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

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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 perfluoroalkyl 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_2F	J_{HF}	CHF_2	J_{HF}	CF_3	J_{FF}[d]	CF_2H	J_{HF}	J_{FF}	CFH_2	J_{HF}	J_{FF}
$Ge(CF_3)_4$	—	—	—	—	−27·0	—	—	—	—	—	—	—
$Ge(CF_3)_3(CF_2H)$	—	—	6·10	45·0	−27·2	3·0	49·0	45·5	3·1	—	—	—
$Ge(CF_3)_2(CF_2H)_2$	—	—	6·23	45·5	−27·6	3·2	49·4	46·0	3·1	—	—	—
$Ge(CF_3)_2(CF_2H)(CFH_2)$	4·98	46·5	6·24	45·7	−26·3	3·3	50·6	45·5	3·0	193·2	46·5	3·3
$Ge(CF_3)(CF_2H)_3$	6·25	—	6·25	45·5	−27·9	3·2	49·7	46·0	3·1	—	—	—
$Ge(CF_3)(CF_2H)_2(CFH_2)$	4·89	46·0	6·15	45·5	−26·75	3·2	50·5	45·6	3·0	193·0	46·0	2·9
$Ge(CF_3)(CF_2H)(CFH_2)_2$	4·90	46·0	6·25	45·6	−25·22	3·2	51·8	45·5	3·0	192·0	46·0	2·7
$Ge(CF_2H)_2(CFH_2)_2$	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 Me_4Si. [c] + ve shifts upfield from CF_3CO_2H. [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

$$\begin{array}{c} Ge(CH_3)_4 + F_2\text{–}He \rightarrow Ge(CF_3)_4 + HF \\ 0{\cdot}87\text{ g} \qquad\qquad\qquad 1{\cdot}45\text{ g }(63{\cdot}5\%) \end{array}$$

used has been discussed previously.[2] The physical and spectral properties of $Ge(CF_3)_4$ 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 cm^3 min^{-1}; helium flow rate 60 cm^3 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 cm^3 min^{-1} and a helium flow of 60 cm^3 min^{-1} at −100 °C for 150 h, the yield of $Ge(CF_3)_4$ is only 1·1%. However, with a fluorine flow of 1 cm^3 min^{-1} and a helium flow of 60 cm^3 min^{-1} at −100 °C for 2 days and a temperature increase of 10 °C per day to −60 °C, the yield of $Ge(CF_3)_4$ increases to 6%.

When the yield of $Ge(CF_3)_4$ is low, one obtains a number of partially fluorinated tetramethylgermanium compounds. Most of the compounds contain CF_3 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 $Ge(CF_3)_2(CF_2H)_2$ gives the following n.m.r. data: ^{1}H: CF_2H, triplet, J_{HF} 45·5 Hz; ^{19}F: CF_3, quintet, J_{FF} 3·2 Hz resulting from coupling of two CF_2H groups; CF_2H, 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 CF_3 groups. The compounds were separated on 10% SE-30 on a Chromsorb P column.

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