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Cleavage Reactions of Group IVa Metal–Metal Bonds

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The reactions of hexamethyldimetal compounds containing unsymmetrical metal–metal bonds with iodine monochloride, hydrogen chloride, and trifluoroiodomethane are reported. The hypothesis that products of similar reactions are determined by polarity of the reacting bonds is critically examined.

Introduction

Cleavage reactions which involve the breaking of two unsymmetrical bonds are usually reported to occur in a manner consistent with bond polarities or differences in electronegativities.[1,2] For example, cleavage of diphenyl(trimethylsilyl)phosphine by iodine monochloride[1] follows eq 1 rather than eq 2. The cleavage

$$(CH_3)_3SiP(C_6H_5)_2 + ICl \longrightarrow (CH_3)_3SiCl + (C_6H_5)_2PI \quad (1)$$

$$(CH_3)_3SiP(C_6H_5)_2 + ICl \not\longrightarrow (CH_3)_3SiI + (C_6H_5)_2PCl \quad (2)$$

of unsymmetrical metal–metal bonds by unsymmetrical reagents was undertaken in this research to determine the influence of bond polarities on the mode of cleavage. Many of these reactions led to the thermodynamically more stable products, not to products arising from a transition state whose geometry was determined by the polarity of the reactant bonds. The products of these and other cleavage reactions were then investigated to find what factors were product determining in specific cases and to account for the differences between our results and those of earlier investigations.[1,2]

The hexamethyldimetal group IVa compounds were selected for this study for several reasons: (1) the simple, distinct nmr[3] signals of the reactants and the expected products permit easy analysis; (2) the compounds are easily handled on a vacuum line; (3) the metal–metal bonds of the hexaalkyldimetals are more reactive toward electrophilic reagents than those of the hexaaryldimetals; (4) methyl groups are less readily cleaved than other alkyl and aryl groups by a variety of reagents. Trimethyl(trimethylsilyl)tin and trimethyl(trimethylgermyl)tin were reported previously.[4] The bond dissociation enthalpy of trimethyl(trimethylsilyl)germane has been reported[5] but not its synthesis or properties.

Few cleavages of bonds between two different group IV elements with unsymmetrical reagents have been reported. Iodine monobromide cleaves an alkyl group from tetraalkyltins in a manner consistent with bond polarities[6]

$$(CH_3)_4Sn + IBr \longrightarrow (CH_3)_3SnBr + CH_3I \quad (3)$$

The reaction of hydrogen halides with R_3M–alkyl and R_3M–aryl linkages consistently gives R_3M–X and HR. Triphenyl(triphenylgermyl)tin reacts with phenyllithium to form an inseparable mixture of tetraphenyltin and tetraphenylgermane and with *n*-butyllithium to form hexaphenyldigermane (20% yield) and, after hydrolysis, triphenylgermylcarboxylic acid (9%).[7] Triphenylsilyllithium and triphenyl(triphenylsilyl)germane form triphenylgermyllithium and hexaphenyldisilane when allowed to react.[8] Cleavage of triphenyl(trichloromethyl)silane by *n*-butyllithium produces *n*-butyltriphenylsilane (15% yield).[9]

Experimental Section

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and Micro-Tech Laboratory of Skokie, Ill. Infrared spectra were recorded with a Beckman IR-10 spectrometer. The ^1H nmr spectra were recorded with a Varian Associates, Inc., T-60 spectrometer and a Varian Associates, Inc., A-60 spectrometer equipped with a V-6040 variable-temperature probe. The ^1H chemical shifts were measured with respect to internal cyclohexane and are reported herein with respect to tetramethylsilane ($\delta_{TMS-C_6H_{12}}$ 1.443 in cyclohexane and $\delta_{TMS-C_6H_{12}}$ 1.433 ppm in carbon tetrachloride). The ^{19}F nmr spectra were recorded with a Bruker HFX-10 spectrometer operating at 84.67 MHz. Mass spectra were obtained with a Consolidated Electrodynamics Corp. 21-104 (180° sector) spectrometer with a slit width of 20 mils and an ionizing current of 10 μA at an energy of 15 eV. A Hewlett-Packard FM 5752A chromatograph, with a thermal conductivity detector, programmable oven control, and 0.5 in. × 8 ft preparative and $^1/_8$ in. × 12 ft analytical columns packed with Apiezon L on firebrick, was used.

Materials.—Hexamethylphosphoric triamide, HMPT (Matheson Coleman and Bell), was stored over 13× molecular sieves and distilled immediately before use. Cyclohexane-d_{12} (Stohler Isotope Chemicals), containing 3% cyclohexane, was dried over Linde 5A Molecular Sieves. Tetrahydrofuran, THF (Matheson Coleman and Bell), was refluxed with lithium aluminum hydride and distilled under nitrogen. Hydrogen chloride (The Matheson Co.), trifluoroiodomethane (Pierce Chemical Co.), lithium hydride, technical grade (Matheson Coleman and Bell), iodine, USP (Baker and Adamson), carbon tetrachloride, spectroquality (Matheson Coleman and Bell), lithium wire, high purity (Foote Mineral Corp.), trimethylchlorosilane, technical grade (Eastman Organic Chemicals), methyl bromide (The Matheson Co.), and trimethyltin chloride (Alpha Inorganics) were used as received. Trimethylbromogermane[10] was prepared by a published procedure and trimethyltin iodide by adaptation of a published procedure.[11] Pure crystals of iodine monochloride, prepared by the method of Buckles and Bader[12] and identified by uv and infrared spectra, grew on the wall of the storage vessel at 0° and were used for chemical and physical studies.

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Trimethyl(trimethylsilyl)germane.—Trimethylbromogermane (0.05 mol), trimethylchlorosilane (0.15 mol), and lithium wire (0.20 mol) were vigorously stirred and refluxed under a helium atmosphere in THF (40 ml). When the nmr spectrum showed that no reaction was occurring, potassium metal and HMPT (10 ml) were added. Potassium metal was added until all the trimethylbromogermane was consumed. Volatile products were removed from the HMPT and salts under vacuum. THF was separated by fractional distillation. Trimethyl(trimethylsilyl)germane was separated from hexamethyldisilane by preparative-scale vpc and purified by low-temperature crystallization in an apparatus described previously.[13] The nmr spectrum and vpc retention time were identical with those of an authentic sample; yield 27%.

The preparation of trimethyl(trimethylsilyl)germane from trimethylgermyllithium was less satisfactory. Trimethylgermyllithium[14] (41 mmol) in HMPT was added to trimethylchlorosilane (41 mmol) in HMPT (25 ml). The volatile components of the resultant mixture were removed under vacuum and then distilled. The fraction boiling between 62 and 200° contained hexamethyldisilane, hexamethyldigermane, and trimethyl(trimethylsilyl)germane in a 3:3:4 ratio. Trimethyl(trimethylsilyl)germane was isolated and purified by vpc; yield, 13% of purified product. The nmr spectrum consisted of two resonances: $\delta_{(CH_3)_3Si}$ 0.11 ppm and $\delta_{(CH_3)_3Ge}$ 0.14 ppm. *Anal.* Calcd for $C_6H_{18}SiGe$: C, 37.76; H, 9.50. Found: C, 37.80; H, 9.38.

Trimethyl(trimethylgermyl)tin was prepared by the method of Schumann and Ronecker,[4] purified by vpc, and identified by infrared and nmr spectra; yield 43%. *Anal.* Calcd for $C_6H_{18}GeSn$: C, 25.60; H, 6.44; Ge, 25.79; Sn, 42.16. Found: C, 25.73; H, 6.87; Ge, 25.43; Sn, 42.39.

Trimethyl(trimethylsilyl)tin was prepared by the method of Schumann and Ronecker,[4] purified by vpc, and identified by infrared and nmr spectra. *Anal.* Calcd for $C_6H_{18}SiSn$: C, 30.41; H, 7.65. Found: C, 30.64; H, 7.55.

Cleavage Reactions.—Components were added directly, by vacuum-line techniques if necessary, to a 5-mm o.d. precision nmr tube. Cyclohexane-d_{12} and carbon tetrachloride were employed as solvents with cyclohexane-h_{12} ($\sim$3%) as the internal nmr standard (all chemical shifts are reported with respect to TMS). Each sealed tube was heated for at least 1 hr at 60° before recording the nmr spectrum.

Reaction of Trimethyl(trimethylgermyl)tin and Iodine Monochloride.—Cyclohexane-d_{12} (0.309 g) and trimethyl(trimethylgermyl)tin (0.865 mmol) were condensed on iodine monochloride (0.234 mmol) in a thin-wall nmr tube which was then sealed under vacuum at $-195°$. An exothermic reaction occurred as the tube warmed to room temperature. New resonances, in addition to those for trimethyl(trimethylgermyl)tin, were observed at δ 0.84 ppm (sharp and $^2J_{^{117,119}SnH}$ = 57.0, 59.5 Hz) and at δ 0.76 ppm (broadened).

Reaction of Trimethyl(trimethylsilyl)tin and Iodine Monochloride.—Cyclohexane-d_{12} (0.358 g) and iodine monochloride (0.23 mmol) were placed in a thin-wall nmr tube. This was attached to a vacuum line and the air was removed. Trimethyl(trimethylsilyl)tin (0.230 mmol) was condensed onto the mixture and the tube was sealed under vacuum and then warmed to 25°. A very rapid reaction occurred. Nmr absorption was observed at δ 0.85 ppm (broad) and δ 0.40 ppm (sharp).

Reaction of Trimethyl(trimethylsilyl)germane and Iodine Monochloride.—Iodine monochloride crystals were dropped into a solution of trimethyl(trimethylsilyl)germane in cyclohexane-d_{12}. The mixture warmed slightly, but reaction proceeded slowly as indicated by the lingering color of iodine monochloride. Strong resonance signals corresponding to trimethyliodogermane and trimethylchlorosilane and a very weak one (probably trimethylchlorogermane) were observed.

Reaction of Hexamethyldigermane and Halogens.—Bromine (0.380 mmol) was added to hexamethyldigermane (0.628 mmol) in carbon tetrachloride (0.3 ml). A vigorous reaction ensued and an nmr signal at δ 0.87 ppm corresponding to trimethylbromogermane was observed.

Hexamethyldigermane reacted slowly with iodine in carbon tetrachloride to form trimethyliodogermane (δ 1.02 ppm). Twenty-five minutes, with occasional shaking, elapsed before the color of the iodine dissipated.

A clump of iodine monochloride crystals (0.265 mmol) was dropped into a solution of hexamethyldigermane (0.321 mmol) in carbon tetrachloride (0.3 ml). A vigorous reaction ensued; the red-brown color of iodine monochloride was replaced by an iodine color which faded away in about 10 min. The ratio of trimethyliodogermane to trimethylchlorogermane was 1.05:1.00.

Addition of hexamethyldigermane (0.231 mmol) to iodine monochloride (0.390 mmol) in carbon tetrachloride (0.3 ml) resulted in a trimethyliodogermane:trimethylchlorogermane ratio of 0.56:1.00. The solution had the color of iodine.

When iodine monochloride crystals were dropped into trimethyliodogermane, elemental iodine precipitated and trimethylchlorogermane was observed in the nmr spectrum of the solution.

Reaction of Hexamethyldisilane and Iodine Monochloride.—Iodine monochloride crystals were dropped into a solution of hexamethyldisilane in carbon tetrachloride. The solution slowly assumed an iodine color which had not disappeared after several hours. The nmr spectrum showed that trimethylchlorosilane and trimethyliodosilane formed in a 2:1 ratio.

Reaction of Trimethyl(trimethylgermyl)tin and Hydrogen Chloride.—Trimethyl(trimethylgermyl)tin (0.162 mmol), hydrogen chloride (0.092 mmol), and cyclohexane-d_{12} (0.30 ml) were sealed into a 5-mm o.d. nmr tube under vacuum and heated for 4 hr at 60°. The nmr spectrum showed the presence of dimethyl(trimethylgermyl)tin chloride (δ 0.57, 0.48 ppm; integration ratio 2.0:3.0), methane (δ 0.17 ppm), and small amounts of trimethylchlorogermane and trimethyltin chloride. The presence of methane and hydrogen in the vapor over the sample at $-195°$ was indicated by the mass spectrum of the vapor.

Reaction of Trimethyl(trimethylsilyl)tin and Hydrogen Chloride.—Trimethyl(trimethylsilyl)tin (0.240 mmol), cyclohexane-d_{12}, and hydrogen chloride (0.240 mmol) were condensed into a thin-wall nmr tube which was then sealed under vacuum and warmed for several hours at 60°. A white precipitate (mp 108°) formed. The solution was transferred to a new tube and the nmr spectrum consisting of resonances corresponding to trimethylchlorosilane, trimethyltin chloride, and trimethyl(trimethylsilyl)tin were observed.

Attempted Reaction of Trimethyl(trimethylsilyl)germane and Hydrogen Chloride.—A sealed nmr tube containing several drops of trimethyl(trimethylsilyl)germane, hydrogen chloride (0.19 mmol), and cyclohexane (0.4 ml) was heated at 70° for 14 hr. The only observable nmr signals were due to starting materials. Similar results were obtained using benzene as the solvent.

Reaction of Trimethyl(trimethylsilyl)tin and Trifluoroiodomethane.—Trifluoroiodomethane (0.18 mmol), trimethyl(trimethylsilyl)tin (0.308 mmol), and cyclohexane-d_{12} were sealed into a heavy-wall nmr tube under vacuum. No reaction occurred after 12 hr at 145°. After 96 hr at 210°, tetramethyltin, trimethyliodosilane, and methane were in the resulting solution; trimethyltin fluoride and elemental tin precipitated. The vapor in equilibrium with the sample exhibited a strong infrared absorption in the C–F stretching region.

Reaction of Trimethyl(trimethylgermyl)tin and Trifluoroiodomethane.—Trimethyl(trimethylgermyl)tin (0.373 mmol), trifluoroiodomethane (0.160 mmol), and cyclohexane (0.2 ml) were condensed into a heavy-wall nmr tube, sealed under vacuum, and heated. During 12 hr at 145° no reaction occurred. After 96 hr at 210°, resonances due to tetramethyltin, trimethyliodogermane, and methane, as well as trimethyl(trimethylgermyl)tin, were observed in the ^1H nmr spectrum. Metallic tin and trimethyltin fluoride precipitated from solution. The vapor over the sample at $-78°$ absorbed strongly in the C–F stretching region.

Pyrolysis of Trifluoroiodomethane (210°).—After 72 hr at 210°, a solution prepared from trifluoroiodomethane (0.14 mmol) and cyclohexane (0.3 ml) sealed into a heavy-wall nmr tube showed no ^{19}F nmr absorption but did have the color of iodine. The vapor over the sample at $-78°$ absorbed strongly in the C–F stretching region.

Attempted Reaction of Trimethyl(trimethylgermyl)tin and Lithium Hydride.—Lithium hydride was placed in an nmr tube into which was condensed cyclohexane-d_{12} and trimethyl(trimethylgermyl)tin. The mixture was warmed to room temperature. After 24 hr at room temperature, the only observable nmr signal was due to trimethyl(trimethylgermyl)tin.

Attempted Reaction of Methyl Bromide and Trimethyltin Iodide.—Methyl bromide (0.414 mmol) was condensed into a tube containing carbon tetrachloride (0.5 ml), cyclohexane (0.05 ml), and trimethyltin iodide (0.210 mmol). The nmr spectrum showed no observable change after 28 hr.

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Reaction of Trimethyliodogermane and Diphenylchlorophosphine.—To trimethyliodogermane, prepared *in situ* by allowing hexamethyldigermane (0.481 mmol) to react with iodine (0.250 mmol) in carbon tetrachloride, were added successive aliquots of diphenylchlorophosphine, until an excess (molar ratio 1.57) was present. The solution turned yellow immediately upon addition of diphenylchlorophosphine. Nmr spectra were recorded after each addition.

Reaction of Trimethyltin Iodide and Diphenylchlorophosphine.—Experiments analogous to the above case were uninterpretable because of rapid halide exchange at the trimethyltin center.

The nmr spectrum obtained by dissolving trimethyltin chloride in pure diphenylchlorophosphine was identical with that obtained by dissolving trimethyltin iodide in diphenylchlorophosphine. The latter solution turned yellow as soon as the trimethyltin iodide was added.

Discussion

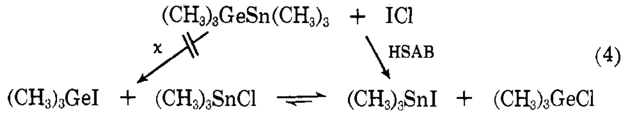
The products from cleavages of group IVa hexamethyldimetal compounds are presented in Table I.

TABLE I

PRODUCTS OF CLEAVAGE REACTIONS

Reactants	Major products
$(CH_3)_3SnGe(CH_3)_3$, ICl	$(CH_3)_3SnI$, $(CH_3)_3GeCl$
$(CH_3)_3SnSi(CH_3)_3$, ICl	$(CH_3)_3SnI$, $(CH_3)_3SiCl$
$(CH_3)_3GeSi(CH_3)_3$, ICl	$(CH_3)_3GeI$, $(CH_3)_3SiCl$
$(CH_3)_3GeGe(CH_3)_3$, ICl	$(CH_3)_3GeI$, $(CH_3)_3GeCl$, I_2
$(CH_3)_3SiSi(CH_3)_3$, ICl	$(CH_3)_3SiI$, $(CH_3)_3SiCl$, I_2
$(CH_3)_3GeGe(CH_3)_3$, Br_2	$(CH_3)_3GeBr$
$(CH_3)_3GeGe(CH_3)_3$, I_2	$(CH_3)_3GeI$
$(CH_3)_3SnGe(CH_3)_3$, HCl	$(CH_3)_3GeSn(CH_3)_2Cl$, CH_4 $(CH_3)_3GeCl$, $(CH_3)_3SnCl$, H_2
$(CH_3)_3SnSi(CH_3)_3$, HCl	$(CH_3)_3SnCl$, $(CH_3)_3SiCl$
$(CH_3)_3GeSi(CH_3)_3$, HCl	No reaction
$(CH_3)_3SnSi(CH_3)_3$, CF_3I	$(CH_3)_3SiI$, $(CH_3)_4Sn$, Sn^0, $(CH_3)_3SnF$, CH_4, fluorocarbons
$(CH_3)_3SnGe(CH_3)_3$, CF_3I	$(CH_3)_3GeI$, $(CH_3)_4Sn$, Sn^0, $(CH_3)_3SnF$, CH_4, fluorocarbons
$(CH_3)_3SnGe(CH_3)_3$, LiH	No reaction

Reactions with iodine monochloride lead in each case to the products predicted by the generalization of hard and soft acids and bases,[15] not to the products predicted by bond polarity (electronegativity) arguments



$$(CH_3)_3GeSn(CH_3)_3 + ICl \quad (4)$$
$$\swarrow \text{x (crossed)} \qquad \searrow \text{HSAB}$$
$$(CH_3)_3GeI + (CH_3)_3SnCl \rightleftharpoons (CH_3)_3SnI + (CH_3)_3GeCl$$

Only for the similar, but unreported, reaction of $(CH_3)_3SnSi(CH_3)_3$ with IBr are thermodynamic data[16,17] available for determining which set of products is thermodynamically favored. The enthalpy data favor the formation of $(CH_3)_3SnBr$ and $(CH_3)_3SiI$ over $(CH_3)_3SnI$ and $(CH_3)_3SiBr$ by 4 kcal/mol in the gas phase. However, solvation effects could readily alter this order.

The reaction of hydrogen chloride with trimethyl(trimethylsilyl)tin to form trimethylchlorosilane and trimethyltin chloride is not unexpected since both trimethylsilane and trimethyltin hydride react with HCl to form the respective chlorides. Trimethyl(trimethylgermyl)tin forms analogous products but also simultaneously reacts to lose a methyl group without rupture of the metal–metal bond

$$(CH_3)_3GeSn(CH_3)_3 + HCl \longrightarrow (CH_3)_3GeSn(CH_3)_2Cl + CH_4$$

$$(CH_3)_3GeSn(CH_3)_3 + 2HCl \longrightarrow (CH_3)_3GeCl + (CH_3)_3SnCl + H_2$$

Hydrogen chloride cleaves a methyl group from pentacarbonyl(trimethylstannyl)manganese without breaking the Mn–Sn bond.[18]

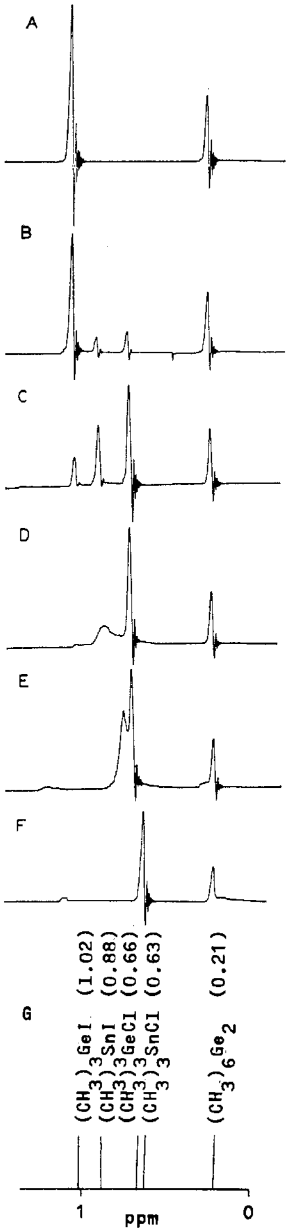


Figure 1.—Nmr spectra of the trimethyliodogermane–trimethyltin chloride system (each solution also contains hexamethyldigermane and the solvent carbon tetrachloride): A, trimethyliodogermane; B, $[(CH_3)_3SnCl]/[(CH_3)_3GeI] = 0.064$; C, 0.451; D, 0.722; E, 1.27; F, trimethyltin chloride; G, chemical shifts of pure compounds.

The trifluoroiodomethane reactions with trimethyl(trimethylsilyl)tin and trimethyl(trimethylgermyl)tin are more complex than the reaction of hexamethylditin and trifluoroiodomethane,[19] presumably because more

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drastic conditions were necessary to induce reaction. Formation of tetramethyltin, methane, and elemental tin, which are also products of trimethyl-*tert*-butyl and dimethyldi-*tert*-butyltin pyrolyses,[20] suggests a free-radical process, but the exact mechanism cannot be inferred from the data presently available.

The reactivity of group IVa metal-metal bonds toward hydrogen chloride and iodine monochloride is Sn–Ge > Sn–Si ≫ Ge–Si > Ge–Ge > Si–Si. The last three bonds are inert to cleavage by HCl under the conditions employed here. The enhanced reactivity of the Ge–Si bond, compared with Ge–Ge and Si–Si bonds, suggests a polar character for the transition state of the reaction with ICl. The reactivity of halogens with hexamethyldigermane, $Br_2 > ICl > I_2$, is consistent with electrophilic attack on the metal–metal bond, but the mechanism may be complex, as it is for reaction 3.

The spectra in Figure 1 indicate that the equilibrium in reaction 4 is labile and that the forward reaction is nearly complete. A single resonance for trimethyltin iodide and trimethyltin chloride (Figure 1F) but separate resonances for the germanium analogs (Figure 1B and C) indicate more rapid halide exchange at the tin centers than at the germanium centers. Rapid halide exchange observed in other studies

$$H_3GeCl + H_3SiI \underset{TMS}{\overset{K_{30^\circ} = 1.87 \times 10^{-4}}{\rightleftharpoons}} H_3GeI + H_3SiCl^{21}$$

$$(CH_3)_3SiI + HCl \underset{TMS}{\overset{K_{30^\circ} = 2 \times 10^{2}}{\rightleftharpoons}} (CH_3)_3SiCl + HI^{21}$$

led to products consistent with the generalization of hard and soft acids and bases. This behavior appears to be a general result for halides of group IVa metals and metalloids.

Diphenylchlorophosphine and trimethyliodogermane (Figure 2) or trimethyltin iodide undergo a rapid halide exchange, leading to products observed in the corresponding bond cleavage reactions

$$(C_6H_5)_2PCl + (CH_3)_3MI \longrightarrow (C_6H_5)_2PI + (CH_3)_3MCl \quad (M = Ge, Sn)$$

Although the products of group IV–group V bond cleavage reactions by interhalogens agree with predictions based on bond polarities,[1,2] the products are, in fact, at thermodynamic equilibrium and the reported agreement with the predictions is fortuitous.

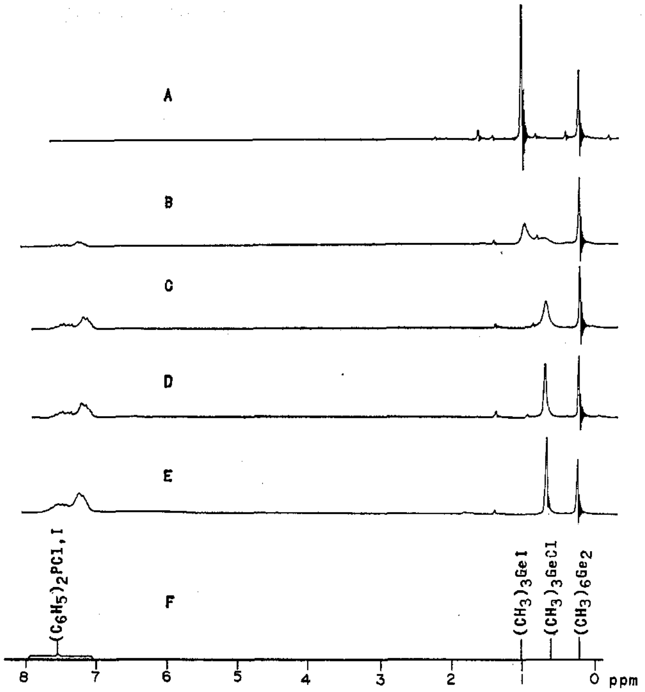

Figure 2.—Nmr spectra of the diphenylchlorophosphine–trimethyliodogermane system (each solution also contains hexamethyldigermane and the solvent carbon tetrachloride): A, trimethyliodogermane; B, $[(C_6H_5)_2PCl]/[(CH_3)_3GeI] = 0.36$; C, 1.03; D, 1.16; E, 1.51; F, chemical shifts of pure compounds.

In contrast to the above cases, the other conceivable products, $(CH_3)_3SnI$ and CH_3Br, from reaction 3 do not undergo exchange to give the observed products. No low-energy pathway is available for halide exchange, and the products of reaction 3 are kinetically controlled and consistent with a transition state determined by bond polarities.

Any arguments based upon the assumption that polarities of the reactant bonds control product formation must be supported by evidence that the observed products arise directly from the transition state and not from subsequent equilibration processes. This condition is not likely to be fulfilled when the products are both metal (metalloid) halides.

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