. In the case of a liquid product, such as *N*-methyl-3-nitraminopropionitrile, a solvent was desirable to extract the nitramine from the acid mixture. Accordingly, the nitration was carried out in methylene chloride, which served not only as a solvent for the starting amine and the product but also as a diluent for the reaction. The importance of keeping the concentration of acetic anhydride at a minimum during the nitration was shown again. By reversing the mode of addition, that is adding the *N*-methyl-3-aminopropionitrile, nitric acid, and hydrochloric acid to acetic anhydride, the yield of *N*-methyl-3-nitraminopropionitrile was decreased to 43–57%.

## EXPERIMENTAL

*Nitriminodipropionitrile.* To 694.5 ml. (16.5 moles) of 98–99% nitric acid was added in 30 min. 900 ml. (7.5 moles) of iminodipropionitrile, keeping the temperature at 0–10° by external cooling. The reaction mixture consisted of a yellow slurry which still could be stirred uniformly. (If all of the amine is added at this point, the mixture becomes too thick for stirring.) The temperature of the reaction mixture was allowed to rise to 15° and the simultaneous addition of 900 ml. (7.5 moles) of iminodipropionitrile, 1980 ml. (21.0 moles) of acetic anhydride, and 62.6 ml. (0.75 mole) of 37% hydrochloric acid was made dropwise in 2.5 hr., keeping the temperature at 15–20° by external cooling. The amine and acetic anhydride were added at the same rate, so as to ensure that the addition of the amine will be completed while only about half of the acetic anhydride has been added. The addition of the acetic anhydride and hydrochloric acid were completed at about the same time. The reaction mixture was stirred for 3 hr. at 25–30°, intermittent cooling being required during this period in order to stay within this temperature range. The mixture was then cooled to 5–10° and quenched with 4 liters of ice water. The white solid was collected, washed thoroughly with ice water, and dried to give 1940.4 g. (77.0%), m.p. 54–55° (lit. value, 53.5–55.5°[2]).

*N-Methyl-3-nitraminopropionitrile.* A solution of 84.1 g. (1.0 mole) of *N*-methyl-3-aminopropionitrile in 100 ml. of methylene chloride was cooled to 0–10° and 46.3 ml. (1.1 moles) of 98–99% nitric acid was added dropwise in 30 min., keeping the temperature at 0–10°. The temperature of the reaction mixture was allowed to rise to 20° and 132 ml. (1.4 moles) of acetic anhydride and 2.5 ml. (0.03 mole) of 37% hydrochloric acid was added dropwise in 30 min., keeping the temperature at 20–25° by external cooling. The reaction mixture was stirred at 25–30° for 2.5 hr., cooled to 5–10° and quenched by the addition of 100 ml. of ice water. The methylene chloride layer was separated and the aqueous layer was extracted with two 100-ml. portions of methylene chloride. The combined methylene chloride extracts were washed with saturated sodium carbonate solution until the aqueous phase reached a *p*H of 8. After a final wash with water, the methylene chloride solution was concentrated *in vacuo* leaving 115.2 g. (89.2%) of light yellow liquid, $n_D^{25}$ 1.4855 (lit. value of distilled product, $n_D^{25}$ 1.4863).[1]

*Acknowledgment.* The authors are indebted to the Bureau of Ordnance for the financial support of this work and to Mr. Otto Schaeffler for aid in the experimental work.

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# Derivatives of *N*-Methylnitraminoacetonitrile

MILTON B. FRANKEL

*Received May 22, 1958*

The preparation of *N*-methyl-3-nitraminopropionitrile and its conversion to *N*-methyl-3-nitraminopropionyl chloride, *N*-methyl-2-nitraminoethyl

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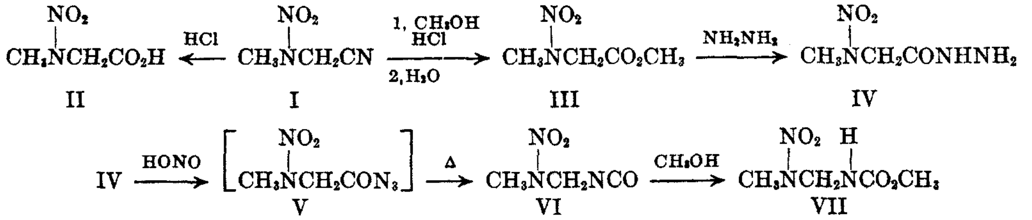
[3] P. Liang, *Org. Syntheses*, Coll. Vol. III, (1955).

isocyanate, and $N$-methyl-2-nitraminoethylamine were recently described.[1] In continuation of the study of the chemistry of simple aliphatic secondary nitramines containing a nitrile group, the synthesis and reactions of the lowest member of this series, $N$-methylnitraminoacetonitrile (I), are reported in the present paper.

$N$-Methyl-3-nitraminopropionitrile was prepared by dehydrating the nitric acid salt of $N$-methyl-3-aminopropionitrile using acetic anhydride and chloride ion catalyst. It was not possible to isolate the nitric acid salt of $N$-methylaminoacetonitrile because of its hygroscopicity. The nitration of $N$-methylaminoacetonitrile was effected by preparing the nitric acid salt *in situ*, and treating it directly with acetic anhydride and chloride ion catalyst to give a 60.9% yield of I. Without the chloride catalyst the yield was decreased to 3.1%.

Hydrolysis of I with concentrated hydrochloric acid gave $N$-methylnitraminoacetic acid (II). Attempts to convert II to the corresponding acid chloride using thionyl chloride or phosphorus pentachloride were unsuccessful owing to the decomposition of II. Methyl $N$-methylnitraminoacetate (III) was prepared by treating I with methanolic hydrogen chloride and hydrolyzing the intermediate imido ester hydrochloride. $N$-methylnitraminoacetohydrazide (IV) was readily formed from III and hydrazine. Compound IV was converted to the corresponding azide (V), which was decomposed *in situ* to give $N$-methylnitraminomethyl isocyanate (VI). The isocyanate reacted very readily with methanol to form the methyl carbamate (VII). Attempts to convert VI to $N$-methylnitraminomethylamine hydrochloride by treatment with concentrated hydrochloric acid, in the same manner in which $N$-methyl-2-nitraminoethylamine hydrochloride was prepared from $N$-methyl-2-nitraminoethyl isocyanate, were unsuccesful. The only compound isolated from this reaction was ammonium chloride. The above reactions are summarized in Chart I.

CHART I



$$\underset{\text{II}}{\mathrm{CH_3\overset{\overset{NO_2}{|}}{N}CH_2CO_2H}} \xleftarrow{\text{HCl}} \underset{\text{I}}{\mathrm{CH_3\overset{\overset{NO_2}{|}}{N}CH_2CN}} \xrightarrow[\text{2, H}_2\text{O}]{\text{1, CH}_3\text{OH}\atop\text{HCl}} \underset{\text{III}}{\mathrm{CH_3\overset{\overset{NO_2}{|}}{N}CH_2CO_2CH_3}} \xrightarrow{\mathrm{NH_2NH_2}} \underset{\text{IV}}{\mathrm{CH_3\overset{\overset{NO_2}{|}}{N}CH_2CONHNH_2}}$$

$$\text{IV} \xrightarrow{\text{HONO}} \underset{\text{V}}{\left[\mathrm{CH_3\overset{\overset{NO_2}{|}}{N}CH_2CON_3}\right]} \xrightarrow{\Delta} \underset{\text{VI}}{\mathrm{CH_3\overset{\overset{NO_2}{|}}{N}CH_2NCO}} \xrightarrow{\mathrm{CH_3OH}} \underset{\text{VII}}{\mathrm{CH_3\overset{\overset{NO_2}{|}}{N}CH_2\overset{\overset{H}{|}}{N}CO_2CH_3}}$$

## EXPERIMENTAL[2,3]

*N-Methylnitraminoacetonitrile* (I). A solution of 490 g. (7.0 moles) of $N$-methylaminoacetonitrile[4] in two liters of methylene chloride was cooled to 0–5° and 325 ml. (7.7 moles) of 98–99% nitric acid was added dropwise with good stirring. After the addition was complete, the temperature was allowed to rise to 20° and 928 ml. (9.8 moles) of acetic anhydride and 17.7 ml. (0.21 mole) of 37% hydrochloric acid were added simultaneously at proportionate rates in 1 hr., keeping the temperature at 20–25°. After the addition was complete, the solution was stirred at 25–30° for 2 hr., then cooled to 5° and quenched by the addition of 400 ml. of ice water. The mixture was stirred for 15 min. and the methylene chloride layer was separated. The aqueous layer was extracted with two 500-ml. portions of methylene chloride. The combined methylene chloride extracts were washed with saturated sodium carbonate solution until the $p$H of the aqueous wash was at least 8, dried over sodium sulfate and concentrated *in vacuo*. The light yellow liquid residue was crystallized at −20° from 750 ml. of methanol to give 490 g. (60.9%) of white needles, m.p. 26–27°, $n_D^{25}$ 1.4792.

*Anal.* Calcd. for $C_3H_5N_3O_2$: C, 31.31; H, 4.38; N, 36.51. Found: C, 31.49; H, 4.39; N, 37.14.

*N-Methylnitraminoacetic acid* (II). One hundred fifteen ml. of 37% hydrochloric acid was warmed to 60° and 111 g. (0.97 mole) of $N$-methylnitraminoacetonitrile was added dropwise. The temperature of the reaction mixture rose to 90° during the addition. After the addition was complete, the mixture was heated on the steam bath with stirring for 5.5 hr. The mixture was cooled and the products were collected and dried to give 159 g. of white solid. The solid was extracted with four 200-ml. portions of ether leaving 44.4 g. (86.0%) of ammonium chloride. The combined ether extracts were concentrated *in vacuo* leaving 111.6 g. (86.5%) of white solid, m.p. 96.5–98.5°. Recrystallization from 37% hydrochloric acid raised the melting point to 99–100°.

*Anal.* Calcd. for $C_3H_6N_2O_4$: C, 26.87; H, 4.51; N, 20.89; Eq. Wt., 134.10. Found: C, 27.02; H, 4.72; N, 20.95; Eq. Wt., 134.06.

*Methyl N-methylnitraminoacetate* (III). A solution of 817 g. (7.1 moles) of $N$-methylnitraminoacetonitrile, 1500 ml. of methanol, and 2500 ml. of absolute ether was cooled to 0–5° and a rapid stream of anhydrous hydrogen chloride gas was bubbled through until the solution was saturated, keeping the temperature at 0–5°. The white crystalline imido ester hydrochloride precipitated. The solid was collected, washed with absolute ether, and added to one liter of water while stirring. The solid dissolved and a colorless oil gradually separated from the solution. The oil was separated and the aqueous phase was extracted with two 1000-ml. portions of methylene chloride. The oil and extracts were combined and washed with 500 ml. of water, 1000 ml. of saturated sodium bicarbonate solution, and 500 ml. of water. The methylene chloride solution was dried over sodium sulfate and concentrated *in vacuo* leaving 869 g. (82.8%) of faint yellow liquid, $n_D^{25}$ 1.4617. Distillation from a Claisen flask gave a colorless liquid, b.p. 87°/0.75 mm., $n_D^{25}$ 1.4615.

*Anal.* Calcd. for $C_4H_8N_2O_4$: C, 32.43; H, 5.44; N, 18.92. Found: C, 32.59; H, 5.40; N, 18.31.

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(1) M. B. Frankel and K. Klager, *J. Am. Chem. Soc.*, **78**, 5428 (1956).

(2) All melting points and boiling points are uncorrected.

(3) Microanalyses by Dr. A. Elek, Elek Microanalytical Laboratories, Los Angeles, Calif.

(4) L. J. Exner, L. S. Luskin, and P. L. deBenneville, *J. Am. Chem. Soc.*, **75**, 4841 (1953).

*N-Methylnitraminoacetohydrazide* (IV). To a solution of 180 ml. (2.39 moles) of 85% hydrazine hydrate and 200 ml. of methanol was added dropwise, with stirring, 235.2 g. (1.60 moles) of methyl *N*-methylnitraminoacetate. The temperature of the solution rose from 25 to 32°. After stirring for 30 min., the solution was cooled and a white solid precipitated. The product was collected, washed with cold methanol, and dried to give 179.3 g. (76.3%) of white solid, m.p. 81–84°. Recrystallization from ethanol raised the melting point to 84–85°.

*Anal.* Calcd. for $C_3H_8N_4O_3$: C, 24.32; H, 5.44; N, 37.83. Found: C, 24.70; H, 5.64; N, 38.00.

*N-Methylnitraminomethyl isocyanate* (VI). A mixture of 14.8 g. (0.1 mole) of *N*-methylnitraminoacetohydrazide, 125 ml. of water, and 125 ml. of chloroform was cooled to 0° and 9.2 ml. (0.11 mole) of 37% hydrochloric acid was added. Then a solution of 10.0 g. (0.11 mole) of 93% potassium nitrite in 20 ml. of water was added dropwise, keeping the temperature at 0–5°. The mixture was stirred for 15 min. and the chloroform layer was separated. The aqueous layer was extracted with two 150-ml. portions of chloroform. The combined chloroform extracts were washed with three 100-ml. portions of ice water, dried over sodium sulfate, and filtered. The solution was concentrated on the water aspirator at a temperature of 10–20° until the volume was decreased by half, to ensure the removal of the last traces of water. The solution was then warmed under a reflux condenser. At 40–50° the decomposition of the azide commenced. After the decomposition started, the solution was slowly heated to reflux. The solution was refluxed until the evolution of nitrogen had ceased (about 2 hr.) and concentrated *in vacuo*. The residue was distilled from a Claisen flask to give 9.0 g. (68.7%) of colorless liquid, b.p. 81–81.5° (2 mm.), $n_D^{25}$ 1.4787.

*Anal.* Calcd. for $C_3H_5N_3O_3$: C, 27.70; H, 3.87; N, 32.30. Found: C, 27.32; H, 3.81; N, 32.74.

*Methyl N-methylnitraminocarbamate* (VII). A solution of 2.62 g. (0.02 mole) of *n*-methylnitraminomethyl isocyanate and 5 ml. of methanol was refluxed for 30 min. and concentrated *in vacuo* to give 3.0 g. (92.1%) of white needles, m.p. 65–67°. Recrystallization from methanol raised the melting point to 66–67°.

*Anal.* Calcd. for $C_4H_9N_3O_4$: C, 29.45; H, 5.56. Found: C, 29.76; H, 5.60.

*Acknowledgment.* The author is indebted to the Bureau of Ordnance for the financial support of this work.

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## Reactions of Aliphatic Nitro Compounds

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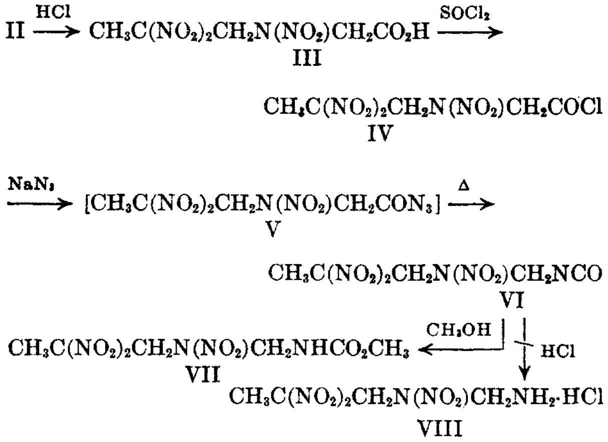
*Received June 9, 1958*

The preparation of derivatives of the carboxylic acid groups in methyl 4,4-dinitropentanoate,[1] methyl 4-nitrazapentanoate,[2] and methyl 3-nitrazabutyrate[3] has been described. Aliphatic monoesters containing both the *gem*-dinitro and nitraza groups have also been reported. Feuer, Bachman, and May[4] prepared ethyl 3,5,5-trinitro-3-azapentanoate (I) and Frankel and Klager[5] reported the synthesis of methyl 3,5,5-trinitro-3-azahexanoate (II). Attempts by Feuer *et al.*[4] to hydrolyze I with concentrated hydrochloric acid resulted only in decomposition with evolution of oxides of nitrogen. The preparation of derivatives of the carboxylic acid group in II is reported in the present work.

$$\underset{\mathrm{I}}{HC(NO_2)_2CH_2N(NO_2)CH_2CO_2C_2H_5}$$

$$\underset{\mathrm{II}}{CH_3C(NO_2)_2CH_2N(NO_2)CH_2CO_2CH_3}$$

Hydrolysis of II with concentrated hydrochloric acid gave 3,5,5-trinitro-3-azahexanoic acid (II) in good yield, indicating that replacement of the acidic hydrogen atom in I with an alkyl group has a stabilizing influence on the molecule. Compound III was converted to 3,5,5-trinitro-3-azahexanoyl chloride (IV) and the corresponding azide (V). The azide was not isolated but decomposed *in situ* to form 2,4,4-trinitro-2-aza-1-pentyl isocyanate (VI). The isocyanate exploded violently on standing at ambient temperature but could be stored safely at −20° for several months. It reacted readily with methanol to form methyl *N*-(2,4,4-trinitro-2-aza-1-pentyl) carbamate (VII). Attempts to convert VI to 2,4,4-trinitro-2-aza-1-pentylamine hydrochloride (VIII) by treatment with concentrated hydrochloric acid were unsuccessful; the only compound isolated from this reaction was ammonium chloride.[6]



$$\mathrm{II} \xrightarrow{HCl} \underset{\mathrm{III}}{CH_3C(NO_2)_2CH_2N(NO_2)CH_2CO_2H} \xrightarrow{SOCl_2} \underset{\mathrm{IV}}{CH_3C(NO_2)_2CH_2N(NO_2)CH_2COCl}$$

$$\xrightarrow{NaN_3} \underset{\mathrm{V}}{[CH_3C(NO_2)_2CH_2N(NO_2)CH_2CON_3]} \xrightarrow{\Delta} \underset{\mathrm{VI}}{CH_3C(NO_2)_2CH_2N(NO_2)CH_2NCO}$$

$$\begin{tikzcd} & \underset{\mathrm{VI}}{CH_3C(NO_2)_2CH_2N(NO_2)CH_2NCO} \arrow[dl, "CH_3OH"'] \arrow[d, "HCl"] \\ \underset{\mathrm{VII}}{CH_3C(NO_2)_2CH_2N(NO_2)CH_2NHCO_2CH_3} & \underset{\mathrm{VIII}}{CH_3C(NO_2)_2CH_2N(NO_2)CH_2NH_2\cdot HCl} \end{tikzcd}$$

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[1] H. Schechter and L. Zeldin, *J. Am. Chem. Soc.*, **73**, 1276 (1951).

[2] M. B. Frankel and K. Klager, *J. Am. Chem. Soc.*, **78**, 5428 (1956).

[3] M. B. Frankel, *J. Org. Chem.*, **23**, 1811 (1958).

[4] H. Feuer, G. B. Bachman, and W. May, *J. Am. Chem. Soc.*, **76**, 5124 (1954).

[5] M. B. Frankel and K. Klager, *J. Am. Chem. Soc.*, **79**, 2953 (1957).

[6] The same results were observed in attempting to convert 2-nitrazapropyl isocyanate to 2-nitrazapropylamine hydrochloride.[3] This is in marked contrast to the facile preparation of 3-nitrazabutylamine hydrochloride from 3-nitrazabutyl isocyanate,[2] where the primary amino group is in a β position to the nitraza group.