were 2.72, 1.48, and 1.18; intensity ratios 4:6:1. The chemical shift of the N-proton was very dependent on concentration; at about 400 mg./ml. it was superimposed on the β- and γ-proton resonances in the spectra of both compounds.

Effect of Solvent on the Cyanoethylation of Acetylacetone.—A mixture of 9.8 g. (0.1 mole) of acetylacetone, 10.7 g. (0.2 mole) of acrylonitrile, and 60 ml. of the solvent was placed in a water bath thermostatted at 25.0 ± 0.1°. After thermal equilibrium had been reached, 10 ml. of triethylamine was added. The mixture was filtered shortly before and shortly after the estimated time required for half-completion of the reaction (as determined by preliminary experiments). The product (I) from each filtration was washed with ethanol, dried, and weighed. The filtrate was maintained at 25° until the reaction was essentially complete and the product removed by filtration, washed, dried, and weighed to obtain the ultimate yield. A graphical interpolation was then used to determine the time required to obtain half of the ultimate yield.

Michael-type Reactions with $\alpha,\alpha,\omega,\omega$-Tetranitroalkanes[1]

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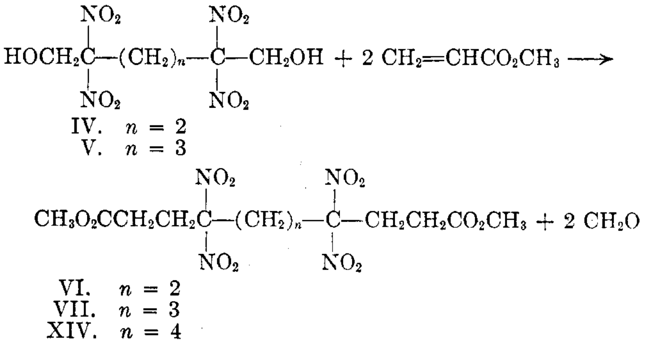
Received September 17, 1962

Michael-type reactions of 1,1,4,4-tetranitrobutane (I), 1,1,5,5-tetranitropentane (II), and 1,1,6,6-tetranitrohexane (III) with a molar excess of acceptor, such as acrylic acid, methyl acrylate, acrylonitrile, acrolein, methyl vinyl ketone, methyl vinyl sulfone, and nitroethylene, afford α,ω-bisadducts in each case. Either the free $\alpha,\alpha,\omega,\omega$-tetranitroalkanes or their α,ω-bismethylol derivatives can be employed, the latter being demethylolated *in situ*. The reaction of the disodium salt of III with 2-bromo-2,2-dinitroethyl acetate and with 2-nitrobutyl acetate leads respectively to 1,1,3,3,8,8,10,10-octanitrodecane (XX) and 3,5,5,10,10,12-hexanitrotetradecane (XXII). The dibasic acids 4,4,7,7-tetranitrodecanedioic acid (XI) and 4,4,8,8-tetranitroundecanedioic acid (XV) are converted, consecutively into their respective acid chloride, diazide, diisocyanate, methyl carbamate, diamine, and diacetamido derivatives.

Michael addition reactions of mononitroalkanes have been studied extensively and numerous examples are known.[3] Fewer examples of additions of 1,1-dinitroalkanes have been reported,[4-9] but the scope of this reaction appears potentially equal to that employing mononitroalkanes. The addition of methyl acrylate to dipotassium 1,1,3,3-tetranitropropane[9] appears to be the only reported example of the Michael-type reaction with an $\alpha,\alpha,\omega,\omega$-tetranitroalkane. In this instance, only monoaddition took place and methyl 3,3,5,5-tetranitropentanoate was obtained.

In continuation of our study of the Michael-type addition with nitroalkanes,[10-13] we are now reporting our findings with $\alpha,\alpha,\omega,\omega$-tetranitroalkanes[14] such as 1,1,4,4-tetranitrobutane (I), 1,1,5,5-tetranitropentane (II), and 1,1,6,6-tetranitrohexane (III), leading to α,ω-disubstituted products. Two procedures were used with such Michael acceptors as methyl acrylate, acrylic acid, acrylonitrile, acrolein, methyl vinyl ketone, methyl vinyl sulfone, and nitroethylene.

Procedure A.—The α,ω-bismethylol-$\alpha,\alpha,\omega,\omega$-tetranitroalkanes[14] were employed, the tetranitroalkanes being generated *in situ* by demethylolation in the presence of catalytic amounts of sodium hydroxide. In the equation below, Procedure A is illustrated by the reactions of 2,2,5,5-tetranitro-1,6-hexanediol (IV) and 2,2,6,6-tetranitro-1,7-heptanediol (V) with methyl acrylate to yield dimethyl 4,4,7,7-tetranitrodecanedioate (VI) and dimethyl 4,4,8,8-tetranitroundecanedioate (VII), respectively.



$$\mathrm{HOCH_2}\underset{\mathrm{NO_2}}{\overset{\mathrm{NO_2}}{\mathrm{C}}}\mathrm{-(CH_2)_{\mathit{n}}-}\underset{\mathrm{NO_2}}{\overset{\mathrm{NO_2}}{\mathrm{C}}}\mathrm{-CH_2OH} + 2\ \mathrm{CH_2{=}CHCO_2CH_3} \longrightarrow$$

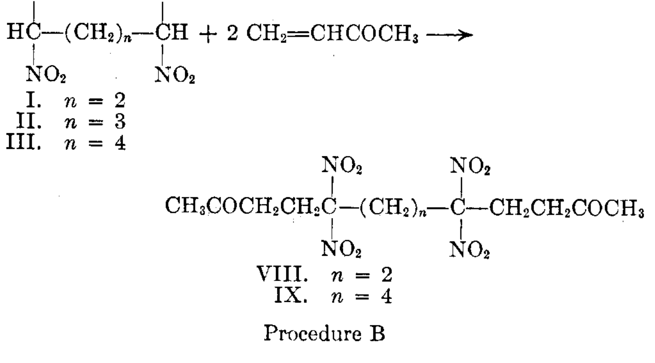
IV. $n = 2$
V. $n = 3$

$$\mathrm{CH_3O_2CCH_2CH_2}\underset{\mathrm{NO_2}}{\overset{\mathrm{NO_2}}{\mathrm{C}}}\mathrm{-(CH_2)_{\mathit{n}}-}\underset{\mathrm{NO_2}}{\overset{\mathrm{NO_2}}{\mathrm{C}}}\mathrm{-CH_2CH_2CO_2CH_3} + 2\ \mathrm{CH_2O}$$

VI. $n = 2$
VII. $n = 3$
XIV. $n = 4$

Procedure A

Procedure B, which was very effective with more reactive or base sensitive acceptors such as methyl vinyl ketone, nitroethylene, or acrolein, employed the free $\alpha,\alpha,\omega,\omega$-tetranitroalkanes with a trace of basic catalyst. Procedure B is illustrated by reactions of 1,1,4,4-tetranitrobutane (I) and 1,1,6,6-tetranitrohex-



$$\mathrm{H}\underset{\mathrm{NO_2}}{\overset{\mathrm{NO_2}}{\mathrm{C}}}\mathrm{-(CH_2)_{\mathit{n}}-}\underset{\mathrm{NO_2}}{\overset{\mathrm{NO_2}}{\mathrm{C}}}\mathrm{H} + 2\ \mathrm{CH_2{=}CHCOCH_3} \longrightarrow$$

I. $n = 2$
II. $n = 3$
III. $n = 4$

$$\mathrm{CH_3COCH_2CH_2}\underset{\mathrm{NO_2}}{\overset{\mathrm{NO_2}}{\mathrm{C}}}\mathrm{-(CH_2)_{\mathit{n}}-}\underset{\mathrm{NO_2}}{\overset{\mathrm{NO_2}}{\mathrm{C}}}\mathrm{-CH_2CH_2COCH_3}$$

VIII. $n = 2$
IX. $n = 4$

Procedure B

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[1] Presented before the Division of Organic Chemistry at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.

[2] Taken, in part, from the Ph.D. theses of Gerd Leston (1952) and Robert Miller (1958), Purdue University.

[3] For a thorough survey of the literature, reference is made to E. D. Bergman, D. Ginsburg, and R. Pappo, *Org. Reactions*, **10**, 179 (1959).

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[11] H. Feuer and R. Harmetz, *ibid.*, **26**, 1061 (1961).

[12] H. Feuer and R. Miller, *ibid.*, **26**, 1348 (1961).

[13] H. Feuer, E. H. White, and S. M. Pier, *ibid.*, **26**, 1639 (1961).

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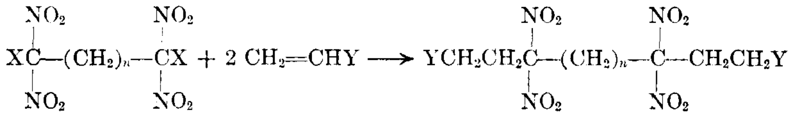
TABLE I

MICHAEL REACTIONS OF $\alpha,\alpha,\omega,\omega$-TETRANITROALKANES


$$XC(NO_2)_2{-}(CH_2)_n{-}C(NO_2)_2X + 2\ CH_2{=}CHY \longrightarrow YCH_2CH_2C(NO_2)_2{-}(CH_2)_n{-}C(NO_2)_2{-}CH_2CH_2Y$$

Nitro cpd., X = ; n = (No.)	Vinyl cpd., Y =	Product	Yield, %[a]	M.p.[b]	Formula	Calcd., % C,	H,	N,	Found, % C,	H,	N,
CH_2OH; 2 (IV)	CN	X	48	148–149°	$C_{10}H_{12}N_6O_8$	34.89	3.51	24.42	34.80	3.40	24.55
CH_2OH; 2 (IV)	CO_2H	XI[c]	60	188°	$C_{10}H_{14}N_4O_{12}$	31.41	3.66	14.66	31.30	3.76	14.80
CH_2OH; 2 (IV)	CO_2CH_3	VI	(68)[a]	157–157.5°	$C_{12}H_{18}N_4O_{12}$	35.12	4.39	13.66	35.42	4.40	13.82
H; 2(I)	$COCH_3$	VIII	(82)[a]	152–153°	$C_{12}H_{18}N_4O_{10}$	38.10	4.80	14.81	38.22	4.89	15.09
H; 2(I)	CHO	XVII[d]	..	Oil[d]	$C_{10}H_{14}N_4O_{10}$						
H; 2(I)	NO_2	XVIII	(58)[a]	147–150°	$C_8H_{12}N_6O_{12}$	25.01	3.14	21.88	24.94	3.12	21.95
CH_2OH; 3 (V)	CN	XII	33	91°	$C_{11}H_{14}N_6O_8$	36.87	3.94	23.46	36.91	3.92	23.42
CH_2OH; 3 (V)	CO_2CH_3	VII	(65)[a]	64.5°	$C_{13}H_{20}N_4O_{12}$	36.79	4.71	13.21	36.85	4.77	13.10
H; 4 (III)	SO_2CH_3	[e]	47	169.5–170°	$C_{12}H_{22}N_4S_2O_{12}$	30.12	4.60	11.71	30.25	4.70	11.45
H; 4 (III)	CN	XIII	54	130–131°	$C_{12}H_{16}N_6O_8$	38.71	4.33	22.58	38.50	4.41	22.74
H; 4 (III)	CO_2CH_3	XIV	83	102.5–103°	$C_{14}H_{22}N_4O_{12}$	38.35	5.02	12.77	38.63	5.00	13.11
H; 4 (III)	$COCH_3$	IX	98	128°	$C_{14}H_{22}N_4O_{10}$	41.38	5.46	13.79	41.24	5.53	13.76

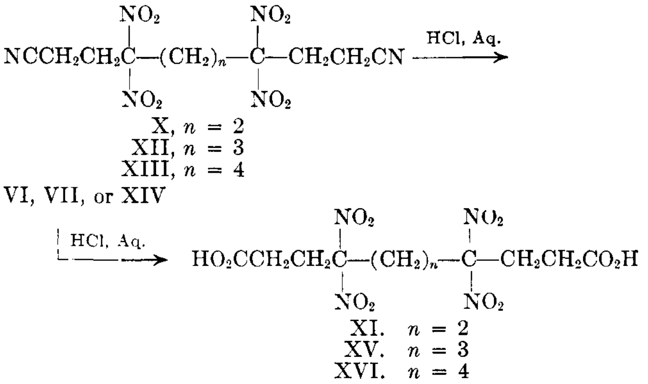
[a] Yields in parentheses are for analytically pure recrystallized samples having melting points reported in table; other yields are for slightly less pure products (melting points given in Experimental). [b] Melting points are for analytically pure samples, recrystallized. [c] Neutral equivalent found, 193; calculated for $C_{10}H_{14}N_4O_{12}$, 191. [d] Product was an oil which could not be distilled without decomposition; isolated as dioxime and bis-2,4-dinitrophenylhydrazone derivatives (analyses in Experimental). [e] Reaction gave mono- and bis-adducts; the latter, 1,10-bis(methylsulfonyl)-3,3,8,8-tetranitrodecane, is listed here.

ane (III) with methyl vinyl ketone to yield 5,5,7,7-tetranitrododecane-2,11-dione (VIII) and 5,5,9,9-tetranitrotetradecane-2,13-dione (IX), respectively.

The reactions were generally conducted in *ca.* 90% methanol or ethanol at 50° with a catalytic amount of sodium hydroxide for six to twenty-four hours. Room temperature or below was employed with the more reactive acceptors methyl vinyl ketone, acrolein and nitroethylene. With one exception (4,4,7,7-tetranitrodecanedial) the products were stable, white crystalline solids, easily purified by crystallization; most were characterized by one or more derivatives. Yields varied considerably (33 to 98%) and were generally superior with the more reactive, base insensitive acceptors (methyl vinyl ketone and methyl acrylate) and poorer with less reactive (acrylonitrile, methyl vinyl sulfone) or base sensitive (nitroethylene) acceptors. A summary of examples studied is presented in Table I.

α,ω-Bis-adducts were obtained in every reaction by employing an excess of the acceptor. With methyl vinyl sulfone, which reacted very slowly with 1,1,6,6-tetranitrohexane, it was possible to isolate both mono- and bis-adducts [1-methylsulfonyl-3,3,8,8-tetranitrooctane and 1,10-bis(methylsulfonyl)-3,3,8,8-tetranitrodecane, respectively].

The bis-adducts derived from 1,1,4,4-tetranitrobutane and acrylonitrile and methyl acrylate [4,4,7,7-tetranitrodecanedinitrile (X) and VI, respectively] could be hydrolyzed by refluxing with dilute hydrochloric acid to form 4,4,7,7-tetranitrodecanedioic acid (XI) in quantitative yield; the same acid was also obtained by addition of IV to sodium acrylate. Also, the bis-adducts of 1,1,5,5-tetranitropentane (II) with acrylonitrile and methyl acrylate [4,4,8,8-tetranitroundecanedinitrile (XII) and VII, respectively] could each be hydrolyzed to 4,4,8,8-tetranitroundecanedioic acid (XV). Similarly, the bis-adducts of 1,1,6,6-tetranitrohexane (III) with acrylonitrile and methyl acrylate [4,4,9,9-tetranitrododecanedinitrile (XIII) and dimethyl 4,4,9,9-tetranitrododecanedioate (XIV), respectively] could each be hydrolyzed to 4,4,9,9-tetranitrododecanedioic acid (XVI).

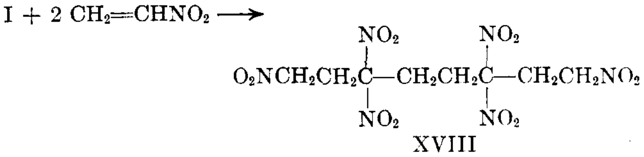


$$NCCH_2CH_2C(NO_2)_2{-}(CH_2)_n{-}C(NO_2)_2{-}CH_2CH_2CN \xrightarrow{HCl,\ Aq.} HO_2CCH_2CH_2C(NO_2)_2{-}(CH_2)_n{-}C(NO_2)_2{-}CH_2CH_2CO_2H$$

$$IV + 2\ CH_2{=}CHCO_2H \xrightarrow{NaOH} XI + 2CH_2O$$

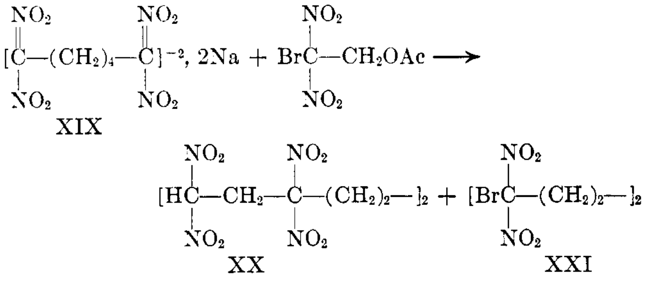
The addition of I to acrolein (sodium ethoxide, ethanol) produced an unstable oil, which could not be crystallized or distilled without decomposition; the oil formed a dioxime and a bis-2,4-dinitrophenylhydrazone derived from the bis-adduct 4,4,7,7-tetranitrodecanedial (XII). Dioxime derivatives were also prepared from the methyl vinyl ketone bis-adducts VIII and IX. Attempts to add I to ethyl propiolate failed to yield a bis-adduct.

The addition of 1,1,4,4-tetranitrobutane to nitroethylene was conducted in tetrahydrofuran solvent at 0° to minimize polymerization of nitroethylene (Triton B catalyst). The reaction gave 1,3,3,6,6,8-hexanitroöctane (XVIII) and appears to be the first example of the use of nitroethylene as an acceptor in the


$$I + 2\ CH_2{=}CHNO_2 \longrightarrow O_2NCH_2CH_2C(NO_2)_2{-}CH_2CH_2C(NO_2)_2{-}CH_2CH_2NO_2$$

XVIII

Michael reaction.[3,15] The α,ω-bismethylol derivative of XVIII was prepared, but this diol could not be oxidatively nitrated[14] to 1,1,3,3,6,6,8,8-octanitroöctane. Reaction of 2-bromo-2,2-dinitroethyl acetate with one mole equivalent of disodium 1,1,4,4-tetranitrohexane (XIX) by the method of Frankel[7] led to 1,1,3,3,8,8,10,10-octanitrodecane (XX) and 1,6-dibromo-1,1,6,6-tetranitrohexane (XXI).



$$[\overset{NO_2}{\underset{NO_2}{C}}-(CH_2)_4-\overset{NO_2}{\underset{NO_2}{C}}]^{-2}, 2Na + Br\overset{NO_2}{\underset{NO_2}{C}}-CH_2OAc \longrightarrow$$

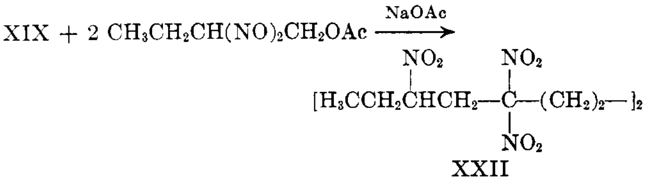
XIX

$$[H\overset{NO_2}{\underset{NO_2}{C}}-CH_2-\overset{NO_2}{\underset{NO_2}{C}}-(CH_2)_2-]_2 + [Br\overset{NO_2}{\underset{NO_2}{C}}-(CH_2)_2-]_2$$

XX XXI

It should be noted that Frankel[7] did not report the formation of the bromonitro compounds in this dinitroethylation reaction.[16]

A very convenient method of conducting Michael-type reactions by generating nitro olefins *in situ* from the corresponding 2-nitroalkyl acetates has been reported recently.[12] It has now been applied successfully to $\alpha,\alpha,\omega,\omega$-tetranitroalkanes. Thus the reaction between 2-nitrobutyl acetate and XIX afforded 3,5,5,10,10,12-hexanitrotetradecane (XXII).

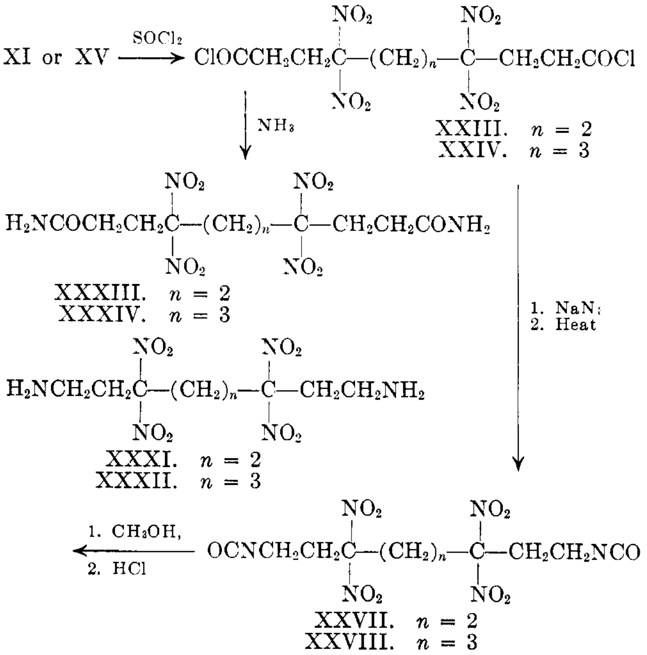


$$XIX + 2\ CH_3CH_2CH(NO)_2CH_2OAc \xrightarrow{NaOAc} [H_3CCH_2\overset{NO_2}{C}HCH_2-\overset{NO_2}{\underset{NO_2}{C}}-(CH_2)_2-]_2$$

XXII

The dibasic acids XI and XV were converted, consecutively, into their respective acid chlorides (XXIII and XXIV), diazides (XXV and XXVI), diisocyanates (XXVII and XXVIII), methyl carbamates (XXIX and XXX), and diamines (XXXI and XXXII). The diazides were obtained by reaction of the acid chlorides with sodium azide. By heating at 50–55° in chloroform solution the diazides decomposed readily to produce the corresponding diisocyanates. The latter compounds were characterized by their carbanilide and methyl carbamate derivatives. Hydrolysis of the carbamates (XXIX and XXX) with refluxing concentrated hydrochloric acid produced the diamine dihydrochlorides which were subsequently converted into the diamines (XXXI and XXXII); the latter substances were rather stable solids which were characterized by their diacetyl derivatives.

The diamides (XXXIII and XXXIV) were obtained from the corresponding acid chlorides by reaction with concentrated ammonia. These substances could not be prepared by condensation of IV or V with acrylamide nor by ammonolysis of esters VI or VII; these esters also failed to produce hydrazides on treatment with hydrazine.



$$XI \text{ or } XV \xrightarrow{SOCl_2} ClOCCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}-(CH_2)_n-\overset{NO_2}{\underset{NO_2}{C}}-CH_2CH_2COCl$$

XXIII. $n = 2$
XXIV. $n = 3$

$$\downarrow NH_3$$

$$H_2NCOCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}-(CH_2)_n-\overset{NO_2}{\underset{NO_2}{C}}-CH_2CH_2CONH_2$$

XXXIII. $n = 2$
XXXIV. $n = 3$

1. NaN_3
2. Heat

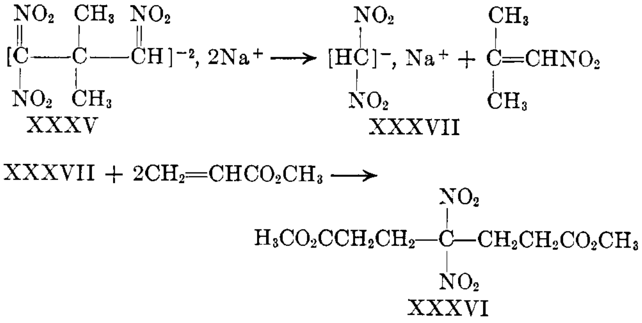
$$H_2NCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}-(CH_2)_n-\overset{NO_2}{\underset{NO_2}{C}}-CH_2CH_2NH_2$$

XXXI. $n = 2$
XXXII. $n = 3$

$$\xleftarrow[2.\ HCl]{1.\ CH_3OH,} OCNCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}-(CH_2)_n-\overset{NO_2}{\underset{NO_2}{C}}-CH_2CH_2NCO$$

XXVII. $n = 2$
XXVIII. $n = 3$

The reaction of the disodium salt of 2,2-dimethyl-1,1,3-trinitropropane (XXXV) with three mole equivalents of methyl acrylate did not give the expected adduct but rather led to dimethyl 4,4-dinitroheptanoate (XXXVI). It was identified by a mixture melting point determination with an authentic sample[4] and by hydrolysis to the known corresponding acid.[4] The unexpected formation of XXXVI most likely proceeded first by fission of XXXV to sodium dinitromethane (XXXVII) and 1-nitro-2-methyl-1-propene followed by the addition of XXXVII to methyl acrylate. The ready cleavage of XXXV was established in a separate experiment, in which XXXVII was obtained in the absence of methyl acrylate under conditions similar to those leading to XXXVI, thus suggesting XXXVII to be a reaction intermediate. Compound XXXVII was characterized by conversion to its potassium salt and also to 2,2-dinitro-1,3-propanediol (XXXVIII). An attempt to synthesize 1,3,3,5-tetranitropentane by base-catalyzed reaction of XXXVII with nitroethylene led to recovered XXXVIII and polynitroethylene.



$$[\overset{NO_2}{\underset{NO_2}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-\overset{NO_2}{C}H]^{-2}, 2Na^+ \longrightarrow [H\overset{NO_2}{\underset{NO_2}{C}}]^-, Na^+ + \overset{CH_3}{\underset{CH_3}{C}}=CHNO_2$$

XXXV XXXVII

$$XXXVII + 2CH_2=CHCO_2CH_3 \longrightarrow H_3CO_2CCH_2CH_2-\overset{NO_2}{\underset{NO_2}{C}}-CH_2CH_2CO_2CH_3$$

XXXVI

Experimental

Dimethyl 4,4,7,7-Tetranitrodecanedioate (VI).—2,2,5,5-Tetranitro-1,6-hexanediol (IV)[14] (2.98 g., 0.01 mole) and 3.44 g. (0.04 mole) of methyl acrylate were dissolved in 30 ml. of 90% aqueous methanol; 0.1 ml. of 50% sodium hydroxide solution was added, the solution stirred at 50° for 6 hr. and then cooled to 25° and filtered. The product was washed with a small volume of methanol and crystallized from benzene giving 2.77 g. of VI

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[15] H. Hopff and M. Capaul, *Helv. Chim. Acta*, **43**, 1898 (1960).

[16] Recently, W. E. McEwen and L. J. Winters reported to have obtained 2-bromo-2,2-dinitro-1-phthalimodoethane and 1,1-dinitro-2-phthalimidoethane on treatment of potassium phthalimide with 2-bromo-2,2-dinitroethyl acetate, [Abstracts, 138th National Meeting of the American Chemical Society, New York, N. Y., September, 1960, p. 25P].

(68% yield), m.p. 157–157.5°[17]; infrared band[17] at 5.75 μ (C═O, ester).

The disodium salt of 1,1,4,4-tetranitrobutane when treated with methyl acrylate in water solvent gave only a 22% yield of VI, m.p. 155–156°.

Dimethyl 4,4,8,8-Tetranitroundecanedioate (VII).—The procedure employed with IV was applied to 2,2,6,6-tetranitro-1,7-heptanediol[14] (V) (3.10 g., 0.01 mole) using a reaction time of 24 hr. (50°). The crude product (3.23 g.) was crystallized from methanol to yield 2.37 g. of VII (65% yield), m.p. 64.5°; infrared band at 5.75 μ (C═O, ester).[17]

4,4,7,7-Tetranitrodecanedinitrile (X).—Diol IV (2.98 g., 0.01 mole) and 2.12 g. (0.04 mole) of acrylonitrile were dissolved in 30 ml. of 90% aqueous methanol; 0.1 ml. of 50% sodium hydroxide solution was added and the solution stirred at 50° for 24 hr. The crude product X was filtered (1.65 g., 48% yield, m.p. 143–149°). Two recrystallizations from absolute ethanol raised the melting point to 148–149°; infrared band at 4.45 μ (C≡N).[17]

4,4,8,8-Tetranitroundecanedinitrile (XII) was prepared in the same manner as X using V (3.12 g., 0.01 mole). After stirring at 50° for 24 hr. and cooling to 5° the crude product XII was filtered (1.17 g., 33% yield, m.p. 89°). Recrystallization from 75% aqueous ethanol solution raised the melting point to 91°; infrared band at 4.45 μ (C≡N).[17]

4,4,7,7-Tetranitrodecanedioic Acid (XI). (a) **From 2,2,5,5-Tetranitro-1,6-hexanediol (IV) and Acrylic Acid.**—Diol IV (2.98 g., 0.01 mole) and 2.88 g. (0.04 mole) of acrylic acid (96% assay) were dissolved in 50 ml. of 90% aqueous methanol. Sodium hydroxide was added to produce the yellow color of the bisnitronate anion (pH *ca.* 6–7). The solution was stirred at 50° for 6 hr. and filtered to remove a small amount of solid; slow acidification of the filtrate with 5 *N* hydrochloric acid at 25° produced a solid which was filtered (4.15 g.). The solid was purified by dissolving in sodium bicarbonate solution, filtering, reprecipitating with hydrochloric acid and recrystallizing from water to yield 2.27 g. (60% yield) of acid XI, m.p. 179–181°. Another recrystallization using charcoal raised the melting point to 182–184°; infrared band at 5.8 μ (C═O, carboxyl).

(b) **From Dimethyl 4,4,7,7-Tetranitrodecanedioate (VI).**—A 6.76-g. sample of the diester (VI) was added to 1 l. of 6 *N* hydrochloric acid and the mixture refluxed for 4 hr. After filtering while hot, the filtrate was chilled and the product filtered. The filtrate was concentrated to yield additional material and the combined crops were recrystallized from large quantities of boiling water to yield 6.2 g. of XI (98%), m.p. 188°.

(c) **From 4,4,7,7-Tetranitrodecanedinitrile (X).**—A 0.2-g. sample of the dinitrile (X) was refluxed with 10 ml. of 18% hydrochloric acid solution for 18 hr. The mixture was filtered while hot to remove unchanged nitrile (0.12 g.) and the filtrate cooled to precipitate the acid. Recrystallization of the crude product from water gave XI, m.p. 187–187.5°.

4,4,8,8-Tetranitroundecanedioic Acid (XV). (a) **From Dimethyl 4,4,8,8-Undecanedioate (VII).**—A 6.36-g. sample of diester VII was refluxed with 250 ml. of 6 *N* hydrochloric acid for 4 hr. The solution was chilled and filtered to yield 5.90 g. (99.3% yield) of acid XV, m.p. 174.4–174.7°; infrared band at 5.8 μ (C═O, carboxyl).

Anal. Calcd. for $C_{11}H_{16}N_4O_{12}$: C, 33.33; H, 4.04; N, 14.14; neut. equiv., 198. Found: C, 33.23; H, 3.91; N, 14.21; neut. equiv., 203.

(b) **From 4,4,8,8-Tetranitroundecanedinitrile (XII).**—A small sample of the dinitrile (XII) was refluxed with 18% hydrochloric acid for 1 hr. and the acid isolated in the usual manner, m.p. 172–173°.

5,5,8,8-Tetranitrododecane-2,11-dione (VIII).—1,1,4,4-Tetranitrobutane[14] (I) (1.19 g., 0.05 mole) was dissolved in 15 ml. of 95% ethanol; 0.9 g. (0.011 mole) of methyl vinyl ketone (85% water azeotrope) was then added and the solution chilled to 3°. Two drops of 50% sodium hydroxide solution was then added, keeping the temperature below 3°; stirring was continued for 1.5 hr. after which time the mixture was allowed to warm to room temperature. A white precipitate formed during the reaction. The mixture was acidified with hydrogen chloride gas, diluted with water, and filtered; the precipitate was washed with water and dried; 1.59 g., m.p. 150–152°. After recrystallizing from ethanol there was obtained 1.51 g. (82% yield) of diketone VIII as long white needles, m.p. 152–153° [17].

The **dioxime** derivative of VIII was prepared by using an excess of hydroxylamine hydrochloride in pyridine solution; white needles from 95% ethanol, m.p. 182–183° (decompn.).

Anal. Calcd. for $C_{12}H_{20}N_6O_{10}$: C, 35.30; H, 4.93; N, 20.58. Found: C, 35.51; H, 4.97; N, 20.83.

Attempts to prepare an adduct of I with ethyl propiolate were unsuccessful. With 0.1 mole equivalent of sodium ethoxide per mole of II, tetrahydrofuran solvent, 0°, no reaction occurred and 71% of I was recovered. The dipotassium salt of I also did not react with ethyl propiolate, 85% of I ultimately being recovered. When sodium ethoxide (0.67 mole equivalent) was added to a mixture of I and ethyl propiolate in tetrahydrofuran solvent at 0°, a vigorous reaction occurred after adding the last portion of base with formation of sodium nitrite, oxides of nitrogen and a trace of crystalline material, m.p. 155–165° (dec.) unidentified.

4,4,8,8-Tetranitrodecanedial Dioxime.—A 1.2-g. sample of I and 0.6 g. (0.01 mole) of acrolein were dissolved in 15 ml. of absolute ethanol and the solution chilled to 3°. To the cold solution was added 0.4 ml. of *N* ethanolic sodium ethoxide solution with stirring. A light yellow precipitate formed at first, and after stirring the cold mixture for 1 hr., the precipitate dissolved. The solution was then warmed to room temperature and allowed to stand for 1 hr. The mixture was acidified with ethanolic hydrogen chloride and concentrated *in vacuo* at room temperature to remove volatile material. There remained 2.0 g. of a pale yellow oil, believed to be mainly the dialdehyde XVII. Attempts to crystallize it failed and on standing in air it produced a brittle substance, containing nitrogen, m.p. 58–65°.

The **dioxime** of XVII was prepared from another similar run by pouring the entire unacidified ethanol solution of the reaction mixture into an aqueous solution containing excess hydroxylamine and ammonium acetate (pH *ca.* 8). After heating on a steam bath for 10 min., cooling, and diluting with water, the crude derivative was removed by filtration. Recrystallization from chloroform containing a small amount of methanol gave white crystals, m.p. 122–123°.

Anal. Calcd. for $C_{10}H_{16}N_6O_{10}$: C, 31.58; H, 4.24; N, 22.10. Found: C, 31.88; H, 4.24; N, 21.45.

The **2,4-dinitrophenylhydrazone** derivative of XVII was prepared from the above yellow oil by the usual procedure. It was very insoluble in a variety of organic solvents but could be crystallized from nitromethane; m.p. 218° (dec.).

Anal. Calcd. for $C_{22}H_{22}N_{12}O_{16}$: C, 37.19; H, 3.12; N, 23.66. Found: C, 37.21; H, 3.22; N, 23.91.

1,3,3,6,6,8-Hexanitroöctane (XVIII).—1,1,4,4-Tetranitrobutane (17.47 g., 0.073 mole) was dissolved in 110 ml. of dry tetrahydrofuran. While maintaining the temperature at −6°, 1 ml. of 35% methanolic Triton B catalyst (benzyltrimethylammonium hydroxide, Rohm and Haas Co.) was slowly added with stirring. Freshly distilled nitroethylene[15] (11.7 g., 0.16 mole) was added with stirring during 25 min. (−5 to 0°). Stirring was continued for 6.5 hr. while the mixture was allowed to warm to 25°. Hydrochloric acid (12 *N*) was added dropwise to the clear dark red solution until the color became light orange; the solution was then concentrated to dryness. The yellow solid remaining was recrystallized from a mixture of ethanol (1 l.) and ethyl acetate (350 ml.) to yield 16.1 g. (58% yield) of XVIII, m.p. 147–150° (dec.). Recrystallization from ethanol gave long, amber colored needles, m.p. 146–147°.[17]

An attempt was made to prepare 1,3,3,5-tetranitropentane by treating nitroethylene (2 mole-equivalents) with 2,2-dinitro-1,3-propanediol (Triton B catalyst, tetrahydrofuran solvent). Polymerization of the nitroethylene occurred very rapidly to yield polynitroethylene (98%) and recovered diol (54%).

2,4,4,7,7,9-Hexanitro-1,10-decanediol.—1,3,3,6,6,8-Hexanitroöctane (XVIII) (3.84 g., 0.01 mole) was suspended in 12 ml. of tetrahydrofuran. Potassium hydroxide (1.32 g., 0.02 mole, 85% assay) dissolved in 10 ml. of 90% methanol was added and the deep-red solution was stirred for 20 min. at 3°. Formalin (1.5 ml., 0.02 mole of formaldehyde) was added and the solution was stirred for 30 min. at 0°. The solution was then acidified with 3 ml. of acetic acid and diluted with 100 ml. of ice–water. A red gum formed which was separated from the solution by decantation. Digestion of the gum with 10 ml. of boiling ethanol followed by addition of water and cooling gave a granular orange-yellow solid which was filtered, washed with water, and dried; 3.39 g., m.p. 125–130°. Crystallization from 15 ml. of ethanol

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[17] Elemental analyses are given in Table I. Infrared spectra were determined as Nujol mulls.

gave 0.70 g. of diol (16% yield), m.p. 155–157°; a second recrystallization raised the melting point to 156–158° (dec.).

Anal. Calcd. for $C_{10}H_{16}N_6O_{14}$: C, 27.03; H, 3.63; N, 18.92. Found: C, 27.33; H, 3.80; N, 18.80.

An attempt to oxidatively nitrate[14] the diol to form 2,2,4,4,7,7,9,9-octanitro-1,10-decanediol was unsuccessful. The reaction, which was carried out in tetrahydrofuran–methanol solution, gave a silver-containing product from which the organic material could not be removed by continuous extraction with boiling ether.

Dimethyl 4,4,9,9-Tetranitrododecanedioate (XIV).—To 1.0 g. (0.0037 mole) of 1,1,6,6-tetranitrohexane[14] (III) dissolved in 15 ml. of 90% aqueous methanol were added 0.78 g. (0.0091 mole) of methyl acrylate and 0.1 ml. of 20% sodium hydroxide solution. The mixture was stirred at 50° for 20 hr. and then acidified with dilute hydrochloric acid and cooled. The crude product, m.p. 100–101°, was filtered (1.36 g.; estimated yield, 83%); m.p. 102.5–103° after recrystallization from methanol.[17]

4,4,9,9-Tetranitro-1,12-dodecanedinitrile (XIII).—The procedure used above for preparation of ester XIV was applied to III (1.0 g.) and acrylonitrile (0.49 g.) to yield 0.75 g. of product (estimated yield, 54%); m.p. 130–131° after recrystallization from absolute methanol.[17]

4,4,9,9-Tetranitrododecanedioic Acid (XVI). (a) From Dimethyl 4,4,9,9-Tetranitrododecanedioate (XIV).—A 1.36 g. sample of ester XIV was refluxed with 50 ml. of 6 *N* hydrochloric acid for 8 hr. After cooling, the product was filtered (1.13 g; estimated yield, 89%); m.p. 182–183° (dec.) after recrystallizing from water.

(b) **From 4,4,9,9-Tetranitrododecanedinitrile (XIII).**—The dinitrile (XIII) was refluxed with 6 *N* hydrochloric acid for 70 hr. to give acid XVI in 87% yield, m.p. 180–181° (dec.); when mixed with the acid obtained from ester XVI, the melting point was not depressed.

Anal. Calcd. for $C_{12}H_{18}N_4O_{12}$: N, 13.65; neut. equiv., 205. Found: N, 13.25; neut. equiv., 204.

5,5,10,10-Tetranitro-2,13-tetradecanedione (IX).—The procedure used above for preparing diketone VIII was applied to III (1.0 g.) and methyl vinyl ketone (1.0 g. of 85% azeotrope). The reaction was run at 27° for 18 hr. employing 3 drops of 40% Triton B catalyst. The mixture was made slightly acidic with dilute hydrochloric acid and chilled to yield 1.5 g. of product, m.p. 126–127.5° (estimated yield, 98%); m.p. 128° after recrystallization from 95% ethanol.[17]

The **dioxime** derivative of IX was prepared by refluxing with an excess of hydroxylamine in ethanol–pyridine solution for 2 hr.; m.p. 163–164° (decompn.) after recrystallization from aqueous ethanol.

Anal. Calcd. for $C_{14}H_{24}N_6O_{10}$: C, 38.50; H, 5.50; N, 19.25. Found: C, 38.73; H, 5.33; N, 19.33.

1,10-Bis(methylsulfonyl)-3,3,8,8-tetranitrodecane.—To a solution of 2.0 g. (0.0075 mole) of 1,1,6,6-tetranitrohexane (III) and 2.06 g. (0.0194 mole) of methyl vinyl sulfone in 30 ml. of 90% ethanol was added 0.15 ml. of 20% sodium hydroxide solution; the mixture was stirred at 50° for 24 hr. After acidification with dilute hydrochloric acid and chilling there was obtained 1.68 g. (47% crude) of material, m.p. 154–161°; m.p. 169.5–170° (dec.) after recrystallization from acetic acid.[17]

From the concentrated ethanol filtrate there was obtained 0.65 g. of material which was recrystallized from aqueous methanol to give **1-methylsulfonyl-3,3,8,8-tetranitroöctane**, m.p. 104–105°.

Anal. Calcd. for $C_9H_{16}N_4SO_{10}$: C, 29.03; H, 4.30; N, 15.05. Found: C, 29.11; H, 4.50; N, 15.08.

The reaction was repeated using 2.0 g. of III and 1.03 g. of methyl vinyl sulfone to yield a product, m.p. 87–91° (0.72 g.) after rubbing on a clay plate; recrystallization from aqueous methanol again gave 1-methylsulfonyl-3,3,8,8-tetranitroöctane, m.p. 104–105°.

1,1,3,3,8,8,10,10-Octanitrodecane (XX).—To a solution of 1.24 g. (0.030 mole) of sodium hydroxide (97.3% assay) in 100 ml. of water was added with stirring 4.0 g. (0.015 mole) of 1,1,6,6-tetranitrohexane, keeping the temperature below 5° until all of the nitro compound was dissolved. While maintaining the temperature at 5° a solution of 3.86 g. (0.015 mole) of 2-bromo-2,2-dinitroethyl acetate[7] in 100 ml. of methanol was added. After warming to 24° the mixture was stirred for 10 hr.; a solid which formed was removed by filtration. The filtrate was concentrated to a small volume under reduced pressure and extracted with ether. The ether extract was evaporated to dryness and the resulting solid was combined with the filtered material (2.88 g. total). After recrystallization, first from hexane, then from ethanol, **1,6-dibromo-1,1,6,6-tetranitrohexane (XXI)** was obtained, m.p. 120–121°; when mixed with an authentic sample, m.p. 120–121°,[14] the melting point was not depressed.

The above aqueous solution remaining after ether extraction was chilled to 0° and acidified with dilute hydrochloric acid; the mixture was extracted with ether and the combined extracts dried over magnesium sulfate. Evaporation of the ether gave an oil which was crystallized from aqueous methanol to yield 1.03 g. (27% yield) of 1,1,3,3,8,8,10,10-octanitrodecane (XXI), m.p. 130–131° (dec.).

Anal. Calcd. for $C_{10}H_{14}N_8O_{16}$: C, 23.90; H, 2.79; N, 22.31. Found: C, 23.91; H, 2.87; N, 22.15.

3,5,5,10,10,12-Hexanitrotetradecane (XXII). –To a cooled solution (0–5°) of 1.63 g. (0.04 mole) of 98% assay sodium hydroxide (65 ml. of methanol and 15 ml. of water) was added with stirring 5.32 g. (0.02 mole) of 1,1,6,6-tetranitrohexane all at once. After salt formation was complete, 6.44 g. (0.04 mole) of 2-nitrobutyl acetate was added all at once, followed by 3.28 g. (0.04 mole) of anhydrous sodium acetate. The mixture was stirred at 6 hr. at 26° and then for 10 more hr. at 40°. Cooling and filtering afforded 6.1 g. (65% yield) of XXII, m.p. 91–95° (mixture of diastereomers). Heating the solid product in 85% aq. methanol and cooling the filtrate gave one of the isomers, m.p. 99–100°.

Anal. Calcd. for $C_{14}H_{24}N_6O_{12}$: C, 35.90; H, 5.13; N, 17.95 Found: C, 35.82; H, 5.02; N, 18.21.

Recrystallization of the insoluble portion with absolute methanol gave the other isomer, m.p. 118–119°. Found: C, 35.90; H, 4.94; N, 18.14.

4,4,7,7-Tetranitrodecanedioyl Chloride (XXIII).—A mixture of 2.0 g. (0.00477 mole) of acid XI and 80 ml. of thionyl chloride was refluxed for 3 hr.; it was then chilled and filtered. The product was dried in a vacuum desiccator; 1.83 g. (83.3%), m.p. 143–144°; by concentrating the mother liquor an additional 0.16 g. was isolated (total yield 90.7%).

Anal. Calcd. for $C_{10}H_{12}Cl_2N_4O_{10}$: C, 28.64; H, 2.86; N, 13.37. Found: C, 28.67; H, 2.89; N, 13.38.

A small sample of the acid chloride was refluxed with methanol for 1 min. to yield the corresponding diester (VI), m.p. 157°. Similarly, refluxing with water produced the acid XI, m.p. 185°.

4,4,8,8-Tetranitroundecanedioyl Chloride (XXIV).—A 2.87-g. (0.0075 mole) sample of acid XV was refluxed with 100 ml. of thionyl chloride for 4 hr. The excess thionyl chloride was then removed *in vacuo* leaving 3.22 g. (99.0%) of the diacid chloride XXIV, m.p. 66–67°; recrystallization from benzene raised the melting point to 66.5–67.5°.

Anal. Calcd. for $C_{11}H_{14}Cl_2N_4O_{10}$: C, 30.48; H, 3.23; N, 12.93. Found: C, 30.79; H, 3.55; N, 12.57.

Dimethyl 3,3,6,6-Tetranitroöctanedicarbamate (XXIX).—A solution of1.05 g. (0.0025 mole) of acid chloride XXIII in 5 ml. of acetone was added dropwise with vigorous stirring to a solution of 0.65 g. (0.01 mole) of sodium azide in 5 ml. of water. After 15 min., 5 ml. of water was added and the product filtered, washed several times with water and dried *in vacuo* to yield 0.94 g. (87%) of **4,4,7,7-tetranitrodecanedioyl azide (XXV)**, m.p. 101° (dec.).

A 1.08-g. (0.0025 mole) sample of the diazide (XXV) in 35 ml. of dry chloroform was heated at 50–55° for 4 hr. The mixture was filtered and refluxed with 1 ml. of methanol for 4 hr. Cooling and filtering gave 0.91 g. (83%) of the dicarbamate XXIX, m.p. 160–163°; recrystallization from methanol raised the melting point to 161–163°.

Anal. Calcd. for $C_{12}H_{20}N_6O_{12}$: C, 32.73; H, 4.55; N, 19.09. Found: C, 32.57; H, 4.60; N, 19.01.

A 0.1-g. sample of the diazide (XXV) in 2 ml. of dry chloroform was heated at 50–55° for 3 hr. The material was filtered and the filtrate cooled to −30°; the **3,3,6,6-tetranitroöctamethylene diisocyanate (XXVII)** was filtered (0.08 g., 92% yield), m.p. 89.5–91°. Recrystallization from dry chloroform raised the melting point to 91–92°.

3,3,7,7-Tetranitroöctanedicarbanilide.—A small sample of the diazide (XXV) was heated in dry chloroform at 50–55° for 1 hr. and then refluxed for 15 min. The mixture was filtered and a few drops of aniline added; the crude product was filtered (m.p. 191°, dec.) and purified by dissolving in hot acetone and reprecipitating with water; m.p. 194.5° (dec.) with previous darkening.

Anal. Calcd. for $C_{22}H_{26}N_8O_{10}$: C, 46.97; H, 4.64; N, 19.93. Found: C, 46.84; H, 4.81; N, 19.31.

Dimethyl 3,3,7,7-Tetranitrononanedicarbamate (XXX).—A solution of 0.86 g. (0.0132 mole) of sodium azide in 10 ml. of acetic acid was added dropwise at 15° to 1.39 g. (0.00321 mole) of acid chloride XXIV in 10 ml. of acetic acid. The mixture was stirred for 15 min. and then diluted slowly with 60 ml. of water. The 4,4,8,8-tetranitroundecanedioyl azide (XXVI) was filtered, washed with water, and dried; 1.35 g. (94%), m.p. 72° (dec.).

A 1.35-g. (0.00303 mole) sample of the azide (XXVI) was dissolved in 13.5 ml. of dry chloroform and heated at 50–55° for 3 hr. The mixture was filtered and refluxed with 1 ml. of methanol for 1 hr. Solvents were removed under reduced pressure to leave 1.34 g. (97.5%) yield of the dicarbamate (XXX), m.p. 91–93°. Two recrystallizations from aqueous ethanol raised the melting point to 93–94°.

Anal. Calcd. for $C_{13}H_{22}N_6O_{12}$: C, 34.36; H, 4.85; N, 18.50. Found: C, 34.20; H, 4.87; N, 18.62.

3,3,7,7-Tetranitrononamethylene diisocyanate (XXVIII) could be isolated after the heating in chloroform in the above experiment, by removing the solvent. The crude material was obtained as an oil which decomposed on attempted distillation at 1 mm.

3,3,7,7-Tetranitrononanedicarbanilide was prepared in the same manner as its lower homolog described above; 67% yield of crude material, m.p. 191° (dec.). It was recrystallized from ethanol; m.p. 196° (dec.), with previous darkening.

Anal. Calcd. for $C_{23}H_{28}N_8O_{10}$: C, 47.92; H, 4.86; N, 19.44. Found: C, 48.10; H, 5.01; N, 19.24.

3,3,6,6-Tetranitroöctanediammonium Chloride.—A 0.21-g. sample of the dicarbamate (XXIX) and 8 ml. of concentrated hydrochloric acid were heated under reflux for 40 hr. The solution was cooled and filtered to yield 0.15 g. (79%) of the dihydrochloride, m.p. 215° (dec.).

Anal. Calcd. for $C_8H_{18}Cl_2N_6O_8$: C, 24.18; H, 4.53; N, 21.16; neut. equiv., 198.5. Found: C, 23.99; H, 4.71; N, 19.3; neut. equiv. 188.

A solution of 30 mg. of the dihydrochloride in water was made basic by adding 1.5 ml. of 0.1 *N* sodium hydroxide solution. White crystals of **3,3,6,6-tetranitro-1,8-octanediamine (XXXI)** slowly formed; these were filtered after 1 hr. and dried *in vacuo;* m.p. 84–85°.

N,N′-Diacetyl-3,3,6,6-tetranitro-1,8-octanediamine was prepared from the amine (XXXI) by reaction with acetic anhydride and sodium acetate in water solvent at room temperature; m.p. 192–192.5° after recrystallizing from water.

Anal. Calcd. for $C_{12}H_{20}N_6O_{10}$: C, 35.29; H, 4.90; N, 20.59. Found: C, 35.21; H, 4.88; N, 19.22.

3,3,7,7-Tetranitrononanediammonium chloride was prepared from the dicarbamate (XXX) (1.49 g., 0.00328 mole) by refluxing with 20 ml. of concd. hydrochloric acid for 6 hr. By concentrating the solution to 5 ml. and cooling, the hydrochloride was precipitated (1.32 g., 98% yield); m.p. 216° with decomposition and darkening at 200°. Recrystallization from 18% hydrochloric acid raised the melting point to 223° (dec.).

Anal. Calcd. for $C_9H_{20}Cl_2N_6O_8$: C, 26.28; H, 4.87; N, 20.44; neut. equiv., 205.5. Found: C, 28.38; H, 5.11; N, 18.9; neut. equiv., 212.

3,3,7,7-Tetranitro-1,9-nonanediamine (XXXII) was prepared in the manner of its lower homolog (XXXI) in the above procedure; m.p. 91.5–92°.

N,N′-Diacetyl-3,3,7,7-tetranitro-1,9-nonanediamine was prepared from XXXII in the manner of its lower homolog XXXI; m.p. 124.5–125°.

Anal. Calcd. for $C_{13}H_{22}N_6O_{10}$: C, 36.97; H, 5.21; N, 19.91. Found: C, 36.91; H, 5.18; N, 19.90.

4,4,7,7-Tetranitrodecanediamide (XXXIII).—A small sample of acid chloride XXIII was added to concentrated ammonium hydroxide and the mixture stirred at 25° for 36 hr. The product was filtered, washed with a small amount of water, and recrystallized from methanol; m.p. 195°.

Anal. Calcd. for $C_{10}H_{16}N_6O_{10}$: C, 31.58; H, 4.21; N, 22.11. Found: C, 31.40; H, 4.13; N, 22.18.

4,4,8,8-Tetranitroundecanediamide (XXXIV) was prepared from acid chloride XXIV in the manner of its lower homolog (XXXIII) and recrystallized from water; m.p. 127–128°.

Anal. Calcd. for $C_{11}H_{18}N_6O_{10}$: C, 33.50; H, 4.57; N, 21.22. Found: C, 33.84; H, 4.71; N, 21.10.

Dimethyl 4,4-Dinitroheptanedioate (XXXVI).—2,2-Dimethyl-1,1,3-trinitropropane[18] (XXXV), 13.8 g. (0.0667 mole) was dissolved in 110 ml. of ether and the solution cooled to 0°. A solution of 3.2 g. (0.139 mole) of sodium in 45 ml. of methanol was added dropwise with vigorous stirring. The disodium salt of XXXV was filtered, washed with a methanol–ether solution, and dried *in vacuo;* yield, 15.3 g. (91.5%) (*explosive*).

A 2.51-g. (0.01 mole) sample of the disodium salt was dissolved in 8 ml. of water 2.86 g. (0.033 mole) of methyl acrylate was added and the mixture stirred at 40° for 48 hr. The organic layer was separated and diluted with 7 ml. of methanol and chilled to −70° to yield 0.71 g. of crude dimethyl 4,4-dinitroheptanedioate, m.p. 41–46°. The material was recrystallized first from methanol and then from petroleum ether (b.p. 60–70°) to yield crystals, m.p. 46.5–47.2°; when mixed with an authentic sample (m.p. 45–46.8°),[4] the melting point was not depressed.

Anal. Calcd. for $C_9H_{14}N_2O_8$: C, 38.85; H, 5.04; N, 10.07; mol. wt., 278. Found: C, 39.10; H, 4.66; N, 10.21; mol. wt., 251; 253 (Rast).

A 0.57-g. sample of the ester was refluxed with 5 ml. of 18% hydrochloric acid for 3 hr. to yield 0.48 g. of crude **4,4-dinitroheptanedioic acid,** m.p. 130–137°; two recrystallizations from ethylene chloride gave crystals; m.p. 139–140°. (Found: neut. equiv., 126; calcd. for $C_7H_{10}N_2O_8$: 125.) When mixed with an authentic sample,[4] m.p. 139–141°, the melting point was not depressed.

An 11.18-g. (0.045 mole) sample of disodium 2,2-dimethyl-1,1,3-trinitropropane was dissolved in 25 ml. of water and the solution stirred at 40° for 72 hr. After concentrating under reduced pressure, a yellow solid precipitated. It was removed by filtration, dissolved in water and treated with concentrated potassium hydroxide solution. **Potassium dinitromethane** was precipitated and recrystallized twice from water; explosion point 202.5° (reported,[19] 207°). This salt (0.90 g.) was suspended in 1.5 ml. of water and 1.8 ml. of formalin was added. After refluxing for 2 min. and cooling, yellow **potassium dinitroethanol** crystallized (explosion point 134°; reported,[20] 140°). The potassium dinitroethanol (0.46 g.) was added to 0.66 mole of water and 0.22 ml. of formalin was added (0.00316 mole of formaldehyde). The mixture was cooled to 0° and stirred while 0.12 g. of acetic acid in 0.2 ml. of water was added dropwise with stirring. The solution was then stirred for 1 hr. at 25°. After extracting with ether, drying and removing the ether, there was obtained **2,2-dinitro-1,3-propanediol**; m.p. 142–143° after two recrystallizations from benzene. When mixed with an authentic sample[20] (m.p. 144–145.5°), the melting point was not depressed.

Acknowledgment.—Support of this work by the Office of Naval Research is gratefully acknowledged.

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