Kinetic Measurements. Rate data were obtained spectrophotometrically by measuring changes of absorbance with time. The complex was dissolved directly in a thermostated cell containing DMSO and the change of absorbance monitored as a function of time. First-order rate constants were calculated from plots of $\ln (A_\infty - A_t)$ against time, where A_t and A_∞ are absorbances at time t and after at least 6 half-lives, respectively. These plots were linear for at least 4 half-lives. The least-squares method was used to fit the experimental data (Table III). A temperature-dependence study was performed in the case of 7. The rate of solvolysis was measured at 30 (Table III), 25 [1.11 (3) $\times 10^{-4}$ and 5.0 (4) $\times 10^{-5}$ s^{-1} for the cis and trans isomers, respectively], and 50 °C [9.5 (3) $\times 10^{-4}$ and 5.8 (4) $\times 10^{-4}$ s^{-1} for the cis and trans isomers, respectively]. The enthalpy and entropy of activation were evaluated from an Eyring plot of $\ln k_{\text{obs.}}$ against $1/T$ [$\Delta H^* = 67$ (3) and 79 (4) kJ mol^{-1} and $\Delta S^* = -96$ (4) and -63 (5) J K^{-1} mol^{-1} for the cis and trans isomers, respectively].

Physical Measurements. IR spectra in the range 4000–400 cm^{-1} were recorded as KBr pellets; spectra in the range 400–200 cm^{-1} were recorded as polythene pellets on Perkin-Elmer 283 and FT1600 spectrophotometers. ^{1}H NMR spectra were obtained with Varian XL 200 and VXR 300 spectrometers. ^{1}H-decoupled ^{195}Pt NMR spectra were recorded on the VXR 300 instrument operating at 64.332 MHz and using a sweep width of 100 kHz, a pulse width of 20 μs, and an acquisition time of 0.096 s; the chemical shift values, referred to $Na_2[PtCl_6]$ used as external standard, are uncorrected for the solvent. UV–vis spectra were recorded on a Varian 2002 double-beam spectrophotometer.

Calculation of ΔG^*. The free energy of activation was calculated by using the expression $\Delta G^*_{T_c} = -RT \ln [\pi(\Delta\nu)h/2^{1/2}kT]$, where $\Delta\nu$ represents the chemical shift difference ($\Delta\delta$ in Hz) of the coalescing peaks in the absence of exchange, T represents the coalescence temperature, and R, k, and h have their normal thermodynamic significances.[22]

Acknowledgment. This work has been supported by the Consiglio Nazionale delle Ricerche and Ministero della Pubblica Istruzione, Rome.

Registry No. 1, 14096-51-6; 2, 33727-98-9; 3, 92283-43-7; *cis*-4, 61848-70-2; *trans*-4, 38780-40-4; 5, 16786-98-4; 6, 123807-65-8; 7, 103601-36-1; 8, 123751-05-3; DMSO, 67-68-5; Pt, 7440-06-4.

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(21) The ^{1}H NMR spectrum taken soon after dissolution of the crystalline compound in D_2O showed only one set of signals; when the solution was left standing for 1 h at room temperature, a new, less intense, set of signals appeared. This indicates that in the crystalline solid the ligand has only one configuration and this is probably trans (only one N–H stretching mode was observed in the IR at 3220 cm^{-1}).

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Contribution from the Department of Chemistry,
University of Illinois at Chicago, Chicago, Illinois 60680

Examination of the Reactivity of Bis(trifluoromethyl)tellurium: Oxidative Trifluoromethylations and Ligand Exchanges with Group 5A and 6A (15 and 16) Elements and Their Halides

E. A. Ganja and J. A. Morrison*

Received May 24, 1989

Bis(trifluoromethyl)tellurium reacts with I_2, S_8, Se, P_4, and As at 220 °C to afford CF_3I, $(CF_3)_2S$, $(CF_3)_2Se$, $(CF_3)_3P$, and $(CF_3)_3As$, which are separated in 97, 92, 92, 70, and 46% yields, respectively. The interaction of $(CF_3)_2Te$ with Sb at 170 °C results in very small amounts of $(CF_3)_3Sb$, ca. 3%, but no (trifluoromethyl)germanes were observed when $(CF_3)_2Te$ was exposed to Ge at 170 °C. At 170 °C the reactions of $(CF_3)_2Te$ with $SeBr_4$, PI_3, and AsI_3 generate $(CF_3)_2Se$, $(CF_3)_3P$, and $(CF_3)_3As$, which can be isolated in 98, 65, and 88% yields, respectively. The reaction of SCl_2 with $(CF_3)_2Te$ at 170 °C, however, is less productive, presumably because there are several alternative pathways that are competitive with the reaction channel that leads to $(CF_3)_2S$. At 170 °C SbI_3 and $(CF_3)_2Te$ form trace amounts (ca. 0.2%) of $(CF_3)_3Sb$, but in the temperature range 120–170 °C, the reaction of GeI_4 with $(CF_3)_2Te$ gave no evidence for the formation of (trifluoromethyl)germanes.

Introduction

For 40 years trifluoromethyl iodide has been by far the most widely utilized reagent in the field of perfluoroalkyl organometallic chemistry. The synthesis and reactivity of this compound were initially examined by Emeleus and his students, who found that CF_3I oxidatively trifluoromethylated elemental P, As, Sb, S, Se, and amalgamated Hg.[1-6] Subsequently, CF_3I was demonstrated to be reactive in ligand exchange reactions with, e.g., the trimethyl derivatives of the main group 5 elements, generating, for example, $CF_3P(CH_3)_2$[7] and $CF_3Bi(CH_3)_2$.[8]

Others, most notably Stone, investigated the reactions between CF_3I and low-valent transition-metal complexes. They found that while CF_3I is not as strong an oxidizing agent as elemental iodine, many trifluoromethyl derivatives, like $CF_3Fe(CO)_4I$ or $CF_3Ni(PPh_3)_2I$, could be formed by the oxidation of appropriate substrates with trifluoromethyl iodide.[9] Ligand interchanges between the iodine center and transition-metal species, for example, platinum(II) dimethyl complexes,[10] have also been demonstrated.[11]

Trifluoromethyl iodide has also been employed as a reagent in organic chemistry but to a much more modest extent. Here, the majority of the reported reactions have been designed to result in the addition of CF_3 and iodine across alkene or alkyne bonds. Typically, the reaction conditions that were employed have been

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Table I. Monoisotopic Mass Spectral Data for Mononuclear Group 5A and 6A (15 and 16) Bis- and Tris(trifluoromethyl) Products from $(CF_3)_2Te$ Reactions[a,b]

$^{130}Te(CF_3)_2$			$^{80}Se(CF_3)_2$			$^{32}S(CF_3)_2$		
mass	ion	abund, %	mass	ion	abund, %	mass	ion	abund, %
268	$Te(CF_3)_2$	97	218	$Se(CF_3)_2$	75	170	$S(CF_3)_2$	100
249	$Te(CF_3)CF_2$	15	199	$Se(CF_3)CF_2$	10	151	$S(CF_3)CF_2$	7
199	$TeCF_3$	100	149	$SeCF_3$	20	101	SCF_3	4
180	$TeCF_2$	47	130	$SeCF_2$	42	82	SCF_2	15
161	TeCF	9	111	SeCF	25	69	CF_3	85
149	TeF	21	99	SeF	3	63	SCF	12
130	Te	86	80	Se	27	50	CF_2	4
69	CF_3	34	69	CF_3	100			
50	CF_2	3	50	CF_2	6			

$^{121}Sb(CF_3)_3$			$^{75}As(CF_3)_3$			$^{31}P(CF_3)_3$		
mass	ion	abund, %	mass	ion	abund, %	mass	ion	abund, %
328	$Sb(CF_3)_3$	6	282	$As(CF_3)_3$	5	238	$P(CF_3)_3$	2
309	$Sb(CF_3)_2CF_2$	1	263	$As(CF_3)_2CF_2$	17	219	$P(CF_3)_2CF_2$	7
259	$Sb(CF_3)_2$	20	213	$As(CF_3)_2$	1	169	$P(CF_3)_2$	1
240	$Sb(CF_3)CF_2$	3	194	$As(CF_3)CF_2$	33	150	$P(CF_3)CF_2$	4
209	$Sb(CF_3)F$	47	175	$As(CF_3)CF$	15	131	$P(CF_3)CF$	19
190	$SbCF_3$	20	163	$As(CF_3)F$	47	119	$P(CF_3)F$	6
171	$SbCF_2$	6	144	$AsCF_3$	31	100	PCF_3/C_2F_4	12
159	SbF_2	51	131	C_3F_5	13	88	PF_3	2
152	SbCF	2	125	$AsCF_2$	20	81	PCF_2/C_2F_3	9
140	SbF	50	119	C_2F_5	18	69	CF_3/PF_2	100
121	Sb	83	113	AsF_2	54	62	PCF	4
69	CF_3	100	106	AsCF	5	50	CF_2/PF	16
50	CF_2	13	94	AsF	34			
			87	AsC	2			
			75	As	29			
			69	CF_3	100			
			50	CF_2	19			

[a] 70-eV mass spectra obtained from a Hewlett Packard 5985A (quadrupole) mass spectrometer with the source at 200 °C. [b] Natural abundances: ^{130}Te, 34.5%; ^{80}Se, 49.8%; ^{32}S, 95.0%; ^{121}Sb, 57.3%; ^{75}As, 100.0%; ^{31}P, 100.0%. The experimental abundances of each ion containing one of these isotopes were divided by the appropriate percentage.

conducive to the formation of radical species, although occasionally conditions that enhance more polar reaction mechanisms have been selected.[12]

In view of the notable successes that have been achieved with CF_3I, it is somewhat surprising that the chemistry of the trifluoromethyl derivatives of the element adjacent to iodine in the periodic table, tellurium, has never been subjected to a systematic evaluation. The potential reagent $(CF_3)_2Te$ was initially synthesized from the reactions between $TeBr_4$ and CF_3 radicals, and the oxidation of $(CF_3)_2Te$ with Cl_2 and Br_2 to form (trifluoromethyl)tellurium(IV) derivatives was also reported at that time.[13] More recently, other preparations of $(CF_3)_2Te$ have been described[14-16] and a few trifluoromethylation reactions of $(CF_3)_2Te$, largely those with hydrocarbons, have been discussed,[14,17] but, overall, the chemistry of $(CF_3)_2Te$ remains almost completely unexplored.

The objective of the present study was to initiate an examination into the chemistry of $(CF_3)_2Te$ in order to begin to detail the instances in which this potential reagent is superior to the classic trifluoromethyl synthon CF_3I and those in which it is less effective. Further, it was of interest to compare the reactivity of $(CF_3)_2Te$ with that recently demonstrated for $Hg(CF_3)_2$.[16] The substrates employed here were drawn from the types of compounds with which the reactivity of CF_3I was first demonstrated, thus two classes of $(CF_3)_2Te$ reactions: oxidative trifluoromethylations and ligand exchanges with representative late main group elements and their halides have been assessed.

Table II. Fluorine NMR Data for Trifluoromethylated Main Group 5A–7A Products from $(CF_3)_2Te$ Reactions[a,b]

Mononuclear Species

group 7A (17)[c]	$\delta(^{19}F)$	group 6A (16)[d]	$\delta(^{19}F)$	group 5A (15)[e]	$\delta(^{19}F)$
CF_3I	70.7	$(CF_3)_2Te$	54.4	$(CF_3)_3Sb$	36.1
CF_3Br	57.2	$(CF_3)_2Se$	43.5	$(CF_3)_3As$	28.9
CF_3Cl	47.1	$(CF_3)_2S$	36.8	$(CF_3)_3P$	24.6

Polynuclear Group 6A (16) Species

CF_3 bonded to Te	$\delta(^{19}F)$	CF_3 bonded to Se	$\delta(^{19}F)$	CF_3 bonded to S	$\delta(^{19}F)$
$(CF_3)_2Te_2$	49.2	$(CF_3)_2Se_2$	37.2	$(CF_3)_2S_2$	28.6
$CF_3SeTeCF_3$	46.6	$CF_3SeTeCF_3$	40.5	$(CF_3)_2S_3$	29.2
CF_3STeCF_3	45.8			$(CF_3)_2S_4$	30.1
				CF_3STeCF_3	35.5

[a] Chemical shifts relative to external TFA; positive values deshielded. All chemical shifts are reasonably in accord with literature values.[16] [b] Supplementary ^{13}C, ^{31}P, ^{77}Se, and ^{125}Te NMR data are contained in ref 16. [c] Additional group 7A compounds: CF_2Br_2, $\delta = 82.3$ ppm; CF_2Cl_2, $\delta = 68.5$ ppm; $CFCl_3$, $\delta = 75.6$ ppm. [d] Additional group 6A compounds: CF_3SeBr, $\delta = 35.7$ ppm; CF_3SCl, $\delta = 25.4$ ppm. [e] Additional group 5A compounds: $(CF_3)_2PI$, $\delta = 20.0$ ppm, $J_{P-F} = 76$ Hz; CF_3PI_2, $\delta = 16.2$ ppm, $J_{P-F} = 48$ Hz; $(CF_3)_2AsI$, $\delta = 24.4$ ppm; CF_3AsI_2, $\delta = 21.2$ ppm.

Experimental Section

All of the synthetic manipulations were carried out either under an inert atmosphere (glovebag or glovebox) or upon a standard vacuum line. The low-temperature distillation column employed during some of the separations described below is of the conventional (Dobson) design. Confirming mass spectral data (Table I) were obtained from an HP 5985A (quadrupole) spectrometer. The ^{19}F NMR spectra (Table II) are from either an IBM 200SY or a Bruker AM-400 instrument. Positive chemical shifts are deshielded relative to the external standard CF_3CO_2H.

Phosphorus triiodide and SbI_3 were prepared by the reaction of the elements with I_2 in CH_2Cl_2; AsI_3 was formed from As_2O_3 and KI in concentrated HCl. All were sublimed prior to use as was GeI_4 (Alfa). Sulfur dichloride (Aldrich) was fractionated to remove Cl_2 and catenated sulfur chlorides. Selenium tetrabromide and $TeBr_4$ (Strem) were used

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as obtained. White phosphorus (ROC/RIC), 325-mesh As (Alfa), 100-mesh Sb (Alfa), 100-mesh S_8 (Fisher), 100-mesh Se (Aldrich), and 325-mesh Ge (Alfa) were also used as received. Bis(trifluoromethyl)tellurium[16] was generated from the reaction of $TeBr_4$ with $(CF_3)_2Hg$[18] at 155 °C and then purified by fractionation or by low-temperature distillation.

As discussed below, many of the reactions between $(CF_3)_2Te$ and the substrates employed during this study appeared to come to an effective equilibrium. In order to follow these interactions more efficiently, they were carried out in sealed Pyrex tubing, 4 mm in diameter by ca. 225 mm in length. The reactors were constructed from 4-mm vacuum valves with a length of 4-mm tubing fused to one arm and an 18/9 ball joint to the other. Where possible, both reagents were sequentially condensed into the reactors, which were then sealed with a hand torch. If this procedure could not be followed, the Teflon plug was removed from the valve and, under inert atmosphere, the nonvolatile reagent was inserted directly into the 4-mm tubing. After reinsertion of the plug and closure of the valve, these vessels were conveyed to the vacuum line, cooled to −196 °C, and evacuated through the 18/9 ball joint. After condensation of the desired amount of $(CF_3)_2Te$ into the vessels, they too were sealed and then heated to the temperatures indicated with a conventional oil bath containing dimethylsilicone. The progress of each reaction was monitored by ^{19}F NMR spectroscopy. At the conclusion of the experiments the vessels were opened and their contents were separated and analyzed.

Oxidative Trifluoromethylations with Bis(trifluoromethyl)tellurium. Formation of Trifluoromethyl Iodide. Iodine, 0.1426 g (0.562 mmol), and $(CF_3)_2Te$, 0.1491 g (0.561 mmol), were sealed into a reactor as described above and heated to 220 °C for a total of 10 h. After 4 h at 220 °C, fluorine NMR spectroscopy indicated that the approximate molar ratio between CF_3I and $(CF_3)_2Te$ was 4.5:1.0. After 6 more hours at 220 °C the vessel was opened and the products were separated. Colorless CF_3I, 0.2129 g (1.087 mmol), which passes through a trap held at −131 °C but is retained at −160 °C, was formed in 97% yield. The residual, yellow $(CF_3)_2Te$, 0.0042 g (0.016 mmol), which passes through at −95 °C but is held at −116 °C, corresponded to 3% of that originally employed. Chemical shift data are contained in Table II.

In a separate experiment, equimolar amounts of I_2 and $(CF_3)_2Te$ were sealed together and maintained at ambient temperature over a period of 17 days. At the conclusion of the experiment CF_3I and $(CF_3)_2Te$ were observed by ^{19}F NMR spectroscopy in the approximate molar ratio 11.5:1.0. At no time during this reaction was a resonance in the 0–45 ppm chemical shift region observed.

Formation of Bis(trifluoromethyl)sulfur. Sulfur, 0.0204 g (0.64 mmol), and $(CF_3)_2Te$, 0.1665 g (0.627 mmol), were allowed to react for a total of 19 h at 220 °C. After 4 h, the relative intensities of the resonances due to $(CF_3)_2Te$, $(CF_3)_2S$, and $(CF_3)_2S_2$ (see Table II) were 1.0:1.4:1.2. As time progressed, the relative intensities of the resonances arising from the first and the last of these compounds decreased while that of $(CF_3)_2S$ continuously increased. After 9 h, for example, the relative intensities were 1.0:8.3:1.5. After 19 h, the reactor was opened and the contents were separated. The clear liquid passing through a −131 °C trap, 0.0977 g (0.574 mmol), was identified as $(CF_3)_2S$, obtained in 92% yield. The disulfide, $(CF_3)_2S_2$, 0.0018 g (0.009 mmol), which is retained at −95 °C, was separated in 1% yield. Ca. 8% of the $(CF_3)_2Te$, 0.0144 g (0.054 mmol), was recovered unchanged.

In a separate experiment, similar amounts of S_8 and $(CF_3)_2Te$ were heated to 170 °C and the reaction was followed by ^{19}F NMR spectroscopy. After 21 h, in addition to the anticipated resonances in the deshielded region of the spectrum (see Table II) there were not less than four different resonances near 29 ppm, the chemical shift region of the (trifluoromethyl)polysulfides, $(CF_3)_2S_x$.[19] All of these resonances were more intense than that of $(CF_3)_2S$, but none were present in concentrations corresponding to as much as 10% of the remaining $(CF_3)_2Te$. After 74 h at 170 °C, the relative amounts of $(CF_3)_2S_3$ (0.53) and $(CF_3)_2S_4$ (0.09) indicated by fluorine NMR were less than that of $(CF_3)_2S$ (1.00), but that of $(CF_3)_2S_2$ (1.45) was not. In addition, two other resonances, at 45.8 and 35.5 ppm, were present in this spectrum in moderate intensity (0.09 each); see Figure 1.

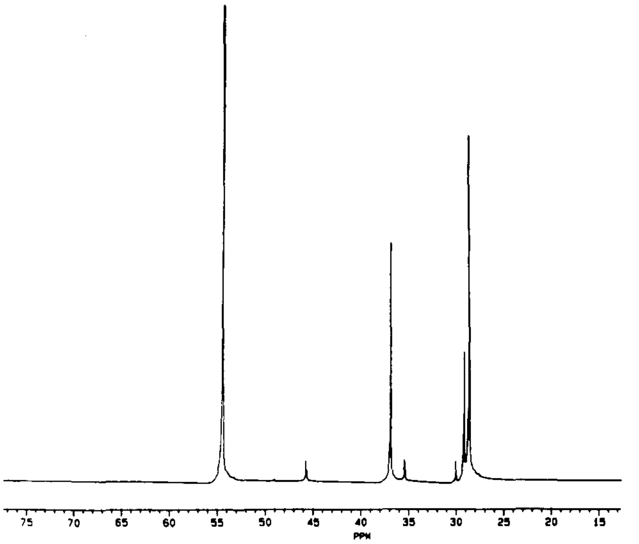

Figure 1. ^{19}F NMR spectrum of the reaction between S_8 and $(CF_3)_2Te$ after 74 h at 170 °C, demonstrating the variety of intermediate products that are formed during this oxidative trifluoromethylation. From left to right, the major resonances arise from $(CF_3)_2Te$ (54 ppm), CF_3TeSCF_3 (46 and 36 ppm), $(CF_3)_2S$ (37 ppm), $(CF_3)_2S_4$ (30 ppm), $(CF_3)_2S_3$ (29 ppm), and $(CF_3)_2S_2$ (28.6 ppm). After 19 h at 220 °C, however, only $(CF_3)_2S$ (92%), $(CF_3)_2Te$ (ca. 8%), and $(CF_3)_2S_2$ (1%) are observed.

Table III. Products from the Oxidative Trifluoromethylation Reactions of $(CF_3)_2Te$ and Comparisons to CF_3I Reactions

reagent	product	conditions: temp, °C/ time, h	$Te(CF_3)_2$ conversion,[a] %	$Te(CF_3)_2$ yield,[b] %	CF_3I yield,[b] %
I_2	CF_3I	220/10	100	97	
S_8	$(CF_3)_2S$	220/19	99	92	0[5]
Se	$(CF_3)_2Se$	220/15	96[c]	92	48[6]
P_4	$(CF_3)_3P$	220/40	87	70	35[2]
As	$(CF_3)_3As$	220/50	81	46	70[3]
Sb	$(CF_3)_3Sb$	170/30		~3[c]	64[4]
Ge	$(CF_3)_4Ge$	170/168		0[c]	*d*

[a] Isolated yields based upon the amounts of $(CF_3)_2Te$ consumed. [b] Isolated yields based upon the amounts of limiting reagent employed. [c] Estimated by fluorine NMR spectroscopy. [d] Reaction not reported.

Formation of Bis(trifluoromethyl)selenium. Elemental Se, 0.0882 g (1.12 mmol), and $(CF_3)_2Te$, 0.2909 g (0.1095 mmol), were sealed together, and the temperature of the reactor was raised to 220 °C. After 2 h at 220 °C, the ratio of the intensities of the resonances arising from $(CF_3)_2Te$ and $(CF_3)_2Se$ in the fluorine spectrum was 1.0:1.2; this spectrum also contained a very small resonance at 37.0 ppm, which corresponds to the chemical shift of $(CF_3)_2Se_2$,[16] two small resonances at 46.6 and 40.5 ppm, and the resonance of $(CF_3)_2Te_2$, 49.2 ppm. After 15 h at 220 °C the smaller resonances were no longer observed and those of $Te(CF_3)_2$ and $(CF_3)_2Se$ were then present in the ratio of 3.6:96.4. The reactor was opened, and $(CF_3)_2Se$, 0.2180 g (1.005 mmol), was identified by NMR spectroscopy and mass spectrometry; see Tables I and II. This colorless compound, which passes through a −116 °C trap but is retained at −131 °C, was isolated in 92% yield; see Table III.

In a separate reaction Se, 0.0510 g (0.65 mmol), and $(CF_3)_2Te$, 0.1898 g (0.715 mmol), were allowed to react at 240 °C for 5 h. Separation then yielded $(CF_3)_2Se$, 0.1165 g (0.537 mmol), 83% based upon the amount of Se originally taken.

Formation of Tris(trifluoromethyl)phosphine. Similarly, a mixture of white phosphorus, 0.0280 g (0.226 mmol), and $(CF_3)_2Te$, 0.3083 g (1.161 mmol), was held at 220 °C. After 20 min the solution had become a red, very viscous oil, but during the next 1 h it transformed into a mobile yellow solution with the precipitation of a grey metallic solid. During the 40-h reaction, the new resonances observed by fluorine NMR spectroscopy were due to very small amounts $(CF_3)_2Te_2$ along with the doublet from $(CF_3)_3P$. At the conclusion of the reaction, the vessel was opened and the contents were separated by low-temperature distillation. The first material came off the column at a head temperature of −102 °C. It was later identified as $(CF_3)_3P$, 0.1284 g (0.540 mmol), 70% based upon the amount of $(CF_3)_2Te$ employed. The second compound from the column was unreacted $(CF_3)_2Te$, 0.0600 g (0.226 mmol); thus, the conversion of $(CF_3)_2Te$ to $(CF_3)_3P$ was 87% based upon $(CF_3)_2Te$ consumed.

Formation of Tris(trifluoromethyl)arsine. Arsenic, 0.0646 g (0.86 mmol), was allowed to react with 0.3344 g (1.259 mmol) of $(CF_3)_2Te$ for 50 h at 220 °C; see Figure 2. After the small amount of SiF_4, ca. 2%, that formed was removed by passage through a −131 °C trap, the products were separated upon a low-temperature column. Unreacted $(CF_3)_2Te$, 0.1428 g (0.538 mmol), preceded $(CF_3)_3As$ from the column,

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Table IV. Relative Molar Ratios of SCl_2 Reaction Components

time, h	$(CF_3)_2Te$	$(CF_3)_2Te_2$	CF_3Cl	CF_2Cl_2	CF_3TeSCF_3[a]	$(CF_3)_2S_4$	$(CF_3)_2S_3$	$(CF_3)_2S_2$	$(CF_3)_2S$
1	65.6	0.5	9.9		3.6	0.9	6.7	9.2	3.6
2	47.1	0.6	19.3	2.8	3.3	0.4	4.4	17.4	4.7
14	25.9		17.1	20.8				23.0	13.2
100	9.9		41.9	30.7				1.5	16.0

[a] Postulated product.

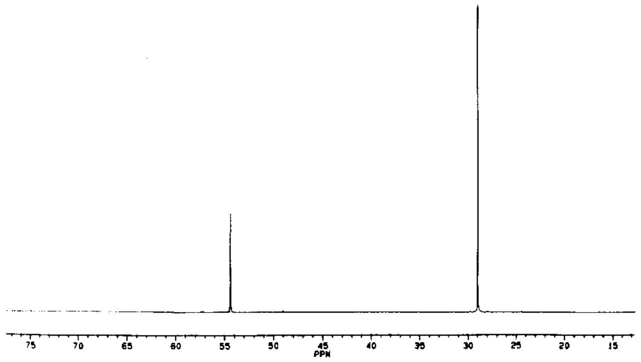

Figure 2. ^{19}F NMR spectrum of the reaction between As and $(CF_3)_2Te$ after 50 h at 220 °C. Throughout this more typical oxidation essentially only $(CF_3)_2Te$ (54 ppm) and $(CF_3)_3As$ (29 ppm) are observed.

Table V. Products from the Ligand-Exchange Reactions of Main Group Halides with $(CF_3)_2Te$ and Comparisons to $(CF_3)_2Hg$ Reactions

reagent	product	conditions: temp, °C/ time, h	yield,[a] %	$(CF_3)_2Hg + MX_n$ yields, %
SCl_2	$(CF_3)_2S$	170/100	16[b]	c
$SeBr_4$	$(CF_3)_2Se$	170/15	98	67[16]
PI_3	$(CF_3)_3P$	170/14	65	55[16]
AsI_3	$(CF_3)_3As$	170/22	88	75[16]
SbI_3	$(CF_3)_3Sb$	165/70	0.2[b]	63[16]
GeI_4	$(CF_3)_4Ge$	120–170/150	0	22[18]

[a] Yields based upon the amount of limiting reagent taken. [b] Not isolated. [c] Reaction not reported.

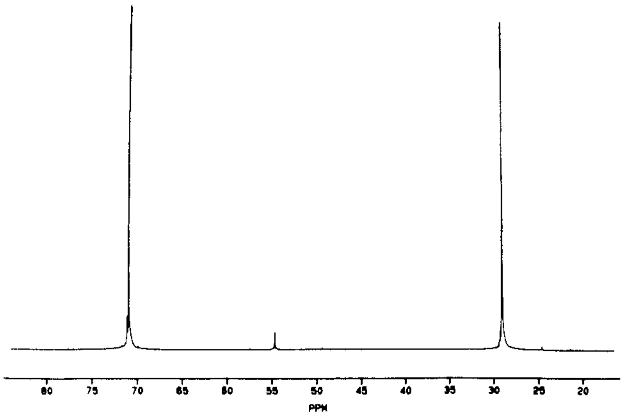

Figure 3. ^{19}F NMR spectrum of the reaction between $(CF_3)_2Te$ and AsI_3 after 22 h at 170 °C. In addition to CF_3I (71 ppm), $(CF_3)_2Te$ (54 ppm), and $(CF_3)_3As$ (29 ppm), very small amounts of $(CF_3)_2Te_2$ (49 ppm), $(CF_3)_2AsI$ (24 ppm), and CF_3AsI_2 (21 ppm) are also apparent.

the latter being evolved at −85 °C. The yield of the arsine, 0.1094 g (0.388 mmol), was 46% based upon the amount of telluride taken and 81% based upon the amount of unrecovered $(CF_3)_2Te$.

Formation of Tris(trifluoromethyl)stibine. Antimony, 0.0555 g (0.456 mmol), and $(CF_3)_2Te$, 0.2393 g (0.901 mmol), were combined and heated to 170 °C. After 3 h a small resonance that corresponded in chemical shift to that of $(CF_3)_3Sb$ (see Table II) was observed. This resonance grew in intensity until it was 4% as intense as that of $(CF_3)_2Te$, slowly declining to ca 3% during the 25th to the 80th hour. After a further 72 h at 170 °C it was no longer detected. Fluorine NMR spectroscopy of the solution indicated the presence of trace amounts of C_2F_4, C_3F_6, and SiF_4, 3% in total, but by far the largest resonance in the spectrum was that of $(CF_3)_2Te$.

Interaction of Germanium with Bis(trifluoromethyl)tellurium. Germanium, 0.0318 g (0.44 mmol), was combined with $(CF_3)_2Te$, 0.2303 g (0.867 mmol), and the vessel was maintained at 170 °C. After 7 days at 170 °C, no evidence for CF_3Ge species had been obtained and the experiment was discontinued. Essentially no decomposition of the reagent, $(CF_3)_2Te$, had occurred.

Ligand Exchange Reactions with Bis(trifluoromethyl)tellurium. Reaction of Sulfur Dichloride with Bis(trifluoromethyl)tellurium. Immediately upon warming, a solution prepared from SCl_2, 0.0783 g (0.760 mmol), and $(CF_3)_2Te$, 0.2087 g (0.786 mmol), began to react, generating a white solid. Fluorine NMR spectra of the resulting slurry contained several very broad resonances, one of which (25.4 ppm) corresponded to that expected of CF_3SCl. After 15 min at 170 °C, however, the solid liquified into a red-brown solution. NMR spectra were periodically obtained during the 100-h course of the reaction, and the relative molar ratios of nine of the components of the mixture, as indicated by four of these ^{19}F spectra, are shown in Table IV.

During the initial 75 h, essentially the only resonances in the spectra were those listed above. After 75 h, however, the resonances of C_2F_4, C_3F_6, SiF_4, TeF_4, and $CFCl_3$ and resonances in the saturated fluorocarbon portion of the spectrum, e.g., −7.1, −12.0, and −13.5 ppm, became apparent. During the last stages of the reaction, these latter resonances all increased in intensity at the expense of the group 6 trifluoromethyl resonances.

Synthesis of Bis(trifluoromethyl)selenium. The reagents $SeBr_4$, 0.2667 g (0.669 mmol), and $(CF_3)_2Te$, 0.3716 g (1.399 mmol), were sealed together and heated to 170 °C for 2 h, and then fluorine NMR data were obtained. By far the largest resonance in the spectrum arose from unreacted $(CF_3)_2Te$; the next largest resonances, each ca. 50% as intense, were due to CF_3Br (57 ppm) and $(CF_3)_2Se$. Additionally, there were very small resonances, ca. 1% each due to $(CF_3)_2Te_2$, $(CF_3)_2Se_2$, and $CF_3TeSeCF_3$; see Table II. After 6 h at 170 °C, the last three were no longer observed. After a total of 15 h at 170 °C, the products were fractionated. The material that passed through a −116 °C bath but was retained at −131 °C was $(CF_3)_2Se$, 0.0994 g (0.458 mmol), isolated in 98% yield; see Table V.

Synthesis of Tris(trifluoromethyl)phosphine. In a glovebag, freshly sublimed PI_3, 0.1634 g (0.397 mmol), was loaded into a reactor, which was then evacuated while the contents were held at −196 °C. Bis(trifluoromethyl)tellurium, 0.3154 g (1.187 mmol), was condensed onto the PI_3. The vessel was sealed and then placed into an oil bath. Fluorine NMR spectra obtained after 7 h at 170 °C contained a large doublet at 24.5 ppm arising from $(CF_3)_3P$ (100%), and singlets at 71 (81%) and 54 (15%) ppm, from CF_3I and $(CF_3)_2Te$, respectively. Traces of $(CF_3)_2Te_2$ and $(CF_3)_2PI$ were also observed. The reactor was heated to 170 °C for a further 7 h, and then the vessel was opened and the volatile contents separated. The trifluoromethyl iodide that had formed was removed by fractionation at −131 °C, and then the residual was separated on a column. Tris(trifluoromethyl)phosphine, 0.0615 g (0.258 mmol), was obtained at a head temperature of −100 °C. The yield was 65%.

Synthesis of Tris(trifluoromethyl)arsine. Arsenic triiodide, 0.2117 g (0.465 mmol), and $(CF_3)_2Te$, 0.3698 g (1.392 mmol), were heated to 170 °C. During the course of the reaction the intensities of the resonances from CF_3I and $(CF_3)_3As$ increased steadily. After 22 h they were present in approximately a 1:1 molar ratio, along with very small resonances from the partially substituted arsines $(CF_3)_2AsI$ and CF_3AsI_2, ca. 1% each; see Figure 3. Separation of the products yielded colorless $(CF_3)_3As$, 0.1151 g (0.408 mmol), 88%.

Exposure of Antimony Triiodide to Bis(trifluoromethyl)tellurium. Triiodoantimony, 0.2013 g (0.401 mmol), and $(CF_3)_2Te$, 0.2997 g (1.128 mmol), were loaded into a reactor and heated to 165 °C. After 1 h small amounts of CF_3I were present, but the fluorine NMR data obtained over the 70-h reaction period never indicated the presence of more than trace amounts (0.2%) of tris(trifluoromethyl)stibine.

Exposure of Germanium Tetraiodide to Bis(trifluoromethyl)tellurium. Freshly sublimed GeI_4, 0.1778 g (0.306 mmol), and $(CF_3)_2Te$, 0.1715 g (0.646 mmol), were allowed to interact at 170 °C. After 10 h CF_3I was observed by ^{19}F NMR spectroscopy, but even after 120 h at 170 °C, although a large amount of CF_3I had formed, no resonances that could be attributed to (trifluoromethyl)germanes were present; the reaction was terminated. Similar results were obtained from reactions carried out at temperatures of 120, 140, and 150 °C, each experiment followed for 150 h. In each case large amounts of $(CF_3)_2Te$ were present at the end of the reaction.

Results and Discussion

Until very recently, the only general synthetic route to the trifluoromethylated derivatives of the group 5A and 6A (15 and 16) elements involved the oxidative trifluoromethylation of the appropriate elemental substrate with CF_3I. Although these reactions have provided reasonable quantities of various trifluoromethylated P, As, Sb, and Se derivatives for many years, there are several aspects of this protocol that are less than completely desirable. One of the important drawbacks is that neither $(CF_3)_2S$ nor $(CF_3)_2Te$ is formed during the interactions of the elements with CF_3I. Additionally, separations of the desired products from the mixtures that are obtained during the CF_3I reactions can be very laborious.

Recently, we have surveyed the reactivity of an alternative trifluoromethylating agent, $(CF_3)_2Hg$, and reported the reactions of the mercurial with a variety of representative group 5A and 6A halides.[16] One of the products that was generated in very high yields (92%) was $(CF_3)_2Te$, a yellow liquid that is easily purified and readily handled with a conventional vacuum line. Since the tellurium–carbon bond has been reputed to be one of the weakest covalent bonds known,[14] and since Te is adjacent to I in the periodic table, it seemed most plausible that $(CF_3)_2Te$ might well find a viable chemical niche as an alternative to CF_3I and $(CF_3)_2Hg$ in the formation of late main group element trifluoromethyl derivatives. In an attempt to ascertain what advantages, if any, $(CF_3)_2Te$ might possess, we have assessed the utility of the telluride in oxidative trifluoromethylations and ligand exchanges of the group 5A and 6A (15 and 16) elements and their halides, the two types of reactions that were originally examined with CF_3I.[2-8]

For spectroscopic convenience all of the reactions that are discussed here were carried out in standard wall Pyrex tubing of a size selected to allow insertion of the entire sample directly into a conventional NMR probe. While we know of no difficulties that might be expected to arise from larger sized reactions, as yet the effects of scaling have not been explicitly addressed and we suggest that appropriate (heavy wall or metallic) pressure vessels be utilized if greater quantities of material are to be employed.

Oxidative Trifluoromethylations with Bis(trifluoromethyl)tellurium. With the exceptions of those employing Ge and Sb, the oxidative trifluoromethylations examined here were carried out at 220 °C, a temperature that was selected since the reactions proceeded at reasonable rates, yet the experiments could be carried out by employing only conventional glassware and laboratory equipment. The studies of elemental germanium and antimony were necessarily conducted at lower temperature because the trifluoromethyl derivatives of both of these elements are known to decompose at temperatures below 200 °C.[4,18]

The results that were obtained from this phase of the investigation have been condensed into Table III, in which the yields based upon the amount of unrecovered trifluoromethylating agent (conversion) and those based upon the amount of limiting reagent utilized (yield) are both displayed. The former values were computed to allow more effective comparisons with the data that Emeleus and his colleagues originally reported during their CF_3I studies.[2-5]

With the sole exception of the antimony reactions all of the yields that were obtained from the $(CF_3)_2Te$ oxidations are higher than those that were reported from the CF_3I oxidations. By far the most dramatic difference is found in the reactions of elemental sulfur. The compound $(CF_3)_2S$, which is obtained nearly quantitatively from $(CF_3)_2Te$ and S_8, is not formed at all when the element reacts with CF_3I.[5]

Although minor amounts of $(CF_3)_2Te_2$ and, in the Sb reactions, traces of SiF_4, C_2F_4, and C_3F_6 were formed, the spectra from the reactions of the group 5A elements were surprisingly free of any products arising from side reactions. Essentially the only resonances that were found were those derived from either $(CF_3)_2Te$ or the fully trifluoromethylated derivative of the element under study. Figure 2 is very typical of the reactions of the group 5A elements with $(CF_3)_2Te$.

Within the series of elements that were examined here the reactions of elemental sulfur are unique in that large amounts of products other than $(CF_3)_2S$ were observed during the intermediate stages. In fact, during the early portions of the reaction between S_8 and $(CF_3)_2Te$ that had been carried out at a lower temperature (170 °C), the polynuclear trifluoromethyl sulfides $(CF_3)_2S_x$, $x = 2$–4, dominated the (trifluoromethyl)sulfur region of the ^{19}F NMR spectra. Even after 74 h at 170 °C, substantial amounts of these intermediate compounds remain; see Figure 1.

These results are derived from the properties of elemental sulfur itself and are most easily interpreted by recalling that when sulfur is heated to 160 °C, the octasulfur rings are cleaved to form the diradical catenasulfur,[20] which, upon exposure to $(CF_3)_2Te$, would be expected to form the trifluoromethylated polysulfides $(CF_3)_2S_x$. Although reasonably chemically robust, the longer chain polysulfides are well-known to be of lesser thermal stability than the shorter,[21] and eventually the longer chain species would be expected to homolytically cleave into two radicals of the type CF_3S_m, which would again be trifluoromethylated by $(CF_3)_2Te$. Smaller amounts of a second type of intermediate, proposed to be the radical cross-product CF_3STeCF_3, are also clearly evident during this early portion of the elemental sulfur reactions; see Figure 1 and Table II. Ultimately, however, all of the reaction channels in the elemental sulfur system lead to the monosulfide, $(CF_3)_2S$, and this is essentially the only sulfur-containing product that is present at the conclusion of the reaction; see Table III.

Overall, the reactions of elemental selenium are very similar to the sulfur reactions, but the Se–Se bond strength, ca. 41 kcal/mol,[22] is significantly lower than the S–S bond strength, ca. 60 kcal/mol;[22] thus, the proportions of $(CF_3)_2Se_2$ that are found in the elemental selenium reactions are always substantially smaller than those of the trifluoromethyl polysulfides in the elemental sulfur reactions. For similar reasons, the concentration of the proposed cross-product, $CF_3SeTeCF_3$, is also much lower than that of CF_3STeCF_3 in the sulfur reactions. The Se reactions are also similar to the sulfur reactions in that at the conclusion of the experiment only the mononuclear $(CF_3)_2Se$ is present in more than trace amounts.

As indicated in the Experimental Section, the fluorine NMR data indicated that all of these oxidative-trifluoromethylation reactions come to an effective equilibrium. This effect was particularly evident in the reactions carried out with the main group 5 elements, where dramatically decreasing molar ratios between the tris(trifluoromethyl) group 5A (15) derivatives and the remaining $(CF_3)_2Te$ were encountered as the location of the group 5A (15) element descended the periodic table; see Table III.

In order to quantitatively compare the reactions of $(CF_3)_2Te$ with the various elements discussed above, the crucial thermodynamic information that would be required is the heats of atomization of the elements and the strengths of the bonds from the elements to carbon. Although reliable bond strength data for trifluoromethyl compounds are very sparse, it is generally accepted that in this portion of the periodic table bond strengths from the elements to carbon decrease substantially as the position of the element becomes lower in the table. In main group 4, for example, this decrease amounts to some 45 kcal/mol.[22] The heats of atomization also decrease (by some 30 kcal/mol in group 5A (15) and 19 kcal/mol in group 6A (16)),[23] and, overall, the former

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(20) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: New York, 1984; p 780 ff.

(21) See, for example: Muller, E.; Hyne, J. B. *J. Am. Chem. Soc.* **1969**, *91*, 1907.

(22) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; pp A-32–A-40. The Te–Te bond strength is given as ca. 30 kcal/mol. Note that in Figure 1 the amount of $(CF_3)_2Te_2$ is much less than that of $(CF_3)_2S_2$.

(23) Jolly, W. L. *The Principles of Inorganic Chemistry*; McGraw-Hill: New York, 1976; p 42.

effect overrides the latter; thus, the formation of the trifluoromethyl derivatives is disfavored for the elements lower in the table relative to those higher up; see Table III.

The reluctance of elemental Ge to enter into the $(CF_3)_2Te$ trifluoromethylation reactions may have arisen from either thermodynamic or kinetic factors, since the heat of atomization of this element (90 kcal/mol)[23] is the largest of the elements surveyed here, yet for the reasons discussed above, the reaction temperatures were required to be among the lowest employed.

Although all of the reactions discussed above involve the formal oxidation of the element by $(CF_3)_2Te$, i.e., $n(CF_3)_2Te + 2M \rightarrow 2(CF_3)_nM + n$Te, the ^{19}F NMR spectra from the elemental iodine reactions were examined for evidence that the reaction might proceed via an oxidative addition of I_2 to $(CF_3)_2Te$, to form $(CF_3)_2TeI_2$, followed by a double reductive elimination that generates elemental tellurium and the 2 mol of CF_3I that were isolated. During these reactions, however, no resonance was observed in the spectral window of interest.[24]

Ligand Exchange Reactions with Bis(trifluoromethyl)tellurium. The reactions between $(CF_3)_2Te$ and the group 5A and 6A halides that have been described here clearly demonstrate that this reagent will easily interchange ligands with representative halides of a variety of relatively electron-rich elements to form the fully substituted trifluoromethyl derivatives in high yields. For example, the products of the ligand exchanges with PI_3 and AsI_3, $(CF_3)_3P$ and $(CF_3)_3As$, were separated in yields that are approximately 10% higher than those that had been previously obtained from the reactions of $(CF_3)_2Hg$ with the same halides; see Table V.

Ligand exchanges between CF_3I and halides like PI_3 cannot be successfully carried out, of course, but the interactions of CF_3I with PMe_3, $AsMe_3$, and $SbMe_3$ have been reported.[7] In these reactions the monotrifluoromethylated compounds, species like CF_3PMe_2, were generated in ca. 50% yield, but derivatives containing more than one CF_3 group were not observed.[7] In a related reaction, that between $BiMe_3$ and CF_3I carried out at 100 °C, the bis(trifluoromethyl) compound $(CF_3)_2BiMe$ was formed (18%), but there was no evidence for $(CF_3)_3Bi$.[8,26]

Reduction of the selenium occurs during the reaction of $SeBr_4$ with $(CF_3)_2Te$, and the overall course of the interaction can be expressed as $SeBr_4 + 3(CF_3)_2Te \rightarrow (CF_3)_2Se + 3Te + 4CF_3Br$. On the basis of this stoichiometry, the yield of $(CF_3)_2Se$ was also very high, 98%, much higher than that found in the reaction of $SeBr_4$ with $(CF_3)_2Hg$; see Table V.

The results obtained from GeI_4 and SbI_3, however, indicate that either the mercurial $(CF_3)_2Hg$[18] or the cadmium reagent $(CF_3)_2Cd\cdot$glyme[27] is far superior for the formation of the trifluoromethylated derivatives of these relatively electron poor, more metallic elements; see Table V.

One potential advantage of the ligand-exchange procedure is that the reactions occur much more quickly and at temperatures that are fully 50 °C lower then the temperatures that were required for the oxidative trifluoromethylations discussed above. This characteristic could be of considerable importance if mixed-ligand species were desired, rather than the homoleptic derivatives that were prepared in this study. One of the disadvantages of the $(CF_3)_2Te$ reactions is that, like the analogous S and Se monotrifluoromethylated derivatives, the tellurium monohalides, e.g., CF_3TeI, are significantly less thermally stable than the parent compound, $(CF_3)_2Te$. The result of this relative instability is that, at 170 °C, only one of the CF_3 groups in $(CF_3)_2Te$ is available for ligand exchange. Except for the SCl_2 reactions discussed below, the second CF_3 group is eventually isolated as one of the trifluoromethyl halides, CF_3Cl, CF_3Br, or CF_3I.

Like the oxidative trifluoromethylations of elemental sulfur, the reactions of the sulfur halide SCl_2 were unique among the halides that were examined. All of the currently available evidence suggests that the first step of this reaction is the formation of CF_3SCl and CF_3TeCl. However, as indicated above, neither of these compounds is very stable thermally; CF_3TeCl gives off CF_3Cl and Te, while (at 170 °C) CF_3SCl forms CF_3S and Cl radicals. The further reactions of CF_3S do result in the formation of the $(CF_3)_2S$ that is observed, but, due to the presence of the chlorine in the system, the yields of this compound that are obtained from the ligand exchange reaction (ca. 15%) are much lower than those obtained from the direct oxidation of sulfur with $(CF_3)_2Te$ (ca. 90%). Because of the excellent yields of $(CF_3)_2S$ from the oxidation reaction, no attempts were made to maximize the amount of $(CF_3)_2S$ generated in the ligand exchange reaction.

There are clearly two previously unobserved reactions that occur in the SCl_2 system. The first is the interchange of chlorine for fluorine on the C_1 tetrahalide CF_3Cl. This is the reaction that is responsible for the formation of CF_2Cl_2 and $CFCl_3$. The second type of reaction, which only became apparent after ca. 75 h at 170 °C, is the accretion of the C_1 hydrocarbons into larger fluorocarbons, the compounds with the chemical shifts of ca. −10 ppm; see the Experimental Section. Both of these organic transformations are under further investigation.

Summary. Recently, Barton has discussed the concept of "disciplined" radicals.[28] These are radical intermediates that eventually lead to only one product, one that is ultimately generated in high yield. The lack of metal fluorides, coupled with the very small amounts of the products that would be expected from difluorocarbene formation, that were observed during the course of the oxidative trifluoromethylations can be taken as an indication that these reactions produce disciplined radicals. This, of course, is merely an alternative way of saying that the number of low-energy reaction channels that are available to the CF_3 radicals is severely restricted, or that, since the chemical integrity of the CF_3 group is maintained throughout the course of the reaction, CF_3 is well described as a pseudohalogen in this type of system.[29] All of the successful oxidations with this reagent were very clean, providing high yields of the desired group 5A, 6A, or 7A products; essentially no thermal decomposition of $(CF_3)_2Te$ was encountered, even at 220 °C.

With the exception of the SCl_2 reactions, all of the ligand-exchange reactions are also very clean. The fluorine NMR spectra contain essentially only the resonances of the appropriate trifluoromethyl halides, $(CF_3)_2Te$, and the CF_3-containing derivatives of the element of interest. Only the SCl_2 reactions are somewhat more complex, since in this system there are a variety of reaction channels that, unlike the oxidations of S_8, do not all merge at $(CF_3)_2S$. Here, presumably because of the near equality of several of the bond strengths in the system,[22] the available reaction channels diverge, eventually leading to many more products than are found in the other halide reactions. These are the results that would be anticipated from "undisciplined" radicals.

Acknowledgment. The experimental assistance of Latif Ahmed and the financial aid of the National Science Foundation are gratefully acknowledged.

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[24] On the basis of previously reported values for (trifluoromethyl)tellurium(IV) chemical shifts,[13,25] the most probable ^{19}F chemical shift of $(CF_3)_2TeI_2$ is ca. 35 ppm.

[25] Herberg, S.; Naumann, D. *Z. Anorg. Allg. Chem.* **1982**, *494*, 151, 159. Naumann, D.; Wilkes, B. *J. Fluorine Chem.* **1985**, *27*, 115.

[26] The reactions of $(CF_3)_2Te$ with main group alkyls have not yet been assessed, but successful ligand interchanges between $(CF_3)_2Te$ and transition-metal alkyls have been reported in: Herberg, S.; Lange, H.; Naumann, D. *J. Fluorine Chem.* **1987**, *35*, 267.

[27] See, for example: Krause, L. J.; Morrison, J. A. *J. Chem. Soc., Chem. Commun.* **1980**, 671; **1981**, 1282. Krause, L. J.; Morrison, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 2995. Ontiveros, C. D.; Morrison, J. A. *Organometallics* **1986**, *5*, 1446. Nair, H. K.; Morrison, J. A. *Inorg. Chem.* **1989**, *28*, 2816. Ontiveros, C. D.; Morrison, J. A. *Inorg. Synth.* **1986**, *24*, 55.

[28] Barton, D. H. R.; Ozbalik, N.; Sarma, J. C. *Tetrahedron Letts.* **1988**, *29*, 6581.

[29] In general, the group 4A (14) trifluoromethyl compounds and $(CF_3)_2Hg$ provide many examples of "undisciplined" radicals. See, for example: Krause, L. J.; Morrison, J. A. *Inorg. Chem.* **1980**, *19*, 604.