F, 4.20; CH_3, 3.32. Found: C, 63.86; H, 7.43; F, 4.22; CH_3, 3.38.

9α-Fluoro-11β,17α,21-trihydroxy-16α-methoxypregn-4-ene-3,20-dione (If). To a solution of 400 mg. of 21-acetoxy-9α - fluoro - 11β,17α - dihydroxy - 16α - methoxypregn-4-ene-3,20-dione (Ie) in 40 ml. of methanol kept under nitrogen was added 1.0 ml. of 10% aqueous potassium carbonate. The reaction mixture was allowed to stand for 20 min. at room temperature, at which time it was neutralized with acetic acid and evaporated until solid had formed. Water was added and the crystals were filtered off and washed with water to give 300 mg. of If, m.p. 240–245°. Several crystallizations from acetone-petroleum ether raised the melting point to 246–249°; λ_{max} 239 mμ (ε 17,800); ν_{max} 3490, 1711, 1680, and 1635 cm.$^{-1}$; $[\alpha]_D^{25}$ +108° (methanol).

Anal. Calcd. for $C_{22}H_{31}O_6F$ (410.47): C, 64.37; H, 7.61; F, 4.63; CH_3, 3.66. Found: C, 64.78; H, 7.93; F, 4.53; CH_3, 3.62.

Compound V. To a solution of 0.64 g. of II in 150 ml. of methanol, previously flushed with nitrogen, was added 2.1 ml. of 10% aqueous potassium carbonate. The reaction mixture was allowed to stand for 20 min. at room temperature and was then neutralized with acetic acid. Evaporation and addition of water gave 0.57 g., m.p. 267–270°. Several crystallizations from acetone–petroleum ether gave compound V, m.p. 277–280°; λ_{max} 240 mμ ($E^{1\%}_{1cm.}$ 378); ν_{max} 3450, 1729, 1670, 1640, and 1620 cm.$^{-1}$; $[\alpha]_D^{25}$ +47° (pyridine).

Anal. Found: C, 65.67, 65.66; H, 7.51, 7.43; F, 4.34, 4.23; CH_3, 8.01.

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Polynitro Aliphatic Esters

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The selective reduction of polynitro acid chlorides to the alcohols with sodium borohydride was reported.[2] The conversion of these alcohols to the nitrate esters and of the acid chlorides to the 2,2,2-trinitroethyl esters is described in the present paper.

4,4-Dinitro-1,7-heptane dinitrate (I), 4,4,6,8,8-pentanitro-1,11-undecane dinitrate (II), 4,4,6,6,8,8-hexanitro-1,11-undecane dinitrate (III), 4,4,6,8,8-pentanitro-6-aza-1,11-undecane dinitrate (IV), and 3,5,5-trinitro-3-aza-1-hexane nitrate (V) were prepared in quantitative yields by treating the corresponding alcohols with absolute nitric acid (Table I). Generally nitrates have a lower melting point than the corresponding alcohols. This was confirmed in compounds I, II, and III which melt 25–47° lower than the alcohols from which they were prepared. However, compounds IV and V melt considerably higher than the corresponding alcohols, a significant factor which must be attributed to the presence of the nitramino group. This is of interest because it is believed that there is a correlation between the melting point and thermal stability of a compound, the higher melting compound being more thermally stable provided that other factors are the same.

The 2,2,2-trinitroethyl esters were generally prepared according to the procedure of Hill,[3] by treating the acid chlorides with 2,2,2-trinitroethanol in the presence of a catalytic amount of aluminum chloride. In this manner bis(2,2,2-trinitroethyl) 4,4-dinitroheptanedioate, bis(2,2,2-trinitroethyl)-4-nitrazaheptanedioate, bis(2,2,2-trinitroethyl) 4,7-dinitrazadecanedioate, and 2,2,2-trinitroethyl 3,5,5-trinitro-3-azahexanoate were synthesized. Bis(2,2,2-trinitroethyl) 4,4,6,6,8,8-hexanitroundecanedioate was prepared from 4,4,6,6,8,8-hexanitroundecanedioic acid and 2,2,2-trinitroethanol using 100% sulfuric acid as the ionizing solvent. The results are summarized in Table II.

EXPERIMENTAL[4,5]

Nitrate esters. The preparation of 4,4,6,6,8,8-hexanitro-1,-11-undecane dinitrate is typical. In a 300-ml. three-necked flask, fitted with a mechanical stirrer and thermometer, was placed 100 ml. of 100% technical nitric acid. The flask was immersed in an ice bath and 10 g. of 4,4,6,6,8,8-hexanitro-1,11-undecanediol was added portionwise in 10 min. The solution was stirred for 10 min. longer at this temperature and poured on ice. The white solid was collected, washed with water, and dried *in vacuo* over potassium hydroxide. The yield of 4,4,6,6,8,8-hexanitro-1,11-undecane dinitrate was 11.4 g. (95.2%).

2,2,2-Trinitroethyl esters. In a 100-ml. round-bottom flask, fitted with a condenser and drying tube, was placed a solution of 3.62 g. (0.02 mole) of 2,2,2-trinitroethanol in 50 ml. of dry ethylene dichloride. Anhydrous aluminum chloride, 0.27 g. (0.002 mole), was added, and the solution turned yellow. To the solution was added 3.31 g. (0.01 mole) of 4,7-dinitrazadecanedioyl chloride. The reaction mixture was refluxed until evolution of hydrogen chloride gas had ceased. The black mixture was cooled and filtered, the solid was washed with cold dilute hydrochloric acid, with water, then dried and recrystallized from ethylene dichloride using charcoal to give 5.3 g. (85.5%) of white crystals, m.p. 126–128°.

In a 500-ml. Erlenmeyer flask was placed 100 g. of 100% sulfuric acid, 18.0 g. (0.1 mole) of 2,2,2-trinitroethanol, followed by 24.3 g. (0.05 mole) of 4,4,6,6,8,8-hexanitroundecanedioic acid and 50 ml. of chloroform. After standing for 5 days with occasional shaking, the copious white solid was collected, washed with ice water, and dried, 35.6 g. (87.8%), m.p. 114–116. Recrystallization from chloroform raised the melting point to 117–118°.

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(1) Present address: Stanford Research Institute, Menlo Park, Calif.

(2) G. B. Linden and M. H. Gold, to be published.

(3) M. E. Hill, *J. Am. Chem. Soc.*, **75**, 3020 (1953); **76**, 2329 (1954).

(4) All melting points are uncorrected.

(5) Microanalysis by Elek Microanalytical Laboratories, Los Angeles, Calif.

TABLE I
NITRATE ESTERS

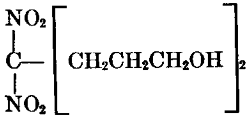
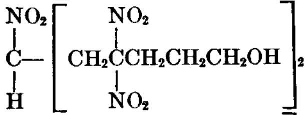
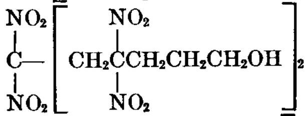
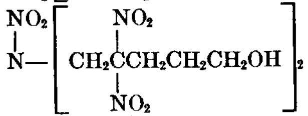
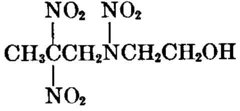
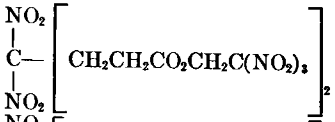
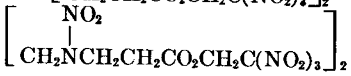
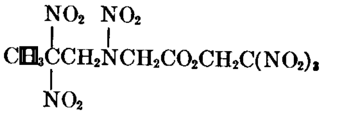
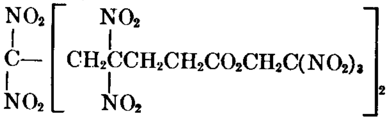
Alcohol	M.P.	Nitrate Ester M.P.	Yield, %	Recryst. Solvent	Formula	Calcd.			Found		
						C	H	N	C	H	N
 $(NO_2)_2C\left[CH_2CH_2CH_2OH\right]_2$	74.5–75	27–28	94.7	Methanol	$C_7H_{12}N_4O_{10}$	26.93	3.88	17.95	27.17	4.15	18.40
 $(NO_2)(H)C\left[CH_2C(NO_2)_2CH_2CH_2CH_2OH\right]_2$	108–109	73–75	96.1	Methanol	$C_{11}H_{17}N_7O_{16}$	26.25	3.41	19.48	26.79	3.64	19.18
 $(NO_2)_2C\left[CH_2C(NO_2)_2CH_2CH_2CH_2OH\right]_2$	125–125.5	100–101	95.2	Methanol	$C_{11}H_{16}N_8O_{18}$	24.09	2.94	20.44	24.54	2.99	19.91
 $(NO_2)N\left[CH_2C(NO_2)_2CH_2CH_2CH_2OH\right]_2$	106–108	133–135	95.0	Methano	$C_{10}H_{16}N_8O_{16}$	23.82	3.20	22.22	23.88	2.96	22.15
 $CH_3C(NO_2)_2CH_2N(NO_2)CH_2CH_2OH$	59–60	117–118	92.1	Methanol	$C_5H_9N_5O_9$	21.21	3.20	24.74	21.74	3.51	25.31

TABLE II

2,2,2-TRINITROETHYL ESTERS

Compound	Yield, %	M.P.	Recryst. Solvent	Formula	Calcd.			Found		
					C	H	N	C	H	N
 $C(NO_2)_2[CH_2CH_2CO_2CH_2C(NO_2)_3]_2$	47.0	170–171	Ethylene dichloride	$C_{11}H_{12}N_8O_{20}$	22.93	2.10	19.45	23.18	2.09	18.74
 $N(NO_2)[CH_2CH_2CO_2CH_2C(NO_2)_3]_2$	35.9	110–111	Chloroform	$C_{10}H_{12}N_8O_{18}$	22.56	2.27	12.05	22.58	2.26	20.93
 $[CH_2N(NO_2)CH_2CH_2CO_2CH_2C(NO_2)_3]_2$	85.5	126–128	Ethylene dichloride	$C_{12}H_{16}N_{10}O_{20}$	23.23	2.60	22.58	23.49	2.90	23.10
 $CH_3C(NO_2)_2CH_2N(NO_2)CH_2CO_2CH_2C(NO_2)_3$	50.3	121–121.5	Ethylene dichloride	$C_7H_9N_7O_{14}$	20.25	2.19	23.62	20.37	2.09	23.70
 $C(NO_2)_2[CH_2C(NO_2)_2CH_2CH_2CO_2CH_2C(NO_2)_3]_2$	87.8	117–118	Chloroform	$C_{15}H_{16}N_{12}O_{28}$	22.18	1.99	20.69	22.06	1.94	20.88

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Preparation of Aliphatic *gem*-Dinitro Monoisocyanates and Derivatives

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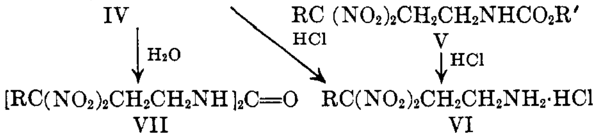
The first aliphatic *gem*-dinitro diisocyanate was reported by Herzog, Gold, and Geckler.[3] This paper describes the preparation of the first aliphatic *gem*-dinitro monoisocyanates by modifications of the original procedure. In general the starting materials were derived from a Michael addition of a *gem*-dinitroalkane[4] to acrylic acid. The nitro acid (I) was converted by the Curtius reaction into the corresponding isocyanate (IV), *via* the respective acid chloride (II) and azide (III).

$$\underset{\text{I}}{RC(NO_2)_2CH_2CH_2CO_2H} \longrightarrow \underset{\text{II}}{RC(NO_2)_2CH_2CH_2COCl} \longrightarrow$$

$$\underset{\text{III}}{RC(NO_2)_2CH_2CH_2CON_3} \longrightarrow \underset{\text{IV}}{RC(NO_2)_2CH_2CH_2NCO}$$

$$R = NO_2,\ CH_3,\ CH_3O_2CCH_2CH_2$$

The nitro isocyanates obtained by these means were isolated from the acid chlorides in over-all yields of 60–71% as viscous distillable liquids. They were characterized by conversion into carbamates (V), hydrolysis of the carbamates or the isocyanates with hydrochloric acid gave the corresponding amine hydrochlorides (VI), while treatment of the isocyanates with water yielded the ureas (VII).



$$\begin{tikzcd}
\underset{\text{IV}}{RC(NO_2)_2CH_2CH_2NCO} \arrow[r, "R'OH"] \arrow[d, "H_2O"] \arrow[dr, "HCl"] & \underset{\text{V}}{RC(NO_2)_2CH_2CH_2NHCO_2R'} \arrow[d, "HCl"] \\
\underset{\text{VII}}{[RC(NO_2)_2CH_2CH_2NH]_2C{=}O} & \underset{\text{VI}}{RC(NO_2)_2CH_2CH_2NH_2\cdot HCl}
\end{tikzcd}$$

The physical properties of these compounds are listed in Table I.

EXPERIMENTAL[5,6]

Nitro acids (I) 4,4-Dinitropentanoic acid was prepared as reported by Shechter[4] and 4,4,4-trinitrobutyric acid was made by the hydrolysis of methyl 4,4,4-trinitrobutyrate.[7] The synthesis of 4,4-dinitro-6-carbomethoxyhexanoic acid is described below. A slurry of 107 g. (0.51 mole) of the sodium salt of methyl 4,4-dinitrobutyrate[8] and 500 ml. of water was warmed to 45° and 180 g. (2.5 moles) of acrylic acid was added. The reaction mixture was stirred at 45° for 3 hr., cooled, and extracted with methylene chloride. The extracts were washed with water and concentrated leaving an oily residue which solidified upon standing at −20°. Recrystallization of the product from isopropyl ether gave 84.5 g. (63.1%) of white crystals, m.p. 92–93°.

Anal. Calcd. for $C_8H_{12}N_2O_8$: C, 36.38; H, 4.58; N, 10.61. Found: C, 37.02; H, 4.53; N, 10.62.

Nitro acid chlorides (II). The acid chlorides were prepared by refluxing the acids with thionyl chloride for 4–6 hr. Generally the crude acid chlorides were not purified but converted directly to the isocyanates. It was found that refluxing 4,4,4-trinitrobutyric acid with thionyl chloride for 4 hr. gave the anhydride while the acid chloride was only obtained after 20 hr., of refluxing.

A mixture of 8.9 g. (0.04 mole) of 4,4,4-trinitrobutyric acid and 10 ml. (0.138 mole) of redistilled thionyl chloride was refluxed for 4 hr. and concentrated *in vacuo*. The residual oil crystallized and was dissolved in 8.5 ml. of benzene. Addition of 30 ml. of hexane caused 2.8 g. (33%) of white solid to separate, m.p. 107–108.5°. Recrystallization from methylene chloride raised the melting point to 109.5–110°.

Anal. Calcd. for $C_8H_8N_6O_{15}$: C, 22.44; H, 1.88; N, 19.63. Found: C, 22.60; H, 2.06; N, 19.44.

A mixture of 49.0 g. (0.22 mole) of 4,4,4-trinitrobutyric acid and 100 ml. (1.38 moles) of thionyl chloride was refluxed for 20 hr. and concentrated *in vacuo*. The residual oil was distilled yielding 44.0 g. (82%), b.p. 65–66°/0.5 mm., n_D^{25} 1.4835, d^{25} 1.5669.

Anal. Calcd. for $C_4H_4ClN_3O_7$: C, 19.89; H, 1.67; N, 17.40 Found: C, 20.28; H, 1.74; N, 17.45.

Nitro isocyanates (IV). The preparation of 3,3-dinitrobutyl isocyanate is given as typical. A mixture of 50 g. (0.26 mole) of 4,4-dinitropentanoic acid and 300 ml. of thionyl chloride was refluxed for 6 hr. and concentrated *in vacuo* to give 55.0 g. (100%) of 4,4-dinitropentanoyl chloride. A solution of the acid chloride in 75 ml. of acetone was added dropwise to a solution of 27.9 g. (0.43 mole) of sodium azide in 279 ml. of water, at a temperature of 10–20°. The solution became cloudy and deposited crystals of the azide. The reaction mixture was stirred for 30 min. and extracted with 500 ml. of chloroform. The chloroform solution was washed with water, dilute sodium bisulfite solution, water, and dried over sodium sulfate. The solution was partially concentrated *in vacuo* to remove the last traces of water and then heated to reflux until the evolution of nitrogen had ceased. The solution was then concentrated *in vacuo* and the residual oil was distilled to give 31.7 g. (63.0%), b.p. 106–110°/1 μ, n_D^{25} 1.4708.

Carbamates (V). The carbamates were prepared in quantitative yields by refluxing the isocyanates with methanol or ethanol.

Amine hydrochlorides (VI). The preparation of 3,3-dinitrobutylamine hydrochloride from 3,3-dinitrobutyl isocyanate and methyl *N*-(3,3-dinitrobutyl)-carbamate is given as typical.

From 3,3-dinitrobutyl isocyanate. A 450-g. (2.38 moles) quantity of 3,3-dinitrobutyl isocyanate was added dropwise with good agitation to 2250 ml. of concentrated hydrochloric

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[3] L. Herzog, M. H. Gold, and R. D. Geckler, *J. Am. Chem. Soc.*, **73**, 749 (1951).

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

[5] All melting points are uncorrected.

[6] Microanalyses by Elek microanalytical Laboratories, Los Angeles, Calif.

[7] Schimmelschmidt, Hunter Report, **BIOS 1919/22 IG**, July 3, 1946.

[8] K. Klager, *J. Org. Chem.*, **16**, 161 (1951).