compounds were disclosed in a series of patents (*3*). The *N*-nitrocarbamates are white crystalline solids with excellent thermal stability, they are generally sensitive to impact and should be handled with care.

EXPERIMENTAL

Preparation of Carbamate. The preparation of *N*-(3,3,3-trinitopropyl)-2,2,2-trinitroethyl carbamate is given as typical. A mixture of 42.2 grams (0.19 mole) of 3,3,3-trinitropropyl isocyanate, 34.7 grams (0.19 mole) of 2,2,2-trinitroethanol, 300 ml. of dry, alcohol free chloroform, and a trace of ferric acetylacetonate was placed in a 1-liter round-bottomed flask, fitted with a condenser and drying tube. The solution was refluxed for 8 hours and concentrated in vacuo to give 62.8 grams (81.7%) of a white solid, m.p. 77 to 86° C. Recrystallization from carbon tetrachloride gave a melting point of 91 to 92° C.

Preparation of *N*-Nitrocarbamate. The preparation of *N*-nitro-*N*-(3,3,3-trinitropropyl)-2,2,2-trinitroethyl carbamate is given as typical. A quantity of 250 ml. of absolute nitric acid (Technical Grade) was cooled in an ice-salt bath, and 250 ml. of acetic anhydride was added dropwise with stirring, while the temperature was kept below 10° C. Then 68.6 grams (0.17 mole) of *N*-(3,3,3-trinitropropyl)-2,2,2-trinitroethyl carbamate was added portionwise at 5° C., and stirring was continued for an additional 30 minutes. The solution was poured with stirring onto cracked ice, the white solid was collected, washed well with cold water, and dried in vacuo over potassium hydroxide to give 68.1 grams (89.4%) of product, m.p. 83 to 90° C. Recrystallization from carbon tetrachloride raised the melting pount to 96 to 97° C.

In those cases in which the carbamate was an oil, the oil was dissolved in the acetic anhydride, and the solution was added dropwise to the absolute nitric acid at 5 to 10° C.

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Polynitro Aliphatic Nitramines

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THE MANNICH condensation of 2,2-dinitro-1-alkanols with ammonia was shown to give *bis*-substituted amines (*1*). This reaction has now been extended to include polynitro aliphatic primary amines and diamines, which were prepared by the acid hydrolysis of the corresponding isocyanates (*3*). The free amines were not isolated but generated in situ from the corresponding hydrochloride salts. Thus, adding an equivalent amount of sodium acetate or sodium hydroxide to an aqueous solution of the alcohol and amine hydrochloride at ambient temperature caused the condensation product to precipitate. The Mannich condensation products were yellow oils or solids of limited stability and difficult to purify. Nitration of this secondary amine with a mixture of absolute nitric acid and acetic anhydride at 5 to 10° C. or with a mixture of absolute nitric acid and concentrated sulfuric acid at 50 to 55° C. gave the corresponding nitramine. The N-nitro derivatives are stable, easily crystallizable white solids; they are sensitive to impact and should be handled with care. The compounds prepared are summarized in Table I, many of these compounds were disclosed in a series of patents (*3*).

EXPERIMENTAL

1,1,1,6,6,6-Hexanitro-3-azahexane. This preparation was typical of the condensation of 2,2-dinitro-1-alkanols and polynitroalkyl amines. An 88-ml. quantity of 1.136*N* sodium hydroxide solution (0.10 mole) was added dropwise at room temperature to a stirred solution of 23.1 grams (0.10 mole) of 3,3,3-trinitropropyl amine hydrochloride, 18.1 grams (0.10 mole) of 2,2,2-trinitroethanol, and 150 ml. of water. A yellow oil immediately separated; on cooling in an ice bath the oil solidified to a yellow solid. The product was collected, washed with water, and dried, 28.2 grams (79%), m.p. 62 to 65° C. Recrystallization from chloroform gave yellow needles, m.p. 64 to 65° C.

1,1,1,3,6,6,6-Heptanitro-3-azahexane. This preparation is typical of the nitration of the Mannich condensation

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Table I. Mannich Condensation Products and *N*-Nitro Derivatives

Alcohol	Amine	Mannich Product	Yield, %	Uncorrected M.P., ° C.
$(NO_2)_3CCH_2OH$	$CH_3C(NO_2)_2CH_2CH_2NH_2$	$CH_3C(NO_2)_2CH_2CH_2NHCH_2C(NO_2)_3$	71.7	Oil
$CH_3C(NO_2)_2CH_2OH$	$(NO_2)_3CCH_2CH_2NH_2$	$CH_3C(NO_2)_2CH_2NHCH_2CH_2C(NO_2)_3$	Quant.	Oil
$(NO_2)_3CCH_2OH$	$(NO_2)_3CCH_2CH_2NH_2$	$(NO_2)_3CCH_2NHCH_2CH_2C(NO_2)_3$	79	64-65
$C(NO_2)_2\text{-}[CH_2OH]_2$	$CH_3C(NO_2)_2CH_2CH_2NH_2$	$C(NO_2)_2\text{-}[CH_2NHCH_2CH_2C(NO_2)_2CH_3]_2$	74.2	95-110
$C(NO_2)_2\text{-}[CH_2OH]_2$	$(NO_2)_3CCH_2CH_2NH_2$	$C(NO_2)_2\text{-}[CH_2NHCH_2CH_2C(NO_2)_3]_2$	83.8	70-80
$(NO_2)_3CCH_2OH$	$CH_2[NH_2]_2$	$CH_2[NHCH_2C(NO_2)_3]_2$	93.1	100-105
$CH_3C(NO_2)_2CH_2OH$	$C(NO_2)_2\text{-}[CH_2CH_2NH_2]_2$	$C(NO_2)_2\text{-}[CH_2CH_2NHCH_2C(NO_2)_2CH_3]_2$	Quant.	Oil
$(NO_2)_3CCH_2OH$	$C(NO_2)_2\text{-}[CH_2CH_2NH_2]_2$	$C(NO_2)_2\text{-}[CH_2CH_2NHCH_2C(NO_2)_3]_2$	65.7	93-95
$(NO_2)_3CCH_2OH$	$N(NO_2)\text{-}[CH_2CH_2NH_2]_2$	$N(NO_2)\text{-}[CH_2CH_2NHCH_2C(NO_2)_3]_2$	33.1	Gum
$(NO_2)_3CCH_2OH$	$[CH_2N(NO_2)CH_2CH_2NH_2]_2$	$[CH_2N(NO_2)CH_2CH_2NHCH_2C(NO_2)_3]_2$	Quant.	100-105
$(NO_2)_3CCH_2OH$	$N(NO_2)\text{-}[CH_2C(NO_2)_2CH_2CH_2NH_2]_2$	$N(NO_2)\text{-}[CH_2C(NO_2)_2CH_2CH_2NHCH_2C(NO_2)_3]_2$	31.3	90-100

Nitrated Mannich Product	Yield, %	Uncorrected M.P. ° C.	Recryst. Solvent	Formula	Analyses: Calculated C	Calculated H	Calculated N	Found C	Found H	Found N
$CH_3C(NO_2)_2CH_2CH_2N(NO_2)CH_2C(NO_2)_3$	38.3	105-107	Chloroform	$C_6H_9N_7O_{12}$	19.41	2.44	26.42	20.18	2.53	26.44
$CH_3C(NO_2)_2CH_2N(NO_2)CH_2CH_2C(NO_2)_3$	63.3	109-109.5	Carbon tetrachloride	$C_6H_9N_7O_{12}$	19.41	2.44	26.42	19.90	2.52	26.91
$(NO_2)_3CCH_2N(NO_2)CH_2CH_2C(NO_2)_3$	86.5	144-145	Chloroform	$C_5H_6N_8O_{14}$	14.93	1.50	27.86	15.23	1.60	28.13
$C(NO_2)_2\text{-}[CH_2N(NO_2)CH_2CH_2C(NO_2)_2CH_3]_2$	61.2	137-139	Ethylene dichloride	$C_{11}H_{18}N_{10}O_{18}$	24.18	3.32	25.64	24.76	3.44	25.52
$C(NO_2)_2\text{-}[CH_2N(NO)CH_2CH_2C(NO_2)_2CH_3]_2$	67.2	124-125	Ethylene dichloride	$C_{11}H_{18}N_{10}O_{14}$	25.69	3.53	27.24	25.36	3.45	26.90
$C(NO_2)_2\text{-}[CH_2N(NO_2)CH_2CH_2C(NO_2)_3]_2$	50.0	157-159	Methanol-water	$C_9H_{12}N_{12}O_{20}$	17.77	1.99	27.64	18.29	2.02	27.40
$CH_2\text{-}[N(NO_2)CH_2C(NO_2)_3]_2$	20.0	84-85	Cyclohexane	$C_5H_6N_{10}O_{16}$	12.99	1.31	30.31	13.44	1.23	30.45
$C(NO_2)_2\text{-}[CH_2CH_2N(NO_2)CH_2C(NO_2)_2CH_3]_2$	78.8	206-208	Acetone	$C_{11}H_{18}N_{10}O_{16}$	24.18	3.32	25.64	24.76	3.35	24.98
$C(NO_2)_2\text{-}[CH_2CH_2N(NO_2)CH_2C(NO_2)_3]_2$	69.8	170-175	100% Nitric acid	$C_9H_{12}N_{12}O_{20}$	17.77	1.99	27.64	18.11	2.00	27.34
$N(NO_2)\text{-}[CH_2CH_2N(NO_2)CH_2C(NO_2)_3]_2$	26.8	158-159	70% Nitric acid	$C_8H_{12}N_{12}O_{18}$	17.03	2.14	29.79	17.57	2.38	29.78
$[CH_2N(NO_2)CH_2CH_2N(NO_2)CH_2C(NO_2)_3]_2$	45.1	166-167	70% Nitric acid	$C_{10}H_{16}N_{14}O_{20}$	18.41	2.47	30.06	18.22	2.38	29.86
$N(NO_2)\text{-}[CH_2C(NO_2)_2CH_2CH_2N(NO_2)CH_2C(NO_2)_3]_2$	40.0	186-187	Nitromethane and carbon tetrachloride	$C_{12}H_{16}N_{16}O_{26}$	18.01	2.02	28.00	18.43	2.42	27.85

products using absolute nitric acid and acetic anhydride. A 150-ml. quantity of absolute commercial nitric acid was cooled in an ice-salt bath and 150 ml. of acetic anhydride was added dropwise, keeping the temperature at 5 to 10° C. Then 28.2 grams (0.079 mole) of 1,1,1,6,6,6-hexanitro-3-azahexane was added. The reaction mixture was warmed to 30° C. to affect solution. (in some cases the amine dissolved at 5 to 10° C. and it was unnecessary to raise the temperature.) The solution was poured on ice. The white solid was collected, washed with water, and dried to give 27.0 grams (86.5%) of product, m.p. 115 to 122° C. Two recrystallizations from chloroform gave white needles, m.p. 144 to 145° C.

2,2,4,7,7,10,12,12-Octanitro-4,10-diazatridecane. This is an example of the preparation of a nitramine using 100% nitric acid and concentration sulfuric acid. To a solution of 53.0 grams (0.20 mole) of 3,3-dinitro-1,5-pentane diamine dihydrochloride, 60 grams (0.40 mole) of 2,2-dinitropropanol, and 400 ml. of water was added dropwise 82 ml. of 4.877*N* sodium hyroxide solution (0.40 mole). A hard yellow solid separated. The water in the flask was decanted and the product in the flask was dried. A solution of 200 ml. of concentrated sulfuric acid and 300 ml. of technical 100% nitric acid was added, and the reaction mixture was warmed to 50 to 55° C. for 20 minutes. On cooling 80 grams of white solid separated, and an additional 6.0 grams was obtained by pouring the filtrate on ice, giving a total over-all yield of 86 grams (79%), m.p. 198 to 200° C. Recrystallization from acetone raised the melting point to 206 to 208° C.

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