

FLUORINE-CONTAINING NITROGEN COMPOUNDS—VI

SULFUR TETRAFLUORIDE FLUORINATION OF ALIPHATIC NITRO ACIDS*

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Abstract—Sulfur tetrafluoride converts aliphatic nitro acids to the corresponding trifluoromethyl compounds. The yield is poor with primary nitro acids; but high yields of fluoronitrocarbons, otherwise difficult to obtain, are produced from certain γ -substituted butyric acids and from substituted acrylic acids. Eleven new fluoronitrocarbons are described.

OF THE wide variety of fluorinating agents used for synthesizing fluorocarbons, remarkably few have been employed successfully for preparing aliphatic fluorocarbons that contain nitro groups. Perchloryl fluoride and elemental fluorine are the only agents extensively studied.¹ Fluorination with chlorine trifluoride, antimony trifluoride, and sodium fluoride has been mentioned in the literature.¹ The discovery several years ago that sulfur tetrafluoride selectively replaces oxygenated functional groups^{2,3} provides another attractive reagent for preparing aliphatic fluoronitrocarbons. Sulfur tetrafluoride was employed recently to convert aliphatic polynitro alcohols to the corresponding polynitrofluoroalkanes,⁴ but its use in fluorinating aliphatic nitro carbonyl compounds has not been previously reported:



In the present investigation, four classes of aliphatic nitro acids, (primary nitro acids, β -substituted butyric acids, γ -substituted butyric acids, and substituted acrylic acids) were treated with sulfur tetrafluoride. The yield of nitro trifluoromethyl product and the optimum temperature for an 8 hr fluorination are given in Table 1. Properties of the fluoronitrocarbons not previously reported are given in Table 2 and NMR data in Table 3.

Primary nitro acids fluorinated poorly. Sulfur tetrafluoride evidently attacks the enol form of the nitro group:



1,1,1,3,3,3-Hexafluoropropane was isolated in about 40% yield from fluorination of 3-nitropropionic acid, and 2,2-bis(trifluoromethyl)propane was isolated in 5% yield from nitropivalic acid. Products of fluorination at the nitro site were not sought in

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other cases. The yield of fluoronitrocarbon increased slightly and the optimum reaction temperature fell as the nitro group was moved further away from the carboxyl. Substituents α to the carboxyl that produce steric hinderance made fluorination more difficult. Difluoronitroacetic acid, which cannot exist in an acinitro form, nevertheless did not fluorinate, probably due to a combination of the added electron-withdrawing effect of the fluorines on the fluorination³ and to the ease with which the acid decarboxylates.

Only one β -substituted butyric acid (2-hydroxy-3,3-dinitro) was fluorinated. No fluorination products insoluble in water were isolated. The acid may have decomposed by reversal of the Henry reaction.

γ -Substituted butyric acids fluorinated well if at least one of the γ substituents, besides the nitro group, was electron-withdrawing. Fluorine, nitro, and trifluoromethyl were all sufficiently electron-withdrawing to stabilize the γ -nitro. In the γ -position, these substituents were far enough away from the carbonyl that they did not affect its reactivity. Where both of the other γ substituents were either H or Me, the nitro group was displaced either through reaction of the acinitro form or through formation of a carbonium ion. γ,γ -dinitrobutyric acid fluorinated only at the carboxyl. Sulfur tetrafluoride is quite different from elemental fluorine or perchloryl fluoride in this respect; either of the latter reagents would have converted the dinitromethyl group to a fluorodinitromethyl group.¹⁵

β -nitro-acrylic acids fluorinated in reasonably good yields under mild conditions, leaving the double bond intact.

The fluorination product from 3-nitroacrylic acid was assigned the *trans* configuration (protons with respect to one another) by comparing its NMR data with those from *cis* and *trans* chloroacrylic acid derivatives.¹⁶ This assignment was supported by the presence of the *trans* CH=CH out-of-plane deformation in the IR spectrum at 10.50 μ . A similar band at 10.38 μ in the IR spectrum of the initial 3-nitroacrylic acid indicated that this too was the *trans* isomer and, therefore, that no isomerization had taken place during fluorination.

Because of the competition between fluorination of the carboxyl and destruction of the nitro, the yield of the desired fluoronitrocarbon shows a fairly strong dependence on the reaction temperature, at least for a fixed reaction time. At too low a fluorination temperature, fluorination of the carboxyl was incomplete; at high a temperature, the product was destroyed by attack on the nitro. A similar situation obtains with respect to time at a fixed temperature. Most of this study was carried out with an 8 hr reaction time, but some yield data were collected for 3-nitropropionic acid at different reaction times. At either 120° or 150°, the yield reached a maximum in about 4 hr, remaining roughly constant to about 12 hr and then gradually decreasing. The decrease past 12 hr was faster at 150° than at 120°.

EXPERIMENTAL

3-Nitromethacrylic acid. 3-Nitromethacrylic acid was prepared by modification of the method of Shechter *et al.*¹⁰ for 3-nitroacrylic acid. Nitryl chloride, generated from 170.5 g freshly redistilled chlorosulfonic acid, 100 g fuming HNO₃, and 123 g of 30% fuming H₂SO₄,¹⁰ was condensed by a dry-ice condenser onto 83.6 g (0.97 mole) of recrystallized methacrylic acid maintained at 0°. When the addition was complete, the reaction mixture was stirred under reflux at room temp for 1 hr. Excess nitryl chloride was removed

TABLE I. FLUORINATION OF ALIPHATIC NITRO ACIDS

| Acid ^a | Fluorination product ^b | Temp ^c (°C) | Yield (%) | Chromatography conditions | |
|---|--|---------------------------|------------------|------------------------------|--------------|
| | | | | Column ^d | Temp (°C) |
| O ₂ NCH ₂ COOH ⁵ | O ₂ NCH ₂ CF ₃ ⁶ | 150 | 18 | A | 50 |
| O ₂ NCF ₂ COOH ⁷ | O ₂ NCF ₂ CF ₃ | 120 | nil | B | 55 |
| O ₂ NCH ₂ CH ₂ COOH ⁸ | O ₂ NCH ₂ CH ₂ CF ₃ ⁹ | 120 | 10 ^e | C | 100 |
| O ₂ NCH ₂ CHClCOOH ¹⁰ | O ₂ NCH ₂ CHClCF ₃ ^f | 60 | 15 | D | 80 |
| O ₂ NCH ₂ C(CH ₃) ₂ COOH ¹¹ | O ₂ NCH ₂ C(CH ₃)CF ₃ | 100 | 5 | D | 75 |
| O ₂ NCH=CHCOOH ¹⁰ | O ₂ NCH=CHCF ₃ ⁴ | 80 | 64 | D | 80 |
| O ₂ NCH=C(CH ₃)COOH | O ₂ NCH=C(CH ₃)CF ₃ | 60 | 37 | D | 60 |
| O ₂ NCH ₂ CH ₂ CH ₂ COOH | O ₂ NCH ₂ CH ₂ CH ₂ CF ₃ | 120 | 20 | C | 128 |
| CH ₃ C(NO ₂) ₂ CHOHCOOH ¹² | CH ₃ C(NO ₂) ₂ CHF ₂ CF ₃ | — | nil ^g | D | 50 |
| (O ₂ N) ₃ CCH ₂ CH ₂ COOH ¹³ | (O ₂ N) ₃ CCH ₂ CH ₂ CF ₃ | 120 | 55 | D | 150 |
| (O ₂ N) ₂ CHCH ₂ CH ₂ COOH | (O ₂ N) ₂ CHCH ₂ CH ₂ CF ₃ | 80 | 90 | D | 130 |
| (O ₂ N) ₂ CFCH ₂ CH ₂ COOH ¹³ | (O ₂ N) ₂ CFCH ₂ CH ₂ CF ₃ | 100 | 87 | D | 100 |
| CH ₃ C(NO ₂) ₂ CH ₂ CH ₂ COOH ¹⁴ | CH ₃ C(NO ₂) ₂ CH ₂ CH ₂ CF ₃ | 120 | 76 | E | 142 |
| (CH ₃) ₂ C(NO ₂)CH ₂ CH ₂ COOH | (CH ₃) ₂ C(NO ₂)CH ₂ CH ₂ CF ₃ | 120 | nil | F | 80 |
| CF ₃ CF(NO ₂)CH ₂ CH ₂ COOH | CF ₃ CF(NO ₂)CH ₂ CH ₂ CF ₃ | 100 | 73 | G | amb |
| CH ₃ (CF ₃)C(NO ₂)CH ₂ CH ₂ COOH | CH ₃ (CF ₃)C(NO ₂)CH ₂ CH ₂ CF ₃ | 100 | 78 | G | 80 |
| (O ₂ N) ₂ C(CH ₂ CH ₂ COOH) ₂ | (O ₂ N) ₂ C(CH ₂ CH ₂ CF ₃) ₂ | 100 | 62 | D | 125 |

^a Further data available from the lit, as indicated.

^b Referenced fluorination products were identified by comparing their physical properties, IR spectra, and NMR spectra with those reported in the lit.

^c Temp affording maximum yield in an 8-hr reaction period.

^d Column descriptions as follows:

A—0.25 in o.d. by 3 m stainless steel packed with 5/100 XE-60 on 60–80 mesh HMDS-treated Chromosorb W.

B—0.13 in o.d. by 1 m stainless steel packed with 100–140 mesh silica gel.

C—0.19 in o.d. by 2 m stainless steel packed with 25/100 XE-60 on 60–70 mesh GC-22 firebrick.

D—Like C, except 0.13 in o.d. and 70–80 mesh.

E—0.19 in o.d. by 2 m stainless steel packed with 25/100 nonylphenoxy(polyethoxy)ethanol on 60–70 mesh GC-22 firebrick.

F—Like E, except Zonyl E91 substrate.

G—0.25 in o.d. by 6 ft aluminium packed with 25/100 XE-60 on 60–80 mesh HMDS-treated Chromosorb W.

^e 13% in 12 hr. Longer reaction periods gave lower yields.

^f Not isolated because of its tendency to dehydrohalogenate.

^g Over the temperature range 100–140°.

TABLE 2. PROPERTIES OF NEW FLUORONITROCARBONS FROM SF₄ FLUORINATION

| Compound | b.p. [°C (mm)] | ρ/temp g/cc/(°C) | n _D ²⁵ | Calc. (%) | | | Found (%) | | |
|---|-------------------|---------------------|------------------------------|-----------|------|-------|-----------|------|-------|
| | | | | C | H | N | C | H | N |
| CF ₃ CH(NO ₂)CH ₃ | 100-2(753) | -- | 1.3424 | 25.19 | 2.82 | 9.79 | 25.33 | 2.75 | 9.80 |
| O ₂ NCH ₂ C(CH ₃) ₂ CF ₃ | 0(5) | -- | -- | 35.09 | 4.71 | 8.19 | 35.21 | 4.58 | 7.90 |
| O ₂ NCH=C(CH ₃)CF ₃ | 110-3(743) | 1.375/24 | 1.3752 | 30.98 | 2.60 | 9.08 | 30.53 | 3.28 | 8.80 |
| O ₂ NCH ₂ CH ₂ CH ₂ CF ₃ | 171-0(743) | 1.325/23 | 1.3665 | 30.58 | 3.85 | 8.92 | 30.73 | 3.42 | 8.73 |
| (O ₂ N) ₂ CCH ₂ CH ₂ CF ₃ | — | 1.597/24 | 1.4062 | 19.44 | 1.63 | 17.01 | 19.52 | 1.39 | 16.98 |
| (O ₂ N) ₂ CHCH ₂ CH ₂ CF ₃ ^a | ~160(742) | 1.526/24 | 1.3982 | 23.87 | 2.50 | 13.92 | 23.64 | 2.48 | 13.89 |
| (O ₂ N) ₂ CFCH ₂ CH ₂ CF ₃ | 155-5(742) | 1.533/24 | 1.3740 | 21.83 | 1.83 | 12.73 | 21.91 | 1.89 | 12.78 |
| CH ₃ C(NO ₂) ₂ CH ₂ CH ₂ CF ₃ | 167(741) | 1.417/23 | 1.3992 | 27.79 | 3.26 | 12.96 | 27.75 | 3.15 | 12.97 |
| CF ₃ CF(NO ₂)CH ₂ CH ₂ CF ₃ | 105-4(744) | 1.519/22 | 1.3178 | 24.68 | 1.66 | 5.76 | 24.71 | 1.65 | 5.80 |
| CH ₃ C(CF ₃)C(NO ₂)CH ₂ CH ₂ CF ₃ | 151-9(738) | 1.446/25 | 1.3440 | 30.57 | 2.99 | 5.94 | 30.07 | 2.87 | 5.87 |
| (O ₂ N) ₂ C(CH ₂ CH ₂ CF ₃) ₂ | — | 1.538/21 | 1.3850 | 28.20 | 2.70 | 9.40 | 28.03 | 2.72 | 9.29 |

^a Neutralization equiv: Calc., 202.1; Found, 201.3; pKa 4.2.

TABLE 3. NMR DATA FOR NEW FLUORONITROCARBONS

| Compound ^a | δ (ppm relative to TMS or CFC1 ₃) | | | | | | J (Hz) |
|--|---|---------|-----------------|---|------|---|--------|
| | CF ₃ | CF | CH ₃ | CH ₂ | CH | | |
| O ₂ NCH ₂ C(CH ₃) ₂ CF ₃ | +78.96 | | 0.98 | 4.18 | | CH ₃ , CF ₃ 0.77 | |
| O ₂ NCH=C(CH ₃)CF ₃ | +71.93 | | 1.83 | | 7.02 | CH ₃ , CH 1.7; CH, CF ₃ 1.45 | |
| O ₂ NCH ₂ CH ₂ CH ₂ CF ₃ | +67.96 | | | (α) 2.14 ^b (β) 2.14 ^b | | CF ₃ , α CH ₂ 10.5; β CH ₂ , γ CH ₂ 6.3 | |
| (O ₂ N) ₂ CCH ₂ CH ₂ CF ₃ | +69.1 | | | (γ) 4.35 (α) 2.51 ^b | | CF ₃ , α CH ₂ 9.4 | |
| (O ₂ N) ₂ CHCH ₂ CH ₂ CF ₃ | +66.7 | | | (β) 2.98 | | | |
| (O ₂ N) ₂ CFCH ₂ CH ₂ CF ₃ | +68.97 | +105.32 | | 2.58 ^b (α) 2.45 (β) 3.05 | 6.28 | CF ₃ , α CH ₂ 10.0; β CH ₂ , CH 6.5 CF ₃ , α CH ₂ 9.5; CF ₃ , CF 1.9 | |
| CH ₃ C(NO ₂) ₃ CH ₂ CH ₂ CF ₃ | +68.2 | | 2.07 | (α) 2.25 (β) 2.54 | | CF ₃ , α CH ₂ 9.9 | |
| CF ₃ CF(NO ₂)CH ₂ CH ₂ CF ₃ | (γ) +67.87 ^c (α) +79.86 | +104.27 | | 2.38 ^b | | CF ₃ (γ), CH ₂ 8.8; CF ₃ (α), CF 4.2 | |
| CH ₃ C(CF ₃)NO ₂ CH ₂ CH ₂ CF ₃ | (γ) +68.12 ^c (α) +76.77 | | 1.80 | 2.37 ^b | | CF ₃ (γ), CH ₂ 9.5 | |
| (O ₂ N) ₂ C(CH ₂ CH ₂ CF ₃) ₂ | +67.0 | | | (α) 2.72 (β) 2.30 | | CF ₃ , α CH ₂ 9.4 | |
| CF ₃ CH(NO ₂)CH ₃ | +76.62 | | 1.45 | | 4.81 | CH ₃ , CH 7.0; CF ₃ , CH 6.2; CF ₃ , CH ₃ 0.6 | |
| CF ₃ C(NO ₂) ₂ CH ₃ | +75.4 | | 2.00 | | | CF ₃ , CH ₃ 1.2 | |

^a First CH₂ adjacent to CF₃ is α , second is β , third is γ .^b Complex multiplet.^c (γ) refers to CF₃ adjacent to CH₂; (α) refers to CF₃ adjacent to C(NO₂).

with a water aspirator, leaving 160.5 g (99%) of blue-to-green, crude, 2-chloro-2-methyl-3-nitropropionic acid, which then was purified by silica gel chromatography and recrystallization from benzene, m.p. 84.5–85.6°. (Found: C, 28.67; H, 3.74; N, 8.42. Calc. for $C_4H_6ClNO_4$: C, 28.67; H, 3.61; N, 8.36%.)

The crude propionic acid was dehydrochlorinated by distillation in a short path still at 140° and about 20 mm. The crude distillate was chromatographed on silica gel and then redistilled to yield 27% of 3-nitromethacrylic acid, m.p. 48–50°. (Found: C, 36.19; H, 3.95; N, 10.51. Calc. for $C_4H_5NO_4$: C, 36.65; H, 3.84; N, 10.69%.)

4-Nitrobutyric acid. A mixture of nitromethane (216 ml; 4 mole) methyl acrylate, (90 ml; 1 mole) and anhyd KF (29.05 g; 0.5 mole) was stirred at room temp for 11 days. The mixture was washed with four 100-ml portions water and dried over $MgSO_4$. Distillation yielded 144.9 g forecut boiling at 80–101°, and 22.3 g (15%) methyl 4-nitrobutyrate boiling at 84–89° (1 mm) [lit.¹⁷ b.p. 92° (3 mm)]. The ester was hydrolyzed by refluxing for 3 hr with 10 times its weight of 10% NaOH aq. yield 56%. Neutralization equiv: Calc: 133; Found: 131. The IR spectrum showed the expected carbonyl and nitro bands.

4,4-Dinitrobutyric acid. Trinitrobutyric acid¹³ was reduced with alkaline hydroperoxide according to the procedure of Glover.¹⁸ The average yield on eight runs was 72%. Neutralization equiv: Calc: 89.1; Found: 91.4. The IR spectrum showed the expected carbonyl and nitro bands.

4-Methyl-4-nitropentanoic acid. Methyl 4-methyl-4-nitropentanoate¹⁹ was hydrolyzed by refluxing for 3 hr with 10 times its weight of 10% NaOH aq. yield 71%, m.p. 42.6–44.8° (lit.²⁰ 47.5–48.5°).

Methyl 4-nitro-4,5,5,5-tetrafluoropentanoate. *t*-BuOK (15 g; 0.13 mole) was added in small amounts over 30–60 min to a stirred soln of 1-nitro-1,2,2,2-tetrafluoroethane²¹ (31.2 g; 0.21 mole) in methyl acrylate (34.5 g; 0.40 mole) maintained at 0°. When the addition was complete, the mixture was stored at room temp for 12 days, then washed with 50 ml water, 20 ml 1N H_2SO_4 , and twice with 20 ml portions water. Drying over $MgSO_4$ and distillation yielded 9.88 g (20%) methyl 4-nitro-4,5,5,5-tetrafluoropentanoate, b.p. 78° (13 mm). The analytical sample was purified by gas chromatography on a 5 ft 20% XE-60 on 50–60 mesh GC-22 firebrick column at 130°; b.p. 179.9° (739 mm); n_D^{25} , 1.3692. (Found: C, 30.87; H, 2.88; N, 6.26. Calc. for $C_6H_7F_4NO_4$: C, 30.91; H, 3.03; N, 6.01%). The IR spectrum showed the expected carbonyl, nitro, and CF bands. The proton NMR spectrum showed a singlet at -3.68 of relative area 3.0 (CH_3) and a complex multiplet of area 3.9 at -2.68 (CH_2CH_2). The F^{19} spectrum showed a doublet at $+79.36$ (CF_3) and a complex multiplet at $+140.6$ (CF); J_{CF,CF_3} , 4.4 Hz.

Either increasing or decreasing the ratio of butoxide to nitroethane decreased the yield of ester. The use of dry DMSO with either normal or reverse addition of the reactants also resulted in lower yields.

4-Nitro-4,5,5,5-tetrafluoropentanoic acid. The methyl ester (20.0 g, 0.086 mole) was refluxed for 15 hr with 90 ml conc HCl and 80 ml water. The cooled mixture was separated, and the aqueous phase was extracted with three 50 ml portions ether. Drying over $MgSO_4$ and removal of the ether left 17.6 g (93%) free acid. The analytical sample was distilled in a short-path still at 100–105° (2 mm); ρ_{22} , 1.555 g/cc; n_D^{25} , 1.3825. (Found: C, 27.27; H, 2.22; N, 6.15; neutralization equiv, 217; pK_a 4.3. Calc. for $C_5H_5F_4NO_4$: C, 27.41; H, 2.30; N, 6.39%; neutralization equiv, 219).

2-Nitro-1,1,1-trifluoropropane

1,1,1-Trifluoroacetone oxime²² (25.4 g, 0.20 mole) was added over 30 min at $+10^\circ$ to a stirred mixture of 100% HNO_3 (30.2 g; 0.40 mole) and NH_4NO_3 (16.0 g; 0.20 mole). The mixture was stirred at $+10^\circ$ for 2 hr. H_2O_2 (20 ml of 30% aqueous) was added over 15 min and the mixture was stirred at $+10^\circ$ for 30 min, then at room temp for 2.5 hr. The mixture was poured into 100 g crushed ice and water. The organic layer was removed, and the aqueous layer was extracted with four 20-ml portions CH_2Cl_2 . Drying over $MgSO_4$ and removing the CH_2Cl_2 left 13.95 g nitration products, which consisted chiefly of 2-nitro-1,1,1-trifluoropropane and 2,2-dinitro-1,1,1-trifluoropropane in roughly a 2:1 ratio.

Methyl 4-nitro-4-trifluoromethylpentanoate

A mixture of crude oxime nitration products containing about 28 g (0.2 mole) 1,1,1-trifluoro-2-nitropropane, 17.2 g (0.20 mole) methyl acrylate and 5.75 g anhyd KF was shaken at room temp for 7 days. The reaction mixture was washed with four 15-ml portions water, dried over $MgSO_4$ and distilled to yield 15.1 g (33%) of the desired methyl ester, b.p. 85–88° (15 mm). The analytical sample was purified by gas chromatography on a 10-ft 20% XE-60 on 50–60 mesh GC-22 firebrick column at 155°; b.p. 207.9° (743 mm); ρ_{23} , 1.356; n_D^{25} , 1.3995. (Found: C, 36.56; H, 4.36; N, 6.07. Calc. for $C_7H_{10}F_3NO_4$: C, 36.70; H, 4.40; N, 6.11%). The IR spectrum showed the expected CO, NO_2 and CF bands. The proton NMR spectrum showed a singlet at -3.70 of area 3.0 (ester CH_3), a complex multiplet of area 4.0 at -2.45 (CH_2CH_2), and a multiplet

of area 3.0 at -1.78 . The F^{19} spectrum showed a multiplet of area 2.9 at $+75.76$; J_{CH_3,CF_3} , 1.1 Hz; J_{CF_3,CH_2} , about 0.5 Hz.

4 Nitro-4-trifluoromethylpentanoic acid. The methyl ester (2.0 g, 0.0087 mole) was refluxed for 15 hr with 9 ml of conc HCl and 8 ml water. The free acid crystallized out on cooling to 0° overnight; yield 1.08 g (58%); m.p. 72.2° . One recrystallization from water raised the m.p. to 73.6° . (Found: C, 33.40; H, 3.38; N, 6.54. Calc. for $C_6H_8F_3NO_4$: C, 33.50; H, 3.75; N, 6.51%.)

Fluorination

A 25-ml stainless steel pressure vessel with a soft copper gasket was charged with 0.03 mole of the acid being fluorinated, 0.09 mole SF_4 , and 0.009 mole BF_3 . SF_4 and BF_3 were measured and transferred in a stainless steel vacuum line and condensed into the reactor with liquid N_2 . The loaded pressure vessel was transferred directly from the nitrogen bath to a rocking heater initially at room temp. Power was supplied to the rocker and heater immediately, and operating temp was reached in 15–30 min. The reaction was carried out behind a barricade and in a well ventilated area. We would not recommend such rapid heating with larger pressure vessels. Caution should be exercised in running these reactions on a larger scale. At the end of the heating period the rocker was turned off, and the reactor was allowed to cool to room temp in the rocker before excess gaseous reactants and byproducts were bled off in a well ventilated hood. Water (1 to 2 ml) was cautiously added to the open vessel (exothermic reaction). The organic phase was removed, washed with four 1-ml portions of 10% Na_2CO_3 aq (omitted for products containing a nitro capable of existing in an aci form), washed with two 1-ml portions water, and dried over $MgSO_4$. The crude reaction mixtures were analyzed, and analytical samples were obtained by gas chromatography.

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