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REACTION OF PERFLUOROALKYLETHYLENS WITH NUCLEOPHILES[†]

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SUMMARY

Perfluoroalkylethylenes react with some carbon-, oxygen-, sulfur-, selenium-, nitrogen-, and phosphorus-based nucleophiles by formal S_N2' displacement of fluoride ion.

INTRODUCTION

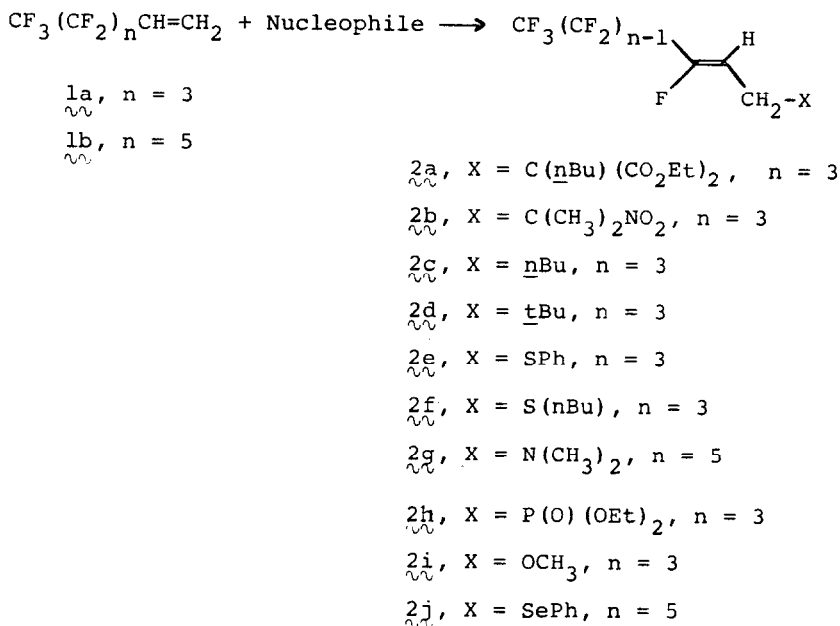
Reactions of nucleophiles with perfluorinated olefins, giving products of addition or addition/elimination, are among the most important reactions in organofluorine chemistry. [1] Additions of nucleophiles to less highly fluorinated olefins are rare unless the olefin is also substituted by some other functional group which could stabilize anionic intermediates [2]. We now describe the reaction of olefins substituted by a single perfluoroalkyl group with a series of nucleophiles [3,4] giving allylically substituted product olefins with high \underline{z} stereoselectivity. Although formally S_N2' processes, these reactions proceed under unusually mild conditions for displacement of a fluoride ion from a perfluoroalkyl group.

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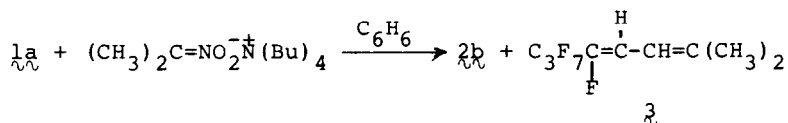
RESULTS AND DISCUSSION

The perfluoroalkylethylenes 1a and 1b reacted under anhydrous conditions with a series of nucleophiles to give the products 2a-j as shown in Table 1. Product yields were not optimized or corrected for the often substantial amounts of unreacted olefin. Olefin stereochemistry was assigned by the NMR signal due to the vinyl hydrogen. In all cases this hydrogen appeared as a doubled triplet at $\delta 5.7$. The coupling to vinyl fluorine was 32 Hz indicating a trans arrangement for the vinyl hydrogen and fluorine. [5] In one case (2b) a small amount ($\sim 5\%$) of the E-isomer was detected by the presence of a second doubled triplet at $\delta 5.8$ with $J_{H-F} = 20$ Hz.

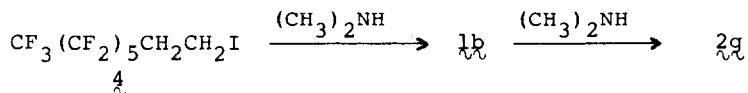


Several entries in Table 1 merit additional comment.

A second product was isolated by preparative GLPC from the reaction of tetrabutylammonium 2-nitropropanide with $1a$. This was identified as the diene 3 , presumably formed by elimination of HNO_2 from the initially formed $2b$.



The reaction with dimethylamine (entry 7) was actually run using a precursor to the perfluorohexylethylene ($1b$), namely the iodide 4 . With an excess of amine, the olefin $1b$ was generated in situ and subsequently reacted with a second mole of amine to give $2g$. It is interesting to note that this sequence



occurs in preference to a simple S_N2 displacement of the iodide.⁴

Formation of the phosphonate derivative $2h$ represents a novel use of the diethyltrimethylsilylphosphite [6] reagent 5 . Attempts to isolate $2h$ using more traditional phosphorus nucleophiles (e.g. triethyl phosphite, sodium diethyl phosphite) failed. The relatively low yield in this case is due to decomposition of 5 at the high reaction temperature. Virtually all the unreacted $1a$ but no 5 could be recovered.

Table 1. Reaction of Perfluoroalkylethylenes with Nucleophiles

Entry	$R_fCH=CH_2$ $R_f = (\text{mol})$	Nucleophile (mol)	Solvent (ml)	Conditions	Product ^a (% yield)
1	C_4F_9 (0.08)	$NaC(CO_2Et)_2C_4H_9$ (0.06)	DMF (100)	25°/17 hr	Zc (60%)
2	C_4F_9 (0.026)	$nBu_3N^+ \bar{C}(CH_3)_2NO_2$ (0.026)	benzene (40)	25°/17 hr	Zb Zc (35%) (20%)
3	C_4F_9 (0.050)	$nBuLi$ (0.050)	Ether (80)	-70° to 20°/3 hr	Zc (80%)
4	C_4F_9 (0.050)	$tBuLi$ (0.054)	Ether (80)	-70° to 20°/3 hr	Zd (76%)
5	C_4F_9 (0.03)	$NaSPh$ (0.04)	DMF (50)	25°/17 hr	Ze (33%)
6	C_4F_9 (0.04)	$NaS(nBu)$ (0.047)	DMF (50)	25°/2 hr	Zf (22%)
7	C_6F_{13} (0.29) ^b	$(CH_3)_2NH$ (0.88)	Ether (100)	25°/2 days	Zg Zh (59%)
8	C_4F_9 (0.03)	$(EtO)_2P(=O)Si(CH_3)_3$ \bar{Z} (0.022)	benzene (30)	180°/16 hr	Zi (24%)
9	C_4F_9 (0.10)	$NaOCH_3$ (0.20)	DMF (200)	25°/62 hr	Zj (9%)
10	C_6F_{13} (0.02)	$NaSePh^c$ (0.02)	CH_3CN (35)	reflux/4 hr	Zk (31%)

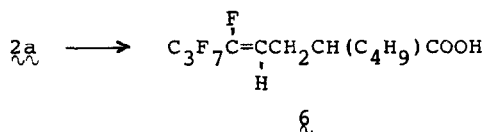
a) Isolated yields, not corrected for recovered perfluoroalkylethylene

b) Substrate was $C_6F_{13}CH_2CH_2I$

c) Generated in situ from diphenyl diselenide (10 mmol) and sodium borohydride (20 mmol)

Reaction of $2a$ with sodium methoxide was unusually complex. Even with prolonged reaction times and an excess of methoxide, at least 50% of the olefin was recovered. The allylic ether $2i$ was the major product but many longer retention time components were also present according to GLPC analysis. This mixture clearly contained OCH_3 and fluorine bound to saturated, allylic, and vinylic carbons by NMR analysis, but pure products have not yet been isolated.

Although the yields in some cases are modest, this chemistry provides a simple route to a great variety of functionalized, fluorine containing olefins. Many of the products 2 could be useful for further transformations. Conversion of $2b$ to diene 3 has already been noted. The malonate derivative $2a$ has been converted to the unsaturated acid 6 by hydrolysis (KOH in refluxing ethanol) and decarboxylation (refluxing acetic acid) in 80% yield.



The reaction mechanism has not yet been investigated. Since these reactions involve displacement of a fluoride ion from a saturated perfluoroalkyl group into a non-hydrogen bonding medium by, in some cases, relatively weak nucleophiles, something other than simple S_N2' displacement may be involved. Since the anions which appear to give the best yields are known^[7] to participate in electron transfer reactions, the possibility that these substitutions involve anion radical intermediates is being investigated.

Table 2. Properties of New Compounds

Compound	bp	¹ H-NMR	¹⁹ F-NMR	Analyses or MS, found (Calcd)
2a u	79-80° (0.3mm)	0.91 (t, 3H); 1.27 (m, 10H); 1.90 (m, 2H); 2.85 (dt, 2H); 4.24 (q, 4H); 5.66 (dt, 1H)	-81.4 (3F); -127.9 (2F); -118.9 (2F); -129.6 (1F)	C, 46.34 (46.16) H, 5.11 (5.01) F, 33.31 (34.36)
2b u	oil	1.63 (s, 6H); 2.88 (m, 2H); 5.62 (dt, 1H)	-81.5 (3F); -119.2 (2F); -127.4 to -128.4 (3F)	C, 34.53 (34.30) H, 2.89 (2.88) F, 48.35 (48.23)
2c u	65-68° (50mm)	0.90 (t, 3H); 1.35 (m, 6H); 2.23 (m, 3H); 5.55 (dt, 1H)	-81.7 (3F); -128.7 (2F); -118.9 (2F); -132.9 (1F)	C, 42.37 (42.26) H, 4.30 (4.26) F, 53.18 (53.48)
2d u	46-47° (33mm)	0.94 (s, 9H); 2.12 (m, 2H); 5.61 (dt, 1H)	-81.6 (3F); -127.9 (2F); -118.6 (2F); -132.0 (1F)	C, 42.61 (42.20) H, 4.28 (4.26) F, 53.01 (53.48)
2e u	oil	3.67 (m, 2H); 5.70 (dt, 1H); 7.2-7.5 (m, 5H)	-81.5 (3F); -128.0 (2F); -119.2 (2F); -130.7 (1F)	C, 43.26 (42.86) H, 2.63 (2.39)
2f u	oil	0.93 (t, 3H); 1.53 (m, 4H); 2.51 (m, 2H); 3.31 (dq, 2H); 5.75 (dt, 1H)	-80.8 (3F); -126.5 (2F); -117.7 (2F); -131.5 (1F)	C, 38.11 (37.98) H, 3.83 (3.82) S, 10.27 (10.14)
2h u	oil	1.35 (t, 6H); 2.79 (ddq, 2H); 4.20 (q, 4H); 5.75 (ddt, 1H)	-80.9 (3F); -126.9 (2F); -118.1 (2F); -128.4 (1F)	C, 33.10 (32.98) H, 3.98 (3.60) P, 8.99 (8.51)
2i u	97-100°	3.38 (s, 3H); 4.20 (m, 2H); 5.80 (dt, 1H)	-80.9 (3F); -118.0 (2F); -127.5 to -126.2 (3F)	m/e = 258.0288 (258.0291)
2j u	98-100° (1mm)	3.53 (dq, 2H); 5.76 (dt, 1H); 7.25 (m, 3H); 7.53 (m, 2H)	-81.5 (3F); -118.1 (2F); -123.5 (4F); -126.8 (2F); -132.1 (1F)	m/e = 483.9628 (483.9599)
3 u	oil	1.83 (s, 3H); 1.90 (s, 3H); 6.0-7.5 (m, 2H)	-81.5 (3F); -127.9 (2F); -118.7 (2F); -134.6 (1F)	m/e = 268 (268)
6 u	oil	0.92 (t, 3H); 1.1-2.0 (m, 6H); 2.25-2.75 (m, 3H); 5.65 (dt, 1H); 11.7 (s, 1H)	-81.6 (3F); -127.9 (2F); -119.0 (2F); -130.1 (1F)	C, 42.06 (42.11) H, 4.13 (4.12) F, 44.74 (44.41)

EXPERIMENTAL

The sodium salts of diethyl butylmalonate, benzenethiol and butanethiol were prepared by reaction of one equivalent of the substrate with sodium ethoxide in ethanol, followed by evaporation of the solvent and drying under reduced pressure. Tetrabutylammonium 2-nitropropanide [8] and diethyltrimethylsilylphosphite [6] were prepared as described. The alkyl lithium reagents were commercial samples obtained as hexane solutions. The sodium salt of benzeneselenol was prepared in situ by reaction of diphenyldiselenide with 2 equivalents of sodium borohydride in acetonitrile.

Proton nmr spectra were obtained on an IBM NR-80 spectrometer at 80 MHz using TMS as internal standard. Fluorine nmr spectra were obtained on a Varian XL-100 spectrometer at 94.1 MHz using fluorotrichloromethane as internal standard.

Reactions were run under argon atmosphere in the solvents and under the conditions indicated in Table 1. In general the nucleophiles were added to a solution of the olefin. After aqueous work-up the products were isolated by standard distillation or chromatography procedures. Properties of new compounds are summarized in Table 2.

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