

**Preservation of Metal–Carbon Bonds During Direct Fluorination;
a Practical Synthetic Method. The Synthesis of
Tetrakis(trifluoromethyl)germanium**

By E. K. LIU and R. J. LAGOW*

(Department of Chemistry, University of Texas at Austin, Austin Texas 78712)

Summary The metal–carbon bonds in tetramethylgermanium have been preserved during direct fluorination; tetrakis(trifluoromethyl)germanium has been produced from the controlled reaction of elemental fluorine with tetramethylgermanium.

RECENTLY we have reported the first cases of preservation of mercury–carbon and silicon–carbon bonds during direct

fluorination.¹ This synthetic method as applied to metal alkyls was regarded even in our laboratory as only a chemical curiosity. Recent results have shown that in some cases direct fluorination may be not only a practical synthetic method but one of choice for the preparation of perfluoro-alkyl organometallic compounds.

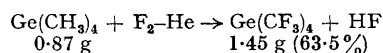
By controlling the fluorine concentration and temperature, we were able to obtain tetrakis(trifluoromethyl)germanium in 63.5% yield from the reaction of tetramethylgermanium

TABLE a

	¹ H ^b				¹⁹ F ^c							
	CH ₂ F	J _{HF}	CHF ₂	J _{HF}	CF ₃	J _{FF} ^d	CF ₂ H	J _{HF}	J _{FF}	CFH ₂	J _{HF}	J _{FF}
Ge(CF ₃) ₄	—	—	—	—	-27.0	—	—	—	—	—	—	—
Ge(CF ₃) ₃ (CF ₂ H)	—	—	6.10	45.0	-27.2	3.0	49.0	45.5	3.1	—	—	—
Ge(CF ₃) ₂ (CF ₂ H) ₂	—	—	6.23	45.5	-27.6	3.2	49.4	46.0	3.1	—	—	—
Ge(CF ₃) ₂ (CF ₂ H)(CFH ₂)	4.98	46.5	6.24	45.7	-26.3	3.3	50.6	45.5	3.0	193.2	46.5	3.3
Ge(CF ₃)(CF ₂ H) ₃	6.25	—	6.25	45.5	-27.9	3.2	49.7	46.0	3.1	—	—	—
Ge(CF ₃)(CF ₂ H) ₂ (CFH ₂)	4.89	46.0	6.15	45.5	-26.75	3.2	50.5	45.6	3.0	193.0	46.0	2.9
Ge(CF ₃)(CF ₂ H)(CFH ₂) ₂	4.90	46.0	6.25	45.6	-25.22	3.2	51.8	45.5	3.0	192.0	46.0	2.7
Ge(CF ₂ H) ₂ (CFH ₂) ₂	4.97	46.0	6.26	45.2	—	—	51.4	46.0	2.5	192.5	46.6	2.5

^a All spectra were recorded for neat liquids. Shifts are in p.p.m., coupling constants in Hz. ^b + ve shifts downfield from external Me₄Si. ^c + ve shifts upfield from CF₃CO₂H. ^d The appropriate fluorine-fluorine coupling pattern was present with *n* fluorine giving an *n* + 1 coupled pattern.

and fluorine [reaction (1)]. The experimental apparatus



used has been discussed previously.² The physical and spectral properties of Ge(CF₃)₄ are identical with those of the same compound first prepared in 1975 in our laboratory using plasma techniques.³ The best fluorination conditions are as follows: fluorine flow rate 1 cm³ min⁻¹; helium flow rate 60 cm³ min⁻¹; starting temperature -100 °C maintained for 48 h; the temperature was then increased in 10 °C steps and maintained at the following temperatures for the following times: -90 °C, 12 h; -80, 14; -70, 8; -60, 14; -50, 10; -40, 12; -30, 10; -20, 14. The reaction is remarkably temperature dependent owing to the extremely low reactivity of the partially fluorinated tetramethylgermanium compounds. If the reaction is conducted with a fluorine flow of 1 cm³ min⁻¹ and a helium flow of 60 cm³ min⁻¹ at -100 °C for 150 h, the yield of Ge(CF₃)₄ is only 1.1%. However, with a fluorine flow of 1 cm³ min⁻¹ and a helium flow of 60 cm³ min⁻¹ at -100 °C for 2 days and a temperature increase of 10 °C per day to -60 °C, the yield of Ge(CF₃)₄ increases to 6%.

When the yield of Ge(CF₃)₄ is low, one obtains a number of partially fluorinated tetramethylgermanium compounds. Most of the compounds contain CF₃ groups, but all contain the four germanium-carbon bonds intact. Several of the compounds along with their n.m.r. data are listed in the Table. Mass spectra and n.m.r. data including proton-fluorine coupling and long-range fluorine-fluorine coupling, along with the appropriate integration are sufficient for identification of the compounds. For example, the compound Ge(CF₃)₂(CF₂H)₂ gives the following n.m.r. data: ¹H: CF₂H, triplet, J_{HF} 45.5 Hz; ¹⁹F: CF₃, quintet, J_{FF} 3.2 Hz resulting from coupling of two CF₂H groups; CF₂H, doublet, J_{HF} 46.0 Hz, with each component of the doublet being a septet, J_{FF} 3.1 Hz resulting from fluorine coupling of two CF₃ groups. The compounds were separated on 10% SE-30 on a Chromsorb P column.

We are grateful for support from the Office of Naval Research for this work.

(Received, 10th February 1977; Com. 119.)

¹ E. Liu and R. J. Lagow, *J. Amer. Chem. Soc.*, 1976, **98**, 8270.

² N. J. Maraschin, B. D. Catsikis, L. H. Davis, G. Jarvinen, and R. J. Lagow, *J. Amer. Chem. Soc.*, 1975, **97**, 513.

³ R. J. Lagow, L. Gerchman, R. Jacob, and J. Morrison, *J. Amer. Chem. Soc.*, 1975, **97**, 518.