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N-PENTAFLUOROSULFANYL-N-NITRO CARBAMATES

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SUMMARY

Unlike N-alkyl carbamates, N-pentafluorosulfanyl carbamates (SF_5NHCO_2R) did not readily undergo nitration to provide the $N-NO_2$ derivatives. Although trifluoroacetyl nitrate did provide nitration, work-up yielded a mixture of $SF_5N(NO_2)CO_2R$ and starting material. The ratio of nitration product to starting material was not changed after prolonged reaction times and the $N-NO_2$ product was stable to the work-up conditions. A rationale for these results as well as the effect of varying R is discussed.

INTRODUCTION

Pentafluorosulfanyl isocyanate ($SF_5N=C=O$), an extremely reactive intermediate that readily combines with a variety of hydrogen active compounds [1], was recently treated with polynitro alcohols to provide dense energetic carbamates [2] (eq. 1). These polynitro SF_5 carbamates (1) have densities of approximately 2.0 g/cc. In an attempt to further increase the density and energy of 1, nitrations to the $N-NO_2$ derivatives (2) were investigated (eq. 2).

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$$\mathrm{SF_5N{=}C{=}O + R(NO_2)_nCH_2OH} \longrightarrow \underset{1}{\mathrm{SF_5NHCO_2CH_2R(NO_2)_n}} \qquad (1)$$

$$1 \xrightarrow{[\mathrm{NO_2}]} \underset{2}{\mathrm{SF_5N(NO_2)CO_2CH_2R(NO_2)_n}} \qquad (2)$$

RESULTS AND DISCUSSION

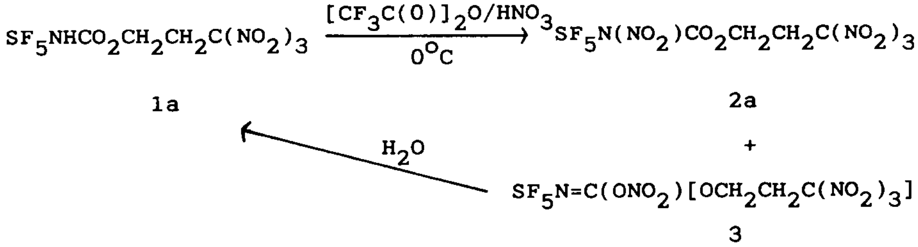
Initially, N-pentafluorosulfanyl-3,3,3-trinitropropyl carbamate (1a) was chosen as a representative 1 for N-nitration. Compound 1a proved to be resistant to nitration, unlike similar polynitroalkyl carbamates which have been shown to readily nitrate with acetic anhydride/nitric acid [3] (as an example, see eq. 3). Thus, 1a was unaffected by acetic

$$\mathrm{C(NO_2)_3CH_2CH_2NHCO_2CH_2C(NO_2)_3} \xrightarrow[5^{\circ}\mathrm{C},\ 30\ \mathrm{min}]{[\mathrm{CH_3C(O)}]_2\mathrm{O/HNO_3}}$$

$$\underset{89\%}{\mathrm{C(NO_2)_3CH_2CH_2N(NO_2)CO_2CH_2C(NO_2)_3}} \qquad (3)$$

anhydride/nitric acid (acetyl nitrate)and by mixed sulfuric-nitric acid. Similarly, nitrogen pentoxide, from 100% nitric acid added to phosphorus pentoxide, left 1a unchanged. Only trifluoroacetyl nitrate (trifluoroacetic anhydride/100% nitric acid) was found to be effective for producing N-pentafluorosulfanyl-N-nitro-3,3,3-trinitropropyl carbamate (2a). However, the product from 1a with trifluoroacetyl nitrate was always a mixture of the N-nitration product (2a) and starting material (1a). The amount of 2a reached a maximum of 43% and could not be increased even with prolonged reaction times. The product 2a can easily be distinguished from 1a by ^{1}H-NMR (2a shows a triplet at 4.86 for $O\text{-}CH_2\text{-}CH_2C(NO_2)_3$ that is shifted from 4.70 in 1a). Because TLC on Silica gel 60 indicated that substantial decomposition of 2a occurred on this adsorbent (trailing on plate), the more acidic Silica gel 40 was used for purification of 2a. The IR and ^1H-NMR spectra of pure 2a (see experimental section) were consistent for the assigned structure. Although other possible structures could include trifluoroacetic anhydride derivatives [for example $SF_5N[C(O)CF_3]CO_2CH_2CH_2C(NO_2)_3]$, they are unlikely since 1a remains unchanged after treatment with trifluoroacetic anhydride alone. A satisfactory elemental analysis for 2a could not be obtained apparently because of the poor stability of this compound. When allowed to stand at room temperature unprotected from moisture, 2a showed substantial hydrolysis to starting material (1a) after a few days. Even when efforts to exclude water were taken, decomposition of 2a occurred.

A rationalization that could account for the fact that only mixtures of 2a and 1a can be obtained is based on competing nitration (on nitrogen or on oxygen of 1a) (see scheme 1). In addition to 2a formed from nitration on nitrogen, nitration on oxygen would produce the imino nitrate 3. During work-up, 3 would be expected to readily hydrolyze to 1a, resulting in the observed mixture (1a and 2a).



Scheme 1

In order to investigate the effect of R on the nitration of SF_5 carbamates, additional SF_5 carbamates (1b-1f) (see TABLE 1) were prepared and treated with trifluoroacetic anhydride/nitric acid to determine the maximum amount of $N-NO_2$ product (2b-2f) formed. As seen in TABLE 1, when R is sufficiently electronegative such as in 1b, nitration does not occur and only recovered starting material is obtained. As R becomes less electronegative (smaller σ^*) the amount of $N-NO_2$ product increases, reaching a limiting amount of about 75% (2e and 2f).

Large molar excesses of trifluoroacetyl nitrate were used to try to drive the nitrations of N-pentafluorosulfanyl carbamates 1 to completion. That only incomplete reactions are obtained is not due to hydrolysis of the $N-NO_2$ derivatives 2 back to 1 under the work-up conditions. As an example, 2d was added to trifluoroacetic anhydride/nitric acid at 0°C and held for 5 min before the solution was poured onto ice. After work-up as usual, ^1H-NMR showed only 2d. This result supports the hypothesis that mixtures of 1 and 2 result from competing O- and N- nitration.

It was anticipated that, in contrast to 1a, N-nitro SF_5 carbamates such as 2d or 2f might be crystallizable or have sufficient stability to give a satisfactory elemental analysis. This was found not to be the case. Thus, although R has a significant effect on the ability to nitrate SF_5NHCO_2R, the $SF_5N(NO_2)$ grouping in $SF_5N(NO_2)CO_2R$ is apparently the dominant factor in the stability of this type of compound.

TABLE 1

Nitration of SF_5 carbamates

$$\underset{\text{1a-1f}}{SF_5NHCO_2R} \xrightarrow[HNO_3]{[CF_3C(O)]_2O} \underset{\text{2a-2f}}{SF_5N(NO_2)CO_2R} + SF_5N{=}C(ONO_2)OR$$

Compound letter	R	σ^* of R	Maximum % $N\text{-}NO_2$ Product^x
b	$CH_2C(NO_2)_2CH_3$	0.99 [4]	0
c	$CH_2C_6H_2(NO_2)_3$	0.65 [5]	41
a	$CH_2CH_2C(NO_2)_3$	0.58 [6]	43
d	$CH_2CH_2C_6H_2(NO_2)_3$	0.26 [5]	51
e	CH_3	0.00 [4,7]	75-80^{xx}
f	$(CH_2)_7\ CH_3$	-0.13 [4,7]	75

x by ^1H NMR
xx based on recovered starting material

N-(2,2,2-Trinitroethyl) carbamates are similar to N-pentafluorosulfanyl carbamates in that there is a strongly electronegative group attached to the carbamate nitrogen. To date there has been no report of successful nitration of N-(2,2,2-trinitroethyl)carbamates; K. Kluger and M. B. Frankel report that conditions were not found for nitration of these types of compounds [8]. Possibly the nitration is similar to that of the N-pentafluorosulfanyl carbamates and the lack of success is due to the production of a mixture of N- and O- nitration products. This is supported by the fact that N-(2,2,2-trinitroethyl) (2-pentafluorothioethyl)carbamate (4) was found to nitrate with mixed sulfuric-nitric acid but only to produce approximately 42% of the N-NO_2 product (5) along with recovered 4 (eq. 4) (acetyl nitrate did not affect 4; trifluoroacetyl nitrate was not tried). Purified 5 gave a satisfactory elemental analysis (see experimental section) and 5 was found to be considerably more stable than the N-pentafluorosulfanyl-N-nitro carbamates 2. A sample of 5, standing exposed to the atmosphere for several weeks, underwent no change as detectable by ^1H NMR.

$$C(NO_2)_3CH_2NHCO_2CH_2CH_2SF_5 \xrightarrow[2.\ H_2O]{1.\ H_2SO_4/HNO_3}$$

4

$$C(NO_2)_3CH_2N(NO_2)CO_2CH_2CH_2SF_5 + 4 \qquad (4)$$

<u>5</u>, 42% 58%

EXPERIMENTAL

<u>Caution</u>: Polynitro compounds are potentially explosive and should be handled with appropriate precautions.

^1H NMR spectra were recorded at 90 MHz with a Varian EM 90 spectrometer; results are given in p.p.m. from tetramethylsilane, used as the internal standard. Infrared spectra were recorded with a Perkin-Elmer model 283 spectrometer (quoted in cm^{-1}) and elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

100% nitric acid was prepared as follows: dry potassium nitrate (32.0 g) was added with cooling to conc. sulfuric acid (54 mL) after which a vacuum (from a water aspirator protected by a tube containing sodium hydroxide pellets) was adjusted so that 100% nitric acid (19g, 95%) distilled at 45-50°C; distillation began when the pot temperature approached 100°C but a slow increase to 150°C was required to complete the distillation.

Pentafluorosulfanyl isocyanate was purchased from the University of Alabama, Tuscaloosa, Alabama (Dr. Joseph S. Thrasher). N-Pentafluorosulfanyl-2,2,2-trinitropropyl carbamate (1a), N-pentafluorosulfanyl-2,2-dinitropropyl carbamate (1b) and N-(2,2,2-trinitroethyl)(2-pentafluorothioethyl)carbamate (4) were prepared as described previously [2][9].

Preparation of N-Pentafluorosulfanyl carbamates

(a) N-Pentafluorosulfanyl-2,4,6-trinitrobenzyl carbamate (1c) (nc)

A solution of 2,4,6-trinitrobenzyl alcohol (1g, 4.1 mmol) in dry acetonitrile (8 mL) was cooled to -78°C before pentafluorosulfanyl isocyanate (0.8 g, 4.7 mmol) was condensed onto the frozen mixture. The mixture was allowed to warm to room temperature and held for 4 h before the volatiles were removed to give 1.68g (100%) of 1c, mp 74-77°C. Crystallization from dichloromethane/hexane raised the melting point to 75-77°C; IR (KBr) 3660, 3580, 3270 (NH), 1758, 1750 (C=O), 1560, 1355 (NO_2), 950-850 (SF_5); ^1H NMR ($CDCl_3$) 5.82 (s, 2 H), 8.03 (bs, 1 H), 9.07 (s, 2 H). Anal. Calcd for $C_8H_5F_5N_4O_8S$: C, 23.31; H, 1.22; F, 23.05; N, 13.59; S, 7.78. Found: C, 23.12; H, 1.34; F, 22.69, N, 13.29; S, 7.95%.

(b) N-Pentafluorosulfanyl-[2-(2,4,6-trinitrophenyl)ethyl]carbamate (1d) (nc)

Pentafluorosulfanyl isocyanate (1.1g, 6.5 mmol) was condensed onto a solution of 2-(2,4,6-trinitrophenyl)ethanol (1.6g, 6.5 mmol) in dry acetonitrile (8 mL) frozen at -78°C. After 4 h at room temperature, the volatiles were removed to give 2.7 g (100%) of 1d, mp 82-84°C. After crystallization from dichloromethane/hexane the melting point was raised to 86-88°C; IR (KBr) 3225(NH), 1780 shoulder, 1752 (C=O), 1550 1355 (NO_2), 960-830 (SF_5); ^1H NMR ($CDCl_3$) 3.60 (t, J = 6Hz, 2 H), 4.60 (t, J = 6Hz, 2 H), 7.73 (bs, 1H), 9.02 (s, 2H). Anal. Calcd for $C_9H_7F_5N_4O_8S$: C, 25.36; H, 1.65; F, 22.29; N, 13.14; S, 7.52. Found: C, 25.48; H, 1.69; F, 21.23; N, 13.06; S, 7.86%.

(c) N-Pentafluorosulfanyl-methyl carbamate (1e)

Compound 1e was prepared by a modification of the procedure described in the literature [1]. To a solution of pentafluorosulfanyl isocyanate (1.5 g, 9 mmol) in dry dichloromethane (10 mL) at -78°C was added methanol (5 mL) drop-wise. The solution was allowed to slowly warm to room temperature before the volatiles were removed under reduced pressure to give 1.65 g (93%) of 1e, mp 67-69°C; the product was identical to an authentic sample supplied by Dr. Joseph S. Thrasher, University of Alabama, Tuscaloosa, Alabama; ^1H NMR ($CDCl_3$) 3.88 (s) (CH_3).

(d) N-Pentafluorosulfanyl-1-octyl carbamate (1f) (nc)

Pentafluorosulfanyl isocyanate (2.4 g, 1.42 mmol) was condensed into dry dichloromethane (9 mL) at -78°C. A solution of 1-octanol (1.8 g, 1.42 mmol) was added dropwise before a dry ice condenser was attached and the mixture was allowed to warm to room temperature. After 2 h, the volatiles were removed to give 4.1 g (97%) of 1f, mp 66-68°C. Crystallization from dichloromethane did not raise the melting point; IR (KBr) 3210 (NH), 1740 (C=O), 875 (SF_5); ^1H NMR ($CDCl_3$) 0.9-1.7 (m), 4.27 (t), 7.87 (bs). Anal. Calcd for $C_9H_{18}F_5NSO_2$: C, 36.11; H, 6.06 F, 31.74. N, 4.68; S, 10.71. Found: 35.83; H, 5.98; F, 31.85; N, 4.71; S, 10.84%.

Preparation of N-Pentafluorosulfanyl-N-Nitro Carbamates

(a) N-Pentafluorosulfanyl-N-nitro-3,3,3-trinitropropyl carbamate (2a) (nc)

Trifluoroacetic anhydride (4 mL, 28 mmol) was stirred in an ice bath during the dropwise addition of 100% nitric acid (0.6 mL, 14 mmol). After 5 min, 1a (0.40 g, 1.1 mmol) was added and the solution was held at 0°C for 17 h before it was poured onto ice. Extraction with dichloromethane, drying (sodium sulfate) and removal of volatiles with a stream of nitrogen gave a residue (0.4 g) which ^1H NMR ($CDCl_3$) showed to be a mixture of 2a (43%) (4.86, t) and 1a (57%) (4.70, t). (A prior run at 0°C for 1.5 h showed 34% of 2a). The residue was dissolved in dichloromethane (1 mL) and chromatographed on Silica gel 40 using dichloromethane as eluant to give pure 2a as an oil; IR (film) 1790 (C=O), 1650 ($N\text{-}NO_2$), 1605 [$C(NO_2)_3$], 910, 800 (SF_5); ^1H NMR ($CDCl_3$) 3.63 (t, J = 6Hz, 2H), 4.86 (t, J = 6Hz, 2H). Compound 2a did not give a satisfactory elemental analysis apparently due to the instability of this material. The unused portion of the sample, that had been submitted for elemental analysis, was returned and examination by ^1H NMR showed 2a had essentially all decomposed.

(b) N-Pentafluorosulfanyl-N-nitro-2,4,6-trinitrobenzyl carbamate (2c) (nc)

100% nitric acid (0.3 ml, 7 mmol) was added dropwise to trifluoroacetic anhydride (4 mL, 28 mmol) stirred in an ice bath. After 5 min, 1c (0.2 g, 0.5 mmol) was added and the solution was stirred at 0^oC. Samples removed (after 1 h, 2 h and 4 h) were poured onto ice and immediately worked-up as described for 2a to give residues which ^1H NMR showed to contain 34%, 41% and 41% of 2c, respectively. A pure sample of 2c was obtained by column chromatography on Silica gel 40 (dichloromethane as eluant); IR (film) 1790 (C=O), 1645 ($N-NO_2$), 1555, 1355 (NO_2), 910-795 (SF_5); ^1H NMR ($CDCl_3$) 9.18 (s, 2 H), 6.03 (s, 2 H).

(c) N-Pentafluorosulfanyl-N-nitro-[2-(2,4,6-trinitrophenyl) ethyl]carbamate (2d) (nc)

A nitration solution, prepared by the dropwise addition of 100% nitric acid (0.6 mL, 14 mmol) to ice cold trifluoroacetic anhydride (6 mL, 42 mmol), was stirred at 0^oC while adding 1d (1.0 g, 2.4 mmol). After 19 h at 0^oC, the reaction solution was poured onto ice; work-up (as described for 2a) gave a residue (1 g) which ^1H NMR showed contained 51% of 2d. (Samples removed after 1.5 h and 3 h showed 37% and 48% of 2d, respectively.). The residue (1 g) was chromatographed on Silica gel 40 using dichloromethane as eluant to give 0.4 g of pure 2d as an oil. IR (film) 1795 (C=O), 1640 ($N-NO_2$), 1555, 1355 (NO_2), 915-800 (SF_5). ^1H NMR ($CDCl_3$) 4.70 (t, J = 6 Hz, 2 H), 4.83 (t, J = 6 Hz, 2 H), 9.10 (s, 2 H).

(d) N-Pentafluorosulfanyl-N-nitro-methyl carbamate (2e)

Compound 1e (0.40 g, 2 mmol) was added at 0°C to a solution prepared by the dropwise addition of 100% nitric acid (0.4 mL, 9.5 mmol) to ice cold trifluoroacetic anhydride (4 ml, 28 mmol). After 16 h at 0°C, the solution was poured onto ice. Work-up, as described for 2a, did not allow determination of the amount of 2e by ^{1}H NMR because 2e was found to be too volatile to be efficiently separated from the dichloromethane extraction solvent. The ^{1}H NMR spectrum of a mixture containing 2e and 1e (also some dichloromethane) showed singlets at 4.10 and 3.88 for 2e and 1e, respectively. Removal of all solvent also removed 2e to leave 0.08 g (20% recovery) of 1e, mp 66-68°C. A control experiment showed that 1e has sufficient volatility that a small amount of 1e may also be lost during removal of the dichloromethane solvent. Thus, it was estimated that the product from the nitration contained 75-80% of 2e. A separate nitration experiment showed that, after 1 h at 0°C, the product was 60% 2e (recovered 1e was 40%).

(e) N-Pentafluorosulfanyl-N-nitro-1-octyl carbamate (2f) (nc)

100% nitric acid (0.6 g, 14 mmol) was added dropwise to trifluoroacetic anhydride (6 ml, 42 mmol) stirred in an ice bath. Compound 1f (1.0 g, 3.3 mmol) was added and the solution was held at 0°C for 4.5 h before it was poured onto ice and worked-up (as described for 2a) to give 1.0 g of product. ^{1}H NMR showed the product was 75% 2f (by comparing triplet at 4.50 for 2f to triplet at 4.27 for 1f). Samples removed after 1 h and 3 h showed 33% and 69% of 2f, respectively. A separate experiment for 16 h at $0^{o}C$ showed the same amount (75%) of 2f as after 4.5 h. The product (1.0 g) was chromatographed on Silica gel 40 using dichloromethane as eluant to give 0.6 g of pure 2f as an oil; IR (film) 1800, 1780 shoulder (C=O), 1645 ($N-NO_2$), 910, 865, 795 (SF_5); ^{1}H NMR ($CDCl_3$) 0.95-1.8 (m), 4.50 (t). Compound 2f was submitted for elemental analysis with the anticipation that 2f would be more stable than 2a. However, a satisfactory analysis could not be obtained for 2f which, in hindsight, was not surprising since a small sample of 2f stored at room temperature in a closed vial (during the time required to obtain the analysis) mostly decomposed.

<u>Preparation of N-(2,2,2-trinitroethyl)-N-nitro-(2-pentafluorothioethyl)carbamate</u> (5) (nc)

To conc. sulfuric acid (3.6 mL) stirred in an ice bath was added 90% nitric acid (1.2 mL) dropwise. Compound 4 (0.42 g, 1.1 mmol) was added and the mixture was stirred at room temperature for 4 h before it was poured onto ice. Work-up as described for 2a gave 0.45 g of oil which ^{1}H NMR showed to be a mixture of 5 (42%) and 4. An independent run at room temperature for 20 h gave the same ratio of 5 to 4. The oil (0.45 g) was dissolved in chloroform, hexane was added, and the solution was cooled to $-10^{o}C$ to give 0.20 g of 4. The product remaining in the mother liquor was chromatographed on Silica gel 40 (dichloromethane as eluant) to give 0.15 g of pure 5 as an oil; IR (film) 1805, 1765, (C=O), 1640 shoulder, 1610 ($N-NO_2$ and NO_2), 800-900 (SF_5); ^{1}H NMR ($CDCl_3$) 4.02

(m, 2 H), 4.85 (t, 2 H), 5.88 (s, 2 H). Anal. Calcd for $C_5H_6F_5N_5O_{10}S$: C,14.19; H, 1.43; F,22.45; N, 16.55; S, 7.58. Found: C, 14.58; H, 1.38; F, 21.35; N, 16.43; S, 7.94%.

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