

Communication

Synthesis of perfluoropropyl and perfluorobutyl germanium by direct fluorination: a potential general synthesis for perfluorinated metal alkyls

Ryan P. Callahan, Cameron R. Youngstrom, Richard J. Lagow *

Department of Chemistry and Biochemistry, College of Natural Sciences, A5300, University of Texas, Austin, TX 7812-1167, USA

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We dedicate this manuscript in honor of Professor F. Albert Cotton, one of the finest men and best chemists in the world, on the occasion of his 70th birthday. R.J. Lagow is extremely grateful for Al's friendship, kindness, advice, and support throughout his academic career.

Abstract

We wish to report a new high-yield synthesis of perfluorotetra-*n*-propyl and perfluorotetra-*n*-butyl germanes from their hydrocarbon analogues. This technique will likely develop into a new general synthesis for perfluorinated organometallic compounds. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The first perfluorinated main group and metal alkyls were reported by Emeléus and co-workers in the year 1948 [1–5]. Emeléus reported compounds such as $\text{Hg}(\text{CF}_3)_2$, $\text{Hg}(\text{CF}_2\text{CF}_3)_2$, $\text{P}(\text{CF}_3)_3$, $\text{As}(\text{CF}_3)_3$, and $\text{Sb}(\text{CF}_3)_3$. Important contributions to the synthesis and literature of trifluoromethyl organometallic compounds have also been made by Burton and MacNeil [6]. Burton and co-workers have also reported a general route to fluorovinyl and perfluorovinyl organometallic compounds [7], as well as a number of perfluoro isopropyl organometallic compounds [8]. The formation of tetrakis(perfluoroalkyl)tellurium compounds by Naumann et al. has also been reported [9].

While the Lagow group has developed several new syntheses for metal trifluoromethyl and trifluorosilyl organometallic compounds [10,11], there has not been a general synthesis for metal alkyls with saturated perfluorocarbon chains, linear or branched, of three to four carbon atoms in length using elemental fluorine.

Utilizing continuous liquid-phase fluorination reaction technology [12], we have been successful with high-yield synthesis of higher-molecular-weight perfluoro germanium alkyls using the hydrocarbon metal alkyls as starting materials and treating these alkyls with fluorine in chlorofluorocarbon solvents, such as 1,1,2-trichlorotrifluoroethane (Freon 113).

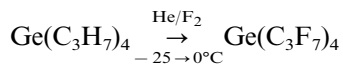
2. Experimental

Tetra-*n*-propylgermane and tetra-*n*-butylgermane were purchased from Gelest Inc. Perfluorinated products were purified by vacuum distillation. Low-resolution mass spectroscopy was performed on a MAT TSQ-70 spectrometer. High-resolution mass spectra were obtained from a VG analytical ZAB2-E mass spectrometer. ^{19}F -NMR was performed using a Varian Unity plus-300 NMR spectrometer. ^{19}F -NMR spectra were recorded at 282 MHz using CDCl_3 as the lock solvent and CFCl_3 as the internal standard.

The direct fluorination reactions were performed in a similar manner to the reactions that have been described in the literature [11].

* Corresponding author.

3. Synthesis of perfluorotetra-*n*-propyl germane



Tetra-*n*-propylgermane (1.5 ml) was added to a round-bottom flask and diluted with 250 ml of 1,1,2-trichlorotrifluoroethane. This solution was then pumped (rate = 25 ml h⁻¹) into a stainless steel reactor that had been cooled to -25°C in an isopropyl alcohol bath and which contained 500 ml of 1,1,2-trichlorotrifluoroethane and 69 g of NaF.

During the addition of tetra-*n*-propylgermane to the stainless steel reactor, a mixture of helium and fluorine was bubbled through the reactor at a rate of 400/100 cc min⁻¹, respectively. After the tetra-*n*-propylgermane solution had been pumped into the reactor, the helium to fluorine flow rate was turned down to 10/10 cc min⁻¹, respectively. The reactor was kept at -25°C with a helium–fluorine flow rate of 10/10 cc min⁻¹ for 24 h. After 24 h, the reactor was warmed to -10°C and kept at this temperature for another 24 h. The helium and fluorine flow rates were not changed at this time. After 24 h at -10°C, the reactor was warmed to 0°C; again the helium and fluorine flow rates were not changed. After 24 h at 0°C, the fluorine was turned off,

and the reactor was allowed to purge for 4 h. The solution in the reactor was then filtered to remove NaF and any NaHF₂ formed during the reaction. 1,1,2-Trichlorotrifluoroethane was removed by simple distillation. Perfluorotetra-*n*-propylgermane was then purified by vacuum distillation (b.p. = 45–6°C/1.7 mmHg) and was obtained in an isolated yield of 76%.

Chemical ionization mass spectral analysis (negative mode): *m/z* (formula, identification, intensity) 750 (C₁₂F₂₈Ge, (M)⁻, 1.83) relative to 581 (C₉F₂₁Ge, (M-C₃F₇)⁻, 100). Elemental compositions were studied by high resolution mass spectroscopy in chemical ionization negative mode. Results were consistent with C₁₂F₂₈Ge (Anal. Calc.: 749.876; Found: 749.878). ¹⁹F-NMR (CFCl₃) δ -80.40 (s, 12F), -106.88 (s, 8F), -120.78 (t, 8F) (Fig. 1).

3.1. High-resolution mass spectrometry of perfluoro-tetra-*n*-propylgermane

	Measured	Calculated
Ge(CF ₂ CF ₂ CF ₃) ⁻	243.918	243.918
Ge(CF ₂ CF ₂ CF ₃) ₂ ⁻	412.907	412.907
Ge(CF ₂ CF ₂ CF ₃) ₃ ⁻	580.888	580.887
Ge(CF ₂ CF ₂ CF ₃) ₄ ⁻	749.878	749.876

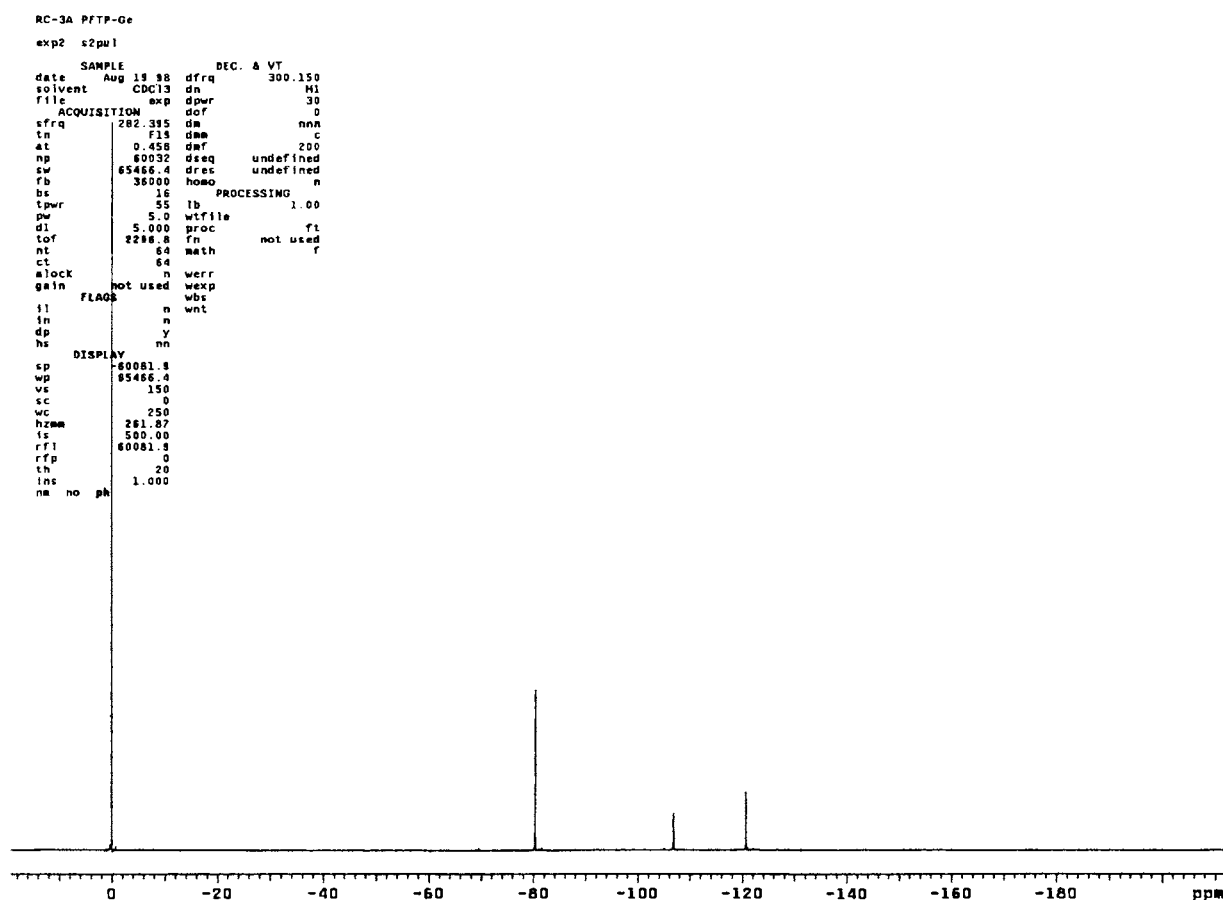


Fig. 1. ¹⁹F-NMR spectrum of perfluoro-tetra-*n*-propylgermane.

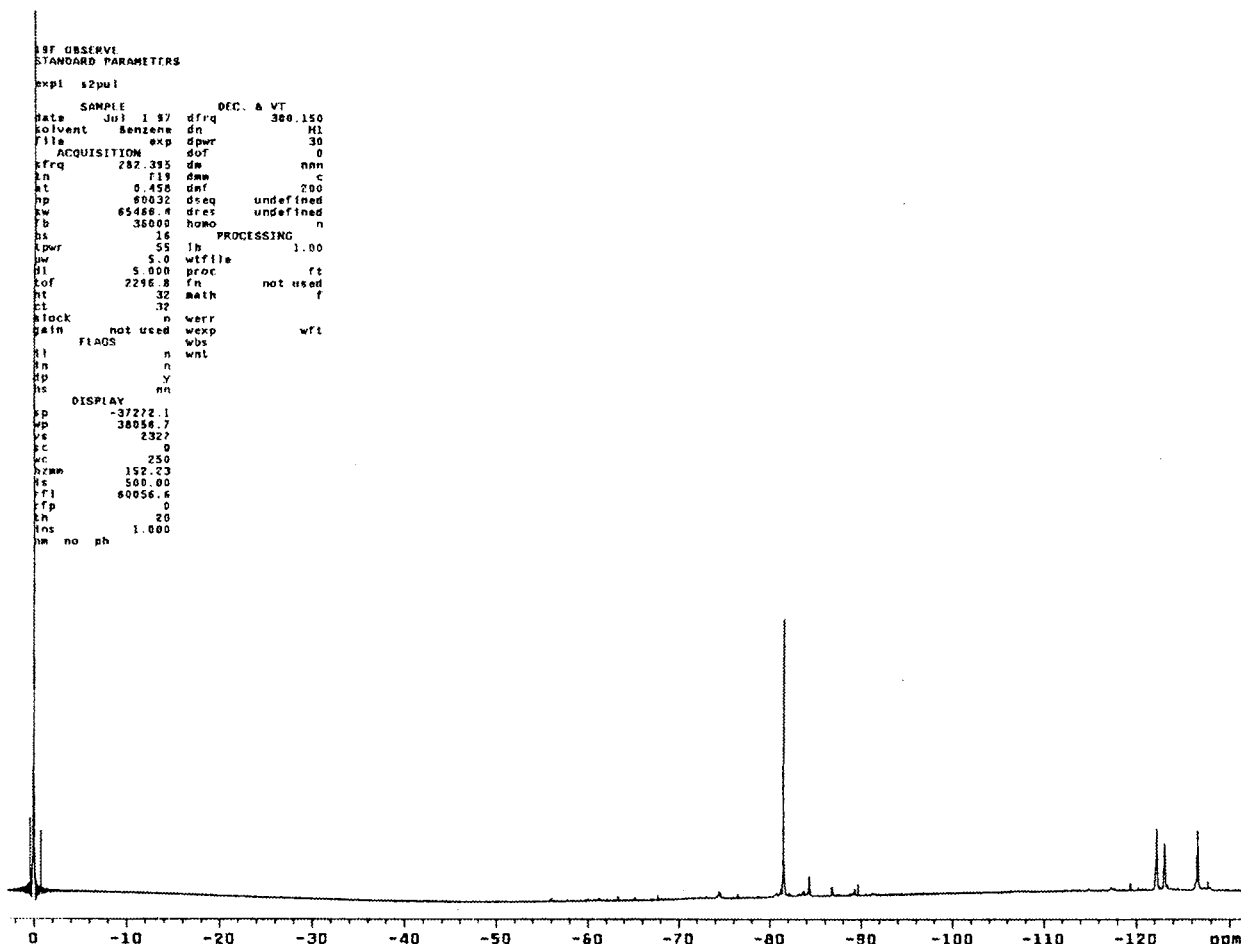
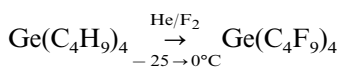


Fig. 2. ^{19}F -NMR spectrum of perfluoro-tetra-*n*-butylgermane.

4. Synthesis of perfluorotetra-*n*-butylgermane



Tetra-*n*-butylgermane (1.62 ml) was added to a round-bottom flask and diluted with 250 ml of 1,1,2-trichlorotrifluoroethane. This solution was then pumped (rate = 25 ml h⁻¹) into a stainless steel reactor that had been cooled to -25°C in an isopropyl alcohol bath and which contained 500 ml of 1,1,2-trichlorotrifluoroethane and 75 g of NaF.

During the addition of tetra-*n*-butylgermane to the stainless steel reactor, a mixture of helium and fluorine was bubbled through the reactor at a rate of 400/100 cc min⁻¹, respectively. After the tetra-*n*-butylgermane solution had been pumped into the reactor, the helium to fluorine flow rate was turned down to 10/10 cc min⁻¹, respectively. The reactor was kept at -25°C with a helium–fluorine flow rate of 10/10 cc min⁻¹ for 24 h. After 24 h the reactor was warmed to -10°C and kept at this temperature for another 24 h. The helium and fluorine flow rates were not changed at this time. After 24 h at -10°C the reactor was warmed to 0°C; again the helium and fluorine flow rates were not changed.

After 24 h at 0°C the fluorine was turned off, and the reactor was allowed to purge for 4 h. The solution in the reactor was then filtered to remove NaF and any NaHF₂ formed during the reaction. 1,1,2-Trichlorotrifluoroethane was removed by simple distillation. Perfluorotetra-*n*-butylgermane was then purified by vacuum distillation (b.p. = 73–75°C/1.7 mmHg) and was obtained in an isolated yield of 72%.

Chemical ionization mass spectral analysis (negative mode): *m/z* (formula, identification, intensity) 948 (C₁₆F₃₆Ge, (M)⁻, 2.18) relative to 730 (C₁₂F₂₇Ge, (M-C₄F₉)⁻, 100). Elemental compositions were studied by high-resolution mass spectroscopy in chemical ionization negative mode. Results were consistent with C₁₆F₃₆Ge (Anal. Calc.: 949.863; Found: 949.868). ^{19}F -NMR (CFCl₃) δ -81.51 (t, 12F), -122.38 (s, 8F), -123.20 (s, 8F), -126.70 (s, 8F) (Fig. 2).

4.1. High-resolution mass spectrometry of perfluoro-tetra-*n*-butylgermane

	Measured	Calculated
Ge(CF ₂ CF ₂ CF ₂ CF ₃) ₄ ⁻	949.868	949.863
Ge(CF ₂ CF ₂ CF ₂ CF ₃) ₃ ⁻	732.890	732.893

$\text{Ge}(\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3)_2^-$	512.899	512.900
$\text{Ge}(\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3)^-$	292.907	292.907

5. Results and discussion

The fluorination of organogermanium compounds using elemental fluorine has produced the perfluorinated analogues in surprising yields (greater than 70% in each case). The perfluorinated analogues of tetra-*n*-propyl and tetra-*n*-butylgermanes are semi-viscous liquids that boil at 45–66°C/1.7 mmHg and 73–75°C/1.7 mmHg, respectively and are stable in air.

We believe that the synthesis of these compounds will give us not only a general route to perfluorinated organogermanium compounds, but will also lead toward a general synthesis for perfluorocarbon analogues of many main group and transition metal alkyls.

Acknowledgements

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References

- [1] H.J. Emeléus, A.A. Banks, R.N. Haszeldine, V. Kerrigan, *J. Chem. Soc.* 2188 (1948).
- [2] H.J. Emeléus, R.N. Haszeldine, *J. Chem. Soc.* 2948 (1949).
- [3] G.R.A. Brandt, H.J. Emeléus, R.N. Haszeldine, *J. Chem. Soc.* 2552 (1952).
- [4] F.W. Bennett, H.J. Emeléus, R.N. Haszeldine, *J. Chem. Soc.* 1565 (1953).
- [5] J.W. Dale, H.J. Emeléus, R.N. Haszeldine, J.H. Moss, *J. Chem. Soc.* 3708 (1957).
- [6] D.J. Burton, J.G. MacNeil, *J. Fluor. Chem.* 55 (1991) 225.
- [7] D.J. Burton, Z. Yang, P.A. Morken, *Tetrahedron* 50 (1994) 2993.
- [8] D.J. Burton, H.K. Nair, *J. Fluor. Chem.* 56 (1992) 341.
- [9] D. Naumann, H. Butler, J. Fischer, J. Hanke, J. Mogais, B. Wilkes, *Z. Anorg. Chem.* 608 (1992) 69.
- [10] R.J. Lagow, T.J. Juhlke, R.W. Braun, T.R. Bierschenk, *J. Am. Chem. Soc.* 101 (1979) 3229.
- [11] R.J. Lagow, T.R. Bierschenk, T.J. Juhlke, *J. Am. Chem. Soc.* 103 (1981) 7340.
- [12] T.R. Bierschenk, T.J. Juhlke, H. Kawa, R.J. Lagow, US Patent No. 5 093 432, 1992.