

caused the peak at δ 4.62 to become a singlet, that at δ 1.66 to become a broad triplet, that at δ 2.57 to become a broad doublet, and the peak at δ 2.80 to become less complex; IR (neat) 1703 (CO), 1640 (C=C) cm^{-1} ; mass spectrum (15 eV), m/e 382 (M^+ , 12%), 273 ($\text{M}^+ - \text{PhS}$, 100%), 163 ($\text{M}^+ - \text{PhS} - \text{PhSH}$, 100%); exact mass calcd for $\text{C}_{23}\text{H}_{26}\text{OS}_2$ 382.1425, found 382.1426.

Epimerization of 7 to 8 and 9 to 10. To a solution of 7 (0.044 g, 1.14 mmol) in 3 mL of THF was added an aqueous solution of sodium hydroxide (0.023 g, 0.58 mmol) in water (2 mL). The mixture was stirred at ambient temperature for 0.5 h. Workup as above gave 8 in quantitative yield.

In a similar experiment, a mixture of 7 (R_f 0.59, reversed-phase TLC, 4:1 methanol-water) and 8 (R_f 0.51) was converted to a mixture of 7 and 10 (R_f 0.48) in quantitative yield.

exo-7-(Phenylthio)bicyclo[4.1.0]heptan-2-one (12). Absolute methanol (0.030 mL, 0.75 mmol) was added to a solution of 3 prepared from 0.75 mmol of tris(phenylthio)methane in THF; the orange-red solution turned light yellow and became turbid. Stirring was continued for 20 min before the addition of hexamethylphosphoric triamide (0.26 mL, 1.50 mmol) and methyl iodide (0.047 mL, 0.75 mmol). The mixture was allowed to warm to 25 °C slowly and was maintained at that temperature for a period of 15 h. Quenching with water, the same workup as above, and flash chromatography gave 0.052 g (32%) of pure *exo*-7-(phenylthio)bicyclo[4.1.0]heptan-2-one (15): mp 62-63 °C; ^1H

NMR δ 1.57-2.38 (m, 8 H), 2.83 (t, $J = 3.84$ Hz, 1 H, CHSPH),¹³ 7.14-7.31 (m, overlapping two singlets at δ 7.29 and 7.31, 5 H); IR (CCl_4) 1695 (CO) cm^{-1} ; mass spectrum (15 eV), m/e 218 (M^+ , 100%); exact mass for $\text{C}_{13}\text{H}_{14}\text{OS}$ (M^+) 218.0765, found 218.0765. The chemical shift of the C-7 proton and the carbonyl frequency are almost identical with those of an analogous compound in the carvone series.⁴

Acknowledgment. We thank Dr. Alvin Marcus for recording the mass spectra and the National Science Foundation for support of this work (CHE 8210245) and for providing the funds for the 300-MHz Bruker NMR instrument used in this study (CHE 7905185).

Registry No. 1, 14572-78-2; 3, 97336-66-8; 4 (isomer I), 97336-59-9; 4 (isomer II), 97336-60-2; 5, 69814-21-7; 6, 89969-02-8; 7, 97336-61-3; 8, 97336-62-4; 9, 97336-63-5; 10, 97336-64-6; 12, 97336-65-7; *sec*-BuSPH, 14905-79-4; tris(phenylthio)methane, 4832-52-4; cyclohex-2-en-1-one, 930-68-7; benzaldehyde, 100-52-7; (-)-carvone, 6485-40-1.

(13) This coupling constant is characteristic of the *exo* phenylthio group in this system.^{4,14}

(14) Schöllkopf, U.; Lehmann, G. J.; Paust, J.; Härtl, H. D. *Chem. Ber.* 1964, 97, 1527.

Reaction of Perfluoroalkyl Iodides with Electron Donor Nucleophiles. Addition of Perfluoroalkyl Iodides to Olefins Initiated by Electron Transfer[†]

Andrew E. Feiring

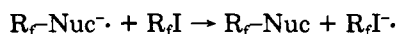
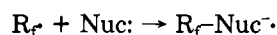
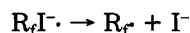
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The radical chain addition of primary and secondary perfluoroalkyl iodides to olefins is initiated by sodium arene- and alkanesulfonates. The process occurs at room temperature and is favored by the use of dipolar aprotic solvents. The reaction of perfluorooctyl iodide with sodium *p*-toluenesulfonate in the absence of olefin requires higher temperatures and gives only 1-H-perfluorooctane; no anion-perfluoroalkyl radical coupling products were detected. Reaction of perfluorooctyl iodide with the sodium salt of diethyl methylmalonate also gives no coupling product; only 1-H-perfluorooctane and a dimer of the malonate anion are produced. These results are compared with the reactions of perfluoroalkyl iodides with nitronate and thiolate anions where formation of $\text{S}_{\text{RN}}1$ substitution products was observed.

Several groups¹⁻⁷ have described the very facile reactions of perfluoroalkyl iodides with certain electron donor nucleophiles. Reactions of the iodides with enamines,³ thiolates,^{2,4} selenates,⁵ sulfonates,⁶ enolates,⁷ and nitronates¹ result in displacement of iodide by the nucleophiles. Since perfluoroalkyl iodides are known to be very resistant to normal nucleophilic attack,⁸ these reactions may proceed by an $\text{S}_{\text{RN}}1$ mechanism⁹⁻¹² (Scheme I).

Scheme I



Recently, we presented firm evidence for the $\text{S}_{\text{RN}}1$ pathway in reactions of the iodides with nitronate¹ and

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- (3) Cantacuzene, D.; Wakselman, C.; Dorme, R. *J. Chem. Soc. Perkin Trans. 1* 1977, 1365.
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- (7) Yagupolskii, L. M.; Matyushcheva, G. I.; Pavenko, N. V.; Boiko, V. N. *J. Org. Chem., USSR (Engl. Transl.)* 1982, 18, 10.
- (8) Chambers, R. D. "Fluorine In Organic Chemistry"; John Wiley & Sons, Inc.: New York, 1973; pp 98-99.

[†] Contribution No. 3349.

Table I. Addition to Perfluoroalkyl Iodides to Olefins

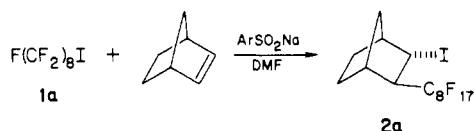
entry	R _f I (mmol)	olefin (mmol)	RSO ₂ Na, (mmol)	solvent	product mixture ^a			isolated yield of 1:1 adduct
					% R _f I	% 1:1 adduct	% olefin ^b	
1	F(CF ₂) ₈ I (20)	norbornene (100)	Ph (30)	DMF	0	100	0	93
2	F(CF ₂) ₈ I (20)	norbornene (50)	<i>p</i> -Tol (20)	DMF	0	100	0	94
3	F(CF ₂) ₂ I (20)	norbornene (100)	CH ₃ (21)	DMF	0	100	0	84
4	F(CF ₂) ₈ I (20)	norbornene (100)	<i>p</i> -CH ₃ CONH-Ph (10)	DMF	0	100	0	84
5	F(CF ₂) ₈ I (10)	norbornene (25)	<i>p</i> -Tol (1)	DMF	0	100	0	90
6	F(CF ₂) ₈ I (20)	norbornene (100)	<i>p</i> -Tol (20)	Me ₂ SO	0	100	0	81
7	F(CF ₂) ₈ I (20)	norbornene (100)	<i>p</i> -Tol (20)	CH ₃ CN	0	100	0	84
8	F(CF ₂) ₈ I (20)	norbornene (100)	<i>p</i> -Tol (20)	benzene	84	16	0	19
9	(CF ₃) ₂ CFI (20)	norbornene (100)	<i>p</i> -Tol (20)	DMF	nm	nm	nm	58
10	C ₇ F ₁₅ CFICF ₃ (10)	norbornene (50)	<i>p</i> -Tol (10)	DMF	0	100	0	85
11	I(CF ₂) ₄ I (20)	norbornene (100)	<i>p</i> -Tol (10)	DMF	0	100 ^c	0	83 ^c
12	F(CF ₂) ₈ I (20)	cyclopentene (60)	<i>p</i> -Tol (10)	DMF	33	63	3	46
13	F(CF ₂) ₈ I (20)	1-octene (80)	<i>p</i> -Tol (20)	DMF	11	62	21	nm
14	F(CF ₂) ₈ I (20)	1-octene (80)	<i>p</i> -Tol (20)	DMF	9	64	21	73
15	F(CF ₂) ₈ I (20)	1-octene (100)	<i>p</i> -Tol (5)	DMF	18	73	5	71
16	F(CF ₂) ₈ I (20)	norbornadiene (100)	<i>p</i> -Tol (20)	DMF	0	100	0	95
17	F(CF ₂) ₈ I (20)	propene (360)	<i>p</i> -Tol (20)	DMF	0	45	44	34
18	F(CF ₂) ₈ I (20)	allylbenzene (40)	<i>p</i> -Tol (5)	DMF	80	15	5	8
19	F(CF ₂) ₈ I (20)	allyl acetate (80)	<i>p</i> -Tol (5)	DMF	59	32	8	29
20	F(CF ₂) ₈ I (20)	methyl 11-undecenoate (20)	<i>p</i> -Tol (5)	DMF	8	61	31	44
21	F(CF ₂) ₈ I (20)	ethene (420)	<i>p</i> -Tol (20)	DMF	31	20		17 (+33% sulfone)

^a By GLPC analysis. ^b Product formed by elimination of HI from 1:1 adduct. ^c 2:1 adduct.

thiolate anions² by trapping the intermediate perfluoroalkyl radicals with a series of olefins which were included in the reaction mixture. These studies have now been extended to sulfinate and methylmalonate anions as nucleophiles. In contrast to the earlier results, these reactions do not lead to net nucleophilic substitution of the iodide. They do lead to perfluoroalkyl radical formation, demonstrated by olefin trapping experiments. The sulfinate salt reaction has been developed into a synthetically useful process for the addition of perfluoroalkyl iodides to olefins. Some additional results on the perfluoroalkyl iodide-nitronate reaction¹ are also reported.

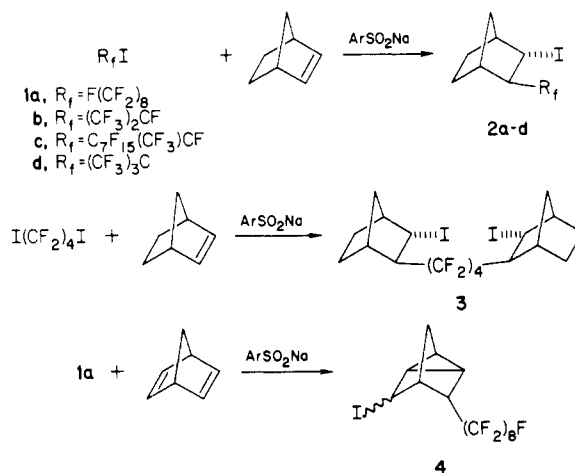
Results

Reactions of Perfluoroalkyl Iodides in the Presence of Sulfinate Salts. Stirring an equimolar mixture of perfluoroalkyl iodide (**1a**) and sodium benzenesulfinate or sodium *p*-toluenesulfinate in DMF or Me₂SO overnight at room temperature gave only unreacted starting materials. Even after one week no reaction was observed. Remarkably, reaction under these conditions in the presence of excess norbornene led to the formation of 2-iodo-3-(perfluoroalkyl)norbornane (**2a**) in nearly quantitative yield in several hours. Appropriate control experiments showed that **2a** was not formed under these conditions in the absence of the sulfinate salt.



The addition of perfluoroalkyl iodides to olefins is an important synthetic procedure¹³ in organofluorine chem-

istry. Since this process seemed to offer the mildest conditions yet known for this addition, the reaction was investigated with different perfluoroalkyl iodides, olefins, solvents, and sulfinate salts. The results are summarized in Table I. The adduct **2a** was formed in high yield from **1a** and norbornene by using the sodium salts of benzene-, *p*-toluene-, *p*-acetamidobenzene-, and methanesulfinic acids as initiators and DMF, Me₂SO, or acetonitrile as solvent. Complete conversion of the perfluoroalkyl iodide occurred with 10 mol % *p*-toluenesulfinate as initiator. The reaction was much slower with benzene as the solvent, although no byproducts were detected. 1,4-Diiodoperfluorobutane reacted cleanly with norbornene giving the 1:2 adduct **3** in high yield. Perfluorooctyl iodide (**1a**) and norbornadiene gave the expected nortricyclene isomers **4**. The facile addition of primary perfluoroalkyl iodides to these strained olefins by using more traditional radical initiators has been noted previously.¹⁴



The secondary iodides **1b** and **1c** also reacted cleanly with norbornene under these conditions giving **2b** and **2c**.

(9) Kornblum, N. *Angew. Chem. Int. Ed. Engl.* 1975, 14, 734. Kornblum, N. In "The Chemistry of Functional Groups; Supplement F: The Chemistry of Amino, Nitroso and Nitro Compounds and their Derivatives"; Patai, S., Ed.; Wiley: New York, 1982. Norris, R. K. In "The Chemistry of Halides, Pseudo-halides and Azides"; Part 2, Patai, S., Rappaport, J., Ed.; Wiley: New York, 1983; Supplement D.

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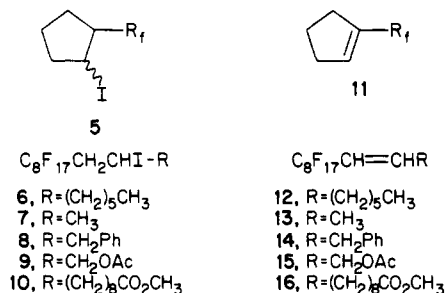
(12) Guthrie, R. D. In "Comprehensive Carbanion Chemistry"; Buncl, E., Durst, T., Eds.; Elsevier: New York, 1980; Chapter 5, Part A.

(13) Sheppard, W. A.; Sharts, C. M. "Organic Fluorine Chemistry"; W. A. Benjamin, Inc.: New York, 1969; p 189-193.

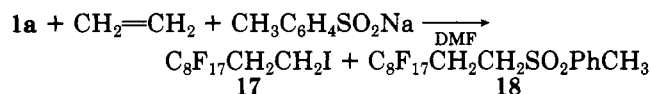
(14) Brace, N. O. *J. Org. Chem.* 1962, 27, 3027. Brace, N. O. *J. Org. Chem.* 1979, 44, 1964.

The latter compound was formed as a mixture of diastereomers. The adduct **2d** of perfluoro-*tert*-butyl iodide and norbornene was detected by fluorine NMR examination of the crude reaction mixture with sodium *p*-toluenesulfinate as initiator. However, the yield was very low, and the compound was not isolated in pure form from this reaction. An authentic sample of **2d** was prepared in good yield by AIBN initiated addition of **1d** to norbornene. Clearly, the latter procedure is preferable with tertiary iodides.

The addition of perfluoroalkyl iodide (**1a**) to other, less strained, olefins gave the results shown in Table I. These results were not optimized; a standard procedure employing a 17-h reaction time at room temperature and DMF as solvent was adopted. The sodium *p*-toluenesulfinate initiator was present in 25–100 mol % based on the iodide. With cyclopentene,¹⁵ 1-octene,¹⁶ propene,¹⁷ allylbenzene,¹⁸ allyl acetate,¹⁹ and methyl undecenoate,²⁰ the yield of primary adducts 5–10 ranged from 8 to 73%. In these cases, secondary products from elimination of HI were also detected. The olefin byproducts 11–16, with the exception of **12** and **16**, were not isolated in pure form. Their presence in the reaction mixtures was detected by proton NMR and confirmed by GC/MS examination of the crude products. With 1-octene, formation of the secondary product could be suppressed by decreasing the amount of sulfinate initiator. Alternatively, the elimination products could be obtained in good yield by treating the crude reaction product with base. A few olefins did not give successful results. Vinyl acetate gave a complex mixture containing essentially none of the expected addition product. 1,1-Difluoroethylene did not react, and tetrafluoroethylene gave unrelated products which will be described separately.



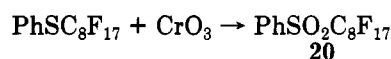
Reaction of perfluoroalkyl iodide (**1a**) with excess ethylene¹⁸ in the presence of 1 equiv of sodium *p*-toluenesulfinate gave a mixture of 17% iodide **17** and 33% sulfone **18**. Control experiments demonstrated formation of **18** from **17** under the reaction conditions, presumably by a straightforward S_N2 substitution process.



Addition of the perfluoroalkyl iodides to olefins was quite sensitive to the presence of oxygen. Identical reactions of perfluoroalkyl iodide (**1a**, 1 equiv), norbornene (3 equiv), and sodium *p*-toluenesulfinate (0.3 equiv) in DMF were monitored by GLPC for unreacted **1a** and the prod-

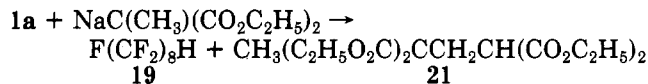
uct **2a**. One reaction was carefully evacuated and filled with argon several times before addition of the salt. The second reaction was run under dry air. The analysis showed complete disappearance of **1a** and formation of **2a** after 2 h in the reaction under argon. After 4 h, the reaction under air showed only a 9% conversion to product. This reaction was then evacuated and filled with argon several times. After an additional 2 h, this reaction also showed a complete conversion of **1a** to **2a**.

To determine the fate of a perfluoroalkyl iodide on reaction with a sulfinate salt in the absence of olefin, a mixture of **1a** (21 g, 0.04 mol) and sodium benzenesulfinate (0.06 mol) was heated at 90 °C for 17 h in DMF. Partial distillation of this solution under vacuum, followed by an aqueous extraction of the distillate, afforded 17 g of water insoluble liquid. This material was a mixture of 20% 1-H-perfluorooctane (**19**) and 80% **1a** by fluorine NMR. No other fluorinated compounds were detected in the distillate or residual material. In particular, no phenyl perfluoroalkyl sulfone (**20**) was observed. An authentic sample of **20** was prepared by oxidation⁴ of the corre-



sponding sulfide. A similar reaction using sodium *p*-toluenesulfinate gave a 77% yield of **19** as the only fluorinated product. The only other fluorinated material was unreacted **1a**. Fate of the sulfinate salt was not investigated; NMR of the crude oily product suggested a complex mixture. Irradiation (3500 Å) of a Me_2SO solution of perfluoroalkyl iodide (**1a**) and sodium benzenesulfinate for 17 h gave a complex mixture. By fluorine NMR, the major fluorinated component was unreacted **1a**, but the spectrum did show other weak, unidentified peaks. Phenyl perfluoroalkyl sulfone (**20**) was not detected by either NMR or GLPC examination of the crude product.

Reaction of Perfluoroalkyl Iodide with the Methylmalonate Anion. Addition of perfluoroalkyl iodide (**1a**) to 1.5 equiv of the sodium salt of diethyl methylmalonate gave, after stirring overnight at room temperature, a 27% yield of 1-H-perfluorooctane (**19**) which was directly distilled from the reaction vessel under vacuum. Further workup of the reaction mixture gave unreacted **1a** and the unsymmetrical dimer of the malonate **21**. No other fluorinated products were detected. A similar reaction with a sample of the malonate salt which was deuterated in the methyl group gave **19** containing 65% deuterium label. Under these conditions no reaction was observed with the sodium salts of either diethyl malonate or diethyl phenylmalonate.



Perfluoroalkyl iodide (**1a**) was reacted with the sodium salt of diethyl methylmalonate (1.2 equiv) in the presence of 5 equiv of norbornene under the conditions described above. Direct GLPC analysis of the reaction mixture showed peaks with the retention times of 1-H-perfluorooctane (**19**) and the norbornene adduct **2a** in a 1:5.7 ratio. The norbornene adduct **2a** was isolated in 67% yield together with the dimer **21** and unreacted malonate.

Reaction of Perfluoroalkyl Iodides with Nitropropanide Anion. As described earlier,¹ reaction of primary perfluoroalkyl iodides with lithium or tetrabutylammonium 2-nitropropanide in DMF or benzene, respectively, affords high yields of 2-perfluoroalkyl-2-nitropropanes (e.g., **22**). When the reaction of per-

(15) Brace, N. O. *J. Org. Chem.* **1963**, *28*, 3093.

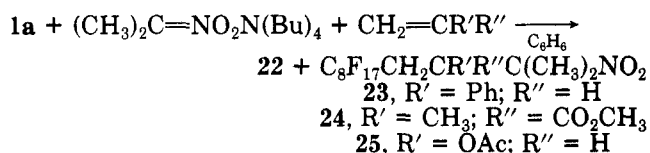
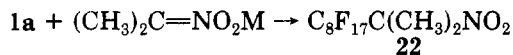
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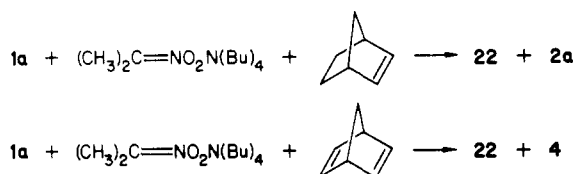
(18) Brace, N. O. U. S. Patent 3 145 223, Aug 18, 1964.

(19) Brace, N. O. *J. Fluorine Chem.* **1982**, *20*, 313.

(20) Brace, N. O. *J. Org. Chem.* **1962**, *27*, 4491.



fluorooctyl iodide with tetrabutylammonium 2-nitropropanide in benzene was conducted in the presence of styrene, vinyl acetate, and methyl methacrylate, products 23–25, incorporating the olefins and the 2-nitropropyl moiety, were also obtained. Somewhat different results are observed by using norbornene or norbornadiene as the trapping reagents. Addition of a benzene solution of tetrabutylammonium 2-nitropropanide to a mixture of 1 equiv of 1a and 5 equiv of norbornene afforded a 30% yield of 22 and a 50% yield of 2-iodo-3-perfluorooctylnorbornane (2a) as the only fluorinated products. A similar reaction in the presence of norbornadiene gave the nortricyclene isomers 4 in 61% yield in addition to 22.

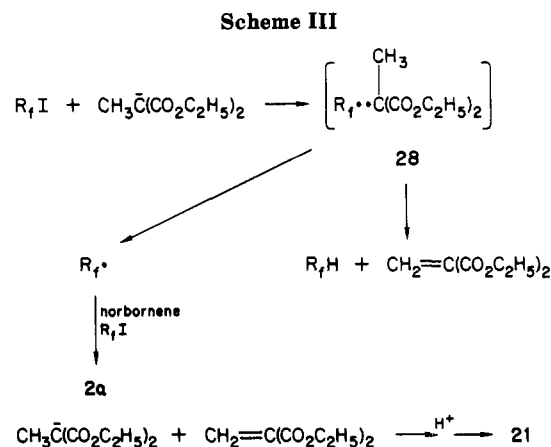
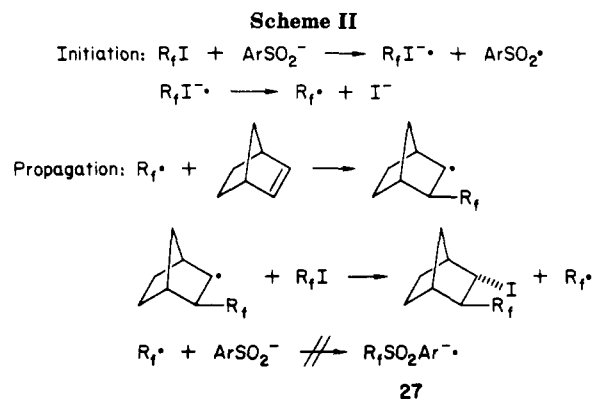


Previously, we noted¹ that a secondary perfluoroalkyl iodide, 2-iodoperfluoropropane (1b) reacted with the 2-nitropropanide ion to give 2,3-dimethyl-2,3-dinitrobutane (26) and a mixture of volatile fluorocarbons; no coupling product like 22 was observed. In the presence of an excess of norbornene, however, reaction of 1b with tetrabutylammonium 2-nitropropanide in benzene gave a 55% yield of the norbornene adduct 2b and about 20% of 26. Again no coupling product like 22 was detected.

Discussion

The addition of perfluoroalkyl iodides to olefins is a well-known process.¹³ The addition may be conducted without any catalyst or initiator but generally requires temperatures in excess of 160 °C. It may be initiated by UV irradiation,²¹ electrochemically,²² or by mercuric salts.²³ More commonly, the addition is initiated by free-radical initiators such as azo compounds and peroxides.^{14–20} The uses of copper chloride and ethanolamine in refluxing *tert*-butyl²⁴ alcohol and amines or amine salts at about 135 °C²⁵ to initiate this addition have been described. The process described here provides a simple alternative which avoids the use of high temperatures, expensive equipment, or hazardous reagents.

A possible mechanism for the sulfinate initiated addition of perfluoroalkyl iodide to norbornene is illustrated in Scheme II. The initiation step involves one electron transfer from the sulfinate anion to the perfluoroalkyl iodide. Loss of iodide ion gives the perfluoroalkyl radical. This species will add to olefins such as norbornene to give an alkyl radical which propagates a normal chain addition process. The perfluoroalkyl radical does not add to the sulfinate salt to give 27 which should propagate an S_{RN}1 substitution process. Clearly the initiation step is very much slower than the propagation sequence as little re-



action is observed in the absence of olefin. The dramatic effect of oxygen on the reaction rate is consistent with a radical chain process. At higher temperatures, the generation of perfluoroalkyl radicals from the iodide and sulfinate followed by hydrogen abstraction from solvent or sulfinate becomes sufficiently rapid to allow formation of observable amounts of product (R_fH) even in the absence of olefin. Formation of R_fH presumably involves a nonchain process.

In contrast to these results, isolation of aryl perfluoroalkyl sulfones from photolysis of perfluoroalkyl iodides and aryl sulfonic acids in liquid ammonia solution has been reported.⁶ The reaction was suggested to proceed by an S_{RN}1 mechanism, although no mechanistic evidence was presented. There is no immediate explanation for this discrepancy, although conditions in these studies were quite different.

Perfluoroalkyl radicals are also clearly generated from the interaction of the perfluorooctyl iodide and the methylmalonate anion, as indicated by the formation of the norbornene adduct 2a. The malonate dimer product 21 is the Michael adduct of methylmalonate anion and methylenemalonate, which could arise from disproportionation of the radical pair 28. In the presence of norbornene, the perfluoroalkyl radicals can initiate a rapid chain addition of 1a to the olefin.

The reaction pathways observed for perfluoroalkyl iodides and the nitronate ion in the presence of styrene or norbornene are collected in Scheme IV. Again the initiation step involves one electron transfer from the anion to generate the perfluoroalkyl radical. Subsequent reactions in the presence and absence of styrene have been discussed.¹ It remains to note the difference in behavior between the benzyl radical 29 and the norbornyl radical 30. The former radical couples with the highly reactive tetrabutylammonium 2-nitropropanide in benzene solution to give the anion radical 31. With less reactive nucleophiles

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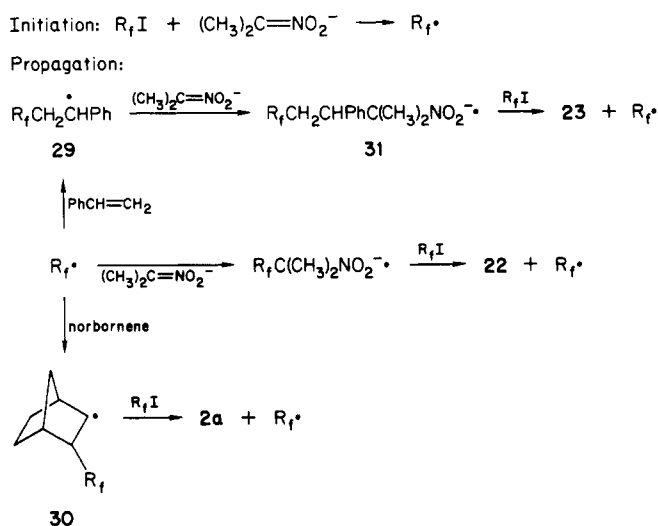
(22) European Patent Appl. 43758; *Chem. Abstr.* 1982, 96, 132156X.

(23) European Patent Appl. 43757; *Chem. Abstr.* 1982, 96, 199075.

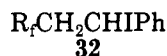
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Scheme IV



(lithium 2-nitropropanide or sodium thiophenoxide in DMF) no reaction is observed, presumably because of failure of this coupling step. Styrene simply inhibits disappearance of the perfluoroalkyl iodide^{1,2} under these conditions. Styrene is known²⁶ to be a poor substrate for perfluoroalkyl iodide addition, presumably because the benzyl radical does not react with perfluoroalkyl iodide at a rate which is competitive with chain termination processes. Thus, the adduct 32 is not likely to be an intermediate to 23. Attempts to prepare 32 using standard radical initiators were unsuccessful.



The more reactive norbornyl radical can abstract iodide from the perfluoroalkyl iodide to continue a chain process by atom transfer. Its failure to react with nitronate anion is presumably due to steric factors. Similarly, failure of the 2-perfluoropropyl radical to couple with the nitronate ion is ascribed to steric factors.¹ The results here confirm that the secondary radical is formed in the interaction of 2b and the nitronate salt.

The nucleophiles employed in the present work (nitronate, thiolate, malonate, and sulfinate) have all been shown in other studies^{9-12,27} to function as electron donor nucleophiles. With appropriate substrates, they can participate in both the initiation and propagation steps required for an $S_{RN}1$ substitution process. In the present series of reactions with perfluoroalkyl iodides as substrates, all the nucleophiles appear to donate an electron to the substrate. However, while nitronate and thiolate can also propagate the chain substitution process, sulfinate and malonate apparently cannot.

The $S_{RN}1$ substitution reactions of perfluoroalkyl iodides are rare examples of such substitutions at sp^3 centers which are not directly bonded to nitro substituted or electro-negatively substituted aryl functions. The other examples generally involve organometallic substrates²⁸ reacting with

nitronate salts. Thus, while single electron transfers between nucleophiles and electrophiles are apparently quite common²⁹ in organic chemistry, coupling processes between radicals and nucleophiles are less frequent. The latter process presumably requires the existence of a relatively low lying orbital to accommodate the extra electron in the anion radical of the substitution product.

Using the competition between addition to norbornene and reaction with the anion, we earlier² found that PhS^- is a better trap than 2-nitropropanide for the perfluoroalkyl radical. We now see that both these anions are better than sulfinate or methylmalonate anion in this process. Presumably, this order reflects the energetics of potential anion radical intermediates.³⁰ The perfluoroalkyl iodide/norbornene or styrene system seems to be quite useful for studying this important anion-nucleophile interaction. Continued studies are planned, including an examination of solvent effects on these reactions.

Experimental Section

Reagents and general procedures were as described in a previous paper.¹ Olefins, solvents, and the sulfinate salts were commercial samples, generally used as received.

Addition of Perfluoroalkyl Iodides to Olefins Initiated by Sulfinate Salts. General Procedure. A solution of perfluoroalkyl iodide (10.9 g, 0.02 mol) and excess olefin in 100 mL of DMF was evacuated and filled with argon several times with a Firestone valve. The sulfinate salt was added, and the resulting solution or suspension was stirred for 17 h at room temperature. The mixture was poured into 300 mL of ether and 300 mL of water. The ether solution was washed with 3×100 mL of water and dried over anhydrous magnesium sulfate. The solution was analyzed by GLPC with a 6 ft \times $1/8$ in. 10% SP-2100 column with a helium carrier gas flow rate of 40 mL/min. An oven temperature program of 70 °C/2 min, 70–230 °C at 16 °C/min, and 230 °C/8 min gave base line separation of all components which eluted in the order: perfluoroalkyl iodide, olefin, 1:1 adduct. The ether solution was concentrated on a rotary evaporator. Proton NMR examination of the crude products showed characteristic absorptions at 4.1–4.5 ppm for the CHI protons, and in cases where the HI elimination products were formed, absorptions in the 5.3–6.7 ppm range. The pure 1:1 adducts could generally be isolated by bulb-to-bulb distillation at 0.5 mm. The results are contained in Table I.

Synthesis of 1-(Perfluoroalkyl)octene (12). The above procedure was followed by using 0.08 mol of 1-octene and 0.02 mol of sodium *p*-toluenesulfinate. GLPC analysis of the crude ether solution showed a mixture of 1a, olefin 12, and the 1:1 adduct 6 in a 9:21:64 ratio (retention times of 1.7, 7.2, and 9.6 min, respectively). Evaporation of the ether solution gave 15.2 g of oil. Bulb-to-bulb distillation at 0.25 mm and a bath temperature of 120 °C gave a colorless liquid. This liquid was dissolved in 100 mL of methanol and added to a solution of 5 g of potassium hydroxide in 100 mL of methanol. After 1 h this solution was poured into 300 mL of ice water containing 20 mL of concentrated HCl. The aqueous solution was extracted with 3×100 mL of 1,1,2-trichlorotrifluoroethane. The combined organic extracts were washed with 2×100 mL of water, dried over anhydrous magnesium sulfate, and concentrated on a rotary evaporator to 7.7 g (73%) of colorless 12. Proton NMR (δ , $CDCl_3/Me_4Si$) 0.90 (3

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H, t), 1.33 (8 H, bs), 2.20 (2 H, bs), 5.2-5.8 (1 H, m), 6.2-6.6 (1 H, m).

Anal. Calcd for $C_{16}H_{15}F_{17}$: C, 36.24; H, 2.85; F, 60.91. Found: C, 36.14; H, 2.94; F, 60.95.

Synthesis of Olefin 16. This compound, prepared as described above from 10.9 g (0.02 mol) of **1a**, 4.1 g (0.021 mol) of methyl undec-10-enoate, and 0.9 g (0.005 mol) of sodium *p*-toluenesulfinate, had the following properties: proton NMR (δ , $CDCl_3/Me_4Si$) 1.1-1.9 (12 H, m), 1.9-2.5 (4 H, m), 3.68 (3 H, s), 5.2-6.0 (1 H, M), 6.0-6.7 (1 H, M); fluorine NMR (δ , $CDCl_3/CFCl_3$) -81.52 (3 F), -126.67 (2 F), -124.04 (2 F), -123.21 (2 F), -122.35 (6 F), -111.79 and -107.14 (2 F).

Anal. Calcd for $C_{20}H_{21}O_2F_{17}$: C, 38.97; H, 3.43; F, 52.40. Found: C, 39.15; H, 3.43; F, 52.40.

Synthesis of 1:2 Adduct 3. The above general procedure with 9.1 g (0.02 mol) of 1,4-diiodoperfluorobutane, 9.4 g (0.1 mol) of norbornene, and 1.8 g (0.01 mol) of sodium *p*-toluenesulfinate gave 12.21 g of crude product. The product was chromatographed over 300 g of silica gel packed in hexane. The column was eluted with 3 L of hexane, taking 100-mL fractions. Fractions 12-25 were combined and concentrated to 10.6 g (83%) of **3** as a white solid: mp 114-115 °C; proton NMR (δ , $CDCl_3/Me_4Si$) 1.1-2.7 (9 H, m), 4.33 (1 H, m); fluorine NMR (δ , $CDCl_3/CFCl_3$) -121.28 (4 F), -117.8 (4 F, AB quartet, $J = 282$ Hz).

Anal. Calcd for $C_{18}H_{20}F_8I_2$: C, 33.66; H, 3.14; F, 23.67. Found: C, 33.58; H, 2.97; F, 23.52.

Reaction of Perfluorooctyl Iodide, Ethene, and Sodium *p*-Toluenesulfinate in DMF. A nitrogen-swept 200-mL pressure vessel was charged with 3.6 g (0.02 mol) of sodium *p*-toluenesulfinate, 90 mL of DMF, and 10.9 g (0.02 mol) of perfluorooctyl iodide. The vessel was closed, cooled in dry ice and acetone, and evacuated. Ethene (10 g, 0.42 mol) was condensed in the vessel. The mixture was agitated overnight at room temperature. The vessel was vented to 1 atmosphere pressure, and the contents were poured into 300 mL of ether and 300 mL of water. The ether solution was washed with 3×100 mL of water and dried over anhydrous magnesium sulfate. GLPC analysis of the ether solution showed three major peaks after the solvent:

peak	R_f , min	area, %
1	1.87	31.2
2	5.18	20.0
3	11.77	34.0

The first peak is unreacted perfluorooctyl iodide. The ether solution was concentrated on the rotary evaporator to 10.03 g of oily orange solid. The crude product adsorbed on 30 g of silica gel was added to a column of 300 g of silica gel packed in hexane. The column was eluted with 1 L of hexane, 1 L of 5% ether in hexane, 0.5 L of 10% ether in hexane, 1 L of 25% ether in hexane,

and 3 L of 35% ether in hexane, taking 100-mL fractions. From fractions 6-9 was isolated 1.92 g (17%) of 1,1,2,2- H_4 -perfluorodecyl iodide (**17**): mp 56-57 °C; proton NMR (δ , $CDCl_3/Me_4Si$) 2.3-3.1 (2 H, m), 3.1-3.5 (2 H, m); fluorine NMR (δ , $CDCl_3/CFCl_3$) -81.38 (3 F), -126.63 (2 F), -122.26 (6 F), -123.15 (2 F), -123.85 (2 F), -115.45 (2 F). From fractions 32-58 was isolated 3.94 g (33%) of $C_8F_{17}CH_2CH_2SO_2C_6H_4CH_3$ (**18**) as a white solid: mp 109-111 °C; proton NMR (δ , $CDCl_3/Me_4Si$) 2.47 (3 H, s) overlapping 2.2-2.9 (2 H, m), 3.1-3.4 (2 H, m), 7.6 (4 H, q); fluorine NMR (δ , $CDCl_3/CFCl_3$) -81.40 (3 F), -126.64 (2 F), -121.8 to -123.9 (12 F).

Anal. Calcd for $C_{17}H_{11}F_{17}SO_2$: C, 33.90; H, 1.84; F, 53.63; S, 5.32. Found: C, 33.83; H, 1.92; F, 53.57; S, 5.49.

Reaction of Perfluorooctyl Iodide with the Sodium Salt of Diethyl Methylmalonate. Perfluorooctyl iodide (10.9 g, 0.02 mol) was added in one portion to a degassed solution of 3.9 g (0.02 mol) of sodium diethyl methylmalonate in 75 mL of Me_2SO . The cloudy yellow solution was stirred overnight. A short-path distillation head and receiver cooled in dry ice and acetone were attached to the flask. The system was gradually evacuated to 0.5 mm. After $1/2$ h, the receiver contained 2.3 g (27%) of 1-*H*-perfluorooctane, identified by GLPC and NMR comparisons with an authentic sample. The liquid remaining in the reaction flask was poured into 200 mL of ice water containing 5 mL of concentrated HCl. The aqueous solution was extracted with 3×100 mL of ether. The combined extracts were washed with 3×100 mL of water and dried over anhydrous magnesium sulfate. GLPC analysis, as above, showed only two peaks after solvent which were assigned to unreacted **1a** and the malonate dimer **21**. The ether solution was concentrated on a rotary evaporator to an oil. Bulb-to-bulb distillation of the oil at 0.5 mm and a bath temperature of 160 °C gave 2.7 g (39%) of **21** as a colorless liquid: proton NMR (δ , $CDCl_3/Me_4Si$) 1.08-1.48 (15 H, two triplets + singlet), 3.51 (1 H, t), 4.14 and 4.16 (8 H, two quartets).

Registry No. **1a**, 507-63-1; **2a**, 89883-21-6; **2b**, 34542-08-0; **2c** (isomer 1), 96791-92-3; **2c** (isomer 2), 96893-59-3; **3**, 96791-83-2; **4**, 96791-88-7; **5** ($R_t = F(CF_2)_8$), 96791-86-5; **6**, 96791-81-0; **7**, 38550-35-5; **8**, 96791-89-8; **9**, 96825-33-1; **11** ($R = F(CF_2)_8$), 96791-87-6; **12**, 96107-50-5; **13**, 67103-04-2; **14**, 96791-90-1; **15**, 96791-91-2; **16**, 96791-82-1; **17**, 2043-53-0; **18**, 96791-84-3; **19**, 335-65-9; **20**, 96791-80-9; **21**, 17696-77-4; Phs C_8F_{17} , 89883-19-2; NaC(CH₃)(CO₂C₂H₅)₂, 18424-77-6; (CF₃)₂CFI, 677-69-0; C₇F₁₅CFICF₃, 96791-85-4; *p*-CH₃CONHC₆H₄SO₂Na, 15898-43-8; sodium diethyl phenylmalonate, 28744-77-6; sodium benzenesulfinate, 873-55-2; sodium *p*-toluenesulfonate, 824-79-3; sodium diethyl methylmalonate, 18424-77-6; sodium diethyl malonate, 996-82-7; norbornene, 498-66-8; 1-octene, 111-66-0; methyl 10-undecenoate, 111-81-9; 1,4-diiodoperfluorobutane, 375-50-8; ethene, 74-85-1; propene, 115-07-1; allylbenzene, 300-57-2; allyl acetate, 591-87-7; norbornadiene, 121-46-0; cyclopentene, 142-29-0; sodium methylsulfinate, 20277-69-4.

Single Electron Transfer in the Reaction of Enolates with Alkyl Halides

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Single electron transfer (SET) in the reaction of a model system consisting of lithiopropiophenone with primary neopentyl type alkyl halides and tosylate was investigated by (1) the use of an appropriate cyclizable alkyl radical probe, (2) observing the effect of varying the leaving group on reaction rate and product distribution, (3) studying the effect of light, di-*tert*-butyl nitroxyl radical, and *p*-dinitrobenzene on the rate of reaction, (4) observing the consequence of varying solvent composition on both the reaction rate and product distribution, and (5) studying the effects of the radical traps, dicyclohexylphosphine and 1,4-cyclohexadiene, on product composition. The results of these studies indicate that single electron transfer is the major reaction pathway involved in the reaction of the enolate with the alkyl iodide in HMPA and that the corresponding bromide and tosylate react by an S_N2 process.

The reaction of an enolate anion with an alkyl substrate (halide or tosylate) is well-recognized as an important

synthetic reaction in organic chemistry.¹ Although the mechanism of this reaction is generally believed to proceed