In another series of experiments without methoxide, the addition of solid sodium borohydride (0.100 mole) to 0.400 mole of cyclohexanone in 200 ml. of methanol produced 0.08 mole (20%) of hydrogen while the addition of cyclohexanone to sodium borohydride in methanol produced 0.32 mole of hydrogen gas.

In one series of experiments cyclohexanone (0.400 mole) in methanol was added very slowly to a well-stirred solution of sodium borohydride (0.100 mole) containing methoxide (0.010 *M*). The products were 0.102 mole of cyclohexanol with 0.291 mole of unreacted cyclohexanone and 0.30 mole of hydrogen gas.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER, CANADA]

Trifluoromethyl Compounds of Germanium[1]

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The interaction of trifluoroiodomethane with germanium(II) iodide or stannous iodide has been examined. Trifluoromethyl-tin derivatives are not obtained, but with germanium(II) iodide, *trifluoromethyltriiodogermane* is formed, together with a trace of *bis-(trifluoromethyl)-diiodogermane*. Trifluoromethyltri-iodogermane has been converted to the corresponding trichloro- and trifluorogermane by reaction with the appropriate silver halide. The thermal and hydrolytic stabilities of the trifluoromethyltrihalogermanes have been investigated. With aqueous potassium fluoride, trifluoromethyltrifluorogermane gives the interesting complex, *potassium trifluoromethyl-pentafluorogermanate*, $K_2CF_3GeF_5$.

Organic derivatives of the group IV elements (Si, Ge, Sn and Pb) have been known for many years but until very recently none of their perfluoroalkyl derivatives had been reported. In alkyl or aryl compounds of the type R_4M the reactivity of the M–carbon bond increases greatly along the series M = Si, Ge, Sn, Pb. It is not surprising, therefore, that, while ultraviolet irradiation of a mixture of tetramethyllead and pentafluoroiodoethane is reported to give trimethylpentafluoroethyllead,[3] similar reactions with tetramethyltin are not successful. An alternative route to trimethyltrifluoromethyltin has been found in the reaction of hexamethylditin with trifluoroiodomethane[4]

$$(CH_3)_3Sn\text{-}Sn(CH_3)_3 + CF_3I \longrightarrow (CH_3)_3SnCF_3 + (CH_3)_3SnI$$

The success of this reaction, which proceeds under ultraviolet irradiation in excess trifluoroiodomethane as solvent, depends on the ease with which the tin–tin bond is broken. Germanium–germanium and silicon–silicon bonds are much more stable, and we have found that hexamethyldigermane and hexamethyldisilane do not react with trifluoroiodomethane under conditions where hexamethylditin reacted in good yield. In order to extend to germanium our studies on perfluoroalkyl derivatives of the group IV elements, it was therefore necessary to devise an alternative approach to the synthesis of the trifluoromethylgermanium compounds, and to this end use has been made of the strong reducing power of the germanium(II) halides.

Experimental

Volatile compounds were manipulated in a conventional vacuum system and purified by trap-to-trap distillation. Molecular weights were determined by Regnault's method.

Reaction of Germanium(II) Iodide with Trifluoroiodomethane.—Germanium(II) iodide was made from germanium(II) hydroxide and hydriodic acid according to Powell and Brewer.[5] Trifluoroiodomethane (112 g., 0.57 mole, a redistilled commercial sample) was condensed onto germanium(II) iodide (59.7 g., 0.183 mole) in a stainless steel autoclave (300 ml.). The autoclave was heated to 130–135° for 10 days and the volatile products then fractionated to give unreacted trifluoroiodomethane (84.2 g., 0.43 mole) and a small amount (0.3 g.) of a colorless liquid having a vapor pressure of about 2 cm. at 25°. Analysis identified this material as slightly impure *bis-(trifluoromethyl)-diiodogermane*.

Anal. Calcd. for $(CF_3)_2GeI_2$: CF_3, 29.7; I, 54.7; mol. wt., 465. Found: CF_3, 27.8; I, 54.2; mol. wt., 434.

Infrared absorption bands (vapor) were present at 1259 (vw), 1227 (vw), 1167 (s), 1148 (vs), 1119 (w), 1030 (w), 1035 (w), 822 (vw) and 730 (w) cm.$^{-1}$. A yellow oil remaining in the autoclave was removed from unreacted germanium(II) iodide by heating under low pressure and then redistilled *in vacuo* to give *trifluoromethyltri-iodogermane* (40 g., 0.078 mole, distillation temperature 40–42° (10^{-3} mm.), vapor pressure at ambient temperatures 0.2–0.5 mm.).

Anal. Calcd. for CF_3GeI_3: CF_3, 13.2; I, 72.9. Found: CF_3, 12.8; I, 72.8, 72.5.

The compound had f.p. 8.4° and $n^{20}{}_D$ 1.6571. Infrared absorption bands (liquid film) were present at 2240 (vw), 1253 (vw), 1126 (vs), 1038 (w) and 729 (m) cm.$^{-1}$. In the vapor phase, only low pressures were possible because of the low volatility of the compound, and absorption bands were seen at 1165 and 1143 cm.$^{-1}$.

Pyrolysis.—Trifluoromethyltri-iodogermane (3.82 g.) in an evacuated silica tube (15 ml.) was heated to 150° for 48 hr., without any change in appearance. After heating to 180° for 3 days some decomposition was apparent and fractionation of the volatile products gave two fractions; the first (0.154 g.) was shown by infrared spectroscopic examination to be mainly perfluorocyclopropane, with some perfluorocyclobutane and fluoro-olefins, while the second (0.120 g.) was shown to be a mixture of germanium tetrafluoride and tetrafluoroethylene, with a trace of silicon tetrafluoride. After removal of unchanged trifluoromethyltri-iodogermane the orange crystals remaining were identified as germanium(IV) iodide (found, m.p. 143°; lit. m.p. 144°). Thus, approximately 40% of the trifluoromethyltri-iodogermane had decomposed under the conditions used.

Trifluoromethyltrichlorogermane.—Trifluoromethyltri-iodogermane (6.75 g.) was added to carefully dried silver chloride (21.1 g.) in a tube cooled to −196°. The tube was evacuated, sealed and allowed to warm to 20°, when a vigorous reaction occurred. After being kept at 20° for 48 hr. the tube was opened and volatile products were removed

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[3] H. D. Kaesz, J. R. Phillips and F. G. A. Stone, *Chem. and Ind.*, 1409 (1959).

[4] H. C. Clark and C. J. Willis, *J. Am. Chem. Soc.*, **82**, 1888 (1960).

[5] H. M. Powell and F. M. Brewer, *J. Chem. Soc.*, 197 (1938).

and fractionated to give *trifluoromethyltrichlorogermane* (1.86 g.).

Anal. Calcd. for CF_3GeCl_3: CF_3, 27.8; Cl, 42.9; mol. wt., 249. Found: CF_3, 28.1; Cl, 41.9; mol. wt., 254.

The compound had a vapor-pressure of about 9 cm. at 20°; attempts were made to estimate its boiling-point by vapor-pressure measurements but considerable reaction with the mercury in the manometer occurred at higher temperatures. The infrared spectrum (vapor) showed the following absorption bands: 1881 (vw), 1425 (vw), 1260 (vw), 1216 (w), 1156 (vs), 1124 (w), 739 (m) cm.$^{-1}$.

Trifluoromethyltrifluorogermane.—Trifluoromethyltri-iodogermane (8.60 g.) was added to carefully dried silver fluoride (20 g.) in a tube cooled to −196°. The tube was evacuated, sealed and allowed to warm up, when a vigorous reaction occurred as the iodo compound melted. After being kept at 20° for 48 hr. the tube was opened and volatile products fractionated to give *trifluoromethyltrifluorogermane* (1.33 g.). Analysis was performed by hydrolyzing the compound with hot water, when the trifluoromethyl group appeared as fluoroform and the remaining three fluorine atoms in the molecule appeared as fluoride ion.

Anal. Calcd. for CF_3GeF_3: CF_3, 34.7; F, 28.7; mol. wt., 199. Found: CF_3, 33.8; F, 28.2; mol. wt., 200.

Vapor-pressure measurements on the solid compound gave the relationship

$$\log p_{(\text{mm.})} = 11.94 - \frac{2451}{T}$$

from which the vapor-pressure is 760 mm. at −1.7°. In a sealed tube, the compound melted at + 3°. Infrared absorption bands (vapor phase) were present at 1179 (s), 1165 (vs), 1131 (w), 1127 (w), 775 (s), 730 (m), 724 (m) and 718 (m) cm^{-1}.

Hydrolytic Reactions.—Hydrolysis of each of the compounds studied was carried out by placing a weighed sample in a tube with water or alkali, evacuating and sealing the tube and then allowing the contents to mix and react for 1-2 days. Any fluoroform produced was weighed and identified by infrared spectroscopic examination. Results are

	Yield of fluoroform		
Compound	Cold water	Hot water	Aqueous alkali
CF_3GeF_3	Nil	97%	94%
CF_3GeCl_3	Nil	71%	100%
CF_3GeI_3	2%	89%	97%

A 92% yield of fluoroform was obtained from an aqueous solution of trifluoromethyltriiodogermane on treatment with silver oxide.

When an aqueous solution of trifluoromethyltrifluorogermane was treated with potassium fluoride solution a precipitate formed immediately. The precipitate was filtered, washed with ethanol and dried to give *potassium trifluoromethylpentafluorogermanate.*

Anal. Calcd. for $K_2CF_3GeF_5$: C, 3.8; F, 48.4. Found: C, 4.0, F, 47.2.

Infrared absorption bands (KBr disc) were present at 1206 (vs), 1045 (vs), 774 (m) and 743 (m) cm.$^{-1}$. The fluorine magnetic resonance spectra of the complex germanate $K_2CF_3GeF_5$, and of the fluoride, CF_3GeF_3, have also been studied. They are fully consistent with the structures proposed below and will be described in detail elsewhere.

Discussion

The di-iodides of tin and germanium are known to react with methyl iodide on heating:

$$CH_3I + MI_2 \longrightarrow CH_3MI_3 \text{ where } M = Sn^6 \text{ or } Ge^7$$

The reaction proceeds readily with germanium (II) iodide at 100°, constituting the most convenient preparation of methyltri-iodogermane, but with stannous iodide a temperature of 160° is necessary and low yields are obtained. This difference is due to the greater reducing power of germanium(II) iodide.

When stannous iodide was heated with trifluoroiodomethane to about 150°, the compound CF_3SnI_3 was not isolated, but quantities of fluorocarbons were produced containing up to 10 carbon atoms per molecule. Trifluoroiodomethane itself is stable under the reaction conditions used, so the formation of fluorocarbons suggests that some reaction with stannous iodide is occurring, but the products are not stable and breakdown occurs, followed by polymerization, coupling etc., to produce fluorocarbons

$$\begin{gathered} \textit{e.g.}\quad CF_3I + SnI_2 \longrightarrow CF_3SnI_3 \\ CF_3SnI_3 \longrightarrow SnI_3F + (\text{-}CF_2\text{-})_n \\ CF_3I + (\text{-}CF_2\text{-})_n \longrightarrow CF_3(CF_2)_nI \\ 2CF_3(CF_2)_nI + SnI_2 \longrightarrow SnI_4 + CF_3(CF_2)_{2n}CF_3 \end{gathered}$$

At lower temperatures, where the trifluoromethyltin tri-iodide might have been stable, no reaction occurred.

Germanium(II) iodide reacted with trifluoroiodomethane much more readily than did stannous iodide, to give largely trifluoromethyltri-iodogermane as a dense, light-yellow liquid.

In the preparation of trifluoromethyl derivatives of the group V elements, *e.g.*, arsenic and phosphorus, it is common practice to heat the element with trifluoroiodomethane, frequently adding iodine as a catalyst. An equilibrium mixture of the products $(CF_3)_3M$, $(CF_3)_2MI$, CF_3MI_2 and MI_3 is then found. On the basis of this and other studies it has been suggested that compounds such as di-iodotrifluoromethylarsine readily disproportionate on heating.[8]

$$\textit{e.g.}\quad 5CF_3AsI_2 \longrightarrow (CF_3)_3As + (CF_3)_2AsI + 3AsI_3$$

The analogous antimony compounds are reported to disproportionate even more readily, making the isolation of di-iodotrifluoromethylstibine particularly difficult.[9] It might have been expected, therefore, that in the reaction of trifluoroiodomethane with germanium(II) iodide a variety of products of formula $(CF_3)_xGeI_{4-x}$, where $x = 1 - 4$ might be obtained. However, the great bulk of the reaction product was the compound CF_3GeI_3 and less than 1% of bis-(trifluoromethyl)-diiodogermane, $(CF_3)_2GeI_2$, was also obtained. The fact that no fluorocarbon material was produced indicates the greater thermal stability of the CF_3–Ge bond compared with the CF_3–Sn bond.

The products of pyrolysis of trifluoromethyltriiodogermane indicate its degree of thermal stability and also emphasize that it does not rearrange easily. At 180° slow decomposition to germanium tetraiodide, germanium tetrafluoride, fluoro-olefins and cyclic fluorocarbons occurs. Such fluorocarbons were found previously in the pyrolysis of trimethyltrifluoromethyltin.[4]

The nature of the products suggests that the initial step in the breakdown of the germanium compound is the transfer of one of the fluorine atoms from the carbon atom to the germanium

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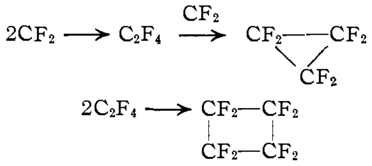
(9) J. W. Dale, H. J. Emeleus, R. N. Haszeldine and J. H. Moss, *ibid.*, 3708 (1957).

atom, followed by elimination of difluorocarbene, rearrangement and polymerization.

$$CF_3GeI_3 \longrightarrow FGeI_3 + CF_2$$

$$4FGeI_3 \longrightarrow 3GeI_4 + GeF_4$$



The pyrolysis products did not include $(CF_3)_2GeI_2$ which would have been produced by disproportionation.

The preparation of trifluoromethyltrichlorogermane and trifluoromethyltrifluorogermane illustrate the usefulness of trifluoromethyltri-iodogermane as an intermediate for the preparation of other trifluoromethyl derivatives of germanium. It is interesting to notice the similarity in physical properties of CF_3GeF_3 and GeF_4. The former has a vapor pressure of 760 mm. at $-2°$ and melts under pressure at $+3°$, while germanium tetrafluoride has a vapor pressure of 760 mm. at $-35°$ and melts under 4 atmospheres pressure at $-15°$.[10]

The hydrolysis of the compounds CF_3GeI_3, CF_3GeCl_3 and CF_3GeF_3 is of considerable interest. Hydrolysis with aqueous sodium hydroxide at room temperature, as with most perfluoroalkyl derivatives of Group IV and V elements (*e.g.*, CF_3AsX_2 where X = Cl, Br or I[8]), gives rapid evolution of fluoroform. Even the weak base silver oxide gave immediate evolution of fluoroform from a solution of trifluoromethyltri-iodogermane at 20°. With cold water, the chloro and fluoro compounds immediately gave clear solutions stable at 25° for at least 48 hr. The iodo-compound, although not immediately miscible with water, gave a clear aqueous solution on prolonged shaking.

The production of stable aqueous solutions of these compounds suggests that interaction with water is occurring, possibly with the production of ionic species, *e.g.*

$$CF_3GeF_3 + 2H_2O \longrightarrow CF_3GeF_3(OH)_2^{2-} + 2H^+$$

Such ions would probably undergo further hydrolysis in solution with production of fluoride ion, *e.g.*

$$CF_3GeF_3(OH)_2^{2-} + H_2O \longrightarrow CF_3GeF_2(OH)_3^{2-} + H^+ + F^-$$

However such hydrolysis must be readily reversible as is shown by the formation of potassium trifluoromethylpentafluorogermanate, $K_2CF_3GeF_5$, on the addition of potassium fluoride solution to an aqueous solution of either trifluoromethyltrifluorogermane or trifluoromethyltri-iodogermane.

$$CF_3GeI_3 + 5F^- \longrightarrow CF_3GeF_5^{2-} + 3I^-$$

In none of the hydrolyses performed was germanium dioxide precipitated. It is reported[10] that germanium tetrafluoride on hydrolysis gives fluorogermanate ion and germanium dioxide

$$3GeF_4 + 2H_2O \longrightarrow 2GeF_6^{2-} + GeO_2 + 4H^+$$

but that germanium dioxide is only precipitated from such a hydrolysis in concentrated solution.

The observed instability of potassium trifluoromethylpentafluorogermanate toward alkali is in sharp contrast to that of the similar boron compound, potassium trifluoromethylfluoborate, $K(CF_3BF_3)$, which is unaffected by alkali.[11] The stability of the boron compound was attributed to the shielding effect produced by the distribution of the negative charge over the six fluorine atoms in the ion. In the case of the trifluoromethylpentafluorogermanate this effect may be reduced by the larger size of the germanium atom.

Another difference between the ions $[CF_3BF_3]^-$ and $[CF_3GeF_5]^=$ was seen in their infrared spectra. In the former, strong absorption bands at 962 and 985 cm.$^{-1}$ were assigned to C–F stretching vibrations, their unusually low frequency being ascribed to the distribution of the negative charge throughout the ion. In the infrared spectrum of the ion $[CF_3GeF_5]^=$ the only strong absorption bands are at 1206 and 1045 cm.$^{-1}$, and these may therefore be assigned to the C–F stretching vibrations. These differences in the positions of the C–F stretching vibrations of the $[CF_3BF_3]^-$ and $[CF_3GeF_5]^=$ ions may be attributed to a number of factors. These include the degree of delocalization of charge which is a double negative charge for the germanium ion and only a single negative charge for $[CF_3BF_3]^-$; the effect of the different masses of the boron and germanium atoms; and the very different symmetries of the two ions. The relative importance of these factors is at present not clear.

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(11) R. D. Chambers, H. C. Clark and C. J. Willis, *J. Am. Chem. Soc.*, **82**, 5298 (1960).