The physical properties of *N*-(1-naphthyl) hydroxamic acids are given in Table I. All the hydroxamic acids are reported for the first time except the *p*-nitro- and *p*-chloro-substituted acids which were reported earlier (*5*). All these acids are white crystalline compounds except the nitro- and iodo-substituted acids which are yellow and pink, respectively. They are sparingly soluble in water but readily soluble in benzene, ethyl alcohol, dioxane, diethyl ether, and chloroform.

The presence of an O–H stretching band is assigned in the region about 3200 cm^{-1} and in conformity with the reported value (*1*, *2*, *6*, *8*, *9*). The lower shift of the O–H band was due to the intramolecular hydrogen bonding of the $-OH{\cdots}C{=}O$. The C=O and N—O bands are assigned at about 1630 and 920 cm^{-1}, respectively.

In the ultraviolet region two characteristic naphthalene bands, I and II, are observed at 225 and 270 nm, respectively. The assignment of these bands is supported by comparing the related compounds (*7*, *10*). In the *N*-(1-naphthyl) hydroxamic acids, the ratio of bands II and I, λ_{II}/λ_{I}, is generally found at about 1.22 (*3*, *4*).

A typical preparation of *N*-(1-naphthyl)benzohydroxamic acid is given below.

The *N*-(1-naphthyl)hydroxylamine was prepared as described elsewhere (*5*). Into a 500-mL three-necked flask equipped with stirrer, dropping funnel, and thermometer, 100 mL of diethyl ether, 10.9 g (0.1 mol) of freshly crystallized (1-naphthyl)-hydroxylamine, and a fine suspension of 12.6 g (0.15 mol) of sodium bicarbonate in 25 mL of water were added. After the mixture was cooled to 0 °C or lower, 9.5 g (0.1 mol) of benzoyl chloride dissolved in 100 mL of diethyl ether was added dropwise over a period of 20–30 min. Some of the product was precipitated as light yellowish solid while the ether layer was separated and ether removed under vaccum. The light yellow residue was combined with the precipitated solid, triturated for about 15 min on a glass mortar with a saturated solution of a sodium bicarbonate to remove the acid impurities, filtered, and washed with cold water. The yield of air-dried product, mp 160 °C, was 70%. Two crystallizations from a mixture of benzene and petroleum ether without the use of charcoal gave white needles, mp 165 °C.

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Synthesis of Novel Energetic Aliphatic Compounds

Edward F. Witucki* and Milton B. Frankel
Rocketdyne, a Division of Rockwell Corporation, Canoga Park, California 91304

Reported here are the syntheses and physical properties of nine novel azides containing other energetic groups. These groups include nitramines, nitro nitramines, nitro esters, nitro ethers, nitrate esters, and (difluoroamino)alkanes. In addition, two new energetic fluorodinitro formals are reported.

The chemistry of aliphatic azido compounds is extensive, dating back to the work of Curtius in 1901. The principal chemical effort, particularly in recent years, has been directed at improving the methods of synthesis rather than the synthesis of new azides. These methods of improvement have included a better choice of leaving groups, reaction solvents, and/or catalysts. A comprehensive account of the chemistry of the azido group has recently been published (*1*). We are extending the synthetic chemistry of aliphatic azides to include other energetic groups. These groups include nitramines, nitro nitramines, nitro esters, nitro ethers, nitrate esters, and (difluoroamino)alkanes. The following nine new azides show the incorporation of these groups.

An example of a nitramine azide is 1,3-diazido-2-nitrazapropane (I) which was prepared by the reaction of sodium azide with 1,3-dichloro-2-nitrazapropane (*2*).

$$N(NO_2)[CH_2Cl]_2 + 2NaN_3 \rightarrow \underset{\text{I}}{N(NO_2)[CH_2N_3]_2}$$

A nitro nitramine azide, *N*-(trinitroethyl)-*N*-(3-azidopropyl)nitramine (III), was prepared by the nitration of *N*-(trinitroethyl)-*N*-(3-azidopropyl)amine (II) with nitric acid–acetic acid. II was obtained by the reaction of (3-azidopropyl)amine hydrochloride with trinitroethanol.

$$(NO_2)_3CCH_2OH + N_3CH_2CH_2CH_2NH_2{\cdot}HCl \rightarrow \underset{\text{II}}{(NO_2)_3CCH_2NHCH_2CH_2CH_2N_3}$$

$$\text{II} + HNO_3\text{–}Ac_2O \rightarrow \underset{\text{III}}{(NO_2)_3CCH_2N(NO_2)CH_2CH_2CH_2N_3}$$

The nitro azido esters prepared were 1,3-diazido-2-propyl-4,4,4-trinitrobutyrate (IV), 1,3-diazido-2-propyl-4,4,4-fluorodinitrobutyrate (V), and bis(1,3-diazido-2-propyl)oxalate (VI). IV was obtained from the reaction of 4,4,4-trinitrobutyryl chloride with 1,3-diazido-2-propanol (*3*).

$$(NO_2)_3CCH_2CH_2COCl + HOCH(CH_2N_3)_2 \rightarrow \underset{\text{IV}}{(NO_2)_3CCH_2CH_2CO_2CH(CH_2N_3)_2}$$

V was prepared from 4,4,4-fluorodinitrobutyryl chloride and 1,3-diazido-2-propanol.

$$F(NO_2)_2CCH_2CH_2COCl + HOCH(CH_2N_3)_2 \rightarrow \underset{\text{V}}{F(NO_2)_2CCH_2CH_2CO_2CH(CH_2N_3)_2}$$

VI was synthesized from oxalyl chloride and 1,3-diazido-2-propanol.

$$[COCl]_2 + 2HOCH(CH_2N_3)_2 \rightarrow \underset{\text{VI}}{[CO_2CH(CH_2N_3)_2]_2}$$

The nitro azido ethers prepared were 1,3-diazido-2-propylfluorodinitroethyl formal (VII) and 1,2-diazido-3-fluorodinitroethoxypropane (VIII). VII was obtained from the reaction of

Table I. Novel Energetic Azides[a]

compound	yield, %	n_D^{25}	d^{25}	mp, °C	bp, °C (mm)
$N(NO_2)(CH_2N_3)_2$	83.2	1.5257			97 (0.45)
$(NO_2)_3CCH_2N(NO_2)CH_2CH_2CH_2N_3$	17.9	1.5124	1.5195		
$(NO_2)_3CCH_2CH_2CO_2CH(CH_2N_3)_2$	66.5	1.5025	1.4640		
$FC(NO_2)_2CH_2CH_2CO_2CH(CH_2N_3)_2$	75.0	1.4869	1.4351		
$[CO_2CH(CH_2N_3)_2]_2$	59.5			54-55	
$FC(NO_2)_2CH_2OCH_2OCH(CH_2N_3)_2$	21.3	1.4798			
$FC(NO_2)_2CH_2OCH_2CH(N_3)CH_2N_3$	18.3	1.4832			
$NO_2OCH(CH_2N_3)_2$	85.6	1.4965	1.3789		
$C(NF_2)_2[CH_2CH_2CH_2N_3]_2$	52.9	1.4635			

[a] Elemental analyses were obtained for all compounds. They were, in every case, consistent with the proposed structure.

Table II. Fluorodinitro Formulas[a]

compound	yield, %	n_D^{25}	d^{25}	bp, °C (mm)
$[CH_2OCH_2OCH_2C(NO_2)_2F]_2$	25.6	1.4420	1.4952	149-150 (0.005)
$CH_2OCH_2OCH_2C(NO_2)_2F$ $CHOCH_2OCH_2C(NO_2)_2F$ $CH_2OCH_2OCH_2C(NO_2)_2F$	51.2	1.4498	1.5190	>184 (0.3)

[a] Elemental analyses were carried out on all compounds. They were, in every case, consistent with the proposed structure.

$$FC(NO_2)_2CH_2OCH_2Cl + HOCH(CH_2N_3)_2 \rightarrow \underset{\text{VII}}{FC(NO_2)_2CH_2OCH_2OCH(CH_2N_3)_2}$$

1,3-diazido-2-propanol and the chloromethyl ether of fluorodinitroethanol. VIII was synthesized in three steps, starting from

$$FC(NO_2)_2CH_2OH + CH_2{=}CHCH_2Br \rightarrow FC(NO_2)_2CH_2OCH_2CH{=}CH_2 \xrightarrow{Br_2} FC(NO_2)_2CH_2OCH_2CH(Br)CH_2Br \xrightarrow{NaN_3} \underset{\text{VIII}}{FC(NO_2)_2CH_2OCH_2CH(N_3)CH_2N_3}$$

fluorodinitroethanol and allyl bromide which yielded fluorodinitroethyl allyl ether. This ether was then brominated to yield the corresponding dibromo analogue which, in turn, was treated with sodium azide to yield VIII. The nitrate ester azide prepared, 1,3-diazido-2-nitratopropane (IX), was obtained from the nitration

$$HOCH(CH_2N_3)_2 + HNO_3 \rightarrow \underset{\text{IX}}{NO_2OCH(CH_2N_3)_2}$$

of 1,3-diazido-2-propanol. It is noted that this azido nitrate is merely the azido analogue of nitroglycerine.

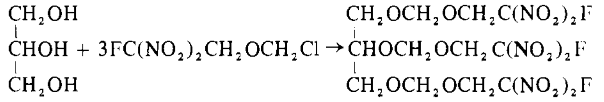
An example of a difluoramino azide is 1,7-diazido-4,4-bis(difluoramino)heptane (X). It was synthesized in two steps starting with the difluoramination of 1,7-dichloro-4-heptanone which was then treated with sodium azide to yield X. Two new

$$O{=}C[CH_2CH_2CH_2Cl]_2 \xrightarrow{HNF_2} C(NF_2)_2[CH_2CH_2CH_2Cl]_2 \xrightarrow{NaN_3} \underset{\text{X}}{C(NF_2)_2[CH_2CH_2CH_2N_3]_2}$$

energetic fluorodinitro formals were also synthesized. They are glycol bis(fluorodinitroethyl formal) (XI) and glycerol tris(fluorodinitroethyl formal) (XII). XI was prepared by the reaction of

$$(CH_2OH)_2 + 2FC(NO_2)_2CH_2OCH_2Cl \rightarrow \underset{\text{XI}}{[CH_2OCH_2OCH_2C(NO_2)_2F]_2}$$

ethylene glycol with the chloromethyl ether of fluorodinitroethanol. XII was prepared by the reaction of glycerine with the chloromethyl ether of fluorodinitroethanol. A summary of these new energetic compounds and their properties are given in Tables I and II.



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3FC(NO_2)_2CH_2OCH_2Cl \rightarrow \begin{array}{l} CH_2OCH_2OCH_2C(NO_2)_2F \\ | \\ CHOCH_2OCH_2C(NO_2)_2F \\ | \\ CH_2OCH_2OCH_2C(NO_2)_2F \end{array}$$

XII

Experimental Section

General Procedures. *Caution!* Most of the products and starting materials described are explosives of moderate to considerable sensitivity to initiation by impact, shock, friction, and other means and should be handled with care.

Melting and boiling points are uncorrected. In cases where the boiling points were high, isolation and purification were accomplished by liquid chromatography for safety reasons. Infrared analyses were carried out with a Perkin-Elmer 137 infrared spectrophotometer. Gas chromatographic analyses were carried out on an F&M 700 instrument using a 10 ft × 3/16 in. stainless steel column packed with 3% QF-1 on 40/80 mesh Chromosorb T.

Final structure proof was obtained in every case with complete elemental analyses.

1,3-Diazido-2-nitrazapropane (I). A solution of 172.6 g (1.09 mol) of 1,3-dichloro-2-nitrazapropane in 500 mL of acetone was added in 30 min to a solution of 195 g (3.0 mol) of sodium azide in 600 mL of water. The reaction was maintained at ambient temperature with mild cooling during the addition. The solution was stirred for 3 h at ambient temperature and extracted with methylene chloride. The methylene chloride solution was washed with water, dried, and concentrated to give 160.6 g of yellow liquid. Distillation of a small portion of the product gave a colorless liquid: boiling point 97 °C (0.45 mm), n_D^{23} 1.5265 (83.2% yield).

N-(Trinitroethyl)-N-(3-azidopropyl)nitramine (III). To a solution of 13.8 g (0.1 mol) of (3-azidopropyl)amine hydrochloride, 21.7 g (0.12 mol) of trinitroethanol, and 60 mL of water was added dropwise a solution of 4.0 g (0.1 mol) of sodium hydroxide in 30 mL of water. The oil, which separated, was extracted with methylene chloride, washed with water, and dried. The methylene chloride solution of *N*-(trinitroethyl)-*N*-(3-azidopropyl)amine was added to a solution of 50 mL of acetic anhydride and 25 mL of 99% nitric acid at 5-10 °C. The reaction mixture was allowed to warm to ambient temperature while being stirred. The methylene chloride layer was separated, washed with water, dried, and concentrated to give 8.2 g of amber oil. The product was purified by liquid chromatography by using a neutral alumina column to give a light yellow liquid; d^{25} 1.5195, n_D^{26} 1.5120 (yield 17.9%).

1,3-Diazido-2-propyl 4,4,4-Trinitrobutyrate (IV). A solution of 25 g (0.1 mol) of 4,4,4-trinitrobutyryl chloride, 14.7 g (0.1 mol) of 1,3-diazido-2-propanol, and 50 mL of ethylene dichloride was refluxed for 1 week. The solution was cooled, washed with water, dried, and concentrated to give 25.5 g of amber liquid. The product was purified by liquid chromatography with a neutral alumina column. This treatment yielded a yellow liquid, n_D^{24} 1.5029, d^{25} 1.4640 (yield 66.5%). The infrared spectrum showed the expected strong absorption for azide (4700 nm), carbonyl (5800 nm), and nitro (6200 nm).

1,3-Diazido-2-propyl 4-Fluoro-4,4-dinitrobutyrate (V). A solution of 6.4 g (0.03 mol) of 4,4,4-fluorodinitrobutyryl chloride, 4.3 g (0.03 mol) of 1,3-diazido-2-propanol, and 25 mL of ethylene dichloride was refluxed for 40 h. The solution was cooled, washed with water, dried, and concentrated to give 8.0 g of light yellow liquid. The product was purified by liquid chromatography with a neutral alumina column to yield 7.2 g (75% yield) of a colorless liquid; $n_D^{23.5}$ 1.4875, d^{25} 1.4351. The infrared spectrum showed the expected strong absorption for azide (4700 nm), carbonyl (5800 nm), and nitro (6200 nm).

Bis(1,3-diazido-2-propyl) Oxalate (VI). A mixture of 8.4 g (0.06 mol) of 1,3-diazido-2-propanol, 3.8 g (0.03 mol) of oxalyl chloride, 1.2 g of anhydrous aluminum chloride, and 45 mL of ethylene dichloride was refluxed for 60 h. The reaction mixture was cooled, washed with dilute hydrochloric acid, dilute sodium bicarbonate solution, and water, dried, and concentrated to give 7 g of liquid product, $n_D^{24.5}$ 1.5140. Purification of the product by liquid chromatography with a basic alumina column yielded 5.95 g (59.5% yield) of a solid, melting at 54–55 °C.

1,3-Diazido-2-propyl 2-Fluoro-2,2-dinitroethyl Formal (VII). A mixture of 10.1 g (0.05 mol) of the chloromethyl ether of fluorodinitroethanol, 7.1 g (0.05 mol) of 1,3-diazido-2-propanol, and 8 drops of stannic chloride was heated at 70 °C for 24 h. The reaction mixture was dissolved in methylene chloride, washed with 1% sodium hydroxide solution and water, dried, and concentrated to give 7 g of yellow liquid. The product was purified by liquid chromatography with a basic alumina column to yield 3.3 g (21.3% yield) of a light yellow liquid; n_D^{25} 1.4798.

1,2-Dibromo-3-fluorodinitroethoxypropane. A solution of 100 g (0.515 mol) of allyl fluorodinitroethyl ether in 200 mL of carbon tetrachloride was cooled in an ice bath and 99 g (0.62 mol) of bromine was added. The mixture was stirred at ambient temperature overnight, refluxed for several hours, and concentrated to give 172.9 g of amber liquid. Distillation at 123 °C (0.25 mm) gave a colorless liquid, n_D^{26} 1.5010, with a GC purity of 100%.

1,2-Diazido-3-fluorodinitroethoxypropane (VIII). A mixture of 114.5 g (0.32 mol) of 1,2-dibromo-3-fluorodinitroethoxypropane, 65 g (1.0 mol) of sodium azide, and 400 mL of dimethylformamide was heated with stirring at 70–80 °C for 3 days. Methylene chloride, 300 mL was added and the mixture was washed with water until free of dimethylformamide. Concentration of the solution gave 19 g of amber liquid; n_D^{28} 1.4930. The product was purified by liquid chromatography with a basic alumina column to give 16.3 g (18.3% yield) of a yellow liquid; n_D^{25} 1.4832.

1,3-Diazido-2-nitratopropane (IX). To a mixture of 18.9 g (0.3 mol) of 99% nitric acid and 30.6 g (0.3 mol) of acetic anhydride at 5 °C was added 150 mL of methylene chloride followed by 14.2 g (0.1 mol) of 1,3-diazido-2-propanol. The resulting reaction mixture was stirred at 10–15 °C for 45 min. The methylene chloride layer was separated, washed with ice water, 5% sodium bicarbonate solution, and water, and dried over $MgSO_4$. The dried solution was then passed through a small neutral alumina column. Concentration of the eluent gave 16 g (85.6% yield) of IX as a colorless oil; n_D^{23} 1.4973, d^{25} 1.3789.

1,7-Dichloro-4,4-bis(difluoramino)heptane. To a solution of 25 mL of difluoraminosulfamic acid and 20 mL of methylene chloride was added dropwise a solution of 1.85 g (0.01 mol) of 1,7-dichloro-4-heptanone in 20 mL of methylene chloride. The temperature rose from 16 to 28 °C. The reaction mixture was stirred for an additional 2 h at ambient temperature. The methylene chloride layer was separated, washed with sodium bicarbonate solution and water, dried over magnesium sulfate, and concentrated to give 2.1 g (77.7% yield) of colorless liquid; n_D^{23} 1.4456.

1,7-Diazido-4,4-bis(difluoramino)heptane (X). A mixture of 2.1 g (0.007 mol) of 1,7-dichloro-4,4-difluoraminoheptane, 2.0 g (0.031 mol) of sodium azide, and 30 mL of dimethylformamide was heated at 85 °C for 3 days. The reaction mixture was cooled to ambient temperature and washed with six 20-mL portions of water, dried, and concentrated to give 1.4 g of crude product. It was purified by liquid chromatography with a small basic alumina column to give 1.16 g (52.9% yield) of pure X; $n_D^{23.5}$ 1.4641.

Glycol Bis(fluorodinitroethyl formal) (XI). A mixture of 47.8 g (0.448 mol) of ethylene glycol, 197.3 g (0.975 mol) of 2-fluoro-2,2-dinitroethyl chloromethyl ether, and 1 mL of $SnCl_4$ was heated under N_2 at 55–60 °C for 24 h. The resulting mixture was dissolved in an equal quantity of methylene chloride and washed first with 4% NaOH and then with water. After drying of the mixture with $MgSO_4$, the solvent was stripped in vacuo yielding 158.6 g of crude reaction mixture. Purification of XI was effected by double distillation under high vacuum through a small Vigreux column. In this way 8.22 g of crude product yielded 2.1 g of pure XI (25.6% yield): bp 149–150 °C (5×10^{-3} mm); n_D^{24} 1.4424, d^{25} 1.4952.

Glycerol Tris(fluorodinitroethyl formal) (XII). A mixture of 23.1 g (0.114 mol) of the chloromethyl ether of 2-fluoro-2,2-dinitroethanol, 2.1 g (0.023 mol) of glycerol, and 0.25 mL of stannic chloride was heated at 50 °C in a nitrogen atmosphere for 4 days. After this time the evolution of hydrogen chloride had ceased and the heterogeneous mixture had become homogeneous. The product was dissolved in methylene chloride, washed with 1% sodium hydroxide and water, dried, and concentrated in vacuo to give 7.72 g of yellow liquid. Attempts to distill the product to 184 °C (0.3 mm) were unsuccessful, as the product was not volatile under these conditions. Pure XII was obtained, however, as a colorless liquid (n_D^{25} 1.4498, d^{25} 1.5190) by liquid chromatography with a silica gel column. Yield of pure XII was 51.2%.

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