identical with that obtained by 2537-Å photolysis of the pentacyclic lactam, **8c**.

**2a,4,5,6,7,7b-Hexahydro-1,2-diphenyl-3H-cyclobuta[*d*]cyclopenta[*b*]pyridin-3-one (16f).**—Irradiation of a mixture of 1.359 g (10.0 mmol) of the pyridone **6f** and 7.5 g (42.0 mmol) of diphenylacetylene as described above gave, in addition to **8f**, 275 mg (8.7%) of cyclobutene derivative, **16f** ($R_f$ ether = 0.65). The product was crystallized from benzene–petroleum ether producing colorless needles: mp 184–186° dec; ir ($CHCl_3$) 1663 (C=C·NH·C=O), 3398 $cm^{-1}$ (NH); nmr ($CDCl_3$) 1.6–2.6 (m, 6, methylene H), 3.88 (diffuse doublet $J$ = 6 Hz, 1, $H_a$), 4.02 (d, $J$ = 5 Hz, 1, $H_b$), 7.0–8.0 $\delta$ (m, 11, aromatic **H** and NH); uv max (EtOH) 224 (log $\epsilon$ 4.45), 277 m$\mu$ (4.08).

*Anal.* Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11. Found: C, 84.45; H, 6.36.

Calcd *m/e* 313. Found: 313.

Fragment peaks at *m/e* 135 (pyridone) and *m/e* 178 (diphenylacetylene were also observed. No attempt was made to obtain this product from the photoisomerization of **8f**.

**2a,4,5,6,7,7b-Hexahydro-7b-methyl-1,2-diphenyl-3H-cyclobuta[*d*]cyclopenta[*b*]pyridin-3-one (16g).**—Irradiation of a mixture of 1.371 g (9.2 mmol) of 4-methylcyclopentano-[*e*]-2-pyridone (**6g**) and 7.5 g (42.0 mmol) of diphenylacetylene as described before gave, in addition to other products, 400 mg (13.3%) of the cyclobutene derivative (**16g**) ($R_f$ ether = 0.75). Crystallization from benzene–petroleum ether furnished colorless needles: mp 202–203°; ir ($CHCl_3$) 1661 (C=C·NH·C=O), 3398 $cm^{-1}$ (NH); nmr ($CDCl_3$) 1.3–2.7 (m, methylene H), 1.5 (s, $CH_3$), 3.58 (s, 1, $H_b$), 7.0–7.85 (m, 10, aromatic H), 8.05 $\delta$ (broad singlet, 1, NH); uv max (EtOH) 225 (log $\epsilon$ 4.37), 263 m$\mu$ (4.17).

*Anal.* Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46. Found: C, 84.51; H, 6.60.

Calcd *m/e* 327. Found: 327.

Fragment peaks at *m/e* 149 (pyridone) and *m/e* 178 (diphenylacetylene) were also observed.

**Stability of 8 at 3500 Å.**—A solution of 10 mg (0.03 mmol) of pentacyclic lactam, **8**, in 20 ml of methanol was irradiated under nitrogen at 3500 Å and the reaction monitored by tlc at various intervals. After 100 hr no spot corresponding to the cyclobutenopyridone, **16**, was detected.

**Photoisomerization of 8 to 16 in Methanol–Ether at 2537 Å.**—A solution of 10 mg (0.03 mmol) of the pentacyclic lactam (**8**) in 2 ml of methanol and 2 ml of anhydrous ether was irradiated at 2537 Å and the reaction followed by tlc. After 12 hr, it was found that isomerization to the cyclobutenopyridone, **16**, had taken place.

**Irradiation of the Pyridone (6) and Diphenylacetylene in Methanol–Ether at 2537 Å.**—A solution of 300 mg (2.0 mmol) of 5,6,7,8-tetrahydro-2-quinolone (**6**) and 750 mg (4.2 mmol) of diphenylacetylene in 8 ml of MeOH and 8 ml of $Et_2O$ was irradiated at 2537 Å for 12 hr. A tlc examination revealed that a minute trace of the pentacyclic lactam, (**8**), was present but no spot due to cyclobutenopyridone (**16**), could be detected.

**Irradiation of the Pyridone (6) and Diphenylacetylene in Benzene at 2537 Å.**—Irradiation of a solution of 100 mg (0.67 mmol) of **6** and 119.3 mg (0.67 mmol) of diphenylacetylene in 10 ml of benzene at 2537 Å for 4 hr followed by an examination by tlc revealed that a trace of cyclobutenopyridone, **16**, was present but no spot corresponding to the pentacyclic lactam, **8**, was visible.

**Photostability of 16 at 2537 Å.**—A solution of 13 mg (0.04 mmol) of cyclobutenopyridone (**16**) in 3 ml of benzene was irradiated at 2537 Å and the reaction checked by tlc after 6 and 17 hr. It was found that some decomposition had taken place as shown by streaking on the plate but the predominant spot was due to unchanged **16**.

**Photostability of 16 at 3500 Å.**—A solution of 27 mg (0.08 mmol) of cyclobutenopyridone (**16**) in 15 ml of methanol was irradiated for 16 hr and the reaction followed by tlc. It was found that some decomposition had taken place but no spots corresponding to new products were seen on the tlc plate.

**Registry No.**—Diphenylacetylene, 501-65-5; **6a**, 25183-42-0; **7**, 25183-43-1; **8**, 20670-50-2; **8a**, 20199-81-9; **8b**, 25183-46-4; **8c**, 25183-47-5; **8d**, 25183-48-6; **8e**, 25183-49-7; **8f**, 25183-50-0; **8g**, 25183-51-1; **11**, R = H, 19734-36-2; **11**, R = Me, 25183-53-3; **16**, 20177-91-7; **16a**, 20177-92-8; **16b**, 25183-56-6; **16c**, 25183-57-7; **16f**, 25183-58-8; **16g**, 25184-11-6.

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# Alkylation Reactions of 2-Fluoro-2,2-dinitroethanol[1]

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2-Fluoro-2,2-dinitroethanol in aqueous alkali reacted with dimethyl sulfate, allyl bromide, acetic anhydride, ethyl chloroformate, and oxalyl chloride yielding 2-fluoro-2,2-dinitroethyl methyl ether, allyl 2-fluoro-2,2-dinitroethyl ether, 2-fluoro-2,2-dinitroethyl acetate, ethyl 2-fluoro-2,2-dinitroethyl carbonate, and 2-fluoro-2,2-dinitroethyl oxalyl chloride, respectively. Ethylene oxide, propylene oxide, epihalohydrins, and butadiene dioxide yielded 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether, 2-fluoro-2,2-dinitroethyl 2-hydroxylpropyl ether, 2-fluoro-2,2-dinitroethyl glycidyl ether, and 4-(2-fluoro-2,2-dinitroethoxy)-3-hydroxybutene 1,2-oxide, respectively. Pyridine-catalyzed reactions of 2-fluoro-2,2-dinitroethanol with thionyl chloride and sulfuryl chloride gave bis(2-fluoro-2,2-dinitroethyl) sulfite and 2-fluoro-2,2-dinitroethyl chloride, respectively. Tris(2-fluoro-2,2-dinitroethyl) borate was obtained in the ester-exchange reaction. Reactions of 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether, 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ether, and 2-fluoro-2,2-dinitroethyl oxalyl chloride were investigated.

Although the synthesis of 2-fluoro-2,2-dinitroethanol was only recently reported,[2,3] the reactions of this unusual polynitro alcohol have been already explored by several groups of investigators.[2-6] 2-Fluoro-2,2-dinitroethanol undergoes deformylation in aqueous alkaline solutions in a manner similar to other 2,2-dinitro alcohols,[7] but unlike the other polynitro alcohols 2-fluoro-2,2-dinitroethanol in basic medium may also exist in equilibrium with its alkoxide ions. The dissociation to alkoxide ions, attributed to the reported

$$FC(NO_2)_2CH_2OH \overset{OH^-}{\rightleftharpoons} FC(NO_2)_2CH_2O^- \rightleftharpoons FC(NO_2)_2^- + CH_2O$$

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[1] This work was supported by the Office of Naval Research under Contract Nonr 2655(OO), by the U. S. Naval Ordnance Laboratory in collaboration with the U. S. Air Force Armament Laboratory, Air Force Systems Command under Contract N60921-67-C-0290, and by the U. S. Air Force Armament Laboratory, Air Force Systems Command under Contract F08635-69-C-0125.

[2] M. J. Kamlet and H. G. Adolph, *J. Org. Chem.*, **33**, 3073 (1968).

[3] V. Grakauskas and K. Baum, *ibid.*, **33**, 3080 (1968).

[4] H. G. Adolph and M. J. Kamlet, *ibid.*, **34**, 45 (1969).

[5] L. T. Eremenko and F. Ya. Natsibullin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **4**, 912, 1968.

[6] V. Grakauskas and K. Baum, *J. Org. Chem.*, **34**, 3927 (1969).

[7] For a review, see P. Noble, Jr., F. G. Borgardt, and W. L. Reed, *Chem. Rev.*, **64**, 19 (1964).

destabilization of nitronate anion by $\alpha$ fluorines,[8] was recently demonstrated in the Michael reaction of 2-fluoro-2,2-dinitroethanol with ethyl propiolate[6] where, in addition to 3-fluoro-3,3-dinitrocrotonate, the "normal" Michael adduct, $\beta$-(2-fluoro-2,2-dinitroethoxy)-acrylate was also obtained. This finding suggested that the observed alkoxide reaction may not be limited to the $\alpha,\beta$ unsaturated carbonyl compounds, but may represent an example of much broader class of nucleophilic reactions of 2-fluoro-2,2-dinitroethoxide anions. With this anticipation in mind, alkali-catalyzed reactions of 2-fluoro-2,2-dinitroethanol with a number of electrophilic reagents were examined and the results are presented in this paper.

Aqueous alkaline 2-fluoro-2,2-dinitroethanol was treated with dimethyl sulfate and allyl bromide at ambient temperature to give 2-fluoro-2,2-dinitroethyl methyl ether[9] (75% yield) and allyl 2-fluoro-2,2-dinitroethyl ether (30% yield), respectively, as shown.

$$FC(NO_2)_2CH_2OH + (CH_3)_2SO_4 \xrightarrow[H_2O]{NaOH} FC(NO_2)_2CH_2OCH_3$$

$$FC(NO_2)_2CH_2OH + CH_2{=}CHCH_2Br \xrightarrow[H_2O]{NaOH} FC(NO_2)_2CH_2OCH_2CH{=}CH_2$$

The Williamson reactions of simple alcohols with dialkyl sulfates or alkyl halides are usually carried out in nonaqueous media under more rigorous reaction conditions.[10] The Williamson reactions of 2,2-dinitro alcohols were not investigated because in alkaline solution these polynitro alcohols undergo deformylation to nitronate salts.[7] Several known polynitro ethers were synthesized indirectly. Thus, 2,2-dinitropropyl ethyl ether was obtained by addition of ethanol to 2-nitropropene, followed by the oxidative nitration of the adduct.[11]

In connection with characterization of polynitro ethers, we synthesized 2,2-dinitropropyl methyl ether by heating 2,2-dinitropropanol with dimethyl sulfate. 2,2-Dinitropropyl methyl sulfate was also obtained.

$$CH_3C(NO_2)_2CH_2OH + (CH_3)_2SO_4 \xrightarrow{95^\circ} CH_3C(NO_2)_2CH_2OCH_3 + CH_3OSO_2OCH_2C(NO_2)_2CH_3$$

This reaction seems to be of general utility in the synthesis of "mixed" nitroalkyl ethers. Thus, 2,2-dinitropropanediol reacted with dimethyl sulfate to give 1,3-dimethoxy-2,2-dinitropropane and 3-methoxy-2,2-dinitropropyl methyl sulfate.

$$(NO_2)_2C(CH_2OH)_2 + (CH_3)_2SO_4 \longrightarrow (NO_2)_2C(CH_2OCH_3)_2 + CH_3OCH_2C(NO_2)_2CH_2OSO_2OCH_3$$

On the other hand, attempts to synthesize 2-fluoro-2,2-dinitroethyl ethers from 2-fluoro-2,2-dinitroethanol were unsuccessful under these reaction conditions.

Acetic anhydride and ethyl chloroformate reacted with aqueous alkaline 2-fluoro-2,2-dinitroethanol to give 2-fluoro-2,2-dinitroethyl acetate[5] and ethyl 2-fluoro-2,2-dinitroethyl carbonate, respectively, in 70–80% yields.

$$FC(NO_2)_2CH_2OH + Ac_2O \xrightarrow[H_2O]{NaOH} FC(NO_2)_2CH_2OCOCH_3$$

$$FC(NO_2)_2CH_2OH + ClCO_2Et \xrightarrow[H_2O]{NaOH} FC(NO_2)_2CH_2OCO_2C_2H_5$$

Pyridine-catalyzed reaction of 2-fluoro-2,2-dinitroethanol with oxalyl chloride yielded, depending on the stoichiometry of reagents, bis(2-fluoro-2,2-dinitroethyl) oxalate[12] and 2-fluoro-2,2-dinitroethyl oxalyl chloride. The bis ester was still the major product at a 1:1 ratio of the reagents but 2-fluoro-2,2-dinitroethyl oxalyl chloride was obtained in 20% yield. The Curtius reaction of this ester chloride gave carbo(2-fluoro-2,2-dinitroethoxy) isocyanate as is depicted below.

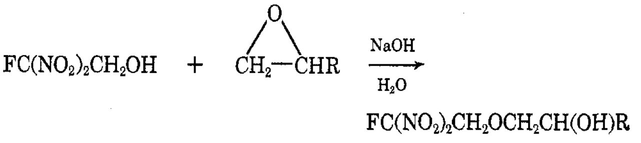
$$FC(NO_2)_2CH_2O_2CCOCl + NaN_3 \xrightarrow[C_2H_4Cl_2]{H_2O} [FC(NO_2)_2CH_2O_2CCON_3] \xrightarrow{\Delta} FC(NO_2)_2CH_2O_2CNCO$$

The isocyanate polymerized readily at room temperature and its elemental analysis was not obtained.[13] The freshly prepared compound exhibited the characteristic NCO infrared absorption peak and reacted with 2-fluoro-2,2-dinitroethanol to give bis(2-fluoro-2,2-dinitroethyl) iminodicarboxylate, which was characterized by elemental analysis and proton nmr spectrum.

$$FC(NO_2)_2CH_2O_2CNCO + HOCH_2CF(NO_2)_2 \longrightarrow NH[CO_2CH_2CF(NO_2)_2]_2$$

Simple carboalkoxy isocyanates could not be synthesized *via* the Curtius reaction[14] and this example seems to represent the first case of this rearrangement.

The above alkylation reactions suggested that in a manner similar to that of simple alkoxides[15] 2-fluoro-2,2-dinitroethoxide may react with 1,2-epoxides to give the corresponding 2-fluoro-2,2-dinitroethyl 2-hydroxyalkyl ethers. This was found to be the case. Ethylene oxide and propylene oxide reacted with 2-fluoro-2,2-



R = H or $CH_3$

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[8] H. G. Adolph and M. J. Kamlet, *J. Amer. Chem. Soc.*, **88**, 4761 (1966).

[9] 2-Fluoro-2,2-dinitroethyl methyl ether was synthesized by Adolph and Kamlet by reacting 2-fluoro-2,2-dinitroethanol with diazomethane,[8] and in the fluorination of 2,2-dinitroethyl methyl ether.[2]

[10] For a review of Williamson reactions, see Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol. VI [3], Georg Thieme Verlag, Stuttgart, 1965, pp 24–33.

[11] H. Schechter, *et al.*, "Research in Nitromonomers and their Applications to Solid Smokeless Propellants," Ohio State University Research Foundation, Report No. 10, March 25, 1954. Available through the Defense Documentation Center, Cameron Station, Alexandria, Va.

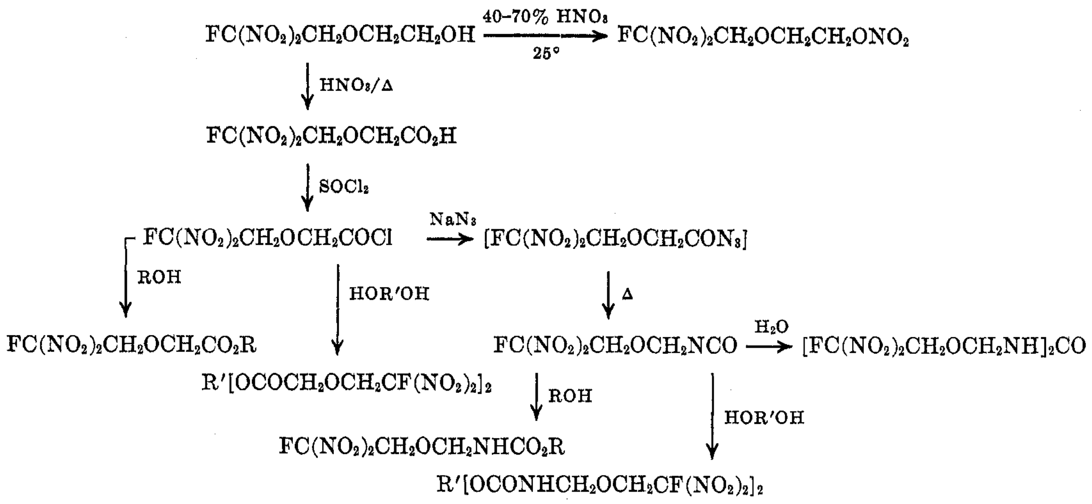
[12] Bis(2-fluoro-2,2-dinitroethyl) oxalate was first synthesized by Dr. M. B. Frankel, Rocketdyne Corp., Canoga Park, Calif. (private communication) whose priority in this regard we herewith acknowledge.

[13] On storage at ambient temperature, the originally mobile liquid turned progressively more viscous and solidified. The resulting solid analyzed for $C_4H_2N_3FO_7$. The material was not characterized but based on the related reaction of ethyl chloroformate with potassium cyanide [O. Diels and K. Jacoby, *Ber.*, **41**, 2393 (1908)], it appears to be tris[carbo(2-fluoro-2,2-dinitroethoxy)]isocyonuric acid.

[14] P. A. S. Smith, *Org. Reactions*, **3**, 337 (1946).

[15] For a general discussion of epoxide-alkoxide reactions, see (a) S. Winstein and R. B. Henderson, *Heterocycl Compounds*, **1**, 47 (1950); (b) G. Dittus in Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol. VI [3], Georg Thieme Verlag, Stuttgart, 1965, pp 40 and 447.

SCHEME I

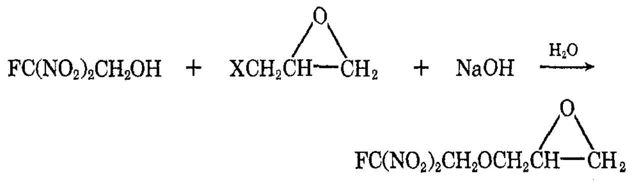


R = $FC(NO_2)_2CH_2$– or $CH_3C(NO_2)_2CH_2$–; R′ = –$CH_2C(NO_2)_2CH_2$–

dinitroethanol in aqueous sodium hydroxide to give 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl and 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ethers, respectively, in 40 to 60% yields.

The product yields were not optimized but a significant increase in yields resulted when excess of an epoxide was used, the concentration of reagents was increased, and the reaction temperature was kept low (0–5°). 2-Fluoro-2,2-dinitroethyl 2-hydroxypropyl ether was also obtained in 12% yield in stannic chloride-catalyzed reaction of 2-fluoro-2,2-dinitroethanol with propylene oxide.

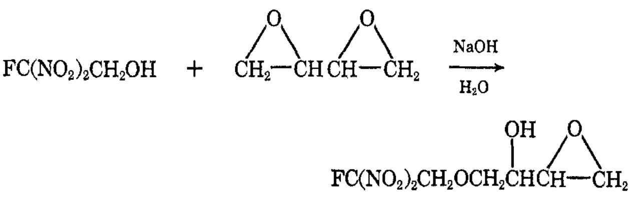
2-Fluoro-2,2-dinitroethanol reacted with epichlorohydrin or epibromohydrin in aqueous sodium hydroxide to give 2-fluoro-2,2-dinitroethyl glycidyl ether in 15 to 30% yields.



X = Cl, Br

At least stoichiometric amounts of sodium hydroxide were required in these reactions to effect the cyclization of halohydrin intermediates.

The reaction of butadiene dioxide with 2-fluoro-2,2-dinitroethane in aqueous sodium hydroxide yielded 4-(2-fluoro-2,2-dinitroethoxy)-3-hydroxybutene 1,2-oxide, identified by elemental analysis and nmr spectra.



The proton nmr spectrum of the distillation residue remaining in the purification of the 1:1 alkylation product suggested that the 1:2 adduct, 1,4-bis(2-fluoro-2,2-dinitroethoxy)-2,3-butanediol, was also produced in the above reaction but the elemental analysis of the material was only in a fair agreement with this structure.

2-Fluoro-2,2-dinitroethyl 2-hydroxyethyl ether and 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ether were found to be useful starting materials in the synthesis of other 2-fluoro-2,2-dinitroethoxy derivatives and their reactions were investigated.

2-Fluoro-2,2-dinitroethyl 2-hydroxyethyl ether was oxidized with 70% nitric acid to give 2-fluoro-2,2-dinitroethoxyacetic acid in 91% yield. The acid was converted to 2-fluoro-2,2-dinitroethoxyacetyl chloride with thionyl chloride. The Curtius reaction of the acid chloride gave 2-fluoro-2,2-dinitroethoxymethyl isocyanate. 2-Fluoro-2,2-dinitroethoxyacetyl chloride was treated with 2-fluoro-2,2-dinitroethanol, 2,2-dinitropropanol, and 2,2-dinitropropanediol to give the corresponding esters quantitatively. 2-Fluoro-2,2-dinitroethoxymethyl isocyanate also reacted with the above nitro alcohols to give the corresponding N-(2-fluoro-2,2-dinitroethoxymethyl)carbamic acid esters. N,N′-Bis[(2-fluoro-2,2-dinitroethoxy)methyl]urea was obtained by reacting the isocyanate with water. Several attempts to oxidize 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether to the corresponding aldehyde with dilute nitric acid under mild conditions failed; small amounts of 2-fluoro-2,2-dinitroethoxyethyl nitrate were obtained. The reactions of 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether are summarized in Scheme I. All the compounds are new and were characterized by their elemental analyses and their infrared and nmr spectra.

The reactions of 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ether were explored to a lesser degree than those of 2-fluoro-2,2-dinitroethyl 2-hydroxylpropyl ether. The compound was oxidized with 70% nitric acid to give 2-fluoro-2,2-dinitroethoxyacetic acid in 40% yield. Oxidation with chromic acid in acetone yielded 2-fluoro-2,2-dinitroethoxyacetone in 95% yield. The ketone was treated with hydroxylamine to give the corresponding oxime, which was nitrated and the resulting nitronitroso intermediate oxidized to 2-fluoro-2,2-dinitroethyl 2,2-dinitropropyl ether, following the procedure of Bull, *et al.*[16] The ether was contaminated with 2-

[16] J. R. Bull, Sir E. R. H. Jones, and G. D. Meakins, *J. Chem. Soc.*, 2601 (1965).

fluoro-2,2-dinitroethoxyacetone and some difficulties were encountered with its purification. The reactions of 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ether are summarized below.

$$\mathrm{FC(NO_2)_2CH_2OCH_2CO_2H}\ \text{and/or}\ \mathrm{FC(NO_2)_2CH_2OCH_2CH_2ONO_2}$$

$$\Big\uparrow\ \mathrm{70\%\ HNO_3}$$

$$\mathrm{FC(NO_2)_2CH_2OCH_2CH(OH)CH_3}$$

$$\Big\downarrow\ \mathrm{CrO_3/acetone}$$

$$\mathrm{FC(NO_2)_2CH_2OCH_2COCH_3}$$

$$\Big\downarrow\ \mathrm{NH_2OH\cdot HCl{-}NaOAc}$$

$$\mathrm{FC(NO_2)_2CH_2OCH_2C({=}NOH)CH_3}$$

$$\text{1. HNO}_3\ \Big\downarrow\ \text{2. H}_2\text{O}_2$$

$$\mathrm{FC(NO_2)_2CH_2OCH_2C(NO_2)_2CH_3}$$

In addition to the reactions of 2-fluoro-2,2-dinitroethanol in aqueous alkali, several related reactions of the alcohol were carried out in the presence of pyridine.[17] Under these conditions, the alcohol reacted with thionyl chloride to give bis(2-fluoro-2,2-dinitroethyl) sulfite[18] (80–85% yield) and a small amount (5–7% yield) of 2-fluoro-2,2-dinitroethyl chloride as is shown below.

$$\mathrm{2FC(NO_2)_2CH_2OH + SOCl_2 + 2C_5H_5N \xrightarrow{CH_2Cl_2} [FC(NO_2)_2CH_2O]_2SO + FC(NO_2)_2CH_2Cl}$$

2-Fluoro-2,2-dinitroethyl chloride was obtained in 75% yield in the pyridine-catalyzed reaction of the alcohol with sulfuryl chloride.

Tris(2-fluoro-2,2-dinitroethyl) borate was obtained quantitatively in the ester-exchange reaction between triethyl borate and 2-fluoro-2,2-dinitroethanol.

$$\mathrm{B(OC_2H_5)_3 + 3FC(NO_2)_2CH_2OH \xrightarrow{90^\circ} B[OCH_2CF(NO_2)_2]_3 + 3C_2H_5OH}$$

2-Fluoro-2,2-dinitroethyl nitrate was obtained in 75% yield in the reaction of 2-fluoro-2,2-dinitroethanol with a sulfuric–nitric acid mixture.

$$\mathrm{FC(NO_2)_2CH_2OH + HNO_3{-}H_2SO_4 \longrightarrow FC(NO_2)_2CH_2ONO_2}$$

The compound has been recently synthesized by Eremenko and Natsibullin[4] in 30% yield.

## Experimental Section

**Caution.**—2-Fluoro-2,2-dinitroethanol is a *severe* skin irritant. Safety shielding should be used in work with fluorodinitro compounds.

**2-Fluoro-2,2-dinitroethyl Methyl Ether.**[2,3]—To a stirred solution of 2.0 g (0.05 mol) of sodium hydroxide and 6.24 g (0.04 mol) of 2-fluoro-2,2-dinitroethanol in 55 ml of water was added dropwise at 25° over a period of 10 min 5.1 g (0.04 mol) of dimethyl sulfate. After 45 min the reaction mixture was extracted with 35 ml of methylene chloride and distilled to give 5.1 g of 2-fluoro-2,2-dinitroethyl methyl ether (75% yield), bp 27° (0.1 mm) [lit.[2] bp 47–48° (4 mm)], $n^{25}\mathrm{D}$ 1.4045.

*Anal.* Calcd for $\mathrm{C_3H_5N_2FO_5}$: C, 21.4; H, 3.0; N, 16.7; F, 11.3. Found: C, 21.2; H, 2.7; N, 16.2; F, 10.6.

Proton nmr ($\mathrm{CDCl_3}$): $\delta$ 4.60 (d, $J_{\mathrm{HF}} = 18$ Hz, $\mathrm{CH_2O}$) and 3.61 (s, $\mathrm{CH_3}$). Fluorine nmr: $\phi$ 110.9 (s).

**Allyl 2-Fluoro-2,2-dinitroethyl Ether.**—A mixture of 1.6 g (0.04 mol) of sodium hydroxide in 30 ml of water, 4.62 g (0.04 mol) of 2-fluoro-2,2-dinitroethanol and 4.85 g (0.04 mol) of allyl bromide was stirred at 25° for 3 hr.

The product was extracted with 30 ml of methylene chloride and distilled to give 2.5 g of alkyl 2-fluoro-2,2-dinotroethyl ether (34% yield), bp 31–32° (0.2 mm).

*Anal.* Calcd for $\mathrm{C_5H_7N_2FO_5}$: C, 30.9; H, 3.6; N, 14.4; F, 9.8. Found: C, 30.6; H, 3.4; N, 13.9; F, 9.9.

Proton nmr ($\mathrm{CDCl_3}$): $\delta$ 5.56–6.20 (d, d, t, $J_{cis} = 9$ Hz, $J_{trans} = 17.5$ Hz, $J_{\mathrm{allyl}} = 5.5$ Hz, CH), 5.06–5.51 (m, $\mathrm{CH_2{=}}$), 4.15 (d, $J_{\mathrm{HH}} = 5.5$ Hz, $\mathrm{CH_2}$), and 4.58 (d, $J_{\mathrm{HF}} = 18$ Hz, $\mathrm{OCH_2CF}$). Fluorine nmr: $\phi$ 111.0 (t, $J_{\mathrm{HF}} = 17.3$ Hz).

**2,2-Dinitropropyl Methyl Ether.**—A mixture of 20 g (0.16 mol) of dimethyl sulfate and 10.0 g (0.067 mol) of 2,2-dinitropropanol was heated at 95–100° for 10 hr and distilled to give 18 g of colorless liquid, bp 30–90° (0.1 mm), and a residue amounting to *ca.* 10 g. The distillate, containing mainly dimethyl sulfate, was stirred with 100 cc of 25% aqueous sodium hydroxide at 25° for 16 hr. An insoluble liquid was extracted with 25 ml of methylene chloride, and distilled to give 2.5 g of 2,2-dinitropropyl methyl ether, bp 35° (0.1 mm), $n^{25}\mathrm{D}$ 1.4295.

*Anal.* Calcd for $\mathrm{C_4H_8N_2O_5}$: C, 29.3; H, 4.9; N, 17.1. Found: C, 29.0; H, 4.8; N, 17.5.

Proton nmr ($\mathrm{CCl_4}$): $\delta$ 4.13 [s, $\mathrm{OCH_2C(NO_2)_2}$], 3.39 (s, $\mathrm{OCH_3}$), and 2.13 (s, $\mathrm{CH_3}$).

**2,2-Dinitropropyl Methyl Sulfate.**—The distillation residue above was washed with 100 ml of water and an insoluble liquid was distilled in a molecular still at 100° (25 $\mu$) to give 1.5 g of colorless oil, $n^{25}\mathrm{D}$ 1.4470.

*Anal.* Calcd for $\mathrm{C_4H_8N_2SO_8}$: C, 19.7; H, 3.3; N, 11.5. Found: C, 20.0; H, 3.3; N, 11.8.

Proton nmr ($\mathrm{CCl_4}$): $\delta$ 4.85 (s, 2), 3.92 (s, 3), and 2.25 (s, 3).

**1,3-Dimethoxy-2,2-dinitropropane.**—A solution of 5.0 g (0.03 mol) of 2,2-dinitropropanediol in 24 g (0.19 mol) if dimethyl sulfate was heated at 90–95° for 7 hr and distilled at 50–90° (0.1 mm) to give 19 g of a colorless liquid (mainly dimethyl sulfate) and a residue amounting to 9.0 g. The distillate was stirred with 200 ml of 10% aqueous sodium hydroxide at 25° for 16 hr. An insoluble liquid was extracted with 15 ml of methylene chloride and distilled to give 0.7 g of 1,3-dimethoxy-2,2-dinitropropane, bp 38° (0.05 mm), $n^{25}\mathrm{D}$ 1.4302.

*Anal.* Calcd for $\mathrm{C_5H_{10}N_2O_6}$: C, 30.9; H, 5.2; N, 14.4. Found: C, 30.7; H, 5.1; N, 14.6.

Proton nmr ($\mathrm{CCl_4}$): $\delta$ 3.47 (s, 3) and 4.28 (s, 2).

**Methyl 3-Methoxy-2,2-dinitropropyl Sulfate.**—The distillation residue above was stirred with 100 ml of water. The product was extracted with 30 ml of methylene chloride and distilled in a molecular still at 100–102° (25 $\mu$) to give 0.9 g of colorless liquid, $n^{25}\mathrm{D}$ 1.4460.

*Anal.* Calcd for $\mathrm{C_5H_{10}N_2SO_9}$: C, 21.9; H, 3.7; N, 10.2. Found: C: 22.2; H, 3.7; N, 11.0.

**2-Fluoro-2,2-dinitroethyl Acetate.**—To a stirred solution of 4.4 g (0.11 mol) of sodium hydroxide and 15.4 g (0.1 mol) of 2-fluoro-2,2-dinitroethanol in 150 ml of water was added dropwise (10 min) with cooling at 0–2° 10.2 g (0.1 mol) of acetic anhydride. The reaction mixture was stirred for 1.5 hr, the product extracted with 50 ml of methylene chloride and distilled to give 16.4 g (83% yield) of 2-fluoro-2,2-dinitroethyl acetate, bp 91° (50 mm), $n^{21}\mathrm{D}$ 1.4198 [lit.[4] bp 90–90.5° (50 mm), $n^{20}\mathrm{D}$ 1.4200].

**2-Fluoro-2,2-dinitroethyl Ethyl Carbonate.**—To a stirred solution of 4.4 g (0.11 mol) of sodium hydroxide and 15.4 g (0.1 mol) of 2-fluoro-2,2-dinitroethanol in 75 ml of water was added at 0–2° with cooling over a period of 15 min 10.8 g (0.1 mol) of ethyl chloroformate. After 45 min the product was extracted with 50 ml of methylene chloride and distilled to give 18.2 g (80% yield) of 2-fluoro-2,2-dinitroethyl ethyl carbonate, bp 53–54° (0.1 mm), $n^{23}\mathrm{D}$ 1.4215.

*Anal.* Calcd for $\mathrm{C_5H_7N_2FO_7}$: C, 26.6; H, 3.1; N, 12.4; F, 8.4. Found: C, 26.3; H, 3.2; N, 13.1; F, 8.5.

Proton nmr ($\mathrm{CCl_4}$): $\delta$ 1.33 (t, $\mathrm{CH_2}$), 4.23 (q, $J = 7.1$ Hz, $\mathrm{CH_2}$), and 5.17 (d, $J_{\mathrm{HF}} = 15.7$ Hz, $\mathrm{CH_2}$). Fluorine nmr: $\phi$ 111.3 (s).

**2-Fluoro-2,2-dinitroethyl Oxalyl Chloride.**—To a stirred solution of 12.7 g (0.1 mol) of oxalyl chloride in 75 ml of diethyl ether was added at 5–10° with cooling over a period of 15 min a solution of 15.4 g (0.1 mol) of 2-fluoro-2,2-dinitroethanol and 7.9 g (0.1 mol) of pyridine in 75 ml of diethyl ether. The reaction mixture was filtered and the filter cake was washed with three 25-ml portions of diethyl ether. The combined filtrate and washings were

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(17) 2-Fluoro-2,2-dinitroethanol forms a sparingly water soluble 1:1 complex with pyridine from which the alcohol can be recovered upon acidification or by removing pyridine at reduced pressure. The complex was examined by nmr but the proton and $^{19}$F spectra did not provide any information regarding its structure.

(18) Bis(2-fluoro-2,2-dinitroethyl) sulfite was reported by K. Baum, *J. Amer. Chem. Soc.*, **91**, 4594 (1969), as a side reaction product in the reaction of sulfur tetrafluoride with 2-fluoro-2,2-dinitroethanol.

distilled to give 4.5 g of 2-fluoro-2,2-dinitroethyl oxalyl chloride, bp 66–67° (0.1 mm).

*Anal.* Calcd for $C_4H_2N_2FClO_7$: C, 19.6; H, 0.8; N, 11.5; F, 7.8. Found: C, 20.0; H, 0.8; N, 11.3; F, 7.4.

**Carbo(2-fluoro-2,2-dinitroethoxy) Isocyanate.**—A solution of 2.45 g (0.01 mol) of 2-fluoro-2,2-dinitroethyl oxalyl chloride in 25 ml of ethylene chloride was added dropwise over a period of 8 min at 12–15° to a stirred solution of 0.8 g (0.012 mol) of sodium azide in 15 ml of water and the mixture was stirred for 15 min. The ethylene chloride solution was washed with 30 ml of ice water, dried over anhydrous sodium sulfate, and filtered. The filtrate was warmed at 50° for 45 min in a distillation apparatus protected from the atmospheric moisture and concentrated at 25 mm. The pale yellow liquid was dried at 35° (0.1 mm); weight 2.0 g. The infrared spectrum of the freshly prepared material showed intense absorption peaks at 4.5 and 6.25 μ, attributed to $-NCO$ and $-NO_2$ groups, respectively.

Soon after its preparation (20–30 min), the clear liquid started to turn turbid and on standing in a closed vial at room temperature for several days it solidified into a white solid.

**2-Fluoro-2,2-dinitroethyl Iminodicarboxylate.**—To a solution of 1.0 g of freshly prepared carbo(2-fluoro-2,2-dinitroethoxy) isocyanate and 0.75 g of 2-fluoro-2,2-dinitroethanol in 15 ml of ethylene chloride was added a catalytic amount of ferric acetylacetonate. After 18 hr a white crystalline solid was filtered, washed with two 1-ml portions of ethylene chloride and dried; wt 1.0 g, mp 182–183°.

*Anal.* Calcd for $C_6H_5N_5F_2O_{12}$: C, 19.1; H, 1.3; N, 18.6; F, 10.1. Found: C, 18.8; H, 1.3; N, 17.8; F, 10.4.

Proton nmr ($d_6$-acetone): δ 10.11 (s, 1, NH) and 5.58 (d, 4, $J_{HF}$ = 16 Hz, $CH_2$).

**2-Fluoro-2,2-dinitroethyl 2-Hydroxyethyl Ether.**—To a stirred solution of 4.0 g (0.1 mol) of sodium hydroxide in 90 ml of water at 0–5° was added 15.5 g (0.1 mol) of 2-fluoro-2,2-dinitroethanol and 5.5 g (0.125 mol) of ethylene oxide. After standing for 16 hr at 0° the reaction mixture was extracted with three 25-ml portions of methylene chloride and the combined extracts were distilled to give 5.4 g (27% yield) of 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether, bp 74–75° (50 μ), $n^{23}_{\mathrm{D}}$ 1.4370.

*Anal.* Calcd for $C_4H_7N_2FO_6$: C, 24.5; H, 3.6; N, 14.1; F, 9.6. Found: C, 24.3; H, 3.6; N, 13.8; F, 9.5.

The infrared spectrum showed absorption peaks at (μ) 3.0 (s), 3.44 (m); 3.50 (sh); 6.27 (s); 6.86 (m); 7.43 (m); 7.62 (s); 8.15 (w); 8.83 (s); 9.40 (s); 11.83 (s); and 12.20 (s).

Proton nmr ($CDCl_3$): δ 4.77 [d, $J_{HF}$ = 18 Hz, $OCH_2CF(NO_2)_2$], 3.82 (s, $CH_2$), and 3.25 (s, OH). Fluorine nmr φ 111.0 (t, $J_{HF}$ = 18 Hz).

Higher yields (68%) and conversion (57%) were observed in a large-scale run using 185 g (1.2 mol) of 2-fluoro-2,2-dinitroethanol, 30 g (0.75 mol) of sodium hydroxide and 125 g (2.86 mols) of ethylene oxide in 750 ml of water. *p*-Toluenesulfonate, bp 160–163° (25 μ) (molecular still), $n^{23}_{\mathrm{D}}$ 1.5035, was obtained quantitatively by treating the hydroxy ether with *p*-toluenesulfonyl chloride in methylene chloride–pyridine solution.

*Anal.* Calcd for $C_{11}H_{13}N_2FSO_8$: C, 37.5; H, 3.7; N, 8.0; F, 5.4. Found: C, 37.7; H, 3.6; N, 7.6; F, 5.5.

**2-Fluoro-2,2-dinitroethyl 2-Hydroxypropyl Ether.**—To a solution of 2.2 g (0.055 mol) of sodium hydroxide in 70 ml of water at 0° was added 9.24 g (0.06 mol) of 2-fluoro-2,2-dinitroethanol and 3.5 g (0.06 mol) of propylene oxide. The reaction mixture was allowed to stand at 0° for 18 hr, extracted with three 30-ml portions of diethyl ether, and the combined ethereal extracts were distilled to give 3.1 g of colorless liquid (25 % yield), bp 62° (0.05 mm), $n^{23}_{\mathrm{D}}$ 1.4325.

*Anal.* Calcd for $C_5H_9N_2FO_6$: C, 28.3; H, 4.3; N, 13.2; F, 9.0. Found: C, 28.0; H, 4.1; N, 13.0; F, 9.3.

Proton nmr ($CDCl_3$): δ 4.75 [d, $J_{HF}$ = 18 Hz, $OCH_2CF(NO_2)_2$], 4.00 (d, q, CH), and 3.6 (s, $OCH_2$ and OH; AB pattern after $D_2O$ exchange). Fluorine nmr: φ 110.8 (t, $J_{HF}$ = 17.5 Hz).

The yield of the product increased to 45 and 63%, respectively, when a 2:1 and a 4:1 molar ratio of propylene oxide to 2-fluoro-2,2-dinitroethanol were employed in the above reaction.

An acid-catalyzed reaction was carried out as follows. To a solution 9.24 g (0.06 mol) of 2-fluoro-2,2-dinitroethanol and 4.0 g (0.068 mol) of propylene oxide in 50 ml of methylene chloride was added 3 drops of stannic chloride and the reaction mixture was allowed to stand at 25° for 18 hr. The solution was washed with 50 ml of water, dried, and distilled to give 1.5 g (12% yield) of 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ether, identified by its infrared spectrum.

*p*-Toluenesulfonate, bp 150–153° (25 μ) (molecular still), $n^{23}_{\mathrm{D}}$ 1.4975, was obtained quantitatively in the same manner as that of 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether (see above).

*Anal.* Calcd for $C_{12}H_{15}N_2FSO_8$: C, 39.4; H, 4.1; N, 7.6; F, 5.2. Found: C, 39.5; H, 4.1; N, 7.2; F, 5.3.

**2-Fluoro-2,2-dinitroethyl Glycidyl Ether.**—Epichlorohydrin, 3.7 g (0.04 mol), and 6.24 g (0.04 mol) of 2-fluoro-2,2-dinitroethanol was added at 0° to a stirred solution of 2.5 g of sodium hydroxide in 75 ml of water. After standing at 0–3° for 48 hr the reaction mixture was extracted with 30 ml of methylene chloride and the extract was distilled to give 2.6 g (31% yield) of 2-fluoro-2,2-dinitroethyl glycidyl ether, bp 70–71° (0.1 mm), $n^{23}_{\mathrm{D}}$ 1.4362.

*Anal.* Calcd for $C_5H_7N_2FO_6$: C, 28.6; H, 3.3; N, 13.3; F, 9.0. Found: C, 28.4; H, 3.2; N, 12.8; F, 8.8.

Proton nmr ($CCl_4$): δ 4.71 [d, $J_{HF}$ = 18 Hz, $OCH_2CF(NO_2)_2$], 4.1 and 3.5 (d, d, $OCH_2$), 3.11 (m, CH), and 3.7 and 3.5 (d, d, ring $CH_2$). Fluorine nmr: φ 111.9 (t, $J_{HF}$ = 18 Hz).

2-Fluoro-2,2-dinitroethyl glycidyl ether was obtained in 15% yield when epibromohydrin instead of epichlorohydrin was used in the above reaction.

**4-(2-Fluoro-2,2-dinitroethoxy)-3-hydroxybutene 1,2-Oxide.**—To a solution of 30.8 g (0.2 mol) of 2-fluoro-2,2-dinitroethanol and 8.6 g (0.1 mol) of butadiene dioxide in 150 ml of water at 0° was added a solution of 8.0 g (0.2 mol) of sodium hydroxide in 75 ml of water. After standing at 0° for 5 days, the product was extracted with 75 ml of methylene chloride and dried to give 19 g of viscous oil. A 1.5 g aliquot of the material was distilled at 120–125° (10 μ) (molecular still) to give 0.9 g of colorless oil.

*Anal.* Calcd for $C_6H_9FN_2O_7$: C, 30.0; H, 3.8; N, 11.7; F, 7.0. Found: C, 29.7; H, 3.8; N, 11.9; F, 7.4.

Proton nmr ($CDCl_3$): δ 4.70 [d, $J_{HF}$ = 18 Hz, $OCH_2CF(NO_2)_2$], 3.75 (m, $CH_2$ and CH), 2.71 (ABM pattern, ring protons), and 3.12 (s, OH; confirmed by $D_2O$ exchange).

**2-Fluoro-2,2-dinitroethoxyacetic Acid.**—2-Fluoro-2,2-dinitroethyl 2-hydroxyethyl ether, 3.1 g (0.02 mol), was added dropwise with stirring at 25° to 6.5 ml of 70% nitric acid and the solution was allowed to stand at 25° for 18 hr. The mixture was heated at 65–70° for 3 hr, evaporated to dryness at reduced pressure (3–5 mm), and a yellow solid was crystallized from methylene chloride to give 3.1 g (91% yield) of 2-fluoro-2,2-dinitroethoxyacetic acid, white crystalline solid, mp 69–70°.

*Anal.* Calcd for $C_4H_5N_2FO_7$: C, 22.6; H, 2.3; N, 13.2; F, 9.0. Found: C, 22.5; H, 2.1; N, 12.9; F, 8.9.

Proton nmr ($d_6$-acetone): δ 10.29 (s, $CO_2H$), 5.00 [d, $J_{HF}$ = 17.2 Hz, $OCH_2CF(NO_2)_2$], and 4.37 (s, $CH_3$).

2-Fluoro-2,2-dinitroethoxyacetic acid was also obtained in the oxidation of 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ether as follows. A solution of the ether, 4.3 g, in 20 ml of 70% nitric acid was allowed to stand at 25° for 18 hr and then was heated at 55–60° for 2 hr. The mixture was evaporated to dryness at reduced pressure, and the product was recrystallized from methylene chloride to give 1.5 g of the acid, 40% yield, mp 68–69°.

**2-Fluoro-2,2-dinitroethoxyacetyl Chloride.**—To a solution of 10.6 g (0.05 mol) of 2-fluoro-2,2-dinitroethoxyacetic acid and 8.0 g (0.067 mol) of thionyl chloride in 30 ml of ethylene chloride was added 2 drops of pyridine and the reaction mixture was warmed at 65–70° until the evolution of hydrogen chloride and sulfur dioxide ceased (30 min). The solution was distilled to give 11.6 g (quantitative yield) 2-fluoro-2,2-dinitroethoxyacetyl chloride, bp 67–68° (0.1 mm), $n^{23}_{\mathrm{D}}$ 1.4505.

*Anal.* Calcd for $C_4H_4N_2ClFO_6$: C, 20.8; H, 1.7; N, 12.2; F, 8.3. Found: C, 20.6; H, 2.1; N, 11.6; F, 8.5.

**2-Fluoro-2,2-dinitroethoxymethyl Isocyanate.**—To a stirred solution of 7.8 g (0.12 mol) of sodium azide in 50 ml of water and 150 ml of ethylene chloride at 15–16° was added dropwise over a period of 10 min 23 g (0.1 mol) of 2-fluoro-2,2-dinitroethoxyacetyl chloride. The reaction mixture was stirred at 10–12° for 35 min, phases separated, and the ethylene chloride solution was dried over anhydrous sodium sulfate and filtered. The filtrate was placed in a 250 ml round-bottomed flash equipped with a reflux condenser protected from the atmospheric moisture by a drying tube, and heated at 60–65° until the evolution of nitrogen ceased (45 min). The solution was distilled to give 20.7 g (100% yield) of 2-fluoro-2,2-dinitroethoxymethyl isocyanate, bp 55–56° (50 μ), $n^{23}_{\mathrm{D}}$ 1.4420.

*Anal.* Calcd for $C_4H_4N_3FO_6$: C, 23.0; H, 1.9; N, 20.1; F, 9.0. Found: C, 22.7; H, 1.9; N, 19.9; F, 8.7.

Proton nmr ($CDCl_3$): $\delta$ 4.93 (s, $CH_2NCO$) and 4.71 (d, $J_{HF}$ = 17.3 Hz, $CH_2$). Fluorine nmr: $\phi$ 110.3 (t, $J_{HF}$ = 16.5 Hz).

**2-Fluoro-2,2-dinitroethyl 2-Fluoro-2,2-dinitroethoxyacetate.**—To a stirred solution of 3.45 g (0.015 mol) of 2-fluoro-2,2-dinitroethoxymethyl chloride and 2.31 g (0.015 mol) of 2-fluoro-2,2-dinitroethanol in 15 ml of methylene chloride was added dropwise over a period of 5 min at 25–28° a solution of 1.2 g (0.015 mol) of pyridine in 15 ml of methylene chloride. After 20 min, the solution was washed with 70 ml of 3% sulfuric acid and distilled in a molecular still at 110–115° (25 $\mu$) to give 5.2 g (100 % yield) of a colorless liquid, $n^{23}\mathrm{D}$ 1.4485.

*Anal.* Calcd for $C_6H_6N_4F_2O_{11}$: C, 20.7; H, 1.7; N, 16.1; F, 10.9. Found: C, 20.5; H, 1.7; N, 15.9; F, 10.8.

Proton nmr ($CDCl_3$): $\delta$ 5.31 (d, 1, $J_{HF}$ = 16 = 16 Hz), 4.73 (d, 1, $J_{HF}$ = 17 Hz), and 4.40 (s, 1). Fluorine nmr: $\phi$ 110.1 (t, $J_{HF}$ = 15 Hz) and $\phi$ 111.1 (t, $J_{HF}$ = 17 Hz).

**2,2-Dinitropropyl 2-Fluoro-2,2-dinitroethoxyacetate.**—2,2-Dinitropropyl 2-fluoro-2,2-dinitroethoxyacetate, bp 138–143° (25 $\mu$) (molecular still), $n^{24}\mathrm{D}$ 1.4645, was obtained quantitatively in the reaction of 2,2-dinitropropanol and 2-fluoro-2,2-dinitroethoxyacetyl chloride following the above described procedure.

*Anal.* Calcd for $C_7H_9N_4FO_{11}$: C, 24.4; H, 2.6; N, 16.3; F, 5.5. Found: C, 24.4; H, 2.6; N, 15.8; F, 5.6.

Proton nmr ($CDCl_3$): $\delta$ 5.00 (s, $OCH_2CO$), 4.73 [d, $J_{HF}$ = 17.5 Hz, $OCH_2CF(NO_2)_2$], 4.33 [s, $OCH_2C(NO_2)_2$–], and 2.23 (s, $CH_3$). Fluorine nmr: $\phi$ 111.2 (t, $J_{HF}$ = 17.4 Hz).

**Bis(2-fluoro-2,2-dinitroethoxyacetate) of 2,2-Dinitropropanediol.**—Bis(2-fluoro-2,2-dinitroethoxyacetate) of 2,2-dinitropropanediol was obtained quantitatively in the reaction of 2,2-dinitropropanediol with 2 mol of 2-fluoro-2,2-dinitroethoxyacetyl chloride following the above procedure. The viscous oil, degassed at 100° (0.1 mm), was not further purified.

*Anal.* Calcd for $C_{11}H_{12}N_6F_2O_{18}$: C, 23.8; H, 2.2; N, 15.2; F, 6.9. Found: C, 23.6; H, 2.1; N, 14.7; F, 6.9.

Proton nmr ($CDCl_3$–$d_6$-acetone): 5.12 (s, 1, $COCH_2O$), 4.78 [d, 1, $J_{HF}$ = 17 Hz, $OCH_2CF(NO_2)_2$], and 4.38 (s, 1, $CH_2$). Fluorine nmr: $\phi$ 111.2 (t, $J_{HF}$ = 16.2 Hz).

**2-Fluoro-2,2-dinitroethyl 2-Fluoro-2,2-dinitroethoxymethylcarbamate.**—To a solution of 2.1 g (0.01 mol) of 2-fluoro-2,2-dinitroethoxymethyl isocyanate and 1.65 g (0.011 mol) of 2-fluoro-2,2-dinitroethanol in 20 ml of methylene chloride at 25° was added a catalytic amount of ferric acetylacetonate (FeAA). The reaction mixture was kept at 35° for 20 min and distilled in a molecular still at 155–160° (25 $\mu$) to give 3.5 g of viscous colorless oil, $n^{25}\mathrm{D}$ 1.4585.

*Anal.* Calcd for $C_6H_7N_5F_2O_{11}$: C, 19.8; H, 1.9; N, 19.3; F, 10.5. Found: C, 19.6; H, 1.8; N, 19.3; F, 10.2.

The infrared spectrum showed major absorption peaks at 2.90, 5.72, 6.25, 7.62, 8.10, 8.95, 11.79, 12.52, and 13.02 $\mu$.

Proton nmr ($CDCl_3$): $\delta$ 6.25 (t, $J$ = 7.5 Hz, NH), 5.30 (d, $J_{HF}$ = 16 Hz), 4.72 [d, $J_{HF}$ = 17.8 Hz, $OCH_2CF(NO_2)_2$], and 4.83, (d, $J$ = 7.5 Hz, $NCH_2$). Fluorine nmr: $\phi$ 110.5 (t, $J_{HF}$ = 15.6 Hz) and $\phi$ 111.0 (t, $J_{HF}$ = 17.4 Hz).

**Bis(2-fluoro-2,2-dinitroethoxymethylcarbamate) of 2,2-Dinitropropanediol.**—Bis(2-fluoro-2,2-dinitroethoxymethylcarbamate)of 2,2-dinitropropanediol was obtained quantitatively in the reaction of 2,2-dinitropropanediol with 2 mol of 2-fluoro-2,2-dinitroethoxymethyl isocyanate following the above procedure. The material, a viscous oil, was purified only by drying at 100° (0.1 mm).

*Anal.* Calcd for $C_{11}H_{14}N_8F_2O_{18}$: C, 22.6; H, 2.4; N, 19.2; F, 6.5. Found: C, 22.4; H, 2.3; N, 19.0; F, 6.4.

The infrared spectrum showed the following major absorption peaks 2.93, 5.76, 6.30, 7.68, 8.20, 9.35, 11.82, and 12.56 $\mu$.

Proton nmr ($d_6$-acetone): $\delta$ 7.90 (t, $J$ = 7.3 Hz, NH), 5.22 [s, $CH_2C(NO_2)_2CH_2$], 4.97 [d, $J_{HF}$ = 18 Hz, $OCH_2CF(N)_2)_2$], and 4.92 (d, $J_{NH-CH_2}$ = 7 Hz, $NCH_2$). Fluorine nmr: $\phi$ 110.8 (t, $J_{HF}$ = 17.7 Hz).

**N,N′-Bis(2-fluoro-2,2-dinitroethoxymethyl)urea.**—A suspension of 0.7 g of 2-fluoro-2,2-dinitroethoxymethyl isocyanate in 5 ml of water was stirred at 25–30° for 45 min. The product, a viscous oil, extracted with 10 ml of methylene chloride, was purified only by drying at 100° (0.1 mm), wt 0.6 g, $n^{23}\mathrm{D}$ 1.4703.

*Anal.* Calcd for $C_7H_{10}N_6F_2O_{11}$: C, 21.4; H, 2.6; N, 21.4; F, 9.8. Found: C, 21.1; H, 2.4; N, 20.6; F, 9.9.

**2-(2-Fluoro-2,2-dinitroethoxy)ethyl Nitrate.**—A solution of 4.0 g of 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether in 10 ml of 70% nitric acid was allowed to stand at 25° for 16 hr. The product was added to 50 ml of ice water and extracted with 30 ml of methylene chloride to give 2.5 g of semisolid. The material was treated with 50 ml of 10% aqueous sodium bicarbonate and extracted with 10 ml of methylene chloride to give 0.5 g of a colorless liquid. [The amount of the material was too small to determine the boiling point, estimated bp 85–90° (0.1 mm)].

*Anal.* Calcd for $C_4H_6N_3FO_8$: C, 19.8; H, 2.5; N, 17.3; F, 7.8. Found: C, 19.8; H, 2.6; N, 16.8; F, 7.8.

Proton nmr ($CDCl_3$): $\delta$ 4.67 [d, $J_{HF}$ = 18 Hz, $OCH_2CF(NO_2)_2$] and 3.9–4.6 (AA′BB′ pattern, $CH_2$).

**2-Fluoro-2,2-dinitroethoxyacetone.**—Sulfuric–chromic acid solution was prepared by adding 8.7 ml of concentrated sulfuric acid to a solution of 10.0 g of chromium trioxide in 19 ml of water following the procedure of Eisenbraun.[19] The chromic acid solution was added dropwise, over a period of 1 hr, at 25–28° to a stirred solution of 15.9 g (0.075 mol) of 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ether in 190 ml of acetone until the color of $Cr^{6+}$ persisted (only *ca* 2/3 of the chromic acid solution was required). The reaction mixture was stirred at 25° for 1.5 hr and the excess $Cr^{6+}$ was destroyed with few drops of 2-propanol. The mixture was filtered and the filter cake was washed with two 35-ml portions of acetone. The combined filtrate and washings were stirred with 10 g of sodium bicarbonate for 25 min, filtered, and concentrated to *ca.* 40 ml. Extraction with 45 ml of methylene chloride and distillation gave 14.5 g (92% yield) of 2-fluoro-2,2-dinitroethoxyacetone, bp 70° (0.05 mm), $n^{23}\mathrm{D}$ 1.4335.

*Anal.* Calcd for $C_5H_7N_2FO_6$: C, 28.6; H, 3.3; N, 13.3; F, 9.0. Found: C, 28.4; H, 3.4; N, 13.2; F, 9.1.

Proton nmr ($CCl_4$): $\delta$ 2.12 (s, $CH_3$), 4.35 (s, $CH_2CO$), and 4.74 [d, $J_{HF}$ = 17.4 Hz, $OCH_2CF(NO_2)_2$]. Fluorine nmr: $\phi$ 109.3 (t, $J_{HF}$ = 17.3 Hz).

**2-Fluoro-2,2-dinitroethoxyacetone Oxime.**—A mixture of 2.3 g (0.033 mol) of hydroxylamine hydrochloride, 2.1 g (0.01 mol) of 2-fluoro-2,2-dinitroethoxyacetone, and 4.53 g (0.033 mol) of sodium acetate trihydrate in 85 ml of absolute ethanol was refluxed for 45 min, and then *ca.* 70 ml of ethanol was removed at 25° (25 mm). The residue was added to 100 ml of ice water and the product was extracted with 40 ml of methylene chloride and dried at 100° (0.1 mm) to give 2.15 g (95.5% yield) of colorless liquid which was not further purified.

*Anal.* Calcd for $C_5H_8N_3FO_6$: C, 26.7; H, 3.6; N, 18.7; F, 8.4. Found: C, 26.5; H, 3.4; N, 18.5; F, 8.3.

Proton nmr ($CCl_4$): $\delta$ 4.52 [d, $J_{HF}$ = 17.0 Hz, $OCH_2CF(NO_2)_2$], 4.20 (s, $CH_2$), 1.91 (s, $CH_3$), and $\delta$ 9.75 (s, NOH). Fluorine nmr: $\phi$ 108.7 (t, $J_{HF}$ = 17.0 Hz).

**2,2-Dinitropropyl 2-Fluoro-2,2-dinitroethyl Ether.**—To a stirred solution of 0.9 g of 2-fluoro-2,2-dinitroethoxyacetone oxime in 25 ml of methylene chloride was added dropwise over a period of 10 min at 0–3° with cooling 5 ml of 100% nitric acid. The deep blue solution was stirred for 45 min and then to it was added dropwise (5 min) 4 ml of 32% hydrogen peroxide. After 15 min, the pale yellow solution was washed with two 25-ml portions of ice water. The methylene chloride solution was distilled in a molecular still at 75° (10 $\mu$) to give 0.45 of colorless liquid. The proton nmr spectrum showed that the distillate was contaminated with 2-fluoro-2,2-dinitroethoxyacetone (13%), which could not be removed by fractionation. An analytical sample of the ether was obtained by washing the mixture with carbon tetrachloride, where the ketone is much more soluble than the ether.

*Anal.* Calcd for $C_5H_7N_4FO_9$: C, 21.0; H, 2.4; N, 19.6; F, 6.6. Found: C, 21.0; H, 2.4; N, 18.6; F, 6.6.

Proton nmr ($d_6$-acetone–$CDCl_3$): $\delta$ 4.95 [d, $J_{HF}$ = 16.8 Hz, $OCH_2CF(NO_2)_2$], 4.65 (s, $CH_2$) and 2.20 (s, $CH_3$). Fluorine nmr: $\phi$ 109.2 (t, $J_{HF}$ = 17.1 Hz).

**Bis(2-fluoro-2,2-dinitroethyl) Sulfite.**[18]—A solution of 3.6 g (0.03 mol) of thionyl chloride in 20 ml of methylene chloride was added at 25–28° to a stirred solution of 9.26 g (0.06 mol) of 2-fluoro-2,2-dinitroethanol and 5.0 g (0.063 mol) of pyridine in 50 ml of methylene chloride. After standing at 25° for 16 hr, the product was washed with 100 ml of cold 2% sulfuric acid and distilled to give 6.8 g (70% yield) of bis(2-fluoro-2,2-dinitroethyl) sulfite, bp 100–105° (25 $\mu$) (moleclar still), $n^{23}\mathrm{D}$ 1.4607.

*Anal.* Calcd for $C_4H_4N_4F_2SO_{11}$: C, 13.6; H, 1.1; N, 15.8; F, 10.7. Found: C, 13.4; H, 1.0; N, 15.2; F, 10.6.

Proton nmr ($CDCl_3$): a pair of very closely spaced doublets centered at 307 Hz. Fluorine nmr: $\phi$ 110.0 (t, $J_{HF}$ = 16.2 Hz).

Fractionation of methylene chloride removed in the purification of the sulfite gave 0.5 g of 2-fluoro-2,2-dinitroethyl chloride, identified by comparing its infrared spectrum with that of an authentic sample (see below).

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[19] E. J. Eisenbraun, *Org. Syn.*, **45**, 28 (1965).

**2-Fluoro-2,2-dinitroethyl Chloride.**—To a stirred solution of 6.24 g (0.04 mol) of 2-fluoro-2,2-dinitroethanol and 3.95 g (0.04 mol) of pyridine in 50 ml of methylene chloride was added dropwise at 0–5° with cooling 2.7 g (0.02 mol) of sulfuryl chloride. No visible reaction. After 45 min, the reaction mixture was warmed to 25° and was allowed to stand for 7 days. The solution was washed with 200 ml of ice-cold 1% sulfuric acid and distilled to give 3.4 g of 2-fluoro-2,2-dinitroethyl chloride, bp 22–23° (0.2 mm), $n^{23}\text{D}$ 1.4270.

*Anal.* Calcd for $C_2H_2N_2ClFO_4$: C, 13.9; H, 1.2; N, 16.2; F, 11.0. Found: C, 13.8; H, 1.0; N, 15.4; F, 11.1.

*Differential thermal analysis showed an endotherm at 156°, the boiling point of the compound.*

Proton nmr ($CCl_4$): $\delta$ 4.60 (d, $J_{HF}$ = 16.1 Hz). Fluorine nmr: $\phi$ 108.2 (s, broad).

**Tris(2-fluoro-2,2-dinitroethyl) Borate.**—A mixture of 10.8 g (0.07 mol) of 2-fluoro-2,2-dinitroethanol and 2.92 g (0.02 mol) of triethyl borate was heated in a distillation apparatus protected from the atmospheric moisture at 95° for 3 hr, and then ethanol was distilled at reduced pressure. The remaining solid was recrystallized from methylene chloride to give 8.9 g of white crystalline solid which hydrolyzed slowly when exposed to the moist air.

*Anal.* Calcd for $C_6H_6N_6BF_3O_{15}$: C, 15.3; H, 1.3; N, 17.9; F, 12.1. Found: C, 15.0; H, 1.3; N, 16.9; F, 11.7.

Proton nmr ($CH_3CN$): $\delta$ 4.96 (d, $J_{HF}$ = 16.5 Hz). Fluorine nmr: $\phi$ 111.9 (t, $J_{HF}$ = 16.2 Hz).

**2-Fluoro-2,2-dinitroethyl Nitrate.**—To a stirred mixture of 12 ml of 100% nitric acid and 12 ml of concentrated sulfuric acid was added dropwise (5 min) at 0–5° 7.7 g of 2-fluoro-2,2-dinitroethanol. The reaction mixture was stirred for 15 min, added to 100 g of crushed ice, a water-insoluble liquid separated, and washed with 50 m of water, wt 7.5 g (75% yield), bp 62–63° (5 mm), $n^{23}\text{D}$ 1.4377 [lit.[4] bp 62–62.5° (5–6 mm), $n^{20}\text{D}$ 1.4372].

**Registry No.**—2-Fluoro-2,2-dinitroethanol, 17003-75-7; allyl 2-fluoro-2,2-dinitroethyl ether, 25171-99-7; 2,2-dinitropropyl methyl ether, 5917-65-7; 2,2-dinitropropyl methyl sulfate, 25172-01-4; 1,3-dimethoxy-2,2-dinitropropane, 25172-02-5; methyl 3-methoxy-2,2-dinitropropyl sulfate, 25172-03-6; 2-fluoro-2,2-dinitroethyl ethyl carbonate, 25172-14-9; 2-fluoro-2,2-dinitroethyl oxalyl chloride, 25172-15-0; 2-fluoro-2,2-dinitroethyl iminodicarboxylate, 25172-16-1; 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether, 25172-17-2; 2-fluoro-2,2-dinitroethanol *p*-toluenesulfonate, 25172-18-3; 2-fluoro-2,2-dinitroethyl 2-hydroxypropyl ether, 25172-19-4; 2-fluoro-2,2-dinitroethyl 2-hydroxyethyl ether *p*-toluenesulfonate, 25172-20-7; 2-fluoro-2,2-dinitroethyl glycidyl ether, 25184-14-9; 4-(2-fluoro-2,2-dinitroethoxy)-3-hydroxybutene 1,2-oxide, 25172-21-8; 2-fluoro-2,2-dinitroethoxyacetic acid, 25172-22-9; 2-fluoro-2,2-dinitroethoxyacetyl chloride, 25172-23-0; 2-fluoro-2,2-dinitroethyoxymethylisocyanate, 25172-24-1; 2-fluoro-2,2-dinitroethyl 2-fluoro-2,2-dinitroethoxyacetate, 25172-25-2; 2,2-dinitropropyl 2-fluoro-2,2-dinitroethoxyacetate, 25172-26-3; bis(2-fluoro-2,2-dinitroethoxyacetate), 25172-27-4; 2-fluoro-2,2-dinitroethyl 2-fluoro-2,2-dinitroethoxymethylcarbamate, 25172-28-5; bis(2-fluoro-2,2-dinitroethoxymethylcarbamate), 25172-29-6; N,N′-bis(2-fluoro-2,2-dinitroethoxymethyl)urea, 25172-30-9, 2-(2-fluoro-2,2-dinitroethoxy)ethyl nitrate, 25172-31-0; 2-fluoro-2,2-dinitroethoxyacetone, 25172-32-1; 2-fluoro-2,2-dinitroethoxyacetone oxime, 25172-33-2; 2,2-dinitropropyl 2-fluoro-2,2-dinitroethyl ether, 25172-34-3; bis(2-fluoro-2,2-dinitroethyl) sulfite, 24590-46-3; 2-fluoro-2,2-dinitroethyl chloride, 25172-36-5; tris(2-fluoro-2,2-dinitroethyl) borate, 25172-37-6.

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# Disproportionation of 3,3-Difluorotetrachloropropene. Application of the Hard and Soft Acids and Bases Principle to Organic Halogen Compounds[1]

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Product distributions from the reaction of 3,3-difluorotetrachloropropene (**1a**) at 50° with aluminum chloride and bromide, titanium tetrachloride, and antimony pentachloride were determined. The aluminum and titanium halides were converted to the fluorides by the reaction; the aluminum fluoride so formed was shown to catalyze the disproportionation of **1a**. 1-Bromo-1,2-dichloro-3,3,3-trifluoropropene (**8**) was formed in the reaction with aluminum bromide and was also independently synthesized. Formation of **8** is rationalized in terms of the hard and soft acids and bases (HSAB) concept; numerous examples from the literature are similarly interpreted. The reactions of $AlCl_3$ with 3-fluoropentachloropropene, 3,3,3-trifluorotrichloropropene, and 1,1-difluorotetrachloroethane were also investigated.

The disproportionation of polyhalogenated aliphatic fluorides has long been recognized, and is of commercial significance, particularly in the case of the fluorochloromethanes, as demonstrated by the profusion of patents in this area. It is also well known that aluminum chloride, a catalyst frequently employed in the disproportionation of fluorochloro compounds, is unsuitable for use in Friedel–Crafts alkylations involving aliphatic fluorides, because of its tendency to abstract organically bound fluorine. Information in the literature which contributes to the general understanding of these processes is meager, however, and little, if any, attempt has been made in the past to determine the extent to which the two occur simultaneously.

The question of the relative effectiveness of various Lewis acids in these two reactions also exists. In the disproportionation of 3,3-difluorotetrachloropropene (**1a**), it is reported that catalytic activity decreases in the sequence[3] antimony pentachloride > titanium tetrachloride > aluminum bromide, aluminum chloride > ferric chloride. The order of activity was determined by the length of time required to produce a

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[1] Taken in part from the Ph.D. Thesis of G. C. B., The University of Iowa, Iowa City, Iowa, 1970.

[2] Shell Foundation Fellow, 1965–1966.

[3] M. Prober, *J. Amer. Chem. Soc.*, **76**, 4189 (1954).