J. Org. Chem. **1983**, *48*, 347–354

Perfluoroalkylation of the 2-Nitropropyl Anion. Evidence for an $S_{RN}1$ Process[†]

Andrew E. Feiring

Central Research & Development Department, E. I. du Pont de Nemours & Company, Inc., Experimental Station, Wilmington, Delaware 19898

Received May 13, 1982

The reaction of primary perfluoroalkyl iodides (R_fI, $R_f = n\text{-}C_6F_{13}$, $n\text{-}C_8F_{17}$) and diiodides $I(CF_2)_nI$ ($n = 4, 6$) with the 2-nitropropyl anion gives 2-(perfluoroalkyl)-2-nitropropanes. The anion was employed as the tetrabutylammonium salt in benzene or in organic solvent/water mixtures or as the lithium salt in dimethylformamide or dimethyl sulfoxide with and without UV irradiation. Evidence is presented for an $S_{RN}1$ process by trapping of radical intermediates with benzene, styrene, methyl methacrylate, and vinyl acetate and by competition experiments with *p*-dinitrobenzene. Substitution of the nitro group in the 2-(perfluoroalkyl)-2-nitropropanes occurs under $S_{RN}1$ conditions with 2-nitropropyl anion, benzenethiolate, and hydride.

Perfluoroalkyl iodides are useful reagents for the perfluoroalkylation of organic compounds. Photolysis or thermolysis of the iodides generate perfluoroalkyl radicals that can add to unsaturated organic compounds.[1] Perfluoroalkyl iodides can couple with organic halides in the presence of copper.[2] Perfluorinated organometallic compounds can be prepared from perfluoroalkyl iodides and can react with organic acceptors.[3] However, perfluoroalkyl iodides are notoriously resistant to displacement of the iodide under S_N1 or S_N2 conditions.[4]

The $S_{RN}1$ reaction is a radical-chain process for nucleophilic substitution.[5-8] A propagation step and usually the initiation step of an $S_{RN}1$ process involves single electron transfer to the substrate. Although perfluoroalkyl iodides are known as good electron acceptors,[9,10] the possibility of substituting the iodide under $S_{RN}1$ conditions has only recently been recognized. The photochemical perfluoroalkylation of aromatic thiols,[11] sulfinic acids,[12] and selenols[13] in liquid ammonia and the spontaneous perfluoroalkylation of certain enamines[14] by perfluoroalkyl iodides have been suggested as $S_{RN}1$ processes. Most recently, the perfluoroalkylation of carbanions including the 2-nitropropanide ion by perfluoroalkyl iodide derivatives was reported.[15] Little evidence has been reported for the mechanism of these reactions.

This paper reports the reaction of perfluoroalkyl iodides with the known $S_{RN}1$ donor, the 2-nitropropanide ion, giving 2-(perfluoroalkyl)-2-nitropropanes. Clear evidence for the intermediacy of perfluoroalkyl radicals, novel solvent/counterion effects, and $S_{RN}1$ substitution reactions of the 2-(perfluoroalkyl)-2-nitropropanes are reported.

Results

Primary Perfluoroalkyl Iodides. The primary perfluoroalkyl iodides **1a** and **1b** reacted with the 2-nitropropanide ion (**2**) to give the (perfluoroalkyl)-2-nitropropane derivatives **3a** and **3b** in good yield. Small amounts (2–3%) of 2,3-dimethyl-2,3-dinitrobutane (**4**) were observed by GLC and NMR examination of crude reaction mixtures. This reaction was studied in different solvent systems and with different 2-nitropropanide counterions under normal laboratory light, in the dark, and with UV irradiation.

$$\underset{\mathbf{1}}{R_fI} + \underset{\mathbf{2}}{(CH_3)_2C{=}NO_2^-} \rightarrow \underset{\mathbf{3}}{R_fC(CH_3)_2NO_2} + \underset{\mathbf{4}}{O_2N(CH_3)_2CC(CH_3)_2NO_2}$$

1a, $R_f = n\text{-}C_6F_{13}$; **1b**, $R_f = n\text{-}C_8F_{17}$; **3a**, $R_f = n\text{-}C_6F_{13}$; **3b**, $R_f = n\text{-}C_8F_{17}$

Reactions of **1** with lithium 2-nitropropanide[16] were run in DMF or Me_2SO solution. The tetrabutylammonium salt of **2** was prepared by addition of 2-nitropropane to an equivalent of 40% tetrabutylammonium hydroxide in water.[17] The resulting aqueous solution was vigorously stirred with a benzene or methylene chloride solution of the perfluoroalkyl iodide. A dried solution of the tetrabutylammonium salt of **2** in benzene was prepared by azeotropic distillation of aqueous tetrabutylammonium hydroxide, 2-nitropropane, and benzene. In a typical synthesis of **3**, the reaction mixture (or an aliquot) was quenched into a mixture of ether and water. The ether solution was washed with several portions of water, dried,

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[†] Contribution No. 3063.

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and analyzed by GLC. The conversion of 1 to 3 was determined from the relative peak areas of 1 and 3 with correction for detector response factors. Results are shown in Table I, including several preparative experiments with isolated product yields.

Reaction of 1 with the lithium salt of 2 in DMF or Me_2SO occurred under ambient laboratory light or in the dark but was modestly accelerated by irradiation with either 300- or 350-nm light. Under the latter conditions, an 82% isolated yield of **3a** was achieved after 2-h irradiation in Me_2SO solution. No other fluorinated products were detected. Similarly, irradiation of a well-stirred mixture of aqueous tetrabutylammonium 2-nitropropanide and a methylene chloride solution of **1a** gave **3a** in 75% yield. With use of benzene as a cosolvent, both thermal (60 °C, 17 h) and photochemical (300 nm) experiments gave **3a** in modest conversion plus smaller amounts of a second fluorinated product. The second material was identified as (perfluorohexyl)benzene (**5**) by comparison with an authentic sample.[18] Remarkably, addition of **1a** to an azeotropically dried solution of the tetrabutylammonium salt of **2** in benzene gave **3a** in good yield and none of the benzene adduct **5**. This reaction occurred

$$\mathbf{1a} + 2\ N(Bu)_4 \xrightarrow{C_6H_6/H_2O} \mathbf{3a} + \underset{\mathbf{5}}{PhC_6F_{13}}$$

somewhat more rapidly under normal laboratory light than the corresponding lithium salt reaction in DMF.

Reaction of **1a** or **1b** with the dried tetrabutylammonium salt of **2** in benzene in the presence of styrene gave **3a,b** plus the novel styrene adducts **6a,b**. This

$$\mathbf{1a,b} + 2\cdot N(Bu)_4 + PhCH{=}CH_2 \xrightarrow{C_6H_6} \mathbf{3a,b} + CF_3(CF_2)_nCF_2CH_2CH(Ph)C(CH_3)_2NO_2$$

$\mathbf{6a}$, $n = 4$
$\mathbf{6b}$, $n = 6$

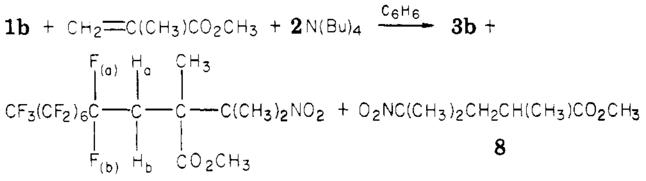
process was studied in greater detail with the C-8 iodide **1b** since all components of the reaction mixture were readily separable by GLC. Conversion of **1b** was noticeably slower in the presence of styrene (compare entries 16 and 19) but ultimately gave **3b** and **6b** in quite good yield. The final ratio of **3b** to **6b** depended on the initial styrene to **1b** ratio, varying from 5:3 with 1 equiv of styrene to 1:2 with 5 equiv of styrene. A preparation-scale experiment with 4 equiv of styrene was halted after partial conversion (3 h). Workup as described in the Experimental Section gave **3b** and **6b** in 13% and 23% isolated yields (not corrected for unreacted **1b**). The product mixture could be distilled essentially to dryness, indicating little polymer formation. Similarly the adduct **6a** was obtained in 33% yield; the presence of **2a** was detected by GLC but not measured quantitatively.

In contrast, irradiation of **1a**, styrene, and lithium 2-nitropropanide in DMF solution gave only traces of **3a** and **6a**. The major product was a nondistillable, oily solid showing broad aliphatic and aromatic NMR absorptions. This material was not characterized further. In the absence of UV irradiation no reaction was observed over 24 h.

Structures of **6a,b** were assigned mainly by their proton NMR spectra as detailed in the Experimental Section. In order to confirm the regiochemistry of the adducts, we prepared the trifluoromethyl derivative **6c** from trifluoromethyl iodide, styrene, and **2**. The fluorine NMR spectrum of this compound showed a clear triplet with $J_{H-F} = 10$ Hz, indicating attachment of the fluorinated group to a methylene carbon.

$$\underset{\mathbf{6c}}{CF_3CH_2CH(Ph)C(CH_3)_2NO_2}$$

In a similar fashion, reaction of perfluorooctyl iodide (1 equiv), methyl methacrylate (2 equiv), and tetrabutylammonium 2-nitropropanide (1 equiv) in benzene gave the adduct **7** (28%), **3b** (25%), and a small amount of the Michael addition[19] product **8**. Reaction in the presence



$$\mathbf{1b} + CH_2{=}C(CH_3)CO_2CH_3 + 2N(Bu)_4 \xrightarrow{C_6H_6} \mathbf{3b} + CF_3(CF_2)_6CF_{(a)}F_{(b)}CH_aH_bC(CH_3)(CO_2CH_3)C(CH_3)_2NO_2 + O_2NC(CH_3)_2CH_2CH(CH_3)CO_2CH_3$$

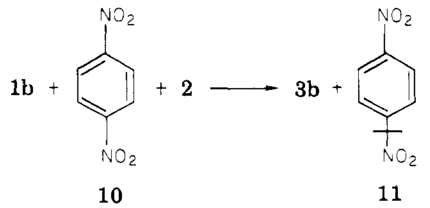
7 **8**

of vinyl acetate (3 equiv) gave **3b** (45%) and the adduct **9** (17%). No oligomerized product was detected in either case.

$$\mathbf{1b} + CH_2{=}CHOAc + 2\cdot N(Bu)_4 \xrightarrow{C_6H_6} \mathbf{3b} + \underset{\mathbf{9}}{CF_3(CF_2)_6CF_2CH_2C(OAc)HC(CH_3)_2NO_2}$$

The adduct **7** shows interesting NMR spectra. In the F-19 NMR spectrum, geminal fluorines $F_{(a)}$ and $F_{(b)}$ appear as two doublets at −116.7 and −105.2 ppm with F–F coupling of 267 Hz. The peaks are too broad to determine F–H coupling constants. Proton NMR spectra were obtained at both 90 and 360 MHz. In both, the geminal methyls appear as well-resolved singlets at δ 1.59 and 1.74. The remaining methyl is a doublet at δ 1.39 with $J = 3.3$ Hz. Since there is no other 3.3-Hz coupling in the proton spectrum, this splitting must arise from long-range coupling to one fluorine. At 90 Mz the methylene hydrogens $H_{(a,b)}$ appear as a complex multiplet. At 360 MHz, they are well-resolved into a pair of multiplets centered at δ 2.64 and 3.14. The higher field signal is a doubled doublet with $J = 15.0$ and 37.5 Hz. The lower field signal could be analyzed as a doubled doubled doublet with $J = 15.0$, 27.1, and 11.7 Hz. Thus the hydrogens are coupled to each other (15.0 Hz) and to the nonequivalent α-fluorines (0, 37.5 Hz and 27.1, 11.7 Hz).

The use of easily reduced *p*-dinitrobenzene (**10**) as an inhibitor for $S_{RN}1$ displacement processes has been described.[5] In the present case, reaction of **2** with mixtures of perfluorooctyl iodide (**1b**) and **10** resulted in competitive reaction with the substrates. Both 2-(perfluorooctyl)-2-nitropropane (**3b**) and α,*p*-dinitrocumene[20] (**11**) were formed. In a typical experiment the anion **2** was reacted with a mixture of **1b** and **10** in excess. The resulting mixture was worked up as usual and the product mixture analyzed by NMR. The components **3b**, **10**, and **11** had well-separated absorptions, and the composition of the



10 **11**

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Table I. Reaction of Perfluoroalkyl Iodides with 2-Nitropropane Salts

exp no.	R_fI (mmol)	$(CH_3)_2C{=}NO_2M$ (mmol)	additive (mmol)	solvent (mL)	conditions	time, min	product analysis^a % $R_fC(CH_3)_2NO_2$	% (other products)
1	1a (20)	Li (20)		DMF (55)	3000 Å	180	86	
2	1a (20)	Li (20)		DMF (55)	3500 Å	180	89	
3	1a (20)	Li (20)		DMF (55)	lab light	180	53	
4	1a (18)	Li (20)		DMF (50)	3500 Å	15	57	
5	1a (18)	Li (20)		DMF (50)	lab light	15	27	
6	1a (9.1)	Li (20)		DMF (50)	lab light	120	51	
7	1a (9.1)	Li (20)		DMF (50)	darkness	120	49	
8	1a (200)	Li (200)		DMF (400)	3500 Å	240	79^b	
9	1a (150)	Li (150)		DMSO (300)	3000 Å	120	82^b	
10	1a (20)	$N(Bu)_4$ (23)		C_6H_6 (30)	lab light	20	71^b	
11	1a (40)	$N(Bu)_4$ (60)		C_6H_6/H_2O (40/24)	darkness, 60 °C	1020	32	5 (5)
12	1a (40)	$N(Bu)_4$ (60)		C_6H_6/H_2O (40/24)	3000 Å	180	39	14 (5)
13	1a (20)	$N(Bu)_4$ (30)		CH_2Cl_2/H_2O (20/12)	3000 Å	180	75^b	
14	1b (200)	Li (200)		DMF (400)	3500 Å	240	58^b	
15	1b (30)	$N(Bu)_4$ (31)		C_6H_6 (40)	lab light	60	79^b	
16	1b (10)	$N(Bu)_4$ (12)		C_6H_6 (45)	lab light	1	51	
						10	65	
						140	76	
17	1a (30)	$N(Bu)_4$ (35)	styrene (110)	C_6H_6 (90)	lab light	130	NM^c	33^b (6a)
18	1b (10)	$N(Bu)_4$ (12)	styrene (10)	C_6H_6 (45)	lab light	1200	51	31 (6b)
19	1b (10)	$N(Bu)_4$ (12)	styrene (30)	C_6H_6 (45)	lab light	1	12	8 (6b)
						10	17	14 (6b)
						140	25	26 (6b)
						1200	34	48 (6b)
20	1b (10)	$N(Bu)_4$ (12)	styrene (50)	C_6H_6 (45)	lab light	1200	27	55 (6b)
21	1b (30)	$N(Bu)_4$ (39)	styrene (120)	C_6H_6 (100)	lab light	180	13^b	23^b (6b)
22	1b (20)	$N(Bu)_4$ (22)	methyl methacrylate (40)	C_6H_6 (50)	lab light	120	25^b	28^b (7)
23	1b (20)	$N(Bu)_4$ (30)	vinyl acetate (60)	C_6H_6 (50)	lab light	300	45^b	17^b (9)

[a] Unless otherwise indicated, product yield by GLC. [b] Isolated yield. [c] NM = not measured.

Table II. Competition Experiments, Perfluorooctyl Iodide and *p*-Dinitrobenzene for 2-Nitropropane Anion

exp no.	perfluorooctyl iodide (1b), mmol	*p*-dinitrobenzene (10), mmol	$(CH_3)_2C{=}NO_2^-$, mmol (cation)	solvent	conditions	$C_8F_{17}C(CH_3)_2NO_2$, mmol	α,*p*-dinitrocumene, mmol	k_1/k_{10}
1	15	15	15 (Li)	DMF	3500 Å, 2 h	7.8	5.5	1.6
2	15	15	10 (Li)	DMF	lab light, 17 h	1.1	8.5	0.09
3	10	10	7.7 (NBu_4)	C_6H_6	lab light, 1 h	1.4	6.3	0.15
4	30	14.9	10 (NBu_4)	C_6H_6	lab light, 17 h	2.6	5.9	0.19

Table III. Reaction of Perfluoroalkyl Diiodides with 2-Nitropropanide Salts

substrate mmol	$(CH_3)_2C{=}NO_2M$ (mmol)	solvent (mL)	conditions	product yield^a 13	14	4
12a (10)	Li (21)	DMF (30)	3000 Å, 2 h			86
12b (50)	Li (150)	DMF (160)	3000 Å, 2 h	16	40	*b*
12b (50)	Li (150)	Me_2SO (160)	3000 Å, 2 h	*b*	60	*b*
12c (43)	Li (100)	DMF (260)	3500 Å, 4 h	*b*	65	*b*
12c (30)	$N(Bu)_4$ (62)	C_6H_6 (100)	lab light, 1.5 h	13	43	

[a] Isolated yield. [b] Product detected by GLC analysis but not isolated.

mixture was calculated from integrals of appropriate peaks. No other significant absorptions were detected in any experiment. Appropriate control experiments were run to ensure that the workup procedure did not result in the selective loss of any component. Relative rates for the disappearance of **1b** and **10** were calculated, assuming first-order processes with each substrate.[21] The data (Table II) indicate similar reactivity of **1b** and **10** toward **2**. With both the tetrabutylammonium salt of **2** in benzene and the lithium salt in DMF under normal laboratory light, *p*-dinitrobenzene reacted faster than perfluorooctyl iodide. On irradiation (350 nm) of the lithium salt in DMF, however, **1b** reacted more rapidly.

Perfluoroalkyl Diiodides. Products from reaction of **2** with the α,ω-perfluoroalkyl diiodides[22] **12a–c** depended on the chain length of the diiodide. The two-carbon diiodide **12a** gave 2,3-dimethyl-2,3-dinitrobutane (**4**) as the only nonvolatile product on photoreaction with lithium 2-nitropropanide in DMF. The longer chain diiodides **12b** and **12c** afforded mixtures of the mono- and dialkylated products **13b,c** and **14b,c** plus traces of **4** and unreacted diiodide. Typical results are shown in Table III.

$$\underset{\mathbf{12a}}{ICF_2CF_2I} + \mathbf{2} \rightarrow \mathbf{4}$$

$$\underset{\substack{\mathbf{12b},\ n = 4\\ \mathbf{12c},\ n = 6}}{I(CF_2)_nI} + \mathbf{2} \rightarrow \underset{\substack{\mathbf{13b},\ n = 4\\ \mathbf{13c},\ n = 6}}{I(CF_2)_nC(CH_3)_2NO_2} + \underset{\substack{\mathbf{14b},\ n = 4\\ \mathbf{14c},\ n = 6}}{O_2NC(CH_3)_2(CF_2)_nC(CH_3)_2NO_2} + \mathbf{4}$$

Secondary Perfluoroalkyl Iodides. The only nonvolatile product isolated from 2-iodoperfluoropropane (**15**) on photoreaction with lithium 2-nitropropanide in benzene was 2,3-dimethyl-2,3-dinitrobutane (**4**). For determination of the fate of the fluorinated molecule, reaction of **15** (0.5 mmol) with tetrabutylammonium 2-nitropropanide (0.4 mmol) in benzene was conducted in a sealed NMR tube containing fluorotrichloromethane as internal standard. After 1 h, fluorine NMR of the solution showed as the major absorptions a doublet (J = 5 Hz) at −70.8 ppm and a heptet at −179.1 ppm (J = 5 Hz) in a 6:1 ratio. The spectrum agreed exactly with that of perfluoro-2,3-dimethylbutane[23] (**16**) run under the same conditions. The reaction mixture spectrum showed in addition to **16** and some unreacted **15** a doubled doublet at −75.7 ppm, which collapses to a doublet on proton decoupling. This absorption was assigned to the methyl fluorines of 2-H perfluoropropane (**17**) with the methylene fluorine too weak to detect. The ratio of **16** to **17** was 3.4:1 by integration.

$$\underset{\mathbf{15}}{CF_3CFICF_3} + \mathbf{2} \rightarrow \mathbf{4} + \underset{\mathbf{16}}{(CF_3)_2CFCF(CF_3)_2} + \underset{\mathbf{17}}{CF_3CFHCF_3}$$

Reactions of 2-(Perfluoroalkyl)-2-nitropropanes. The chemistry of these derivatives was briefly studied especially regarding displacement of the nitro group. Three examples were uncovered with replacement of NO_2 by 2-nitropropyl, benzenethiol, and hydride.

A solution of **3a** and tetrabutylammonium 2-nitropropanide in benzene was irradiated with 300-nm light until GLC showed complete consumption of **3a** (ca. 6 h). The major product was **18**, isolated in 43% yield. Several

$$\mathbf{3a} + \mathbf{2}\cdot N(Bu)_4 \xrightarrow[h\nu]{C_6H_6} \underset{\mathbf{18}}{C_6F_{13}C(CH_3)_2C(CH_3)_2NO_2}$$

minor products were observed by GLC. 2,3-Dimethyl-2,3-dinitrobutane (**4**) was identified, the others remain unknown. This reaction proceeded under normal laboratory light but was slower (ca. 17% conversion after 4 h). GLC analysis showed the same products as with the photoassisted process.

Irradiation of a solution of **3a** and sodium thiophenoxide in DMF with 3000-Å light gave a complex mixture of products. The major isolable material was diphenyl disulfide, which by GLC analysis was not present before addition of **3a** and irradiation. A small amount of oil, tentatively identified as the sulfide **19**, was obtained by column chromatography.

$$\mathbf{3a} + PhSNa \xrightarrow[h\nu]{DMF} PhSSPh + \underset{\mathbf{19}}{C_6F_{13}C(CH_3)_2SPh}$$

Addition of **3a** to 2 equiv of lithium aluminum hydride in ether resulted in a vigorous reaction. Workup with aqueous sodium hydroxide, followed by careful distillation of the ether, gave an oily product. GLC analysis showed the presence of three products in a 1.0:3.2:0.71 ratio. These materials were subsequently identified as the fluorocarbon **20**, the hydroxylamine **21**, and the amine **22a**. Each of

$$\mathbf{3a} \xrightarrow[ether]{LiAlH_4} \underset{\mathbf{20}}{C_6F_{13}C(CH_3)_2H} + \underset{\mathbf{21}}{C_6F_{13}C(CH_3)_2NHOH} + \underset{\mathbf{22a}}{C_6F_{13}C(CH_3)_2NH_2}$$

the products was obtained as the predominant material under different conditions. Reduction of **3a** with lithium aluminum hydride in THF at 35 °C proceeded with visible gas evolution. GLC examination on the crude product showed **20** as the major component with only traces of **21** and **22a**. Isolation of pure **20** was difficult due to its volatility. In one experiment (Experimental Section), a 44% yield of pure **20** was attained. Reduction of **3a** with excess stannous chloride in ethanolic hydrochloric acid afforded the hydroxylamine **21** as the major product. Attempted Pt- or Pd-catalyzed hydrogenation of **3a** in ethanol or acetic acid at 50 psi and room temperature resulted in no hydrogen uptake. At 90 °C and 1000 psi, hydrogen pressure **3a** was smoothly reduced over palladium on charcoal in ethanol to **22a**, isolated in 62% yield. Similarly, 2-(perfluorooctyl)-2-nitropropane (**3b**) and the dinitro compounds **14b** and **14c** were readily reduced to the corresponding amines **22b**, **23b**, and **23c**, respectively, in good yield. Properties of these interesting poly-

$$\mathbf{14b,c} \xrightarrow[Pd/C]{H_2} \underset{\substack{\mathbf{23b},\ n = 4\\ \mathbf{23c},\ n = 6}}{H_2NC(CH_3)_2(CF_2)_nC(CH_3)_2NH_2}$$

fluorinated alkylamines[24] have not yet been examined in detail. The monoamines **22a,b** readily form stable crystalline hydrochloride salts. The amine **22b** was converted to the tertiary amine **24** with formic acid and formaldehyde, but efforts to convert **24** to a quaternary ammonium salt using methyl iodide have been unsuccessful.

$$\underset{\mathbf{22b}}{C_8F_{17}C(CH_3)_2NH_2} \xrightarrow[HCHO]{HCOOH} \underset{\mathbf{24}}{C_8F_{17}C(CH_3)_2N(CH_3)_2}$$

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Scheme I

$$R_fI + (CH_3)_2C{=}NO_2^- \longrightarrow \underset{\mathbf{25}}{R_fI^{-\bullet}} + (CH_3)_2\dot{C}NO_2 \quad (M1)$$

$$\mathbf{25} \longrightarrow \underset{\mathbf{26}}{R_f\bullet} + I^- \quad (M2)$$

$$\mathbf{26} + (CH_3)_2C{=}NO_2^- \longrightarrow \underset{\mathbf{27}}{[R_fC(CH_3)_2NO_2]^{-\bullet}} \quad (M3)$$

$$\mathbf{27} + R_fI \longrightarrow R_fC(CH_3)_2NO_2 + \mathbf{25} \quad (M4)$$

Scheme II

28 (M6)

$$\mathbf{28} + (CH_3)_2C{=}NO_2^- \longrightarrow \underset{\mathbf{29}}{R_fCH_2C(R',R'')C(CH_3)_2NO_2^{-\bullet}} \quad (M7)$$

$$\mathbf{29} + R_fI \longrightarrow R_fCH_2C(R',R'')C(CH_3)_2NO_2 + R_fI^{-\bullet} \quad (M8)$$

6, R' = Ph; R = H
7, R' = CH_3; R = CO_2CH_3
9, R' = OAc; R'' = H

Scheme III

$$R_fC(CH_3)_2NO_2 + \mathbf{2} \longrightarrow \underset{\mathbf{27}}{[R_fC(CH_3)_2NO_2]^{-\bullet}} + (CH_3)_2\dot{C}NO_2$$

$$\mathbf{27} \longrightarrow \underset{\mathbf{30}}{R_fC(CH_3)_2\bullet} + NO_2$$

$$\mathbf{30} + \mathbf{2} \longrightarrow \underset{\mathbf{31}}{[R_fC(CH_3)_2C(CH_3)_2NO_2]^{-\bullet}}$$

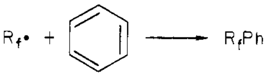
$$\mathbf{31} + \mathbf{3} \longrightarrow \mathbf{18} + \mathbf{27}$$

Discussion

The reaction of primary perfluoroalkyl iodide with 2-nitropropane anion (**2**) exhibits characteristics of an $S_{RN}1$ process.[5-8] The reaction occurs readily under mild conditions with a substrate resistant to normal nucleophilic attack on carbon. Alkylation of **2** is on carbon rather than oxygen. The process can be accelerated by light.[5]

The $S_{RN}1$ mechanism as applied to this process is shown in Scheme I. The initiation step is likely to be electron transfer from anion **2** to the perfluoroalkyl iodide **1**. A true thermodynamic reduction potential for **1** is not available due to the irreversibility of the process. Preparative electrochemical reductions[9] of **1** have been carried out at −0.6 V vs. SCE, suggesting that the effective reduction potential of **1** is well within a range for electron transfer from **2**. The anion radical **25** should rapidly decompose to the perfluoroalkyl radical and iodide ion. The CF_3I anion radical,[10] observed as a stable species in solid solution at 77 K, decomposed above 100 K to the trifluoromethyl radical and iodide ion. Addition of the perfluoroalkyl radical to **2** generates a second anion radical **27**. Although this species can expel nitrite anion (see below), it prefers in the presence of **1** to transfer an electron, continuing the chain process. The reversible one-electron reduction potential of 2-(perfluorohexyl)-2-nitropropane in acetonitrile is −1.285 V vs. SCE.[26] Thus the electron transfer of equation M4 is likely to be an exothermic process.

The formation of perfluoroalkyl radicals **26** from reaction of **1** and **2** is strongly suggested by the formation of perfluoroalkylated benzene **5** and the olefin adducts **6**, **7**, and **9**. The radical perfluoroalkylation of aromatics is

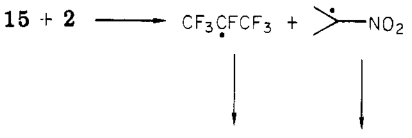


(M5)

well-known,[18] as is the addition of perfluoroalkyl radicals to olefins.[1] The regiochemistry of the adducts indicates initial attack on the olefin by the perfluoroalkyl radical. The formation of **6**, **7**, and **9** can be included within the $S_{RN}1$ scheme by equations M6–M8 (Scheme II). The observed decrease in the rate of disappearance of **1** in the presence of styrene could be explained by a slower rate of capture of **28** compared to **26** by the 2-nitropropanide ion ($k_{M7} < k_{M3}$). Alternatively, the anticipated longer lifetimes of radicals **28** may permit reaction with the 2-nitropropyl radical produced in the initiation step (M1). This chain-terminating process could result in a net decrease in the rate of disappearance of **1**.

The absence of significant olefin telomer formation in benzene suggests that the 2-nitropropanide ion is an efficient radical trap under these conditions. Yet the perfluoroalkyl radical adds to three olefins of differing polarity even in the presence of this efficient radical sink. This unusual result suggests that the primary perfluoroalkyl radical is highly indiscriminate in addition processes.

The reaction of **2** with the secondary perfluoroalkyl iodide **15** is also likely to begin with an electron-transfer process followed by loss of iodide ion. The resulting secondary radical, for steric or electronic reasons, fails to react with **2** (or the process is reversible). Dimers of the radicals are produced in a presumably nonchain process. Both the



16 **4**

ease of formation and stability of perfluoroalkyl radicals are known[27] to increase with branching of the perfluoroalkyl chain. Thus, the secondary radical should form more rapidly and react with **2** more slowly than the primary radical, permitting the alternative dimerization process.

Reactions of **3** with **2**, sodium thiophenoxide and lithium aluminum hydride can be explained as $S_{RN}1$ processes (Scheme III). The displacement of nitro from a saturated carbon by **2** and thiolate anions under $S_{RN}1$ conditions is well-known.[5] Typically, but not always,[28] the α-carbon bears conjugating substituents such as phenyl or a second nitro group. The perfluoroalkyl group presumably facilitates the process by stabilizing the anion radical **27**. The half-wave reduction potential[26] of **3a** is −1.285 V compared to −1.70 V for a nonfluorinated model compound, 2-methyl-2-nitropropane.[25] The anion radical **27** formed from **3** and **2** is also an intermediate in the synthesis of **3** from **1** and **2** (Scheme I). In the earlier case, presence of a more easily reduced species in solution (R_fI) permits electron transfer to occur. In the absence of such a species, the anion radical **27** loses nitrite anion to generate radical **30**, which reacts with the nucleophile.

The reduction of **3a** to **20** with $LiALH_4$ may involve a single-electron-transfer mechanism. Single-electron-

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[25] Geske, D. H.; Ragle, J. L.; Bambenek, M. A.; Balch, A. L. *J. Am. Chem. Soc.* **1964**, *86*, 987.

[26] The reduction potential of **3a** was measured by differential pulse polarography in acetonitrile/0.1 M tetrabutylammonium tetrafluoroborate at 1 mM concentration.

[27] Fisher, J. P.; Homer, J. B.; Lossing, F. P. *J. Am. Chem. Soc.* **1965**, *87*, 957.

[28] Kornblum, N.; Carlson, S. C.; Smith, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 647. Russell, G. A.; Jawdosiuk, M.; Makozza, M. *Ibid.* **1979**, *101*, 2355. Kornblum, N.; Erickson, A. S. *J. Org. Chem.* **1981**, *46*, 1038.

transfer processes with metal hydrides and several easily reducible functional groups have been reported,[29] but the replacement of nitro by hydrogen using $LiAlH_4$ appears to be novel.[30]

Medium Effects. Several interesting medium effects on the reaction of the perfluoroalkyl iodides with **2** were noted. These can be summarized as follows: (1) the reaction of **1** with the tetrabutylammonium salt of **2** in benzene was faster than with the lithium salt in DMF, (2) the byproduct, (perfluorohexyl)benzene was formed with use of benzene/water mixtures as solvent but not in pure benzene, (3) the styrene adducts **6** were formed cleanly from **1** and styrene with the tetrabutylammonium salt of **2** in benzene but not with the lithium salt in DMF. In the latter case, photostimulated reaction gave mostly material believed to be styrene oligomers.

Each of these effects suggest that the anion is more reactive as its tetrabutylammonium salt in benzene compared to benzene/water mixtures or to the lithium salt in DMF.[17] Thus under the former conditions either the rate of initiation (M1) or the efficiency of the chain-carrying step (M3) could be enhanced, resulting in a faster overall conversion of **1** to **3**. A more efficient chain-carrying step (M3) in benzene relative to a benzene/water mixture could explain the absence of the perfluoroalkylated benzene product in pure benzene. Similarly, the efficiency of the chain-carrying step (M7) in the process with styrene may be greater with the tetrabutylammonium salt in benzene compared to the lithium salt in DMF, becoming fast enough to overcome the rate of an alternative olefin polymerization process. The propagation rate constants, k_p, for the olefins employed in this study range from about 10^2L/mol s for styrene to 4×10^3 L/mol s for vinyl acetate.[31] Thus in benzene solution the rate of step M7 must be greater than 4×10^3 since little or no oligomer was product.

The reason for the varying reactivity of the nitronate anion under the above conditions cannot yet be defined since the effects of solvent and counterion have not been separated. The solvent polarity, ion pairing,[32] and the rate of phase transfer in the mixed solvent system could be important factors. Also, termination processes[33] that result in little product formation but significant kinetic effects have not been considered. Studies in these areas are continuing.

Finally the competitive reactions of perfluorooctyl iodide and *p*-dinitrobenzene (**10**) should be discussed. The use of even catalytic amounts of **10** to inhibit $S_{RN}1$ processes with substrates such as *p*-nitrobenzyl chloride is well-known. Presumably this inhibition results from the ability of **10** or its transformation products under the reaction conditions to accept electrons more readily than the substrate. The formation of significant amounts of the product **3** from the perfluoroalkyl iodide (**1**) even in the presence of an equivalent of **10** suggests that the perfluoroalkyl iodide (**1**) and **10** are comparable in their ability to accept an electron. Note that this argument does not require the actual transformation of **10** to α,β-dinitrocumene (**11**) to be an electron-transfer process, only that **10** or its transformation products can function as electron acceptors. In fact, the conversion of **10** to **11** is likely not an $S_{RN}1$ process.[6] The selective enhancement of the reaction of **1** in competition with **10** on photolysis may derive from the fact that the two substrates react with the nitronate anion by a different mechanism with the $S_{RN}1$ process selectively enhanced. Rate enhancements by long-wavelength UV irradiation have often been observed in $S_{RN}1$ processes.[5,6]

Conclusion

The chemistry described here provides a new route for the functionalization of readily available perfluoroalkyl iodides. The process clearly involves the intermediacy of perfluoroalkyl radicals and is consistent with the well-established $S_{RN}1$ mechanism. Notable variations in the process can be observed by changing reaction conditions. These variations may enhance synthetic utility of the $S_{RN}1$ process and provide mechanistic information.

Experimental Section

Proton NMR spectra were measured in $CDCl_3$ solutions on a Varian EM-390 spectrometer at 90 MHz, an IBM NR-80 spectrometer at 80 MHz, or an N-360 WB spectrometer at 360 MHz. Fluorine NMR spectra were measured in $CDCl_3$ solution on a Varian XL-100 spectrometer at 94.1 MHz; chemical shifts are reported in parts per million relative to fluorotrichloromethane as internal standard. Negative values are upfield from the standard. Irradiations were conducted in a Rayonet photochemical reactor, using 16 300- or 350-nm lamps. Pyrex vessels were equipped with cold finger condensers.

All reactions were conducted under a positive pressure of argon. In general, reaction vessels were repeatedly evacuated and filled with argon, using a Firestone valve after the addition of each reagent. Solvents were reagent grade, transferred by syringe, and maintained under an argon blanket after opening. Tetrabutylammonium hydroxide (40% in water; Alfa) and 2-nitropropane (Aldrich) were used as received. Styrene and thiophenol were distilled and maintained under argon. Lithium 2-nitropropanide,[16] sodium thiophenoxide,[16] 1,2-diiodoperfluoroethane,[22] 1,4-diiodoperfluorobutane,[22] and 1,6-diiodoperfluorohexane[22] were prepared as described. Perfluorohexyl iodide, perfluorooctyl iodide (Chemicals and Pigments Department, E. I. du Pont de Nemours & Co.), and 2-iodoperfluoropropane (PCR, Inc.) were washed with 0.5 N sodium thiosulfate solution to remove iodine, dried ($MgSO_4$), filtered, and stored under argon in foil-wrapped bottles.

GLC analyses were run on a Hewlett-Packard 5710A instrument with thermal conductivity detector using a 6 ft × $^1/_8$ in. 10% SP-2100 column. Peak areas were measured with a Hewlett-Packard 3390A integrator and are corrected for detector response factors.

Tetrabutylammonium 2-Nitropropanide. A mixture of 100 g of 40% tetrabutylammonium hydroxide in water, 2-nitropropane (15 mL), and benzene (250 mL) was subjected to azeotropic distillation until 60 mL of water was collected. Benzene (100 mL) was then removed by distillation. The solution was cooled to room temperature and transferred by syringe to a 200-mL volumetric flask. The solution was diluted to the mark, giving a nominally 0.77 M solution of tetrabutylammonium 2-nitropropanide in benzene, clear and faintly yellow. The solution was stored in a brown bottle under argon.

2-(Perfluoroalkyl)-2-nitropropanes. A. From Lithium 2-Nitropropanide. A 470-mL photolysis vessel was charged with 89.2 g (0.2 mol) of perfluorohexyl iodide, 400 mL of DMF, and 19 g (0.2 mol) of lithium 2-nitropropanide. The stirred solution was irradiated for 4 h using 350-nm lamps. The solution was poured into 1 L of ice water and extracted three times with 300

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(29) Ashby, E. C.; Goel, A. B. *Tetrahedron Lett.* **1981**, *22*, 4783. Ashby, E. C.; Goel, A. B.; DePriest, R. N. *Ibid.* **1981**, *22*, 3729. Singh, P. R.; Khurana, J. M.; Nigam, A. *Ibid.* **1981**, *22*, 2901. Ashby, E. C.; Goel, A. B. *Ibid.* **1981**, *22*, 1879.

(30) The conversion of nitro to hydride by tributyltin hydride (Ono, N.; Miyake, H.; Tamura, R.; Kaji, A. *Tetrahedron Lett.* **1981**, *22*, 1705; Tanner, D. D.; Blackburn, E. V.; Diaz, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 1557) and by methanethiolate (Kornblum, N.; Carlson, S. C.; Smith, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 647) has been reported. Anion radical intermediates were suggested.

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(32) Russell, G. A.; Ros, F.; Mudryk, B. *J. Am. Chem. Soc.* **1980**, *102*, 7601. Gussell, G. A.; Ros, F.; Hershberger, J.; Tashtoush, H. *J. Org. Chem.* **1982**, *47*, 1480.

(33) Termination processes in aromatic $S_{RN}1$ reactions have been considered in detail: Amatore, C.; Pinson, J.; Saveant, J. M.; Thiebault, A. *J. Am. Chem. Soc.* **1981**, *103*, 6930.

mL of ether. The combined ether extracts were washed three times with 300 mL of water, dried, and concentrated on a rotary evaporator to 70.9 g of white solid. Kugelrohr distillation at 20 mm and bath temperature of 130 °C gave 64.6 g (79%) of colorless liquid **3a**, which crystallized on standing.

A duplicate reaction using 109 g (0.2 mol) perfluorooctyl iodide gave 90 g of crude product. The product was recrystallized from 150 mL of boiling ethanol and dried at 50 mm and 70 °C, giving 58.4 g (58%) of **3b** as white plates.

B. From Tetrabutylammonium 2-Nitropropanide in Benzene. Perfluorohexyl iodide (8.9 g, 0.02 mol) was added in one portion to 30 mL of the tetrabutylammonium 2-nitropropanide solution in benzene. The solution immediately turned bright red and the temperature rose to 53 °C. The solution was stirred for 20 min and poured into 200 mL of ether and 200 mL of water. The ether solution was washed three times with 100 mL of water, dried ($MgSO_4$), and concentrated on a rotary evaporator to 7.3 g of oil. Kugelrohr distillation as above gave 5.8 g (71%) of **3a**.

A similar run using 16.4 g (0.03 mol) of perfluorooctyl iodide and 40 mL of the salt solution gave 9.3 (61%) of **3b** after recrystallization from 40 mL of ethanol.

C. From Tetrabutylammonium 2-Nitropropanide in Benzene/Water. A solution of 40 mL of 40% tetrabutylammonium hydroxide in water and 5.4 mL of 2-nitropropane was treated with a solution of 17.8 g of perfluorohexyl iodide in 40 mL of benzene. The vigorously stirred mixture in a foil-wrapped flask was maintained at 60 °C for 17 h. The mixture was added to 500 mL of water and extracted twice with 150 mL of ether. The combined ether extracts were washed three times with 100 mL of water, dried ($MgSO_4$), and concentrated on a rotary evaporator to 9 g of brown oil. Kugelrohr distillation at and 120 °C (20 mm) gave 6.2 g of distillate as an oily solid. GLC analysis (oven temperature 100–102 min, 100–200 °C at 8 °C/min) showed two major peaks, identified as **3a** (84%) and **5** (14%) by coinjection with authentic samples.

A similar run except that the vigorously stirred mixture was irradiated for 3 h with 300-nm lamps gave 9 g after Kugelrohr distillation. GLC analysis showed **3a** (70%) and **5** (24%).

Reaction of α,ω-Diiodoperfluoroalkanes with 2-Nitropropanide. A. A solution of 14.3 g (0.15 mol) of lithium 2-nitropropanide, 160 mL of DMF, and 22.7 g (0.05 mol) of 1,4-diiodoperfluorobutane was irradiated for 2.5 h with 300-nm lamps. The solution was poured into 500 mL of water and extracted twice with 250 mL of ether. The combined ether extracts were washed three times with 100 mL of water, dried ($MgSO_4$), and concentrated on the rotary evaporator to 17.5 g of yellow sticky solid. GLC analysis (oven 100 °C–4 min, 100–200 °C at 16 °C/min) showed five peaks (retention time, area percent): **12b** (2.04 min, 10.7%), **4** (4.30 min, 2.4%), unknown (6.39 min, 6.3%), **13b** (6.96 min, 32.1%), and **14b** (10.01 min, 48.5%). The crude product was recrystallized from 100 mL of boiling absolute ethanol, giving 7.6 g (40%) of **14b**. The mother liquor was concentrated to 9.1 g of oily solid, which was chromatographed on 430 g of silica gel. The column was eluted with 1.5 L of hexane, followed by 1.5 L of 5% ether in hexane, taking 100-mL fractions. Fractions 25–29 contained 3.3 g (16%) of **13b**.

B. A solution of 16.6 g (0.03 mol) of 1,6-diiodoperfluorohexane (**12c**) in 30 mL of benzene was added dropwise over 0.5 h to 80 mL of the benzene solution of tetrabutylammonium 2-nitropropanide. Temperature rose to 42 °. The solution was stirred for 1 h and then added to 300 mL of ether and 300 mL of water. The organic phase was washed three times with 100 mL of water, dried ($MgSO_4$), and concentrated on the rotary evaporator to 14.3 g of yellow oily solid. GLC analysis as above showed **12c** (4.19 min, 18.5%), **13c** (8.31 min, 22.4%), and **14c** (11.04 min, 53.1%). The crude product was recrystallized from 200 mL of boiling ethanol, giving 5.0 g (35%) of **14c**. The mother liquor was concentrated to 8.7 g of oily solid, which was chromatographed on 320 g of silica gel. The column was eluted with 1 L of hexane, 1 L of 5% ether in hexane, and 2 L of 10% ether in hexane, taking 100-mL fractions. Fractions 20–22 contained 2.05 g (13%) of **13c**. Fractions 34–37 contained 1.15 g of **14c** for a total **14c** yield of 43%.

C. A solution of 2.0 g (0.021 mol) of lithium 2-nitropropanide, 30 mL of DMF, and 3.5 g (0.01 mol) of 1,2-diiodotetrafluoroethane was irradiated with 300-nm light for 2 h. The solution was poured into 150 mL of water and extracted twice with 50 mL of ether. The ether extracts were washed three times with 100 mL of water, dried ($MgSO_4$), and concentrated on the rotary evaporator to 1.52 g of white solid identified as **4** by NMR and GLC.

Reaction of Perfluorooctyl Iodide, Tetrabutylammonium 2-Nitropropanide, and Styrene. A 50-mL portion of the tetrabutylammonium 2-nitropropanide solution in benzene was added over 0.25 h to a stirred solution of 16.4 g (0.03 mol) of perfluorooctyl iodide and 12.5 g (0.12 mol) of styrene in 50 mL of benzene. The solution was stirred 3 h and poured into 300 mL of ether + 200 mL of water. The organic solution was washed three times with 100 mL of water, dried ($MgSO_4$), and concentrated on the rotary evaporator to 23.8 g of a faintly yellow oil. The oil was Kugelrohr distilled to give three fractions. The first (100 °C (50 mm), 10.4 g) was mostly unreacted perfluorooctyl iodide and styrene by GLC. The second (150 °C (30 mm), 2.0 g, 13%) was **3b**. The third fraction (160 °C (0.25 mm), 5.5 g) was recrystallized from 60 mL of methanol to give 4.2 g (23%) of **6b**.

A similar experiment using 13.5 g (0.03 mol) of perfluorohexyl iodide gave 5.0 g (33%) of **6a**.

Reaction of Perfluorooctyl Iodide, Tetrabutylammonium 2-Nitropropanide, and Methyl Methacrylate. A 28-mL (0.022 mol) portion of the tetrabutylammonium 2-nitropropanide solution in benzene was added to a solution of 10.9 g (0.02 mol) of perfluorooctyl iodide, 4.0 g (0.04 mol) of methyl methacrylate, and 25 mL of benzene. The solution temperature rose to 48 °C. After 2 h the orange solution was poured into 200 mL of water and 300 mL ether. The ether solution was washed three times with 100 mL of water, dried ($MgSO_4$), and concentrated on a rotary evaporator to 9.4 g of yellow solid. The solid was chromatographed on 230 g of silica gel packed in hexane. The column was eluted with 1 L of hexane, 1 L 5% ether in hexane, 1 L 10% ether in hexane, and 1 L of 25% ether in hexane, taking 100-mL fractions. Fractions 19 and 20 contained 2.49 g of **3b**, fractions 24–29 contained 3.45 g of **7**, and fractions 32–38 contained 0.73 g of **8**.

Reaction of Perfluorooctyl Iodide, Tetrabutylammonium 2-Nitropropanide, and Vinyl Acetate. A 39-mL (0.03 mol) portion of the tetrabutylammonium 2-nitropropanide solution in benzene was added to a solution of 10.9 g (0.02 mol) of perfluorooctyl iodide, 5.2 g (0.06 mol) of vinyl acetate, and 30 mL of benzene. After 5 h, workup as above gave 11.4 g of crude product. The material was chromatographed on 300 g of silica gel packed in hexane. The column was eluted with 1 L of hexane, 1 L of 5% ether in hexane, 1 L of 10% ether in hexane, and 1 L of 15% ether in hexane, taking 100-mL fractions. Fractions 18–23 contained 4.6 g of **3b**, and fractions 30–33 contained 2.0 g of **9**.

Reaction of 2-(Perfluorohexyl)-2-nitropropane (3a) with Tetrabutylammonium 2-Nitropropanide. A solution of 10.2 g of **3a** in 50 mL of benzene and 50 mL of the tetrabutylammonium 2-nitropropanide solution in benzene was irradiated with 300-nm light for 6 h. The solution was poured into 200 mL of ether. The organic phase was washed three times with 200 mL of water, dried ($MgSO_4$), and concentrated on a rotary evaporator to 9.6 g of a yellow oily solid. Two recrystallizations of the material from 30 mL of boiling ethanol gave 3.6 g of pure **18**. The combined mother liquors was concentrated on the rotary evaporator to a multicomponent yellow solid (4.5 g). Chromatography on 130 g of silica gel (1 L of hexane, 2 L of 10% 1,1,2-trichlorotrifluoroethane in hexane, 100-mL fractions) gave in fractions 12–16 an additional 1.23 g of **18**, for a total yield of 43%.

Reaction of 2-(Perfluorohexyl)-2-nitropropane (3a) with Sodium Thiophenoxide. A solution of 4.1 g (0.01 mol) of **3a**, 2.0 g (0.015 mol) of sodium thiophenoxide, and 40 mL of DMF was irradiated for 3 h with 300-nm lamps. The solution was poured into 500 mL of ice water and extracted three times with 200 mL of ether. The combined ether extracts were washed three times with 100 mL of water, dried ($MgSO_4$), and concentrated on the rotary evaporator to 3.1 g of oil. GLC analysis (oven 100 °C–2 min, 100–200 °C at 16 °C/min) showed a complex series of peaks. There were two major peaks 7.4 min (23%) and 12.65 min (44%), the second having the retention time of diphenyl disulfide. The crude product was chromatographed on 120 g of silica gel (1 L of hexane, 1 L of 5% ether in hexane, 100-mL fractions). About 37 mg of material in fraction 6 was pure 7.4-min material by GLC. Its structure was assigned as **19** by NMR. Some diphenyl disulfide was isolated from later fractions.

Catalytic Hydrogenation of 2-(Perfluoroalkyl)-2-nitropropanes. A 400-mL stainless steel pressure vessel was charged with 24.4 g (0.06 mol) of 2-(perfluorohexyl)-2-nitropropane (**3a**), 1.5 g of 10% Pd/C, and 200 mL of ethanol. The vessel was pressured to 1000 psi with H_2 and agitated at 80 °C overnight. The vessel was cooled and vented, and the contents were filtered to remove the catalyst. The filtrate was treated with 15 mL of concentrated HCl and concentrated on a rotary evaporator to a white solid. The solid was treated with 100 mL of 1 N KOH. A lower layer was separated, and the upper aqueous layer was extracted twice with 40 mL of ether. The combined organic layers were washed with 10 mL of water and dried ($MgSO_4$). The ether was removed by distillation through a 6-in. Vigreux column. The residue was distilled through a short-path still at 80 mm, giving 14 g (62%) of 2-(perfluorohexyl)-2-aminopropane (**22a**).

Reduction of 2-(perfluorooctyl)-2-nitropropane (**3b**; 25.4 g, 0.05 mol) in 200 mL of ethanol with 2.0 g of 10% Pd/C as above gave 16.9 g (71%) of 2-(perfluorooctyl)-2-aminopropane (**22b**).

The diamines **23b** and **23c** were prepared similarly except that the crude products were isolated by concentration on a rotary evaporator of the ethanol solutions after filtration. The perfluorobutyl (**23b**) derivative was purified by Kugelrohr distillation at 10 mm and 110 °C (81% yield). The perfluorohexyl derivative (**23c**) was recrystallized from hexane in 76% yield.

Reduction of 2-(Perfluorohexyl)-2-nitropropane (3a) with Lithium Aluminum Hydride. A mixture of 2.6 g of lithium aluminum hydride and 50 mL of tetrahydrofuran was warmed to 35 °C and the heat was removed. A solution of 10.2 g (0.025 mol) of **3a** in 50 mL of THF was added dropwise over 1 h. The temperature remained at about 35 °C and a slow gas evolution was evident. The mixture was stirred for 0.25 h after the addition was complete. The mixture was chilled in ice water and quenched by the dropwise addition of 1 N KOH. The mixture was filtered. The filtrate was diluted to 400 mL with ether and washed five times with 100 mL of water. The dried ($MgSO_4$) ether solution was carefully concentrated on the rotary evaporator to 6.4 g of clear oil. GLC analysis (oven 100 °C–2 min, 100–200 °C at 16 °C/min) showed four peaks (retention time, area percent): 2-(perfluorohexyl)propane (0.67, 68.4), 2-(perfluorohexyl)-2-aminopropane (1.04, 4.7), unreacted **3a** (2.41, 22.8), and 2-(perfluorohexyl)-2-(hydroxyamino)propane (2.89, 3.3). Distillation of the crude product through a short path still gave 4.0 g (44%) of colorless liquid bp 65–66 °C (60 mm) identified as pure **20**.

Reduction of 2-(Perfluorohexyl)-2-nitropropane (3a) with Stannous Chloride. A solution of 4.1 g (0.01 mol) of **3a** in 30 mL of ethanol was added over 0.5 h to a solution of 11.3 g (0.05 mol) of stannous chloride dihydrate in 15 mL of concentrated hydrochloric acid. The solution temperature was checked with an ice bath at 40 °C. After addition the solution was stirred for 1 h at room temperature. The solution was cooled in ice water, diluted with 90 mL of 6 N NaOH, and extracted twice with 30 mL of ether. Combined ether extracts were washed twice with 50 mL of 1 N NaOH and twice with 50 mL of water, dried ($MgSO_4$), and concentrated on the rotary evaporator to 3.3 g of oil, which crystallized on standing. GLC analysis (oven 100 °C–2 min, 100–200 °C at 8 °C/min) showed two peaks. The first peak (retention time = 1.01 min, 14 area %) had the retention time of authentic 2-(perfluorohexyl)-2-aminopropane (**22a**). A pure sample of the second peak material (retention time = 3.10 min, 80 area %) was obtained by two recrystallizations of the crude product from boiling hexane, followed by drying in a vacuum oven at 60 °C. The yield of purified material was 1.9 g (48%), identified as the hydroxylamine **21**.

Methylation of 2-(Perfluorooctyl)-2-aminopropane. A mixture of 14.4 g (0.03 mol) of 2-(perfluorooctyl)-2-aminopropane (**22b**), 7.8 g of formic acid, and 9.0 mL of 37% formaldehyde was heated to 90 °C (foaming!). After 17 h, the mixture was cooled to room temperature and transferred to a separatory funnel, using 50 mL of 2 N hydrochloric acid. The solution was made basic with 1 N sodium hydroxide and extracted three times with 75 mL of ether. Combined ether extracts were washed three times with 50 mL of water, dried ($MgSO_4$), and concentrated on a rotary evaporator. The residue was distilled through a short-path condenser, giving 13.8 g (91%) of colorless **24**, bp 88–90 °C (10 mm).

Properties of New Compounds. Satisfactory combustion analytical data for C, H, N were obtained. Proton NMR were obtained at 80 or 90 MHz unless otherwise indicated. Only the first two CF_2 groups of the straight-chain perfluoroalkyl derivatives are shifted significantly with substitution in the fluorine NMR and are indicated below. The terminal CF_3, adjacent CF_2, and central CF_2 resonances always appeared at −81.5, −126.7, and −122 to −124 ppm, respectively. $CF_3(CF_2)_4CF_2C(CH_3)_2NO_2$ (**3a**): mp 43–44 °C; H NMR δ 1.87 (singlet with fine structure); F NMR −118.6 (2 F), −115.6 (2 F). $CF_3(CF_2)_6CF_2C(CH_3)_2NO_2$ (**3b**): mp 72–73 °C; H NMR δ 1.90 (singlet with fine structure); F NMR δ −118.7 (2 F), −115.7 (2 F). $CF_3(CF_2)_4CF_2CH_2CH(Ph)C(CH_3)_2NO_2$ (**6a**): mp 63–64 °C; H NMR δ 1.48 (s, 3 H), 1.59 (s, 3 H), 2.50 (m, 2 H), 3.80 (dd, 1 H), 7.1–7.5 (m, 5 H); F NMR δ −123.7 (2 F), −112.3 (1 F), −114.9 (1 F). $CF_3(CF_2)_6CF_2CH_2CH(Ph)C(CH_3)_2NO_2$ (**6b**): mp 73–74 °C; H NMR δ 1.50 (s, 3 H), 1.62 (s, 3 H), 2.58 (m, 2 H), 3.83 (dd, 2 H), 7.1–7.5 (m, 5 H); F NMR δ −123.8 (2 F), −113.1 (1 F), −114.0 (1 F). $CF_3CH_2CH(Ph)C(CH_3)_2NO_2$ (**6c**): mp 59 °C; H NMR δ 1.43 (s, 3 H), 1.57 (s, 3 H), 2.60 (m, 2 H), 3.66 (dd, 1 H), 7.1–7.5 (m, 5 H); F NMR δ −64.5 (t, J_{H-F} = 10 Hz). $CF_3(CF_2)_6CF_2CH_2C(CH_3)(CO_2CH_3)C(CH_3)_2NO_2$ (**7**): mp 95–96 °C; H NMR (360 MHz) δ 1.39 (d, J = 3.3 Hz, 3 H), 1.59 (s, 3 H), 1.74 (s, 3 H), 2.64 (m, 1 H), 3.14 (dd, J = 15.1, 37.5 Hz, 1 H), 3.76 (s, 3 H); F NMR δ −122.6 (2 F), −116.7 (1 F), −105.2 (1 F). $CF_3(CF_2)_6CF_2CH_2CH(O_2CCH_3)C(CH_3)_2NO_2$ (**9**): mp 66–67 °C; H NMR (360 MHZ) δ 1.62 (s, 3 H), 1.65 (s, 3 H), 2.10 (s, 3 H), 2.40 (m, 2 H), 5.88 (m, 1 H); F NMR δ −122.6 (2 F), −114.9 (2 F). $I(CF_2)_4C(CH_3)_2NO_2$ (**13B**): bp 72–74 °C (2.5 mm); H NMR δ 1.87 (singlet with fine structure); F NMR δ −59.0 (2 F), −113.3 (2 F), −115.8 (2 F), −117.8 (2 F). $I(CF_2)_6C(CH_3)_2NO_2$ (**13C**); mp 54–57 °C; H NMR δ 1.84 (singlet with fine structure); F NMR δ −59.3 (2 F), −113.5 (2 F), −121.3 (2 F), −122.1 (2 F), −118.7 (2 F), −115.8 (2 F). $O_2N(CH_3)_2C(CF_2)_4C(CH_3)_2NO_2$ (**14b**): mp 119–120 °C; H NMR δ 1.84 (singlet with fine structure); F NMR −115.7 (4 F), −118.5 (4 F). $O_2N(CH_3)_2C(CF_2)_6C(CH_3)_2NO_2$ (**14c**): mp 129–131 °C; H NMR δ 1.87 (singlet with fine structure); F NMR−115.7 (4 F), −118.6 (4 F), −121.9 (4 F). $CF_3(CF_2)_4CF_2C(CH_3)_2C(CH_3)_2NO_2$ (**18**): mp 77–78 °C; H NMR 1.40 (s, 6 H), 1.75 (s, 6 H); F NMR δ −117.1 (2 F), −110.7 (2 F). $CF_3(CF_2)_4CF_2C(CH_3)_2SPh$ (**19**): oil; H NMR δ 1.47 (s, 6 H), 7.2–7.4 (m, 3 H), 7.4–7.7 (m, 2 H); F NMR δ −117.1 (2 F), −111.3 (2 F). $CF_3(CF_2)_4CF_2C(CH_3)_2H$ (**20**): bp 60–62 °C (50 mm); H NMR δ 1.13 (d, 6 H), 2.43 (m, 1 H); F NMR−121.2 (2 F), −119.8 (2 F). $CF_3(CF_2)_4CF_2C(CH_3)_2NHOH$ (**21**): mp 51–52 °C; H NMR δ 1.37 (singlet with fine structure, 6 H), 5.23 (br s, 1 H), 5.70 (br s, 1 H); F NMR δ −119.5 (2 F), −117.6 (2 F). $CF_3(CF_2)_4CF_2C(CH_3)_2NH_2$ (**22a**): bp 88–90 °C (80 mm); H NMR δ 1.32 (singlet with fine structure, 6 H), 1.55 (br s, 2 H); F NMR −121.0 (2 F), −118.7 (2 F). $CF_3(CF_2)_6C(CH_3)_2NH_2$ (**22b**): bp 94–95 °C (35 mm); H NMR δ 1.30 (singlet with fine structure, 6 H), 1.53 (br s, 2 H); F NMR δ −121.0 (2 F), −118.5 (2 F). $H_2NC(CH_3)_2(CF_2)_4C(CH_3)_2NH_2$ (**23b**): mp 74–75 °C; H NMR δ 1.30 (singlet with fine structure, 12 H), 1.57 (br s, 4 H); F NMR δ −118.6 (4 F), −121.1 (4 F). $H_2NC(CH_3)_2(CF_2)_6C(CH_3)_2NH_2$ (**23c**): mp 88–89 °C; H NMR δ 1.30 (singlet with fine structure, 12 H), 1.57 (br s, 4 H); F NMR δ −122 (4 F), −121.1 (4F), −118.7 (4F). $CF_3(CF_2)_6CF_2C(CH_3)_2N(CH_3)_2$ (**24**): bp 88–90 °C (10 mm); H NMR δ 1.32 (singlet with fine structure, 6 H), 2.43 (s, 6 H); F NMR δ −119.3 (2 F), −112.6 (2 F).