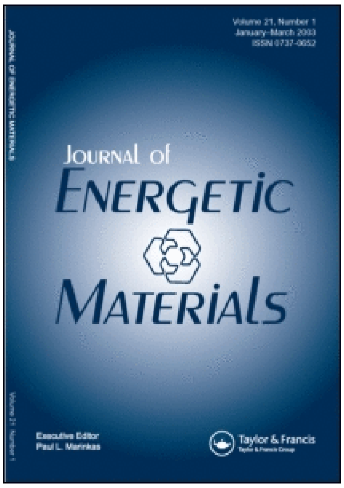

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Dinitronitramino-hydroxyesters, hydroxyacids, polyesters and diols

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DINITRONITRAMINO-HYDROXYESTERS, HYDROXYACIDS, POLYESTERS AND DIOLS

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ABSTRACT

The synthesis of difunctional dinitronitramino compounds, R-$C(NO_2)_2CH_2N(NO_2)$-R', where either R or R' or both contain a hydroxyl group, is described. The compounds include hydroxyesters, hydroxyacids and diols. Energetic polyesters were prepared from the hydroxyacids.

INTRODUCTION

Our interest in more stable difunctional energetic intermediates containing the hydroxyl function led us to investigate the synthesis of dinitronitramines, R-$C(NO_2)CH_2N(NO_2)$-R', where either R or R' or both contain a hydroxyl group. The synthesis of these intermediates was designed so that the dinitromethylene and nitramino groups are more than one carbon atom removed from the hydroxyl function. This arrangement provides compounds with increased stability since they

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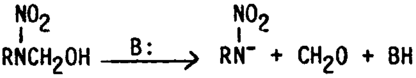
are not susceptible to a reverse Henry[1] type reaction (eq. 1 and eq. 2) that could occur if the hydroxyl group was separated by only one carbon atom.

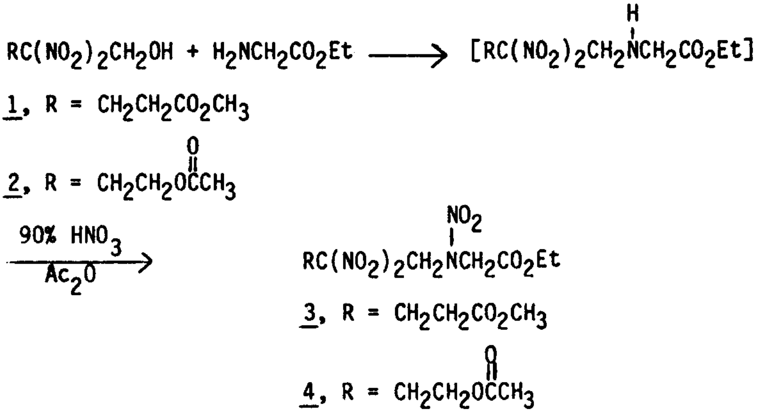
$$RC(NO_2)_2CH_2OH \xrightarrow{B:} RC(NO_2)_2^- + CH_2O + BH \qquad \text{eq. 1}$$



$$R\overset{NO_2}{\overset{|}{N}}CH_2OH \xrightarrow{B:} R\overset{NO_2}{\overset{|}{N^-}} + CH_2O + BH \qquad \text{eq. 2}$$

RESULTS AND DISCUSSION

The starting materials for the dinitronitramino compounds were the diesters 3 and 4 which were prepared by nitration of the condensation product (not isolated) from B-dinitroalcohols 1 and 2 and glycine ethyl ester.



$$RC(NO_2)_2CH_2OH + H_2NCH_2CO_2Et \longrightarrow [RC(NO_2)_2CH_2\overset{H}{\overset{|}{N}}CH_2CO_2Et]$$

1, $R = CH_2CH_2CO_2CH_3$

2, $R = CH_2CH_2O\overset{O}{\overset{\|}{C}}CH_3$

$$\xrightarrow[Ac_2O]{90\%\ HNO_3} RC(NO_2)_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CO_2Et$$

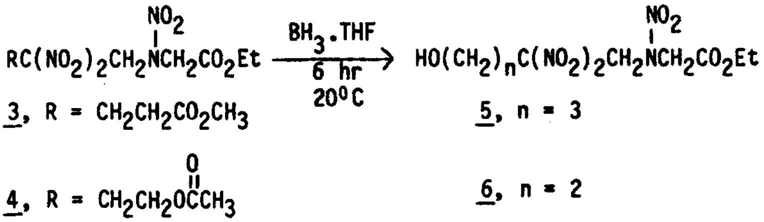
3, $R = CH_2CH_2CO_2CH_3$

4, $R = CH_2CH_2O\overset{O}{\overset{\|}{C}}CH_3$

The dinitronitramines are comprised of three types of compounds: (A) hydroxyesters; (B) hydroxyacids; (C) diols.

(A). Dinitronitramino Hydroxyesters

The diesters 3 and 4 each contain an ethyl ester along with a methyl ester at the opposite end of the molecule. One might expect a difference in the rate of reduction of the two ester groups with borane-THF due to unequal effects of the electron withdrawing groups [$-C(NO_2)_2-$ and $-N(NO_2)-$] on the electron densities at the ester carbonyls.[2] In practice, the difference in the reactivities of the ester groups was found to be quite large with the one nearest to the nitramino function being considerably more difficult to reduce.[3] Thus, by controlling the time and temperature of the reaction, the partial reduction of 3 and 4 to give good yields of the hydroxyesters, ethyl 3-aza-3,5,5-trinitro-8-hydroxyoctanoate 5 and ethyl 3-aza-3,5,5-trinitro-7-hydroxyheptanoate 6, was readily achieved.



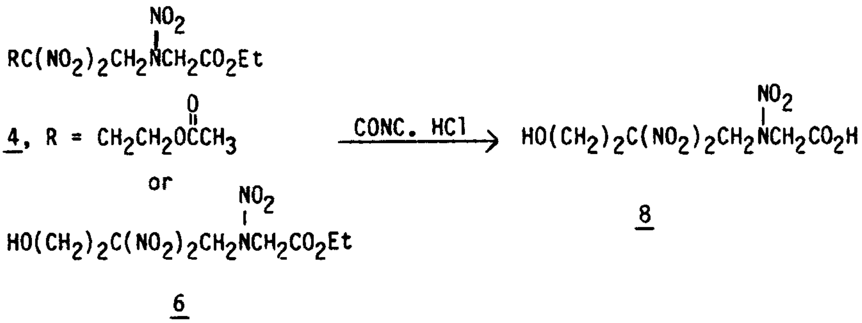
$$\mathrm{RC(NO_2)_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CO_2Et} \xrightarrow[\substack{6\ \mathrm{hr} \\ 20^{\circ}\mathrm{C}}]{\mathrm{BH_3.THF}} \mathrm{HO(CH_2)_nC(NO_2)_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CO_2Et}$$

3, $R = CH_2CH_2CO_2CH_3$ 5, $n = 3$

4, $R = \mathrm{CH_2CH_2O\overset{O}{\overset{\|}{C}}CH_3}$ 6, $n = 2$

(B). Dinitronitramino Hydroxyacids for Energetic Polyesters

Hydrolysis of the hydroxyesters 5 and 6 produced the dinitronitramino hydroxyacids, 3-aza-3,5,5-trinitro-8-hydroxyoctanoic acid 7, and 3-aza-3,5,5-trinitro-7-hydroxyheptanoic acid 8 which were of interest as monomers for the synthesis of energetic polyesters. The synthesis of 8 was straightforward and this hydroxyacid was readily formed by treatment of either the diester 4 or the hydroxyester 6 with conc. hydrochloric acid.



$RC(NO_2)_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CO_2Et$

4, R = $CH_2CH_2O\overset{O}{\overset{\|}{C}}CH_3$ $\xrightarrow{\text{CONC. HCl}}$ $HO(CH_2)_2C(NO_2)_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CO_2H$

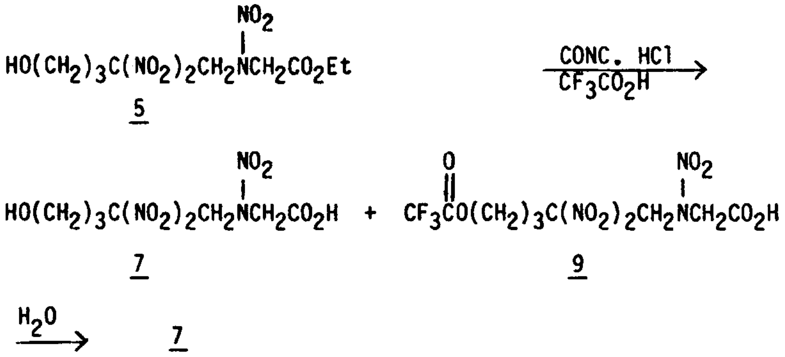
or

$HO(CH_2)_2C(NO_2)_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CO_2Et$

6

8

The synthesis of the hydroxyacid 7 was more complicated because, unlike 8, compound 7 apparently has a strong tendency toward ester formation in the presence of strong acid. Thus, attempts to prepare 7 by direct hydrolysis of 5 with conc. hydrochloric acid gave mainly polyester from self-condensation of 7. When trifluoroacetic acid and conc. hydrochloric acid were used to hydrolyze 5, a mixture of 7 and the trifluoroacetate 9 was obtained. This mixture, however, could be converted to 7 by hydrolysis with water.



$HO(CH_2)_3C(NO_2)_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CO_2Et$ $\xrightarrow[CF_3CO_2H]{\text{CONC. HCl}}$

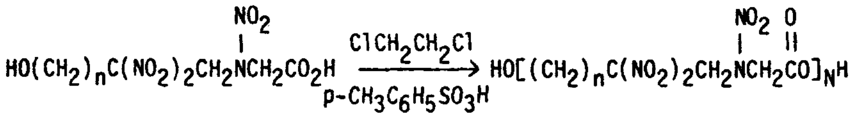
5

$HO(CH_2)_3C(NO_2)_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CO_2H + CF_3\overset{O}{\overset{\|}{C}}O(CH_2)_3C(NO_2)_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CO_2H$

7 9

$\xrightarrow{H_2O}$ 7

The hydroxyacid monomers 7 and 8 can be self-condensed to give energetic polyesters. Thus, heating 7 or 8 with p-toluenesulfonic acid in 1,2-dichloroethane with azeotropic removal of water gave polyesters (characterized by gel permeation chromatography, see experimental section).

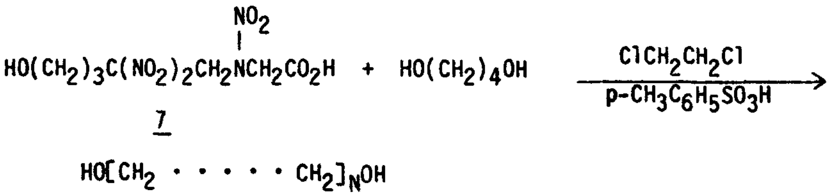


$$HO(CH_2)_nC(NO_2)_2CH_2\overset{NO_2}{N}CH_2CO_2H \xrightarrow[p\text{-}CH_3C_6H_5SO_3H]{ClCH_2CH_2Cl} HO[(CH_2)_nC(NO_2)_2CH_2\overset{NO_2}{N}CH_2\overset{O}{C}O]_NH$$

7, n = 3
8, n = 2

To our knowledge, there has been no previous example of energetic polyester formation from single monomers. Generally, the synthesis of energetic polyesters has been accomplished only through the preparation and reaction of two separate starting materials, a diol and either a diacid or a diacid derivative. For example, AFNOL was prepared from 2,2,8,8-tetranitro-4,6-dioxanonane-1,9-diol and 4,4-dinitropimeloyl chloride[4].

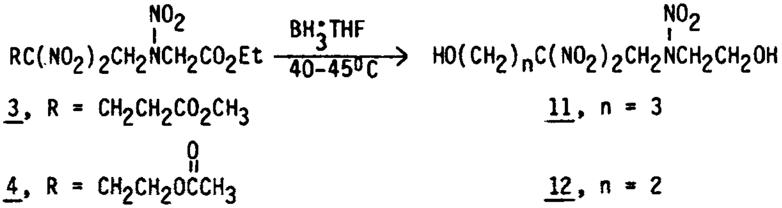
A hydroxy terminated copolymer was obtained from the reaction of 7 with butane-1,4-diol. Calculations showed that the mole ratio of 7 to butane-1,4-diol should be 5.25 to give a theoretical no. average molecular weight of approx. 1550. The observed value was 1470 (by gel permeation chromatography).



$$\underset{7}{HO(CH_2)_3C(NO_2)_2CH_2\overset{NO_2}{N}CH_2CO_2H} + HO(CH_2)_4OH \xrightarrow[p\text{-}CH_3C_6H_5SO_3H]{ClCH_2CH_2Cl} HO[CH_2 \cdot \cdot \cdot \cdot \cdot CH_2]_NOH$$

(C). Dinitronitramino Diols

Although the ester group nearest the nitramino function in diesters 3 and 4 is resistant to reduction with borane-THF, prolonged treatment of 3 and 4 with borane-THF at slightly elevated temperatures gave the diols, 3-aza-3,5,5-trinitrooctane-1,8-diol 11 and 3-aza-3,5,5-trinitroheptane-1,7-diol[5] 12.



$$RC(NO_2)_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CO_2Et \xrightarrow[40\text{-}45^{\circ}C]{BH_3\cdot THF} HO(CH_2)_nC(NO_2)_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CH_2OH$$

3, $R = CH_2CH_2CO_2CH_3$ 11, $n = 3$

4, $R = CH_2CH_2O\overset{O}{\overset{\|}{C}}CH_3$ 12, $n = 2$

Because diols 11 and 12 have the dinitromethylene and nitramino functions more than one carbon atom removed from the hydroxyl groups, they will not fragment under weakly basic conditions to give formaldehyde and unstable dinitrocarbanions. By contrast, B-dinitrodiols, $R[C(NO_2)_2CH_2OH]_2$, do readily fragment and this gives rise to problems when energetic prepolymers prepared from this type of diol are treated with isocyanates to form urethane crosslinks. The urethane linkages are sufficiently basic to cause any remaining B-dinitroalcohol end groups to form dinitrocarbanions.[6] The unstable dinitrocarbanions lead to bubble formation in gumstocks and provide sites for the initiation of thermal decomposition and other chemical reactions which cause degradation during aging. Diols 11 and 12, which cannot lose formaldehyde, are not similarly affected by urethanes.

Thermal Stability of Dinitronitramines

To test the thermal stability of the $-C(NO_2)_2CH_2N(NO_2)-$ linkage, the diester 3 (mp 77-79°C) was held at 100°C for 48 hr. The linkage apparently has good thermal stability as the amount of gas evolved per gram of 3 was only 0.75 cc. (A material is considered thermally stable if the gas evolved per gram is less than 2.0 cc.) Thus, materials containing the $-C(NO_2)_2CH_2N(NO_2)-$ linkage would be expected to have good thermal stability unless other groups are present that either have poor inherent thermal stability or will interact with the linkage.

EXPERIMENTAL

^1H NMR spectra were determined on a Varian EM-390 spectrometer with TMS as the internal standard. IR spectra were obtained with a Beckmann model 167 spectrometer and elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee 37921. Melting points are uncorrected.

1-Ethyl-8-methyl 3-aza-3,5,5-trinitrooctanedioate (3).

A solution containing 12.0 g (0.054 mole) of methyl 4,4-dinitro-5-hydroxypentanoate,[7] 11.4 g (0.082 mole)of glycine ethyl ester hydrochloride and 1.4 ml (0.05 mole) of 37% aqueous formaldehyde in 56 ml of methanol and 28 ml of water was stirred in an ice bath while 3.0 g of sodium hydroxide in 25 ml of water was added dropwise to give a final pH of 6.5. The mixture was allowed to warm to room temperature and then 1.4 ml of acetic acid was added dropwise to lower the pH to 5. After 1.5 hr. the mixture was extracted with methylene chloride and the extract was washed with water, dried over sodium sulfate, and the methylene chloride was removed to give 16.1 g of oil. The oil was slowly added to a nitric acid-acetic anhydride solution (prepared by dropwise addition of 20 ml of 90% nitric acid to 66 ml of acetic anhydride with cooling below 25°C) stirred in an ice-salt bath to keep the temperature below 5°C. The solution was then stirred at room temperature for 2.5 hr. before it was poured into 500 ml of ice water. The mixture was stirred for 1 hr. and the solid 13.84 g, mp 67-72°C, was removed by filtration. Crystallization from methanol gave 11.2 g (61%), mp 76-78°C. Recrystallization raised the melting point to 77-79°C: ^1H NMR ($CDCl_3$) 1.33 (t, 3H), 2.60 (t, 2H), 3.03 (t, 2H), 3.80 (s, 3H), 4.35, 4.48 (q overlap s, 4H) 5.00 (s, 2H); IR (KBr) 1750 (C=O), 1550-1590 (NO_2)cm^{-1}.

Anal. Calcd for $C_{10}H_6N_4O_{10}$: C, 34.10; H, 4.58; N, 15.90.

Found: C, 34.24; H, 4.48; N, 15.95.

Ethyl 3-aza-3,5,5-trinitro-7-acetoxyheptanoate (4).

A solution containing 6.0 g (0.27 mole) of 2,2-dinitrobutane-1,4-diol-4-acetate,[8] 5.7 g (0.041 mole) of glycine ethyl ester hydrochloride and 0.66 ml of aqueous 37% formaldehyde in 28 ml of methanol and 14 ml of water was stirred in an ice bath while 1.48 g of sodium hydroxide in 12.5 ml of water was added dropwise to give pH 6 to 6.5. The solution was then stirred at ambient temperature while 0.66 ml of acetic acid was added dropwise to give a pH of 5. After 1.5 hr. the mixture was extracted with methylene chloride and the extract was washed with water and dried over sodium sulfate. Removal of solvent gave 8.3 g of oil which was slowly added to nitric acid-acetic anhydride (prepared from dropwise addition of 10 ml of 90% nitric acid to 33 ml of acetic anhydride with cooling below 25°C) stirred in an ice-salt bath to keep the temperature below 5°C. The solution was then stirred at ambient temperature for 2.5 hr. before it was poured into 300 ml of ice water. Stirring for 30 min. gave a solid which was removed by filtration and washed with water to yield 7.66 g, mp 45-50°C. The solid was crystallized from methanol-water to give 6.03 g (63%) of product, mp 53-54.5°C. ^1H NMR ($CDCl_3$) 1.33 (t, 3H), 2.05 (s, 2H), 3.03 (t, 2H), 4.22-4.48 (overlapping s, t and q, (6H), 5.03 (s, 2H). IR (KBr) 1752 (C=0), 1598, 1577 (NO_2)cm^{-1}.

Anal. Calcd for $C_{10}H_{16}N_4O_{10}$: C, 34.10; H, 4.58; N, 15.90.

Found: C, 34.15; H, 4.70; N, 16.04.

Ethyl 3-aza-3,5,5-trinitro-8-hydroxyoctanoate (5).

A 1 M solution of borane-THF (32.5 ml, 0.0325 mole) was stirred under a nitrogen atmosphere in an ice bath while 10.9 g (0.031 mole) of 1-ethyl-8-methyl 3-aza-3,5,5-trinitrooctanedioate was added in portions. The solution was then held at 20°C for 6 hr. before 5.5 ml of water was slowly added dropwise. The mixture was warmed to 60°C for 5 min. and then was poured into 45 ml of water. The mixture was extracted with ether and the ether extract was washed with aqueous sodium carbonate, then with water and dried over magnesium sulfate. Removal of the volatiles on a rotary evaporator gave 9.03 g of an oil which was chromatographed on silica gel 60 (110 g) using methylene chloride and then methylene chloride-ethyl acetate (80/20) as eluent to give the pure product (7.5 g, 75%) as an oil. ^{1}H NMR ($CDCl_3$ + D_2O) 1.35 (t, 3H), 1.74 (m, 2H), 2.79 (t, 2H), 3.80 (t, 2H) 4.24-4.47 (q overlapping s, 4H) 4.70 (OH), 5.00 (s, 2H); IR (film) 3650-3100 (OH), 1750 (C=O), 1600-1550 (NO_2)cm^{-1}.

Anal. Calcd for $C_9H_{16}N_4O_9$: C, 33.34; H, 4.97; N, 17.28. Found: C, 33.61; H, 5.25; N, 17.32.

Ethyl 3-aza-3,5,5-trinitro-7-hydroxyheptanoate (6).

To 10 ml (10 mmol) of 1 M borane-THF solution stirred under a nitrogen atmosphere in an ice bath was added 3.33 g (9.5 mmol) of ethyl 3-aza-3,5,5-trinitro-7-acetoxyheptanoate. After 6 hr. at 20°C, water (2 ml) was slowly added dropwise and the mixture was warmed to 60°C for 5 min. before it was poured into 15 ml of water. Extraction with ether and washing the ether with aqueous sodium carbonate and then with water followed by drying over magnesium sulfate and removal of volatiles on the rotary evaporator gave 2.52 g of oil. The oil was chromatographed on silica gel 60 (60 g) using methylene chloride and then methylene chloride-ethyl acetate (80/20) as eluent to give pure product (2.1 g, 71%) as an oil. ^{1}H NMR ($CDCl_3$ + D_2O) 1.34 (t, 3H), 2.94 (t, 2H), 3.94 (t, 2H), 4.34 (q, 2H), 4.64 (s, 2H) 4.70 (OH), 5.12 (s, 2H); IR (film) 3650-3200 (OH), 1745 (C=O), 1575 (broad) (NO_2)cm^{-1}.

Anal. Calcd for $C_8H_{14}N_4O_9$: C, 30.97; H, 4.55; N, 18.06. Found: C, 30.99; H, 4.74; N, 18.07.

3-Aza-3,5,5-trinitro-8-hydroxyoctanoic acid (7).

A solution of 7.4 g (0.0228 mole) of ethyl 3-aza-3,5,5-trinitro-8-hydroxyoctanoate in 20 ml of trifluoroacetic acid and 40 ml of conc. hydrochloric acid was heated at 70-73°C for 22 hr. before it was poured into 180 ml of water. The solution was extracted with ether and the ether extract was dried over sodium sulfate before the volatiles were removed on a rotary evaporator to give an oil. Carbon tetrachloride was added and the volatiles were again removed on the rotary evaporator. This was repeated several times to help remove trifluoroacetic acid from the oil which was shown by ^1H NMR to be a mixture of the free hydroxy acid (the title compound) and its trifluoroacetate derivative. The oil was then stirred with 150 ml of water at 75°C for 2 hr. before the hot solution was decanted from some insoluble oil. The cooled solution was extracted with ether and the volatiles were removed on a rotary evaporator to give an oil which by NMR analysis still contained an appreciable amount of the trifluoroacetate. The oil was stirred with 150 ml of water at 75°C for 1.5 hr. before the hot solution was decanted, cooled and extracted with ether to give an oil which NMR showed to contain only the title compound. Stirring the oil with methylene chloride gave 3.75 g (56%), mp 104-108°C. Crystallization from acetone-methylene chloride raised the melting point to 108-109°C. ^1H NMR $[(CD_3)_2C=O]$ 1.65 (m, 2H), 2.88 (m, 2H), 3.73 (t, 2H), 4.20 (broad), 4.84 (s, 2H), 5.27 (s, 2H); IR (KBr) 3450 (OH), 3000-2500 (CO_2H), 1727 (C=O), 1590 (shoulder) 1567 (NO_2).

Anal. Calcd for $C_7H_{12}N_4O_9$: C, 28.38; H, 4.08; N, 18.92. Found: C, 28.40; H, 4.16; N, 18.74.

The title compound has a strong tendency to form the trifluoroacetate in the presence of trifluoroacetic acid. Thus, heating the hydroxy acid 7 (0.10 g) with 2.5 ml of trifluoroacetic acid at 72-75°C for 16 hr. followed by removal of volatiles gave 0.14 g (100%) of the trifluoroacetate 9, mp 94-95°C. ^1H NMR [$(CD_3)_2C{=}O$] 1.9 (m, overlap with NMR solvent), 3.00 (m, 2H), 3.93 (broad) 4.67 (t, 2H), 4.80 (s, 2H), 5.32 (s, 2H); IR (KBr) 1793, 1725 (C=O), 1575 (NO_2)cm^{-1}.

Anal. Calcd for $C_9H_{11}F_3N_4O_{10}$: C, 27.56; H, 2.83; F, 14.53; N, 14.28. Found: C, 27.45; H, 2.87; F, 14.58, N, 14.24.

Aza-3,5,5-trinitro-7-hydroxyheptanoic acid (8).

A mixture of 4.4 g (0.0125 mole) of ethyl 3-aza-3,5,5-trinitro-7-acetoxyheptanoate and 36 ml of conc. hydrochloric acid was stirred at 70-74°C for 20 hr. before it was poured into 75 ml of water. Extraction with ether followed by removal of solvent gave an oil which turned to a solid (2.82 g, mp 139-141) (80%) when stirred with 20 ml of chloroform. Recrystallization from acetone-chloroform raised the melting point to 140-141°C. ^1H NMR [$(CD_3)_2C{=}O$] 3.03 (t, 2H), 3.88 (t, 2H), 4.53 (broad), 4.89 (s, 2H), 5.26 (s, 2H); IR (KBr) 3445 (OH), 3000-2500 (CO_2H), 1735

(C=O), 1590 (shoulder) 1565 (NO_2)cm^{-1}.

Anal. Calcd for $C_6H_{10}N_4O_9$: C, 25.54; H, 3.57; N, 19.86. Found: C, 25.69; H, 3.54; N, 19.71.

3-Aza-3,5,5-trinitrooctanedioic acid (10).

A mixture of 4.3 g (0.012 mole) of 1-ethyl-8-methyl 3-aza-3,5,5-trinitrooctanedionate and 40 ml of conc. hydrochloric acid was stirred at 70-72°C for 18 hr. before it was allowed to cool to room temperature. The solid precipitate was removed by filtration and washed with cold water to give 3.0 g (79%), mp 171-174°C. Crystallization from acetone-chloroform raised the melting point to 173-174°C. ^1H NMR [$(CD_3)_2C=O$] 2.60 (t, 2H), 3.11 (t, 2H), 4.64 (broad), 4.79 (s, 2H), 5.27 (s, 2H); IR (KBr) 3600-2500 (CO_2H), 1730 (C=O), 1587, 1563 (NO_2)cm^{-1}.

Anal. Calcd for $C_7H_{10}N_4O_{10}$: C, 27.10; H, 3.25; N, 18.06. Found: C, 27.13; H, 3.46; N, 17.83.

Polyester from 3-Aza-3,5,5-trinitro-8-hydroxyoctanoic acid.

A reverse Dean Stark trap was attached to a flask containing a stirred mixture of 0.72 g (2.43 mmole) of 3-aza-3,5,5-trinitro-8-hydroxyoctanoic acid, 0.05 g (0.24 mmole) of p-toluenesulfonic acid monohydrate and 10 ml of 1,2-dichloroethane. The flask was placed in an oil bath and the oil bath temperature was raised to 125°C and held for 20 hr. The reaction mixture was cooled to room temperature and the solid (0.68 g) was removed by filtration. The solid was then stirred with 10 ml of diethyl ether for 24 hr. at room temperature. The insoluble solid (0.59 g, mp 135-160) was removed by filtration and was shown by gel permeation chromatography to be a polymer with number average molecular weight of 1361 with dispersity equal to 2.49. IR (KBr) 1755 (ester C=O), 1570 (NO_2)cm^{-1}. ^1H NMR [$(CD_3)_2C=O$] showed no monomer was present by the absence of the triplet at 3.73 (corresponding to $\underline{CH_2}OH$). A new triplet at 4.34 (corresponding to $\underline{CH_2}$-O-C=O) is present in the polyester.

Polyester from 3-Aza-3,5,5-trinitro-7-hydroxyheptanoic acid.

A reverse Dean Stark trap was attached to a flask containing 0.69 g (2.43 mmole) of 3-aza-3,5,5-trinitro-7-hydroxyheptanoic acid, 0.05 g (0.24 mmole) of p-toluenesulfonic acid monohydrate and 15 ml of 1,2-dichloroethane. The mixture was stirred in an oil bath while the bath temperature was raised to 115°C and held for 20 hr. The insoluble material (0.56 g) was removed from the cooled mixture by filtration and then was stirred with 15 ml of diethyl ether for 16 hr. The ether insoluble solid (0.38 g, mp 150-165°C) was removed and was shown by gel permeation chromatography to be a polymer with number average molecular weight of 1234 and dispersity equal to 1.80 (the ether soluble material was mainly the starting hydroxy acid monomer). ^1H NMR [$(CD_3)_2C=O$] of the ether insoluble solid shows a triplet at 4.56 (corresponding to $\underline{CH_2}OC=O$) instead of the triplet at 3.88 (corresponding to $\underline{CH_2}OH$) present in the monomer.

Polyester from Copolymerization of 3-Aza-3,5,5-trinitro-8-hydroxyoctanoic acid and butane-1,4-diol.

A reverse Dean Stark trap was attached to a flask containing 0.85 g (2.87 mmole) of 3-aza-3,5,5-trinitro-8-hydroxyoctanoic acid, 0.05 g (0.545 mmole) of butane-1,4-diol, 0.06 g (0.288 mmole) of p-toluenesulfonic acid monohydrate and 25 ml of 1,2-dichlorethane. The reaction mixture was stirred in an oil bath which was held at 100°C for 20 hr. The volatiles were then removed on a rotary evaporator to yield a gummy solid which was stirred with 30 ml of water for 6 hr. The water-insoluble solid (0.81 g, mp 60-110°C) was shown by gel permeation chromatography to be a polymer with a number average molecular weight of 1470 and a dispersity equal to 1.35. IR (KBr) 1757 (C=O)cm^{-1}; no CO_2H absorption.

3-Aza-3,5,5-trinitrooctane-1,8-diol (11).

To a 1 M solution of borane-THF (105 ml, 0.105 mole) stirred in a cold water bath under a nitrogen atmosphere was added 15.5 g (0.044 mole) of 1-ethyl-8-methyl 3-aza-3,5,5-trinitrooctanedioate 3 rapidly in portions. After the mild exothermic reaction was over, the solution was stirred overnight at room temperature and was then heated at 40-43°C for 4 days before it was cooled in a cold water bath while 11 ml of water was slowly added dropwise. Most of the THF was then removed by distillation to give a thick slurry of insoluble boric acid. Diethyl ether was added and the boric acid was removed by filtration. The ether filtrate was washed with aqueous sodium carbonate, then with water, and was dried over sodium sulfate. Removal of the ether with a rotary evaporator gave an oil which was dissolved in 175 ml of warm methylene chloride. Cooling in a dry ice-acetone bath gave 10.5 g (85%), mp 51-53°C. ^{1}H NMR (CD_2Cl_2 + D_2O) 1.64 (m, 2H) 2.60-2.87 (m, 2H) 3.75 (t, 2H) 3.97 (s, 4H) 4.70 (OH) 5.12 (2H); IR (KBr) 3650-3100 (OH), 1595, 1570, 1542 (NO_2)cm^{-1}.

Anal. Calcd for $C_7H_{14}N_4O_8$: C, 29.79; H, 5.00; N, 19.85. Found: C, 29.82; H, 5.04; N, 19.75.

3-Aza-3,5,5-trinitroheptane-1,7-diol[5] (12).

A 1 M solution of borane-THF (50 ml, 0.05 mole) was stirred in an ice bath under a nitrogen atmosphere while 6.42 g (0.0182 mole) of ethyl 3-aza-3,5,5-trinitro-7-acetoxyheptanoate 4 was added. The solution was stirred at room temperature overnight and then was heated at 45-46°C for 24 hr. before it was cooled and 6 ml of water was slowly added dropwise. Most of the THF was then removed by distillation, diethyl ether was added and the insoluble boric acid was removed by filtration. The ether filtrate was washed with aqueous sodium carbonate, then with water and dried over sodium sulfate. Removal of solvent on a rotary evaporator gave an oil which was dissolved in 75 ml of warm methylene chloride. Cooling in a dry-ice acetone bath gave 2.9 g (60%) of crystals, mp 50-51.5°C. ^{1}H NMR (CD_2Cl_2 + D_2O) 2.89 (t, 2H), 3.87 (t, 2H), 4.02 (s, 4H), 4.70 (OH), 5.17 (s, 2H); IR(KBr) 3650-3100 (OH), 1595, 1572, 1542 (NO_2)cm^{-1}.

Anal. Calcd for $C_6H_{12}N_4O_8$: C, 26.87; H, 4.51; N, 20.89. Found: C, 26.76; H, 4.40; N, 20.60.

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