

Perfluoroalkylation of simple inorganic molecules: A one step route to novel perfluoroalkylated compounds

Rajendra P. Singh and Jean'ne M. Shreeve*

Department of Chemistry, University of Idaho, Moscow, ID 83844-2343, USA.

E-mail: jshreeve@uidaho.edu; Fax: +1 208-885-9146

Received (in Corvallis, OR, USA) 24th May 2002, Accepted 5th July 2002

First published as an Advance Article on the web 19th July 2002

Reactions of $(\text{CH}_3)_3\text{SiR}_f$ ($\text{R}_f = \text{CF}_3, \text{C}_2\text{F}_5$) with NOCl , NO , NO_2 , SO_2 , CO_2 , in the presence of caesium fluoride provide a one step synthetic route to perfluoroalkylated compounds in very good yields.

Straightforward and reliable synthetic methods for the incorporation of perfluoroalkyl groups are highly desirable. (Perfluoroalkyl)trimethylsilanes are effective reagents that, in the presence of fluoride ion, have been used for the introduction of perfluoroalkyl groups into a variety of substrates, including aldehydes, hydrocarbons, ketones, esters and sulfur-based electrophiles.^{1–9} For nearly twenty years, (perfluoroalkyl)trimethylsilanes have been used in the synthesis of a variety of perfluoroalkylated compounds which have found applications in the fields of materials science, agrochemistry and pharmaceuticals.^{10–16} Our continuing interest in (perfluoroalkyl)trimethylsilane reagents prompted us to demonstrate applications with inorganic substrates. This methodology has allowed us to prepare several valuable perfluoroalkylated compounds in good to excellent yields in a manner that is much simpler and more straightforward than the traditional routes. The details of the reactions are described as follows.

Perfluoronitrosoalkanes have been studied for their use as monomers in the synthesis of nitroso rubbers and other novel polymers.¹⁷ In the 1950s, the syntheses of polyfluoroalkylnitroso compounds were first reported^{18–22} by Haszeldine and Banus when a mixture of perfluoroalkyl iodide and nitric oxide were subjected to ultraviolet irradiation in the presence of mercury. In general, conversions did not exceed 50% and, in addition, it was difficult to remove traces of unreacted iodide, the presence of which could result in low molecular weight polymers due to chain transfer reactions. Other methods involved the photolysis or pyrolysis of a perfluoroacyl nitrite which required rather drastic reaction conditions ($> 190^\circ\text{C}$).²³ In some of the syntheses, the toxic $(\text{CF}_3)_2\text{Cd}$ compound has been employed as the transfer reagent with products being isolated in low yields.²⁴

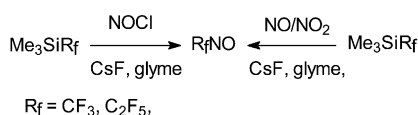
We now report a simple and efficient method to prepare perfluoronitrosoalkanes in very good yield. The reaction of (perfluoroalkyl)trimethylsilane (Me_3SiR_f , $\text{R}_f = \text{CF}_3, \text{C}_2\text{F}_5$) with nitrosyl chloride in the presence of caesium fluoride led to the formation of perfluoronitrosoalkanes in $> 90\%$ yields.[†] Since the reaction did not proceed without solvent, ethylene glycol dimethyl ether (monoglyme) was used. The reaction was started at -196°C and the mixture was allowed to warm slowly to 25°C . The formation of the blue gaseous product (CF_3NO or $\text{C}_2\text{F}_5\text{NO}$) was complete within 3 h. Stoichiometric amounts of caesium fluoride were required due to the simple metathetical nature of the reactions (Scheme 1). However, with the higher perfluoroalkyl homologues (Me_3SiR_f , $\text{R}_f = \text{C}_6\text{F}_{13}, \text{C}_7\text{F}_{15}, \text{C}_8\text{F}_{17}$) the reaction was found to proceed slowly, and over an 8

h reaction time, the yields of the anticipated nitroso compounds were $< 20\%$.

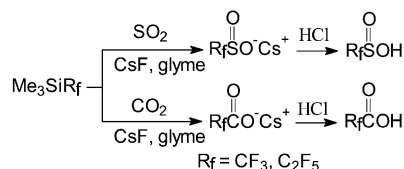
Although while not surprising, (perfluoroalkyl)trimethylsilane did not react with nitric oxide, the presence of an equimolar amount of nitrogen dioxide led to the formation of perfluoronitrosoalkane in $< 15\%$ yields. It is likely that the reaction occurred because of the presence of NO^+ resulting from the equilibrium, $\text{NO} + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_3 \rightarrow \text{NO}^+\text{NO}_2^-$. The perfluoronitrosoalkanes were purified by low temperature trap-to-trap distillation. Products were characterized by comparison with the spectroscopic data reported in the literature.^{19,20}

Perfluoroalkanesulfonic acids and their derivatives are useful compounds in the preparation of wetting agents, impregnants, or surfactants.²⁵ Earlier perfluoroalkanesulfonic acids were synthesized either by electrochemical methods²⁶ or by the reduction of perfluoroalkanesulfonic fluorides with hydrazine hydrate in refluxing ether.²⁷ While the yield of trifluoromethanesulfonic acid in the latter synthesis was not reported, the overall yield reported for perfluorobutanesulfonic acid was about 20%. Also, there is a report about the reaction of SO_2 with TMSCF_3 in the presence of TBAF but the final oxidized product is reported in 30% yield and no details of experimental and characterization data are mentioned.²⁸ We report a very facile, efficient, and high yield synthesis of the caesium salts of trifluoro and pentafluoroalkanesulfonic acids. Reactions of (perfluoroalkyl)trimethylsilanes with SO_2 and CsF in equimolar ratios in monoglyme led to the formation of the caesium salt of perfluoroalkanesulfonic acids in almost quantitative yields (Scheme 2).[‡] The salts were characterized by comparing the spectroscopic data with the sodium and potassium salt of the acids reported in the literature.²⁹ These salts were converted into the free acids in $\sim 60\%$ yields by reacting with anhydrous HCl gas neat and characterized by comparing with the literature data.²⁷

The reactions of (perfluoroalkyl)trimethylsilane have been extensively studied with carbonyl compounds but remain unexplored with carbon dioxide. We have found that CO_2 with Me_3SiR_f ($\text{R}_f = \text{CF}_3, \text{C}_2\text{F}_5$) in the presence of an equimolar amount of CsF in monoglyme produced $\text{R}_f\text{CO}_2^- \text{Cs}^+$ in quantitative yields.[§] The reaction does not proceed in the absence of solvent. Reaction with equimolar amounts of anhydrous HCl neat gave trifluoroacetic acid in 90% yield and pentafluoropropionic acid in 85% yield (Scheme 2). Catalytic amounts of CsF gave the products in traces. Even in the presence of an excess perfluoroalkylating reagent (Me_3SiR_f), only the monoaddition product was formed with no evidence for interaction with the remaining carbonyl moiety. Reaction of COS with Me_3SiCF_3 in the presence of CsF under identical reaction conditions led to the formation of a mixture of



Scheme 1



Scheme 2

CF₃COSH and CF₃CSOH.³⁰ Carbon disulfide was reported to react with Me₃SiCF₃.³¹

The present report describes a powerful and simple method for the preparation of several fluorinated compounds with some advantages in comparison with some other routes.

This work was supported by the National Science Foundation (Grant No. CHE-9720365) and by the Petroleum Research Fund, administered by ACS.

Notes and references

† Caesium fluoride (0.30 g, 2.0 mmol) and ethylene glycol dimethyl ether (1 mL) were added in a dry flask (100 mL), cooled to -196 °C. The flask was evacuated to remove any air or nitrogen gas. NOCl (2.0 mmol) was transferred under vacuum followed by the condensation of Me₃SiCF₃ (2.0 mmol) at -196 °C. The cold bath was removed. The formation of the blue gas (CF₃NO) commenced shortly after the reaction reached 25 °C. The reaction mixture was stirred for 3 h. Based on the gas phase IR, all of the NOCl was consumed. CF₃NO was separated from other volatile compounds by trap-to-trap distillation. It was isolated in 92% yield. Product was characterized by comparing the spectroscopic data reported in the literature.¹⁹ C₂F₅NO was prepared in the similar way in 85% isolated yield.²⁰

‡ In general, caesium fluoride was added in a flask and 1.5 equiv. of Me₃SiR_f was added at -196 °C followed by monoglyme. The mixture was evacuated and 1.5 equiv. of sulfur dioxide were added. After warming slowly to 25 °C the reaction mixture was stirred for 24 h. Removal of volatile materials at reduced pressure gave the caesium salt of perfluoroalkylated sulfinic acids. CF₃SO₂-Cs⁺: Yield, 95%; IR (nujol mull): 1260, 1219, 1190, 1121, 1026, 945, 801 cm⁻¹. ¹⁹F NMR (DMSO-d₆): δ -85.63 (s); ¹³C NMR (DMSO-d₆): δ 125.5 (q, J_{C-F} = 360 Hz); C₂F₅SO₂-Cs⁺: Yield, 95%; IR (nujol mull): 1262, 1163, 1132, 1083, 1022, 958, 801, 723 cm⁻¹. ¹⁹F NMR (DMSO-d₆): δ -78.17 (s, 3F), -131.91 (s, 2F); ¹³C NMR (DMSO-d₆): δ 120.3 (triplet of quartets, J_{C-F} = 287.5 Hz, J_{C-C-F} = 34 Hz).

§ Prepared by the similar procedure as used for SO₂ reaction. CF₃COO-Cs⁺: Yield: 95%. IR (nujol mull): 1665, 1456, 1417, 1205, 1228, 984, 828, 801, 720 cm⁻¹. ¹⁹F NMR (DMSO-d₆): δ -73.35 (s, 3F); ¹³C NMR (DMSO-d₆): δ 122.7 (q, J_{C-F} = 293 Hz, CF₃COO); 164.3 (q, J_{C-C-F} = 37.5 Hz, CF₃COO). To the salt was added an equimolar amount of anhydrous HCl and after the flask was agitated for 1 h, CF₃COOH was separated in 90% yield by distillation from caesium chloride and characterized by comparing the spectroscopic data with authentic samples. C₂F₅COO-Cs⁺: Yield: 95%. IR (nujol mull): 1689, 1455, 1366, 1322, 1195, 1113, 1024, 984, 935, 806, 730 cm⁻¹. ¹⁹F NMR (DMSO-d₆): δ -81.30 (s, 3F), -118.10 (s, 2F); ¹³C NMR (DMSO-d₆): δ 114.7 (quartet of troplet, 2F, J_{C-F} = 262 Hz, CF₃CF₂, J_{C-C-F}, 37.5 Hz, = CF₃CF₂); 125.0 (triplet of quartet, 3F, J_{C-F} = 285 Hz, CF₃CF₂, J_{C-C-F}, 37.5 Hz, CF₃CF₂, 163.8 (q, J_{C-C-F} = 22.5 Hz, CF₃CF₂COO).

- 1 G. K. S. Prakash and A. K. Yudin, *Chem. Rev.*, 1997, **97**, 757.
- 2 R. P. Singh and J. M. Shreeve, *Tetrahedron*, 2000, **56**, 7613.
- 3 R. Krishnamurti, D. R. Bellew and G. K. S. Prakash, *J. Org. Chem.*, 1994, **56**, 984.
- 4 D. W. Nelson, N. J. O'Reilly, J. Speier and P. G. Gassman, *J. Org. Chem.*, 1994, **59**, 8157.

- 5 S. P. Kotun, J. D. O. Anderson and D. D. DesMarteau, *J. Org. Chem.*, 1992, **57**, 1124.
- 6 J. Wiedemann, T. Heiner, G. Mloston, G. K. S. Prakash and G. A. Olah, *Angew. Chem., Int. Ed.*, 1998, **37**, 820.
- 7 A. A. Kolomeitsev, V. N. Movchun, N. V. Kondratenko and Y. L. Yagupolski, *Synthesis*, 1990, 1155.
- 8 R. P. Singh, R. L. Kirchmeier and J. M. Shreeve, *J. Org. Chem.*, 1999, **64**, 2579.
- 9 R. P. Singh, G. Cao, R. L. Kirchmeier and J. M. Shreeve, *J. Org. Chem.*, 1999, **64**, 2873.
- 10 *Organofluorine Chemistry: Principles and Commercial Applications*, eds. R. E. Banks, B. E. Smart and J. C. Tatlow, Plenum, New York, 1994.
- 11 *Biomedical Frontiers of Fluorine Chemistry*, eds. I. Ojima, J. R. McCarthy and J. T. Welch, ACS Symposium Series 639; American Chemical Society, Washington, DC, 1996.
- 12 *Organic Chemistry in Medicinal Chemistry and Biomedical Applications*, ed. R. Filler, Elsevier, Amsterdam, 1993.
- 13 J. T. Welch and S. Eswarakrishnan, *Fluorine in Bioorganic Chemistry*, John Wiley and Sons, New York, 1991.
- 14 R. Filler and K. Kirk, *Biological Properties of Fluorinated Compounds in Chemistry of Organic Fluorine Compounds II: A Critical Review*, eds. M. Hudlicky and A. E. Pavlath, ACS Monograph 187; American Chemical Society, Washington, DC, 1995, pp. 1011.
- 15 *Recent Developments in Fluorine-Containing Agrochemicals in Organic Fluorine Chemistry: Principles and Commercial Applications*, eds. R. E. Banks, B. E. Smart and J. C. Tatlow, Plenum, New York, 1994, pp. 237.
- 16 R. W. Lang, *Fluorinated Agrochemicals in Chemistry of Organic Fluorine Compounds II*; eds. M. Hudlicky and A. E. Pavlath, ACS Monograph 187; American Chemical Society, Washington, DC, 1995, pp. 1143.
- 17 D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 1955, 1881.
- 18 R. N. Haszeldine, *Nature*, 1951, **168**, 1028.
- 19 J. Jander and R. N. Haszeldine, *J. Chem. Soc.*, 1954, 912.
- 20 R. N. Haszeldine, *J. Chem. Soc.*, 1953, 2075.
- 21 J. Banus, *Nature*, 1953, **171**, 173.
- 22 J. Banus, *J. Chem. Soc.*, 1953, 3775.
- 23 R. E. Banks, M. G. Barlow, R. N. Haszeldine and M. K. McCreath, *J. Chem. Soc.*, 1966, 1350.
- 24 K. Ludovici, D. Naumann, G. Siegmund, W. Tyrra, H.-G. Varbelow and H. Wrubel, *J. Fluorine Chemistry*, 1995, **73**, 273.
- 25 H. W. Roesky, H. Niederpruem and M. Wechsberg, *Ger. Offen.* 2, 1973, **148**, 597.
- 26 J. C. Folest, J. Y. Nedelec and J. Perichon, *Synth. Commun.*, 1988, **18**, 1491.
- 27 H. W. Roesky, *Angew. Chem., Int. Ed.*, 1971, **10**, 810.
- 28 *Nucleophilic Perfluoroalkylation of Organic Compounds Using Perfluoroalkyltrialkylsilanes in Synthetic Fluorine*, eds. G. A. Olah, R. D. Chamber and G. K. S. Prakash, John Wiley, New York, 1992, pp. 227.
- 29 H. W. Roesky and J. Holtschneider, *J. Fluorine Chemistry*, 1976, **7**, 77.
- 30 W. A. Sheppard and E. L. Muetterties, *J. Org. Chem.*, 1960, **25**, 180.
- 31 Y. L. Yagupolskii, V. N. Movchun, N. V. Kirij, D. Naumann, N. Magiarosa and W. Tyrra, 16th International Symposium Fluorine Chemistry, University of Durham, UK, July 16-21, 2000, Abstract No. A38.