furic acid. This was extracted with methylene chloride, the extract was dried and freed from solvent, and the residue was washed twice with water and dried over magnesium sulfate. Distillation of the oil afforded 25 g of XIV (55.3%), bp 44–45° (15 mm).

Anal. Calcd for $C_3H_2F_4N_2O_5$: N, 12.62; F, 34.22. Found: N, 12.34; F, 33.84.

Fluorodinitromethyl Azide (XV).—To a solution of 85 g of fluorotrinitromethane in 175 ml of dimethylformamide was added, at −15 to −20° and over a period of 10–15 min, 40 g of sodium azide. The mixture was stirred 2 hr at −15 to −20° (*Caution! at higher temperatures the reaction may get out of hand*) and then poured into ice–water (strong gassing). The product was extracted into methylene chloride, the solvent was removed at a temperature below 65°, and the residue was washed with water, dried, and fractionated at 40 mm of pressure. At *ca.* 40°, 31.5 g of crude XV containing *ca.* 10% starting material distilled over (yield *ca.* 34%). Refractionation at 60 mm (bp 45°) gave a material which appeared to be pure by glpc (silicon oil on Teflon column), but which exhibited a weak band in the 1700-cm^{-1} region of the infrared spectrum which suggested the presence of an impurity. The spectrum also showed a strong azide band at 2200 cm^{-1} in addition to the usual nitro bands at 1325 and 1610 cm^{-1}.

Fluorodinitromethyl azide decomposes slowly at room temperature and should be handled with care. Further characterization and reactions of this material will be described in a subsequent paper.

Difluorodinitromethane (XVI).—A 500-ml, four-necked flask was fitted with a stirrer, thermometer, and a vented addition funnel whose stem extended almost to the bottom of the vessel. The fourth neck was connected to a cold trap held at −70° during the experiment. The system was purged with a slow stream of dry nitrogen through the vent of the addition funnel, the flask was charged with 35 g of anhydrous potassium fluoride and 250 ml of sulfolane, and the mixture was heated to 150° for 15 min and allowed to cool to 95°. At this temperature, 50.7 g of fluorotrinitromethane was added over a period of 1.5 hr; the mixture was stirred an additional 0.5 hr at 100° and allowed to cool. The trap contents were dried over magnesium sulfate and were shown by glpc and by comparison of the infrared spectrum with that of a sample prepared by the method of Mitsch[27] to be essentially pure XVI, yield 25 g (58.7%).

2-Fluoro-2,2-dinitroethanol (VII) by FTM Reduction.—Methanol (90 ml) and 42 ml of 30% aqueous hydrogen peroxide were mixed at 0° in a 500-ml, three-neck flask fitted with stirrer, thermometer, and vented addition funnel. A solution of 14.5 g of sodium hydroxide in 70 ml of water was prepared and 1 ml of this was added at −5 to −10°. At the same temperature, 30 ml of 36–37% aqueous formaldehyde solution was added gradually (exotherm) followed by 50 g of fluorotrinitromethane. With the temperature kept at −5 to −10°, the remainder of the sodium hydroxide solution was added over a 30-min period; the yellow solution was then stirred an additional 15 min while the temperature was allowed to rise to 0°.

Dilute sulfuric acid (equivalent to 5 ml of concentrated H_2SO_4) was added dropwise to the reaction mixture with the temperature maintained at 0° until, toward the end of the addition, a strong exotherm raised it to 10–15°. After saturation of the reaction mixture with sodium chloride, it was extracted with one 100-ml and two 50-ml portions of methylene chloride and the extracts were dried and freed from solvent. Vacuum fractionation of the residual oil gave 41.3 g VII (90.6%) of excellent purity (glpc), bp 55° (0.5 mm).

Anal. Calcd for $C_2H_3FN_2O_5$: N, 18.20; F, 12.33. Found: N, 18.51; F, 12.01.

Fluorodinitromethane (X) by FTM Reduction.—To a solution of 5 g of fluorotrinitromethane in 10 ml of methanol was added dropwise at −10° a mixture of 6.7 g of 30% hydrogen peroxide and 3.3 g of potassium hydroxide in 15 ml of methanol. A thick yellow precipitate formed (efficient stirrer necessary). The mixture was poured into ice-cold dilute sulfuric acid, the resulting clear solution extracted with methylene chloride, the extracts dried, and the solvent distilled off through a Vigreaux column. The residue on fractionation gave 1.5 g (41%) of crude X. The product was identical with, although less pure than, the material obtained as a by-product in the aqueous fluorination of potassium ethyl dinitroacetate.

Registry No.—I, 17003-70-2; II, 17003-71-3; III, 13214-58-9; IV, 17003-25-7; V, 15895-14-4; VI, 15895-15-5; VII, 17003-75-7; VIII, 17003-76-8; IX, 17003-77-9; X, 7182-87-8; XI, 17003-79-1; XII, 17003-80-4; XIII, 17021-83-9; XIV, 17003-81-5; XV, 17003-82-6; XVI, 1185-11-1; $FC(NO_2)_3$, 1840-42-2.

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Aqueous Fluorination of Nitronate Salts[1]

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The fluorination of aqueous solutions of nitronate salts gave *gem*-fluoronitro compounds. The following compounds were synthesized by this reaction: fluorotrinitromethane, 1-fluoro-1,1-dinitroethane, 1-fluoro-1,1-dinitropropane, 2-fluoro-2,2-dinitroethanol, 1-fluoro-1-nitroethane, and 1-fluoro-1-nitropropane.

Although many examples of the direct chlorination and bromination of nitronate salts to give α-halonitro compounds are known,[2] only indirect methods have been reported for fluorination. Perchloryl fluoride has been used to convert *gem*-nitronitronate salts[3] and simple secondary nitronate salts[4] into the corresponding fluorine derivatives, but attempts to apply this reaction to simple primary nitronate salts were unsuccessful. Perfluoropiperidine has also been used as a fluorinating agent to prepare 2-fluoro-2-nitropropane.[5]

The present investigation concerns the preparation of fluoronitro compounds by the direct fluorination of aqueous solutions of nitronate salts, under conditions similar to those generally used for chlorination and bromination of nitronate salts. Although the fluorination of sodium hydroxide in aqueous solution is the standard

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method of preparing oxygen difluoride,[6] this technique has only recently been shown to be applicable to organic substituents with the fluorination of urea,[7] and, subsequently, other nitrogenous compounds such as alkyl carbamates,[8] sulfamides,[9] and cyanamide.[10]

The fluorinations were conducted simply by bubbling fluorine diluted with nitrogen into aqueous solutions of the nitronate salts. Salts of terminal *gem*-dinitro compounds and of nitroform gave high yields of the corresponding fluoronitro compounds. Thus, the sodium salt of nitroform gave a 92.3% yield of fluorotrinitromethane, bp 81–82°. Similarly, the salts of 1,1-dinitroethane and 1,1-dinitropropane gave 1-fluoro-1,1-dinitroethane and 1-fluoro-1,1-dinitropropane in yields of 82 and 70%, respectively. The fluorination of the salt of 2,2-dinitroethanol[11] gave 2-fluoro-2,2-dinitroethanol in 84% yield. The same yield was obtained when this salt was prepared *in situ* by the addition of sodium hydroxide to a solution of 2,2-dinitro-1,3-propanediol; the liberated formaldehyde did not interfere with the fluorination. 1-Fluoro-1,1-dinitroethane, 1-fluoro-1,1-dinitropropane, and 2-fluoro-2,2-dinitroethanol were prepared previously using perchloryl fluoride as the fluorinating agent.[3]

$$HOCH_2C(NO_2)_2CH_2OH \xrightarrow{OH^-} HOCH_2C(NO_2)_2^- + CH_2O$$

$$\downarrow F_2$$

$$HOCH_2C(NO_2)_2F$$

The aqueous fluorination technique was less satisfactory as a preparative method when salts of simple mononitroalkanes were used as starting materials. The sodium salts of nitroethane and 1-nitropropane gave 1-fluoro-1-nitroethane and 1-fluoro-1-nitropropane in yields of 5.5 and 14%, respectively. The products were contaminated by large amounts of the unsubstituted nitroalkanes and were isolated by gas chromatography. The yields were much more sensitive to reaction conditions than those for the fluorination of *gem*-nitronitronate salts. For example, when the rate at which fluorine was introduced into a solution of the sodium salt of 1-nitropropane was increased threefold, only 1-nitropropane was isolated, although the fluorine was still consumed smoothly. The yields can, no doubt be improved if the reaction parameters are varied systematically. Simple 1-fluoro-1-nitroalkanes have not been reported previously.

The acid-forming side reaction that results in low yields of fluorinated mononitro compounds appears to be the fluorination of hydroxide ion; the pK_a values of mononitro compounds exceed those of the corresponding terminal *gem*-dinitro compound by about 3 units.[2]

The nmr spectral data for the fluoronitro compounds are shown in Table I. The ^{19}F septet observed for fluorotrinitromethane indicates coupling to three nitrogens. The fact that the nitrogen quadruple effect does not obscure the coupling indicates that the electric fields surrounding the nitrogen nucleus are highly symmetrical.[12] Coupling to nitrogen is also evident in the ^{19}F spectra of 1-fluoro-1,1-dinitroethane and 1-fluoro-1,1-dinitropropane, but not in that of 2-fluoro-2,2-dinitroethanol. The hydroxyl of the latter thus distorts the field around the nitrogens enough to prevent observable coupling.

TABLE I
NMR DATA[a]

Compd	Proton	Fluorine
$FC(NO_2)_3$	...	φ 86.3 septet
		J_{F-N} = 9.8 cps
$FC(NO_2)_2CH_3$	δ 2.47 d	φ 97.6 m
	J_{HF} = 17.7 cps	(>7 lines)
$FC(NO_2)_2CH_2CH_3$	δ 1.17 t (CH_3)	φ 106.3 m
	J_{HH} = 7.3 cps	(>9 lines)
	δ 2.83 d, q (CH_2)	
	J_{HH} = 7.3 cps	
	J_{HF} = 19.7 cps	
$FC(NO_2)_2CH_2OH$	δ 3.97 t (OH)	φ 111.3 t
	J_{HH} = 7.0 cps	J_{HF} = 15 cps
	δ 5.80 d, d (CH_2)	
	J_{HH} = 7.0 cps	
	J_{HF} = 15.9 cps	
$FCH(NO_2)CH_3$	δ 1.88 d, d (CH_3)	φ 144.2 d, q
	J_{HF} = 21 cps	$J_{HF_{gem}}$ = 51 cps
	J_{HH} = 6.3 cps	$J_{HF_{vic}}$ = 21 cps
	δ 5.84 d,q (C—H)	
	J_{HF} = 51 cps	
	J_{HH} = 6.3 cps	
$FCH(NO_2)CH_2CH_3$	δ 5.75 d,t (CH)	φ 149.3 d, t
	J_{HF} = 51 cps,	$J_{HF_{gem}}$ = 54 cps
	J_{HH} = 5 cps	$J_{HF_{vic}}$ = 23 cps
	δ 2.20 d,d,q (CH_2)	
	J_{HF} = 22 cps	
	δ 1.09 t (CH_3)	
	J_{HH} = 7.5 cps	

[a] Abbreviations used are d = doublet, t = triplet, q = quartet, m = symmetrical multiplet.

Infrared spectra are described in the Experimental Section.

Experimental Section

General.—Fluorinations were conducted in a glass, standard taper, three-necked flask fitted with a mechanical stirrer, a glass tube extending below the liquid level used as a gas inlet, and a standard taper thermometer well with an opening for gas exit. Standard fluorine-handling hardware[13] was used and the fluorine was diluted threefold with nitrogen. Exit gases were vented through an aqueous potassium iodide trap. Safety shielding is strongly recommended because of the potentially explosive nature of the products. Particular care should be exercised in handling 2-fluoro-2,2-dinitroethanol to prevent contact with the skin; painful inflamation can result.

Fluorotrinitromethane.—A solution prepared from 78.5 g (0.50 mol) of nitroform and 20.0 g (0.50 mol) of sodium hydroxide in 700 ml of water was fluorinated at 0–5°; 0.50 mol of fluorine was absorbed over a 1.5-hr period. The mixture was saturated with sodium chloride. The lower layer was separated, dried over sodium sulfate, and distilled to give 78 g (92.3% yield) of colorless liquid: bp 81–82°; $n^{25}D$ 1.3930.

Anal. Calcd for CFN_3O_6: C, 7.1; H, 0.0; F, 11.2, N, 24.9. Found: C, 7.0; H, 0.1; F, 11.0, N, 24.6.

The infrared spectrum consisted of the following peaks (μ): 3.36(w), 3.45(w), 3.78(w), 3.88(w), 6.19(vs), 7.38(w), 7.72(vs), 8.20(w), 9.90(w), 11.20(w), 12.55(vs).

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1-Fluoro-1,1-dinitroethane.—A solution of 20.0 g (0.50 mol) of sodium hydroxide and 60.0 g (0.50 mol) of 1,1-dinitroethane in 300 ml of water was fluorinated at 0–5° with 0.5 mol of fluorine over a 2-hr period. The product was extracted with two 75-ml portions of methylene chloride and the solution was dried over sodium sulfate and distilled to give 57 g (82% yield) of colorless liquid: bp 42–43° (30 mm); $n^{25}D$ 1.3960.

Anal. Calcd for $C_2H_3FN_2O_4$: C, 17.4; H, 2.2; F, 13.8, N, 20.3. Found: C, 17.2, H, 2.1; F, 13.5; N, 20.1.

The infrared spectrum consisted of the following peaks (μ): 3.3(w), 3.4(w), 3.45(w), 6.25(vs), 6.98(m), 7.2(s), 7.37(w), 7.55(s), 7.83(s), 8.60(s), 8.90(s), 10.35(w), 11.4(w), 11.75(s), 13.05(s).

1-Fluoro-1,1-dinitropropane.—A solution of 13.6 g (0.10 mol) of 1,1-dinitropropane and 4.0 g (0.10 mol) of sodium hydroxide in 300 ml of water was fluorinated at 0–5°, using 0.1 mol of fluorine in 45 min. The product was extracted with three 30-ml portions of methylene chloride, dried, and distilled to give 9.5 g (70% conversion) of colorless liquid: bp 43–44° (25 mm); $n^{25}D$ 1.4050.

Anal. Calcd for $C_3H_5FN_2O_4$: C, 23.7; H, 3.3; F, 12.5; N, 18.4. Found: C, 23.6; H, 3.3; F, 12.1; N, 17.8.

Unreacted 1,1-dinitropropane, 1.4 g, was recovered from the distillation residue.

The infrared spectrum showed the following bands (μ): 3.3(w), 3.37(w), 3.44(w), 6.26(vs), 6.82(w), 6.98(w), 7.17(w), 7.30(w), 7.53(m), 7.64(m), 8.00(w), 8.73(w), 9.18(m), 9.75(m), 10.21(w), 11.82(s), 12.39(s), 12.90(m).

2-Fluoro-2,2-dinitroethanol.—A solution of 20 g (0.5 mol) of sodium hydroxide in 100 ml of water was added dropwise at 0–5° to a solution of 83 g (0.5 mol) of 2,2-dinitro-1,3-propanediol in 400 ml of water. The solution was fluorinated at 0–5° with 0.5 mol of fluorine over a 2.5-hr period. The solution was then saturated with sodium chloride and was extracted with four 100-ml portions of methylene chloride. The methylene chloride solution was dried over sodium sulfate and distilled to give 65 g (84% yield) of colorless liquid: bp 38–39° (0.1 mm); $n^{25}D$ 1.4430.

Anal. Calcd for $C_2H_3FN_2O_5$: C, 15.6; H, 1.9; F, 13.0; N, 18.2. Found: C, 15.5; H, 2.0, F, 13.0, N, 18.1.

The infrared spectrum showed the following peaks (μ): 2.8 (s); 2.9(s), 3.4(w), 3.43(w), 6.25(vs), 6.93(m), 7.4(w), 7.6(s), 7.95(w), 8.2(w), 9.3(vs), 10.0(m), 10.95(w), 11.45(w), 11.79(s), 12.55(vs), 13.20(w).

1-Fluoro-1-nitroethane.—Nitroethane (41.2 g, 0.55 mol) was dissolved in a solution of 22 g (0.55 mol) of sodium hydroxide in 70 ml of water. The solution was diluted to 650 ml and was reacted with 0.55 mol of fluorine over a 5-hr period at 0–5°. The product was extracted with three 50-ml portions of methylene chloride, dried, and distilled to give 14 g of colorless liquid, bp 22–23° (25 mm). Analysis by gas chromatography (4 ft × 3/16 in. column of 5% diethylene glycol adipate on Chromosorb P, 60°, He flow 50 cc/min) showed the distillate was an 80:20 mixture of nitroethane and 1-fluoro-1-nitroethane (5.5% yield). An analytical sample was isolated by gas chromatography.

Anal. Calcd for $C_2H_4FNO_2$: C, 25.8; H, 4.3; N, 15.0, F, 20.4. Found: C, 25.4; H, 4.4; N, 14.5; F, 20.0.

The infrared spectrum showed the following bands (μ): 3.40(w), 6.34(vs), 6.91(m), 7.18(m), 7.32(m), 7.42(m), 7.63(w), 8.63(s), 8.82(m), 9.47(m), 10.94(w), 11.60(w).

1-Fluoro-1-nitropropane.—The above procedure starting with 49 g (0.55 mol) of 1-nitropropane gave 32 g of distillate, bp 33–35° (25 mm), which was found by gas chromatography to consist of 75% 1-nitropropane and 24% of 1-fluoro-1-nitropropane (14% yield).

Anal. Calcd for $C_3H_6FNO_2$: C, 33.6; H, 5.6; N, 13.1; F, 17.7. Found: C, 33.2; H, 5.8; N, 12.7; F, 17.4.

Registry No.—Fluorotrinitromethane, 1840-42-2; 1-fluoro-1,1-dinitroethane, 13214-58-9; 1-fluoro-1,1-dinitropropane, 17003-25-7; 2-fluoro-2,2-dinitroethanol, 17003-75-7; 1-fluoro-1-nitroethane, 17003-27-9; 1-fluoro-1-nitropropane, 17003-28-0.

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Reactions of Phosphorus Compounds. XVII. Reactions of Cyclopropylmethyl and Certain C_4-Triphenylphosphonium Salts

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Certain reactions of cyclopropylmethyltriphenylphosphonium bromide were examined. No products derived from ring opening were found. It was shown that no equilibration exists between the ylide **4** and an acyclic isomer, **5**. No cyclopropane derivatives were detected in the reactions of crotyl- or 3-butenyltriphenylphosphonium halides under basic conditions. No products attributable to ring opening were observed in the reactions of cyclobutyltriphenylphosphonium bromide. Preparations are described for *o*-hydroxybenzylidenecyclobutane, benzylidenecyclobutane, and 1-cyclopropyl-2-phenylethylene. Also prepared were cyclobutyl-, 3-butenyl-, crotyl-, and cyclopropylmethyldiphenylphosphine oxides. The lithium aluminum hydride reduction of cyclopropylmethyltriphenylphosphonium bromide (**3**) gave triphenylphosphine.

It has been shown[2-4] that the cyclopropylcarbinyl anion (**1**) may exist in reversible equilibrium with the acyclic carbanion **2**. The stability of the acyclic isomer compared with that of the cyclic form is profoundly affected both by the nature of the cation (M^+) and by the polarity of the solvent.[5,6]

1 **2**

In view of Maercker's recent communication[7] we wish to report our work involving cyclopropylmethyltriphenylphosphonium bromide (**3**) and certain other C_4-triphenylphosphonium halides.

The reactions of salt **3** were examined with the thought that the equilibration of the ylide **4** with **5** followed by proton migration to the crotyl ylide **6a–b** was a distinct possibility (Scheme I). Reaction of **4** with benzaldehyde in dimethylformamide (DMF) gave only *cis–trans* mixtures of 1-cyclopropyl-2-phenylethylene (**7a**). Even under conditions expected[4,6] to favor ring opening to the acyclic ylide **5**, the reaction of **4** with benzaldehyde (eq 1)

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