(0.40 mol) of 2,2,2-trifluoroethyl trifluoroacetate, and 50 g (0.50 mol) of TFE was shaken at ambient temperature for 8 h. The volatiles were removed from the reaction mixture under reduced pressure to give a viscous residue which was treated with 400 mL of water and 200 mL of concentrated H_2SO_4. The mixture was stirred at 25 °C for 3 days and then at 70–80 °C for 3 days. The mixture was continuously extracted with ether for 12 h and the extract was distilled to a head temperature of 66 °C to remove the volatiles. The residual crude acid (118 g) was stirred with 100 g (1.0 mol) and 2,2,2-trifluoroethanol and 150 mL of concentrated H_2SO_4 for 3 days. The mixture was distilled to give 179.4 g of liquid, bp ≤30 °C (1 mm) which was redistilled to remove most of the unreacted 2,2,2-trifluoroethanol. To the higher boiling residue was added 15 g of P_2O_5 and the distillation was continued to give 20.7 g (16%) of **28** containing about 3% of **30** (IR: 1860 cm^{-1} (C=O)) by GC. A sample of pure **28**, bp 65–66 °C (100 mm), was analyzed: IR 2990 (saturated CH), 1800 (C=O), 1300–1100 cm^{-1} (CF, CO); ^1H NMR δ 4.64 (q, J_{HF} = 7.7 Hz, OCH_2); ^{19}F NMR ϕ −74.9 (t, 3 F, J_{HF} = 7.7 Hz, CH_2CF_3), −75.7 (t of t, 3 F, J_{FF} = 8.2, 2.9 Hz, $CF_3C{=}O$), −119.5 (sextet, 2 F, J_{FF} = 3.3 Hz, CF_2), −120.5 (q of t, 2 F, J_{FF} = 8.2, 3.5 Hz, CF_2). Anal. Calcd for $C_7H_2F_{10}O_3$: C, 25.94; H, 0.62. Found: C, 25.79; H, 0.62.

Derivatives of Functionalized Fluoro Esters and Fluoro Ketones. New Fluoro Monomer Syntheses

Carl G. Krespan

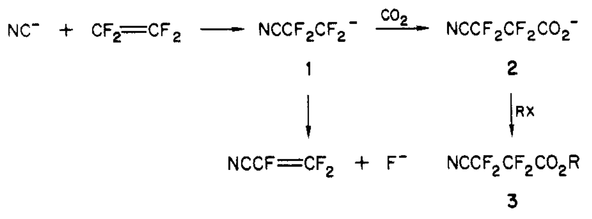
Central Research and Development Department,† E. I. du Pont de Nemours and Co., Inc.,
Wilmington, Delaware 19898

Received April 23, 1985

New reactions of functionalized fluoro esters are described, including reaction with tertiary amines to form quaternary ammonium carboxylates in high yield. Efficient schemes for conversion of these salts to trifluorovinyl ethers and perfluoroallyl ethers, two types of comonomer, are presented. Similar reactions are also available for conversion of functionalized fluoro ketones to copolymerizable fluoro olefins. Many of the examples involve fluoroalkyl azides, previously a relatively inaccessible and unstudied class.

Fluoro esters and fluoro ketones containing one or more functionalities are now readily available from a one-pot synthesis of broad scope involving a nucleophilic anion, a fluoro olefin (especially tetrafluoroethylene), and carbon dioxide[1] or a fluoro ester.[2] It was of interest to bring about transformations of the ester and carbonyl groups of these intermediates, while preserving the accompanying functions for later use. As can be seen from the following discussion, this approach was successful, even with azido and cyano present as functions. In addition, reactions of the fluoro carboxylate salts obtained as primary products of the carbanion trapping with CO_2 were examined.

Fluoro Carboxylate Alkylation. The yield of 3-cyanotetrafluoropropionate anion **2** as a function of variables such as solvent, temperature, and cyanide counterion was studied in conjunction with an appraisal of common alkylating agents as to their effectiveness in converting the carboxylate into a readily isolated ester. The results, which are summarized in Table I, allow several conclusions to be drawn, as follows. Best yields of anion **2** are obtained with a solvent in which the cyanide salt employed has appreciable solubility. Sodium cyanide offers the advantage over potassium cyanide of minimizing formation of product derived from fluoride ion (pentafluoropropionate anion) but requires a very polar medium such as dimethyl sulfoxide for good results. The 3-cyanotetrafluoropropionate salts form readily at 25 °C and are reasonably stable up to 100 °C but decompose at 150 °C. A source of yield loss in addition to elimination of fluoride ion from the intermediate carbanion **1**[1] is attack on the product by cyanide ion. Fluorinated nitriles are subject to addition of nucleophiles, including cyanide ion,[3] so that the low yield from entry 15 in Table I is explicable as the result of generating **2** in the presence of excess cyanide. The slightly exothermic reaction of cyanide with **2** in dimethyl sulfoxide, carried out separately, was shown to give unidentified condensation products.



Reactive alkylating agents, dimethyl sulfate and methyl fluorosulfate, converted the fluoro carboxylate anions to the esters easily and in good yield. Dimethyl sulfate appeared to be effective across the entire spectrum of solvents used. Less active reagents (methyl, ethyl, and allyl bromide) gave the corresponding esters **3** slowly and in lower yield, and they tended to interact with dimethyl sulfoxide even at room temperature.

Fluoro Ester Chemistry. Reactions of the cyano group in **3** (R = CH_3) can be complicated by involvement of the ester group. Thus, an attempt to trimerize **3** (R = CH_3) to the triazine with tetraphenyltin led instead to *N*-methyltetrafluorosuccinimide, a rearrangement product. The cyano ester does, however, serve as a convenient high-yield source of dimethyl tetrafluorosuccinate by reaction with methanol and the calculated amount of water in the presence of sulfuric acid.

Highly selective attack on the ester function can be carried out with a soft nucleophile such as a tertiary amine.[4] Triethylamine reacts slowly with **3** (R = CH_3)

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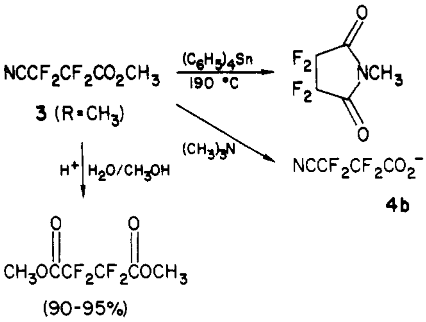
† Contribution No. 3742.

[1] (a) Krespan, C. G.; Van-Catledge, F. A.; Smart, B. E. *J. Am. Chem. Soc.* **1984**, *106*, 5544. (b) Krespan, C. G. U.S. Patent 4474700, 1984.

[2] Krespan, C. G.; Smart, B. E. *J. Org. Chem.*, submitted for publication.

[3] For example, see: Middleton, W. J.; Krespan, C. G. *J. Org. Chem.* **1968**, *33*, 3625.

0022-3263/86/1951-0326$01.50/0



in ether solution by S_N2 attack on methyl to give methyltriethylammonium 3-cyanotetrafluoropropionate (**4a**) in 90–95% yield as a low-melting deliquescent solid. Trimethylamine reacts more rapidly to give pure salt **4b** in similar yield. Although **4b** is stable below its melting point (147–148 °C), the crude methyltriethylammonium salt **4a** pyrolyzes at about 100 °C to ethylene, carbon dioxide, and tarry residue.

The loss of carbon dioxide in the latter decomposition suggests that a reversal of the reaction by which carboxylate **2** is formed will occur in solution at 100–150 °C to give carbanion **1**. The presence of **1** was demonstrated by conducting a pyrolysis of **4b** in the presence of iodine to trap **1** as the iodide **5**, a reaction which offers a new synthesis of functionalized iodides.[5]

$$\mathbf{4b} + I_2 \xrightarrow{\Delta} \underset{\mathbf{5}}{NCCF_2CF_2I}$$

Subsequently, functionalized tetramethylammonium fluoro carboxylates **6**–**8** were also prepared from the corresponding methyl esters and trimethylamine. Pyrolysis

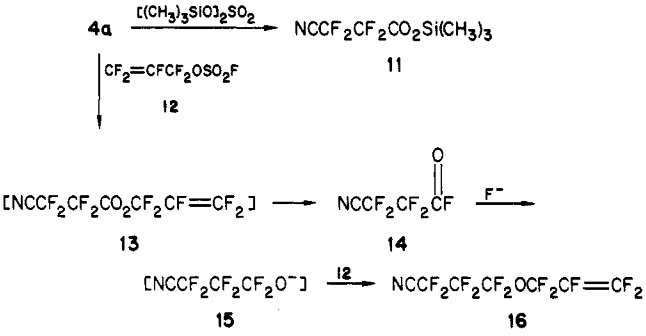
$$\underset{\mathbf{6}}{N_3CF_2CF_2CO_2^-N^+(CH_3)_4} \underset{T}{\xrightarrow[\Delta]{I_2}} \underset{\mathbf{9}}{N_3CF_2CF_2I}$$

$$\underset{\mathbf{7}}{CH_3OCF_2CF_2CO_2^-N^+(CH_3)_4} \qquad \underset{\mathbf{8}}{CH_3SO_2CF_2CF_2CO_2^-N^+(CH_3)_4}$$

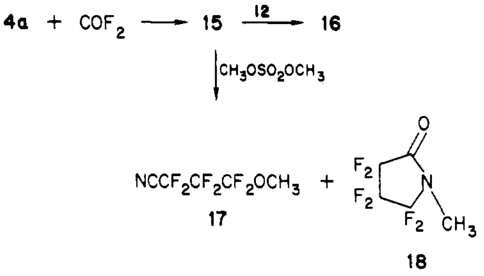
of **6** with iodine did produce iodide **9**, but several attempts to prepare iodide **10** from **7** gave mainly byproducts such as CO_2, CH_3F, CH_3I, and $CH_3OCF_2CF_2COF$. Little **10** was formed in these reactions, apparently due a tendency for loss of fluoride ion to dominate reactions of $CH_3OCF_2CF_2^-$ at elevated temperature. A synthesis of iodide **10** via radical intermediates was more successful.[6]

$$CH_3OCF_2CF_2COCl + KI \xrightarrow{\Delta} \underset{\mathbf{10}}{CH_3OCF_2CF_2I}$$

The functionalized fluoro carboxylate salts react as such, however, near room temperature. For example, salt **4a** is converted by bis(trimethylsilyl) sulfate to trimethylsilyl 3-cyanotetrafluoropropionate (**11**), and it readily displaces fluorosulfate anion from perfluoroallyl fluorosulfate (**12**).[7] The latter reaction, presumed to form the perfluoroallyl ester **13** as an intermediate, gave instead the fluoride ion catalyzed decomposition product of **13**, 3-cyanotetrafluoropropionyl fluoride (**14**).[8] A byproduct, cyano olefin **16**, was also isolated in low yield, indicating that fluoride ion generated from side reactions added to **14** with formation of **15**, which then displaced fluorosulfate from **12** to give product **16**. An even higher yield of **16** (34%) was obtained with a 100% excess fluorosulfate **12**.



Carbonyl fluoride was examined as a reagent for making intermediate **15** more directly from **4a**; when the reaction mixture was treated with dimethyl sulfate at 10 °C, both the acyclic derivative **17** and the product of cyclization followed by rearrangement and methylation (**18**) were obtained.



Treatment of **15** (prepared from either **4a** or **4b** and carbonyl fluoride) with the reactive perfluoroallylating agent **12** at 0 °C, however, gave only the acyclic derivative **16** in 50% yield. The series of reactions starting from ester **3** (R = CH_3) to prepare cyano olefin **16** in 50–60% overall yield can also be conducted as a one-pot reaction in diglyme solvent. Similarly, methyl 3-azidotetrafluoropropionate was reacted with triethylamine to form a crude methyltriethylammonium salt **19**, which was transformed by carbonyl fluoride and then **12** to azido olefin **20** in 35% overall yield.

$$N_3CF_2CF_2CO_2CH_3 + N(CH_2CH_3)_3 \rightarrow \underset{\mathbf{19}}{N_3CF_2CF_2CO_2^-N^+(CH_2CH_3)_3CH_3} \xrightarrow{COF_2} \xrightarrow{\mathbf{12}} \underset{\mathbf{20}}{N_3CF_2CF_2CF_2OCF_2CF{=}CF_2}$$

These relatively direct syntheses of **16** and **20** from tetrafluoroethylene illustrate the versatility of the synthetic scheme in its ability to provide a spectrum of functionalized terminal fluoro olefins. The perfluorallyloxy end group they contain has been shown to be a site which undergoes radical copolymerization,[9] and comonomers **16** and **20** are no exception. Both participated in copolymerizations with tetrafluoroethylene without appre-

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[4] Krespan, C. G. *J. Org. Chem.* **1978**, *43*, 637. The behavior of methyl chlorodifluoroacetate as a methylating agent with heptafluoroisopropoxide ion is reported.

[5] Paskovitch, D.; Gaspar, P.; Hammond, G. S. *J. Org. Chem.* **1967**, *32*, 833. Pyrolysis of sodium perfluoroalkylcarboxylates in the presence of iodine in dimethylformamide solution is shown to give perfluoroalkyl iodides.

[6] Krespan, C. G. *J. Org. Chem.* **1958**, *23*, 2016. Simple fluoro acid chlorides are converted to fluoroalkyl iodides by thermolysis of intermediate acyl iodides.

[7] Krespan, C. G.; England, D. C. *J. Am. Chem. Soc.* **1981**, *103*, 5598. The facile displacement of fluorosulfate ion from perfluoroallyl fluorosulfate by a variety of anions is reported, but none have the low reactivity of a fluoro carboxylate anion.

[8] Dorfman, E.; Emerson, W. E.; Carr, R. L. K. U.S. Patent 3 795 693, 1974. A multistep route to ω-cyanoperfluoroalkanoyl fluorides such as **14** is described.

[9] Krespan, C. G. U.S. Patent 4 349 650, 1982.

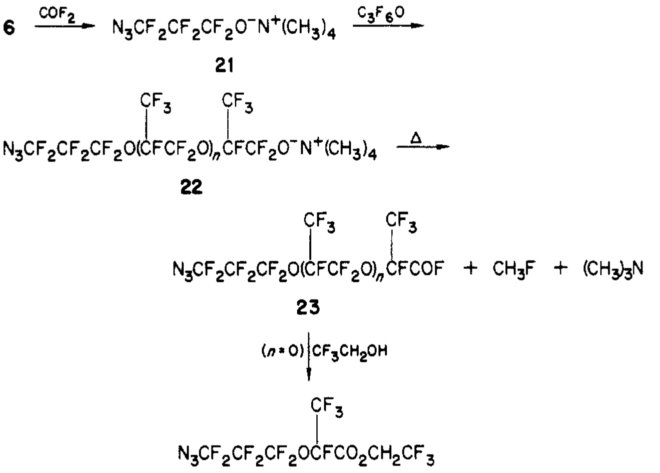
Table I. Formation and Alkylation of $NCCF_2CF_2CO_2^-$

reactants (mol)	solvent[a]	temp (°C)/time	alkylating agent	yield of ester (%)
0.40 KCN, 0.50 TFE, 0.75 CO_2	DMF	100/8 h	$CH_3OSO_2OCH_3$	24[b]
0.40 NaCN, 0.50 TFE, 0.75 CO_2	DMF	50–100/6 h	$CH_3OSO_2OCH_3$	11
0.50 KCN, 0.50 TFE, 0.75 CO_2	tetraglyme	100/8 h	$CH_3OSO_2OCH_3$	40[c]
0.50 NaCN, 0.50 TFE, 0.75 CO_2	tetraglyme	100/8 h	$CH_3OSO_2OCH_2$	39
0.50 NaCN, 0.50 TFE, 0.75 CO_2	5:1 tetraglyme/18-crown-6	50/4 h, 100/8 h	$CH_3OSO_2OCH_3$	28
0.50 NaCN, 0.50 TFE, 0.75 CO_2	diglyme	100/10 h	$CH_3OSO_2OCH_3$	5
0.50 NaCN, 0.50 TFE, 0.75 CO_2	5:1 diglyme/18-crown-6	100/10 h	$CH_3OSO_2OCH_3$	24
0.40 Et_4NCN, 0.40 TFE, 0.75 CO_2	CH_3CN	100/8 h	CH_3OSO_2F	46
0.40 NaCN, 0.50 TFE, 0.75 CO_2	CH_3CN	100/6 h	$CH_3OSO_2OCH_3$	(low)
0.50 NaCN, 0.50 TFE, 0.75 CO_2	HMPA	100/3 h[d]	$CH_3OSO_2OCH_3$	61
0.40 NaCN, 0.50 TFE, 0.75 CO_2	Me_2SO	100/1 h	$CH_3OSO_2OCH_3$	58
0.25 NaCN, 0.50 TFE, 0.75 CO_2	Me_2SO	100/1 h	$CH_3OSO_2OCH_3$	65
0.50 NaCN, 0.50 TFE, 0.75 CO_2	Me_2SO	150/15 min	$CH_3OSO_2OCH_3$	(very low)
0.50 NaCN, 0.50 TFE, 0.75 CO_2	Me_2SO	25[e]	$CH_3OSO_2OCH_3$	58
0.50 NaCN, 0.50 TFE, 0.75 CO_2	Me_2SO	25	$CH_3OSO_2OCH_3$	5[f]
0.25 $Ca(CN)_2$, 0.50 TFE, 0.75 CO_2	Me_2SO	50/6 h, 100/4 h	$CH_3OSO_2OCH_3$	16
0.50 NaCN, 0.50 TFE, 0.75 CO_2	Me_2SO	50/20 h	CH_3Br	20
0.50 NaCN, 0.50 TFE, 0.75 CO_2	Me_2SO	100/1 h	CH_3CH_2Br	28
0.40 NaCN, 0.50 TFE, 0.75 CO_2	Me_2SO	100/1 h	$CH_2{=}CHCH_2Br$[g]	35

[a] 150 mL of solvent; run in a 400-mL metal tube. [b] Plus 33% of $CF_3CF_2CO_2CH_3$. [c] Plus 14% of $CF_3CF_2CO_2CH_3$. [d] Strong initial exotherm. [e] Rapid pressure drop; agitated 20 h. [f] Tetrafluoroethylene injected portionwise at temperature; a similar yield was obtained at 100 °C. [g] Allyl chloride reacted poorly, if at all.

ciable involvement of the azido or cyano moieties.

It is also possible to divert this chemistry to the synthesis of trifluorovinyl ethers, another class of comonomer. For example, azidocarboxylate **6** is converted in the normal manner to alkoxide **21** by carbonyl fluoride and then to low oligomers **22** by reaction with hexafluoropropene epoxide. Upon warming, tetramethylammonium fluoride in equilibrium is conveniently lost as methyl fluoride and trimethylamine,[10] and the residual mixture of volatile acid fluorides **23** can be purified by fractionation.



$$6 \xrightarrow{COF_2} N_3CF_2CF_2CF_2O^-N^+(CH_3)_4 \xrightarrow{C_3F_6O}$$

21

$$N_3CF_2CF_2CF_2O(\overset{CF_3}{\overset{|}{C}}FCF_2O)_n\overset{CF_3}{\overset{|}{C}}FCF_2O^-N^+(CH_3)_4 \xrightarrow{\Delta}$$

22

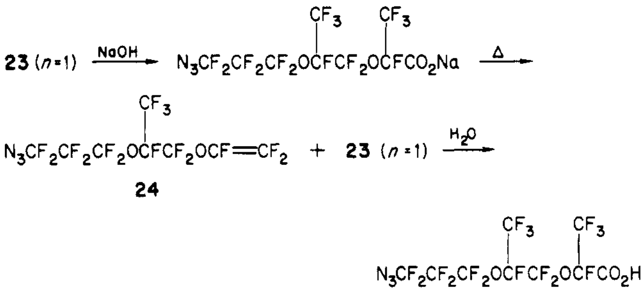
$$N_3CF_2CF_2CF_2O(\overset{CF_3}{\overset{|}{C}}FCF_2O)_n\overset{CF_3}{\overset{|}{C}}FCOF + CH_3F + (CH_3)_3N$$

23

$$\downarrow (n=0)\ CF_3CH_2OH$$

$$N_3CF_2CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCO_2CH_2CF_3$$

The compound **23** ($n = 1$) was selected as having a (C + O)/N ratio sufficiently large to negate any vigorous accidental detonation[11,12] and treated with aqueous sodium hydroxide. The resulting salt was dried under vacuum and then pyrolyzed at 225–230 °C, a temperature range just under the lowest azide decomposition temperature observed in this work. Trifluorovinyl ether **24** was obtained in 37% yield along with regenerated **23**. Elastomeric terpolymers containing 2–4% of **24** with $CF_2{=}CF_2$ and $CF_2{=}CFOCF_3$ were readily prepared by radical initiation in aqueous emulsion.[13]



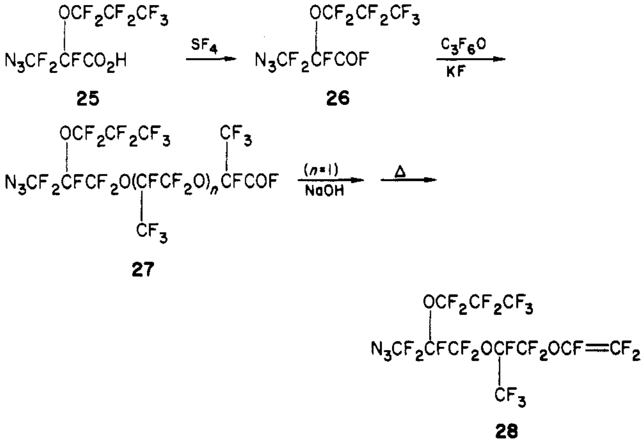
$$\mathbf{23}\ (n=1) \xrightarrow{NaOH} N_3CF_2CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2O\overset{CF_3}{\overset{|}{C}}FCO_2Na \xrightarrow{\Delta}$$

$$N_3CF_2CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2OCF{=}CF_2 + \mathbf{23}\ (n=1) \xrightarrow{H_2O}$$

24

$$N_3CF_2CF_2CF_2O\overset{CF_3}{\overset{|}{C}}FCF_2O\overset{CF_3}{\overset{|}{C}}FCO_2H$$

In most cases, the functionalized fluoro carboxylates can also be converted to the acid fluoride, which will undergo fluoride ion catalyzed condensation with hexafluoropropene epoxide. This sequence is illustrated by the reaction of acid **25** with sulfur tetrafluoride to give acid fluoride **26** and then the condensation of **26** with hexafluoropropene epoxide to give **27**. Conversion of **27** (n = 1) to the trifluorovinyl ether **28** is by the usual sequence of reactions. A copolymer of **28** with tetrafluoroethylene showed the expected DSC exotherm, $T_p \sim 290$ °C, for decomposition of the azide group.



$$N_3CF_2\overset{OCF_2CF_2CF_3}{\overset{|}{C}}FCO_2H \xrightarrow{SF_4} N_3CF_2\overset{OCF_2CF_2CF_3}{\overset{|}{C}}FCOF \xrightarrow[KF]{C_3F_6O}$$

25 **26**

$$N_3CF_2\overset{OCF_2CF_2CF_3}{\overset{|}{C}}FCF_2O(\underset{CF_3}{\underset{|}{C}}FCF_2O)_n\overset{CF_3}{\overset{|}{C}}FCOF \xrightarrow[NaOH]{(n=1)} \xrightarrow{\Delta}$$

27

$$N_3CF_2\overset{OCF_2CF_2CF_3}{\overset{|}{C}}FCF_2O\underset{CF_3}{\underset{|}{C}}FCF_2OCF{=}CF_2$$

28

Fluoro Ketone Chemistry. The functionalized fluoro ketones available from tetrafluoroethylene,[2] particularly

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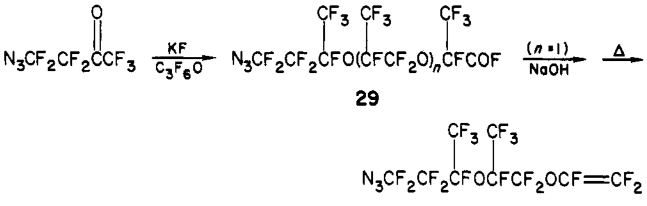
(10) Collie, N. *Trans. Chem. Soc. (London)* **1889**, *55*, 110.

(11) Smith, P. A. S. "Open-Chain Nitrogen Compounds"; W.A. Benjamin, Inc., New York, 1966; Vol. II, p 214. For nonfluorimated azides, (C + O)/N ratio greater than 3 generally assures lack of explosiveness.

(12) Studies carried out in these laboratories showed $N_3CF_2CF_2CO_2CH_3$ to be relatively insensitive to mechanical and electrical shock, but to decompose with near explosive violence when heated to 230–240 °C. On the other hand, $N_3CF_2CF(OCF_2CF_2CF_3)CO_2CH_3$ decomposed near 266 °C at a modest rate.

(13) These copolymers were prepared by Dr. C. A. Aufdermarsh, Polymer Products Dept., Du Pont.

the trifluoromethyl ketones which tend to form stable fluoroalkoxides with fluoride ion,[14] condense directly with hexafluoropropene epoxide in the presence of fluoride ion. These adducts are also precursors to copolymerizable trifluorovinyl ethers such as **30**, obtained from **29**.

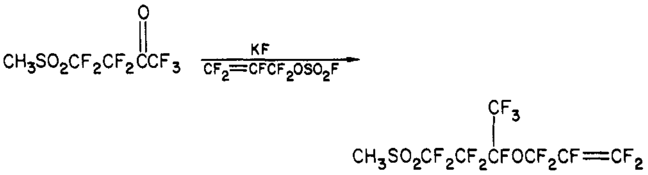


$$N_3CF_2CF_2C(=O)CF_3 \xrightarrow[C_3F_6O]{KF} N_3CF_2CF_2CF(CF_3)O(CF(CF_3)CF_2O)_nCF(CF_3)COF \xrightarrow[NaOH]{(n=1)} \xrightarrow{\Delta} N_3CF_2CF_2CF(CF_3)OCF(CF_3)CF_2OCF{=}CF_2$$

29

30

In addition, these fluoro ketones give functionalized fluoro olefins directly when reacted with fluoride ion/perfluoroallyl fluorosulfate. Thus, sulfone **31** is obtained from the appropriate keto sulfone as indicated.



$$CH_3SO_2CF_2CF_2C(=O)CF_3 \xrightarrow[CF_2=CFCF_2OSO_2F]{KF} CH_3SO_2CF_2CF_2CF(CF_3)OCF_2CF{=}CF_2$$

31

Experimental Section

Unless noted otherwise, IR and NMR spectra were taken on CCl_4 solutions.

Ethyl and Allyl 3-Cyanotetrafluoropropionates (3, R = CH_3CH_2; $CH_2{=}CHCH_2$). A sample of methyltriethylammonium salt **4a** was reacted with excess ethyl bromide in dimethyl sulfoxide at 25 °C for 5 days. The volatile product was tranferred at 2 mm and then fractionated to give 30% of ethyl 3-cyanotetrafluoropropionate, bp 58 °C (100 mm): IR: 2990 (saturated CH), 2250 (CN), 1775 (CO), and 1300–1100 cm^{-1} (CF, CO); ^1H NMR δ 4.53 (q, J_{HH} = 7.3 Hz, 2 H, CH_2), 1.43 (t, J_{HH} = 7.3 Hz, 3 H, CH_3); ^{19}F NMR ϕ −107.6 (t, J_{FF} = 6.0 Hz, 2 F, CF_2CN), −123.3 (t, J_{FF} = 6.0 Hz, 2 F, $CF_2C{=}O$); MS, *m/e* 199.0265 (M^+; calcd for $C_6H_5F_4NO_2$, 199.0256). Anal. Calcd for $C_6H_5F_4NO_2$: C, 36.19; H, 2.53; N, 7.04. Found: C, 36.55; H, 2.74; N, 6.99.

Allyl 3-cyanotetrafluoropropionate, bp 55 °C (50 mm), was prepared as indicated in Table I: IR 3090 (unsaturated CH), 2960 and 2860 (saturated CH), 2260 (CN), 1785 (CO), 1650 (C=C), and 1200–1100 cm^{-1} (CF, CO); ^1H NMR δ 5.6 (2nd order m, 3 H, =CH), 4.92 (d, J_{HH} = 5.4 Hz, 2 H, CH_2); ^{19}F NMR ϕ −107.5 (t, J_{FF} = 5.8 Hz, 2 F, CF_2CN), −119.5 (t, J_{FF} = 5.8 Hz, 2 F, $CF_2C{=}O$). Anal. Calcd for $C_7H_5F_4NO_2$: C, 39.82; H, 2.39; N, 6.64. Found: C, 39.92; H, 2.49; N, 6.75.

Isomerization to *N*-Methyltetrafluorosuccinimide. A 250-mL Carius tube charged with 45.0 g (0.243 mol) of **3** (R = CH_3) and 2.0 g of tetraphenyltin was heated at 150–160 °C for 1 day, 175 °C for 1 day, and 185–195 °C for 1 day. Crystalline product formed on cooling. The mixture was heated at 185–195 °C for 2 more days, and then volatile products were separated from tetraphenyltin at 0.01 mm. Starting cyano ester, 22.1 g (49%), identified by IR, was recovered by warming the volatile products at 45 °C (10 mm). The residual solid was sublimed at 50 °C (1 mm) to give 21.4 g (48% conversion, 93% yield) of *N*-methyltetrafluorosuccinimide, mp 96–97 °C: IR (KBr) 1792 and 1755 (imide CO), 1165 and 1080 cm^{-1} (CF); ^1H NMR (acetone-d_6) δ 3.28 (m, NCH_3); ^{19}F NMR ϕ −126.9 (m, CF_2), with multiplets weakly coupled to each other; MS, *m/e* 185 (M^+), 157 (M^+ − CO), 128 (M^+ − CH_3NCO), 100 ($C_2F_4^+$); mass measured M^+ 185.0095, calcd for $C_5H_3F_4NO_2$ 185.0098. Anal. Calcd for $C_5H_3F_4NO_2$: C, 32.45; H, 1.63; N, 7.57. Found: C, 32.21; H, 1.60; N, 7.72.

Synthesis of Dimethyl Tetrafluorosuccinate. A mixture of 224 g (1.21 mol) of $NCCF_2CF_2CO_2CH_3$, 112 g (3.5 mol) of methanol, 120 g (1.22 mol) of 97% H_2SO_4, and 18.0 g (1.0 mol) of water was stirred at 60–65 °C for 2 days. Fractionation afforded 213 g (80%) of dimethyl tetrafluorosuccinate, bp 50–54 °C (4.2 mm), identified by comparison of the IR spectrum to that of an authentic sample.

Methyltriethylammonium 3-Cyanotetrafluoropropionate (4a) and Tetramethylammonium 3-Cyanotetrafluoropropionate (4b). Most nucleophiles attack cyano ester **3** (R = CH_3) rather indiscriminately, but amines under mild conditions react selectively at the ester group. A homogeneous solution of 9.3 g (0.05 mol) of the cyano ester and 5.1 g (0.05 mol) of triethylamine in 25 mL of ether was stirred at 25 °C while a second layer formed slowly over 4 days; no increase was observed in an additional 2 days. Removal of volatiles under vacuum at 25 °C gave 92% of a deliquescent yellow solid, **4a**: mp 52–55 °C; IR ($CDCl_3$) 2965 (saturated CH), 2255 (CN), 1690 (CO_2^-), and 1250–1100 cm^{-1} (CF); ^1H NMR ($CDCl_3$) δ 3.47 (q, J_{HH} = 7.1 Hz, 6 H, CH_2N), 3.08 (s, 3 H, CH_3N), 1.37 (t, J_{HH} = 7.1 Hz, of m, 9 H, CH_3); ^{19}F NMRϕ −108.5 (t, J_{FF} = 8.4 Hz, 2 F, CF_2CN), −119.3 (t, J_{FF} = 8.4 Hz, 2 F, CF_2 C=O).

A solution of 40.7 g (0.22 mol) of methyl 3-cyanotetrafluoropropionate in 50 mL of ether was stirred while 11.8 g (0.20 mol) of trimethylamine was distilled in. A mildly exothermic reaction was accompanied by precipitation of colorless solid. The mixture was stirred for 1 h and allowed to stand overnight. Volatiles were removed at full pump vacuum to leave 44.6 g (91%) of pure tetramethylammonium 3-cyanotetrafluoropropionate, mp 147–148 °C dec, not deliquescent and insoluble in chloroform: IR (Nujol) 2260 (CN), 1680 (broad, CO_2^-), 1140 cm^{-1} (CF); ^1H NMR (Me_2SO-d_6) δ 3.13 (s, CH_3); ^{19}F NMR ϕ −107.8 (t, J_{FF} = 9.5 Hz, 2 F, CF_2CN), −118.8 (t, J_{FF} = 9.5 Hz, 2 F, $CF_2C{=}O$). Anal. Calcd for $C_8H_{12}F_4N_2O_2$: C, 39.35; H, 4.95; N, 11.47. Found: C, 39.30; H, 4.89; N, 11.37.

3-Iodotetrafluoropropionitrile (5). A mixture of 44 g (0.18 mol) of **4b**, 63.5 g (0.25 mol) of iodine, and 200 mL of dry dimethylformamide was stirred and heated slowly to reflux. Reaction commenced at about 140 °C and the pot was ultimately taken to 160 °C while distillate was removed over a 1-h period, bp 77–150 °C. Fractionation of the distillate afforded 18.9 g (42%) of 3-iodotetrafluoropropionitrile, bp 60 °C, GC pure; IR 2260 (CN), 1250–1100 cm^{-1} (CF); ^1H NMR none; ^{19}F NMR ϕ −63.4 (t, J_{FF} = 10.7 Hz, 2 F, CF_2I), −100.8 (t, J_{FF} = 10.7 Hz, 2 F, CF_2CN); MS, *m/e* 253 (M^+), 177 (ICF_2^+), 127 (I^+), 126 (M^+ − I), 107 ($CF_2{=}CFCN^+$), 100 ($C_2F_4^+$), 76 ($NCCF_2^+$). Anal. Calcd for C_3F_4IN: C, 14.24; N, 5.54. Found: C, 14.22; N, 5.67.

Tetramethylammonium 3-Azidotetrafluoropropionate (6) and 1-Azido-2-iodotetrafluoroethane (9). Procedure for **6** is the same as for **4b**: 68% yield; mp 144–145 °C dec; IR (Nujol) 2170 (N_3), 1680 (br, CO_2^-), 1250–1100 cm^{-1} (CF); ^1H NMR (Me_2SO-d_6) δ 3.25 (s, CH_3); ^{19}F NMR ϕ −90.8 (t, J_{FF} = 6.2 Hz, 2 F, CF_2N_3), −115.8 (t, J_{FF} = 6.2 Hz, 2 F, $CF_2C{=}O$). Anal. Calcd for $C_7H_{12}F_4N_4O_2$: C, 32.31; H, 4.65; N, 21.53. Found: C, 32.23; H, 4.56; N, 21.30.

A mixture of 41.4 g (0.16 mol) of azidopropionate **6**, 63.5 g (0.25 mol) of iodine, and 200 mL of dry dimethylformamide was stirred and heated to 135 °C, where gas evolution commenced. Heating was continued while distillate was collected, bp 50–149 °C, and the strong gas evolution subsided. Redistillation afforded 13.4 g (31%) of 1-azido-2-iodotetrafluoroethane, bp 41–43 °C (150 mm): IR 2160 (N_3), 1300–1100 cm^{-1} (CF); ^1H NMR none; ^{19}F NMR ϕ −62.9 (t, J_{FF} = 7.7 Hz, 2 F, CF_2I), −90.2 (t, J_{FF} = 7.7 Hz, 2 F, CF_2N_3). The compound is too volatile for conventional weighing techniques, and an attempt to flame seal it in a capillary tube for weighing caused it to detonate. Elemental analyses were, therefore, unsatisfactory.[15] Anal. Calcd for $C_2F_4IN_3$: F, 28.26; I, 47.19. Found: F, 24.58; I, 44.59.

Tetramethylammonium 3-Methoxytetrafluoropropionate (7) and Methyl 2-Iodotetrafluoroethyl Ether (10). Trimethylamine and methyl 3-methoxytetrafluoropropionate were

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[14] Evans, F. W.; Litt, M. H.; Weidler-Kubranek, A. M.; Avonda, F. P. *J. Org. Chem.* **1968**, *33*, 1837.

[15] Banks, R. E.; McGlinchey, M. J. *J. Chem. Soc. C* **1971**, 3971. These authors report the synthesis of N_3CF_2CFXI (X = Cl, CF_3) by azide-catalyzed addition of IN_3 to the olefins. Their elementary analyses were also unsatisfactory.

reacted for 6 h in acetonitrile and then volatiles were removed to leave 89% of tetramethylammonium 3-methoxytetrafluoropropionate as a deliquescent solid, mp 110–115 °C; IR ($CDCl_3$) 2890 and 2950 (saturated CH), 1685 (CO_2^-, br), 1250–1100 cm^{-1} (CF); ^1H NMR (CD_3CN) δ 3.60 (s, 3 H, CH_3O), 3.21 (s, 12 H, CH_3N); ^{19}F NMR ϕ −90.6 (t, J_{FF} = 4.5 Hz, 2 F, CF_2O), −117.5 (t, J_{FF} = 4.5 Hz, 2 F, $CF_2C{=}O$).

Reactions of **7** with iodine in dimethylformamide and in diglyme gave little if any of iodide **10**. However, formation and thermolysis of the acyl iodide did provide **10**. 3-Methoxytetrafluoropropionyl chloride, bp 85–86 °C, was prepared by heating sodium 3-methoxytetrafluoropropionate with benzotrichloride. Then KI (166 g, 1.0 mol) and 97.0 g (0.50 mol) of 3-methoxytetrafluoropropionyl chloride were heated at 200 °C for 8 h under autogenous pressure. The reaction mixture was poured into 1 L of water, and the lower layer was washed with water, dried, and distilled to give 23.7 g (18%) of methyl 2-iodotetrafluoroethyl ether, bp 89–90 °C: IR 3010, 2960, and 2860 (saturated CH), 1250–1100 cm^{-1} (CF, CO); ^1H NMR δ 3.67 (s, CH_3O); ^{19}F NMR ϕ −63.1 (t, J_{FF} = 7.0 Hz, 2 F, CF_2I), −93.2 (t, J_{FF} = 7.0 Hz, 2 F, CF_2O). Anal. Calcd for $C_3H_3F_4IO$: C, 13.97; H, 1.17. Found: C, 14.39; H, 1.38.

Methyl 3-(Methylsulfonyl)tetrafluoropropionate and Tetramethylammonium 3-(Methylsulfonyl)tetrafluoropropionate (8). $NaSCH_3$ was prepared by distilling 24 g (0.50 mol) of methyl mercaptan into a stirred suspension of 24 g (0.50 mol) of 50% NaH/mineral oil in 170 mL of dimethyl sulfoxide over a 2-h period. The mixture was charged into a 400-mL tube with 27 g (0.6 mol) of CO_2 and 50 g (0.50 mol) of tetrafluoroethylene and shaken at 50 °C for 8 h. The reaction mixture was poured into a cold solution of 300 mL of concentrated HCl in 1 L of water, and the resulting mixture was extracted continuously with ether. Removal of volatiles from the extracts at 5 mm gave 94.6 g of crude $CH_3SCF_2CF_2CO_2H$. This product was stirred at 85–95 °C while a mixture of 125 mL (ca. 1.2 mol) of 30% H_2O_2 and 75 mL of acetic acid was added dropwise over 2 h. The mixture was then stirred at 90–95 °C for 3 h, after which volatiles were removed under vacuum. The residual oil was extracted with pentane to remove mineral oil and then refluxed 1 h with 500 mL of methanol and 2 mL of concentrated HCl. Chloroform (500 mL) was added, the mixture was distilled to a head temperature of 63 °C. Another 500 mL of methanol and 1 ml of concentrated HCl were added, and the esterification was allowed to proceed at 25 °C for 3 days. Chloroform (500 mL) was added and the mixture was fractionated to give 64.0 g (54%) of methyl 3-(methylsulfonyl)tetrafluoropropionate,[16] bp 75 °C (1.2 mm): IR (neat) 3020, 2970, 2940, and 2860 (saturated CH), 1780 (C=O), 1355 (SO_2), 1250–1100 cm^{-1} (CF, CO, SO_2); ^1H NMR ($CDCl_3$) δ 3.99 (s, 3 H, CH_3O), 3.16 (t of t, J_{HF} = 1.8, 0.7 Hz, 3 H, CH_3SO_2); ^{19}F NMR ϕ −116.4 (t, J_{FF} = 3.8 Hz, of t, J_{HF} = 2 Hz, 2 F, CF_2SO_2), −117.5 (t, J_{FF} = 3.8 Hz, 2 F, $CF_2C{=}O$). Anal. Calcd for $C_5H_6F_4O_4S$: C, 25.22; H, 2.54. Found: C, 25.49; H, 2.98.

Procedure for **8** was the same as for **4b**: 88% yield; mp 98–100 °C, deliquescent crystals; ^1H NMR (Me_2SO-d_6) δ 3.40 (t, J_{HF} = 2 Hz, 3 H, CH_3SO_2), 3.17 (s, 12 H, $(CH_3)_4N^+$); ^{19}F NMR ϕ −112.3 (t, J_{FF} = 3.0 Hz, 2 F, $CF_2C{=}O$), −114.4 (t, J_{FF} = 3.0 Hz, of m, 2 F, CF_2SO_2). Anal. Calcd for $C_8H_{15}F_4NO_4S$: C, 32.32; H, 5.09; N, 4.71. Found: C, 32.20; H, 5.17; N, 4.44.

Trimethylsilyl 3-Cyanotetrafluoropropionate (11). A sample of cyano ester **3** (R = CH_3) was reacted with an equivalent of triethylamine in ether at 25 °C for 6 days to give 55.6 g (0.2 mol) of crude methyltriethylammonium salt. The salt was dissolved in 150 mL of tetraglyme and stirred while a solution of 24.2 g (0.10 mol) of bis(trimethylsilyl) sulfate[17] in 150 mL of tetraglyme was added rapidly. The mixture was stirred overnight, and volatiles were removed under vacuum. Fractionation of the volatiles gave 17.3 g (36%) of trimethylsilyl 3-cyanotetrafluoropropionate, bp 73 °C (100 mm): IR 2980 (saturated CH), 2250 (CN), 1765 (C=O), 1200–1100 cm^{-1} (CF); ^1H NMR δ 0.40 (s, CH_3); ^{19}F NMR ϕ −108.0 (t, J_{FF} = 6.5 Hz, 2 F, CF_2CN), −120.2 (t, J_{FF} = 6.5 Hz, 2 F, $CF_2C{=}O$). Anal. Calcd for $C_7H_9F_4NO_2Si$: C, 34.57; H, 3.72; N, 5.76. Found: C, 34.80; H, 3.84; N, 5.98.

3-Cyanotetrafluoropropionyl Fluoride (14) and Perfluoro-5-oxa-7-octenenitrile (16). A solution of 53.9 g (0.2 mole of salt **4a** in 300 mL of diglyme was stirred at −10 to −5 °C while 46.0 g (0.20 mol) of perfluoroallyl fluorosulfate was added rapidly. The mixture was stirred at −10 to −5 °C for 1 h and then at −5 to 0 °C for 4 h. Removal of volatiles at 35 °C (5 mm) through a liquid N_2 trap and fractionation gave 10.0 g (29%) of 3-cyanotetrafluoropropionyl fluoride, bp 19–20 °C: IR (gas phase) 2265 (CN), 1888 (COF), 1300–1100 cm^{-1} (CF); ^{19}F NMR (0 °C) ϕ 25.8 (t of t, J_{FF} = 10.1, 5.0 Hz, 1 F, COF), −106.7 (d of t, J_{FF} = 5.0, 4.6 Hz, 2 F, CF_2CN), −118.5 (d of t, J_{FF} = 10.1, 4.6 Hz, 2 F, $CF_2C{=}O$).

Further fractionation gave 3.9 g of recovered perfluoroallyl fluorosulfate, bp 62–63 °C, and then 8.0 g (12%) of perfluoro-5-oxa-7-octenenitrile, bp 81–83 °C: IR 2265 (CN), 1790 (C=C), 1300–1100 cm^{-1} (CF, CO); ^{19}F NMR ϕ −71.9 (d of d of t of d, J_{FF} = 25.2, 13.9, 11.6, 7.3 Hz, 2 F, $CCF_2C{=}$), −83.7 (t of t of m, J_{FF} = 11.6, 9, 2 F, OCF_2), −91.0 (d of d of t, J_{FF} 50.8, 39.5, 7.3 Hz, 1 F, *cis*-$CF_2CF{=}CF\mathbf{F}$), −104.7 (d of d of t, J_{FF} = 118.0, 50.8 25.2 Hz, 1 F, *trans*-$CF_2CF{=}C\mathit{F}F$, −106.4 (t of t of d, J_{FF} = 8.8, 4.4, 1.6 Hz, 2 F, CF_2CN), −127.5 (t of t, J_{FF} = 4.4, 2.3 Hz, 2 F, CF_2), −190.8 (d of d of t of t, J_{FF} = 118.0, 39.5, 13.9, 1.6 Hz, 1 F, $CF_2C\mathbf{F}{=}$). Anal. Calcd for $C_7F_{11}NO$: C, 26.02; N, 4.34. Found: C, 26.36; N, 4.41.

Higher yields of **16** are available when carbonyl fluoride is used to prepare intermediate alkoxide **15**. Dry salt **4b**, obtained from 13.6 g (0.23 mol) of trimethylamine and 42.6 g (0.23 mol) of **3** (R = CH_3), was dissolved in 300 mL of diglyme and stirred at −15 °C while 16.8 g (0.255 mol) of carbonyl fluoride was passed in slowly. The mixture was stirred at −10 to −3 °C for 1 h and then cooled at −20 °C while 58.2 g (0.25 mol) of perfluoroallyl fluorosulfate was added all at once. The stirred mixture (mechanical stirrer) was allowed to come to −5 °C and held at −5 °C to 0 °C for 1 h and then poured into 1.5 L of ice water. The lower layer was washed with water, dried, and distilled to afford 36.8 g (50%) of perfluoro-5-oxa-3-octenenitrile, bp 83–85 °C.

4-Methoxyhexafluorobutyronitrile (17) and *N*-Methylhexafluorobutanelactam (18). A solution of 53.2 g (0.2 mol) of crude **4a** in 300 mL of diglyme was stirred at −15 to −10 °C while 15 g (0.23 mol) of carbonyl fluoride was passed in slowly enough to be absorbed. At this point, uptake of COF_2 had become extremely slow. The mixture was stirred at −10 to −5 °C for 2.5 h. Dimethyl sulfate (31.5 g, 0.25 mol) was added, and the mixture was stirred at −5 to 0 °C for 30 min. No precipitate was noted, so the reaction was continued at 10 °C for 1.5 h, where solid did form. Volatiles were removed at 45 °C (5 mm) and fractionated to give 13.6 g (33%) of 4-methoxyhexafluorobutyronitrile, bp 65–67 °C: IR 3010, 2960, and 2870 (saturated CH), 2250 (CN), 1250–1100 cm^{-1} (CF, CO); ^1H NMR δ 3.73 (s, OCH_3); ^{19}F NMR ϕ −88.9 (t of t, J_{FF} = 7.7, 4.5 Hz, 2 F, CF_2O), −106.8 (t of t, J_{FF} = 7.7, 5.5 Hz, 2 F, CF_2CN), −128.0 (p, J_{FF} = 5 Hz, 2 F, CF_2).

Further distillation afforded 5.5 g (13%) of *N*-methylhexafluorobutanelactam, bp 94–98 °C, ca. 90% pure: GC/MS, largest minor component is **17**; major component *m/e* 207 (intense M^+), 188 (M^+ − F), 150 ($C_3F_6^+$), 131 ($C_3F_5^+$), 100 ($C_2F_4^+$), 79 ($CF_2{=}NCH_3^+$), 78($CF_2{=}NCH_2^+$), 69(CF_3^+), and 57 ($CH_3N{=}C{=}O^+$) (the fragmentation pattern and intense parent ion support the cyclic structure); IR 3000 and 2960 (saturated CH), 1785 (C=O), 1250–1100 cm^{-1} (CF); ^1H NMR δ 3.07 (s, NCH_3); ^{19}F NMR ϕ −100.9 (t after H decoupling, J_{FF} = 3.5 Hz, 2 F, CF_2N), −127.2 (t, J_{FF} = 5.5 Hz, 2 F, $CF_2C{=}O$), 134.3 (t of t, J_{FF} = 5.5, 3.5 Hz, 2 F, CF_2).

Methyltriethylammonium 3-Azidotetrafluoropropionate (19) and Perfluoro-4-oxa-6-heptenyl Azide (20). For **19**: 99% yield; IR ($CHCl_3$) 3020 (saturated CH), 2170 (N_3), 1690 (CO_2^-), 1250–1100 cm^{-1} (CF); ^1H NMR (Me_2SO-d_6) δ 3.31 (q, J_{HH} = 7 Hz, 6 H, CH_2), 2.93 (s, 3 H, NCH_3), 1.22 (t, J_{HH} = 7 Hz, 9 H, CH_3); ^{19}F NMR ϕ −90.8 (t, J_{FF} = 6.3 Hz, 2 F, CF_2N_3), −115.6 (t, J_{FF} = 6.3 Hz, 2 F, $CF_2C{=}O$).

Crude salt **19** (54.9 g, ca. 0.18 mol) was dissolved in 300 mL of diglyme and stirred at −20 to −15 °C while 13.5 g (0.20 mol) of COF_2 was passed in slowly enough to be completely absorbed. The mixture was stirred at 0 °C for 1 h, after which 46.0 g (0.20 mol) of perfluoroallyl fluorosulfate was added rapidly at −5 to 0 °C. Solids were broken up, and the mixture was stirred at −5

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[16] Kimoto, K.; Miyauchi, H.; Ohmura, J.; Ebisawa, M.; Hane, T., U.K. Patent Appl. 2 051 831, 1981. An alternative synthetic scheme is used to prepare the corresponding ethyl ester.

[17] Schmidt, M.; Schmidbauer, H. *Chem. Ber.* **1961**, *94*, 2446. A convenient preparation of bis(trimethylsilyl) sulfate is reported.

to 0 °C for 1.5 h and at 0–5 °C for 1 h, and then was poured into 1.5 L of cold water. The organic layer was washed with 200 mL of cold water, dried over $CaSO_4$, and distilled to give 21.3 g (35% from $N_3CF_2CF_2CO_2CH_3$) of perfluoro-4-oxa-6-heptenyl azide, bp 59–60 °C (110 mm): IR 2160 (N_3), 1790 (C=C), 1250–1100 cm^{-1} (CF, CO); ^{19}F NMR ϕ −72.0 (d of d of t of d, J_{FF} = 25.0, 14.0, 12.3, 7.3 Hz, 2 F, $OCF_2{=}$), −84.3 (t of t of m, J_{FF} = 12.3, 9 Hz, 2 F, OCF_2CF_2), −89.6 (t of m, J_{FF} = 9 Hz, 2 F, CF_2N_3), −92.0 (d of d of t, J_{FF} = 52.3, 39.1, 7.3 Hz, 1 F, *cis*-$\mathrm{CF_2CF{=}CF}F$), −105.3 (d of d of t, J_{FF} = 117.7, 52.3, 25.0 Hz, 1 F, *trans*-$\mathrm{CF_2CF{=}CF}F$), −128.3 (br s, 2 F, CF_2), −190.5 (d of d of t of t, J_{FF} = 117.7, 39.1, 14.0, 1.6 Hz, 1 F, $\mathrm{CF_2C}F{=}$). Anal. Calcd for $C_6F_{11}N_3O$: C, 21.25; N, 12.39. Found: C, 21.85; N, 12.86.

Perfluoro-6-azido-2-methyl-3-oxahexanoyl Fluoride (23, *n* = 0) and Perfluoro-9-azido-2,5-dimethyl-3,6-dioxanonanoyl Fluoride (23, *n* = 1). A mixture of 163.9 g (0.63 mol) of salt **6** and 1 L of tetraglyme was stirred at 0 °C while 61 g (0.92 mol) of carbonyl fluoride was added over 4.5 h. Absorption of carbonyl fluoride slowed at this point. The mixture was stirred at 15–20 °C while 207 g (1.25 mol) of hexafluoropropene epoxide was distilled in over 1.3 h and then stirred overnight at 25 °C. The reaction mixture was warmed to 55 °C (~2.5 mm) to volatilize 258.3 g of product, which was fractionated. There was thus obtained 101.3 g (45%) of **23** (*n* = 0), bp 50–55 °C (100 mm), containing 5–10% of fluoride ion initiated oligomers: IR 2160 (N_3), 1880 (COF), 1300–1100 cm^{-1} (CF, CO): ^{19}F NMR ϕ 25.9 (m, 1 F, COF), −79.2 (A branch d of d of t, J_{FF} = 149, 19.5, 9.0 Hz, 1 F, CFFO), −82.6 (m, 3 F, CF), −86.5 (B branch d of t, J_{FF} = 149, 7.5 Hz, 1 F, CFFO), −89.4 (t, J_{FF} = 8.1 Hz, 2 F, CF_2 N_3), −128.1 (m, 2 F, CF), −131.1 (d of m, J_{FF} = 19.5 Hz, 1 F, CF). Further distillation gave 51.7 g (16%) of pure **23** (*n* = 1), bp 50 °C (9.4 mm): IR (neat) 2160 (N_3), 1880 (COF), 1300–1100 cm^{-1} (CF, CO); ^{19}F NMR ϕ 28.9 (m, 1 F, COF), −79.1 (A branch m, 1 F, CFFO), −80.6 (m, 3 F, CF_3), −81.0 (m, 2 F, CF_2O), −82.7 (m, 3 F, CF_3), −86.0 (B branch m, 1 F, CFFO), −89.6 (t, J_{FF} = 7.5 Hz, 2 F, CF_2N_3), −128.0 (m, 2 F, CF_2), −131.2 (d, J_{FF} = 19 Hz, 1 F, CF), −145.5 (t, J_{FF} = 21.1 Hz, 1 F, CF).

A pure derivative of **23** (*n* = 0) was readily obtained by esterification and fractionation. A mixture of 101 g (0.285 mol) of **23** (*n* = 0) (ca. 90% pure), 23.9 g (0.57 mol) of NaF, and 200 mL of ether was cooled and stirred while 30 g (0.30 mol) of trifluoroethanol was added. The mixture was stirred overnight, after which IR analysis indicated only partial reaction. Another 10 g (0.10 mol) of trifluoroethanol was added and the mixture stirred 5 more days, filtered, and distilled. There was thus obtained 65.1 g (53%) of the 2,2,2-trifluoroethyl ester of **23** (*n* = 0), bp 68–70 °C (20 mm): IR (neat) 2980 (saturated CH), 2160 (N_3), 1800 (C=O), 1300–1100 cm^{-1} (CF, CO); ^1H NMR δ 4.68 (q, J_{HF} = 8.0 Hz, CH_2); ^{19}F NMR ϕ −75.0 (t, J_{HF} = 8.0 Hz, of d, J_{FF} = 2.5 Hz, 3 F, $\mathrm{C}F_3\mathrm{CH_2}$), −79.0 (A branch d of d of t, J_{FF} = 149, 19.6, 8.1 Hz, 1 F, OCFF), −82.9 (d, J_{FF} = 3 Hz, 3 F, CF_3), −86.6 (B branch d of m, J_{FF} = 149 Hz, 1 F, OC*F*F), −89.6 (t of m, J_{FF} = 8.1 Hz, 2 F, CF_2N_3), −128.2 (s, 2 F, CF_2), −129.2 (d of m, J_{FF} = 19.6 Hz, 1 F, CF). Anal. Calcd for $C_8H_2F_{13}N_3O_2$: C, 22.08; H, 0.46; N, 9.66. Found: C, 22.18; H, 0.71; N, 9.80.

Perfluoro-9-azido-5-methyl-3,6-dioxanon-1-ene (24). Compound **23** (*n* = 1) (51.0 g, 0.098 mol) and 150 mL of water were stirred and cooled while a solution of 8.8 g (0.22 mol) of NaOH in 50 mL of water was added slowly to a phenolphthalein end point. Water was evaporated in a stream of air until the residue was semisolid, and the salt was dried at 140–150 °C under vacuum. Pyrolysis was carried out at 225–230 °C, where the pressure dropped from 3.5 mm to 0.2 mm over 5 h. The contents of the −80 °C trap were washed with water, dried, and distilled to afford 16.6 g (37%) of perfluoro-9-azido-5-methyl-3,6-dioxanon-1-ene, bp 55 °C (20 mm): IR (neat) 2160 (N_3), 1840 ($OCF{=}CF_2$), 1300–1100 cm^{-1} (CF, CO); ^1H NMR none; ^{19}F NMR ϕ −80.6 (m, 3 F, CF_3), −81.1 (br m, 2 F, CF_2O), −85.3 (m, 2 F, CF_2O), −89.6 (t, J_{FF} = 7.8 Hz, 2 F, CF_2N_3), −114.4 (2nd order m, 1 F, =CF), −122.6 (2nd order m, 1 F, =CF), −128.0 (s, 2 F, CF_2), −136.2 (2nd order m, 1 F, =CF), −145.5 (t, J_{FF} = 21.0 Hz, 1 F, CF). Anal. Calcd for $C_8F_{15}N_3O_2$: C, 21.11; F, 62.62, N, 9.23. Found: C, 21.11; F, 62.87, N, 9.04.

An undesired side reaction of the salt results in reformation of acid fluoride **23** (*n* = 1) as a byproduct which was converted to the corresponding acid during the water wash. Therefore, the fractionation also gave 7.9 g (16%) of carboxylic acid, bp 63–67 °C (0.06 mm): IR (neat) 3200 (br, OH), 2150 (N_3), 1770 (C=O), 1300–1100 cm^{-1} (CF, CO); ^1H NMR (acetone-d_6) δ 13.3 (s, CO_2H); ^{19}F NMR ϕ −80.2 (m, 3 F, CF_3), −80.5 (br m, 2 F, OCF_2), −82.7 (m, 3 F, CF_3), −83.8 (m, 2 F, OCF_2), −88.8 (m, 2 F, CF_2N_3), −127.5 (m, 2 F, CF_2), −131.5 (m, 1 F, CF), −145.1 (t, J_{FF} = 22 Hz, 1 F, CF). Anal. Calcd for $C_9HF_{16}N_3O_4$: C, 20.78; H, 0.39; N, 8.08. Found: C, 20.88; H, 0.27; N, 8.47.

3-Azido-2-(heptafluoro-*n*-propoxy)trifluoropropionyl Fluoride (26). A 400-mL tube charged with 26.0 g (0.40 mol) of NaN_3, 150 mL of dimethyl sulfoxide, 33 g (0.75 mol) of CO_2, and 106 g (0.40 mol) of perfluoro(propyl vinyl ether) was agitated at room temperature for 8 h and then at 50 °C for 2 h. The reaction mixture was poured into a cold solution of 250 mL of concentrated H_2SO_4 in 900 mL of water and extracted continuously with ether for 7 h. Evaporation of the extracts at 10 mm gave 140 g of crude acid **25** as the hydrate.

The crude acid hydrate, 80 mL of $CF_2ClCFCl_2$, 84 g (2.0 mol) of NaF, and 150 g (1.4 mol) of SF_4 were heated at 80 °C for 12 h in a metal tube. The reaction mixture was filtered, the filter cake rinsed with a little $CFCl_2CF_2Cl$, and the filtrates were distilled to afford 82.9 g (58%) of 3-azido-2-heptafluoro-*n*-propoxytrifluoropropionyl fluoride, bp 51–53 °C (100 mm): IR 2150 (N_3), 1875 (COF), 1300–1100 cm^{-1} (CF, CO); ^{19}F NMR ϕ 26.0 (p, J_{FF} = 6 Hz, 1 F, COF), −79.6 (A branch, d of d of q, J_{FF} = 150, 20, 7.5 Hz, 1 F, CF_2O), −82.0 (t, J_{FF} = 7.5 Hz, 3 F, CF_3), −87.7 (B branch, d of q, J_{FF} = 151, 7.5 Hz, 1 F, OCF_2), −88.6 (A branch, d of t, J_{FF} = 186, 5.5 Hz, 1 F, CF_2N_3), −90.9 (B branch, d of t, J_{FF} = 186, 6.2 Hz, 1 F, CF_2N_3), −129.3 (d of p, J_{FF} = 20, 6 Hz, 1 F, CF), −130.2 (s, 2 F, CF_2).

Perfluoro-6-azido-2-methyl-5-*n*-propoxy-3-oxahexanoyl Fluoride (27, *n* = 0) and Perfluoro-9-azido-2,5-dimethyl-8-*n*-propoxy-3,6-dioxanonanoyl Fluoride (27, *n* = 1). A suspension of 10.0 g (0.17 mol) of flame-dried KF in 72 g (0.20 mol) of **26** and 100 mL of 9:1 adiponitrile/tetraglyme was stirred at 20 °C while hexafluoropropene epoxide was introduced on demand at ca. 1 atm. After a very short induction period, 67 g (0.40 mol) of epoxide was taken up in 2 h while the temperature rose steadily to 42 °C. Distillation of volatiles up to bp 50 °C (0.3 mm) afforded 136 g of liquid, which was then fractionated to give recovered **26** contaminated with epoxide dimer and trimer, bp 51–65 °C (100 mm), followed by 35.0 g (34%) of **27** (*n* = 0), bp 46–47.5 °C (9.5 mm), and 5.2 g (4%) of **27** (*n* = 1), bp 43–46 °C (1.2 mm).

For **27** (*n* = 0): IR (neat) 2170 (N_3), 1890 (COF), 1300–1100 cm^{-1} (CF, CO); ^{19}F NMR ϕ 25.9 (m, 1 F, COF), −77.9 (A branch, d, J_{FF} = 143 Hz, 1 F, OCF_2), −81.8 (AB m, 2 F, OCF_2), −82.2 (t, J_{FF} = 6.4 Hz, 3 F, CF_3), −82.7 (m, 3 F, CF_3), −85.2 (B branch, d of m, J_{FF} = 143 Hz, 1 F, OCF_2), −87.9 (m, 2 F, CF_2N_3), −130.3 (s, 2 F, CF_2), −131.3 (d, J_{FF} = 20.4 Hz, 1 F, CF), −144.5 (t, J_{FF} = 22 Hz, 1 F, CF). Anal. Calcd for $C_9F_{17}N_3O_3$: C, 20.74; N, 8.06. Found: C, 20.47; N, 8.14.

For 2:1 adduct **27** (*n* = 1): IR (neat) 2170 (N_3), 1890 (COF), 1300–1100 cm^{-1} (CF, CO); ^{19}F NMR ($CCl_4/CFCl_3$) ϕ 25.8 (m, 1 F, COF), −79.5 (m, 2 F, OCF_2), −79.9 (A branch, d of m, J_{FF} = 150 Hz, 1 F, OCF_2), −80.5 (m, 3 F, CF_3), −81.8 (m, 2 F, OCF_2), −82.1 (t, J_{FF} = 6.4 Hz, 3 F, CF_3), −82.7 (m, 3 F, CF_3), −85.6 (B branch of d of m, J_{FF} = 150 Hz, 1 F, OCF_2), 88.1 (m, 2 F, CF_2N_3), −130.1 (s, 2 F, CF_2), −130.9 (d, J_{FF} = 20.2 Hz, 1 F, CF), −143.6 (m, 1 F, CF), −145.2 (t, J_{FF} = 22 Hz, 1 F, CF). Anal. Calcd for $C_{12}F_{23}N_3O_4$: C, 20.98; N, 6.12. Found: C, 21.26; N, 6.39.

Perfluoro-9-azido-5-methyl-8-*n*-propoxy-3,6-dioxanon-1-ene (28). An 18.0-g sample (0.026 mol) of **27** (*n* = 1) was stirred with 50 mL of water while 10% NaOH was added dropwise to a permanent phenolphthalein end point. Most of the water was evaporated from the gelatinous mixture in a stream of air, and the residual salts were dried at 140 °C (0.1 mm). Pyrolysis of the dry salts was carried out by raising the temperature from 220 to 235 °C over 5 h; maximum pressure was 1.8 mm. The pyrolyzate which collected in a −80 °C trap was washed with water, dried over $CaSO_4$, filtered, and distilled to afford 7.7 g (48%) of perfluoro-9-azido-5-methyl-8-*n*-propoxy-3,6-dioxanon-1-ene, bp 64–68 °C (9.5 mm): IR (neat) 2150 (N_3), 1835 (C=C), 1300–1100 cm^{-1} (CF, CO). Anal. Calcd for $C_{11}F_{21}N_3O_3$: C, 21.27; N, 6.76. Found: C, 21.10; N, 6.88.

Perfluoro-6-azido-2,4-dimethyl-3-oxahexanoyl Fluoride (29, *n* = 0), Perfluoro-9-azido-2,5,7-trimethyl-3,6-dioxano-

nanoyl Fluoride (29, *n* = 1), and Perfluoro-12-azido-2,5,8,10-tetramethyl-3,6,9-trioxadodecanoyl Fluoride (29, *n* = 2). For **29**, the procedure for **27** was followed with tetraglyme as solvent. For **29** (*n* = 1) 27% yield, bp 58–59 °C (8 mm); IR 2150 (N_3), 1880 (COF), 1300–1100 cm^{-1} (CF, CO); ^{19}F NMR is in accord with a mixture of racemates of $N_3CF_2CF_2CF(CF_3)OCF(CF_3)CF_2OCF(CF_3)COF$. Anal. Calcd for $C_{10}F_{19}N_3O_3$: C, 21.03; N, 7.36. Found: C, 21.12; N, 7.84.

In a similar reaction, 88 g (0.37 mol) of 4-azidoheptafluorobutan-2-one in 100 mL of tetraglyme was added to 5.8 g (0.10 mol) of flame-dried KF in 300 mL of tetraglyme, followed by 125 g (0.75 mol) of hexafluoropropene epoxide added at 0 to −10 °C over 1.5 h. Mixed products were distilled up to bp 92 °C (0.5 mm), a small upper layer of tetraglyme was removed, and the product was fractionated to give 58.1 g (27%) of **29** (*n* = 1), bp 57–65 °C (7.8 mm). For **29** (*n* = 2): 22% yield; bp 60 °C (1.1 mm); IR (neat) 2150 (N_3), 1880 (COF), 1300–1100 cm^{-1} (CF, CO). Anal. Calcd for $C_{13}F_{25}N_3O_4$: C, 21.18; N, 5.70. Found: C, 21.59; N, 6.15.

A similar reaction conducted at 10–20 °C led to 31% of **29** (*n* = 0), 29% of **29** (*n* = 1), and 21% of **29** (*n* = 2).

Perfluoro-9-azido-5,7-dimethyl-3,6-dioxanon-1-ene (30). The procedure was similar to that for **28**: 54% yield; bp 64–66 °C (20 mm); IR (neat) 2150 (N_3), 1840 (C=C), 1300–1100 cm^{-1} (CF, CO). The ^{19}F NMR spectrum was compatible with the assigned structure. Anal. Calcd for $C_9F_{17}N_3O_2$: C, 21.40; N, 8.32. Found: C, 21.58; N, 8.48.

7-(Methylsulfonyl)-5-(trifluoromethyl)-4-oxadecafluorohept-1-ene (31). A mixture of 12.76 g (0.046 mol) of 4-(methylsulfonyl)heptafluorobutanone-2,[2] 2.91 g (0.05 mol) of flame-dried KF, and 100 mL of diglyme was stirred for 15 min. Stirring was continued at 0–5 °C while 10.6 g (0.046 mol) of perfluoroallyl fluorosulfate was added dropwise. The mixture was stirred at 0–5 °C for another 2 h and then poured into 500 mL of cold water. The lower layer was washed with 100 mL of water, dried over $CaSO_4$, and fractionated to give 4.3 g (22%) of **31**: bp 83 °C (1.9 mm); IR (neat) 3040, 3020, and 2930 (saturated CH), 1790 (C=C), 1380 (SO_2), 1250–1100 cm^{-1} (CF, CO); ^1H NMR δ 3.08 (t of t, J_{FF} = 1.8, 0.7 Hz, CH_3); ^{19}F NMR ϕ −69.8 (m, 2 F, OCF_2C=), −78.7 (m, 3 F, CF_3), −92.1 (d of d of t, J_{FF} = 52.8, 39.3, 7.2 Hz, 1 F, *cis*-CF_2CF=CFF), −105.3 (d of d of t, J_{FF} = 117.7, 52.8, 25.1 Hz, 1 F, *trans*-CF_2CF=CFF), −112.6 (A branch d of d, J_{FF} = 266, 13 Hz, 1 F, CF), −116.0 (B branch d of d, J_{FF} = 266, 13 Hz, 1 F, CF), −120.1 (m, 2 F, CF_2), −141.0 (m, 1 F, CF), −190.7 (d of d of t, J_{FF} = 117.7, 39.3, 13.1 Hz, 1 F, CF_2CF=). Anal. Calcd for $C_8H_3F_{13}O_3S$: C, 22.55; H, 0.71. Found: C, 22.26; H, 0.84.

Registry No. **3** (R = CH_2CH_3), 99643-22-8; **3** (R = CH_2=$CHCH_2$), 86413-97-0; **3** (R = CH_3), 86414-22-4; **4a**, 86414-24-6; **4b**, 99643-23-9; **5**, 99643-24-0; **6**, 86414-13-3; **7**, 99643-27-3; **8**, 86414-21-3; **9**, 99643-25-1; **10**, 73606-09-4; **11**, 99643-29-5; **12**, 67641-28-5; **14**, 86414-10-0; **16**, 86402-61-1; **17**, 99643-30-8; **18**, 78159-16-7; **19**, 86414-12-2; **20**, 86402-59-7; **23** (*n* = 0), 99643-31-9; **23** (*n* = 1), 99643-32-0; **23** (2,2,2-trifluoroethyl ester, *n* = 0), 99655-34-2; **24**, 99643-33-1; **25**, 95906-13-1; **26**, 86414-16-6; **27** (*n* = 0), 86414-17-7; **27** (*n* = 1), 86414-18-8; **28**, 86402-57-5; **29** (*n* = 0), 99643-34-2; **29** (*n* = 1), 99605-47-7; **29** (*n* = 2), 99617-52-4; **30**, 99643-36-4; **31**, 99643-37-5; TFE, 116-14-3; CH_3CH_2Br, 74-96-4; KCN, 151-50-8; NaCN, 143-33-9; Et_4NCN, 13435-20-6; $Ca(CN)_2$, 592-01-8; $CF_3CF_2CO_2CH_3$, 378-75-6; $H_3COSO_2OCH_3$, 77-78-1; H_3COSO_2F, 421-20-5; CH_3Br, 74-83-9; CH_2=$CHCH_2Br$, 106-95-6; Ph_4Sn, 595-90-4; $H_3CO(CF_2)_2CO_2CH_3$, 755-73-7; $H_3CO(CF_2)_2COCl$, 85036-72-2; $H_3CO(CF_2)_2CO_2H$, 99643-28-4; $PhCCl_3$, 98-07-7; H_3CSN_9, 5188-07-8; $H_3CS(CF_2)_2CO_2H$, 77705-92-1; $H_3CSO_2(CF_2)_2CO_2CH_3$, 86414-19-9; $[(CH_3)_3SiO]_2SO_2$, 18306-29-1; COF_2, 353-50-4; F_3CCH_2OH, 75-89-8; $N_3(CF_2)_2COCF_3$, 99643-35-3; $H_3CSO_2(CF_2)_2COCF_3$, 99655-35-3; $H_3CO_2C(CF_2)_2CO_2CH_3$, 356-36-5; *N*-methyltetrafluorosuccinimide, 356-39-8; hexafluoropropene epoxide, 428-59-1; perfluoro(propyl vinyl ether), 1623-05-8.

Fluoroalkyl Azide Chemistry

Carl G. Krespan

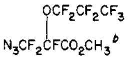
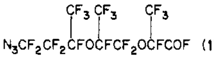
Central Research and Development Department,[†] *E. I. du Pont de Nemours and Co. Inc.,*
Wilmington, Delaware 19898

Received April 24, 1985

A study of the chemistry of newly available functionalized fluoroalkyl azides has uncovered novel transformations of the azide group, indicating its value in the synthesis of nitriles and isocyanates. In addition, conditions for synthesis of functionalized difluoromethylenimines and functionalized azo compounds are outlined. A synthesis of perfluoroallyl azide is presented.

Few polyfluoroalkyl azides were known[1-3] until the recently discovered synthesis based on azide ion, fluoro olefin, and a carbanion trap made a selection of functionalized fluoroalkyl azides readily available.[4-6] A common denominator in the properties of trifluoromethyl azide[2] and the various fluoro azides containing two or more saturated carbons adjacent to the azide group is their relative insensitivity to heat. Makarov et al. reported that CF_3N_3 does explode at 330 °C, while Christe and Schack found[7] that it is stable at room temperature. Similarly, our experience with azides of the type N_3CF_2CFXY (X = F, OR_F; Y = ester, fluoroacyl, fluoroalkyl) indicated them to be stable to over 100 °C but to decompose exothermically at 230–260 °C. Table I summarizes results on thermolysis of four azides of increasing molecular weight. Clearly, the expected trend toward less powerful detonations with decreasing weight percent of azide content in

Table I. Azide Thermal Stability Tests[a]

compd	exotherm onset (°C)	decompstn temp (°C)	max d*p*/d*t* (ϕ/s)
$N_3CF_2CF_2CO_2CH_3$ (**2**)	232	245	420000
$N_3CF_2CF_2CF_2OCF_2CF$=CF_2	250	267	1000
 $N_3CF_2CF(OCF_2CF_2CF_3)CO_2CH_3$ [b]		266	280
 $N_3CF_2CF_2CF(CF_3)OCF(CF_3)CF_2OCF(CF_3)COF$ (17)[b]		265	<1

[a] Conducted in a sealed 100-mL stainless steel pressure vessel where 0.037 mol of compound was heated at 10 °C/min. [b] Stable to the mechanical impact from a 5-kg weight dropped from a height of 55 in. and insensitive to a 10-kV continuous electrostatic arc.

[†] Contribution No. 3741.