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=CF**F**), −105.3 (d of d of t, J_{FF} = 117.7, 52.8, 25.1 Hz, 1 F, *trans*-CF_2CF=C**F**F), −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

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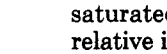
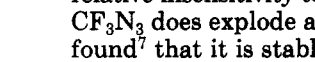
A study of the chemistry of newly available functionalized fluoroalkyl azides has uncovered novel transformations of the azide group, indicating its value in the synthesis of nitriles and isocyanates. In addition, conditions for synthesis of functionalized difluoromethylenimines and functionalized azo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

Table I. Azide Thermal Stability Tests[a]

compd	exotherm onset (°C)	decompstn temp (°C)	max dp/dt (ϕ/s)
$N_3CF_2CF_2CO_2CH_3$ (**2**)	232	245	420000
$N_3CF_2CF_2CF_2OCF_2CF$=CF_2	250	267	1000
		266	280
		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.

Clearly, the expected trend toward less powerful detonations with decreasing weight percent of azide content in

† Contribution No. 3741.

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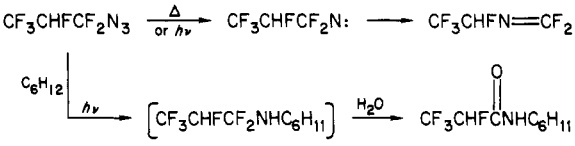
the molecule is observed. The smallest azide, which contains four C atoms, has a rate of decomposition nearly in the explosive range, while even the increase to seven C atoms reduced the rate by a factor of 420 to a decomposition of low power. The low sensitivity to moderate heating extends to mechanical and electrical shock, as indicated in Table I. Indeed, attempts to detonate small samples of several azides with a hammer failed, and distillations were routinely carried out in platinum spinning band stills without incident.

While it is true that detonations have been avoided by working with azides having no unsaturation closer than three carbon atoms (γ, δ) to the azide group and by keeping temperatures below 125 °C at all times, *the potential for violent decomposition is clearly present*, especially in the lower members of the series. Appropriate precautions are, therefore, recommended, including adequate shielding, restricted run size, dilution with several-fold amounts of solvent, and the use of leather gloves and gauntlets.

Other groups, working with two saturated polyfluoroalkyl azides, have found evidence that pyrolysis[8] and photolysis[9] reactions involve nitrene intermediates (e.g., eq 1). The report from one group[9] noted the occurrence



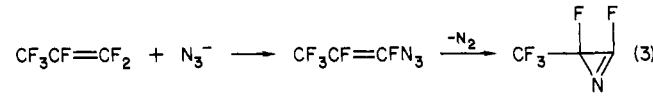
of several violent explosions. One was triggered thermally during attempted combustion analysis, but no explanation is offered for the others, implying a degree of capricious behavior in their azides.

Our sole example of a β,γ-unsaturated azide has been perfluoroallyl azide (1), prepared from azide ion and perfluoroallyl fluorosulfate (eq 2). This material was

$$N_3^- + CF_2{=}CFCF_2OSO_2F \rightarrow \underset{\mathbf{1}}{N_3CF_2CF{=}CF_2} \quad (2)$$

manipulated several times at 25 °C with no noticeable decomposition, but one attempt to transfer a neat sample led to an explosion.[10] While the cause is unknown, the ease with which 1 was set off indicates much greater sensitivity than that of the fluorinated γ,δ-unsaturated azides.[11]

The limited number of known α,β-unsaturated azides (i.e., polyfluorovinyl azides), decompose at 25–60 °C and they have been shown to give 2*H*-azirines[12-15] (as in eq 3).

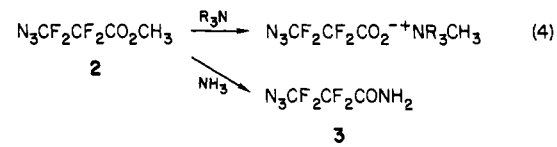


These systems, as well as the fluoroacyl azides, must be handled with care, since neat or concentrated samples may well explode unexpectedly. The ready thermolyses of α,β-unsaturated azides suggest participation of the unsaturated center in a concerted decomposition reaction, but free nitrene has not been excluded as an intermediate.[13,15]

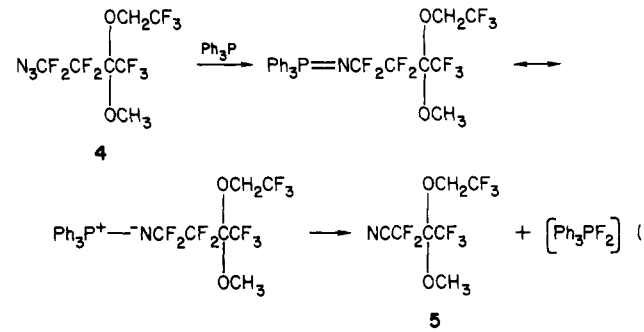
Fluoroaryl azides, which may be viewed as a special class of α,β-unsaturated azide, decompose at intermediate temperatures (80–160 °C).[16,17] In contrast to the tendency to form 2*H*-azirines observed with the fluorovinyl azides, none of the related 3*H*-azepine derivatives could be isolated from fluoroaryl azide decompositions in aromatic amines.[17] Instead, trapping by C–H and N–H insertion reactions provided evidence for at least partial decomposition to a reactive nitrene intermediate.

Herewith are reported details of our studies on the chemistry of the azide group in functionalized fluoroalkyl azides.

Reaction with Acids and Bases. Although a fluoroalkyl group might be expected to render an attached azide group more susceptible than usual to nucleophilic attack, amines do not react appreciably with a fluoroalkylated azide at 25 °C. Thus, trialkylamines react with a methyl ester such as 2 to give a quaternary ammonium salt in good yield by selective attack at the ester group.[6] Similarly, ammonia reacts readily with 2 to form amide 3 (eq 4).



Phosphines such as triphenylphosphine, however, combine readily with the azides, presumably to give phosphatriazines and then phosphazo compounds as normal Staudinger reaction products. As carried out at ca. 25 °C in ether solution, these reactions proceed with fluorine α to nitrogen finally being eliminated to provide nitriles in good yield. Conversion of azide 4 to nitrile 5 is an example (eq 5). Interestingly, related phosphazo derivatives in



which phosphorus is substituted with chlorine rather than

(1) Knunyants, I. L.; Bykhovskaya, E. G. *Proc. Acad. Sci. USSR Chem. Sect. (Engl. Transl.)* **1960**, *131*, 411. Addition of HN_3 to hexafluoropropene gives $CF_3CHFCF_2N_3$.

(2) Makarov, S. P.; Yakubovich, A. Y.; Filatov, A. S.; Englin, M. A.; Nikiforova, T. Y. *Zh. Obshch. Khim.* **1968**, *38*, 709. CF_3N_3 is prepared starting from CF_3NO.

(3) Banks, R. E.; McGlinchey, M. J. *J. Chem. Soc.* **1971**, 3971. Addition of IN_3 to hexafluoropropene and to chlorotrifluoroethylene is reported to give N_3CF_2CFClI and $N_3CF_2CFICF_3$, albeit in modest yields.

(4) (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 4 474 700, 1984.

(5) Krespan, C. G.; Smart, B. E. *J. Org. Chem.*, first paper in a series of three in this issue.

(6) Krespan, C. G. *J. Org. Chem.*, previous paper in this issue.

(7) Christe, K. O.; Schack, C. J. *Inorg. Chem.* **1981**, *20*, 2566.

(8) Knunyants, I. L.; Bykhovskaya, E. G.; Frosin, V. N. *Dokl. Akad. Nauk SSSR* **1960**, *132*, 357.

(9) Banks, R. E.; Berry, D.; McGlinchey, M. J.; Moore, G. J. *J. Chem. Soc. C* **1970**, 1017.

(10) Observation by Dr. D. Ballargeon of these laboratories.

(11) Logothetis, A. L. *J. Am.* Chem. *Soc.* **1965**, *87*, 749. The decomposition of hydrocarbon-based olefinic azides is studied. Thermolysis of allyl azide occurred at 75 °C, while 4-azido-1-pentene required ca. 180 °C. A dipolar intermediate similar to that in eq 8 is proposed for triazoline decompositions.

(12) Knunyants, I. L.; Bykhovskaya, E. G. *Zh. Vses. Khim. Ova. im. D. I. Mendeleeva* **1962**, *7*, 585.

(13) Cleaver, C. S.; Krespan, C. G. *J. Am. Chem. Soc.* **1965**, *87*, 3716.

(14) Krespan, C. G. *J. Org. Chem.* **1969**, *34*, 1278.

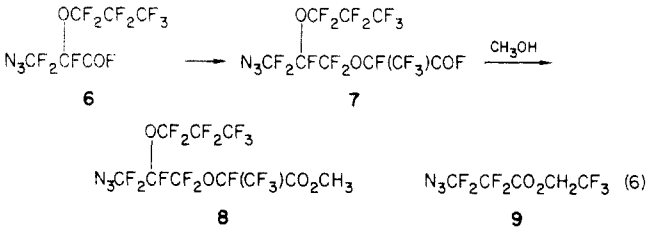
(15) Banks, R. E.; McGlinchey, M. J. *J. Chem. Soc. C* **1970**, 2172.

(16) Birchall, J. M.; Haszeldine, R. N.; Parkinson, A. R. *J. Chem. Soc.* **1962**, 4966.

(17) Banks, R. E.; Prakash, A. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1365.

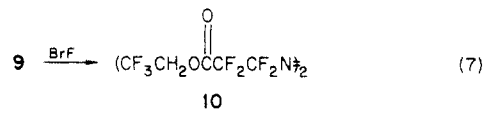
phenyl groups have been isolated and found to be stable to 100 °C.[18] Presumably the trichlorophosphazo derivatives possess a more covalent π system than the triphenyl analogues.

Concentrated sulfuric acid destroys the azide group slowly at 25 °C and rapidly at 75 °C, giving unidentified products. More weakly acidic media can be tolerated, as indicated by the synthesis of acid fluoride **6** from the carboxylic acid and sulfur tetrafluoride,[6] and by the esterification of **7** to give **8** (eq 6).



The acid-catalyzed transesterification of **2** to form **9** was also carried out at 25 °C with preservation of the azide group.[5]

Lewis acids can attack fluoroalkyl azides. Schack and Christe[19] investigated reactions of trifluoromethyl azide with fluorine and halogen fluorides; in the reaction with bromine fluoride, a high yield of perfluoroazomethane was obtained. This reaction can be used to prepare functionalized azo compounds, e.g. **10**, provided the functionality to be carried along is not readily oxidized (eq 7). Sulfur

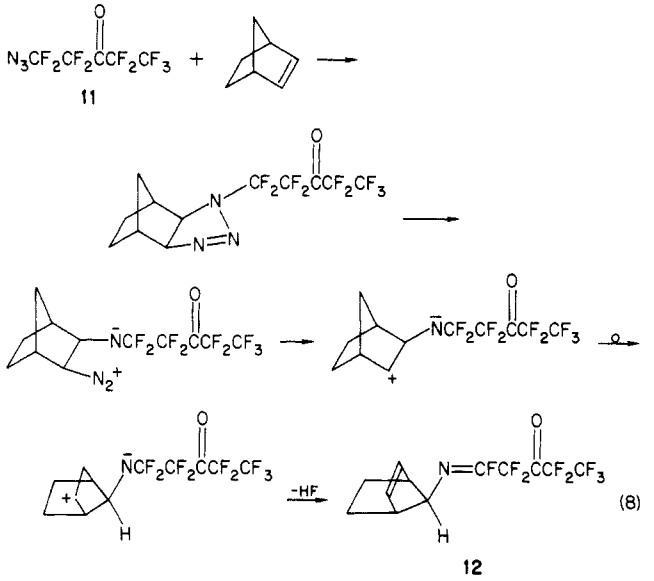


trioxide also reacts slowly with azide, e.g., **11**, at 25 °C, but gives a mixture of sulfonyl fluorides, nitrile, and high-boiling adducts.

Addition to Carbon–Carbon Unsaturation. Addition of azide to olefin generally proceeds by 1,3-cycloaddition to give a triazoline which may readily give secondary products after loss of N_2.[20,21] Simple olefins react so slowly at ordinary temperatures as to be considered unreactive, and one of the known polyfluoroalkyl azides ($CF_3CHFCF_2N_3$) has been reported to be unreactive toward cyclohexene in the dark at room temperature.[9] When the reaction of $N_3CF_2CF(OCF_3)CO_2CH_3$ with 2,3-dimethylbutadiene was run at 25 °C, slow darkening and formation of only traces of precipitate over 10 days indicated a sluggish nonspecific reaction.

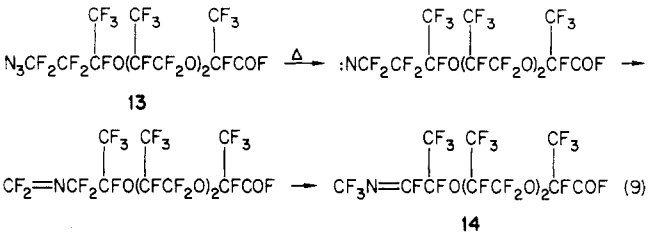
Norbornene, a strained olefin, undergoes a mildly exothermic with azide **11** accompanied by steady evolution of nitrogen. Rearranged adduct **12** was isolated; higher adducts which probably arise from further reaction of **12** with **11** were present, but were not purified.

Norbornenes undergo retro-Diels–Alder reactions in the mass spectrometer to form cyclopentadiene radical cation and neutral olefin fragments. The appearance of a strong $M^+ - C_2H_4$ mass in the spectrum of **12** is thus in accord with a bridgehead substituent. The syn configuration is assigned to this substituent as being the most likely stereochemistry to result from a carbonium ion mechanism operative after formation of a 1,3-dipolar adduct (eq 8).[11]

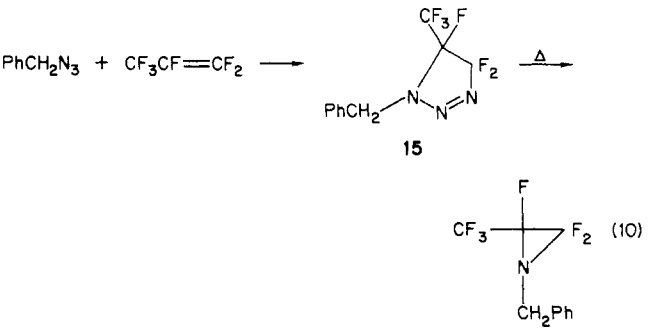


No cycloaddition of azide **3** to the triple bond of diphenylacetylene was observed in acetonitrile at reflux, or at 130 °C in a sealed tube. Decomposition products were obtained at 180 °C.

Thermolysis. Thermolysis of $CF_3CHFCF_2N_3$ in a hot tube at high temperatures (200–280 °C) cleanly afforded $CF_3CHFN{=}CF_2$, provided the reaction is carried out in a platinum tube to avoid migration of the double bond to an internal position.[8] This migration was also observed in the thermolysis of **13** at 280 °C in a static system to give imine **14**. The sequence involving formation of an intermediate nitrene, 1,2-fluoroalkyl shift, and 1,3-migration of fluoride is proposed (eq 9).



The high temperature required for thermolysis to the reactive nitrene and its facile rearrangement discouraged attempts at nitrene addition to a fluoro olefin as a fluoroaziridine synthesis. Slow cycloaddition of benzyl azide to hexafluoropropene at 150 °C has been reported to give triazoline **15**, which could be pyrolyzed to the aziridine with loss of nitrogen (eq 10).[22] This approach has not been successful with the fluoroalkyl azides.



(18) Leidinger, W.; Sundermeyer, W. *J. Fluorine Chem.* **1981/82**, *19*, 85.

(19) Schack, C. J.; Christe, K. O. *Inorg. Chem.* **1983**, *22*, 22.

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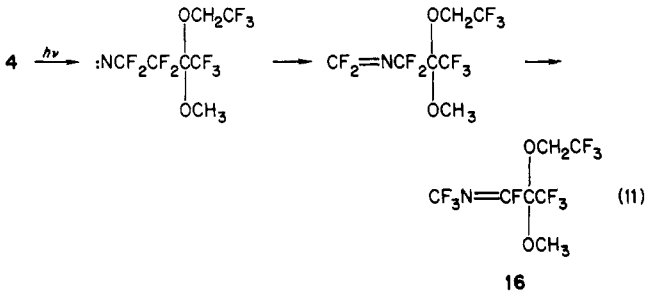
(21) "The Chemistry of the Azido Group"; Patai, S., Ed.; John Wiley: New York, 1971.

(22) Carpenter, W.; Haymaker, A.; Moore, D. W. *J. Org. Chem.* **1966**, *31*, 789.

Photolysis. Photodecomposition of alkyl azides tends strongly toward rearranged imine and N_2 as products,[23] and photolysis of two simple polyfluoroalkyl azides has also been reported to give the corresponding imines.[9] In the fluoroalkyl cases, an indication that nitrene is a discrete intermediate was obtained by photolyses in the presence of cyclohexane and cyclohexene, from which products of fluoroalkylnitrene insertion into CH bonds (not usually seen in intermolecular reactions) were obtained.

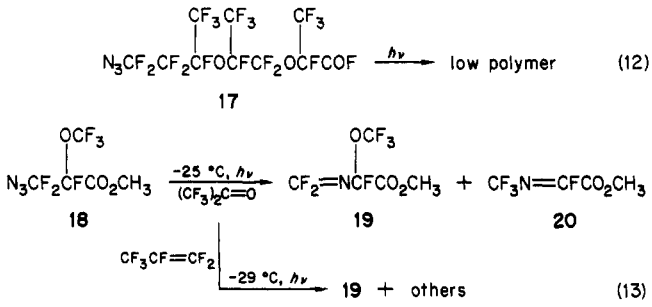
Azide **4**, which contains no UV-active function other than the azide group, exhibits UV absorption of $\epsilon_{254\,nm}^{isooctane}$ 63.6, readily accessible in quartz equipment. Irradiation of **4** in refluxing perfluorodimethylcyclobutane (ca. 40 °C) proceeded with some attack on CH bonds to generate HF and with formation of imine **16** by migration of the C=N to the thermodynamically favored internal position (eq 11).



(11)

16

Since HF formed by side reactions during the photolysis may have caused the 1,3-fluorine migration, azide **17** was photolyzed under the same conditions as **4** in the hope of isolating an unrearranged difluoromethylenimine. The result was formation of low polymer, perhaps through interaction of nitrene with the acid fluoride (eq 12). As a test for oxaziridine or poly(oxaziridine)[24] formation, azide **18** was photolyzed at −25 °C in the presence of excess hexafluoroacetone. Instead of oxaziridine or its polymer, mainly unrearranged imine **19** and a lesser amount of internal imine **20** were obtained (eq 13).



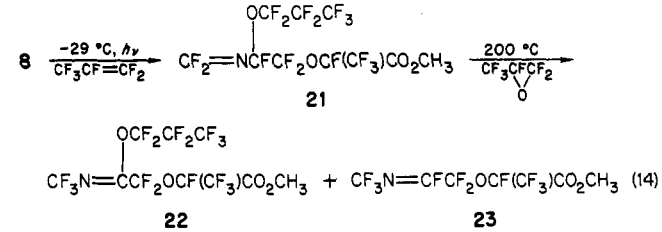
(12)

17

(13)

18 **19** **20**

Not only is hexafluoroacetone unreactive to azide/nitrene under these conditions but the hexafluoropropene does not give aziridine under similar conditions. Thus, with the possible exception of the acid fluoride function, the presumed nitrene intermediate rearranged rather than cycloadd intermolecularly to C=O or C=C. The tendency for **18** to form multiple products at −25 °C, including rearranged imine in which trifluoromethoxy was eliminated rather than fluorine, and the nearly exclusive formation of rearranged imine from **4** at 40 °C suggested that low-temperature photolysis of an azide such as **8** might provide a preferred synthesis of unrearranged imine. Intramolecular insertion of nitrene into CH will be minimized with the two functions appropriately far apart, so the reaction can cleanly give **21** (eq 14).

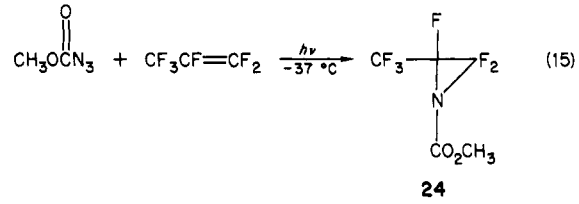


(14)

21 **22** **23**

The availability of difluoromethylenimine **21** prompted an attempt to add difluoromethylene to the double bond. The addition to form aziridine did not appear to go; rather, double bond migration occurred with loss of perfluoropropoxy as well as fluoride.

Fluoroalkylnitrenes appear to be reactive, electrophilic intermediates having a relatively short half-life with respect to a migration of fluoroalkyl from C to N. If this tendency to rearrange is mainly responsible for lack of addition to a fluoro olefin to form aziridine, a negatively substituted nitrene with longer lifetime should form an aziridine. Ethyl azidoformate could not be added thermally to hexafluoropropene, but the photochemically activated azide or resulting nitrene did add to hexafluoropropene to give aziridine **24** (eq 15).[25]



(15)

24

Reaction with Ni(CO)$_4$. When azide **2** was added to a solution of nickel carbonyl in acetonitrile, an exothermic reaction occurred. The two products which were formed (eq 16) are best rationalized by an intermediate nitrenoid

$$2 + Ni(CO)_4 \rightarrow (CO)_3Ni(:NCF_2CF_2CO_2CH_3) \rightarrow \underset{\mathbf{25}}{} NCCF_2CO_2CH_3 + O{=}C{=}NCF_2CF_2CO_2CH_3 \quad (16)$$

26 **27**

species, i.e., nitrene bonded to nickel as in **25**. Elimination of α-fluorine would lead to nitrile **26** and nickel fluoride, while insertion of carbon monoxide also coordinated to nickel into the Ni–N bond followed by dissociation would lead to isocyanate **27**. This combination of nitrene with carbon monoxide (as moderated by Ni(0)) promises to be an easy, direct route to functionalized fluoroalkyl isocyanates, a little known class of compound.

Experimental Section

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

Caution! Since the azide group is of such high energy that it can cause violent detonations, the precautions noted in the Discussion section are recommended for handling these and related fluoroalkyl azides.

Perfluoroallyl Azide (1). A mixture of 3.30 g (0.05 mol) of sodium azide, 0.4 g of methyltricaprylylammonium chloride, 50 mL of toluene, and 50 mL of water was stirred while 11.5 g (0.05 mol) of perfluoroallyl fluorosulfate was added dropwise. The temperature rose to 34 °C during the addition. The mixture was stirred for 3 h and then the toluene layer was dried, and volatiles were distilled trap to trap several times at 25 °C (50 mm) to give 5.2 g (60%) of colorless perfluoroallyl azide: IR (gas phase) 2155 (N_3), 1800 (C=C), 1300–1100 cm^{-1} (CF); ^{19}F NMR ϕ −76.0 (d of d of d, J_{FF} = 22.8, 16.8, 6.9 Hz, 2 F, CF_2), −93.4 (d of d of t, J_{FF}

(23) Kyba, E. P.; Abramovitch, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 735.
(24) Sekiya, A.; Des Marteau, D. D. *Inorg. Chem.* **1979**, *18*, 919. The synthesis and polymerization of a perfluorooxaziridine are described.

(25) This experiment was carried out by Dr. J. Lazar of these laboratories.

= 55.2, 38.1, 6.9 Hz, 1 F, *cis*-$CF_2CF{=}CF$), -106.1 (d of d of t, J_{FF} = 117.0, 55.2, 22.8 Hz, 1 F, *trans*-$CF_2CF{=}CF$), -188.8 (d of d of t, J_{FF} = 117.0, 38.1, 16.8 Hz, 1 F, $CF_2CF{=}$). A small amount (<5%) of starting fluorosulfate was present along with another impurity, probably $CF_2{=}CFCF_2Cl$.

3-Azidotetrafluoropropionamide (3). A mixture of methyl and 2,2,2-trifluoroethyl esters of 3-azidotetrafluoropropionic acid (74.5 g, ca. 0.25 mol of mixed esters) was stirred at 30 °C (cooling) while 7.0 g (0.4 mol) of ammonia was distilled in. The mixture was stirred 1 h at 25 °C and evaporated to dryness at 25 °C (10 mm) to give 38.9 g (84%) of crystalline 3-azidotetrafluoropropionamide, mp 62–63 °C. An analytical sample sublimed at 60 °C (5 mm) had mp 62.5–63.5 °C: IR (Nujol) 3410, 3190 (NH_2), 2140 (N_3), 1665 (amide CO + NH_2, br), 1300–1100 cm^{-1} (CF); ^1H NMR (acetone-d_6) δ 7.93 (br m) and 3.33 (br s) for NH suggesting restricted rotation; ^{19}F NMR ϕ -91.4 (t, J_{FF} = 5.2 Hz, 2 F, CF_2N_3) with apparent central peaks of an AB for $CF_2C{=}O$ at -120.6 (t, J_{FF} = 5.2 Hz, of d, J_{HF} = 2 Hz, 1 F) and -120.7 (t, J_{FF} = 5.2 Hz, of d, J_{HF} = 1.5 Hz, 1 F). Anal. Calcd for $C_3H_2F_4N_4O$: C, 19.36; H, 1.09; N, 30.11. Found: C, 19.58; H, 1.06; N, 30.37.

3-Methoxy-3-(trifluoromethyl)-2,2,6,6,6-pentafluoro-4-oxahexanenitrile (5). A solution of 17.7 g (0.050 mol) of azide **4** in 25 mL of ether was added to a solution of 13.1 g (0.050 mol) of triphenylphosphine in 100 mL of ether. A yellow-orange color developed along with a slight exotherm and slow gas evolution. White solid slowly deposited as the mixture was stirred for 1 day. The solid was filtered off, rinsed with ether, and dried; 12.9 g (87%) of triphenylhydroxyphosphonium fluoride or bifluoride, mp 160–162 °C, was thus obtained: ^1H NMR (acetone-d_6) δ 7.6 (m, Ar CH) with active H exchanged into the acetone-d_6; ^{19}F NMR ϕ -182 (very br, F^-).

The filtrate, shown by IR to contain virtually no N_3, was evaporated to low volume, and product was then transferred under high vacuum to remove solid. Fractionation gave 10.4 g (72%), bp 54 °C (40 mm), of 3-methoxy-3-(trifluoromethyl)-2,2,6,6,6-pentafluoro-4-oxahexanenitrile: IR 3030, 2990, 2910, and 2870 (saturated CH), 2270 (CN), 1250–1100 cm^{-1} (CF, C–O); ^1H NMR δ 4.11 (q, J_{HF} = 7.8 Hz, 2 H, CH_2CF_3), 3.72 (s, 3 H, CH_3O); ^{19}F NMR ϕ -74.4 (t, J_{FF} = 10.0 Hz, 3 F, CF_3), -75.2 (t, J_{HF} = 7.8 Hz, 3 F, CF_3CH_2), -101.2 (q, J_{FF} = 10.0 Hz, 2 F, CF_2). Anal. Calcd for $C_7H_5F_8NO_2$: C, 29.28; H, 1.76; N, 4.88. Found: C, 29.49; H, 1.59; N, 5.10.

Methyl Perfluoro-6-azido-5-*n*-propoxy-2-methyl-3-oxahexanoate (8). A mixture of 51 g (0.10 mol) of **7**, 100 mL of ether, 7 mL of methanol, and 8.4 g (0.20 mol) of NaF was stirred overnight, filtered, and distilled to give 46.6 g (87%) of ester **8**, bp 59 °C (3 mm): IR 3000, 2960, 2850 (saturated CH), 2150 (N_3), 1760 (C=O), 1300–1100 cm^{-1} (CF, CO); ^1H NMR δ 3.93 (s, CH_3O); ^{19}F NMR ϕ -78.1 (A branch, d of m, J_{FF} = 150 Hz, 1 F, CF_2O), -81.7 (m, 2 F, CF_2O), -82.0 (t, J_{FF} = 6 Hz, 3 F, CF_3), -83.1 (s, 3 F, CF_3), -85.0 (B branch, d of m, J_{FF} = 150 Hz, 1 F, CF_2O), -88.2 (m, 2 F, CF_2N_3), -130.2 (s, 2 F, CF_2), -132.3 (d of m, J_{FF} = 19 Hz, 1 F, CF), -144.4 (t, J_{FF} = 23 Hz, 1 F, CF).

3,3'-Azobis(2,2,2-trifluoroethyl tetrafluoropropionate) (10). A mixture of 11.2 g (0.07 mol) of bromine and 6.9 g (0.05 mol) of bromine trifluoride was stirred for 30 min in a Teflon-brand pot with Teflon condenser attached. Then 8.8 g (0.033 mol) of 2,2,2-trifluoroethyl 3-azidotetrafluoropropionate was added and stirring was continued. A very mild exotherm and steady gas evolution ensued. The mixture was stirred overnight and then volatiles (mainly Br_2) were removed at 25 °C (15 min). KF (5.8 g, 0.10 mol) was added, the mixture was stirred for 1 h, and then unreacted azido ester (3.2 g, 36%) was removed at 0.2 mm. Azo compound **10**, 0.7 g (14%) was then volatilized out slowly at 25 °C (0.05 mm): IR (neat) 3000 (saturated CH), 1800 (C=O), 1300–1100 cm^{-1} (CF); Raman (neat) 1590 (N=N), 1800 cm^{-1} (C=O).

The sample was 96% pure: GC/MS, *m/e* 463 (M^+ - F), 444 (M^+ - 2F), 425 (M^+ - 3F), 383 (M^+ - CF_3CH_2O), 355 (M^+ - CF_3CH_2OCO), 317 (M^+ - 2F - CF_3CH_2OCO), 227 ($CF_3CH_2O_2CCF_2CF_2^+$), 208 ($CF_3CH_2O_2CCF{=}CF_2^+$), 177 ($CF_3CH_2O_2CCF_2^+$, weak), 127 ($CF_3CH_2O_2C^+$), 100 ($C_2F_4^+$), 83 ($CF_3CH_2^+$), 69 (CF_3^+).

7-*syn*-[(Octafluoro-3-oxopentylidene)amino]norbornene (12). A mixture of 9.4 g (0.10 mol) of norbornene and 50 mL of CH_2Cl_2 was stirred at 25 °C while 28.9 g (0.10 mol) of 1-azidononafluoropentan-3-one was added dropwise. Gas evolution and a mild exothermic reaction occurred during and after the addition. The mixture was stirred for 2 h, allowed to stand overnight, and distilled to give 12.3 g (37%) of rearranged adduct **12**, bp 28–30 °C (0.5 mm): IR (neat) 3070 (unsaturated CH), 2980 and 2880 (saturated CH), 1790 (C=O), 1755 (C=N), 1575 (C=C, weak), 1250–1100 cm^{-1} (CF); ^1H NMR δ 5.90 (m, 2 H, =CH), 3.73 (s, 1 H, CHN), 2.82 (m, 2 H, bridgehead CH), 1.77 (m, 2 H, CH_2), 1.11 (m, 2 H, CH_2); ^{19}F NMR ϕ-49.3 (t, J_{FF} = 24.3 Hz, 1 F, =CF), -82.6 (m, 3 F, CF_3), -113.4 (d of m, J_{FF} = 24.3 Hz, 2 F, CF_2), -120.4 (t of q, J_{FF} = 7.9, 1.5 Hz, 2 F, CF_2); MS (E.I.), *m/e* 335.0552 (M^+, calcd for $C_{12}H_9F_8NO$, 335.0556), 307.0209 (M^+ - C_2H_4; calcd 307.0243), 188.0687 (M^+ - CF_3CF_2CO; calcd 188.0687), 160.0365 (M^+ - C_2H_4 - CF_3CF_2CO; calcd 160.0374), 138.0714 (M^+ - $CF_3CF_2COCF_2$; calcd 138.0714). Anal. Calcd for $C_{12}H_9F_8NO$: C, 43.00; H, 2.71; N, 4.18. Found: C, 43.25; H, 2.57; N, 4.66.

Perfluoro-11-(methylimino)-2,5,8,10-tetramethyl-3,6,9-trioxaundecanoyl Fluoride (14). A solution of 16.0 g (0.022 mol) of **13** in 20 mL of hexafluoropropene cyclodimer was heated in a 100-mL metal tube at 280 °C for 1 h. Distillation gave 10.2 g (65%) of imine **14**, bp 70 °C (8 mm): IR (neat) 1875 and 1880 (COF), 1770 (N=CF), 1300–1100 cm^{-1} (CF, CO); ^{19}F NMR ϕ 25.4 (m, 1 F, COF), -20.7 (m, 1 F, N=CF), -58.1 (d, J_{FF} = 14 Hz, 3 F, $CF_3N{=}$), -78.9 (m, 3 F, CF_2O + A branch (CFFO), -80.0 (m, 6 F, CF_3), -82.3 (m, 6 F, CF_3), -85.5 (B branch d of m, J_{FF} = 150 Hz, 1 F, CFFO), -126.4 (br m, 1 F, CF), -129.9 (m, 1 F, CF), -142.6 (m, 1 F, CF), -144.3 (t, J_{FF} = 21 Hz, 1 F, CF). Anal. Calcd for $C_{13}F_{25}NO_4$: C, 22.02; N, 1.98. Found: C, 21.80; N, 1.70.

1-[(Trifluoromethyl)imino]-2-methoxy-2-(trifluoromethyl)-1,5,5,5-tetrafluoro-3-oxapentane (16). A two-phase mixture of 25 mL of hexafluoropropene cyclodimer and 17.7 g (0.05 mol) of azide **4** was stirred in a quartz vessel while it was irradiated for 19 h with a spiral 10-W quartz mercury resonance lamp. Some etching, color formation, and precipitation of a small amount of flocculent solid occurred. Fractionation of the single liquid phase gave 6.8 g (42%) of imine **16**, bp 33–34 °C (15 mm): IR (neat) 2970 and 2860 (saturated CH), 1780 (N=CF), 1300–1100 cm^{-1} (CF, CO); ^1H NMR δ 4.10 (2nd order m, 2 H, OCH_2), 3.61 (s, 3 H, OCH_3); ^{19}F NMR ϕ -18.0 (m, 1 F, N=CF), -57.0 (d, J_{FF} = 14 Hz, 3 F, CF_3N), -74.6 (t, J_{HF} = 8 Hz, 3 F, CF_3), -76.3 (d, J_{FF} = 8 Hz, 3 F, CF_3). Anal. Calcd for $C_7H_5F_{10}NO_2$: C, 25.86; H, 1.55, N, 4.31. Found: C, 25.96; H, 1.50; N, 4.56.

Photolysis of 17. A solution of 17 g (0.03 mol) of azide **17** in 25 mL of hexafluoropropene cyclodimer was exposed to the spiral 10-W mercury lamp for 2 days. Distillation of the reaction mixture afforded 7.4 g of fractions with increasing viscosity, bp 60 °C (3.8 mm) -99 °C (0.3 mm), along with 3.5 g of viscous residue. All fractions showed IR bands at 2290 (CN or N=C=O), 1880 (COF), and 1800 cm^{-1} (C=O and/or $CF_2{=}N$).

Methyl 2-[(Difluoromethylene)amino]-2-(trifluoromethoxy)fluoroacetate (19) and Methyl [(Trifluoromethyl)imino]fluoroacetate (20). A mixture of 26.7 g (0.10 mol) of methyl 3-azido-2-(trifluoromethoxy)trifluoropropionate and 66.4 g (0.40 mol, 40 mL at -80 °C) of hexafluoroacetone was stirred under reflux (ca. -25 °C) for 2 days while it was irradiated with a spiral 10-W low-pressure Hg resonance lamp. Solvent was evaporated and product distilled to give early fractions enriched in imine **20**, bp 39–43 °C (50 mm), 4.5 g, and then 9.8 g (41%) of impure imine **19**: IR 2960 (saturated CH), 1800 (C=O, $N{=}CF_2$), 1300–1100 cm^{-1} (CF); ^1H NMR δ 3.93 (s, OCH_3); ^{19}F NMR ϕ-30.7 (br, 1 F, N=CF), -47.9 (br, 1 F, N=CF) -55.2 (d, J_{FF} = 10 Hz, 3 F, OCF_3), -89.9 (q, J_{FF} = 10 Hz, 1 F, CF); MS (C.I.), *m/e* 240 (M + H^+), 211 (M^+ - CO). For **20**: IR 2960 (saturated CH), 1770 (sh) and 1740 (C=N, conjugated C=O), 1300–1100 (CF); ^1H NMR δ 3.97 (s, OCH_3); ^{19}F NMR ϕ -23.3 (q, J_{FF} = 14 Hz, 1 F, N=CF), -57.2 (d, J_{FF} = 14 Hz, 3 F, CF_3N).

A similar reaction carried out in hexafluoropropene as solvent gave a similar yield of **19** along with many byproducts.

Methyl Perfluoro-5-(methyleneamino)-2-methyl-3,6-dioxanonanoate (21). A solution of 45.7 g (0.086 mol) of ester **8** in 80 mL of hexafluoropropene was stirred under reflux and irradiated for 2 days with a spiral 10-W low-pressure Hg resonance lamp. The liquid product after evaporation of volatiles, 45.3 g, was shown by IR to contain only traces of azide. Fractionation afforded 32.3 g (74%) of imine **21**, bp 42–44 °C (3 mm): IR 2960 (saturated CH), 1780 (C=O and $CF_2{=}N$), 1250–1100 cm^{-1} (CF,

CO) (Reference 9 reports an 1805-cm^{-1} IR band for CF_2=N in CF_2=NCHFCF_3); ^{1}H NMR δ 3.96 (s, CH_3O); ^{19}F NMR ϕ -29.3 (very br A branch, d, J_{FF} = 84 Hz, 1 F, N=CF_2), -42.8 (very br B branch, d, J_{FF} = 84 Hz, 1 F, N=CF_2), -82.2 (m, 3 F, CF_3), -83.0 (A branch, d, J_{FF} = 143 Hz, 1 F, CF_2O), -83.3 (m, 3 F, CF_3), -84.9 (br, 2 F, CF_2O), -91.2 (B branch, d, J_{FF} = 143 Hz, 1 F, CF_2O), -100.6 (m, 1 F, =NCF), -130.7 (m, 2 F, CF_2), -132.9 and -133.8 (m's, 1 F, CF of two racemates). Similar chemical shifts for CF_2=NR_F have been reported previously (e.g., ref 26). Anal. Calcd for $C_{10}H_3F_{16}NO_4$: C, 23.78; H, 0.60; N, 2.77. Found: C, 23.69; H, 0.64; N, 2.61.

Methyl Perfluoro-5-(methylimino)-2-methyl-3,6-dioxanonanoate (22) and Methyl Perfluoro-5-(methylimino)-2-methyl-3-oxapentanoate (23). A mixture of 21.5 g (0.043 mol) of imine **21**, 25 mL of hexafluoropropene cyclodimer, and 20 g (0.12 mol) of hexafluoropropene epoxide was heated at 200 °C in a 100-mL metal tube for 8 h. Distillation afforded 3.1 g (21%) of imine **23**, bp 40-41 °C (20 mm): IR (neat) 2970 (saturated CH), 1780 (C=O, CF=N), 1300-1100 cm^{-1} (CF, CO); ^{1}H NMR δ 4.00 (s, OCH_3); ^{19}F NMR ϕ -31.3 (q, J_{FF} = 14 Hz, 1 F, N=CF), -57.3 (d, J_{FF} = 14 Hz, 3 F, CF_3N), -70.7 (A branch d of d, J_{FF} = 168, 14 Hz, 1 F, OCFF), -80.0 (B branch d of d, J_{FF} = 168, 10 Hz, 1 F, OCFF), -82.4 (s, 3 F, CF_3), -129.6 (t, J_{FF} = 12 Hz, 1 F, CF). Anal. Calcd for $C_7H_3F_{10}NO_3$: C, 24.79; H, 0.89. Found: C, 24.82; H, 0.93.

Imine **22**, 4.2 g (19%), bp 47-58 °C (10 mm), was contaminated with a little isocyanate impurity: IR (neat) 2970 (saturated CH), 1790 (C=O), 1750 (C=N), 1300-1100 cm^{-1} (CF, CO) with a band at 2280 cm^{-1} for impurity (N=C=O); ^{1}H NMR δ 3.96 (s, CH_3O); ^{19}F NMR ϕ -54.8 (m, 3 F, CF_3N), -66.2 (A branch d of m, J_{FF} = 168 Hz, 1 F, =CCFFO), -76.9 (B branch d of p, J_{FF} = 168, 12 Hz, 1 F, =CCFFO), -81.7 (t, J_{FF} = 8 Hz, 3 F, CF_3), -82.5 (s, 3 F, CF_3), -88.4 (br, 2 F, CF_2O), -129.1 (t, J_{FF} = 12 Hz, 1 F, CF), -129.4 (s, 2 F, CF_2). Anal. Calcd for $C_{10}H_3F_{16}NO_4$: C, 23.78; H, 0.60. Found: C, 23.88; H, 0.56.

***N*-Methoxycarbonyl (Trifluoromethyl)trifluoroaziridine (24).** A solution of 25.0 g (0.25 mol) of methyl azidoformate in 500 mL of hexafluoropropene was irradiated with a Hanovia 679-A-36 lamp in a quartz vessel at -37 °C for 18 h. Fractionation afforded 11.4 g (20%) of 90% pure aziridine **24**, bp 88 °C. The other component of the mixture was identified as methyl azidoformate. An analytical sample of **24** was obtained by preparative GC: ^{1}H NMR δ 3.95; ^{19}F NMR ϕ -74.8 (m, 3 F, CF_3), -121.5 (m, 2 F, CF_2), -171.3 (m, 1 F, CF). Anal. Calcd for $C_5H_3F_6NO_2$: C, 27.12; H, 1.36; N, 6.78. Found: C, 27.42; H, 2.12; N, 6.52.

Methyl Cyanodifluoroacetate (26) and Methyl 3-Isocyanatotetrafluoropropionate (27). A mixture of 18.5 g (0.10 mol) of methyl 3-azidotetrafluoropropionate, 100 mL of acetonitrile, and 8.55 g (6.5 ml, 0.05 mol) of nickel carbonyl under nitrogen reacted vigorously after a short induction period. The temperature was maintained at 25 °C with an ice-water bath until gas evolution subsided, and the mixture was then stirred at 25 °C for 3 days. Volatiles were removed under reduced pressure and fractionated to give 3.7 g of a mixture of the known nitrile **26** (identified by IR) and the isocyanate **27**, bp 50-69 °C (150 mm), followed by 4.1 g (20%) of methyl 3-isocyanatotetrafluoropropionate, bp 69-70 °C (150 mm); IR 3020, 2970, and 2860 (saturated CH), 2280 (NCO), 1785 (CO), 1250-1100 cm^{-1} (CF); ^{1}H NMR δ 3.97 (s, OCH_3); ^{19}F NMR ϕ -83.3 (m, 2 F, CF_2NCO), -120.3 (t, J_{FF} = 3.8 Hz, 2 F, CF_2C=O). Anal. Calcd for $C_5H_3F_4NO_3$: C, 29.87, H, 1.50; N, 6.97; F, 37.79. Found: C, 30.17, H, 1.73; N, 7.11; F, 37.56.

Registry No. **1**, 99605-38-6; **2**, 86414-01-9; **3**, 99605-39-7; **4**, 99605-40-0; **5**, 99605-41-1; **7**, 86414-17-7; **8**, 99605-42-2; **10**, 99605-43-3; **11**, 99605-56-8; **12**, 99605-44-4; **13**, 99617-52-4; **14**, 99605-45-5; **16**, 99605-46-6; **17**, 99605-47-7; **18**, 86414-03-1; **19**, 99605-48-8; **20**, 99605-49-9; **21**, 99605-50-2; **22**, 99605-51-3; **23**, 99605-52-4; **24**, 99605-53-5; **26**, 99605-54-6; **27**, 99605-55-7; perfluoroallyl fluorosulfate, 67641-28-5; 3-azidotetrafluoropropionate, 99617-53-5; norbornene, 498-66-8; methyl azidoformate, 1516-56-9.

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Addition Compounds of Alkali Metal Hydrides. 28. Preparation of Potassium Dialkoxymonoalkylborohydrides from Cyclic Boronic Esters. A New Class of Reducing Agents

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The reaction of cyclic boronic esters possessing a wide range of steric requirements with excess potassium hydride to form the corresponding potassium dialkoxymonoalkylborohydrides was explored. In cases involving a less hindered diol such as ethylene glycol, 2,3-butanediol, or 1,3-propanediol, the reaction is slightly exothermic and quite facile, being complete in less than 1 h at 25 °C. In cases involving a highly hindered diol such as pinacol, the reaction is very sluggish, even at 65 °C. The stability of the potassium dialkoxymonoalkylborohydrides is strongly dependent upon the steric bulkiness of the alkyl groups of the boronic ester. Thus, for R = *n*-hexyl, 3-hexyl, *tert*-butyl, or thexyl, the addition product is quite stable to disproportionation. However, for R = methyl, the corresponding borohydride is unstable, undergoing rapid redistribution to form a white precipitate. The stable potassium dialkoxymonoalkylborohydrides thus formed reduce 2-methylcyclohexanone with moderate stereoselectivity, giving the cis isomer preferentially, with selectivities of 73-84%.

Trisubstituted borohydrides such as trialkylborohydrides and trialkoxyborohydrides constitute a highly attractive class of reducing agents in organic synthesis. Trialkylborohydrides have been synthesized by several different routes, such as the reaction of trialkylboranes with alkali metal hydrides[2] (LiH, NaH, KH), or with

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