

Reactions of Triethylgermylpentafluorobenzene with Some Electrophilic Agents

Vadim V. Bardin,* Ljudmila N. Rogoza, and Georgii G. Furin

Institute of Organic Chemistry, 630090, Novosibirsk, Russia

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ABSTRACT

Triethylgermylpentafluorobenzene $C_6F_5GeEt_3$ reacts with CF_3SO_3H , HSO_3Cl , Me_3SiOSO_2Cl , chlorine, bromine, $Cl_2/AlCl_3$, or $Br_2/AlBr_3$ with cleavage of the $C_{aryl}-Ge$ bond. Cesium fluoride promotes electrophilic degermylation of $C_6F_5GeEt_3$, possibly via the intermediate formation of a tetraorganylfluorogermanate.

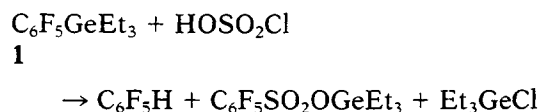
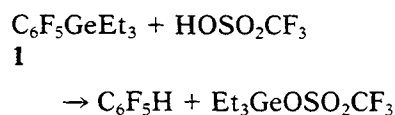
INTRODUCTION

The interaction of arylalkylgermanes with electrophilic agents usually results in cleavage of the $C_{aryl}-Ge$ bond [1]. Replacement of hydrogen by fluorine in the aromatic ring increases electrophilicity of the aryl group. For instance, substitution of a hydrogen atom in pentafluorobenzene by an electrophilic agent requires more drastic conditions than those required for substitution in benzene or monofluorobenzene (cf. Ref. [2]). The data about the reactions of polyfluoroaromatic derivatives of germanium with electrophilic agents are rather scarce. Thus, tetrakis(pentafluorophenyl)germane does not react with aq 6N HCl (reflux, 8 hours), 6N HCl in THF (reflux, 5 hours) [3], Br_2 in dibromioethane (reflux, 5–6 hours) [4], $Br_2/AlBr_3$ [3], or I_2 (250°C, 40 days) [4]. Bromination of tris(pentafluorophenyl)germane or bis(pentafluorophenyl)germane by bromine (benzene, 100°C, 6 hours) gives $(C_6F_5)_3GeBr$ [5] or $(C_6F_5)_2GeBr_2$ [6] in high yield. Xenon difluoride fluorinates the aromatic ring of

triethylgermylpentafluorobenzene in the presence of $BF_3 \cdot OEt_2$ to form 1-triethylgermylheptafluoro-1,4-cyclohexadiene [7]. These data point to the high stability of the $C_{aryl}-Ge$ bond in pentafluorophenylgermanium derivatives to electrophilic attack. In continuation of our study of the reactivity of polyfluoroaryl derivatives of silicon and germanium, we have investigated the reactions of triethylgermylpentafluorobenzene with some electrophilic agents.

RESULTS AND DISCUSSION

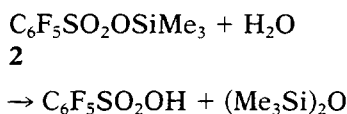
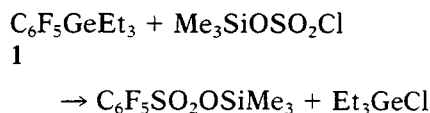
Just as with perfluorotetraphenylgermane, triethylgermylpentafluorobenzene **1** is stable to concd HCl, to a boiling anhydrous HCl solution in ether, and to CF_3COOH (80°C, 14 hours). However, a stronger acid, CF_3SO_3H , quickly reacted with **1** to give pentafluorobenzene. The latter was also obtained in the reaction of the germylbenzene **1** with chlorosulfonic acid, but $C_6F_5SO_2OGeEt_3$ was also formed. Hydrolysis of the reaction mixture and subsequent extraction with dichloromethane gave C_6F_5H and Et_3GeCl (organic layer) and $C_6F_5SO_3H$ (aqueous solution). Presumably, chlorotriethylgermane was also a product of the transformation of Et_3GeOSO_2Cl under the action of HCl or HSO_3Cl .



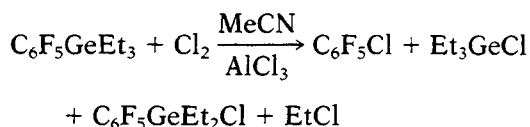
Use of Me_3SiOSO_2Cl instead of HSO_3Cl prevented protodegermylation of compound **1**, and penta-

*To whom correspondence should be addressed.

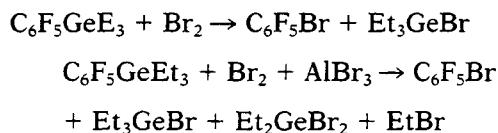
fluorobenzenesulfonic acid trimethylsilyl ester **2** was formed in a high yield. Hydrolysis of compound **2** gave pentafluorobenzenesulfonic acid and hexamethyldisiloxane. Pentafluorobenzene was found to be stable either to $\text{Me}_3\text{SiOSO}_2\text{Cl}$ or HSO_3Cl under these conditions and, consequently, is not an intermediate product.



Heating of the germylbenzene **1** with chlorine (1.6–4 equiv) in acetonitrile (55–60°C, 27 hours) gave chloropentafluorobenzene, Et_3GeCl , and a trace of chlorodiethylgermylpentafluorobenzene. Addition of AlCl_3 did not affect the reaction route, but the extent of conversion of substrate **1** decreased, possibly because of the side reaction of chlorine with the $\text{AlCl}_3/\text{CH}_3\text{CN}$.

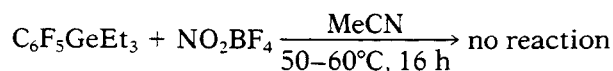
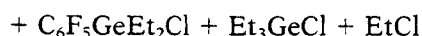
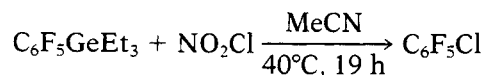


Treatment of compound **1** with liquid bromine (1.9 equiv) (20–22°C) afforded bromopentafluorobenzene and bromotriethylgermane; the ratio of $\text{C}_6\text{F}_5\text{GeEt}_3:\text{C}_6\text{F}_5\text{Br}$ was 28:72 (0.5 hours) and 5:95 (4 hours). In the presence of a larger excess of bromine (2.6 equiv), germylbenzene **1** was completely converted to bromopentafluorobenzene, bromotriethylgermane, and hexaethyldigermoxane (after hydrolysis of the reaction mixture) during 4 hours. In the presence of AlBr_3 , bromodegermylation of substrate **1** was completed during 30 minutes. Bromotriethylgermane was partially converted to Et_2GeBr_2 [1], but no compounds of the type $\text{C}_6\text{F}_5\text{GeEt}_n\text{Br}_{3-n}$ ($n = 0-2$) were obtained. In acetonitrile, the reaction of **1** with bromine proceeded more slowly than in the absence of a solvent. Indeed, the extent of conversion of **1** was 57% (6 hours) and 100% (24 hours) at 20–22°C. In the nonpolar CCl_4 , the bromination was still slower, but the products formed were the same.



The lability of germylbenzene **1** with strong acids hinders investigation of its nitration with nitric acid or its reactions in the presence of other strong acids. Therefore, we have studied the reaction of **1** with nitril chloride and nitronium te-

trafluoroborate. Triethylgermylpentafluorobenzene remained unchanged after having been stirred with NO_2BF_4 in MeCN at 50–60°C during 16 hours. However, chloropentafluorobenzene and chlorodiethylgermylpentafluorobenzene were obtained by reaction of germylbenzene **1** with NO_2Cl in acetonitrile at 40°C (19 hours). No nitropentafluorobenzene was detected (^{19}F NMR). Taking into account thermal dissociation of nitril chloride, $2\text{NO}_2\text{Cl} \rightarrow \text{N}_2\text{O}_4 + \text{Cl}_2$ [8], both chlorocontaining products could have arisen from chlorination of compound **1**. The stability of the latter toward a typical electrophile, NO_2BF_4 , together with the predominant formation of $\text{C}_6\text{F}_5\text{GeEt}_2\text{Cl}$ in reaction with NO_2Cl allows one to assume a radical type of carbon-germanium bond cleavage by the action of chlorine. Also, radical assistance by NO_2 is not excluded.



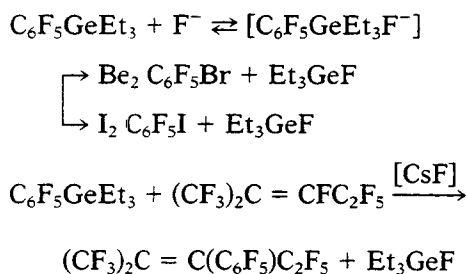
Triethylgermylpentafluorobenzene is stable toward alkylating and acylating agents and remains unchanged when boiled in acetyl chloride in the presence of AlCl_3 (4 hours) or heated with benzyl bromide and AlBr_3 (1:1) (MeCN, 50°C, 6 hours). It has been shown by a control experiment that AlBr_3 does not react with **1** in ether (reflux, 6 hours).

It is known that treatment of phenyltrimethylgermane with HCl in Bu_2O (room temperature) [9] or of phenyltriethylgermane with boiling 48% HBr [1] gives benzene and the corresponding halotrialkylgermane. Halogenation of phenyltrimethylgermane with chlorine, bromine, or iodine or ICl in CCl_4 , MeOH, or HOAc at 25°C led to the formation of $\text{C}_6\text{H}_5\text{X}$, Me_3GeX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), or Me_3GeCl (ICl as electrophile); in polar solvents, the reaction terminated after several minutes [10]. Bromination of $\text{C}_6\text{H}_5\text{GeMe}_3$ in the presence of FeBr_3 (40°C, heptane) [11] and chlorination in the presence of FeCl_3 (60°C, no solvent) [12] gave not only the above products but also some isomeric bromo(chloro)phenyltrimethylgermanes. No compounds of the type $\text{C}_6\text{H}_5\text{GeMe}_n\text{X}_{3-n}$ or $\text{C}_6\text{H}_5\text{GeMe}_2\text{CH}_2\text{X}$ were formed in this reaction. Hence, triethylgermylpentafluorobenzene reacts with electrophilic agents just as nonfluorinated phenyltrialkylgermanes do. The hypothetical dealkylation of **1** by electrophiles and subsequent splitting of the $\text{C}_{\text{arv}}-\text{Ge}$ bond in $\text{C}_6\text{F}_5\text{GeEt}_n\text{X}_{3-n}$ should be excluded, because there are no nonaromatic germanium derivatives $\text{GeEt}_n\text{X}_{4-n}$ among the products (except for Et_2GeBr_2 , see above). However, the rate of bromo(chloro)degermylation of the fluorine-containing germylbenzene **1** is much lower

than that for phenyltrimethylgermane. Comparison of the reactivities of $C_6F_5GeEt_3$ and pentafluorobenzene in their reactions with HSO_3Cl , bromine, $Br_2/AlBr_3$, and Me_3SiOSO_2Cl shows faster degermylation of **1** than deprotonation of pentafluorobenzene. Bromination and chlorosulfonylation of pentafluorobenzene occur under more rigid conditions [2].

The action of Lewis acids (aluminium halides) in electrophilic halodegermylation of triethylgermylpentafluorobenzene consists in activation of the electrophilic reagent. The reactions of a related compound, trimethylsilylpentafluorobenzene, with electrophilic agents are essentially accelerated by the presence of a Lewis base, the fluoride ion (from CsF), due to coordination of the fluoride ion by the silicon atom [13]. For germanium compounds, such coordination with F^- is less typical than for silicon compounds, though there are some examples of syntheses of organylfluorogermanates, e.g., $K_2[CF_3GeF_5]$ [14], $K_2[(CF_3)_3GeF_3]$, and $K_2[(CF_3)_4GeF_2]$ [15].

We found that cesium fluoride also promotes the reaction of germylbenzene **1** with electrophilic agents. Thus, its bromination in acetonitrile in the presence of CsF is completed during 1 hour at $20^\circ C$, while iodination takes 3 hours. In the absence of cesium fluoride, **1** does not react with iodine within 24 hours. The ^{19}F NMR spectra of both reaction mixtures contain the signals of C_6F_5X ($X = Br, I$) and fluorotriethylgermane ($\sim 1:1$). Even the weaker electrophile, perfluoro-2-methyl-2-pentene, is arylated with triethylgermylpentafluorobenzene in the presence of CsF . A similar reaction had been performed earlier with trimethylsilylpentafluorobenzene [16]. The activating effect of cesium fluoride possibly consists in the intermediate formation of a fluorogermanate which reacts with the electrophile.



EXPERIMENTAL

The 1H and ^{19}F NMR spectra were recorded on a Bruker WP 200 SY instrument at frequencies of 200 (1H) and 188.28 (^{19}F) MHz (with TMS and C_6F_6 as internal references). The products were identified by comparing NMR spectra with those of authentic samples. Yields of products were determined from ^{19}F NMR spectra using benzotrifluoride as a quantitative internal reference. The GLC analysis

was performed on an LKhM-72 chromatograph (15% SE-30, SKTFV-803, or QF-1 on chromosorb W). Acetonitrile was refluxed over P_2O_5 and distilled.

Triethylgermylpentafluorobenzene 1 was obtained from C_6F_5Br , Et_3GeCl , and $P(NEt_2)_3$ [17]. 1H NMR ($CDCl_3$), δ : 0.79–1.16 ($GeEt_3$); ^{19}F NMR ($CDCl_3$), δ : 36.0 (F–2, 6), 9.07 (F–4), 0.90 (F–3, 5); $J(2,4) = J(4,6) = 2.48$ Hz, $J(3,4) = J(4,5) = 19.4$ Hz.

Reactions of Germylbenzene 1 with Acids

A. A mixture of $C_6F_5GeEt_3$ (2.15 g, 6.58 mmol) and concd HCl (1 mL) was stirred for 1 hour at room temperature and diluted with water, and the organic layer was collected, washed with water, and dried with $CaCl_2$ to yield 1.92 g (90%) of $C_6F_5GeEt_3$.

B. A mixture of $C_6F_5GeEt_3$ (2.04 g, 6.25 mmol) and 7N HCl in ether (16 g) was refluxed for 5 hours with stirring. Germylbenzene **1** remained unchanged (^{19}F NMR).

C. $C_6F_5GeEt_3$ remained unchanged after being heated with an excess of CF_3COOH in a sealed tube ($80^\circ C$, 14 hours) (^{19}F NMR).

D. Trifluoromethanesulfonic acid (0.4 g, 2.66 mmol) was dropped into stirred germylbenzene **1** (0.45 g, 1.38 mmol) at room temperature. As a result of an exothermic reaction, pentafluorobenzene was immediately obtained (quantitative yield, ^{19}F NMR).

E. Chlorosulfonic acid (0.77 g, 6.61 mmol) and $C_6F_5GeEt_3$ (0.62 g, 1.90 mmol) were kept for 1 hour at $20^\circ C$. The ^{19}F NMR spectrum contained the signals of C_6F_5H (85% yield) and $C_6F_5SO_3GeEt_3$ (15% yield).

F. Germylbenzene **1** (7.55 g, 23.1 mmol) was added dropwise with stirring to HSO_3Cl (11.35 g, 97.4 mmol) and kept for 1 hour at $20^\circ C$. The mixture was poured onto ice and extracted with dichloromethane, the extract was dried with $CaCl_2$, and the solvent was distilled to afford 3.30 g (85%) of C_6F_5H and 4.31 g (96%) of Et_3GeCl (^{19}F NMR, GLC). The aqueous layer contained 0.96 g (15%) of $C_6F_5SO_3H$ (^{19}F NMR).

Reaction of Germylbenzene 1 with Me_3SiOSO_2Cl

A mixture of germylbenzene **1** (19.6 g, 60.0 mmol) and Me_3SiOSO_2Cl (11.3 g, 60.0 mmol) was stirred for 2 hours at $50-70^\circ C$ under a dry argon atmosphere. Vacuum distillation gave 16 g (83%) of $C_6F_5SO_3SiMe_3$, bp $89.5-91^\circ C$ (3 mm Hg). 1H NMR ($CDCl_3$), δ : 0.38 ($SiMe_3$); ^{19}F NMR ($CDCl_3$), δ : 24.8 (F–2, 6), 15.2 (F–4), 1.88 (F–3, 5) [Ref. [18] bp $87^\circ C$ (0.5 mm Hg); ^{19}F NMR (CCl_4-CDCl_3), δ : 26.5 (F–2, 6), 15.8 (F–4), 2.8 (F–3, 5)]. This substance is highly sensitive to moisture, and we were unable to obtain the correct analytical data by microanalysis. Hydrolysis of 7.36 g (23 mmol) of the freshly dis-

tilled product **2** gave 1.4 g (75%) of hexamethyldisiloxane. The aqueous layer was treated with a saturated solution of S-benzylthiuronium chloride. The precipitate that had formed was filtered off, washed twice with water, and dried over P₂O₅ to give 4.78 g (55%) of S-benzylthiuronium pentafluorobenzenesulfate, mp 178–179°C. Found, %: C41.0, H2.70, F23.4, N6.50, S15.5. C₁₄H₁₁F₅N₂O₃S₂. Required, %: C40.6, H2.65, F22.9, N6.76, S15.5

Reaction of Germylbenzene **1** with Chlorine

A. Chlorine (0.5 g, 7.0 mmol) was condensed into a solution of germylbenzene **1** (1.4 g, 4.3 mmol) in acetonitrile (2 mL). The mixture was heated in a sealed tube for 27 hours at 55–60°C, cooled, diluted with CH₂Cl₂ (2 mL), washed with concd HCl followed by water, and dried with MgSO₄, and then the solvent was evaporated off to give a mixture of C₆F₅GeEt₃ (conversion 83%), Et₃GeCl, C₆F₅Cl (yields 81 and 51%), and C₆F₅GeEt₂Cl (traces) (GLC and NMR data).

B. Chlorine (0.5 g, 7.0 mmol) was condensed into a solution of sublimed AlCl₃ (0.7 g, 5.26 mmol) in MeCN (3 mL), and germylbenzene **1** (1.15 g, 3.52 mmol) was added. The mixture was heated in a sealed ampoule for 22 hours at 55–60°C and then cooled and extracted with hexane, and the solvent was evaporated off to give C₆F₅GeEt₃ (36% conversion), Et₃GeCl, C₆F₅Cl (yields 44 and 32%), and C₆F₅GeEt₂Cl (trace).

Reaction of Germylbenzene **1** with Bromine

A. Germylbenzene **1** (0.80 g, 2.45 mmol) and bromine (0.75 g, 4.68 mmol) were mixed at 20–22°C. The ratio C₆F₅GeEt₃:C₆F₅Br was 28:72 after 30 minutes and 5:95 after 4 hours (¹⁹F NMR).

B. Germylbenzene **1** (1.2 g, 3.6 mmol) and bromine 1.5 g, 9.3 mmol) were stirred for 4 hours at 20–22°C. Dichloromethane (4 mL) was added, the resulting solution washed with 10% Na₂S₂O₅ followed by water and dried with MgSO₄, and the solvent was distilled to give a residue of 2.3 g of a mixture of bromopentafluorobenzene, bromotriethylgermane, and hexaethylgermanoxane (yields 86, 42, and 52%, respectively) (GLC data).

C. Germylbenzene **1** (1.28 g, 3.92 mmol), bromine (1.28 g, 8.0 mmol), and acetonitrile (5 mL) were stirred for 6 hours at 20–22°C. The reaction mixture was washed with 10% Na₂S₂O₅ followed by water and extracted with dichloromethane, and the extract was dried with CaCl₂. The solvent was distilled to give a residue of 0.56 g of **1** (conversion 56%) and 0.47 g (83%) of C₆F₅Br (¹⁹F NMR).

D. Germylbenzene **1** (1.0 g, 3.06 mmol), bromine (1.2 g, 7.5 mmol), and MeCN (2 mL) were stirred for 24 hours at 20–22°C. Excess bromine was removed with metallic mercury, the solution was filtered, and the residue was washed with dichlo-

romethane. The solvent was evaporated from the extract to give 1.6 g of a mixture of bromopentafluorobenzene and bromotriethylgermane (yields 93 and 100%, respectively) (NMR, GLC).

E. Germylbenzene **1** (0.6 g, 1.84 mmol), bromine (0.6 g, 3.75 mmol), and CCl₄ (2 mL) were stirred at 20–22°C. The ratio C₆F₅GeEt₃:C₆F₅Br was 70:30 after 24 hours (¹⁹F NMR).

F. C₆F₅GeEt₃ (1.6 g, 5 mmol) was added dropwise with cooling to a solution derived from the action of aluminum (0.1 g, 3.7 mg-at) on bromine (2.4 g, 15 mmol). The mixture was stirred for 0.5 hours at room temperature. As shown by ¹⁹F NMR spectroscopy, the reaction mixture contained bromopentafluorobenzene, but no signals of C₆F₅GeEt_nBr_{3-n} (n = 0–3) compounds were observed. The solution was diluted with pentane, the liquid was decanted and diluted with MeCN (0.5 mL), the upper layer was separated, and the volatile compounds were removed under reduced pressure. The residual products were C₆F₅Br, Et₃GeBr, and Et₂GeBr₂ (yields 88, 5, and 70%, respectively) (¹⁹F NMR and GLC).

G. CsF (0.48 g, 3.2 mmol) was added to a stirred solution of germylbenzene **1** (1.0 g, 3.0 mmol) and bromine (0.5 g, 3 mmol) in MeCN (3 mL). After 1 hour (22°C), the bromine coloration vanished. According to ¹⁹F NMR spectroscopy, the reaction products were bromopentafluorobenzene and fluorotriethylgermane. The reaction mixture was diluted with water, and the organic layer was washed with 10% Na₂S₂O₅ followed by water and then dried with MgSO₄. The products were C₆F₅Br and (Et₃Ge)₂O (yields 83 and 82%).

Reaction of Germylbenzene **1** with Iodine

A. Germylbenzene **1** (1.1 g, 3.37 mmol) and iodine (1.2 g, 4.72 mmol) in MeCN (3 mL) were stirred for 24 hours at 20°C. Substrate **1** was unchanged (¹⁹F NMR).

B. Germylbenzene **1** (1.1 g, 3.37 mmol), iodine (0.9 g, 3.54 mmol), and CsF (0.6 g, 3.95 mmol) in MeCN (3 mL) were stirred for 3 hours at 20–22°C until the iodine coloring vanished. The mixture was diluted with water and extracted with dichloromethane (4 mL), and the extract was washed with 10% Na₂S₂O₅ followed by water and dried with MgSO₄, and the solvent was distilled off. The product was 1.6 g of a mixture of iodopentafluorobenzene, Et₃GeF, and (Et₃Ge)₂O (yields 73, 32, and 32%, respectively).

Reaction of Germylbenzene **1** with Nitrating Agents

A. NO₂Cl (1.89 g, 23.2 mmol) was condensed into a glass tube, and then a solution of C₆F₅GeEt₃ (3.79 g, 11.6 mmol) in acetonitrile (4 mL) was added. The sealed tube was kept for 19 hours at 40°C and

for 28 hours at room temperature. The reaction mixture was treated with mercury and filtered through a glass filter. The filtrate contained 1.82 g of germylbenzene **1** (conversion 52%), 1.32 g of $C_6F_5GeEt_2Cl$, and 0.19 g of chloropentafluorobenzene (yields 66 and 15%, respectively, based on the reacted germylbenzene **1**) (^{19}F NMR).

B. A mixture of $C_6F_5GeEt_3$ (0.54 g, 1.65 mmol), 0.44 g (3.31 mmol) of NO_2BF_4 , and acetonitrile (5 mL) was stirred in a sealed tube with a magnetic stirrer for 16 hours at 50–60°C. Germylbenzene **1** did not react (^{19}F NMR).

Attempted Reaction of Germylbenzene 1 with $AcCl$ and $AlCl_3$

$C_6F_5GeEt_3$ (1.6 g, 4.9 mmol) was added to a solution of $AlCl_3$ (0.7 g, 5.24 mmol) in CH_3COCl (5.5 g, 70 mmol) and refluxed for 4 hours. Then the mixture was cooled and hydrolyzed with dilute HCl, the organic layer was washed with water, and the aqueous layer was extracted with dichloromethane. The extracts were combined and dried with $CaCl_2$ and Na_2CO_3 . Germylbenzene **1** had not reacted (^{19}F NMR).

Attempted Reaction of Germylbenzene 1 with Benzyl Bromide and $AlBr_3$

A. A solution of $AlBr_3$ (1.36 g, 5.1 mmol), $C_6H_5CH_2Br$ (0.87 g, 5.1 mmol), and $C_6F_5GeEt_3$ (0.83 g, 2.5 mmol) in acetonitrile (5 mL) was heated for 6 hours at 50°C. Germylbenzene **1** had not reacted (^{19}F NMR).

B. Heating of $AlBr_3$ (1.48 g, 5.5 mmol), germylbenzene **1** (1.81 g, 5.5 mmol), and benzyl bromide (0.94 g, 5.5 mmol) in anhydrous ether (13 mL) (6 hours, 50°C) gave the same result.

Reaction of Germylbenzene 1 with Perfluoro-2-Methyl-2-Pentene

Germylbenzene **1** (1.1 g, 3.37 mmol), perfluoro-2-methyl-2-pentene (1.8 g, 6.0 mmol), CsF (0.6 g, 3.95 mmol), and 2 mL of MeCN were refluxed with stirring for 5 hours. The mixture was diluted with water, dried with $MgSO_4$, and concentrated under reduced pressure to give perfluoro-2-methyl-3-phenyl-2-pentene [16] and Et_3GeF (yields 71 and 97%, respectively) (GLC, ^{19}F NMR data).

Attempted Reaction of Pentafluorobenzene with Me_3SiOSO_2Cl

Me_3SiOSO_2Cl (0.28 g, 1.48 mmol) and pentafluorobenzene (0.25 g, 1.49 mmol) were heated in a sealed tube for 2 hours at 50–70°C. No evidence of reaction was detected (^{19}F NMR).

Attempted Reaction of Pentafluorobenzene with Bromine

Bromine (0.45 g, 2.81 mmol), acetonitrile (1 mL), and pentafluorobenzene (0.25 g, 1.49 mmol) were placed in an NMR tube and kept for 6 hours at room temperature. As shown by ^{19}F NMR, pentafluorobenzene had not reacted.

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