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Silyl and Germyl Derivatives of Trifluoroacetic and Trichloroacetic Acids

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Silyl and germyl derivatives of trifluoroacetic and trichloroacetic acids, $R_3MOC(O)CX_3$ (R = H, CH_3; M = Si, Ge; X = F, Cl), have been prepared either by facile cleavage of the parent carbodiimide with trifluoroacetic and trichloroacetic acids or by exchange of a fluorogermane with the corresponding trimethylsilyl trihaloacetate. The compounds are characterized by ^1H NMR, infrared, Raman, and x-ray photoelectron spectroscopy and mass spectrometry. Cleavage reactions involving the addition of a hydrogen halide to trimethylsilyl trichloroacetate do not give quantitative yields of the familiar halo(trimethyl)silane but proceed only to partial completion according to the series HCl > HBr > HI. When excess difluoro(dimethyl)germane is used, the trimethylsilyl trichloroacetate is totally consumed affording $(CH_3)_2Ge(OC(O)CCl_3)_2$ and $(CH_3)_2GeFOC(O)CCl_3$.

The use of silver salts in the preparation of silyl and germyl acetates and trifluoroacetates has been well documented,[1-6] including a recent report by Stobart on the preparation of germyl trifluoroacetate and germyl formate.[4] Similarly, it has been reported that bis(silyl)- and bis(germyl)carbodiimides are quite useful as synthetic intermediates in the preparation of chalco- and pseudohalosilanes and -germanes.[7-9] In the present study, the preparation of $R_3MOC(O)CX_3$ (R = H, CH_3; M = Si, Ge; X = F, Cl) is described by synthetic routes described in previous work.[8,9]

Results and Discussion

The heavy metal salt exchange reaction has been an invaluable source for the interconversion of silanes and germanes.[1-6,8,10,11] This method is limited, however, due to a lack of availability of these silver salts. As a result, other synthetic routes to their preparation were investigated. One method which has proved quite useful involves the reaction of bis(silyl)- or bis(germyl)carbodiimide with a wide variety of protic reagents, viz., H_2E, ROH, R′SH (E = O, S, Se, Te; R, R′ = alkyl, aryl).[7-9,12] The advantage of this reaction is that the

$$(H_3SiN:)_2C + 2HOC(O)CF_3 \xrightarrow{\text{room temp}} 2H_3SiOC(O)CF_3 + 0.5(H_2NCN)_2$$

$$((CH_3)_3GeN:)_2C + 2HOC(O)CCl_3 \xrightarrow{\text{room temp}} 2(CH_3)_3GeOC(O)CCl_3 + 0.5(H_2NCN)_2 \qquad (1)$$

secondary product, dicyanodiamide, is a white involatile solid which may easily be separated from the other products, thus the attractiveness of this method to prepare silyl and germyl trihaloacetates. When silyl trichloroacetate is prepared, there is a strong tendency for side reactions to occur, resulting in the formation of hydrogen and monosilane. Although similar observations have been noted in the preparation of silyl acetate and silyl trifluoroacetate,[13] this does not occur when the analogous germyl trichloroacetate is prepared.

A comparative route to the formation of the germyl trihaloacetates involves the rapid exchange of an excess of a fluorogermane with a trimethylsilyl trihaloacetate at room temperature. The reaction is virtually quantitative and the

$$H_3GeF + (CH_3)_3SiOC(O)CCl_3 \rightarrow H_3GeOC(O)CCl_3 + (CH_3)_3SiF \qquad (2)$$

separation of volatile products is relatively simple, provided an excess of the fluorogermane is used. When trimethylsilyl trichloroacetate and excess difluoro(dimethyl)germane are mixed, the reaction favors exchange with one fluorine group rather than with two by approximately a 6:1 margin

$$(CH_3)_2GeF_2 + (CH_3)_3SiOC(O)CCl_3 \rightarrow \underset{(86\%)}{(CH_3)_2GeFOC(O)CCl_3} + \underset{(14\%)}{(CH_3)_2Ge(OC(O)CCl_3)_2} + (CH_3)_3SiF \qquad (3)$$

The silyl and germyl trihaloacetates are clear, colorless liquids which are all, except for trimethylgermyl trichloroacetate, sufficiently volatile to be handled easily under vacuum-line conditions. As is the case with its acetate[2,14] and trifluoroacetate[4] counterparts, germyl trichloroacetate undergoes decomposition on prolonged standing at room temperature to yield trichloroacetic acid, germane, and polygermane $(GeH)_x$. Apart from this observation the remainder of the trichloroacetates demonstrate marked thermal stability.

Cleavage Reactions. Chemical characterization of the R_3M moiety in the trifluoroacetates and trichloroacetates may be achieved via cleavage of the Ge–O or Si–O bond with an excess of a gaseous halogen halide. In the case of silicon, the Si–O bond is stronger than the Si–X (X = Cl, Br, I) counterpart; thus reactivity will depend upon pressure and the amount of the hydrogen halide used. Under similar conditions, trimethylsilyl trichloroacetate was allowed to react with HCl, HBr, and HI. The results showed that the degree of cleavage was of the order Cl > Br > I which is also the trend for the Si–X bond energies.

^1H NMR Spectra. The ^1H NMR parameters for the silyl and germyl trihaloacetates are summarized in Table I. The chemical shifts of the M–H resonances in Table I may be compared to those of the related acetate,[13,15] thiolacetate,[9] and formate[13] species, viz., $H_3SiOC(O)CH_3$ 4.47, $H_3SiOC(S)CH_3$ 4.61, $H_3SiOC(O)H$ 4.55, $H_3GeOC(O)CH_3$ 5.36, $H_3GeSC(O)CH_3$ 4.62, and $H_3GeOC(O)H$ 5.51 ppm downfield of internal tetramethylsilane. The $\delta(CH_3)$ resonance for the germyl trihaloacetates shifts to lower field as the methyl substitution increases and as the halide changes from fluorine to chlorine. This is the case with the corresponding halo(methyl)germanes.[1,16] A less pronounced shift occurs in the silicon counterparts. When observing the M–H resonances, the Si–H resonances are to higher field than the corresponding Ge–H resonances and there is a shift to lower field with increasing methyl substitution in the germyl trihaloacetates. However, as one goes from the trifluoroacetates to the trichloroacetates, the M–H resonance shifts to lower field which is the opposite effect to the related halosilanes and -germanes.[17,18]

Mass Spectra. The polyisotopic nature of silicon and particularly of germanium combined with extensive hydrogen stripping hinders the detailed assignment of the mass spectra of $H_3MOC(O)CCl_3$. However, fragmentation patterns can be obtained (Table II) by summing the hydrogen loss. This pattern parallels that of the trifluoroacetate analogues.[4] The predominant ion for $H_3GeOC(O)CCl_3$ is $[GeH_n]^+$ suggesting

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Table I. ^1H NMR Parameters[a] of the Silyl and Germyl Trihaloacetates

Compd	$\delta(CH_3)$	$\delta(MH)$ (M = Si, Ge)	$\lvert J_{HH}^{vic} \rvert$	$\lvert J_{CH} \rvert$	$\lvert J_{^{29}SiH} \rvert$
$H_3SiOC(O)CF_3$ [b,c]		4.68			242.1
$(CH_3)_3SiOC(O)CF_3$	0.43			120.1	7.5
$H_3SiOC(O)CCl_3$		4.79			241.9
$(CH_3)_3SiOC(O)CCl_3$	0.44			120.7	7.3
$H_3GeOC(O)CF_3$ [d]		5.88			
$CH_3GeH_2OC(O)CF_3$	0.95	6.01	2.93	132.9	
$(CH_3)_2GeHOC(O)CF_3$	0.83	6.09	2.48	130.1	
$(CH_3)_3GeOC(O)CF_3$	0.69			128.4	
$H_3GeOC(O)CCl_3$		5.89			
$(CH_3)_2GeHOC(O)CCl_3$	0.92	5.94	2.93		
$(CH_3)_3GeOC(O)CCl_3$	0.74			129.1	

[a] The spectra were recorded at room temperature in CCl_4 solution (ca. 5% v/v). Chemical shifts ($\delta \pm 0.02$ ppm) are in ppm to the low field of tetramethylsilane as internal standard. Coupling constants are in Hz; deviations are $J_{HH} \pm 0.05$, $J_{^{13}CH} \pm 0.2$, and $J_{^{29}SiH} \pm 1$ Hz (neat liquid). [b] Reference 13. [c] Reference 15. [d] Reference 4.

Table II. Mass Spectra of Silyl and Germyl Trichloroacetates[a]

Ion family	Percentage of metal-containing ions[b] Si	Ge
$[MH_n(O_2CCCl_3)]^+$		
$[MH_n(O_2CCCl_2)]^+$	0.2	13.0
$[MH_n(O_2CCCl)]^+$	0.3	
$[MH_n(O_2CC)]^+$	2.7	1.4
$[MH_n(O_2CCl)]^+$	3.0	1.4
$[MH_n(OCCl)]^+$	0.6	0.6
$[MH_n(O_2Cl)]^+$	7.9	2.5
$[MH_n(O_2C)]^+$	36.8	12.4
$[MH_n(OC)]^+$	0.9	1.9
$[MH_nCl]^+$	7.9	12.2
$[MH_nO]^+$	9.3	4.2
$[MH_nC]^+$	4.9	4.4
$[MH_n]^+$	25.5	46.0

[a] The mass spectra are summed over n in each ion family from 0 to 3. [b] Other non-metal-containing peaks may be attributed to $[C(O)Cl]^+$, $[OCO]^+$, $[CO]^+$, $[CCl_3]^+$, $[CCl_2]^+$, $[CCl]^+$, and $[Cl]^+$.

a loss of CCl_3CO_2 via Ge–O bond cleavage. The silicon species is less susceptible to such cleavage, as expected from the relative strength of the Si–O bond, and its predominant ion $[SiH_nO_2C]^+$ arises from loss of CCl_3. Rearrangements occur by Cl migration giving $[MH_nOC(O)Cl]^+$ and $[MH_nCl]^+$ and by CO_2 elimination giving $[MH_nC]^+$.

Vibrational Spectra. The infrared and Raman spectra of silyl and germyl acetates and trifluoroacetates have appeared elsewhere.[3,4,14,19] Principal features for the new trichloroacetate species are based on these results, as well as on the spectra of the parent acid[20] and trimethyltin trichloroacetate.[21] Assignmments above 500 cm^{-1} agree well with the related compounds, but due to the complexity of the molecular skeleton, assignments below 500 cm^{-1} are only generalized to include δ skeleton and skeletal modes. Peaks attributable to $\delta(CCO)$, $\rho(CCl_3)$, and $\delta(COM)$ should occur in this region. A comparison of the $\nu(C{=}O)$ and $\nu_{as}(M{-}H)$ frequencies in the infrared for the $H_3MOC(O)CX_3$ (M = C, Si, Ge; X = H, F, Cl) derivatives is displayed in Table III. From this, it can be seen that the carbonyl frequencies are in the order C > Si > Ge when referring to the metal atom and F > Cl > H when observing the acid substituent. A shift in the carbonyl frequency to higher wavenumber reflects the presence of more electron-withdrawing groups in the molecule. A similar but less pronounced effect exists with the $\nu_{as}(M{-}H)$ mode where the trifluoroacetate species affords the highest frequency followed by the trichloroacetate and acetate derivatives. The changes in the values of $\nu(Si{-}H)$ in the $H_3SiOC(O)CX_3$ series match the value of the corresponding direct coupling constant J_{Si-H}, namely: $\nu(Si{-}H)$ 2226 (F),[19] 2224 (Cl), 2214 cm^{-1} (H);[19] J_{Si-H} (Hz) = 242.1 (F),[13] 241.9 (Cl), 231.3 (H).[13] This is consistent with the concept that the apparently stronger bond (as is indicated by the high frequency) will have the higher s-bond character for silicon (as is indicated by the coupling constant assuming the Fermi contact term is the most important). The remainder of the spectra for the silyl and germyl trichloroacetates are comparable to the acetate and trifluoroacetate analogues and are summarized in Table IV.

X-Ray Photoelectron Spectra. All of the core-level binding energies for the series $(CH_3)_3SiOC(O)CX_3$ are displayed in Table V. The changes in the carbon 1s binding energy of the methyl groups attached to silicon parallel closely the changes in chemical shift noted in the ^1H NMR spectra: thus for $(CH_3)_3SiOC(O)CX_3$ for X = F, 290.1 (0.43); X = Cl, 290.1 (0.44); X = H, 289.7 eV (0.25 ppm). For the similar germanium series the effect is identical: X = F, 290.7 (0.83); X = Cl, 290.4 (0.74); X = H, 290.2 eV (0.53 ppm). Thus the increased shielding of the proton along the series X = F → Cl → H is paralleled by the lowering in the binding energy as is generally to be expected.[22]

There are more marked changes in the binding energies of the carbon atom directly attached to F, Cl, or H. With the CX_3 groups of both the silicon and germanium series, the highest binding energy and hence relatively highest positive charge reside on carbon attached to fluorine. Indeed, as has been noted elsewhere,[23] all of the corresponding binding energies, O 1s, Si 2p, and Ge 3d, parallel this increase indicating the greater "stiffness" of the molecule with fluorine relative to hydrogen.

The two O 1s peaks are clearly separated in the spectra of $(CH_3)_3GeOC(O)CCl_3$ and $(CH_3)_3GeOC(O)CH_3$ and the binding energy chemical shifts are typical of an acetate (e.g., methyl acetate).[24] In this respect we apparently have another example of germanium "behaving more like carbon than silicon". In the silicon series, the two oxygen-binding energies were so close as to only give one envelope. It is tempting to speculate that this could indicate that both oxygen atoms, in the silicon cases, are involved in π interactions, in contrast to no significant π-bonding participation by carbon or germanium in the single bond to oxygen.

Experimental Section

The apparatus and ^1H NMR, infrared, and Raman techniques were as described previously.[8] Mass spectral data were obtained using a Varian MAT CH5 double-focusing spectrometer equipped with an INCOS 2000 computer system at an ionizing potential of 70 eV. Core-electron binding energies were determined on a McPherson ESCA-36 photoelectron spectrometer, using magnesium Kα x radiation (1253.6 eV) for photoelectron excitation. Silyl and germyl halides were prepared from the parent hydride by standard methods[1,26] while $(CH_3)_3SiCl$ and $(CH_3)_3GeBr$ were obtained commercially. Conversion to the corresponding carbodiimide was accomplished by halide metathesis reactions with lead cyanamide.[8] Trifluoroacetic and trichloroacetic acids were degassed at −45 °C prior to use. Fluo-

Table III. Comparison of $\nu(C{=}O)$[a] and $\nu_{as}(M{-}H)$ Infrared Frequencies (cm^{-1}) for $H_3MOC(O)CX_3$ Species: M = C, Si, Ge; X = H, F, Cl

Mode	$H_3MOC(O)CF_3$			$H_3MOC(O)CCl_3$			$H_3MOC(O)CH_3$		
	C[b]	Si[c]	Ge[d]	C[b]	Si	Ge	C[b]	Si[c]	Ge[d]
$\nu(C{=}O)$	1805	1795	1775	1775	1759	1739	1748	1750	1730
$\nu_{as}(M{-}H)$		2226	2159		2224	2152		2214	2143

[a] The parent acids show infrared (CCl_4 solution) absorptions for $\nu(C{=}O)$ as follows: HOC(O)CF_3 1785 cm^{-1}, HOC(O)CCl_3 1750 cm^{-1}, HOC(O)CH_3 1695 cm^{-1}. [b] Reference 32. [c] Reference 19. [d] Reference 4.

Table IV. Vibrational Spectra (cm^{-1}) of Silyl and Germyl Trichloroacetate Derivatives[a]

$H_3SiOC(O)CCl_3$[b]		$(CH_3)_3SiOC(O)CCl_3$		$H_3GeOC(O)CCl_3$		$(CH_3)_3GeOC(O)CCl_3$		
IR (soln)	Raman (liq)	IR (soln)	Raman (liq)	IR (soln)	Raman (liq)	IR (soln)	Raman (liq)	Tentative assign (M = Si, Ge)
		2985 sh	2992 sh			2988 sh	3000 mw	$\nu(CH_3)$
		2964 mw	2969 mw, dp			2968 mw		
		2903 w	2908 s, p			2917 w	2925 s	
2224 ms	2243 sh			2152 m	2173 sh			$\nu(MH_3)$
2208 sh	2213 vs, p			2130 m	2136 vs, p			
1759 s	1753 m, p	1757 s	1752 m, p	1739 s	1722 w, p	1731 s	1740 mw	$\nu(C{=}O)$
		1411 w	1412 w, dp			1410 w	~1402 vvw	$\delta(CH_3)$
		1260 s	1262 w, sh			1263 mw	1265 vw	
						1248 mw	1241 w	
1265 s	1262 w, p	1271 s	1270 w, p	1277 s	1294 w, p	1285 s	~1291 vvw	$\nu(C{-}O)$
980 w	979 sh	972 m	971 w	969 w	965 w	962 m	967 w	$\nu(C{-}C)$
949 m	942 m, dp			862 m	848 m, dp			$\delta(MH_3)$
931 vs	931 sh, dp			833 s	838 sh, dp			
790 sh	790 m, p	776 mw[c]	776 mw, p	775 sh	772 m, p	~780 sh	772 vw	$\nu(CCl_3)$
678 mw	684 sh, dp	681 m	683 sh, dp	690 m	690 mw, dp	686 s	683 w	$\pi(CCO_2)$?
		860 s	863 mw, dp			851 s	868 w	$\rho(CH_3)$
		832 m	834 mw, dp			834 s	839 w	
						743 ms	743 w	
728 sh	731 m, p	736 mw[c]	732 m, p					$\nu(Si{-}O)$
		701 sh	697 m, dp					
		622 vw[c]	616 s, p			597 m	579 s	$\nu(M{-}C)$
~716 sh	718 sh, dp			625 mw	632 sh, dp			$\rho(MH_3)$
661 sh	669 m, dp			575 vw	589 sh, dp			
				639 w	632 sh	634 ms	631 m	$\nu(Ge{-}O)$
573 w	~576 vvw	568 vw	575 vw	530 vw	522 w, p	~519 vvw	513 vw	$\delta(OCO)$
435 vw	437 vs, p	445 vw	436 vs, p	437 vw	435 vw, p	448 vw	434 m	δ(skeleton and skeletal modes)
370 w	381 ms, p	381 sh	377 m, p	370 w	362 s, p	351 w	357 mw	
	280 ms, dp		277 m, dp		285 s, dp		289 mw	
	263 sh		261 sh		238 sh		240 sh	
	239 m, dp		237 m, dp		223 s, dp		231 m	
	202 m, dp		184 m, dp		205 s, dp		195 sh	
	187 ms, p		168 m, dp?)		173 vs, p		166 s	
	131 mw						112 mw	
			85 sh		99 sh		72 sh	

[a] The spectra were recorded at room temperature. Key: s, strong; m, medium; w, weak; v, very; sh, shoulder; p, polarized; dp, depolarized. [b] Unassigned bands (cm^{-1}) in the infrared (Raman) at 858 m (861 m, dp), 829 m (834 m, dp), and (314 m, p). [c] Gas-phase spectrum.

Table V. Core-Electron Binding Energies[a] (eV) for the Silyl and Germyl Acetates and Trihaloacetates

	Compd (M = Si, Ge)					
	$(CH_3)_3MOC(O)CF_3$		$(CH_3)_3MOC(O)CCl_3$		$(CH_3)_3MOC(O)CH_3$	
Core level	Si	Ge[b]	Si	Ge	Si	Ge
C 1s *C*H$_3$	290.10	290.71	290.10	290.37	289.71	290.21
C 1s O(*C*)O	290.10	290.71	290.10	290.37	289.71	290.21
C 1s *C*X$_3$	295.72	295.57	295.09	295.24		
O 1s M*O*C	539.15	539.61	538.75	538.60	537.25	538.20
O 1s C=O	539.15	539.61	538.75	540.13	537.25	540.05
Si 2p	107.13		106.78		106.52	
Ge 3d		37.79		37.27		37.02
F 1s	694.37	694.58				
Cl $2p_{3/2}$			206.66	n.o.[c]		

[a] Values corrected to Ar $2p_{3/2}$ = 248.63 eV, uncertainty ±0.05 eV, except that Si 2p and Ge 3d are reported relative to Ne 2s at 48.47 eV.[33] [b] For the Ge species, the compound was $(CH_3)_2GeHOC(O)CF_3$. [c] Due to the small quantity of $(CH_3)_3GeOC(O)CCl_3$ used, the Cl $2p_{3/2}$ level could not be observed.

Table VI. Protolysis Reactions of $(R_3MN:)_2C$ Species with Trifluoro- and Trichloroacetic Acids[a]

$$\underset{\text{I}}{(R_3MN:)_2C} + 2HOC(O)CX_3 \rightarrow \underset{\text{II}}{2R_3MOC(O)CX_3} + 0.5(H_2NCN)_2$$

	X = F			X = Cl		
R_3M	Amt of I, mmol	Amt of II, mmol	Yield, %	Amt of I, mmol	Amt of II, mmol	Yield, %
H_3Ge	0.21	0.36	86	0.61	1.01	83
$(CH_3)_3Ge$	1.65	2.91	88	0.43	0.73	86[b]
H_3Si	0.42	0.70	83	2.99	4.83	81
$(CH_3)_3Si$	0.65	1.17	90	1.13	2.10	93[c]

[a] Ca. 5% excess acid used in all cases. [b] Found for $(CH_3)_3GeOC(O)CCl_3$: mp 54.6 ± 0.2 °C; vp (25 °C) <1 Torr. [c] Found for $(CH_3)_3SiOC(O)CCl_3$: mp 18.7 ± 0.2 °C; vp (25 °C) ca. 1.5 Torr.

Table VII. Exchange Reactions of Fluorogermanes with Trimethylsilyl Trihaloacetates[a]

$$\underset{\text{I}}{R_3GeF} + (CH_3)_3SiOC(O)CX_3 \rightarrow \underset{\text{II}}{R_3GeOC(O)CX_3} + (CH_3)_3SiF$$

	X = F			X = Cl		
R_3Ge	Amt of I, mmol	Amt of II, mmol	Yield, %	Amt of I, mmol	Amt of II, mmol	Yield, %
H_3Ge	0.72	0.68	94	1.38	1.15	92
CH_3GeH_2	0.95	0.85	89	0.94	0.86	91
$(CH_3)_2GeH$	0.76	0.69	91			
$(CH_3)_3Ge$	0.25	0.23	92	0.51	0.48	94

[a] Excess of the fluoride was used in most cases.

rogermanes were prepared by the reaction of iodogermanes with PbF_2.[1,16,27]

Preparation of the Silyl and Germyl Trihaloacetates. (a) Reaction of $(R_3MN:)_2C$ with $HOC(O)CX_3$ (R = H, CH_3; M = Si, Ge; X = F, Cl). In a typical experiment, $HOC(O)CCl_3$ (6.84 mmol) was placed into a reaction vessel (volume ca. 50 mL equipped with a Teflon stopcock) and degassed at −45 °C. Next, $(H_3SiN:)_2C$ (2.99 mmol) was condensed into the reaction vessel at −196 °C. The mixture was isolated and allowed to warm to room temperature and react for ca. 10 min. Fractionation of volatile products through traps at −78 and −196 °C gave $H_3SiOC(O)CCl_3$ (4.83 mmol, 81%; vp ca. 3 Torr at 25 °C; P *m/e* 154–161 $(C_2H_nSiO_2Cl_2)^+$) in the former and traces of monosilane, identified by its IR spectrum,[28] in the latter. Some hydrogen was formed (in all other cases, no hydrogen was formed). An involatile white material remaining in the vessel (mp ca. 210 °C; soluble in H_2O, acetone; insoluble in CCl_4, CS_2, C_6H_6) was shown from its IR spectrum[29] to be dicyanodiamide. Details of all reactions are given in Table VI.

(b) Reaction of $(CH_3)_nH_{3-n}GeF$ with Trimethylsilyl Trihaloacetates. Typically, $(CH_3)_3SiOC(O)CCl_3$ (1.38 mmol) and H_3GeF (1.25 mmol) were condensed into a reaction vessel (see part a) held at −196 °C. The vessel was isolated, and the contents were allowed to warm to room temperature and react for 30 min. The volatile products were distilled through traps at −45 and −196 °C. The −45 °C trap retains $H_3GeOC(O)CCl_3$ (1.15 mmol, 92%; vp <1 Torr at 25 °C; P *m/e* 196–209 $(C_2H_nGeO_2Cl_2)^+$) and a slight trace of $(CH_3)_3SiOC(O)CCl_3$ (ca. 0.1 mmol) identified by its ^1H NMR spectra. The −196 °C trap contains $(CH_3)_3SiF$ (ca. 1.20 mmol) identified by its ^1H NMR parameters.[30] No hydrogen was formed. Details of all reactions are given in Table VII.

Cleavage Reactions Of Trimethylsilyl Trichloroacetate. (a) Reaction of Trimethylsilyl Trichloroacetate with Hydrogen Halides. Typically, $(CH_3)_3SiOC(O)CCl_3$ (1.23 mmol) and HCl (ca. 4 mmol) were condensed, in vacuo, into a reaction flask (as described in the preceding section a) held at −196 °C. The vessel was isolated, and the contents were allowed to warm to room temperature and react for 45 min. The volatile components were then fractionated through traps held at −78 and −196 °C. The former trap contained trichloroacetic acid, trimethylchlorosilane (1.07 mmol, 87%), and unreacted trimethylsilyl trichloroacetate (0.16 mmol, 13%). The latter trap held unreacted HCl (ca. 2.8 mmol). When HBr was used in an analogous procedure, the products were trimethylbromosilane (1.31 mmol, 75% conversion based on $(CH_3)_3SiOC(O)CCl_3$), trimethylsilyl trichloroacetate (0.43 mmol, 25%), trichloroacetic acid, and unreacted HBr, while with HI the products were trimethyliodosilane (0.15 mmol, 10% conversion based on $(CH_3)_3SiOC(O)CCl_3$), trimethylsilyl trichloroacetate (1.33 mmol, 90%), trichloroacetic acid, and unreacted HI. All components in the above reactions were identified by their ^1H NMR spectra.

(b) Reaction of Trimethylsilyl Trichloroacetate with Me_2GeF_2. Trimethylsilyl trichloroacetate (1.24 mmol) and difluoro(dimethyl)germane (1.72 mmol) were distilled into a Pyrex-glass tube (ca. 2-mm o.d.) held at −196 °C and sealed, and the contents were allowed to react overnight at room temperature. The subsequent ^1H NMR spectra showed peaks attributable to Me_3SiF (34.5% based on integration), $Me_3SiOC(O)CCl_3$ (2.7%), Me_2GeF_2 (31.8%), $Me_2Ge(OCOCCl_3)_2$ (δ(Me) 1.30 ppm, 4.3%), and $Me_2GeFOC(O)CCl_3$ (δ(Me) 1.08 ppm, $\delta(Si^{19}F)$ −4.47 ppm relative to Me_3SiF, $J_{HF}{}^{vic}$ = 6.1 Hz, 26.7%).

(c) Reaction of Trimethylsilyl Trichloroacetate with BF_3. Trimethylsilyl trichloroacetate (1.56 mmol) and boron trifluoride (ca. 3 mmol) were distilled, in vacuo, into a reaction vessel as described previously. The contents were isolated and allowed to react at room temperature for 45 min. The volatile products were subsequently fractionated using baths held at −112 and −196 °C. The latter contained BF_3, identified by its infrared spectrum,[31] while the former contained trimethylsilyl trichloroacetate (0.80 mmol, 51% based on integration) and trimethylfluorosilane (49%). The other product from the reaction was assumed to be $BF_n(OC(O)CCl_3)_{3-n}$, $n = 0 \rightarrow 2$.

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Registry No. $H_3GeOC(O)CF_3$, 58272-98-3; $(CH_3)_3GeOC(O)CF_3$, 7610-08-4; $H_3SiOC(O)CF_3$, 6876-44-4; $(CH_3)_3SiOC(O)CF_3$, 400-53-3; $H_3GeOC(O)CCl_3$, 62600-93-5; $(CH_3)_3GeOC(O)CCl_3$, 62600-94-6; $H_3SiOC(O)CCl_3$, 62600-95-7; $(CH_3)_3SiOC(O)CCl_3$, 25436-07-1; $CH_3GeH_2OC(O)CF_3$, 62625-10-9; $(CH_3)_2GeHOC(O)CF_3$, 62600-96-8; $CH_3GeH_2OC(O)CCl_3$, 62600-97-9; $(CH_3)_3SiOC(O)CH_3$, 2345-38-2; $(CH_3)_3GeOC(O)CH_3$, 1118-13-4;

HOC(O)CF$_3$, 76-05-1; HOC(O)CCl$_3$, 76-03-9; (H$_3$GeN:)$_2$C, 10592-53-7; ((CH$_3$)$_3$GeN:)$_2$C, 30006-65-6; (H$_3$SiN:)$_2$C, 4468-88-6; ((CH$_3$)$_3$SiN:)$_2$C, 1000-70-0; H$_3$GeF, 13537-30-9; CH$_3$GeH$_2$F, 30123-02-5; (CH$_3$)$_2$GeHF, 34117-35-6; (CH$_3$)$_3$GeF, 661-37-0; (CH$_3$)$_3$SiCl, 75-77-4; (CH$_3$)$_3$SiBr, 2857-97-8; (CH$_3$)$_3$SiI, 16029-98-4; (CH$_3$)$_3$SiF, 420-56-4; Me$_2$GeF$_2$, 811-70-1; Me$_2$Ge(OC(O)CCl$_3$)$_2$, 62600-98-0; Me$_2$GeFOC(O)CCl$_3$, 62600-99-1; BF$_3$, 7637-07-2; HCl, 7647-01-0; HBr, 10035-10-6; HI, 10034-85-2; (CH$_3$)$_2$GeHOC(O)CCl$_3$, 62601-00-7.

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Photoelectron Spectra of Tris(dialkylaminophosphines). A Controversy

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The photoelectron spectra of tris(dimethylaminophosphine) (I), tris (diethylaminophosphine) (II), and tris(dipropylaminophosphine) (III) have been studied in an effort to resolve a controversy pertaining to the interpretation of the spectrum of I. The current interpretation concludes that I, II, and III have C_s skeletal symmetry with two nitrogen lone pairs interacting in a σ manner, while the remaining nitrogen lone pair interacts in a π fashion with the phosphorus lone pair. The second and third ionization bands correspond to the phosphorus–nitrogen lone-pair interaction.

Several laboratories recently have been using ultraviolet photoelectron spectroscopy to predict conformational geometries, particularly for molecules containing "lone-pair" electrons.[1] The rapid time scale of the ionization process in photoelectron spectroscopy (Franck–Condon transitions) permits observation of the spectrum of the predominant conformation (or conformations) of a molecule even though low barriers to bond rotations allow rapid equilibration of geometries. This technique therefore avoids the "time-averaged" spectra which complicate the utilization of NMR in conformational analysis studies. This technique is particularly useful in studying compounds having electrons in nonbonding orbitals on adjacent atoms since such orbitals interact to produce symmetric and antisymmetric molecular orbitals if they are oriented in a manner such that the two orbitals are not orthogonal. The magnitude (or presence or absence) of these interactions can therefore be utilized to deduce the conformations of this type of molecule.

Cowley and co-workers[2] first reported the photoelectron spectrum of tris(dimethylaminophosphine) (I). On the basis primarily of comparison with the spectra of several aminophosphines which contain one or more fluorine atoms, they concluded that I must have C_s symmetry with two of the nitrogen lone pairs interacting in a σ fashion, while the remaining N lone pair interacts in a π manner with the phosphorus lone pair. Furthermore, they assigned the first and third ionization bands for I ($I_1 = 7.61$ eV, $I_3 = 8.86$ eV) to correspond to the two interacting sets of N lone pairs, while the second and fourth bands ($I_2 = 7.89$ eV, $I_4 = 9.98$ eV) were attributed to the interacting N and P lone pairs. The authors suggested that an early electron diffraction study[3] of I, which was interpreted to indicate that the molecule has a C_3 axis of symmetry, needed to be reinterpreted. Later, Lappert and co-workers[4] reexamined the photoelectron spectrum of I in connection with a study of several haloaminophosphines. The latter workers criticized the Cowley interpretation and suggested that I has C_{3v} symmetry with all of the N lone pairs interacting in a π fashion with P and with each other. Such an interpretation dictates that bands I_1 and I_4 at 7.30 and 9.80 eV in their spectrum be assigned to the a_1 combination of N and P, while bands I_2 and I_3 at 7.95 and 8.60 eV must be attributed to the Jahn–Teller split ^{2}E ionic state which has no P lone-pair contribution.[5] Thus, the Cowley interpretation proposes that the highest occupied molecular orbital for I