Reactions of trimethylsilylpentafluorobenzene and triethylgermylpentafluorobenzene with nucleophilic reagents

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Abstract

This paper reports the results of studies on the reactions of trialkylsilyl- and germyl-pentafluorobenzenes with O-, N, S- and C-nucleophiles, and with $LiAlH_4$. Depending on the nature of the nucleophilic reagent, its attack is oriented towards a heteroatom (RO^-, RS^-), the C-4 atom of the pentafluorophenyl ring (BuLi, $LiAlH_4$, piperidyl-lithium) or at both electrophilic centres (piperidine, RS^-).

Introduction

The nucleophilic substitution reactions of fluorine atoms in the series of polyfluoroaromatic compounds have been extensively studied [1]. The orientation of nucleophilic defluorination in pentafluorobenzene derivatives C_6F_5X is predominantly determined by the electronic effect of the substituent X and, to a lesser extent, by the nature of the solvent. There are also examples of reactions where two sites are susceptible to nucleophilic attack depending on the nature of the nucleophilic reagent: at the C-4 carbon atom of the pentafluorophenyl ring and at the atom of the functional group directly bonded with the pentafluorophenyl ring [2–4]. These are illustrated in the reactions of pentafluorobenzophenone [2, 3] and perfluorodiphenylmercury [4] with MeONa in MeOH, with hydrazine in EtOH or THF, and with $LiAlH_4$ in THF. However, the results cannot be compared directly, since they were carried out in different solvents [1].

The reactions of nucleophilic reagents with polyfluoroaryl-containing organoelemental compounds remain almost uninvestigated. This limits our knowledge about the effect of a heteroatom substituent on the reactivity of polyfluoroaromatic compounds and prevents selective modification of the polyfluoroaryl group bonded with the heteroatom.

We report here the results of our studies on the reactions of trialkylsilyl- and germylpentafluorobenzenes with O-, N-, S- and C-nucleopohiles, and with $LiAlH_4$.

Experimental

The ^1H NMR spectra were recorded on a Varian A56/60A instrument (60 MHz, TMS as an internal standard) and the ^{19}F NMR spectra on Varian

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A56/60A (56.4 MHz) and Bruker WP 200 SY (188.28 MHz, internal standard C_6F_6) instruments. The IR spectra were measured on UR 20 and Specord IR 75 instruments either using a thin layer or in CCl_4 (1%) solution. The GLC analysis was carried out on an LKhM-72 chromatograph (15% SE-30, SKTFW-803 or QF-1 on Chromosorb W).

Ethanol was dried with magnesium ethoxide, while propanol and diglyme were distilled over sodium and stored over 4 Å molecular sieves. THF and ether were dried over sodium benzophenone ketyl. Piperidine was distilled over KOH. Tables 1–3 list the NMR, IR and analytical data for the new compounds obtained.

Treatment of $C_6F_5MR_3$ with aqueous THF, EtOH, PrOH or PrSH

Method (a)

$C_6F_5MR_3$ (1 mmol) was placed into an NMR tube, then 80% aq. THF or 80% aq. propanol was added to 1 ml volume. The mixture was stirred and allowed to stand at room temperature in sealed tubes. After 20 h, the ^{19}F NMR spectra showed only the signals of the starting compounds **1** and **11** in both cases.

Method (b)

Arylsilane (**1**) was stirred with anhydrous propanol or propanethiol in acetonitrile at 20 °C over a period of 1–3 h. The mixture was poured into water, the organic layer separated, washed with water and dried over $MgSO_4$. The initial arylsilane (**1**) was isolated (90–95% yield).

TABLE 1

^1H and ^{19}F NMR spectra

Compound	Solvent	^1H NMR spectrum, δ (ppm)	F NMR spectrum, δ (ppm)	
			F-2,6	F-3,5
3 (nc)	CCl_4	6.68 ($1H_{ar}$); 4.15 (OCH_2); 1.77 (CH_2); 1.00 (CH_3).	5.14	22.2
4 (nc)	CCl_4	7.14 ($1H_{ar}$); 2.88 (SCH_2); 1.59 (CH_2); 0.95 (CH_3).	28.0	23.8
5 (nc)	CCl_4	7.25 (SC_6H_4); 6.95 (C_6F_4H); 1.22 (CH_3).	29.1	24.1
6 (nc)	–	3.20 (4H-2,6); 0.18 ($SiMe_3$); 1.47 (4H-3,5 + 2H-4).	36.2	15.1
12 (nc)	$CFCl_3$	2.85 (SCH_2); 1.50 (CH_2); 1.08 ($GeEt_3$); 0.98 (CH_3).	35.9	28.8
13 (nc)	$CFCl_3$	3.18 (4H-2,6); 1.12 ($GeEt_3$); 1.64 (4H-3,5 + 2H-4).	33.4	12.3
14 (nc)	–	2.63 (CH_2); 1.37 (CH_2); 1.08–1.05 (CH_3CH_2); 1.07 ($GeEt_3$).	34.6	18.1
15 (nc)	$(CD_3)_2CO$	7.30 ($1H_{ar}$); 1.17, 1.12 ($GeEt_3$).	35.6	24.3

TABLE 2

Infrared spectra

Compound	Frequency (cm^{-1})
3 (nc)	3078; 2963; 2875; 1633; 1524; 1511; 1483; 1464; 1382; 1167; 1087; 990; 943.
4 (nc)	3080; 2964; 2930; 1630; 1545; 1492; 1437; 1385; 1293; 1243; 1231; 1140; 1127; 919; 892.
5 (nc)	3075; 2962; 2869; 1627; 1527; 1489; 1433; 1232; 1172; 915.
6 (nc)	2946; 2862; 1646; 1500; 1463; 1419; 1394; 1294; 1261; 1236; 1166; 1128; 1113; 1012; 967; 912; 898; 857; 832.
12 (nc)	2960; 2938; 2913; 2880; 1624; 1524; 1442; 1382; 1359; 1295; 1249; 1232; 1082; 1020; 975; 947; 783; 723; 711.
13 (nc)	2944; 2911; 2876; 2860; 1638; 1511; 1492; 1460; 1396; 1333; 1287; 1271; 1238; 1165; 1127; 1111; 1022; 1010; 965; 865.
14 (nc)	2953; 2942; 2913; 2867; 1441; 1370; 1256; 1244; 1134; 1018; 960; 907; 719.
15 (nc)	3095; 2960; 2943; 2914; 2878; 1608; 1473; 1434; 1385; 1360; 1241; 1220; 1175; 1023; 909; 852; 716.

Method (c)

Similarly, after treatment of germylbenzene (**11**) with anhydrous ethanol or propanol (20 °C, 1–8 h) or an acetonitrile solution of propanethiol (60–70 °C, 18 h), the starting product was isolated in 90–95% yield.

Reactions of silylbenzene (1) and germylbenzene (11) with PrONa, EtONa and RSNa

A mixture of silylbenzene (**1**) [or germylbenzene (**11**)], the nucleophilic reagent and the solvent were stirred under the conditions indicated in Table 4, poured into water, acidified with HCl, the organic layer separated and washed with water, dried over $MgSO_4$, weighed and analysed by GLC and NMR methods.

Reactions of silylbenzene (1) with piperidine

Method (a)

Silylbenzene (**1**) (1 mmol), solvent (1 ml) and piperidine (2 mmol) were placed in an NMR tube. The mixture was stirred and maintained at 20 °C. Formation of the products and their ratio were recorded by ^{19}F NMR spectroscopy (Table 5).*

Method (b)

To 2.9 mmol of arylsilane (**1**) was added 9.4 mmol of piperidine in 2 ml acetonitrile. The mixture was stirred with a magnetic stirrer for 2 h at 20 °C. It was then diluted with 15 ml of 5% HCl, the organic layer washed with water, dried over $MgSO_4$ and weighed. According to the GLC data, the

*1-Piperidino-2,3,5,6-tetrafluorobenzene (**7**) has been described earlier [5].

TABLE 3

Analytical data

Compound	B.p. (°C/Torr)	Found (%) / Calculated					Formula
		C	H	F	N	S	
3 (nc)	173–174	51.9	3.37	36.8			$C_9H_8F_4O$
		51.9	3.85	36.5			
4 (nc)	200–202	48.6	3.52	33.9		14.3	$C_9H_8F_4S$
		48.2	3.57	33.9		14.3	
5 (nc)	170–172/4	62.1	4.12	24.3		11.0	$C_{16}H_{14}F_4S$
		61.1	4.47	24.2		10.2	
6 (nc)	120–123/50	55.5	6.17	25.3	4.87		$C_{14}H_{19}F_4NSi$
		55.1	6.23	24.9	4.59		
12 (nc)	138–140/1	47.2	5.73	20.4		8.48	$C_{15}H_{22}F_4GeS$
		47.0	5.75	19.9		8.36	
13 (nc)	148–149/5	51.9	6.43	19.3	3.60		$C_{17}H_{25}F_4GeN$
		52.1	6.38	19.4	3.37		
14 (nc)	98–100/3	52.7	6.57	21.2			$C_{16}H_{24}F_4Ge$
		52.7	6.58	20.9			
15 (nc)	60–61/2	47.1	5.20	24.4			$C_{12}H_{16}F_4Ge$
		46.7	5.18	24.6			

yields of compounds **2**, **6** and **7** were 64, 10 and 2% respectively, and the conversion of arylsilane (**1**) was 59%.

Method (c)

Similarly, incubating a mixture of 5 mmol arylsilane (**1**) 10 mmol piperidine and 4 ml acetonitrile for 6 h at 40–50 °C afforded a mixture of compounds **2**, **6** and **7** in 15, 51 and 23% yield, respectively (GLC data) [100% conversion of arylsilane (**1**)].

*Reactions of silylbenzene (**1**) and germylbenzene (**11**) with piperidyl-lithium*

Method (a)

A solution consisting of 48 mmol ethyl-lithium in 35 ml ether cooled to −30 °C was added dropwise in dry argon, with stirring, to a solution of 129 mmol piperidine in 60 ml ether also cooled to −30 °C. The mixture was stirred for 5 min, then 56.3 mmol silylbenzene (**1**) in 10 ml ether was

TABLE 4

Reactions of trimethylsilylpentafluorobenzene (**1**) and triethylgermylpentafluorobenzene (**11**) with PrONa, EtONa and RSNa (at 20 °C)

Compound (mmol)		Nucleophile (mmol)		Solvent (ml)		Time (h)	Conversion of **1** (**11**) (%)	Yield (%)
1	(2.5)	EtONa	(5)	THF	(1)	3	100	**2** (98)
1	(5)	PrONa	(5)	PrOH	(2)	1	100	**2** (57), **3** (27)
1	(5)[a]	PrONa	(5)	PrOH	(2)	18	100	**2** (2), **3** (80)
1	(5)	PrSNa	(5)	PrOH	(2)	1	100	**2** (40), **4** (48)
1	(5)[a]	PrSNa	(5)	PrOH	(2)	12	100	**2** (9), **4** (61)
1	(10)	PrSNa	(4)	THF	(4)	1.5	80	**2** (65), **4** (15)
1	(10)	PrSNa	(9)	THF	(4)	3	100	**2** (33), **4** (37)
1	(6.3)	RSNa[b]	(6.3)			2	86	**2** (54), **5** (23)
11	(1.8)	EtONa	(2.6)	THF	(1)	3	50	**2** (88)
11	(5.0)	PrONa	(6.5)	PrOH	(13)	1	50	**2** (88)
11	(2.4)	PrSNa	(2.3)	THF	(1.5)	3	97	**2** (9.5), **12** (73)
11	(10)	PrSNa	(13)	PrOH	(25)	10	100	**4** (19), **12** (66)

[a]At 40–50 °C.
[b]4-Bu^{t}C$_6$H$_4$SNa in diglyme (2.5 ml).

TABLE 5

Reactions of silylbenzene (**1**) with piperidine

Solvent	Time (h)	Product yield (%)				Product ratio (%)
		1	**2**	**6**	**7**	(**2**+**7**)/(**2**+**7**+**6**)
Et_2O	4.5	71	29			
	7	68	32			
	24	52	36	12		0.75
	28[a]	43	39	14	4	0.75
	144[a]	13	52	23	12	0.74
THF	4.2	69	31			
	7.1	64	36			
	24	32	44	24		0.65
	30[a]	24	48	24	4	0.68
	144[a]		52	20	28	0.80
MeCN	12[a]	20	47	23	10	0.71
PrOH	4	10	90			
	7		100			
	144		88		12	

[a]The ^{19}F NMR spectrum contained a signal corresponding to $FSiMe_3$.

added. The mixture was stirred for 1 h at −20 to −30 °C and poured on to ice and 200 ml 5% HCl. The organic layer was separated, the aqueous layer extracted with ether, the combined extract washed with water, dried over $CaCl_2$ and the solvent then distilled off. As shown by the ^{19}F NMR data,

the residue did not contain compounds **2** and **7**. Vacuum distillation gave 16.7 mmol silylbenzene (**1**) (70% conversion) and 19.8 mmol compound **6** (50% conversion).

Method (b)

The reaction of 18 mmol germylbenzene (**11**) with 64 mmol piperidine and 46 mmol ethyl-lithium in 45 ml ether was performed in a similar manner to Method (a), but after adding germylbenzene (**11**) the reaction mixture was stirred for 2 h at 18–20 °C. Distillation *in vacuo* produced germylbenzene (**11**) (7 mmol, 61% conversion) and compound **13** (6 mmol, 55% conversion).

*Reaction of germylbenzene (**11**) with piperidine*

Method (a)

Experiments in ether and THF were conducted similarly to those with silylbenzene (**1**). After 7 h (in THF) and 25 h (in ether), the ^{19}F NMR spectra contained only signals corresponding to compound **11**. After 144 h, the signals corresponding to germylbenzene (**11**) disappeared, and compounds **2**, **7** and **13** were formed in a 36:41:23 ratio.

Method (b)

A mixture of 0.37 mmol germylbenzene (**11**) and 1.17 mmol piperidine in 0.3 ml acetonitrile was heated in a sealed tube for 12 h at 60–70 °C. The ^{19}F NMR data obtained indicated that the only fluorine-containing product formed was compound **7**.

Method (c)

Germylbenzene (**11**) (9 mmol) was added with stirring to a solution of 28 mmol piperidine in 6 ml diglyme heated to 100 °C. The mixture was then stirred for 3.5 h at 145 °C, cooled, poured on to water acidified with HCl and extracted with ether. The extract was dried over $CaCl_2$. After the solvent had been distilled off, the residue was distilled in *vacuo* to produce 2.8 mmol compound **7** (31% conversion) and 1.4 mmol compound **13** (16% conversion).

Competing reactions of $C_6F_5SiMe_3$ and $C_6F_5GeR_3$ with piperidine

Method (a)

Piperidine (0.45 mmol) was added to a solution of 0.69 mmol $C_6F_5SiMe_3$ and 0.70 mmol $C_6F_5GeMe_3$ in 0.15 ml CD_3CN and stored at 20 °C in a sealed tube. After 3 h, the ratio of these compounds was 1:1.1, after 5 h the ratio was 1:1.6 and after 12 h it was 1:2.8 (mol) (^{19}F NMR data).

Method (b)

Likewise, a solution consisting of 0.80 mmol $C_6F_5SiMe_3$, 0.80 mmol $C_6F_5GeEt_3$ and 0.85 mmol piperidine in 0.6 ml acetonitrile was stored in a sealed ampoule (20 °C), after which, in addition to the products, it contained the starting compounds in a 1:1.8 ratio (26 h), whilst after 6 d there were

no fluorine signals corresponding to $C_6F_5SiMe_3$ although those of $C_6F_5GeEt_3$ persisted.

*Reactions of silylbenzene (**1**) and germylbenzene (**11**) with $LiAlH_4$*

Silylbenzene (**1**) (42 mmol) and 70 ml THF were placed in a flask equipped with a stirrer and reflux condenser. Then 42 mmol $LiAlH_4$ was added portion by portion in dry argon. The mixture was stirred for 24 h at 20 °C, then carefully poured into 300 ml of 5% HCl, the organic layer separated, the aqueous layer extracted with dichloromethane, the combined extract dried over $CaCl_2$ and the solvent distilled off. According to the ^{19}F NMR data, the residue contained only 1-trimethylsilyl-2,3,5,6-tetrafluorobenzene, which was isolated by distillation to give 36 mmol of compound **8** (86% conversion), similar to that previously described [6].

Similarly, from 3 mmol germylbenzene (**11**), 3.4 mmol $LiAlH_4$ and 20 ml ether, 2.6 mmol of germylbenzene (**15**) was obtained (87% conversion) together with traces of the *ortho* isomer (^{19}F NMR data).

*Reaction of germylbenzene (**11**) with butyl–lithium*

To a stirred solution of 10 mmol germylbenzene (**11**) in 30 ml ether was added 20 ml of 1 M BuLi in hexane (20 mmol), the mixture being stirred for 20 h at 20 °C. The latter was then poured on to water, the organic layer washed with water, dried over $CaCl_2$, the solvent distilled off and the residue distilled *in vacuo* to give 6.4 mmol of compound **14** (64% conversion).

*1-Propoxy-2,3,5,6-tetrafluorobenzene (**3**) (nc)*

A solution of 50 mmol pentafluorobenzene and 60 mmol sodium propylate in 20 ml propanol was refluxed for 7.5 h. The solution was then cooled, poured into water, extracted with dichloromethane and the extract dried over $MgSO_4$. The solvent was distilled off and the residue distilled. The yield of compound **3** was 77%.

*1-Propanethio-2,3,5,6-tetrafluorobenzene (**4**) (nc)*

A solution of 50 mmol propanethiol in 5 ml diglyme was added to a mixture of 50 mmol pentafluorobenzene, 55 mmol calcinated K_2CO_3 and 10 ml diglyme. The mixture was heated with stirring for 1.5 h at 60–70 °C. Then it was poured into water, extracted with dichloromethane, the extract was washed three times with water and dried over $MgSO_4$. The solvent was distilled off and the residue was distilled. The yield of compound **4** was 55%.

*4-5-Butyl-2',3',5',6'-tetrafluorodiphenyl sulphide (**5**) (nc)*

A mixture of 90 mmol pentafluorobenzene, 70 mmol 4-t-butylthiophenol, 90 mmol calcinated K_2CO_3 and 22 ml acetonitrile was refluxed with stirring for 2 h. The mixture was treated as described above to give compound **5** in a 38% yield.

Results and discussion

Trimethylsilylpentafluorobenzene (**1**) was inert to 80% aqueous THF, 80% aqueous and anhydrous propanol (20 °C, 3–20 h), but after treatment with sodium propylate in propanol (20 °C), the C_{aryl}—Si bond was cleaved to form pentafluorobenzene (**2**) and 1-propoxy-2,3,5,6-tetrafluorobenzene (**3**). Increasing the temperature to 40–50 °C led to complete transformation of compound **1** into **3**. Substitution of PrONa in propanol by sodium ethoxide in THF did not affect the reaction route (Table 4).

$$\underset{(1)}{C_6F_5SiMe_3} \xrightarrow[2.\ H_2O]{1.\ EtONa} \underset{(2)}{C_6HF_5}$$

Compound **1** did not react at room temperature with propanethiol, but its treatment with sodium propanethiolate in PrOH or sodium 4-t-butylthiophenolate in diglyme under the same conditions led to pentafluorobenzene, 1-propanethio-2,3,5,6-tetrafluorobenzene (**4**) and 4-t-butyl-2′,3′,5′,6′-tetrafluorodiphenyl sulphide (**5**), respectively (Table 4).

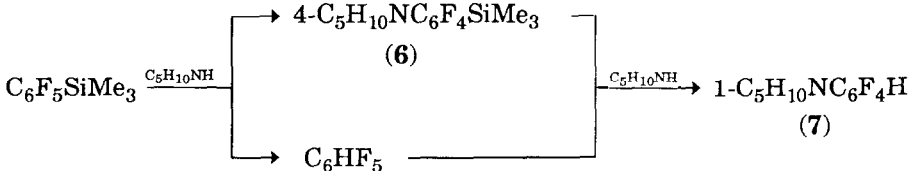
$$C_6F_5SiMe_3 \xrightarrow[2.\ H_2O]{1.\ RSNa} C_6HF_5 + 1\text{-}RSC_6F_4H$$

R = Pr, **4**

= 4-Bu^{t}C$_6$H$_4$, **5**

When the temperature was raised (40–50 °C) and the process was prolonged, the yield of compound **4** increased with a simultaneous decrease in the yield of compound **2**.

In contrast to water, propanol and propanethiol, piperidine reacted with silylbenzene (**1**) at room temperature (Table 5). According to the ^{19}F NMR spectra, the reaction of 2 equiv. piperidine with 1 equiv. silylbenzene (**1**) in ether or THF yielded, at first, pentafluorobenzene and 1-trimethylsilyl-4-piperidinotetrafluorobenzene (**6**), and after some time the spectra also showed signals corresponding to 1-piperidino-2,3,5,6-tetrafluorobenzene (**7**). Reaction in acetonitrile proceeded similarly. An increase in the relative amount of piperidine did not affect the relationship between the two reaction routes at 20 °C. At 40–50 °C, the main product was compound **6**.



In propanol, C_{aryl}—Si bond cleavage occurred faster than the process of nucleophilic aminodefluorination. Treatment of silylbenzene (**1**) with piperidine in propanol (20 °C) gave only pentafluorobenzene (**2**), which was further slowly converted to compound **7** (Table 5). The ^{19}F NMR spectra did not show signals corresponding to fluorotrimethylsilane and product **6**.

It is interesting that treatment of silylbenzene (**1**) with piperidyl–lithium at −20 °C gave only **6**.

$$C_6F_5SiMe_3 + C_5H_{10}NLi \xrightarrow{-20\ ^\circ C} 4\text{-}C_5H_{10}NC_6F_4SiMe_3$$

(**6**)

Interaction of silylbenzene (**1**) with lithium aluminium hydride proceeded readily at 20 °C in THF, the only product being 1-trimethylsilyl-2,3,5,6-tetrafluorobenzene (**8**).

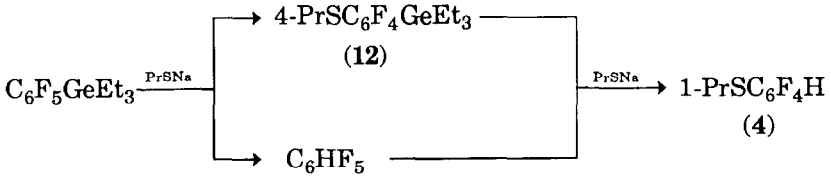
Three more examples of selective defluorination of trimethylsilylpentafluorobenzene are known. Fearon and Gilman [7, 8] have shown that treatment of compound **1** with butyl-lithium or triphenyl-lithium leads to 1-trimethylsilyl-4-butyltetrafluorobenzene (**9**) and 1-trimethylsilyl-4-triphenylsilyltetrafluorobenzene (**10**), respectively. A similar result was obtained by Dua and Gilman [9] who treated compound **1** with Bu^{t}Li in THF.

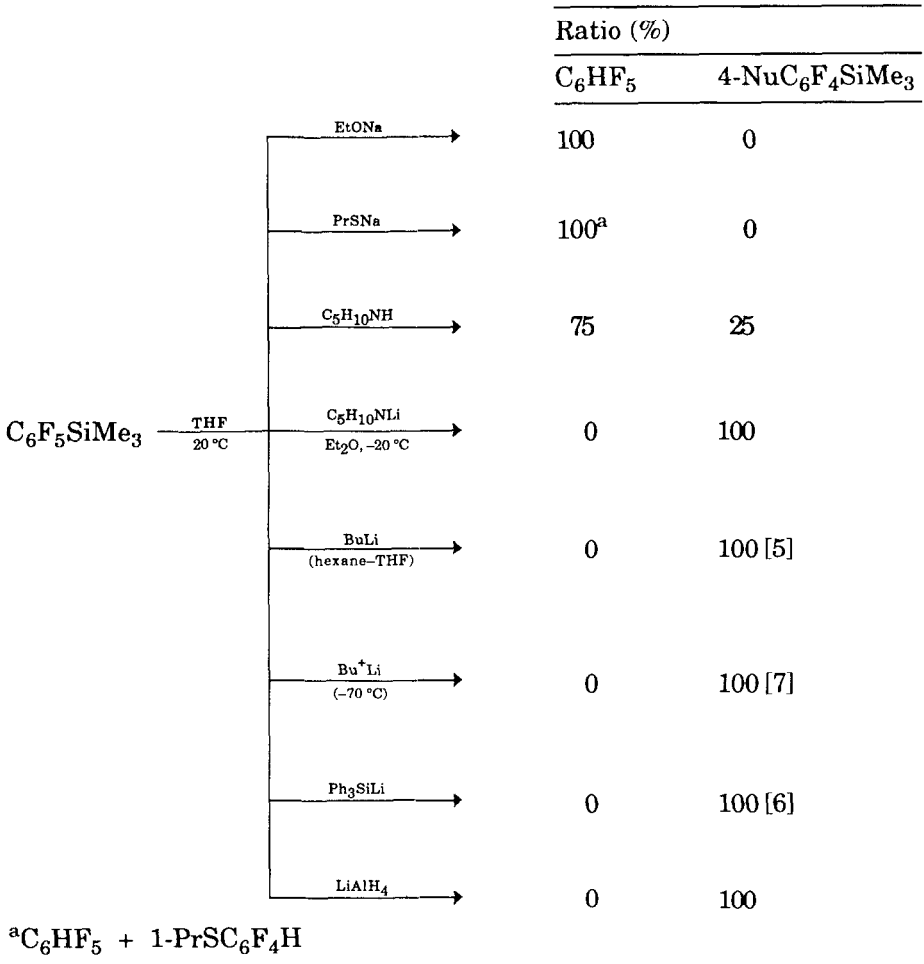
Summing up the results of the reactions of trimethylsilylpentafluorobenzene with nucleophiles, it should be noted that this compound shows dual reactivity. Orientation in these reactions is determined by the nature of nucleophile: O- and S-nucleophiles attack the silicon atom, Si- and C-nucleophiles, $LiAlH_4$ and piperidyl-lithium attack the C-4 atom of the pentafluorophenyl group, and piperidine attacks both reaction centres. Scheme 1 shows the product ratios in the reactions of trimethylsilylpentafluorobenzene with nucleophiles.

The reactions of triethylgermylpentafluorobenzene (**11**) with nucleophilic agents are similar in many respects to the reactions of trimethylsilylpentafluorobenzene. Germylbenzene (**11**) was stable towards anhydrous ethanol and propanol, 80% aqueous THF and 80% propanol. However, EtONa in THF cleaved the C_{aryl}–Ge bond to form pentafluorobenzene. The reaction of compound **11** with sodium propylate in propanol proceeded in a similar manner.

$$\underset{(11)}{C_6F_5GeEt_3} \xrightarrow[2.\ H_2O]{1.\ RONa} C_6HF_5\ (R = Et,\ Pr)$$

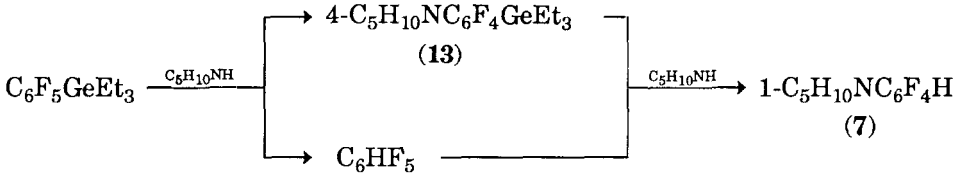
Germylbenzene (**11**) did not react with propanethiol (60–70 °C, 18 h). With sodium propanethiolate in THF it reacted at 20 °C forming pentafluorobenzene and substituted triethylgermylarene (**12**), the latter being the main product. Substitution of THF by propanol did not alter the main direction of nucleophilic attack, but at longer reaction times pentafluorobenzene vanished and compound **4** appeared. In contrast to silylbenzene (**1**) reacting with S-nucleophiles only by protodesilylation, germylbenzene (**11**) gave predominantly the nucleophilic defluorination product. The contribution of the protodegermylation product in this case was small.





Scheme 1.

The reaction of piperidine with germylbenzene (**11**) proceeded in a similar manner to that with the silylbenzene (**1**) but much more slowly. The ^{19}F NMR spectrum of the solution of compound **11** and piperidine (1:2, mol) in ether (20 °C, 25 h) or THF (20 °C, 7 h) showed only the signals of the starting compound **11**. Only after 144 h was germylbenzene (11) transformed to 1-triethylgermyl-4-piperidinotetrafluorobenzene (**13**), and to compounds **2** and **7**.



With **11** and excess piperidine in acetonitrile at 60–70 °C for 12 h, compound **7** was the only fluoro-organic product. This suggests that substituted germylbenzene (**13**) probably protodegermylated by piperidine. At the same time, addition of 1 equiv. germylbenzene (**11**) to the hot solution of 3 equiv. piperidine in diglyme and subsequent mixing at 145 °C gave a mixture of the piperidinobenzenes **7** and **13**. Hence it appears that the degermylation rate of **13** under these conditions is less than the rate of reaction of compound **11**.

It should be noted that treatment of germylbenzene (**11**) with piperidyllithium gave only compound **13**.

$$C_6F_5GeEt_3 + C_5H_{10}NLi \longrightarrow 4\text{-}C_5H_{10}NC_6F_4GeEt_3$$

Lithium aluminium hydride and butyl-lithium react with germylbenzene (11) exclusively by nucleophilic substitution of fluorine in the pentafluorobenzene ring.

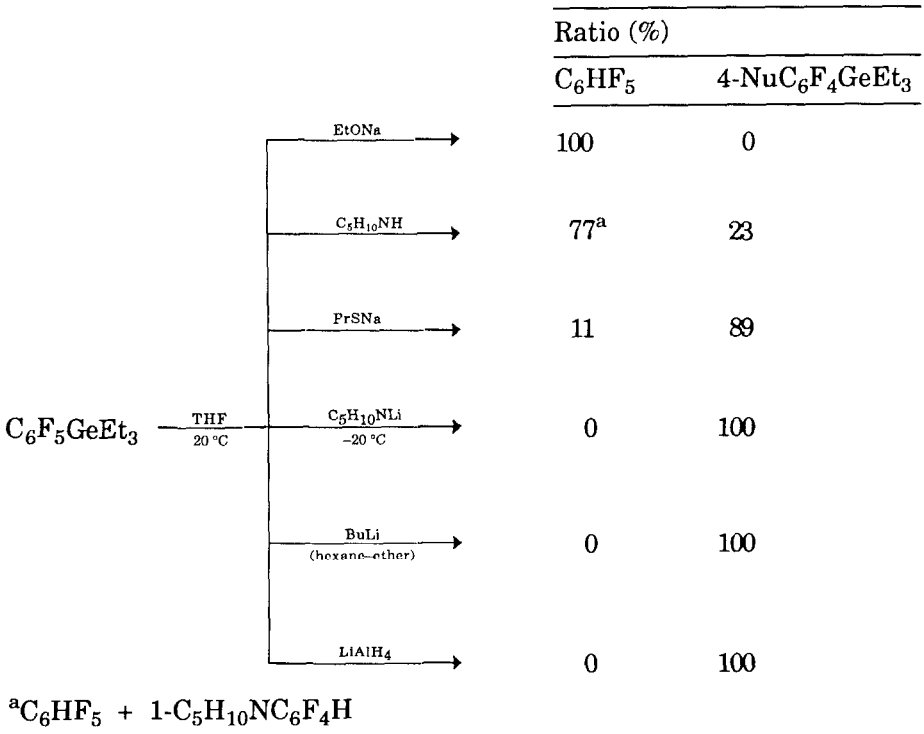
$$C_6F_5GeEt_3 \xrightarrow{BuLi} 4\text{-}BuC_6F_4GeEt_3 \quad (\mathbf{14})$$

$$C_6F_5GeEt_3 \xrightarrow{LiAlH_4} 4\text{-}HC_6F_4GeEt_3 \quad (\mathbf{15})$$

All these reactions are summarized in Scheme 2. Thus, triethylgermylpentafluorobenzene reacts with nucleophiles at two reaction centres, the results of the reactions depending on the nature of the nucleophile but, apparently, being independent of the solvent.

Comparison of the results of nucleophilic reactions of trialkylsilyl- and germylpentafluorobenzene (Schemes 1 and 2) shows that, despite their similarities, there are distinct differences. One is the orientation of the attack by S-nucleophiles. Another difference is the lower rate of reaction of piperidine with germylbenzene (**11**) relative to silylbenzene (**1**) (at 20 °C). This is confirmed by the results of competing reactions of compounds **1** and **11** with piperidine. With the initial ratio of piperidine:**1**:**11** equal to 1:1.1, after 26 h the ratio of **1**:**11** was 1:1.8, and after 144 h no silylbenzene (**1**) existed in the reaction mixture whereas germylbenzene (**11**) still remained present. A similar picture was presented by the pair $C_6F_5SiMe_3$:$C_6F_5GeMe_3$. This latter observation shows that the reactivities of $C_6F_5GeMe_3$ and $C_6F_5GeEt_3$ are not essentially different in this case. Equally, it should be noted that the ratio (**2** + **7**)/(**2** + **7** + **6**) (or **13**) observed in the reaction of piperidine with silylbenzene (**1**) or with germylbenzene (**11**) is equal to 0.65–0.80 in both cases and is virtually independent of the degree of reaction or the solvent employed (except for PrOH).

An important distinction between the reactions of compounds **1** and **11** is that attack by the nucleophile depends on the nature of the latter. 'Soft' nucleophiles, such as butyl-lithium, piperidyl-lithium and lithium aluminium hydride attack only the C-4 atom of the benzene ring. The 'hard' alkoxy



Scheme 2.

oxygen attacks only the heteroatom. The diminished bond ionicity inherent in piperidine relative to piperidyl-lithium results in the nitrogen of piperidine being 'harder' so that piperidine reacts at two electrophilic centres. In other words, the interaction follows the 'hard'–'hard' and 'soft'–'soft' principle (see ref. 10). It would be useful to compare these results with data on the nucleophilic reactions of $C_6F_5GeBr_3$ and $C_6F_5SiCl_3$ [11–14]. Substitution of the electron-donating alkyl groups in compounds **1** and **11** by electron-accepting halogen atoms increases the electron deficiency on the silicon and germanium atoms. Exchange of, for example, the $GeEt_3$ group for $GeBr_3$ group also results in an increase in the partial positive charge on the C-4 atom of the pentafluorophenyl ring. However, experiments have shown the 'hard' and 'soft' nucleophiles react with such compounds only at the silicon and germanium atoms [11–14]. Moreover, substitution of one CH_3 group in compound **1** by a more electronegative H atom, or of two methyl groups by H and C_6F_5 also leads to exclusive attack of the silicon atom by alkyl-magnesium halides, MeLi and BuLi [15–17].

In conclusion, the NMR data indicate that nucleophilic attack on the pentafluorophenyl group in compounds **1** and **11** results in fluorine substitution at the 4 position. No *ortho* substitution relative to the trialkylsilyl (germyl) group was observed with S- and N-nucleophiles, and only traces (<5%) of

the *ortho* isomer were obtained in the reaction of $LiAlH_4$ with compound **11**.

Such regiospecificity of nucleophilic defluorination is apparently due to the electron-accepting resonance effect of the $MAlk_3$ groups, as reported in refs. 1 and 8.

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