coupling constants because the value of γ is still unknown for covalently bonded bromine.

Registry No. $POBr_3$, 7789-59-5.

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Germanium Atoms in Synthesis

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The low-temperature cocondensation technique, originally developed for synthetic purposes by Skell,[1] has been extended to many elements and other short-lived molecular species,[2] and this, combined with the advances in matrix-isolation spectroscopy,[3] has opened new vistas to the chemist. Although carbon has been extensively studied,[4] few forays have been made into the chemistry of the remaining group IV elemental species.[5] We now wish to report on some reactions of germanium atoms whereby halides of carbon and silicon are converted, in modest yields, into trihalogermyl derivatives

$$Ge + 3MX_n \rightarrow MX_{n-1}GeX_3 + (MX_{n-1})_2$$

Experimental Section

Atomic germanium vapor, produced in an evacuated apparatus described elsewhere,[2c,6] was codeposited at −196° with the appropriate group IV halide, the excess unreacted substrate was removed at −78°, and the less volatile products were fractionally sublimed *in vacuo*. The products were identified mass spectrometrically. The mass spectra of compounds containing both chlorine and germanium are complicated by the relationship $2 \times {}^{35}Cl \equiv 1 \times {}^{70}Ge$ ($= m/e$ 70). To avoid fallacious assignments the previously tabulated[7] isotopic contributions of various combinations of Ge_xCl_y were used.

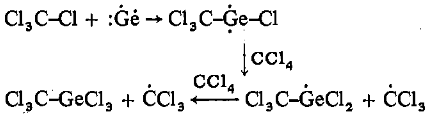
Trichloromethyltrichlorogermane was identified by comparison of its mass spectrum and melting point (106°) with published data.[7,8] CCl_3GeCl_3 sublimes as colorless leaf-shaped crystals. Dichloromethyltrichlorogermane is a high-boiling liquid[9] showing ν_{max}(C–H) at 2975 cm^{-1}. The mass spectrum shows major peaks attributable to $CGeCl_5^+$, $CGeCl_4^+$, $CGeCl_3^+$, $GeCl_3^+$, $GeCl_2^+$, CCl_3^+, and $CHCl_2^+$. Trichlorosilyltrichlorogermane is an involatile liquid showing major peaks assignable to $SiGeCl_6^+$, $SiGeCl_5^+$, $GeCl_4^+$, $SiCl_4^+$, $GeCl_3^+$, and $SiCl_3^+$. Mass spectra were recorded on a CEC 21-110-B spectrometer operating at 70 eV with an inlet temperature of 150°.

Results and Discussion

Reaction of Ge atoms with CCl_4 yields CCl_3GeCl_3 (20%) and C_2Cl_6. The fact that $(GeCl_3)_2CCl_2$ is readily isolable[7] from the reaction of carbon atoms with $GeCl_4$ precludes the possibility that $(CCl_3)_2GeCl_2$ was produced but not isolated in the present reaction; the latter compound would be expected to be even more volatile and hence more easily pumped out of the reaction system. $SiCl_4$ reacts similarly to produce $GeCl_3SiCl_3$ (10%); this compound had previously been postulated as an intermediate in the reaction of $GeCl_2$ with $SiCl_4$ but was claimed to be unstable.[10] A tentative claim has also been made by Urry[11] that $GeCl_3SiCl_3$ is formed upon heating $Cl_3Si{-}Hg{-}GeCl_3$. The physical similarities of that compound and of the one produced in the present study indicate that Urry's tentative assignment was probably correct. When $CHCl_3$ was used as the substrate, the only germane formed was $CHCl_2GeCl_3$ (8%) indicating that no C–H insertion or abstraction occurred; presumably this is a reflection of the relative C–H and C–Cl bond strengths (96 and 72 kcal/mol, respectively).[12]

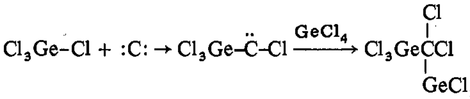
It is interesting to note that ethyl chloride fails to react under cocondensation conditions, perhaps indicating that the well-known direct synthesis of alkylgermanium halides[13] does not involve germanium insertion to give intermediate germenes but is rather a radical-initiated process. Moreover, these industrial processes are catalyzed by copper which Timms[14] has shown to be an excellent dehalogenating agent.

Germanium atoms possess a ^3P ground state and at the temperature of vaporization (~1250°) less than 0.1% would be expected to be in the ^1D or ^1S excited states.[15] Thus, unlike carbon[4] and silicon[5c] atoms which are best generated using an arc or electron gun, respectively, the chemistry should be essentially that of ground-state germanium. The data are rationalizable on the basis of an intermediate triplet germene which then abstracts halogens in a stepwise manner characteristic of radicals



$$\begin{tikzcd}[column sep=small] Cl_3C{-}Cl + :\dot{G}\dot{e} \arrow[r] & Cl_3C{-}\dot{G}\dot{e}{-}Cl \arrow[d, "CCl_4"] \\ Cl_3C{-}GeCl_3 + \dot{C}Cl_3 & Cl_3C{-}\dot{G}eCl_2 + \dot{C}Cl_3 \arrow[l, "CCl_4"'] \end{tikzcd}$$

Such a scheme is analogous to the reactions of ^3P carbon atoms with alkyl halides to produce trihalomethyl derivatives[4] and contrasts with the behavior of ^1D or ^1S carbon atoms which undergo double insertions characteristic of successive singlet carbene reactions[7]



$$Cl_3Ge{-}Cl + :C: \rightarrow Cl_3Ge{-}\ddot{C}{-}Cl \xrightarrow{GeCl_4} Cl_3Ge\overset{Cl}{\underset{GeCl_3}{C}}Cl$$

Mechanistic analogies may also be found in the elegant studies of the chemistry of SiF_2 and GeF_2 by Margrave and his coworkers.[16,17]

Thus, the cocondensation procedure provides another viable synthetic route to organogermanium compounds; it is also more selective in its mode of attack than "hot" Ge atoms produced by nuclear recoil methods.[5d]

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Registry No. Ge, 7440-56-4.

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Synthesis of Organotin Mixed Dihalides

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A study of functional group exchange on both methylsilicon and methylgermanium residues shows it not to deviate substantially from randomness in the case of halogens,[1] except with fluorine, when the least methylated silicon residue is preferentially fluorinated.[2] Consequently yields of mixed dihalogenosilanes are less than 50%.[3] Exchange between methylsilicon and methylgermanium moieties shows the heavier halogen to prefer the heavier metalloid,[1] as would be predicted from bond energies.[4]

Mixed organotin dihalides were first reported almost a century ago. Ph_2SnClX (X = Br or I) were prepared from the dichloride and the corresponding hydrogen halide. Bromination of 1,3-dichlorotetra-*n*-butylditin oxide yields di-*n*-butyltin chloride bromide in 60% yield as the only tin dihalide. This is also formed in good yield by recrystallizing or redistilling an equimolar mixture of $(n\text{-Bu})_2SnCl_2$ and $(n\text{-Bu})_2SnBr_2$.[5]

This note describes the synthesis of the dialkyltin dihalides R_2SnXY (R = Me, Et, or *n*-Bu; XY = ClBr, ClI, or BrI) by the redistribution method (A) just mentioned or by the halogen exchange (B) between silicon and tin. This latter method is

$$R_2SnX_2 + R_2SnY_2 \rightarrow 2R_2SnXY$$

$$R_2SnX_2 + Me_3SiY \rightarrow R_2SnXY + Me_3SiX$$

normally exothermic for monohalogen-substituted species with the heavier halogen preferring tin and can also be used to prepare the dialkyltin dihalides R_2SnX_2

$$R_3SnX + Me_3SiY \rightarrow Me_3SiX + R_3SnY$$

(R = Me or *n*-Bu; X, Y = Cl, Br, or I with Y heavier than X)

$$R_3SnF + Et_3SiX \rightarrow R_3SnX + Et_3SiF$$

(R = *n*-Bu or Ph; X = Cl, Br, or I)

e.g.

$$(n\text{-Bu})_2SnCl_2 + 2Et_3SiI \rightarrow (n\text{-Bu})_2SnI_2 + 2Et_3SiCl$$

Though all the mixed dihalides can be prepared by one of these two methods, few can be made by both. Neither method has been found suitable for tin fluoride halides, though two such compounds have been reported, using NaF or HF as the fluorinating agent[6]

$$(R = t\text{-Bu})\ R_2SnClF \xleftarrow{NaF} R_2SnCl_2 \xrightarrow{HF} R_2SnClF\ (R = Me)$$

Table I gives the physical characteristics of the dihalides along with the method(s) of synthesis. Yields were excellent and, apart from di-*n*-butyltin bromide iodide, were crystalline solids melting sharply at temperatures near or above those of their symmetrical precursors. All analyzed well (Table II) and their Mössbauer spectra, which show the presence of only one kind of tin nucleus as a single doublet having values of the quadrupole splitting ΔE_Q ranging from 3.0 to 3.5 mm sec^{-1}, support the absence of mixtures.[7]

Apart from diethyltin chloride iodide, all the mixed dihalides appear to be stable pure, but in solution the ^{119}Sn nmr spectra show the mixed methyl and ethyl iodides to randomize.[8] Only one absorption is observed for $R_2SnClBr$ (R = Me or Et) supporting a single species or very rapid halogen exchange. This parallels the proton nmr observations on methyltin mono-, di-, and trihalide mixtures, which showed the presence of mixed species.[9] None were isolated so, apart from di-*n*-butyltin chloride bromide, all the mixed dihalides reported here are new compounds.

Details of the spectroscopic results will be reported later and it is hoped to couple this with a structural study.

Experimental Section

Trimethylchlorosilane was purchased from Fluka while the bromide and iodide were prepared in good yield from $(Me_3Si)_2O$ and PBr_3 or AlI_3.[10] Triethylhalogenosilanes resulted from Et_3SiH, prepared from trichlorosilane and a Grignard reagent, using the appropriate allyl halide.

R_3SnF (R = *n*-Bu, Ph) were obtained from Phase Separations Ltd. and M and T Chemicals Inc., while Me_3SnCl and Me_2SnCl_2 resulted from the arrangement of Me_4Sn with $SnCl_4$.[11] Di-*n*-butyltin dichloride was commercially available from Albright and Wilson (Mfg.) Ltd. Diethyltin dichloride (mp 85°)[12] was prepared in almost quantitative yield by warming the oxide with excess trimethylchlorosilane.

All compounds were characterized either by analysis for at least carbon and hydrogen or by comparison of their physical properties with those of reported authentic samples. Care was taken to exclude moisture from the reactions and typical among them are the following ones.

Reaction of Me_3SiI with Me_3SnCl and with Me_2SnCl_2. The iodide (4.10 g, 1 mol) was added dropwise to trimethyltin chloride (4.06 g, 1 mol) with cooling. An exothermic reaction occurred, and after the addition was completed, the mixture was heated overnight. Volatile constituents were pumped off, trapped, and fractionated giving trimethylchlorosilane (1.6 g, 73%), bp 57°, n^{22}D 1.3884,[10] while distillation of the residue yielded trimethyltin iodide (4.7 g, 80%), bp 59° (12 mm), mp 4°, n^{22}D 1.5682 (4.7 g, 80%).[13]

Table I. Physical Characteristics of Dialkyltin Dihalides R_2SnXY and R_2SnX_2 [mp, °C (bp, °C (*P*, mm)]

	XY					
R	ClBr	ClI	BrI	Cl_2	Br_2	I_2
Me	81 (A[a])	35 (B)	48–49 (A, B)	106–107	77–78	36 (62 (1))
Et	62–63 (B[a])	*b*	47–48 (B)	85	62–64	45–46
n-Bu	33–34 (A, B) (88 (0.04))	25 (A, B) (86 (0.01)) n^{28}D 1.5378	(104 (0.04)) (A) n^{28}D 1.5635	41–42	22–23	(110 (0.01)) n^{25}D 1.6044

[a] Method of preparation of mixed dihalides: A, redistribution; B, halogenosilane exchange. [b] Et_2SnClI appeared to be labile, even as a solid.