Angewandte Chemie International Edition

DOI: 10.1002/anie.201410639

Perfluorinated Alkoxides

A Convenient Route to Tetraalkylammonium Perfluoroalkoxides from Hydrofluoroethers[**]

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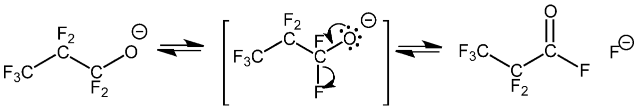
Abstract: *Hydrofluoroethers are shown to alkylate tertiary amines readily under solvent-free conditions, affording valuable tetraalkylammonium perfluoroalkoxides bearing α-fluorines. The reaction of* $R_FCF_2{-}OCH_3$ *(*$R_F = CF_2CF_3$*,* $CF_2CF_2CF_3$*, and* $CF(CF_3)_2$*) with* $NR^1R^2R^3$ *produces twenty new α-perfluoroalkoxides,* $[(CH_3)NR^1R^2R^3][R_FCF_2O]$ *under mild conditions. These α-perfluoroalkoxides are easy to handle, thermally stable, and can be used for the perfluoroalkoxylation of benzyl bromides.*

The fully fluorinated (perfluoro-) alkoxy moiety can impart a range of desirable properties including high metabolic stability, increased lipophilicity, and a degree of thermal and chemical stability that is unprecedented with other functional groups.[1] Furthermore, perfluoroalkoxides have demonstrated ability as inductively electron-withdrawing ancillary ligands in the design of olefin metathesis catalysts,[2] have been proposed as a precursor to solvents for metal/air batteries,[3] and are the active, but not well-studied, species in the anionic ring-opening polymerization of commercially available perfluoropolyalkylethers.[4] Whereas the number of strategies for the late stage incorporation of fluorine,[1c,5] perfluoroalkyl,[6] and perfluorothiolate[7] moieties continues to increase, the perfluoroalkoxylation of aliphatic and aryl substrates has been hindered in part by the lack of a convenient, fluoride-free preparation of thermally stable perfluoroalkoxides. Recent reports have shown the need for a convenient and practical preparation of this underrepresented functional group for pharmaceutical, agrochemical, and industrial applications.[1c,f,8]

Unlike their hydrocarbon analogues, perfluoroalkoxides with α-fluorines cannot be derived from the corresponding perfluoroalcohols and therefore have been difficult to prepare and isolate.[9] Perfluoroalcohols are thermodynamically unstable, because the elimination of HF affords the corresponding acyl fluoride even at very low temperatures.[10] Rather, perfluoroalkoxides have been accessed through the formation of adducts between alkali metal fluorides and perfluorinated carbonyl derivatives as first reported by Willis and Redwood more than 50 years ago.[11] However, these products can readily revert back to their starting point with elimination of an alkali metal fluoride (Scheme 1) and hence have limited synthetic utility beyond ring opening of perfluoro-epoxides.[4]



Scheme 1. Elimination of fluoride from α-perfluoroalkoxides.

However, the presence of a nonmetal cation tends to shift the equilibrium to the perfluoroalkoxide and improve the synthetic utility significantly.[12] The first structurally characterized nonmetal perfluoroalkoxide, tris(dimethylamino)sulfonium (TAS^+) trifluoromethoxide, was prepared by Farnham and Middleton in 1985[13] and has been utilized in the trifluoromethoxylation of aryl boronic acids and stannanes by Ritter et al.[14] More recently, four additional examples were reported between the reaction of an anhydrous fluoride ion and the corresponding perfluorocarbonyl or trifluoromethyl trifluoromethanesulfonates (Scheme 2).[12,15] Particularly noteworthy is the preparation of the only two isolated transition metal complexes bearing a trifluoromethoxide moiety by Vicic et al.[8f,16] However, the high cost, toxicity of low-molecular-weight carbonyl fluorides, air sensitivity of the required reagents, the need for an anhydrous fluoride source, the difficulty of having a fluoride-free perfluoroalkoxide as well as the often in situ preparation of the perfluoroalkoxides, had severely limited synthetic applications to date.

We have found commercially available hydrofluoroethers (HFEs) such as methoxy heptafluoropropane (HFE-7000) (**1**) and methoxy nonafluorobutane (HFE-7100) (**2**) to be particularly good and inexpensive, laboratory cosolvents for the manipulation of organofluorine compounds as both are fluorophilic and relatively polar solvents (Figure 1).[17] Bearing both fluorinated and hydrocarbon segments, HFEs display a combination of physical properties such as low surface

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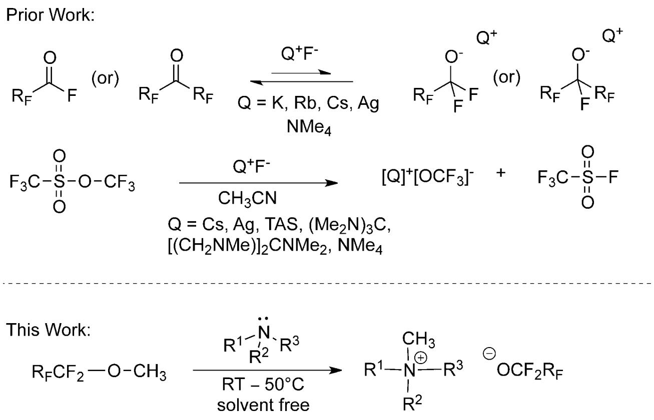
[**] The authors acknowledge funding from the Natural Sciences and Engineering Research Council of Canada (NSERC), Simon Fraser University (SFU), and Trinity Western University (TWU). In addition, we thank J. Ovens (SFU) for assistance with the structural determination of **6a** and A. Simonson (U of Utah) for assistance with TGA-MS.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201410639.



Scheme 2. Representative methods for the preparation of perfluoroalkoxides bearing α-fluorines.

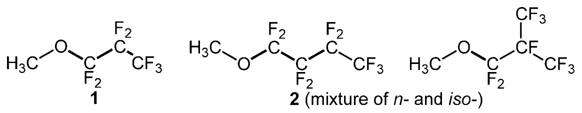


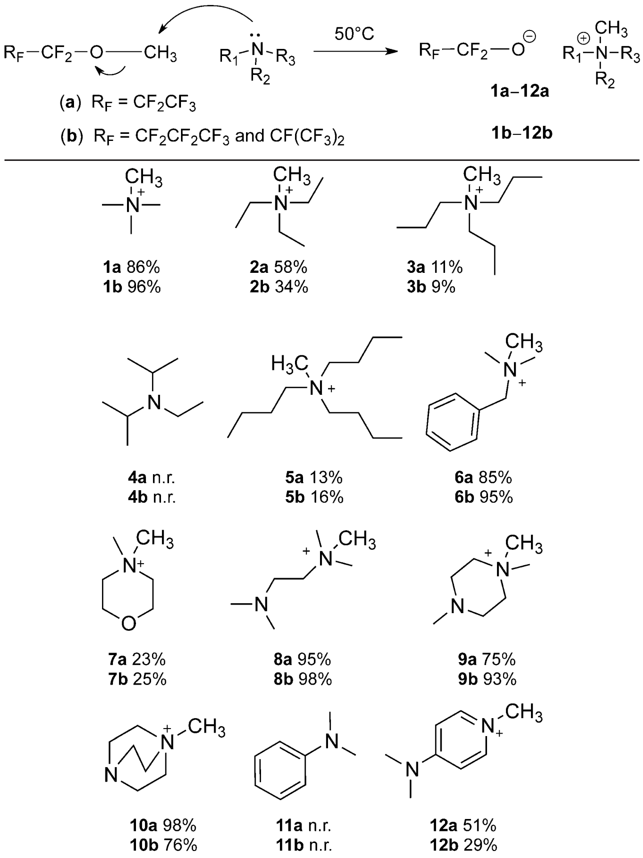
Figure 1. Commercially available hydrofluoroethers HFE-7000 (**1**) and HFE-7100 (**2**), a nearly equimolar mixture of *n*- and *iso*-isomers.

tension, low flammability, and low toxicity, which allow this class of compounds to find application in a wide range of commercial uses as refrigerants, solvents in precision cleaning, fingerprinting agents, blowing agents, and lithium battery cosolvents.[18] Overall, this utility is underpinned by the chemical inertness of HFEs.

Despite their chemical inertness, we observed a rather unexpected but noteworthy degradation pathway for HFEs.[19] Thus, rather than being inert, methoxy hydrofluoroethers (HFE-7000 and HFE-7100) alkylate tertiary amines under mild conditions in moderate to good yields, affording tetraalkylammonium perfluoroalkoxides as highly moisture-sensitive solids. To probe the scope of this reaction, we investigated the reactivity of 12 tertiary amines, including trialkylamines, diamines, and aromatic amines with both HFE-7000 and HFE-7100 (Table 1). In most cases, the perfluoroalkoxide, which is the only detectable product, precipitates out of the reagent mixture, enabling a clean workup by filtration or, if the amine is volatile, both reagents can be simply removed under reduced pressure to afford multigram quantities of the desired perfluoroalkoxide adduct.

Each of the twenty new perfluoroalkoxides reported herein was characterized by ^{1}H and ^{19}F NMR spectroscopy, IR spectroscopy, and elemental analysis (see the Supporting Information, SI). In addition, the X-ray crystal structure of **6a** was determined (Figure 2) and clearly depicts a methylated *N,N*-dimethylbenzylamine with a perfluoropropoxide anion. The bond lengths are consistent with the other four known perfluoroalkoxide structures, including a significantly short C–O bond (1.28 Å) and elongated C–F bonds, ostensibly due to negative hyperconjugation. This is further corroborated by the increased ν_{C-O} frequency (1540 cm^{-1}) in each of the reported perfluoroalkoxides due to an increase in bond order of the C–O bond, irrespective of the associated cation. At ambient temperature, the α-fluorines of the perfluoroalkoxide tend to appear as a broad signal in the ^{19}F NMR spectrum, a not well-understood phenomenon which has been attributed to slow fluoride exchange.[13,15d] However, at no point do we observe free fluoride or the corresponding acyl fluoride (see SI). Upon cooling in CH_2Cl_2 in 10° intervals

Table 1: Substrate scope for the methylation of tertiary amines by hydrofluoroethers.[a]



1a 86% **1b** 96%	**2a** 58% **2b** 34%	**3a** 11% **3b** 9%
4a n.r. **4b** n.r.	**5a** 13% **5b** 16%	**6a** 85% **6b** 95%
7a 23% **7b** 25%	**8a** 95% **8b** 98%	**9a** 75% **9b** 93%
10a 98% **10b** 76%	**11a** n.r. **11b** n.r.	**12a** 51% **12b** 29%

[a] Yields refer to the isolated material of > 98% purity unless otherwise noted. n.r. = no reaction.

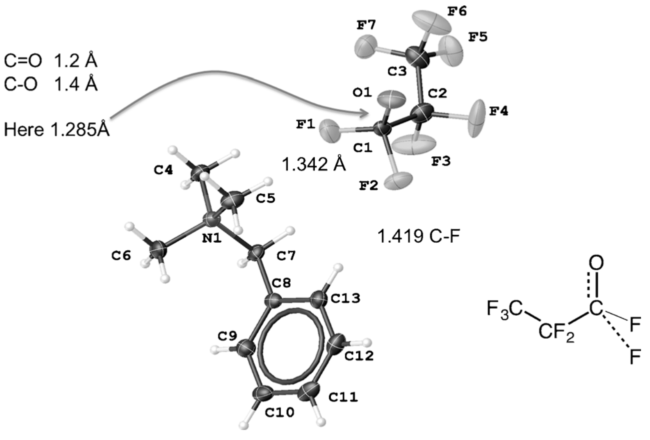
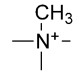
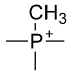
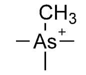


Figure 2. X-ray structure of **6a** showing the thermal ellipsoids at the 30% probability level (*P*21/*c*, 150 K, *R* = 7.11%).

from room temperature to −80 °C, the α-difluoromethylene signal of **6a** sharpens and then splits into a multiplet below −30 °C.

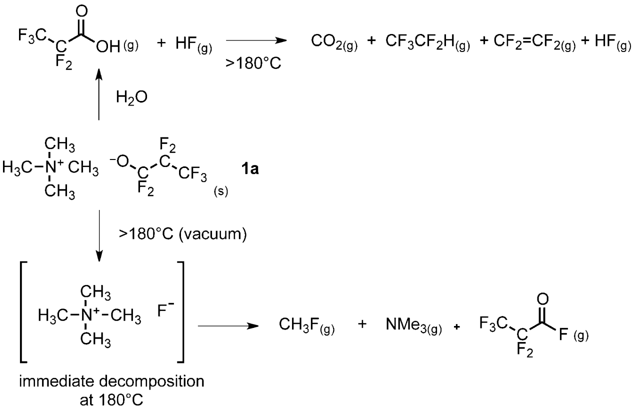
To further survey the methylating ability of HFEs, we targeted analogous Group 15 substrates and observed that the yield unsurprisingly decreases (Table 2). The spectroscopic details of **13a** are entirely consistent with a tetramethylphosphonium perfluoropropoxide rather than a pentacoordinate phosphorane with perfluoroalkoxy or fluoride moiety.[20]

Table 2: Methylation of homologous Group 15 substrates by $CH_3OCF_2CF_2CF_3$.[a]

		
1a 77%	**13a** 12%	**14a** trace

[a] 25 °C, 48 h, yields are of isolated products.

Since perfluoroalkoxides tend to eliminate fluoride with concomitant formation of perfluoroacyl fluoride at elevated temperatures, we hypothesized that thermal decomposition of tetraalkylammonium perfluoroalkoxides could enable a facile route to truly anhydrous tetraalkylammonium fluorides. The prepared tetramethylammonium perfluoropropoxide was subjected to thermal analysis in a glovebox equipped with a thermogravimetric analyzer/mass spectrometer (TGA-MS). As shown in Scheme 3, adventitious amounts of moisture were sufficient to catalytically decompose the tetraalkylammonium perfluoroalkoxides to the carboxylic acid. The carboxylic acid then underwent decarboxylation of the anion and concomitant Hofmann elimination of the cation between 185–200 °C, affording a mixture of volatile products, including tetrafluoroethylene. However, with careful handling in the appropriate Schlenkware on a stainless steel vacuum line equipped with a gas cell IR spectrometer, we were able to determine that the tetramethylammonium perfluoroalkoxide were surprisingly stable at 150 °C at 1 torr for a period of 1 h and partial decomposition did not occur until 180 °C.



Scheme 3. Thermal and hydrolysis decomposition routes for tetramethylammonium perfluoropropoxide (**1a**) determined by TGA-MS, IR spectroscopy, GC/MS, and ^{19}F NMR spectroscopy.

However, at this temperature, the tetramethylammonium perfluoropropoxide underwent immediate decomposition of the tetramethylammonium fluoride to fluoroform and trimethylamine based on gas-phase IR and GC/MS analysis of the trapped off-gas and ^{19}F NMR analysis of the residue (see SI).

Having established a convenient route to thermally stable perfluoroalkoxides, we then explored the reactivity of **1a** with benzyl bromide substrates in solution. We had a particular interest in the ratio of perfluoroalkoxylation to fluoro derivatives. After optimizing the solvent and temperature, we found that acetonitrile at 45 °C gave the highest conversion (see SI). Surprisingly, even at 45 °C, with 2.0 equivalents of tetramethylammonium perfluoropropoxide, only 1 % of 4-bromobenzyl fluoride was obtained. However, at 75 °C the same conversion of ether was obtained but an increase in 4-bromobenzyl fluoride. We hypothesized that the newly formed ether was in a reversible reaction. With the addition of 1.0 equivalent of $AgBF_4$, the conversion reached 94 % with less than 1 % benzyl fluoride after 8 h. The volatility of the ethers resulted in a lower isolated yield (Figure 3).

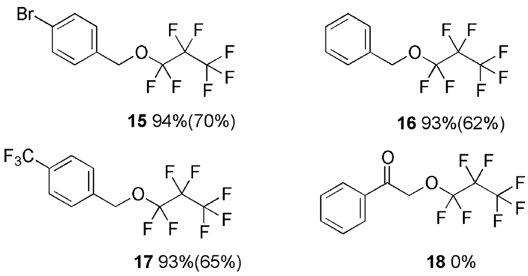


Figure 3. Perfluoroalkoxylation of alkyl bromides with $NMe_4OCF_2CF_2CF_3$ at 45 °C in CH_3CN for 8 h. Conversions were determined by GC/MS and yields of the pure isolated compound are reported in parentheses.

The solution state stability of perfluoroalkoxides may be related to methods of preparation as was recently observed by Vicic et al. in the preparation of the analogous $[NMe_4][SCF_3]$.[7b] Even though the substrates reported herein are simple (Figure 3) with no competing elimination pathway, the perfluoroalkoxides are able to tolerate higher temperatures than previously reported with high conversion of the ether and only minor amounts of fluoride substitution (Figure 3).[15a,c,21] However, even if the perfluoroalkoxide is not in equilibrium with free fluoride, the newly formed ethers can still be susceptible to β-fluoride elimination. For instance, no product was observed with 2-bromoacetophenone derivative **18** but substantial amounts of benzoyl fluoride derivatives.

In summary, we have observed that two commercially available methyl hydrofluoroethers are not inert but act as electrophilic methylating agents of tertiary amines and PMe_3, affording quaternary ammonium or phosphonium perfluoroalkoxides, respectively. Furthermore, these thermally stable salts are isolable, stable in the absence of moisture, and react with benzyl bromides to form perfluoropropoxy benzyl ethers. Hydrofluoroethers provide access to new tetraalkylammonium perfluoroalkoxides and future work will seek to explore perfluoroalkoxylation of more complex aliphatic substrates.

Experimental Section

General procedure for the preparation of perfluorinated alkoxides: In a sealed 20 mL vial with a resin-lined screw cap under nitrogen atmosphere, the respective tertiary amine (0.6 mol) and hydrofluoroether (5 equiv) were combined and the vial was sealed. The vials were then agitated and heated at 50.0 °C. Reactions with trimethylamine were performed by vacuum transfer technique of the amine to a 60 mL Pyrex^{TM} high-pressure tube. After 48 h, excess reagents were removed in vacuo and the perfluoroalkoxide was collected in a fine-fritted disk in a glovebox and washed with anhydrous hexanes (3 × 3 mL) and further dried in vacuo. Although extremely moisture sensitive, the resulting perfluoroalkoxides can be stored in dry borosilicate vials for an extended period of time at ambient temperature under a moisture-free atmosphere without decomposition.

Received: October 31, 2014
Revised: December 10, 2014

Keywords: alkylation · fluorine · hydrofluoroether · perfluoroalkoxide · reactive intermediates

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Communications

Perfluorinated Alkoxides

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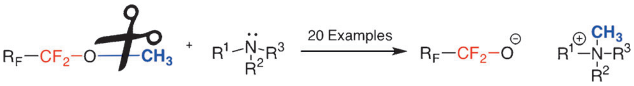
C. M. Friesen* ______ ■■■–■■■

A Convenient Route to Tetraalkylammonium Perfluoroalkoxides from Hydrofluoroethers



Fluoride free! The preparation of a series of tetraalkylammonium perfluoroalkoxides under mild, fluoride-free conditions is achieved by the methylation of tertiary amines with commercially available, partially fluorinated ethers. This practical synthesis paves a new way to an under-represented class of thermally stable compounds bearing α-fluorines.