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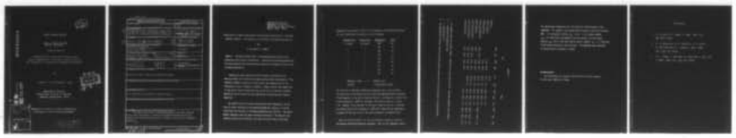

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PRESERVATION OF METAL-CARBON BONDS DURING DIRECT FLUORINATION, A PRACTICAL SYNTHETIC METHOD. THE SYNTHESIS OF TETRAKIS(TRIFLUOROMETHYL)GERMANIUM.

by

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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.

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Contribution from the
Department of Chemistry
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Preservation of Metal-Carbon Bonds During Direct Fluorination, a Practical Synthetic Method. The Synthesis of Tetrakis(trifluoromethyl)germanium.

by

E. Liu and R. J. Lagow*

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 organometallics.

By controlling the fluorine concentration and temperature, we are able to obtain tetrakis(trifluoromethyl)germanium, $Ge(CF_3)_4$, in 63.5% yield from the reaction of tetramethylgermanium and fluorine. The experimental apparatus 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 the following:

Fluorine Flow	Helium Flow	Temperature	Hours
1 cc/min	60 cc/min	-100^{0}	48
"	"	-90	12
"	"	-80	14
"	"	-70	8
"	"	-60	14
"	"	-50	10
"	"	-40	12
"	"	-30	10
"	"	-20	14

$$\underset{0.87\ \text{gm}}{Ge(CH_3)_4} + F_2/He \longrightarrow \underset{1.45\ \text{gm (63.5\% yield)}}{Ge(CF_3)_4} + HF$$

The reaction is remarkably temperature dependent due to the extremely low reactivity of the partially fluorinated tetramethylgermanium compounds. If the reaction is run with a fluorine flow of 1 cc/minute to a helium flow of 60 cc/minute at $-100^{0}C$ for 150 hours, the yield of $Ge(CF_3)_4$ is only 1.1%. However if the reaction is run with a fluorine flow of 1 cc/minute to a helium flow of 60 cc/minute at $-100^{0}C$ for 2 days and the temperature increased 10^{0} per day to -60^{0}, 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

Table 1[a]

	^1H[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 samples were run as neat liquids. Shifts are in parts per million. Coupling constants are in hertz.

[b] + dounfield from external TMS

[c] + upfield from TFA

[d] The appropriate fluorine-fluorine coupling pattern present with n fluorine giving n+1 coupled pattern.

the appropriate integration are sufficient for identification of the compounds. For example, the compound $Ge(CF_3)_2(CF_2H)_2$ gives the following NMR: H: CF_2H group; triplet, $J_{HF} = 45.5$; F: CF_3 group, pentet, $J_{FF} = 3.2$ resulting from coupling of two CF_2H groups, and CF_2H group, doublet, $J_{HF} = 46.0$, with each doublet being a septet, $J_{FF} = 3.1$ resulting from fluorine coupling of two CF_3groups. The compounds were separated on 10% SE-30 on a chromsorb P columns.

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