In conclusion, the present method, though empirical, gives the results comparable to the method of Chang and Lu in predicting heat of mixing data for ternary alcohol-alcohol-saturated hydrocarbon mixtures from binary parameters.

Acknowledgment

The author thanks the Computer Center, Osaka University, and the Data Processing Center, Kyoto University, for the use of their facilities.

Nomenclature

h_a = enthalpy of formation of a hydrogen bond, −6.0 kcal/mol
h^E = heat of mixing, cal/mol
K = chemical equilibrium constant of pure alcohol
$\bar{K}$ = chemical equilibrium constant of pseudo-single alcohol
R = gas constant
T = absolute temperature, K
v = molar volume, ml/mol
x = liquid mole fraction
$\bar{x}_a = x_a/(x_a + x_b)$

Greek Letters

β = physical interaction parameter, cal/cc
ϕ = volume fraction
$\bar{\phi}$ = volume fraction of pseudo-single alcohol

Subscripts

a, b = alcohols
h = hydrocarbon
i = alcohol monomer

Superscript

° = property of a pure substance in its particular reference state

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NEW COMPOUND SECTION

Synthesis of 1-Fluoro-1,1,3,3-tetranitro-5-oxahexane, 3-Trifluoromethoxy-2,2-dinitropropanol, and 3-Fluoro-2,2-dinitropropanol

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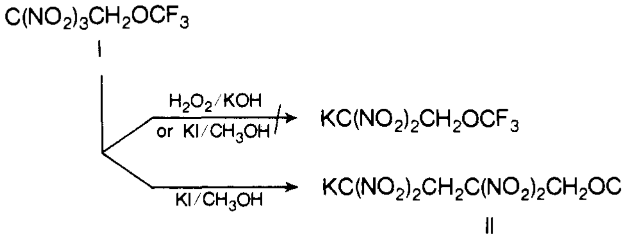
The synthesis of 1-fluoro-1,1,3,3-tetranitro-5-oxahexane by an aqueous fluorination procedure is described. The intermediate, potassium, 1,1,3,3-tetranitro-5-oxahexane, was obtained unexpectedly by basic reduction of 2,2,2-trinitroethyl trifluoromethyl ether. A limited amount of sulfur tetrafluoride produced two novel alcohols, 3-trifluoromethoxy-2,2-dinitropropanol and 3-fluoro-2,2-dinitropropanol. The acetate, acrylate, and formal derivatives of the alcohols were also prepared. The physical properties of the compounds are given.

A report in the Russian literature by Eremenko et al. (*3*) on the preparation of 1-fluoro-1,1,3,3-tetranitro-5-oxahexane, III, prompts us to report our recent synthesis and characterization of this compound.

In our research on the synthesis and reactions of fluorinated nitroaliphatic compounds (*10–12*), it was desirable to prepare potassium 2,2-dinitroethyl trifluoromethyl ether, $KC(NO_2)_2CH_2OCF_3$, as an intermediate. The reduction of a terminal trinitromethyl group to a potassium dinitromethyl group is well established (*7, 8*). Therefore, we anticipated that I would undergo this reaction to give the desired intermediate, $KC(NO_2)_2CH_2OCF_3$, as shown in Reaction 1.



$$C(NO_2)_3CH_2OCF_3 \quad \mathrm{I}$$

$$\not\xrightarrow[\text{or KI/CH}_3\text{OH}]{\text{H}_2\text{O}_2\text{/KOH}} KC(NO_2)_2CH_2OCF_3 \qquad (1)$$

$$\xrightarrow[\text{KI/CH}_3\text{OH}]{} KC(NO_2)_2CH_2C(NO_2)_2CH_2OCH_3 \quad \mathrm{II} \qquad (2)$$

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When I was treated with 3% hydrogen peroxide and potassium hydroxide, Reaction 1, decomposition resulted. This reaction was unexpected because many nitro compounds are stable to basic conditions. We then attempted the reduction using potassium iodide and methanol, Reaction 2, and isolated two unexpected products, potassium bifluoride, KHF_2, and potassium 1,1,3,3-tetranitro-5-oxahexane, $KC(NO_2)_2CH_2C(NO_2)_2CH_2OCH_3$, II. The products suggest the formation of a dinitroethylene intermediate. Since other workers have observed analogous nucleophilic additions to nitroethylenes (*5*), the following mechanism is suggested as a possible explanation for the experimental results, Reaction 3.

$$\begin{tikzcd}
(O_2N)_3CCH_2OCF_3 + KI \arrow[r, "CH_3OH"] & {} \\
\text{I} & {[KO_2N{=}C(NO_2)CH_2OCF_3] + I_2 + KNO_2} \arrow[d, "-KOCF_3"] \\
KC(NO_2)_2CH_2OCH_3 & {[(O_2N)_2C{=}CH_2]} \arrow[l, "KOCH_3"', "MeOH"] \arrow[d, "KC(NO_2)_2CH_2OCH_3"] \\
& KC(NO_2)_2CH_2C(NO_2)_2CH_2OCH_3
\end{tikzcd} \qquad (3)$$

$$KOCF_3 + CH_3OH \longrightarrow KOCH_3 + HOCF_3$$

$$HOCF_3 \longrightarrow COF_2 + HF \xrightarrow{KF} KHF_2$$

In a similar manner we attempted to obtain potassium 2,2-dinitroethyl fluoride, $KC(NO_2)_2CCH_2F$, as an intermediate by the reduction of 2,2,2-trinitroethyl fluoride (*1*). Again, the hydrogen peroxide-potassium hydroxide reduction was too severe, and decomposition products were obtained. Potassium iodide-methanol reduction also produced II, but in lower yield than was observed in Reaction 1.

$$\begin{tikzcd}
& KC(NO_2)_2CH_2F \\
C(NO_2)_3CH_2F \arrow[ur, "H_2O_2/KOH", "KI/CH_3OH"', "/" marking] \arrow[dr, "KI{,}CH_3OH"'] & \\
& \text{II}
\end{tikzcd} \qquad (4)$$

We assume that the ether, II, was produced by the same series of reactions previously observed in Reaction 3.

The fluoro derivative, III, was prepared to complete the structure proof of the ether. Eremenko and Oreshko (*4*) have reported that aqueous fluorination of the salts of different polynitro compounds is not applicable to salts of Michael adducts with 1,1-dinitroethylene, since they are unstable under the reaction conditions of fluorination in neutral and alkaline aqueous solutions. However, we found that II was easily converted to III in an aqueous fluorination, Reaction 5.

$$\underset{\text{II}}{KC(NO_2)_2CH_2C(NO_2)_2CH_2OCH_3} \xrightarrow[H_2O]{F_2/N_2} \underset{\text{III}}{FC(NO_2)_2CH_2C(NO_2)_2CH_2OCH_3} \qquad (5)$$

Our research program on the synthesis and reactions of fluorinated nitroaliphatic compounds (*10, 11*) required the synthesis of 3-trifluoromethoxy-2,2-dinitropropanol, IV, and 3-fluoro-2,2-dinitropropanol, V.

Hasek et al. (*9*), found that dicarboxylic acids treated with an excess of sulfur tetrafluoride produced the corresponding hexafluoroalkane. However, when sebacic acid was treated with a limited amount of sulfur tetrafluoride, only partial fluorination occurred. We reasoned that the same type of limited fluorination might occur when the bisfluoroformate, VII, was treated with a limited amount of sulfur tetrafluoride. Thus, Compound IV was prepared in 50–60% yields according to the following reaction sequence, Reactions 6, 7, and 8. The reaction conditions required only one equivalent of sulfur tetrafluoride with the bisfluoroformate, VII, Reaction 7.

$$\underset{\text{VI}}{HOCH_2C(NO_2)CH_2OH} \xrightarrow[NaF]{COF_2} \underset{\text{VII}}{FCOOCH_2C(NO_2)_2CH_2OCOF} \qquad (6)$$

$$\underset{\text{VII}}{FCOOCH_2C(NO_2)_2CH_2OCOF} \xrightarrow[HF]{1 \text{ equiv. } SF_4} \underset{\text{IX}}{CF_3OCH_2C(NO_2)_2CH_2OCOF} \; 52\% \qquad (7)$$

91%

$$\underset{\text{VIII}}{CF_3OCH_2C(NO_2)_2CH_2OCF_3} \; 23.9\%$$

$$\underset{\text{VII}}{FCOOCH_2C(NO_2)_2CH_2OCOF} \; 23.9\%$$

(separable by distillation)

$$\underset{\text{IX}}{CF_3OCH_2C(NO_2)_2CH_2OCOF} \xrightarrow[HNO_3]{H_2O} \underset{\text{IV}}{CF_3OCH_2C(NO_2)_2CH_2OH} \qquad (8)$$

91%

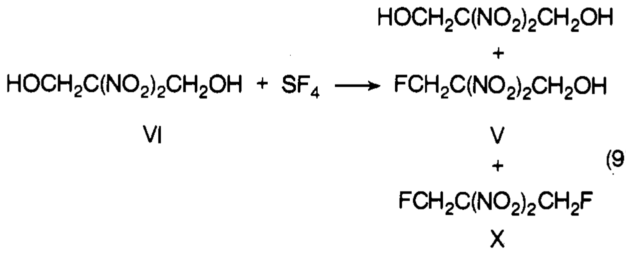
Recently, Baum (*1*) reported the synthesis of 1,3-difluoro-2,2-dinitropropane, 1-fluoro-3,3,3-trinitropropane, and 2,2-dinitro-1-fluoropropane by treatment of the corresponding alcohols with excess sulfur tetrafluoride. We ex-

Table I. Physical Properties of Fluoronitroalkyl Compounds[a]

Compound	Structure	Empirical formula	Yield, %	Bp, °C (mm)	*n* D (°C)	*ρ*, 20°C
II	$KC(NO_2)_2CH_2C(NO_2)_2CH_2OCH_3$	$C_5H_7KN_4O_9$	60	[Mp 165–6 (dec)]	. . .	. . .
III	$FC(NO_2)_2CH_2C(NO_2)_2CH_2OCH_3$	$C_5H_7FN_4O_9$	36	85–90 (0.4)	. . .	. . .
IV	$CF_3OCH_2C(NO_2)_2CH_2OH$	$C_4H_5F_3N_2O_6$	91.7	75–78 (0.1)	1.4005 (25)	1.69
V	$FCH_2C(NO_2)_2CH_2OH$	$C_3H_5FN_2O_5$	18.5	63 (0.01)	. . .	. . .
IX	$CF_3OCH_2C(NO_2)_2CH_2OCOF$	$C_5H_4F_4N_2O_7$	69	45–55 (1.0)	1.3857 (23)	. . .
		53% Conversion				
XI	$CF_3OCH_2C(NO_2)_2CH_2OCOCH_3$	$C_6H_7F_3N_2O_7$	83	50–52 (0.5)	1.3952 (25)	1.56
XII	$CF_3OCH_2C(NO_2)_2CH_2OCOCH{=}CH_2$	$C_7H_7F_3N_2O_7$	74	50–55 (0.05)	1.4085 (25)	1.49
XIII	$[CF_3OCH_2C(NO_2)_2CH_2O]_2CH_2$	$C_9H_{10}F_6N_4O_{12}$	50	130–135 (0.01)	1.4048 (25)	1.58
XV	$FCH_2C(NO_2)_2CH_2OCOCH_3$	$C_5H_7FN_2O_6$	54	53–54 (0.2)	1.3952 (25)	1.56
XVI	$FCH_2C(NO_2)_2CH_2OCOCH{=}CH_2$	$C_6H_7FN_2O_6$	59	65–70 (0.02)	1.4085 (25)	. . .

[a] Elemental analyses (C, H, N) in agreement with theoretical values were obtained and submitted for review.

tended this work by treating VI with a limited amount of sulfur tetrafluoride to obtain V, Reaction 9. V was separated from the other components in 20% yield by vacuum distillation. No attempt was made to improve the yield of this reaction.



$$\underset{\text{VI}}{HOCH_2C(NO_2)_2CH_2OH} + SF_4 \longrightarrow \begin{array}{c} HOCH_2C(NO_2)_2CH_2OH \\ + \\ FCH_2C(NO_2)_2CH_2OH \\ \text{V} \\ + \\ FCH_2C(NO_2)_2CH_2F \\ \text{X} \end{array} \qquad (9)$$

The physical properties of these compounds are shown in Table I, and the spectral properties in Table II.

Experimental

Fluorine was obtained from the General Chemical Division of the Allied Chemical Corp. and was always diluted in stream with nitrogen prior to fluorination.

Melting points and boiling points are uncorrected. Elemental analyses were performed by E. McCarthy, and the nmr data were obtained by H. C. Barrett. Nmr spectra were run on a Varian HA-100 spectrometer. Values for the ^1H chemical shifts are given in δ units with respect to tetramethylsilane as an internal reference, and values for the ^{19}F chemical shifts are given in φ^* units (6) with respect to trichlorofluoromethane as an internal reference.

Table II. Spectral Properties of Fluoronitroalkyl Compounds

Compound	Structure	Ir bands	Nmr data	
II	$KC(NO_2)_2CH_2C(NO_2)_2CH_2OCH_3$	1595 (s, CNO_2)	δ	3.45 (s, $\underline{3}$, OCH_3)
		1100–1200 (m, OCH_3)		4.38 (s, $\underline{2}$, CH_2O)
				4.59 (s, $\underline{2}$, CH_2)
III	$FC(NO_2)_2CH_2C(NO_2)_2CH_2OCH_3$	1600 (s, ON_2)	δ	3.28 (s, $\underline{3}$, OCH_3)
		11.25 (m, COC)		4.25 (s, $\underline{2}$, OCH_2)
				4.48 (s, $\underline{2}$, CH_2)
			φ^*	100.3 (bt, FC)
IV	$CF_3OCH_2C(NO_2)_2CH_2OH$	3500 (m, OH)	δ	2.76 (s, $\underline{1}$, CH_2OH)
		3000 (w, CH)		4.56 (s, $\underline{2}$, CH_2OH)
		1600 (s, CNO_2)		4.86 (s, $\underline{2}$, CF_3OCH_2)
		1400– (bs, CF)		
		1175	φ^*	62.0 (s, CF_3)
		1080 (s, COC)		
V	$FCH_2C(NO_2)_2CH_2OH$	3600 (m, OH)	δ	2.56 (s, $\underline{1}$, $CH_2O\underline{H}$)
		3000 (w, CH)		4.54 (d, $\underline{2}$, $J_{HF} = 2$ Hz, CH_2OH)
		1600 (s, CNO_2)		
		1100–1000 (s, CF)		5.22 (d, $\underline{2}$, $J_{HF} = 45$ Hz, FCH_2)
IX	$CF_3OCH_2C(NO_2)_2CH_2OCOF$	3000 (w, CH)	δ	5.20 (s, $\underline{2}$, CF_3OCH_2)
		1840 (s, O═C—F)		4.90 (s, $\underline{2}$, CH_2OCOF)
		1600 (s, CNO_2)		
		1300–1150 (bs, CF)		
XI	$CF_3OCH_2C(NO_2)_2CH_2OCOCH_3$	3000 (w, CH)	δ	2.06 (s, $\underline{3}$, CH_2COO)
		1750 (s, C═O)		4.90 (s, $\underline{2}$, CF_3OCH_2)
		1600 (s, CNO_2)		5.01 (s, $\underline{2}$, CH_2OCOCH_3)
			φ^*	62.4 (s, CF)
XII	$CF_3OCH_2C(NO_2)_2CH_2OCOCH{=}CH_2$	3000 (w, CH)	δ	4.86 (s, $\underline{2}$, CF_3OCH_2)
		1750 (s, C═O)		5.08 (s, $\underline{2}$, $CH_2C{=}O$)
		1640 (m, C═C)		6.2 (m, $\underline{3}$, $CH{=}CH_2$)
		1600 (s, CNO_2)		
		1400 (m, CNO_2)	φ^*	62.4 (s, CF_3)
XIII	$[CF_3OCH_2C(NO_2)_2CH_2O]_2CH_2$	3000 (w, CH)	δ	4.44 (s, $\underline{4}$, CH_2O)
		1590 (s, CNO_2)		
		1150–1350 (bs, CF)		4.80 (s, $\underline{2}$, OCH_2O)
				4.88 (s, $\underline{4}$, CF_3OCH_2)
		1060 (m, COC)	φ^*	62.6 (s, CF_3)
XV	$FCH_2C(NO_2)_2CH_2OCOCH_3$	3000 (w, CH)	δ	2.08 (s, $\underline{3}$, CH_3CO)
		1750 (s, C═O)		4.99 (d, $\underline{2}$, $J_{HF} = 2$ Hz CH_2O)
		1600 (s, CNO_2)		5.20 (d, $\underline{2}$, $J_{HF} = 48$ Hz FCH_2)
		1100 (m, CF)	φ^*	240.0 (t of t, $J_{HF} = 2.5$ Hz $J_{HF} = 58$ Hz, FCH_2)
XVI	$FCH_2C(NO_2)_2CH_2OCOCH{=}CH_2$	3000 (w, CH)	δ	5.09 (d, $\underline{2}$, J_{HF}, 2 Hz, FCH_2)
		1750 (s, C═O)		
		1640 (m, C═C)		5.22 (d, $\underline{2}$, J_{HF}, 46 Hz, CH_2O)
		1600 (s, CNO_2)		
		1400 (m, CNO_2)		6.02 (m, $\underline{3}$, $CH{=}CH_2$)
		1100–1025 (bs, CF)		

In nmr descriptions, s = singlet, d = doublet, t = triplet, q = quadruplet, and m = multiplet. The infrared spectra were obtained on a Perkin-Elmer 237B grating infrared spectrometer. In infrared descriptions, s = strong, m = medium, w = weak, and b = broad.

An F&M Model 500 gas chromatograph equipped with a thermal conductivity detector was used for all glpc analyses. Unless otherwise noted, samples were analyzed using a 30% SE-30 column, 4 ft × ¼ in. Infrared spectra were run on a Perkin-Elmer 237 infrared spectrophotometer. In ir descriptions, s = strong, m = medium, w = weak, and b = broad.

Caution: Carbonyl fluoride and sulfur tetrafluoride are highly reactive and highly toxic gases; $LD_{50} \sim 10\text{–}20$ ppm. Toxicities and mode of action are similar to those of phosgene. Also, both reagents react with water to liberate hydrogen fluoride; care must be taken to avoid hydrogen fluoride burns. The reactions are usually performed in a well-ventilated hood using shields, masks, and rubber gloves.

The fluorodinitro compounds described in this paper are explosive and sensitive to initiation by impact, shock, friction, or other means. Many fluorodinitro compounds are toxic and may cause burns when brought into contact with the skin. Therefore, care should be taken when handling these compounds.

Potassium 1,1,3,3-tetranitro-5-oxahexane, II. *From 2,2,2-trinitroethyl trifluoromethyl ether, I.* Potassium iodide (2.46 grams, 0.160 mole) was dissolved in 20 ml of methanol. To this solution, in a 5-min period, was added dropwise at 25°C with stirring I (2.0 grams, 0.010 mole). The mixture turned dark after 1 hr of stirring and was allowed to stir an additional 2 hr. Potassium bifluoride precipitated and was filtered and washed well with ether to remove iodine. The methanol and ether filtrates were combined and concentrated at 18 mm, leaving a dark solid. The solid was washed well with ether to remove iodine; 1.0 gram (83%) of crude material remained. Recrystallization of this product from ethanol gave 0.7 gram (60%) of II, mp 165–166°C (dec.).

From 2,2,2-trinitroethyl fluoride. Potassium iodide (3.65 grams, 0.022 mole) was dissolved in 50 ml of methanol. A solution of 1-fluoro-2,2,2-trinitroethane (1.83 grams, 0.010 mole) in 20 ml of methanol was added. The brown reaction mixture was refluxed for 2 hr and concentrated at 18 mm, leaving a dark crystalline solid. The solid was washed with ether until the iodine was removed. The yellow solid was recrystallized from water to give 0.60 gram (36%) of II.

1-Fluoro-1,1,3,3-tetranitro-5-oxahexane, III. A stream of fluorine:nitrogen (5:45 cc/min) was passed through a stirred solution of II (3.0 grams, 0.0098 mole) in 90 ml of water with 15 ml of methylene chloride as a second phase in a glass reactor at 0–5°C. After 55 min the yellow solution turned colorless. The organic phase was separated, dried over magnesium sulfate, and evaporated in vacuo leaving 2.33 grams of liquid. The liquid was run through a 60-cm silica-gel (90-200 mesh) column using a 1:1 mixture of chloroform:hexane. The solvent was removed from the eluent, and the residue was distilled to give 1.0 gram (36%) of III:

3-Trifluoromethoxy-2,2-dinitropropanol, IV. IX (5.0 grams, 0.018 mole), 10 ml of cold water, and one drop of concentrated nitric acid were combined. The clear two-phase system was stirred rapidly and warmed to 25°C. Very slow evolution of gas was observed. The mixture was heated at 50–60°C for 1 hr at which time all CO_2 evolution had ceased. The layers were separated, and the aqueous layer was washed with methylene chloride (6 × 10 ml) and dried over magnesium sulfate. The solids were removed by filtration, and methylene chloride was removed under vacuum, leaving a colorless liquid, 4.0 grams (96% crude yield). Purification by distillation gave 3.1 grams (74% yield) of colorless IV.

The reaction was scaled up sixfold. IX (30.07 grams, 0.107 mole) was stirred with water (20 ml) and concentrated nitric acid for 2 hr at 50°C. The water wash was omitted. After filtering and removal of solvent by distillation, the colorless fraction boiling at 75–78°C (0.1 mm) was collected as IV, 23.10 grams (91.7% yield).

3-Trifluoromethoxy-2,2-dinitropropyl fluoroformate, IX. To a 300-ml stainless-steel autoclave was added VII (15.48 grams, 0.060 mole). The autoclave was cooled to −78°C, flushed twice with nitrogen, and evacuated to 0.5 mm. Sulfur tetrafluoride (7.40 grams, 0.068 mole) and anhydrous hydrogen fluoride (40 grams, 2.0 mole) were distilled into the vessel. After sealing, the autoclave was heated at 80°C for 42 hr with gentle rocking. The autoclave was cooled to −78°C, and the toxic gases were vented into a 10% potassium hydroxide solution (100 ml). The residual fuming brown liquid was decanted into 50 ml of methylene chloride containing 20 grams of 1:1 sodium fluoride: magnesium sulfate. The vessel was washed with methylene chloride (2 × 35 ml). The solids were removed by filtration, and solvent was removed at 15 mm, leaving a brown liquid, 15.1 grams (90% crude recovery).

Glpc (SE-30, 4 ft × ¼ in., 100°C, programmed to 125° and 150°C; He flow rate, 46 ml/min) of this residue showed three products, which were subsequently identified as the following compounds: VIII 23.9%, bp 27–28°C (1.0 mm), R_f 3.6 min; IX 52.0%, bp 48–52°C (1.0 mm), R_f 10 min; and VII 23.9%, bp 68–70°C (0.1 mm); R_f 18 min. The residue was fractionally distilled through a 4-in. Vigreux column at reduced pressure. Fraction three was obtained as a colorless liquid: bp 48–52°C (1.0 mm); 6.5 grams of 96% pure IX (33% distilled yield). A second fractional distillation produced 2.6 grams of an analytical sample which was +99% pure, bp 44–45°C (0.8 mm), $n^{23}D$ 1.3857.

The reaction was scaled up using 70 grams (0.271 mole) of 2,2-dinitropropyl bis(fluoroformate), 27.5 grams (0.25 mole) of sulfur tetrafluoride, and 100 grams (5 mole) of anhydrous hydrogen fluoride. After working up the reaction mixture as described, the following products were obtained: VIII, 9.4%; IX, 53.0%; VII, 37.0%.

3-Trifluoromethoxy-2,2-dinitropropyl acetate, XI. The general procedure of Bourne and coworkers (2) was adapted for this and subsequent ester preparations. To 2.34 grams of IV (0.01 mole) were added 0.90 gram (0.015 mole) of glacial acetic acid and 3.0 grams (0.014 mole) of trifluoroacetic anhydride. Within 2 min a mild exotherm occurred, which lasted for 10 min. The colorless liquid was stirred 16 hr at ambient temperature. The solution was diluted with methylene chloride (30 ml) and washed with water (10 ml), 5% sodium bicarbonate solution (10 ml), and water (10 ml). The aqueous washes were each extracted with methylene chloride (2 × 5 ml), and the methylene chloride fractions were combined and dried with magnesium sulfate. The solids were removed by filtration, and the methylene chloride was removed at 15 mm, leaving a clear tan liquid, 2.5 grams (90% crude yield). The fraction boiling at 50–52°C (0.5 mm) was collected as VII, 2.3 grams (83% yield).

3-Trifluoromethoxy-2,2-dinitropropyl acrylate, XII. To 2.34 grams (0.01 mole) of IV were added 1.0 gram (0.014 mole) of acrylic acid and 3.0 grams (0.014 mole) of trifluoroacetic anhydride. Within a few minutes a mild exotherm occurred which lasted for 10 min. The solution was stirred at 50°C for 15 min, cooled to room temperature, and diluted with methylene chloride. The solution was washed with water (10 ml), 5% sodium bicarbonate (10 ml), and water (10 ml). Each aqueous wash was extracted with methylene chloride (2 × 5 ml). The methylene chloride fractions were combined and dried over magnesium sulfate. After filtration to remove the solids, the solvent was removed at ~15 mm, leaving a colorless liquid, 2.56 grams (90% crude yield). The product was purified by vacuum distillation, and the colorless fraction boiling at 50–55°C (0.05 mm) was collected as XII, 2.12 grams (74% yield), $n^{25}\mathrm{D}$ 1.4055.

Bis (3-trifluoromethoxy-2,2-dinitropropyl) formal, XIII. Paraformaldehyde (0.11 gram, 3.7 mole as HCHO) was added to 10 grams of 90% sulfuric acid and heated to 50°C for 1 hr with stirring. The solution was cooled to 10°C, and 1.96 grams (8.4 mole) of IV was added. The temperature rose to 20°C as phasing out occurred. The mixture was stirred vigorously for 15 min, poured onto 50 grams of ice, and extracted with methylene chloride (5 × 10 ml). The methylene chloride solution was dried over magnesium sulfate and filtered. Solvent was removed at 15 mm, leaving 1.5 grams of crude liquid. Distillation of the liquid gave 1.24 grams (64% yield); bp 110–115°C (0.05 mm), glpc (4% poly-*m*-phenyl ether on 80/100 Chromosorb G AW/DMCS, 10 ft × ⅛ in., 200°C, He 10 ml/min, R_f 4.7 min) 96% pure. Liquid chromatography on silica gel eluted with chloroform produced 1.09 grams of colorless liquid which was distilled at 130–135°C (0.01 mm), producing 1.0 gram (50% yield) of XIII (>98% pure).

3-Fluoro-2,2-dinitropropanol, V. VI (10.0 grams, 0.06 mole) was added to a 300-ml autoclave, cooled to −78°C, evacuated to 1 mm, and flushed twice with nitrogen. After the final evacuation to 1 mm, sulfur tetrafluoride (6.9 grams, 0.064 mole) was distilled into the autoclave. The reaction mixture was heated at 80 ± 5°C for 4 days with gentle rocking. The autoclave was cooled to −78°C, and the toxic gases were vented into a 10% potassium hydroxide solution (1000 ml). The fuming reaction mixture was decanted into sodium fluoride to remove the residual hydrogen fluoride. The autoclave was washed with methylene chloride (5 × 20 ml). The solids were removed by filtration, and solvent was removed at 15 mm, leaving a semisolid, 8.4 grams (84% crude yield). After purification by vacuum distillation, colorless semisolid, II, was collected boiling at 63°C (0.01 mm), 1.85 grams (18.5%).

3-Fluoro-2,2-dinitropropyl acetate. To 2.1 grams (0.012 mole) of V was added 1.8 gram (0.30 mole) of glacial acetic acid and 4.5 grams (0.0215 mole) of trifluoroacetic anhydride. Within 2 min a mild exotherm (~5°C) occurred which lasted for 10 min. The colorless liquid was stirred at 50°C for 1 hr. The solution was diluted with methylene chloride (30 ml) and washed with water (10 ml), 5% sodium bicarbonate solution (10 ml), and water (10 ml). The aqueous washes were each extracted with methylene chloride (2 × 5 ml), and the methylene chloride fractions were combined and dried with magnesium sulfate. The solids were removed by filtration, and the methylene chloride was removed at 15 mm, leaving a clear tan liquid, 2.2 grams (84% crude yield). The fraction boiling at 53–54°C (0.2 mm) was collected as XV; 1.4 grams (54% yield).

3-Fluoro-2,2-dinitropropyl acrylate, XVI. To 0.75 gram (4 mmol) of V was added 0.36 gram (5.0 mmol) of acrylic acid and 1.0 gram (5.0 mmol) of trifluoroacetic anhydride. Within a few minutes a mild exotherm (~5°C) occurred which lasted for 10 min. The solution was stirred at 50°C for 1 hr, cooled to room temperature, and diluted with methylene chloride. The solution was washed with water (10 ml), 5% sodium bicarbonate solution (10 ml), and water (10 ml). Each aqueous wash was extracted with methylene chloride (2 × 5 ml). The methylene chloride fractions were combined and dried over magnesium sulfate. After filtration to remove the solids, the solvent was removed at ~15 mm, leaving a colorless liquid, 0.84 gram (85% crude yield). The product was purified by vacuum distillation, and the colorless fraction boiling at 65–70°C (0.02 mm) was collected as XVI, 0.58 gram (59% yield).

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