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TRIMETHYLGERMYL–METHANE AND -TRIFLUOROMETHANE–SULFONATES

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Abstract—$Me_3GeOS(O_2)CH_3$ and $Me_3GeOS(O)_2CF_3$ have been prepared and characterised by their ^1H, ^{13}C, ^{19}F NMR, IR, Raman and mass spectra.

INTRODUCTION

Although several organotin and organosilicon derivatives of trifluoromethanesulfonic acid are known[1], only one example of an organogermanium trifluoromethanesulfonate has been cited[1, 2]. Its IR spectrum was reported brieflly without a description of its synthesis. Because of our interest in the chemistry of germanium compounds, we have initiated studies into the synthesis and spectroscopic properties of trimethylgermyl–trifluoromethanesulfonate $Me_3GeOS(O_2)CF_3$ and -methanesulfonate $Me_3GeOS(O_2)CH_3$. In this paper we report their synthesis, N.M.R., IR, Raman and mass spectra.

EXPERIMENTAL

All reagents were obtained commercially and were used without further purification. Chloro- and bromotrimethylgermanes were obtained from Laramie Chemical Co., methane- and trifluoromethane- sulfonic acids and their silver salts from Aldrich Chemical Co., and lead cyanamide from ROC/RIC Chemical Co. Bis-trimethylgermanium carbodimide $[(CH_3)_3GeN:]_2C$ was prepared as described previously[3].

The ^1H and ^{19}F NMR spectra of the neat liquids were recorded on a JEOL C-60 HL spectrometer while ^{13}C NMR spectra were obtained using the Brucker CPX 100 multinuclear pulsed Fourier transform NMR spectrometer operating at 22.64 MHz at a probe temperature of 35°C. All ^{13}C NMR spectra were recorded under ^1H noise-decoupling conditions. Samples were sealed in capillaries which were then placed in the 5 mm tubes containing TMS (as internal standard) and deuterochloroform (as lock for the ^{13}C NMR spectra). ^{19}F chemical shifts were measured relative to trifluoroacetic acid as external reference.

The IR spectra were recorded on a Beckman IR 12 (4000–400 cm^{-1}) by placing a drop of the sample between two KBr windows. Raman spectra were recorded in the range 3000–100 cm^{-1} on a Spectra-Physics 700 instrument, in conjunction with a 164 argon ion Laser and model 265 exciter. Mass spectra were obtained using a Varian MAT CH5 double focussing spectrometer equipped with an INCOS 2000 computer system at an ionizing energy of 70 eV. The ion clusters suggested in Table 2 were checked for "best fits" with the program (MASPEC).† A linear least-square iterative computer program (SMASBD)† was used to fit theoretical polyisotopic patterns. Typically, for isotopic distributions involving one species, e.g. $Me_2GeOS(O_2)CF_3^+$ or Me_3GeOSO^+, the average deviation was in the range 0.4–1.1. For a more complex cluster, such as that from m/e 115 to 125, the average deviation was still less than 2 for a distribution of the ions Me_3Ge^+, Me_2GeO^+, Me_2GeF^+ and $HGeOS^+$ in the ratio of 10.0:0.4:5.6:4.0.

All manipulations involved either the use of a dry box in a dry nitrogen atmosphere or standard vacuum line techniques

Reaction of Me_3GeX *with* $AgOS(O_2)CF_3/CH_3$. Typically, $AgOS(O_2)CF_3/CH_3$ (*ca.* 4 mmol) was placed into a reaction vessel (*ca.* 25 ml capacity) equipped with a high vacuum Teflon stopcock. The vessel, which was wrapped with aluminum foil to protect the silver salt from light, was then degassed. Me_3GeCl or Me_3GeBr (*ca.* 5 mmol) and CH_2Cl_2 (*ca.* 5 ml) were distilled into the vessel held at −196°C. The mixture was allowed to warm up to room temperature and kept at that temperature for 24 hr with occasional shaking. Unreacted silver salt and the silver halide that precipitated were then filtered in a dry nitrogen-atmosphere box, using Wattman filter paper No. 41. Volatiles from the filtrate were then removed under vacuum leaving $Me_3GeOS(O_2)CF_3/CH_3$ in the flask as a non-volatile liquid. The yield based on the amount of Me_3GeX was ≃10% for both chloride and bromide starting materials.

Reaction of $[Me_3GeN:]_2C$ *with* $HOS(O_2)CF_3/CH_3$. Bis-trimethylgermylcarbodiimide $[Me_3GeN:]_2C$ (*ca.* 6 mmol) was distilled into a reaction vessel (*ca.* 25 ml capacity) held at −196°C containing $HOS(O_2)CF_3/CH_3$ (*ca.* 5 mmol). The mixture was allowed to react (room temperature, 10 minutes). The ^1H NMR spectrum of the mixture indicated the existence of some unreacted $[Me_3GeN:]_2C$ but none of the acid. The polymeric $(H_2NCN)_n$ [4] was obtained as a white solid and was filtered through a Wattman filter paper No. 41 in the nitrogen atmosphere box. The filtrate was pumped for 30 min to ensure the removal of volatiles from the product (yield ~50%).

RESULTS AND DISCUSSION

Our initial attempts to prepare trimethylgermyl trifluoromethane-sulfonate, $Me_3GeOS(O_2)CF_3$ and trimethylgermylmethanesulfonate, $Me_3GeOS(O_2)CH_3$ involved the reaction shown in eqn (1).

$$Me_3GeX + AgOS(O_2)CF_3/CH_3 \xrightarrow{CH_2Cl_2} Me_3GeOS(O_2)CF_3/CH_3 + AgX (X = Cl \text{ or } Br). \quad (1)$$

Unfortunately, the yield (10%) is most unsatisfactory. The ^1H NMR and IR spectra indicate the presence of unreacted germyl halide. Thus, an alternative route was developed as is indicated by eqn (2).

$$(Me_3GeN:)_2C + HOS(O_2)CF_3/CH_3 \xrightarrow{40\ min} Me_3GeOS(O_2)CF_3/CH_3 + \tfrac{1}{2}(H_2NCN)_n. \quad (2)$$

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†MASPEC and SMASBD were obtained from J. Miller of the Chemistry Department, Brock University.

The susceptibility of the Ge–N bond in germyl carbodiimides towards protic species has been investigated earlier[3]. The carbodiimide reaction appears to be quantitative, but recovery of $Me_3GeOS(O_2)CF_3/CH_3$ from this reaction is still only about 50%. In this relatively small-scale reaction, much of the product is lost during the filtration step. The compound $Me_3GeOS(O_2)CF_3$ is a yellowish viscous liquid, while $Me_3GeOS(O_2)CH_3$ is colourless. Both are sensitive to hydrolysis even on exposure to air and decompose on heating.

The ^1H, ^{13}C and ^{19}F NMR Chemical shifts for these compounds are given in Table 1. The assignments for Me(Ge) and Me(S) are based upon the ratio of the intensity of the two signals in the ^1H NMR spectra. The value of δMe(S) in $Me_3GeOS(O_2)CH_3$ (2.93 ppm) is appreciably to low field of that in Me_3GeSMe (1.96 ppm)[5] but very close to the value in the acid, $HOS(O_2)CH_3$ (3.2 ppm). Thus, the substitution of the Me_3Ge-group for the proton has but a small effect on the chemical shift of the methyl group attached to sulfur.

The values of δMe(Ge) in the two compounds change even less for substitution of CF_3 for CH_3 on sulfur, the change being appreciably less than that found when comparing trimethylgermyltrifluoroacetate (0.69 ppm)[6] and trimethylgermylacetate (0.53 ppm)[7]. The ^{13}C NMR spectrum of $Me_3GeOS(O_2)CF_3$ shows a quartet centered at 118.98 for the $C(F_3)$ resonance with $J_{CF} = 316.2$ Hz. This compares with a value of 132.3 ppm for the CF_3 resonance in Me_3GeSCF_3, in which the value of J_{CF} is 306 Hz. The ^{13}C chemical shift for the methyl carbon atoms is 2.77 and 3.18 ppm respectively for $Me_3GeOS(O_2)CF_3$ and $Me_3GeOS(O_2)CH_3$; both values being very close to that found in $(Me_3Ge)_2O$ of 3.25 ppm[8]. Thus, the presence of the oxygen atom, rather than the $OS(O_2)$ grouping apparently predominates in determining these shifts. Similarly, the ^{13}C chemical shift for the methyl group attached to sulfur (40.32) is close to that observed in $Me_3GeSCMe_3$ at 43.65[9]. The ^{19}F NMR spectrum shows a chemical shift of 0.24 ppm relative to CF_3COOH. This value is close to that reported for $Me_3SnN(Me)S(O_2)CF_3$[10].

In the mass spectra of both species, $Me_3GeOS(O_2)CX_3$, X = F or H, there are no peaks corresponding to the parent ions. However, both do show distinct features corresponding to the ion resulting from the loss of one methyl group. The cluster of ions centered at m/e = 255 corresponding to the ion $[Me_2GeOS(O_2)CF_3]^+$ accounts for 8.54% of the ion current. The relative peak heights match the expected isotopic distribution as do those of the ion $[Me_2GeOS(O_2)CH_3]^+$ which account for 38.25% of the ion current of the methyl derivative. In view of the similarity between the two spectra of the analogues, it seems reasonable to assume that the loss of methyl is mainly, if not totally, from the germanium atom rather than the sulfur atom especially as there is no significant cluster in the fluoride spectrum corresponding to the loss of CF_3. Thus, the marked increased relative intensity of the $Me_2GeOS(O_2)Me^+$ ion may be due in part to the fact that the methyl analogue is a poorer leaving group so that the Ge–O bond is less readily broken. Both spectra show weak features centered at m/e 183. Given the poor statistics at this level of intensity, it is reasonable to assume that in both cases the ion is $[Me_3GeOSO]^+$ arising from rearrangements resulting in the loss of CF_3O and CH_3O respectively. Again, both spectra show similar features around m/e 139 which apparently arise from the ion $HGeOSO^+$. It is interesting to note that there is no indication of the ion Me_3GeO^+. Thus, the initial fragmentation of the parent apparently results in the breaking of the Ge–O bond or the Ge–CH_3 bond, but not the O–S bond. Very weak features can be distinguished in both spectra centered at m/e 168 and 153, suggesting successive loss of two CH_3 radicals and one CH_2 from $[Me_3GeOSO]^+$. The cluster of greatest intensity in the perfluoride derivative, and of major importance in the methyl analogue, is the cluster centered at m/e = 119 which clearly corresponds to the Me_3Ge^+ ion. However, the relative peak heights and extent of the cluster indicate the presence of a second ion containing a germanium atom centered at m/e = 123. The transfer of fluorine during the unimolecular dissociation of perfluorogermanes has been noted[11] and it is tempting to suggest that the ion corresponds in the perfluoro compound, to the ion Me_2GeF^+. However, the ion is also present in the methyl derivative so it may well correspond to $HGeOS^+$ in both cases. It is also possible that a small amounnt of Me_2GeO^+ is present, centered at m/e 120. The best computer fit suggests that the ions present in the CF_3 compound are Me_3Ge^+, Me_2GeO^+, Me_2GeF^+ and $HGeOS^+$ in the ratio 10:0.4:5.6:4 and those of the CH_3 compound are Me_3Ge^+, Me_2GeO^+ and $HGeOS^+$ in the ratio 10:0.7:3.4. Thus, in neither case is the contribution from Me_2GeO^+ particularly significant and no ion was seen corresponding to Me_3GeO^+. The relatively broad, but weak, cluster between m/e 99 and 109 is probably a mixture of several ions. The predominant species are Me_2GeH^+ and

Table 1. The nuclear magnetic resonance spectra of $Me_3GeOS(O_2)X$, ($X = CH_3$ and CF_3)

X	δ^1H*		$\delta^{13}C$*		$\delta^{19}F$*
	δMe(Ge)	δMe(S)	δ_C(Ge)	δ_C(S)	
CH_3	0.8^b	2.93^b	3.18	40.32	
CF_3	0.85	-	2.77	118.98#	0.24

* ^1H and ^{13}C chemical shifts are in ppm with reference to TMS; positive values denote downfield shifts. The ^{19}F chemical shift is in ppm to high field of CF_3OOH.

\# $J_{CF} = 316.2$ Hz.

Me_2Ge^+, both of these having been noted in other trimethyl derivatives[12]. However, the cluster also apparently contains $MeGeCH_2^+$, $MeGeO^+$, and, in the case of the fluoride, $MeGeHF^+$. The cluster around m/e = 89 is very similar to that found for $Me_3GeNCNGeMe_3$[13], where metastable studies confirmed the dissociation of Me_3Ge^+ to $MeGe^+$ and $MeGeH_2^+$ in approximately equal amounts. The presence of small amounts of GeF^+ are indicated in the fluoride, so there is an accumulation of weak evidence to support fluorine transfer to germanium. The germanium cluster around m/e 70–77 contains a little more GeH^+ than Ge^+, while the fluoride spectrum also contains a small amount of CF_3^+ (m/e = 69). Finally, the fragmentation patterns in the mass spectra confirmed the presence of monomeric compounds in contrast to those formed from reacting Me_3SnCl with (CF_3SO_3H), where bridging, bidentate fluoro-sulfonate ligands have been identified by X-ray diffraction[14] and Mössbauer spectra[15, 16].

The observed IR frequencies and Raman shifts and the descriptions of the fundamental frequencies of $Me_3GeOS(O_2)CX_3$, X = F or H are presented in Table 3. The molecules are assumed to have C_s symmetry leading to thirty-two a' modes (IR active and Raman polarized) and twenty-five a'' modes (IR active and Raman depolarized). The assignment of the vibrations associated with the Me_3Ge-moiety are based on the vibrational assignments of Me_3GeX[17] (where X = halogen) and $(Me_3Ge)_2O$[18]. Two distinct methyl vibrations are apparent in both species, corresponding to the asymmetric and symmetric CH_3 stretches as expected. Similarly, the corresponding CH_3 deformation and CH_3 rocking modes are assigned to the expected region of the spectrum. There are pronounced shoulders on the higher energy side of the CH_3 stretches of $Me_3GeOS(O_2)CH_3$ at *ca.* 3010 and 2940 cm^{-1} which must correspond to the asymmetric and symmetric CH_3 stretches associated with the methyl group attached to sulfur. In Me_3GeSMe, the CH_3- symmetric stretches for the methyl group are assigned at 2921 cm^{-1} for the CH_3S group and 2906 cm^{-1} for those attached to germanium[19]. In the methyl deformation region, the spectra of the two compounds are again similar with the asymmetric $CH_3(Ge)$ band at 1420 cm^{-1} having a shoulder for the $Me_3GeOS(O_2)Me$ compound at 1435 cm^{-1}. However, in the methyl rocking region there is a distinct separation for the CH_3 groups attached to germanium (*ca.* 830 cm^{-1}) and that attached to sulfur (*ca.* 950 cm^{-1}) as was found for the methylthiogermanes[20]. The (C–S) and (Ge–C) stretching assignments are largely based on the proposed assignment for Me_3GeSMe and Me_3SnSMe[19], as well as the previous IR data on the $Me_3GeOS(O_2)CF_3$[2] compound. A very strong band at 574 cm^{-1}, which is polarized in the Raman, and the medium intensity band at 625 cm^{-1} are assigned as the symmetric and asym-

Table 2. Mass spectra of $Me_3GeOS(O_2)CX_3$ where X = CF_3 and CH_3

CF_3			CH_3		
m/e	Int	Ion family (%RA)	m/e	Int	Ion family (%RA)
255	4.7		201	23.3	
254	1.1		200	5.8	
253	20.2	$Me_2GeOS(O_2)CF_3^+$	199	100.0	$Me_2GeOS(O_2)Me^+$
252	4.7		198	23.4	
251	16.2	(8.54)	197	74.5	(38.25)
250	0		196	2.5	
249	10.4		195	50.2	
185	3.7		185	3.8	
184	1.0		184	1.0	
183	4.5	Me_3GeOSO^+	183	6.0	Me_3GeOSO^+
182	1.0		182	1.0	
181	3.1	(2.21)	181	4.9	(2.61)
180	0		180	0	
179	1.5		179	2.4	
141	8.1		141	3.2	
140	1.6		140	0.5	
139	16.9	$HGeOSO^+$	139	5.9	$HGeOSO^+$
138	3.5		138	2.0	
137	13.4	(7.62)	137	5.3	(2.75)
136	0		136	0	
135	7.6		135	3.2	
125	15.4		125	2.4	
124	3.7		124	0	
123	67.9	Me_2GeF^+(?)/$HGeOS^+$	123	11.5	$HGeOS^+$
122	19.8		122	2.9	
121	68.1		121	28.3	
120	60	Me_2GeO^+	120	6.4	Me_2GeO^+

Table 2.(b) (continued)

		CF_3			CH_3
m/e	Int	Ion family (%RA)	m/e	Int	Ion family (%RA)
119	100.0	Me_3Ge^+	119	54.9	Me_3Ge^+
118	18.0		118	12.9	
117	46.7	(57.18)	117	36.2	(24.71)
116	3.3		116	25	
115	34.6		115	22.7	
109	2.9		109	0	
108	0		108	0	
107	4.8	$MeGeHF^+$	107	4.2	
106	2.6		106	2.3	
105	6.3	$Me_2GeH^+/MeGeO^+$	105	13.0	$Me_2GeH^+/MeGeO^+$
104	7.2	Me_2Ge^+	104	6.5	Me_2Ge^+
103	5.8	$MeGeCH_2^+$	103	13.8	$MeGeCH_2^+$
102	4.0		102	4.9	
101	4.1	(6.31)	101	8.7	(8.03)
100	3.2		100	3.0	
99	1.4		99	2.3	
95	0		95	0	
94	0		94	0	
93	5.5	GeF^+?	92	0	
91	13.8	$MeGeH_2^+$	91	16.6	$MeGeH_2^+$
90	3.2		90	4.8	
89	22.7	$MeGe^+$	89	24.1	$MeGe^+$
88	6.9		88	7.0	
87	16.5	(12.52)	87	18.0	(19.75)
86	3.3		86	2.6	
85	9.3		85	9.3	
77	1.6		77	1.6	
76	1.0		76	1.0	
75	7.1	GeH^+	75	6.6	GeH^+
74	4.9	Ge^+	74	4.7	Ge^+
73	5.6		73	5.6	
72	2.5	(4.14)	72	2.5	(3.91)
71	3.3		71	5.0	
70	1.8		70	1.6	
69	9.9	CF_3^+	69	0	

metric (Ge–C) stretching modes. The corresponding bands are seen at 581 cm^{-1} and 625 cm^{-1} in the IR spectra of both compounds.

The (C–S) stretching vibration is assigned at *ca.* 770 cm^{-1} for both species, which agrees with the previous studies on $FXeOS(O_2)CF_3$[21], $Me_3GeOS(O_2)CF_3$ and $I(OSO_2CF_3)_3$[2] but is in contrast to the assignment in the compounds $Me_3SnOS(O_2)CF_3$ and $Me_3SnOS(O_2)CH_3$ which placed the (C–S) stretches at 347 and 425 cm^{-1} respectively[22]. It is interesting to note that in other studies on C–S containing compounds the (C–S) stretch has been assigned either in the 750 cm^{-1} region (where a methyl group is attached to sulfur as in CH_3SO_2Cl)[23] or to the 470 cm^{-1} region (where CF_3 is attached to sulfur as in CF_3SH[24] and $N(SCF_3)_3$[25]. The spectrum of the 450 cm^{-1} region of $Me_3GeOS(O_2)CF_3$ shows no distinct peaks and looks very similar to the spectrum of $Me_3GeOS(O_2)Me$. The intensity of the peaks is rather high, relative to other C–S containing compounds and it is proposed that there is an accidental overlap with the Me_3Ge rocking modes, which are typically also found in this region.

The assignment of the Ge–O stretching vibration in the two compounds is more difficult since there is mixing with the SO_3 stretching modes and CH_3 rocking modes. A literature survey on germyl oxides such as $(H_3Ge)_2O$, H_3GeOMe[26], MeH_2GeOAc[27] and $(Me_3Ge)_2O$,[18], reveals a similar difficulty in assigning the Ge–O stretching band which has been rationalized to be anywhere within a region from 900 to 500 cm^{-1}. A further complication that increases the ambiguity of vibrational assignments arises from the fact that sulfur–oxygen (OSO_2) and carbon–fluorine (CF_3) vibrations of identical symmetry are found in the same spectral range. The above confusion was not resolved by the Raman spectra because only very fragmentary Raman data could be obtained due to strong scattering over the whole spectral range. Thus, the assignment of the $OS(O_2)CF_3$ vibrations

Table 3. Vibrational frequencies from 3010 to 100 cm^{-1}

$Me_3GeOS(O_2)CF_3$		$Me_3GeOS(O_2)CH_3$		
IR(liquid)	Raman(liquid)	IR(liquid)	Raman(liquid)	Description
		3011 mw	3005 mw,dp	CH_3(S)st(a)
2995w	2998 mw,dp	2999 mw	3000 mw,dp	CH_3(Ge)st(a)
		2940 m	2937 ms,p	CH_3(S)st(s)
2920 w	2921 s,p	2920 m	2925 s,p	CH_3(Ge)st(s)
		1435 sh	1423 vw	CH_3(S)def(a)
1415 sh	1409 w,dp	1420 m	1417 w,dp	CH_3(Ge)def(a)
1365 m,sh	1346 w,dp	1351 m,sh	1379 vw	SO_2 st(a)
		1332 } s 1320 } m,sh	1334 } vw 1320 } vw,sh	CH_3(S)def(s) CH_3(Ge)def(s)
1290 s				
1275 m		1286 w,sh	1275 w	SO_2st(a)
1245 s	1248 w,dp	-	-	CF_3st(a)
		1235 s		
1200 sh	1193 w,dp	1210 vs	1200 vw	SO_3st(s)
		1196 vs	1182 vw	+
1175 s	1081 mw,p	-	1155 m,p	CF_3st(s)
1032 vs	1028 m,p	1062 vs	1072 vw	
980 m,sh	975 w	990 m	982 w,p	S–O(Ge)st· +(Ge–O)st
		952 w,sh } 945 m	950 vw } 931 vw	CH_3(S) rock
831 m	831 w	833 s,br	837 vw	CH_3(Ge) rock
800 sh,sh	-	-	777 sh	CH_3(Ge) rock
769 m	762 m,p	787 s	768 m,p	(C–S) st
690 sh,w				
652 s	668 w	-	-	CF_3def(a)
	630 vw	636 m	629 m,p	SO_2 Scissor
625 m,sh 581 m	625 m,dp	625 } m 580 } m,sh		GeC_3st(a)
570 sh	576 vs,p	569 w	574 vs,p	GeC_3st(s)
530 w	534 v,p	542 ms	540 ms,p	SO_2 wag
		528 m	527 ms,sh	SO_2 twist
515 m	494 w	-		CF_3def(S)
-	360 w,dp	-	377 w,dp	SO_2 rock
-	323 m,dp	-	-	CF_3 rock
	260 245 } mw, dp	-	265 244 } mw,dp	SO_3 rock
	185 m,dp		190 } m,dp 182 } m,sh	GeC_3def(a)
	172 sh		170 sh,dp	GeC_3def (s)
	120 w,p		122 w,p	Ge–O–S bend

is based largely on comparisons with similar molecules such as $Ag(SO_3CF_3)_2$[28], $FXOSO_2CF_3$[21], $Me_3SnSO_3CF_3/CH_3$[22], $I(OSO_2CF_3)_3$ and $Me_3GeOSO_2CF_3$[2], and also with other molecules such as $CsOCF_3$[29], CF_3SF_3[30], $N(SCF_3)_3$[25]. In spite of the extensive mixing, it seems reasonable to assume that the peaks that only occur in the fluoride correspond to the CF_3 modes while the common features arise from OSO_2 stretching and bending vibrations. The most intense envelope observed in the IR spectra occurs between 1150 and 1350 cm^{-1} in both compounds. This region is expected to contain the SO_2 asymmetric (1365 mm^{-1}) and symmetric 1275 cm^{-1}) stretches, as well as the SO_3 symmetric (1195 cm^{-1}) stretch in agreement with the frequency assignments in CH_3SO_2Cl and CD_3SO_2Cl which were supported by calculation[23]. According to some reports published on compounds containing the CF_3 group[25, 30], the vibrational activity of the latter (i.e. its stretching mode) falls in a narrow range between 1275 and 1072 cm^{-1} and this fits this proposal. The OSO_2 skeletal bends are found in a region that overlaps with the CF_3 bends, as well as the GeC_3 stretches. The $\nu_s(GeC_3)$ stretching mode is assigned to the most intense and highly polarized bands in the Raman at (CH_3) 574 and 576 cm^{-1} (CF_3), while the $\nu_{as}(GeC_3)$ stretching modes are assigned at 580 cm^{-1} in both compounds. The GeC_3 deformations and rocks are assigned in the region under 200 cm^{-1} which is basically isolated from the SO_3 and CF_3 rocking deformation modes. These were assigned with respect to the reported literature values and are displayed in Table 3.

In summation, the preparation of organogermanium derivatives of methane or trifluoromethanesulfonic acid is achieved either by the silver salt method which has been known for quite some time in the preparation of silyl and germylacetates and trifluoroacetates [31, 32], or by the acid solvolysis of organogermanium derivatives. The former method gives very poor yields but the latter method, which gives much better yields, involves the reaction of bis-germylcarbodiimide with the protic reagent [$HOS(O_2)CF_3/CH_3$], similar to that used for the preparation of $Me_3GeO(CO)CF_3$ [6]. The advantage of this reaction is that the secondary product dicyano diamide is a white involatile solid which can be easily separated from the other products, but the disadvantage is that it involves the use of a relatively corrosive acid and therefore needs careful handling.

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