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Articles

Difluoroorganometalate-Assisted Generation of Perfluorocarbanions from Trimethylsilyl Synthons and Their Interactions with Perfluoroaryl Compounds[†]

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Barbier-type reactions of $ICF_2CF_2OCF_2CF_2SO_2F$, $I(CF_2CF_2)_4OCF_2CF_2SO_2F$, and $I(CF_2CF_2)_4OCF(CF_3)_2$ with MeMgBr and $ClSiMe_3$ in 3:1 tetrahydrofuran (THF)/diethyl ether mixtures at −78 °C gave $Me_3SiCF_2CF_2OCF_2CF_2SO_2F$ (**1**), $Me_3Si(CF_2CF_2)_4OCF_2CF_2SO_2F$ (**2**), and $Me_3Si(CF_2CF_2)_4OCF(CF_3)_2$ (**3**) in 65−89% yields. The anions in three difluorometalates, $[(Me_2N)_3S]^+[Me_3SiF_2]^-$ (TASF), $[Bu_4N]^+[Me_3SiF_2]^-$ (TBAT), and $[(Pip_2N)_3S]^+[Me_3SnF_2]^-$ (TPSF), were reacted with **1**−**3**, to generate 2 equiv of Me_3SiF for TASF and TBAF or 1 equiv each of Me_3SnF and Me_3SiF for TPSF, and the perfluoroalkyl ether nucleophiles $^-CF_2CF_2OCF_2CF_2SO_2F$, $^-(CF_2CF_2)_4OCF_2CF_2SO_2F$, and $^-(CF_2CF_2)_4OCF(CF_3)_{2,}$ respectively. The sulfonium or ammonium countercation interacted with hexafluorobenzene, monosubstituted pentafluorobenzenes, and pentafluoropyridine over a range of temperatures between −78 and 25 °C to also generate aryl carbocationic species that reacted with $^-CF_2CF_2OCF_2CF_2SO_2F$ to give $XC_6F_4CF_2CF_2OCF_2CF_2SO_2F$, where C−X = C−F (**4**), $C-NO_2$ (**5**), C−CN (**6**), $C-CF_3$ (**7**), $C-CH{=}CH_2$ (**8**), N (**9**), with $^-(CF_2CF_2)_4OCF_2CF_2SO_2F$ to give $XC_6F_4(CF_2CF_2)_4OCF_2CF_2SO_2F$, where C−X = $C-NO_2$ (**10**), C−CN (**11**), $C-CF_3$ (**12**), N (**13**), and with $^-(CF_2CF_2)_4OCF(CF_3)_2$ to give $XC_6F_4(CF_2CF_2)_4OCF(CF_3)_2$, where C−X = C−F (**14**), $C-NO_2$ (**15**), C−CN (**16**), $C-CF_3$ (**17**), $C-CH{=}CH_2$ (**18**), N (**19**). The new products were obtained in 22−73% yields, and purification was carried out by separation of fractions either by silica gel preparative thin-layer chromatography (TLC) by using a diethyl ether/cyclohexane mixture as the mobile phase eluent ($XC_6F_4(CF_2CF_2)_4OCF(CF_3)_2$ type compounds) or by octadecyl bonded reverse-phase thin-layer chromatography (rp-TLC) by using an acetonitrile/water mixture as eluent. Reaction of compound **16** with 2 mol equiv of $Me_3SiOOCMe$ resulted in the disubstitution product at *ortho* positions of the nitrile. Compound **5** was transformed via a five-step process to the tricarboxylate *o*-$(MeCOO)_2O_2NC_6F_4CF_2CF_2OCF_2COOMe$ (**24**). The new products were characterized by elemental analyses and NMR and high-resolution mass spectral analysis.

Introduction

The substitution or addition of the simplest perfluoroalkyl group, CF_3, onto organic compounds for medicinal and agrochemical applications has been achieved by nucleophilic and electrophilic displacement reactions.[1] Trifluoromethylation increases lipophilicity, capacity for hydrogen bonding, and polar interactions and helps to block unwanted biochemical reactions.[2] Substitution of longer chain perfluoroalkyl groups, i.e., when $n \geq 3$ in C_nF_{2n+1}, onto organic substrates occurred by cross-coupling reactions via organocopper intermediates or by first forming their unstable organometallic derivatives.[3] Generally, polyfluorinated organic compounds have lower surface tensions and higher densities, which are very useful in some specialized medicinal and industrial applications.[4] Recent studies show that nucleophilic perfluoroalkylation by Me_3SiCF_3 involved less rigorous processes, resulting in higher yields and fewer reaction side products than achieved via either the respective Grignard reagent or copper-assisted cross

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[†] Dedicated to Professor Dr. Herbert Schumann on his 65th birthday.

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coupling.[5] Both procedures involve cationic exchanges. Interestingly, there are limited reports on addition of or substitution by nucleophiles of higher ($n \geq 3$) perfluoroalkyls or their perfluoroalkyl ether relatives onto organic substrates.[6] There are even fewer reports of substitution of nucleophiles from $Me_3SiOCH_2R_f$, $Me_3SiOC_6F_5$, or $Me_3SiOC_6F_4X$ (X = H, NO_2, CN, CF_3) onto perfluoroaromatic substrates.[7] Recent advances in metal-catalyzed polymerization of perfluoroaromatic compounds, due in large part to C−F activation, also is one area that will find application for new compounds derivable from long-chain perfluoroalkylation of perfluoroaryl compounds.[8] Perfluoroaromatic compounds are susceptible to nucleophilic substitution, which makes them useful as substrates to build bigger molecules that contain functional perfluoroalkyl groups: e.g., the oxo-linked stepwise polymerization of perfluoroaryl units.[7a] Hence, it was of interest to explore the generation of C-nucleophiles from the Me_3Si derivatives of some iodoperfluoroalkyl ethers.

Simple metal fluorides, copper salts, tetraalkylammonium fluorides ($Me_4N^+F^-$ and $Bu_4N^+F^-$), and fluoride ions from hypervalent difluorosilicates or difluorostannates were reacted with Me_3SiCF_3 to generate the reactive nucleophile CF_3^-.[1,9] There is limited information on the generation of $C_nF_{2n+1}^-$ ($n \geq 3$) nucleophiles from their trimethylsilyl synthons.[6] Carbanions of long-chain perfluoroalkylsilanes, e.g. $Me_3SiC_8F_{17}$, generally react with acid fluorides to give perfluoro ketones in good yields (eq 1).[6]

$$R_fC(O)F + Me_3SiC_8F_{17} \xrightarrow{5\%\ TASF} R_fC(O)C_8F_{17} + Me_3SiF \quad (1)$$

$$TASF = [(Me_3N)_3S]^+[Me_3SiF_2]^-$$

Farnham reported lower chemo- and regioselectivities as well as fragmentation of the long chain in $C_8F_{17}^-$ when $Me_3SiC_8F_{17}$ was reacted with terminal alkenes.[6] Fragmentation was a serious side reaction when long-chain perfluoroalkyl carbanions were reacted with weak electrophiles.[6] Yields in the 30−50% range were suggested for reactions of long-chain perfluoroalkyl nucleophiles with fluorinated aromatic substrates.[6] Unfortunately, no experimental evidence was provided to explain the conditions that permit control of selectivity.

Some of the known fluoride ion sources appear to have limited ability to generate such C-nucleophiles or carbanions. The tris(amino)sulfonium cation (TAS^+) occasionally had performed as a more aggressive cation than Cs^+. For example, whereas tetrasubstituted olefins, e.g. $(CF_3)_2{=}C(CF_3)_2$, do not form carbanions with CsF, they react with tris(dimethylamino)sulfonium (trimethylsilyl)difluorosilicate (TASF) to liberate Me_3SiF.[6] This phenomenon is encountered also in their different abilities to facilitate exchange of β-fluorides with excess olefins.[6] To explain this phenomenon, cumulative energies of all species involved would be required to account for the thermodynamic stability of each constituent of the reaction mixture. Our work reconfirms the superiority of difluorosilicate or difluorostannate compounds as fluoride ion sources for the generation of long-chain C-nucleophiles. We also report on the selective reactivity of carbanions with perfluorinated aromatic substrates.

Results and Discussion

Three trimethylsilyl perfluoroalkyl ethers, Me_3SiR_f (R_f = $(CF_2)_2OCF_2CF_2SO_2F$ (**1**), $(CF_2)_8OCF_2CF_2SO_2F$ (**2**),[3] $(CF_2)_8OCF(CF_3)_2$ (**3**)) were reacted with cesium fluoride, tetrabutylammonium fluoride, two hypervalent difluorosilicates (tris(dimethylamino)sulfonium trimethyldifluorosilicate (TASF),[10] tetrabutylammonium triphenyldifluorosilicate (TBAT)[2]), and one difluorostannate compound (tris(piperidino)sulfonium triphenyldifluorostannate (TPSF)[11]) in order to generate the respective C-nucleophile. In the last three cases concomitant formation of Me_3SiF or Me_3SnF aided in driving the reactions to completion. Hexafluorobenzene, four other substituted pentafluorobenzene compounds (XC_6F_5, X = NO_2, CN, F, CF_3), and pentafluoropyridine (NC_6F_5) were employed as substrates in reaction with each of the C-nucleophiles at −78 °C for 3−7 h. This was followed by slow warming to room temperature. The difluorometalates have different physical properties and nucleophilicities. For example, whereas TASF is very hygroscopic, both TBAT and TPSF are not. TBAT, the ammonium-based salt, is less nucleophilic than $Bu_4N^+F^-$, and the sulfonium-based salts are strong nucleophiles.[2]

It was not possible to generate the respective C-nucleophile from **1**−**3** in the presence of either catalytic or stoichiometric quantities of CsF or $Bu_4N^+F^-$. Despite varying the thermal conditions and reaction times during different runs, we found no evidence that any substitution of the perfluoroaryl compounds had occurred. This result was surprising, since both had catalyzed the reactions of $Me_3SiC_8F_{17}$ and $Me_3SiCF(CF_3)[OCF_2CF(CF_3)]_2OC_3F_7$, with cyanuric fluoride, at −5 °C to give the trisubstituted triazine derivatives.[12] In our work, they also catalyzed the reactions of **1** and **2** with cyanuric fluoride to give **4** and **5**, which were characterized by their molecular ions at m/z 975 and 1875, respectively, in the mass spectra (eq 2).

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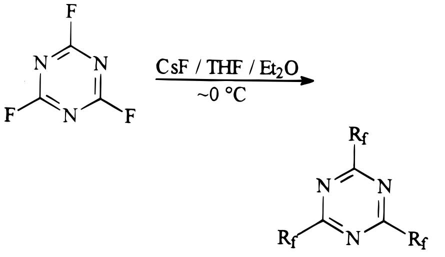


(2)

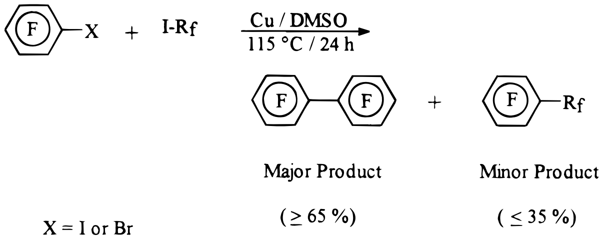
$R_f = C_8F_{17}$,[12] $CF(CF_3)O[CF_2OCF(CF_3)]_2OC_3F_7$,[12]

$CF_2CF_2OCF_2CF_2SO_2F$ (**4**), $(CF_2)_8OCF_2CF_2SO_2F$ (**5**)

Catalytic amounts of both CsF and $Bu_4N^+F^-$ have generated O- and C-nucleophiles from $Me_3SiOCH_2R_f$ (R_f = perfluoroalkyl, perfluoroaryl) and Me_3SiCF_3 at room temperature, and their reactions with different organic substrates are the subject of several recent publications.[1,7] However, in addition to being useful in the reactions between $Me_3SiC_8F_{17}$ and acid fluorides,[6] TASF has been used as a fluoride ion source for promoting Me_3SiCF_3-trifluoromethylation of substituted pentafluorobenzenes (Ar_F-F), Ar_F-CF_3 = 4-C_5F_4N, 4-$CF_3C_6F_4$, 4-$C_6F_5C_6F_4$, 4-$C_6F_5C_6F_4$-4′, in 40−70% yield.[13] TSAF was used for fluorination of hydroxy-containing compounds and for alkylation of haloalkyl, haloaryl, and haloarylalkyl organic compounds as well as in generation of the weakly nucleophilic carbanion, i.e., $CF_3CF_2CF_2C^-(CF_3)_2(TAS)^+$ from $CF_3CF_2CF{=}C(CF_3)_2$ and TASF, for reaction with a number of halides, hydrides, and azides.[6]

On the basis of the mechanism previously suggested for TASF in alkylation reactions,[14] it is likely that the anion, i.e., $[Me_3SiF_2]^-$, promoted the cleavage of the Me_3Si-CF_2 bond in **1**−**3** by reacting with the Me_3Si moiety to produce 2 equiv of Me_3SiF and TAS^+ stabilized the nucleophile as R_f-TAS^+.[6,14] It is attractive to consider further reaction as nucleophilic attack by a fluorine atom of the perfluoroaromatic substrate. However, in the absence of evidence from mechanistic studies, we rely on the mechanism published earlier[14] and on the ambiguity in the products of reactions of Me_3SiR_f/CsF and Me_3SiR_f/TASF with cyanuric fluoride and perfluoroaromatic compounds to treat this as an electrophilic attack by TAS^+ leading to generation of a carbocationic center. Reactions did not occur when catalytic amounts of TASF were used, but the desired products were formed with stoichiometric quantities of the difluorometalate. Success and failure of O-nucleophilic substitution of fluorine atoms in poorly activated or nonactivated perfluoroaryl compounds appear to depend on the nucleophile used. For example, while $HC_6F_4OSiMe_3$ did not substitute any fluorine atom in hexafluorobenzene, $CH_2{=}CHC_6H_4C_6H_4OSiMe_3$ did.[7a]

The C-nucleophiles from **1**−**3** were reacted with hexafluorobenzene at −78 °C to form the monosubstituted products in 22−27% yields, as confirmed by NMR and MS spectral evidence. The same compounds were obtained as minor products when the iodoperfluoroalkyl ether precursors of **1**−**3** were reacted with iodo- or bromopentafluorobenzene (eq 3).[15]



(3)

X = I or Br

Rf = $CF_2CF_2OCF_2CF_2SO_2F$

$(CF_2CF_2)_4OCF_2CF_2SO_2F$

$(CF_2CF_2)_4OCF_2CF(CF_3)_2$

Higher yields, between 45 and 73% (see Table 1), were obtained when substituted pentafluorobenzene substrates were reacted with the trimethylsilyl synthons **1**−**3** at subzero temperatures. When an excess of the perfluoroaryl substrates was used, spectroscopic evidence suggests that only *para*-substituted products were obtained. Earlier studies of the substitution of pentafluoroaryl compounds by organometallic intermediates and O-nucleophiles demonstrated that the *para* fluorine atom in substituted pentafluorobenzene is most activated,[7b] although other recent results indicate that the O-nucleophile may also contribute to regioselectivity in the obtained substitution products. For example, interaction of $CH_2{=}CHC_6H_4C_6H_4OSiMe_3$ with BrC_6F_5 produced a mixture of *ortho*-, *meta*-, and *para*-substituted products that was inseparable in our hands.[7a] The controlled *para* substitution in the new compounds does not conform to earlier expectations that perfluorinated, long-chain, weak nucleophiles do not react regioselectively with substituted pentafluorobenzene.[6] The reactions of the nucleophile and the carbocation proceeded over 3−7 h while the temperature was raised slowly from −78 to 25 °C, to give the products **4**−**19** (Table 1). Also, no significant increase in the yields was observed as a function of the methodology employed, i.e., by abruptly quenching at subzero temperatures and working up the reaction (by hydrolysis and separation) or after slowly warming the reaction mixture to 25 °C.

A 3:1 excess of the perfluorinated substrate was used in order to ensure regioselective *para* substitution. On the basis of earlier reports on related chemistry, *ortho* and *meta* substitutions may have occurred if equimolar amounts of reagent or a slight excess of equimolar quantities of the trimethylsilyl synthon and the difluorometalate were used on perfluoroaryl compounds.[7a] In our case, evaluation of the GC-MS chromatogram did not indicate more than one substitution. The chemical shifts and integration of signals from ^{19}F NMR confirm that the products were exclusively *para*-substituted perfluoroaryl products. The complete disappearance of the signal for the *para* fluorine atom in the NMR spectra is the strongest evidence for the success of these reactions. The conversion was not quantitative under the experimental conditions utilized, and products were obtained in 22−73% isolated yields, based on the amount of **1**, **2**, or **3** used (Table 1). Isolation of the products was carried out on silica gel thin-layer chro-

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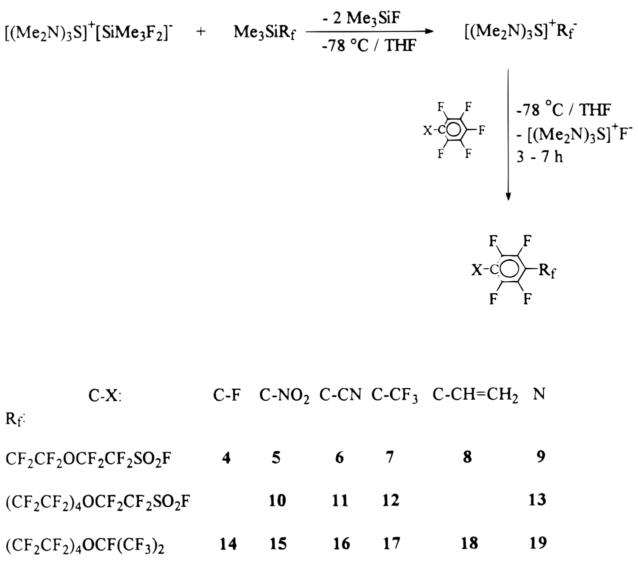
(15) Unpublished results in our laboratory show that the reaction between iodoperfluoralkyl ethers and iodo- or bromopentafluorobenzene via the organocopper intermediate proceeded to give decafluorobiphenyl as the major product (about 70%) and the cross-coupled compound as the minor product (about 30%). No other side products were formed in these reactions.

Table 1. Summary of Physical Properties and Analytical Data of Products of C-nucleophilic Substitution of Perfluoroaryls

compd	yield (%)	bp (°C/mm)	F^- [a]	formula	anal. (%) calcd/found C	H	N
1	72	84/3		$Me_3Si(CF_2)_2OCF_2CF_2SO_2F$	22.58/22.46	2.42/2.35	
3	89	94/1		$Me_3Si(CF_2)_8OCF(CF_3)_2$	25.53/25.60	1.37/1.43	
4	24	*b*	TPSF	$C_6F_5(CF_2)_2OCF_2CF_2SO_2F$	25.75/25.55		
5	72	104/0.5	TBAT	$O_2NC_6F_4(CF_2)_2OCF_2CF_2SO_2F$			
6	73	106/1	TBAT	$CNC_6F_4(CF_2)_2OCF_2CF_2SO_2F$	27.91/27.72		2.96/3.05
7	69	99/1	TPSF	$CF_3C_6F_4(CF_2)_2OCF_2CF_2SO_2F$	25.58/25.33		
8	26	*b*	TASF	$ViC_6F_4(CF_2)_2OCF_2CF_2SO_2F^{\#}$			
9	68	124/3	TASF	$NC_6F_4(CF_2)_2OCF_2CF_2SO_2F$	24.05.23.88		3.12/2.99
	56		TABT	$NC_6F_4(CF_2)_2OCF_2CF_2SO_2F$			
	65		TPSF	$NC_6F_4(CF_2)_2OCF_2CF_2SO_2F$			
10	67	67/25	TASF	$O_2NC_6F_4(CF_2)_8OCF_2CF_2SO_2F$	24.21/23.79		1.77/1.66
11	71	69/28	TBAT	$CNC_6F_4(CF_2)_8OCF_2CF_2SO_2F$			
12	64	64/25	TPSF	$CF_3C_6F_4(CF_2)_8OCF_2CF_2SO_2F$			
13	60	62/20	TASF	$NC_6F_4(CF_2)_8OCF_2CF_2SO_2F$	24.03/23.88	-	1.87/1.94
	59		TPSF	$NC_6F_4(CF_2)_8OCF_2CF_2SO_2F$			
	52		TBAT	$NC_6F_4(CF_2)_8OCF_2CF_2SO_2F$			
14	24	*b*	TASF	$C_6F_5(CF_2)_8OCF(CF_3)_2$	27.13/26.97		
15	48	108/3	TBAT	$O_2NC_6F_4(CF_2)_8OCF(CF_3)_2$			
16	57	*c*	TPSF	$CNC_6F_4(CF_2)_8OCF(CF_3)_2$	26.93/27.08		1.85/1.80
17	49	*c*	TASF	$CF_3C_6F_4(CF_2)_8OCF(CF_3)_2$			
18	22	*b*	TPSF	$ViC_6F_4(CF_2)_8OCF(CF_3)_2{}^{d}$	30.00/29.86	0.40/0.46	
19	62	102/0.5	TASF	$NC_6F_4(CF_2)_8OCF(CF_3)_2$	26.12/25.97	1.91/1.88	
20	63	92/1		*e*	31.47/31.92	0.72/0.76	1.67/1.53
21				Scheme 2			
22	90	95/5		Scheme 2			
23	85	92/3		Scheme 2			
24	56	108/0.5		Scheme 2	36.07/35.86	1.80/1.68	2.81/2.72

[a] The difluorosilicates (TBAT and TASF) and difluorostannate (TPSF) sources of fluoride ion initiators. [b] The yields were too small for any useful distillation. Estimations were made from GC-MS chromatograms. [c] Estimation was made after rp-TLC purification. [d] Vi = $CH_2{=}CH$.

Scheme 1. Likely Mechanism for Reaction of the Dimetalates as Represented by Reactions of TASF



R_f \ C-X:	C-F	C-NO_2	C-CN	C-CF_3	C-CH=CH_2	N
$CF_2CF_2OCF_2CF_2SO_2F$	**4**	**5**	**6**	**7**	**8**	**9**
$(CF_2CF_2)_4OCF_2CF_2SO_2F$		**10**	**11**	**12**		**13**
$(CF_2CF_2)_4OCF(CF_3)_2$	**14**	**15**	**16**	**17**	**18**	**19**

matography (TLC) by using a 1:2 diethyl ether/cyclohexane mixture as the mobile phase.

TPSF and TBAT are stable, and their activities are not dependent on temperature.[2,9a] The difluorosilicates (TSAF and TBAT) reacted faster than the difluorostannate (TPSF), most likely because the five-coordinate anionic stannate $[Ph_3SnF_2]^-$ is more stable than the silicate $[Me_3SiF_2]^-$. The Me_3Si signal usually disappeared completely in the proton NMR after 2 h (TSAF and TBAT) and 3 h (TPSF) at −78 °C. The relative nucleophilicities of these difluorometalates have been discussed in earlier publications,[2,11] and the results show that the different fluoride ion sources, i.e., $Me_3SiF_2^-$ and $Ph_3SnF_2^-$, had different influences on the rate of completion of this step of the reaction. Since the signal for Me_3Si eventually disappears anyway, this is probably not a very significant difference.

The reactions of either the sulfonium (TPSF and TASF) or ammonium (TBAT) cations and hexafluorobenzene, substituted pentafluorobenzenes, or pentafluoropyridine, appear to determine the yield of reaction. The exchange of R_f^- in $TAS^+R_f^-$ (Scheme 1) and $TBA^+R_f^-$ or $TPS^+R_f^-$ for F^- in the perfluoroaryl compounds Ar_F-F, which led to the formation of Ar_F-R_f, appears to depend on the driving force for formation of the respective complex side products, i.e., TAS^+F^-, TBA^+F^-, or TPS^+F^-. All six fluorine atoms of hexafluorobenzene are symmetric and equally weakly activated, which results in their weak response to nucleophilic substitution. Hence, when this occurred at all as in compounds **4** and **14**, it is not surprising that the yields are low. However, the *para*- or *meta*-directing characteristics of pentafluoropyridine O_2N-, CN-, and CF_3-substituted pentafluorobenzenes are known to preferentially influence the ease with which, at least, the activated aryl fluorine atom is substituted.[13b] The relative drive of this reaction eventually determines the yield of the reaction.

Surprisingly, the GC chromatogram of products obtained after hydrolysis and removal of volatile solvent show no reaction side products. The yields also depended on the extent of activation of the fluorine substituents of the perfluoroaryl compounds. Generally, high yields were obtained from C_6F_5N or C_6F_5X (where X = NO_2, CN, CF_3), and low when X = $CH{=}CH_2$ and F (Table 1).

Table 2. Summary of Characteristic NMR and MS Data for 1−24

	NMR data (ppm)			
compd	^{1}H	^{29}Si	^{19}F	MS data (*m*/*e*)
1	0.28	9.3	+44.8, −82.3, −87.7, −114.9, −117.9	372 [M$^+$]
3	0.27	9.4	−81.3 to −81.7, −118.9, −122.9 −126.0, −137.8, −146.1	658 [M$^+$]
4			+44.8, −82.3, −87.7, −114.9, −117.9 −151.4, −161.8	466 [M$^+$], 447 [M$^+$ − F] 283 [M$^+$−OCF$_2$CF$_2$SO$_2$F]
5			+44.8, −82.3, −87.7, −114.9, −117.9 −146.6, −159.1	493 [M$^+$], 474 [M$^+$ − F] 310 [M$^+$ − OCF$_2$CF$_2$SO$_2$F]
6			+44.8, −82.3, −87.7, −114.9, −117.9 −132.6, −159.2	473 [M$^+$], 454 [M$^+$ − F] 290 [M$^+$ − OCF$_2$CF$_2$SO$_2$F]
7	5.64−5.75 5.96−6.27		+44.8, −82.3, −87.7, −114.9, −117.9 −56.7, −152.3, −160.3	516 [M$^+$], 497 [M$^+$ − F] 333 [M$^+$ − OCF$_2$CF$_2$SO$_2$F]
8			+44.9, −82.3, −87.5, −114.9, −117.9 −144.0, −163.9	474 [M$^+$], 455 [M$^+$ − F] 311 [M$^+$ − OCF$_2$CF$_2$SO$_2$F]
9			+44.8, −82.3, −87.7, −114.9, −117.9 −86.3, −160.3	449 [M$^+$], 430 [M$^+$ − F] 266 [M$^+$ − OCF$_2$CF$_2$SO$_2$F]
10			+44.7, −82.7, −87.3, −114.9, −117.9 −122, −146.4, −158.8	793 [M$^+$], 774 [M$^+$ − F] 610 [M$^+$ − OCF$_2$CF$_2$SO$_2$F]
11			+44.8, −82.3, −87.6, −114.9, −117.9 −122.6, −132.1, −159.9	773 [M$^+$], 754 [M$^+$ − F] 590 [M$^+$ − OCF$_2$CF$_2$SO$_2$F]
12			+44.9, −56.8, −82.1, −87.4, −114.9, −117.9, −122, −152.1, −159.7	816 [M$^+$], 797 [M$^+$ − F] 633 [M$^+$ − OCF$_2$CF$_2$SO$_2$F]
13			+44.8, −82.3, −87.6, −114.9, −117.9 −122, −86.4, −159.9	749 [M$^+$], 730 [M$^+$ − F] 566 [M$^+$ − OCF$_2$CF$_2$SO$_2$F]
14			−81.3 - −81.7, −118.9, −122.9, 126.0 −137.8, −146.1, −146.6, 151.4, −161.8	752 [M$^+$], 733 [M$^+$ − F] 574 [M$^+$ − OCF(CF$_3$)$_2$]
15			−81.3 to −81.7, −118.9, −122.9 −126.0, −137.8, −146.1, −146.9, −158.6	779 [M$^+$], 760 [M$^+$ − F] 594 [M$^+$ − OCF(CF$_3$)$_2$]
16			−81.3 to −81.7, −118.9, −122.9 −126.0, −137.8, −146.1, −132.6, −159.2	759 [M$^+$], 740 [M$^+$ − F] 574 [M$^+$ − OCF(CF$_3$)$_2$]
17			−56.4, −81.1 to −81.6, −118.7, −122.9 −126.0, −137.8, −140.8, −152.1, −160.3	802 [M$^+$], 783 [M$^+$ − F] 617 [M$^+$ − OCF(CF$_3$)$_2$]
18	5.64−5.75 5.96−6.27 6.54−7.63		−81.3 to −81.7, −118.9, −122.9 −126.0, −137.8, −144.0, −146.1, −163.9	760 [M$^+$], 741 [M$^+$ − F] 574 [M$^+$ − OCF(CF$_3$)$_2$]
19			−81.5 to −81.9, −86.6, −118.8, −122.9 −126.0, −137.8, −146.1, −160.8	735 [M$^+$], 716 [M$^+$ − F] 550 [M$^+$ − OCF(CF$_3$)$_2$]
20	0.68		−81.2 to −81.7, −118.9, −146.6	839 [M$^+$], 721 [M$^+$ − 2(OAc)] 654 [M$^+$ − OCF(CF$_3$)$_2$]
21				
22	10.42 0.49		−81.3 to −81.7, −118.8, −151.3, −162.2	437 [M$^+$], 420 [M$^+$ − OH] 326 [M$^+$ − OCF$_2$COOH]
23	 0.51		−81.3 to −81.7, −118.9, −122.3 −151.3, −162.4	451 [M$^+$] 567 [M$^+$ − OCF(CF$_3$)$_2$]
24	0.68 0.78		−81.3 to −81.7, −118.7, −122.7 −151.5	499 [M$^+$], 381 [M$^+$ − 2(OAc)] 388 [M$^+$ − OCF$_2$COOH]

There was no evidence for even trace level substitution when the difluorometalates promoted the reaction of **1**−**3** with pentafluoroiodobenzene. Although the corresponding signals for the protons of the Me_3Si moiety had disappeared in the ^{1}H NMR, the GC-MS chromatogram indicated that both the nucleophile and the pentafluoroiodobenzene had undergone some unexplainable transformation. This suggested that it was possible that the countercations in the difluorometalates were capable of more than simple fluoride ion abstraction, depending on the composition of the reaction mixture. Although fragmentation of the perfluoroalkyl carbanion of $Me_3SiC_8F_{17}$ was reported earlier,[6] we have no experimental evidence to support this in our work.

Although the same mechanism[14] (Scheme 1) is assumed for all three difluorometalates in these reactions, the chemoselectivity of the countercation for the aryl fluorine compared to other vulnerable fluorine atoms was not studied previously. An investigation of this phenomenon was a reason to choose the trimethylsilyl synthons **1** and **2**, which have the terminal $-SO_2F$ functionality known to be very sensitive to nucleophilic attack by amines and hydroxides and to attack Grignard reagents.[3,16] The ^{19}F NMR spectra revealed that the countercation (TAS$^+$, TPS$^+$, or TBA$^+$) preferentially reacted with the aromatic fluoride and that there were no significant side reactions under these experimental conditions. As evidence (Table 2), there was no reduction in the integrated amount of the $-SO_2F$ signal at +44.9 ppm in the ^{19}F NMR spectra of compounds **4**−**13**. Instead, the signals of the *para* fluorine in the aryl compounds **4**−**13** and *meta* fluorine in **7**, **12**, and **17** disappeared. The GC-MS chromatogram contained the peaks of $XC_6F_4(CF_2CF_2)_nOCF_2CF_2SO_2F$ ($n = 1$ (**4**−**9**), 4 (**10**−**13**)) as the major products in high yields (Table 2).

The usual workup involved phase distribution of products between a 1:3 water/ether mixture of solvents. The organic phase was concentrated, and compounds **14**−**19** (of the type $XC_6F_4(CF_2CF_2)_4OCF(CF_3)_2$) were purified on silica gel by thin-layer chromatography (TLC) by using a 1:2 diethyl ether/cyclohexane mixture as the mobile phase while **4**−**13** (of the type $XC_6F_4(CF_2CF_2)_nOCF_2CF_2SO_2F$ ($n = 1, 4$)) were eluted by using a

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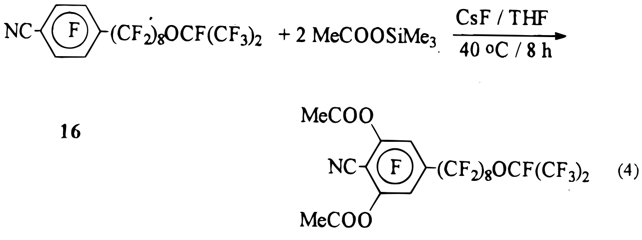
[16] Holbrook, G. W.; Steward, O. W. (to Dow Corning Co.) U.S. Patent 3,012,006, 1961.

1:1 acetonitrile/water mixture on octadecane-bonded reverse-phase thin-layer chromatographic plates (rp-TLC), to give analytically pure products based on elemental analyses (Table 1) and GC-MS evidence (Table 2).

Some of the new compounds were reacted with nucleophiles to produce newer derivatives that were stable to oxidizing or reducing agents and have potential for use as solubilizers and/or conductors. Hexamethyldisilazane was reacted with acetic acid to produce $MeCOOSiMe_3$. The latter was reacted with half the stoichiometric quantity of $CNC_6F_4(CF_2CF_2)_4OCF(CF_3)_2$ at 25 °C, in THF. CsF catalyzed disubstitution at the positions *ortho* to the nitrile moiety to form *o*-$(OOCMe)_2$-$[CNC_6F_4(CF_2CF_2)_4OCF(CF_3)_2]$ (**20**) (eq 4). The position of the substitution was confirmed from ^{19}F NMR spectra, and further substitution of the remaining fluorine atoms did not occur.

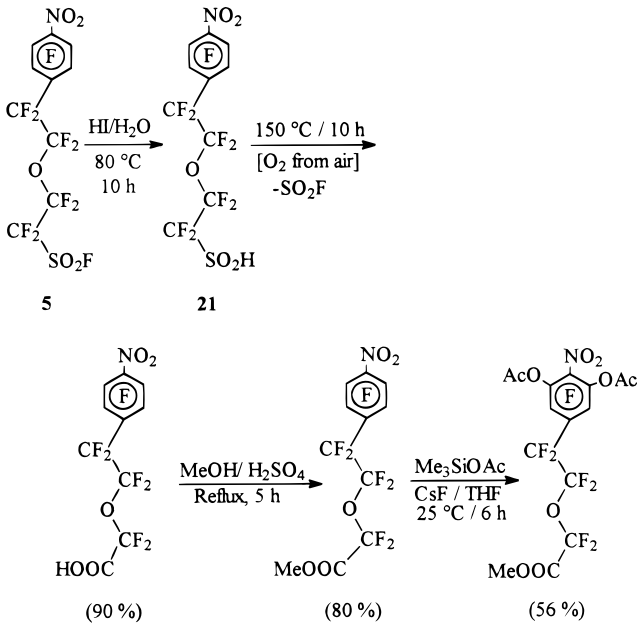


16 (4)

20

Compound **5**, $O_2NC_6F_4CF_2CF_2OCF_2CF_2SO_2F$, was transformed via the process described in Scheme 2 to give the tricarboxylate **24**. The carboxylic acid **22** was obtained by a modification of an earlier literature procedure.[17] This involved quantitative conversion of the sulfonyl fluoride functionality, $-SO_2F$, to the sulfinic acid on reduction with aqueous hydroiodic acid and subsequent heating at 150 °C for 10 h. Refluxing the acid and a catalytic amount of H_2SO_4 in methanol gave the methyl estee **23** in 80% yield. Further reaction with $Me_3SiOOCMe$ resulted in nucleophilic disubstitution at positions *ortho* to the nitro substituent. This fluorinated tricarboxylate, **24**, was obtained as a colorless liquid, bp 108 °C/0.5 mm. The material properties of compounds **20** and **24** are currently being investigated.

Scheme 2. Transformation of Compound 5 to the Tricarboxylate 23



5 **21**

22 **23** **24**

Experimental Section

General Considerations. The solvents, THF and diethyl ether, were dried with sodium and distilled over a purple solution of benzophenone. A standard Schlenk line system was used for handling the air- and moisture-sensitive reactions under anaerobic (dry nitrogen) conditions. Infrared spectra were recorded on a Bio-Rad FTS 3000 Excalibur series infrared spectrometer as neat liquids between KBr plates. ^1H, ^{13}C or $^{13}C\{^{19}F\}$, ^{19}F, and ^{29}Si NMR spectra were obtained on a Bruker AMX spectrometer (200, 300, or 500 MHz) at 200, 50, 188, and 59 MHz, respectively, by using $CDCl_3$ as locking solvent except where otherwise indicated. Chemical shifts were reported relative to Me_4Si or $CFCl_3$. Routine mass spectra (EI) were obtained with a Finnigan GCQ spectrometer. High-resolution mass spectral data were obtained on a JEOL JMS-AX505HA mass spectrometer connected to a Hewlett-Packard HP 6890 series GC system. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ.

Preparation of Me_3SiR_f (R_f = $(CF_2)_2OCF_2CF_2SO_2F$ (1), $(CF_2)_8OCF_2CF_2SO_2F$ (2), $(CF_2)_8OCF(CF_3)_2$ (3)). These compounds were prepared according to the procedure described earlier for **2**.[3] Compounds **1** and **3** were obtained as clear, colorless distillates.

Properties of 1. Bp: 84 °C/3 mm. Yield: 72%. NMR ($CDCl_3$): ^1H, δ 0.28 (CH_3Si, 9H, s); ^{13}C, δ 1.1, 105−121 (m); ^{19}F, δ +44.8, −82.3, −87.7, −114.9, −117.9 ppm; $^{29}Si\{^1H\}$, δ 9.3 (t) ppm, $^2J_{Si-CF_2}$ = 57.2 Hz ($^{29}Si\{^{19}F\}$ δ 9.3 (s) ppm). MS (EI) (*m*/*z*, species, %): 372, M^+, 60. Anal. Calcd for $C_7H_9O_3SF_9Si$: C, 22.58; H, 2.42. Found: C, 22.46; H, 2.35.

Properties of 3. Bp: 94 °C/1 mm. Yield: 89%. NMR ($CDCl_3$ + Freon 113): ^1H, δ 0.27 (CH_3Si, 9H, s); ^{13}C, δ 1.1, 102−122 (m); ^{19}F, δ −81.3 to −81.7, −118.9, −122.9, − 126.0, −137.8, −146.1; $^{29}Si\{^1H\}$, δ 9.4 (t) ppm, $^2J_{Si-CF_2}$ = 57.2 Hz ($^{29}Si\{^{19}F\}$ δ 9.4 (s) ppm). MS (EI) (*m*/*z*, species, %): 658, M^+, 64. Anal. Calcd for $C_{13}H_9O_3SF_{21}Si$: C, 25.53; H, 1.37. Found: C, 25.60; H, 1.43.

General Procedure for C-Nucleophilic Substitution of Aryl Fluorides Promoted by Difluorometalates (TBAT, TASF, and TPSF). The reaction between **3**, pentafluorobenzonitrile, and tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) is given to describe the general procedures used for the difluorosilicate and difluorostannate nucleophilic reactions with the perfluoroaryl systems. Data for the other compounds are summarized in Tables 1 and 2.

A mixture of 2.90 g (15.0 mmol) of pentafluorobenzonitrile in 5 mL of THF and 3.29 g (5.0 mmol) of **3** was stirred in a flame-dried two-necked 100 mL flask under a dry nitrogen atmosphere and maintained at −78 °C. A 20 mL brown THF solution of 1.13 g (5.07 mmol) of **3** was added dropwise from a syringe over 20 min. The resulting mixture was warmed slowly to room temperature and stirred for 3 h. Hexane (100 mL) was added to the stirred mixture, which was then stirred for another 15 min. The unreacted difluorometalate was hydrolyzed with 50 mL of water. The organic layer was dried over anhydrous magnesium sulfate and concentrated by distilling off the solvents at atmospheric pressure. Separation by silica gel preparative TLC by using a 1:2 diethyl ether/cyclohexane mixture as the mobile phase gave 1,4-$CNC_6F_4(CF_2CF_2)_4OCF$-

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(17) Sako, M.; Miyauchi, H. Ohmura, J.; Kimoto, K. In *Modern Chlor-Alkali Technology*; Jackson, C., Ed.; Ellis Horwood: Chichester, U.K., 1983. Vol. 3, p 76.

$(CF_3)_2$ (**16**) as a clear colorless liquid (bp 105 °C/2 mm) in 69% yield. NMR ($CDCl_3$): ^{19}F, δ −81.3 to −81.7, −118.9, −122.9, −126.0, −132.6, −137.8, -146.1, −159.2 ppm. High-resolution mass MS (*m*/*z*): calcd, 759.000; found, 758.895. Anal. Calcd: C, 26.93; H, 1.85. Found: C, 27.08; H, 1.80.

Synthesis of Trimethylsilyl Acetate ($Me_3SiOOCMe$). Hexamethyldisilazane (16.1 g, 100 mmol) was added slowly to a stirred mixture of 3.0 g (50 mmol) of acetic acid and 30 mL of toluene in a flame-dried 100 mL two-necked flask that was connected to a reflux condenser and kept under nitrogen flow. The mixture was gently warmed to reflux at 110 °C for 10 h. The product, trimethylsilyl acetate ($Me_3SiOOCMe$; bp 75 °C), was obtained as a colorless liquid by fractional distillation of the crude product in 78% yield. NMR ($CDCl_3$): ^1H, δ 0.27 (CH_3Si, 9H, s), 0.48 ppm (CH_3CO, 3H, s). MS (*m*/*z*): 132, M^+, 100%.

Nucleophilic Disubstitution of 16 by $Me_3SiOOCMe$ To Give 20. In a flame-dried 100 mL two-necked flask connected to a reflux condenser under nitrogen flow, trimethylsilyl acetate (0.24 g, 2.00 mmol) was added to the stirred solution of 0.76 g (1.00 mmol) of **16** in 25 mL of THF. Catalytic amounts of oven-dried anhydrous cesium fluoride (0.04 g, 0.26 mmol) were added to the mixture, and stirring was continued for 6 h at 25 °C. A mixture of 50 mL of diethyl ether and 3 mL of water was used to separate the organic product from the residual cesium fluoride. Fractional distillation of the organic layer gave a colorless distillate at 92 °C/1 mm, which was analyzed to be **20**. This disubstituted product was obtained in 63% yield. NMR ($CDCl_3$): ^1H, δ 0.68 ppm (CH_3COO, 6H, s). ^{19}F, δ −81.2 to −81.7, −118.9, −146.6 ppm. High-resolution mass MS (*m*/*z*): calcd, 839.000; found, 838.996. Anal. Calcd for $C_{22}H_6NO_5F_{25}$: C, 31.47; H, 0.72; N, 1.67. Found: C, 31.92; H, 0.76; N, 1.53.

Synthesis of 24 from 5. In a flame-dried 100 mL two-necked flask that was connected to a reflux condenser under nitrogen flow was placed 2.47 g (5 mmol) of **5** and 44 mL of 0.2 M (10.2 mmol) hydroiodic acid. A $CaCl_2$ drying tube connected to an aspirator was fitted at the top of the reflux condenser to gently evacuate the reaction medium. The mixture was warmed slowly to 80 °C and stirred for 10 h. The mixture was cooled to 25 °C, and any volatile compounds were evacuated under aspirator vacuum for 3 h. The mixture was heated to 150 °C for another 10 h in a setup that allowed air to pass through the flask by decreasing the pressure with an aspirator and was then cooled. Fractional distillation of the crude product under vacuum gave 1.82 g (4.49 mmol) of **22** as a colorless liquid at 95 °C/5 mm; 90% yield. Methanol (15 mL) and 0.3 mL of concentrated H_2SO_4 were added to 1.82 g of **22**, and the mixture was refluxed for 5 h. After the workup, 1.60 g (3.82 mmol; 80% yield) of **23** was isolated by distillation. To a 20 mL solution of 1.50 g (3.58 mmol) of **23** in THF was added catalytic amounts of oven-dried anhydrous cesium fluoride (0.04 g, 0.26 mmol), and the mixture was stirred for 6 h at 25 °C. A mixture of 100 mL of diethyl ether and 3 mL of water was used to separate the organic product from the residual cesium fluoride. Fractional distillation of the organic layer gave the tricarboxylate **24** as a colorless distillate at 108 °C/0.5 mm in 56% yield. NMR ($CDCl_3$): ^1H, δ 0.68 (CH_3OCO, 6H, s), 0.78 ppm (CH_3COO, 3H, s). ^{19}F, δ −81.3 to −81.7, −118.7, −122.7, −151.1 ppm. MS (EI; *m*/*z*): 499, M^+, 83%; 374, [M^+ − OCF_2COOMe], 62%; 324, [M^+ − CF_2OCF_2COOMe], 100%. Anal. Calcd for $C_{15}H_9NO_9F_8$: C, 36.07; H, 1.80; N, 2.81. Found: C, 35.86; H, 1.68; N, 2.72.

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