Reactions of polyfluoroaromatic compounds with electrophilic agents in the presence of tris(dialkylamino)phosphine

6.* Reactions of halogenotetrafluorobenzenes RC_6F_4X (X = Cl, Br, or I) with chlorotrimethylsilane

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The rate of replacement of the halogen atom in isomers of RC_6F_4X (X = Cl, Br, or I) by the $SiMe_3$ group under the action of Me_3SiCl and $P(NEt_2)_3$ depends on the nature and the mutual arrangement of the substituents X and R. In addition to silyldehalogenation, compounds C_6HF_4X (X = Br or I) undergo silyldeprotonation and reduction to tetrafluorobenzenes.

Key words: halogenotetrafluorobenzenes, dihalogenotetrafluorobenzenes, tris(diethylamino)phosphine, silyldehalogenation, silyldeprotonation.

Previously,[1-4] we have reported the new synthesis of polyfluoroaryl organometallic compounds (derivatives of silicon, germanium, tin, and lead) by the reaction of polyfluoroaryl bromide or iodide with Alk_3EX in the presence of tris(dialkylamino)phosphines. The replacement of fluorine atoms in the aromatic ring by the Et_3Ge group has also been observed.[5] In many cases, this method of nucleophilic polyfluoroarylation is more convenient than the standard synthesis *via* polyfluoroarylmagnesium or polyfluoroaryllithium compounds. First, the reaction occurs in various solvents (CH_2Cl_2, alkanes, *etc.*) and is completed at ~20 °C. Second, in the isolation of products, poorly soluble phosphonium salts that form are easily removed by filtration or washing with acid.

In this work, we studied the dependence of the reactivity of aryl halides RC_6F_4X (X = Cl, Br, or I) in the model reaction with Me_3SiCl in the presence of $P(NEt_2)_3$ on the nature of the substituent R and its position in the ring.

Isomeric dichlorotetrafluorobenzenes (**1**—**3**) slowly react (Scheme 1) in hexane at ~20 °C to form "normal" products (**4**—**6**) and the reduction products (**7** and **8**).

Scheme 1

$$\underset{\mathbf{1}}{1,2\text{-}Cl_2C_6F_4} + \underset{\mathbf{2}}{1,3\text{-}Cl_2C_6F_4} + \underset{\mathbf{3}}{1,4\text{-}Cl_2C_6F_4} \longrightarrow$$

$$\xrightarrow[-20\ ^\circ C]{Me_3SiCl,\ P(NEt_2)_3} \underset{\mathbf{4}}{1\text{-}Me_3Si\text{-}2\text{-}ClC_6F_4} +$$

$$+ \underset{\mathbf{5}}{1\text{-}Me_3Si\text{-}3\text{-}ClC_6F_4} + \underset{\mathbf{6}}{1\text{-}Me_3Si\text{-}4\text{-}ClC_6F_4} +$$

$$+ \underset{\mathbf{7}}{1\text{-}Cl\text{-}2,3,4,5\text{-}C_6F_4H} + \underset{\mathbf{8}}{1\text{-}Cl\text{-}2,3,4,6\text{-}C_6F_4H}$$

The reactions of isomeric dibromotetrafluorobenzenes (**9**—**11**) with equimolar amounts of the reagents in hexane are completed in 1 h to form products **12**—**14** in quantitative yields (Scheme 2) (Table 1).

Scheme 2

$$\underset{\mathbf{9-11}}{1,n\text{-}Br_2C_6F_4} + Me_3SiCl + P(NEt_2)_3 \longrightarrow$$

$$\longrightarrow \underset{\mathbf{12-14}}{1\text{-}Me_3Si\text{-}n\text{-}BrC_6F_4}$$

n = 2 (**9**, **12**), 3 (**10**, **13**), 4 (**11**, **14**)

The reactions of tetrafluorodiiodobenzenes with an excess of Me_3SiCl and $P(NEt_2)_3$ (Scheme 3) are completed in 24—65 h at ~20 °C and also yield products of replacement of only one iodine atom (**18**—**20**) together with the monohydrodeiodination products (**21**—**23**) (see Table 1). The latter compounds are apparently formed independently because interconversion of the products does not occur in the course of the reaction: when conversion of diiodobenzene **17** was 77 and 100% (after 24 and 50 h), the ratios of products **20** : **23** were 90 : 10 and 92 : 8, respectively (^{19}F NMR).

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[*] For Part 5, see Ref. 1.

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Table 1. Reactions of polyfluoroaryl halides with Me_3SiCl and $P(NEt_2)_3$ in hexane

Sub-strate	Number of mmoles			Time /h	Reaction product (yield (%))
	Substrate	Me_3SiCl	$P(NEt_2)_3$		
9	8.8	8.9	8.9	1	**12** (100) (85)[a]
10	1.4	1.7	1.5	1	**13** (100) (75)[a]
11	10	11	10	1	**14** (100), **29**[b]
15	0.72	1.10	0.89	65	**18** (23), **21** (77)[c]
16	5.7	7.3	6.4	24	**19** (86) (66)[a], **22** (14)
17	5.2	6.4	6.0	50	**20** (92), **23** (8)
22	0.58	0.64	0.64	16[d]	**26** (79), **19** (6), **27** (15)[c]
23	1.2	1.4	1.6	20	**29** (46), **20** (23), **30** (31)[c]
24	1.0	1.0	1.0	36	[e]
24	1.7	1.8	1.7	12[d]	[e]
25	1.3	1.8	1.7	47	**26** (31), **13** (21), **27** (48)
25	1.3	1.8	1.6	4[d]	**26** (68), **27** (27), **45** (5)
25	1.3	1.8	1.6	66[f]	**26** (77), **27** (13), **45** (8), **46** (2)
28	1.0	1.3	1.0	3	**29** (67), **14** (23), **30** (10)
31	2.0	2.0	2.2	140	[e]
32	3.8	3.8	3.8	0.3[d]	**6** (100) (61)[a]
33	5.0	11.0	6.0	68	**34** (93), **35** (7)[c]
33	6.4	13.7	7.3	6[g]	**34** (92), **35** (8)[c]
35	2.0	2.2	2.0	40[d]	[e]
C_6F_6	0.80	1.83	1.00	15[g]	[e]

[a] The yield of the isolated product. [b] Traces. [c] Conversion of the substrate: **15**, 70%; **22**, 84%; **23**, 93%; **33**, 60%; and **33**, 72% (at 50 °C). [d] CH_2Cl_2. [e] The reaction did not occur. [f] C_6H_6. [g] At 50 °C.

Scheme 3

$$\underset{\mathbf{15-17}}{1,n\text{-}I_2C_6F_4} + Me_3SiCl + P(NEt_2)_3 \longrightarrow$$

$$\longrightarrow \underset{\mathbf{18-20}}{1\text{-}Me_3Si\text{-}n\text{-}IC_6F_4} + \underset{\mathbf{21-23}}{1\text{-}I\text{-}n\text{-}HC_6F_4}$$

n = 2 (**15**, **18**, **21**), 3 (**16**, **19**, **22**), 3 (**17**, **20**, **23**)

In the case of monohalogenotetrafluorobenzenes, the rate of silyldehalogenation decreases, and unexpected silyldeprotonation and protodehalogenation occur. 1-Bromo-2,3,4,5-tetrafluorobenzene (**24**) remained unchanged under the action of Me_3SiCl and $P(NEt_2)_3$ in hexane (36 h) or in CH_2Cl_2 (12 h). The isomeric 1-bromo-2,3,4,6-tetrafluorobenzene (**25**) gave in hexane the silyldeprotonation product **13**, 1-trimethylsilyl-2,3,4,6-tetrafluorobenzene (**26**), and 1,2,3,5-tetrafluorobenzene (**27**) (conversion was 42% in 4 h). In CH_2Cl_2, this reaction noticeably accelerated to give 1,3-bis(trimethylsilyl)tetrafluorobenzene instead of compound **13** (see Table 1). The reaction of 1-bromo-2,3,5,6-tetrafluorobenzene (**28**) in hexane was completed in 2—3 h to yield silylbromotetrafluorobenzene **14**, 1-trimethylsilyl-2,3,5,6-tetrafluorobenzene (**29**), and 1,2,4,5-tetrafluorobenzene (**30**).

The isomeric iodotetrafluorobenzenes react analogously (Scheme 4).

Scheme 4

$$\underset{\mathbf{22}}{1\text{-}I\text{-}2,3,4,6\text{-}F_4C_6H} + Me_3SiCl + P(NEt_2)_3 \longrightarrow$$

$$\longrightarrow \mathbf{26} + \mathbf{19} + \mathbf{27}$$

$$\underset{\mathbf{23}}{1\text{-}I\text{-}2,3,5,6\text{-}F_4C_6H} + Me_3SiCl + P(NEt_2)_3 \longrightarrow$$

$$\longrightarrow \mathbf{29} + \mathbf{20} + \mathbf{30}$$

However, silyldeprotonation was not observed in the case of pentafluorobenzene (CH_2Cl_2, 40 h), 1-chloro-2,3,5,6-tetrafluorobenzene (**31**) (hexane, 140 h), and tetrafluorobenzenes (hexane, 40 h) at ~20 °C, nor was the replacement of the chlorine atom observed in 1-bromo-4-chlorotetrafluorobenzene (**32**), which rapidly afforded **6** in quantitative yield (Scheme 5, Table 1).

Scheme 5

$$\underset{\mathbf{32}}{1\text{-}Br\text{-}4\text{-}ClC_6F_4} + Me_3SiCl + P(NEt_2)_3 \longrightarrow$$

$$\longrightarrow \underset{\mathbf{6}}{1\text{-}Me_3Si\text{-}4\text{-}ClC_6F_4}$$

In the polyfluoroaromatic ring, the replacement of the Cl atom by the Me_3Si group under the action of $P(NEt_2)_3$ proceeded substantially more slowly than the replacement of Br and I. Chloropentafluorobenzene (**33**) remained virtually unchanged in pentane at ~20 °C for 1 h.[2,3] After 68 h, its conversion into trimethylsilylpentafluorobenzene (**34**) was 60% (72% at 50 °C for 6 h). In the last-mentioned case, pentafluorobenzene (**35**) formed in addition to silylbenzene **34**. Note that hexafluorobenzene remained unchanged under these conditions.

The more precise determination of the dependence of the reactivity of compounds RC_6F_4X on the type and positions of the halogen atom X and the substituent R was made using the method of competitive reactions (Table 2). According to the data from ^{19}F NMR, bromopentafluorobenzene (**36**) reacts with Me_3SiCl and $P(NEt_2)_3$ in CH_2Cl_2 or hexane faster than iodopentafluorobenzene (**37**) (see Table 2), which qualitatively agrees with the results of silyldehalogenation of other RC_6F_4X compounds (see Table 1). It is remarkable that the conversion of bromo- and iodopenta-

Table 2. Competitive reactions of ArX and Ar′X with Me_3SiCl and $P(NEt_2)_3$

ArX, Ar′X (number of mmoles)	Number of mmoles		Time /h	The ArX : Ar′X ratio after the reaction (%)
	Me_3SiCl	$P(NEt_2)_3$		
2 (0.20), **3** (0.17)	0.26	0.13	24	**2** : **3** = 53 : 47
3 (0.23), **33** (0.26)	0.27	0.11	5	**3** : **33** = 46 : 54
			20	**3** : **33** = 42 : 58
9 (1.34), **11** (1.34), **13** (1.34)[b]	0.86	0.80	1	**9**[a] : **11** : **13** = 75 : 20 : 15
13 (0.39), **28** (0.33)	0.55	0.40	2	**13** : **28** = 25 : 75
13 (0.16), **36** (0.16)	0.20	0.13	1	**13** : **36** = 47 : 53
14 (0.20), **40** (0.21)	0.30	0.04	2	**14** : **40** = 61 : 39
16 (0.11), **17** (0.13)	0.18	0.10	5	**16** : **17** = 61 : 39
			20	**16** : **17** = 58 : 42
22 (0.14), **23** (0.13)[b]	0.18	0.14	20	**22** : **23** = 84 : 16
25 (0.43), **28** (0.43)	0.55	0.44	2	**25** : **28** = 81 : 19
28 (0.42), **40** (0.42)	0.51	0.40	2	**28** : **40** = 50 : 50
31 (0.77), **33** (0.59)	1.04	0.13	66	**31**[a] : **33** = 65 : 35
32 (0.59), **36** (0.55)	0.29	0.15	0.6	**32** : **36** = 51 : 49
36 (0.45), **37** (0.45)[b]	0.26	0.10	1	**36** : **37** = 28 : 72
36 (1.25), **37** (1.25)	1.25	1.21	0.3	**36** : **37** = 16 : 84
37 (0.47), **44** (0.47)	0.61	0.20	0.3	**37**[a] : **44** = 63 : 37
36 (0.20), **38** (0.20)	0.38	0.37	1	**36** : **38** = 70 : 30
38 (0.13), **39** (0.14)	0.20	0.05	1	**38** : **39** = 50 : 50

[a] The compound did not react. [b] In hexane.

fluorobenzenes in a competitive reaction with Mg in ether was the same.

Therefore, the rate of silyldehalogenation decreases in the order $C_6F_5Br > C_6F_5I >> C_6F_5Cl >> C_6F_6$.

When the positions of the substituent R and the halogen atom X in 2- and $3\text{-}RC_6F_4Br$ compounds are fixed, the rate of silyldehalogenation is determined by the nature of R and changes in the following order (see Table 2): F > Br >> H ≥ Me_3Si and F > Br > H > Me_3Si for 2-R and 3-R, respectively. Note the absence of bis(trimethylsilyl)tetrafluorobenzenes in the products of the reaction of compounds $C_6F_4X_2$ (X = Cl, Br, or I), which indicates that the rate of silyldehalogenation of these compounds is higher than that of silyltetrafluorohalogenobenzenes $C_6XF_4SiMe_3$ regardless of the nature of X and its position relative to the Me_3Si group.

Derivatives of 1-bromo-2,3,5,6-tetrafluorobenzene are more readily available, which made it possible to use a wider range of compounds $4\text{-}RC_6F_4Br$, in particular, 4-bromoheptafluorotoluene (**38**), 4-bromotetrafluorobenzonitrile (**39**), and 4-bromo-2,3,5,6-tetrafluoroanisole (**40**), which are transformed into the known 4-trimethylsilylheptafluorotoluene (**41**), 4-trimethylsilyl-2,3,5,6-tetrafluorobenzonitrile (**42**), and 4-trimethylsilyl-2,3,5,6-tetrafluoroanisole (**43**), respectively.[3] It was demonstrated that the activation effect of the substituent R on the rate of the reaction of $4\text{-}RC_6F_4Br$ with Me_3SiCl and $P(NEt_2)_3$ varies in the series CN = CF_3 > F = Cl ≥ Br > H = OMe > $SiMe_3$. An analogous situation was observed for polyfluorinated aryl chlorides and aryl iodides. Thus, the rates of the reactions of C_6F_5Cl and $1,4\text{-}C_6Cl_2F_4$ are identical and are higher than that of the reaction of $4\text{-}HC_6F_4Cl$, whereas 4-iodoheptafluorotoluene (**44**) is consumed faster than iodopentafluorobenzene.

The rates of the reactions of compounds RC_6F_4X with Me_3SiCl and $P(NEt_2)_3$ also depends on the mutual arrangement of R and X. It was found that for each of R = X = Cl, Br, and I, the rate of consumption decreases in going from the *para* to *ortho* isomer. The difference in the conversion of the *para* and *meta* isomers is substantially smaller than that between the *meta* and *ortho* isomers: $1,4\text{-}C_6F_4X_2 \geq 1,3\text{-}C_6F_4X_2 >> 1,2\text{-}C_6F_4X_2$ (X = Cl, Br, or I). It is interesting to note that all isomers of $C_6F_4Cl_2$ are transformed into ClC_6F_4Li under the action of BuLi. The reaction of ClC_6F_4Li with Me_3SiCl yields silylbenzenes **4**, **5**, and **6** in a ratio identical to that of the initial dichlorotetrafluorobenzenes **1**, **2**, and **3**.

The tendency of the reactivity to decrease in going from the *para* to *ortho* isomer holds for bromo- and iodotetrafluorobenzenes in spite of the fact that silyldeprotonation competes with hydrodehalogenation of the substrates: $1\text{-Br-}2,3,5,6\text{-}C_6F_4H > 1\text{-Br-}2,3,4,6\text{-}C_6F_4H >> 1\text{-Br-}2,3,4,5\text{-}C_6F_4H > 1\text{-I-}2,3,5,6\text{-}C_6F_4H > 1\text{-I-}2,3,4,6\text{-}C_6F_4H$.

Therefore, the relative rate of the reaction of polyfluoroaryl halides RC_6F_4X with Me_3SiCl and $P(NEt_2)_3$ is determined by the nature of the halogen X and the substituent R and their mutual arrangement. An analogous effect of the substituent R manifests itself in the reaction of polyfluoroaromatic compounds with nucleophilic agents. Therefore, it was reasonable to compare both types of the reactions.

According to the data of kinetic measurements, the relative rates of the reaction of derivatives C_6F_5R with MeONa in MeOH (50 °C) are 1, 5, 21, 20, $1.6 \cdot 10^4$, $4.8 \cdot 10^5$, and $3.2 \cdot 10^6$ for R = H, F, Cl, Br, CF_3, CN, and NO_2, respectively,[6] which qualitatively agrees with the results of the competitive reactions of $4\text{-}RC_6F_4X$ with Me_3SiCl and $P(NEt_2)_3$. However, the relative amount of the isomers of NuC_6F_4R decreases in the series 4-Nu > 2-Nu >> 3-N in the nucleophilic defluorination of compounds C_6F_5R (R = Cl, Br, or I), which may be attributed to a decrease in the relative stability of intermediate anionic σ-complexes.[7] In the reactions of silyldehalogenation of compounds RC_6F_4X, the dependence of the rate of the reaction on the mutual arrangement of R and X is quite different and, apparently, reflects the relative stability of the aryl anion or the structurally similar intermediate state, which appears when the halogen atom X is transferred from ArX to $P(NEt_2)_3$. In this case, the inductive effect of substituents at the C-2 and C-6 atoms of the $RC_6F_4^-$ anion is the governing factor, whereas the replacement of F atoms at positions 3 and 4 by the less electronegative Cl, Br, or H atoms has a substantially weaker effect due to damping of the inductive effect. The relatively small change in the rate of silyldehalogenation in the series of various $4\text{-}RC_6F_4X$ derivatives compared to that observed

Table 3. ^1H and ^{19}F NMR spectra (in $CDCl_3$)

Compound	δ ^1H	δ ^{19}F					J/Hz
		F(2)	F(3)	F(4)	F(5)	F(6)	
4	0.45		25.95	9.81	5.31	37.62	$^5J_{H-CSiCC-F} = 2.3$, $J_{3,4} = 20$, $J_{3,6} = 11$, $J_{4,5} = 19$, $J_{4,6} = 4$, $J_{5,6} = 22$
6	0.42	35.33	20.95		20.95	35.33	$^5J_{H-CSiCC-F} = 1.5^a$
10	0.46		35.61	10.21	6.24	38.69	$^5J_{H-CSiCC-F} = 2.5$, $J_{3,4} = 21.5$, $J_{3,5} = 3.5$, $J_{3,6} = 11$, $J_{4,5} = 19$, $J_{4,6} = 5$, $J_{5,6} = 22.5$
12	0.38	65.10		38.39	−0.16	40.36	$^5J_{H-CSiCC-F} = 1.5$, $J_{2,5} = 11$, $J_{4,5} = 20.5$, $J_{4,6} = 7.6$, $J_{5,6} = 23$
18[b]	0.46		53.73	10.98	8.13	41.17	$J_{3,4} = 22$, $J_{3,5} = 4.5$, $J_{3,6} = 11.5$, $J_{4,5} = 17$, $J_{4,6} = 5.5$, $J_{5,6} = 20$
19	0.41	78.53		51.28	0.05	41.57	$J_{2,5} = 11$, $J_{4,5} = 22$, $J_{4,6} = 8$, $J_{5,6} = 22$
20[b]	0.42	36.02	41.68		41.68	36.02	[a]
29[c]	0.39, 7.00	33.45	22.63		22.63	33.45	[a]

[a] The AA′BB′ spin system. [b] In hexane. [c] *cf.* Ref. 14.

in the nucleophilic defluorination of RC_6F_5 compounds is also explained by the fact that the difference in the electronegativities of the substituents R removed from the reaction center has a lesser effect. These results agree with the decrease in the kinetic and equilibrium acidities in the series C_6F_5H > 1,4-$C_6H_2F_4$ > 1,3-$C_6H_2F_4$ > 1,2-$C_6H_2F_4$.[8]

However, the pathways of reduction of diiodotetrafluorobenzenes to iodotetrafluorobenzenes is still a question. Although the reduction of 4-I-C_6F_4CN [9] and 4-iodotetrafluoropyridine[10] by iodide anions in polar solvents has been previously reported, we demonstrated that a mixture of IC_6F_5 and diiodotetrafluorobenzene **16** remained unchanged under the action of $P(NEt_2)_3ClI$ (in CH_2Cl_2) for 6 days. The replacement of the halogen atom by H may be the result of competitive processes, including those with the participation of polyfluoroaryl radicals. To check this possibility, we carried out the reaction of bromotetrafluorobenzene **25** with Me_3SiCl and $P(NEt_2)_3$ in benzene, which is the radical scavenger. Actually, 2,3,4,6-tetrafluorobiphenyl was found in the reaction mixture, but its concentration was ~ one sixth of that of 1,2,3,5-tetrafluorobenzene, which is indicative of an insignificant contribution of radical reactions. For comparison, radical pentafluorophenylation of benzene afforded 2,3,4,5,6-pentaflurobiphenyl in high yield, whereas pentafluorobenzene was absent.[11]

The mechanism of the replacement of the hydrogen atom by the trimethylsilyl group in halogenotetrafluorobenzenes **22**, **23**, **25**, and **28** is also unclear. Taking into account that fluorobenzenes $C_6F_4H_2$, C_6F_5H, and 4-ClC_6F_4H are inert with respect to Me_3SiCl and $P(NEt_2)_3$, it should be suggested that silyldeprotonation of halides RC_6F_4H (R = Br or I) is preceded by coordination of $P(NEt_2)_3$ to the Br or I atom.

Unlike silyldehalogenation of polyfluoroaryl halides, the replacement of the F atom by the Et_3Ge group under the action of Et_3GeCl and $P(NEt_2)_3$, which we have observed previously for fluorobenzenes C_6F_5R (R = CF_3, CO_2Me, CN, or NO_2), occurs according to the mechanism whose key stage is, apparently, the nucleophilic attack of $P(NEt_2)_3$ on the C atom at the *para* position with respect to the substituent R.[5] This reaction is regiospecific, and the dependence of the rate of germyldefluorination on the nature of the substituent R is close to that for methoxydefluorination with sodium methoxide. Using competitive reactions of fluorobenzenes $C_6F_5CN-C_6F_5NO_2$ and $C_6F_5CN-C_6F_5CF_3$ with Me_3SiCl and $P(NEt_2)_3$ as an example, it was demonstrated that this dependence exists in the silyldefluorination. It should be noted that in the competitive reaction, C_6F_5CN reacts substantially faster than octafluorotoluene, whereas the rates of consumption of 4-BrC_6F_4CN and 4-$BrC_6F_4CF_3$ are almost identical.

Compounds **6**, **12**, **13**, and **19**, which have not been reported previously, were isolated by distillation and identified based on the data of elemental analysis, IR spectra, and ^1H and ^{19}F NMR spectra (Table 3). Compound **4** was isolated together with isomers **6** and **5**. Isomer **5** was described previously[12] and characterized by the ^1H and ^{19}F NMR spectra. The structures of silylbenzenes **18** and **20** were established based on the ^1H and ^{19}F NMR spectra of their mixtures with other reaction products and on results of hydrodesilylation with KF [13] to the known iodotetrafluorobenzenes **21** and **23**, respectively. Silylbenzenes **14**,[3] **26**,[12] and **29**,[14] 1,3-bis(trimethylsilyl)tetrafluorobenzene (**45**),[12] and 2,3,4,6-tetrafluorobiphenyl (**46**)[15] were identified by comparing their ^1H and ^{19}F NMR spectra with the spectra of the known compounds.

Experimental

The ^1H (200 MHz) and ^{19}F (188.3 MHz) NMR spectra were recorded on Bruker WP 200 SY and AC 200 spectrometers (Me_4Si and C_6F_6 as internal standards). The IR spectra were recorded on a Specord M-80 instrument in CCl_4 (3%).

Me_3SiCl was distilled over CaH_2 before use. $P(NEt_2)_3$ was purified according to the known procedure.[4] Hexane and CH_2Cl_2 were dried with $CaCl_2$ and distilled over CaH_2. Compound **15** was synthesized according to the modified procedure[16] developed for the synthesis of diiodobenzene **16**.

1,2-Diiodotetrafluorobenzene (15). KI (8.2 g, 49.3 mmol) was added portionwise to a stirred solution of KIO_4 (3.9 g, 17 mmol) in concentrated H_2SO_4 (45 mL) chilled with cold water. Then 1,2,3,4-tetrafluorobenzene (2.5 g, 16.7 mmol) was added, and the reaction mixture was heated at 70 °C for 8 h, whereupon iodine sublimed in the upper part of the vessel. The mixture was cooled, and the dark solution was poured onto ice and extracted with CH_2Cl_2. The extract was washed with an aqueous $Na_2S_2O_3$ solution and water and dried with $MgSO_4$. The solvent was removed by distillation *in vacuo*. The residue was chromatographed on a short column with SiO_2 (pentane was used as the eluent). After the removal of the solvent, compound **15** was obtained in a yield of 4.1 g (63%). The IR spectra and the ^{19}F NMR spectra of **15** are identical to those of an authentic sample.

Chlorotetrafluorotrimethylsilylbenzenes. A solution of dichlorotetrafluorobenzenes (*o* : *m* : *p* = 23 : 65 : 12) (5.5 g, 25 mmol) in ether (30 mL) was cooled to −10—−12 °C under an atmosphere of argon and a cooled (−10 °C) 2 *M* etheral solution of BuLi (18 mL, 36 mmol) was added dropwise at ≤ −5 °C. The mixture was stirred at −5—−8 °C for 30 min, and then Me_3SiCl (3 mL) was added with a syringe. The mixture was stirred at −5—−8 °C for 25 min. Cooling was discontinued, and after 20 min, the solution was poured into dilute HCl. The organic layer was washed with water and dried with $CaCl_2$. The solvent was removed by distillation, and the residue was distilled. A mixture of isomeric *o*-, *m*-, and *p*-chlorotetrafluorotrimethylsilylbenzenes was obtained in a ratio of 22 : 67 : 11 in a yield of 4.6 g (72%). B.p. 204—206 °C. Found (%): C, 42.5; H, 3.92; Cl, 14.0; F, 29.6. $C_9H_9ClF_4Si$. Calculated (%): C, 42.1; H, 3.51; Cl, 13.8; F, 29.6.

Silyldehalogenation of tetrafluorobenzenes RC_6F_4X (general procedure). Compound RC_6F_4X (X = Cl, Br, or I) and Me_3SiCl were dissolved in hexane (dichloromethane). $P(NEt_2)_3$ was added dropwise with stirring. The course of the reaction was monitored by ^{19}F NMR spectroscopy. The reaction mixture was washed with concentrated HCl or 50% aqueous H_2SO_4 and water and dried with $MgSO_4$. The solvent was evaporated, and the residue was distilled to give compounds **6**, **12**, **13**, and **19** (see Tables 1 and 2).

The reaction of dichlorotetrafluorobenzene (*o* : *m* : *p* = 23 : 65 : 12) (32 mmol) with Me_3SiCl (37 mmol) and $P(NEt_2)_3$ (34 mmol) in hexane (35 mL) yielded after 7 days a mixture containing compounds **1** (16%), **2** (5%), **3** (traces), **4** (3%), **5** (54%), **6** (10%), **7** (4%), and **8** (8%). The conversion of dichlorotetrafluorobenzenes **1**, **2**, and **3** was 40, 94, and 100%, respectively (^{19}F NMR).

The reactions of diiodotetrafluorobenzenes **15** and **17** were carried out analogously (see Tables 1 and 3). The NMR spectra were recorded, and then the solvent was evaporated *in vacuo*. The residue was dissolved in MeCN (1—2 mL) and MeOH (0.5 mL), and KF (0.5 g) was added. The reaction mixture was stirred at ~20 °C for 12—22 h. Volatile compounds were distilled off *in vacuo*. The residue was extracted with CH_2Cl_2, washed with water, and dried with $CaCl_2$. The solvent was distilled off. Compound **15** gave a mixture of products **15** and **21** (yield 83% with respect to the consumed substrate **15**). Compound **17** gave iodobenzene **23** (yield 57%).

Polyfluoroarenes remained unchanged upon treatment of 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-tetrafluorobenzenes (14 : 77 : 9) (1 mmol) with Me_3SiCl (1.6 mmol) and $P(NEt_2)_3$ (1.1 mmol) in hexane (1 mL) at 20—22 °C for 40 h (^{19}F NMR).

2-Bromo-1-trimethylsilyltetrafluorobenzene (12). B.p. 100—103 °C (15 Torr). Found (%): C, 36.0; H, 2.97; Br, 27.0; F, 25.2. $C_9H_9BrF_4Si$. Calculated (%): C, 35.9; H, 2.99; Br, 26.6; F, 25.2. IR, ν/cm^{-1}: 2960, 2903, 1620, 1604, 1500, 1462, 1428, 1360, 1328, 1302, 1250, 1192, 1120, 1100, 1027, 1000, 867, 850.

3-Bromo-1-trimethylsilyltetrafluorobenzene (13). B.p. 122—124 °C (25 Torr). Found (%): C, 36.0; H, 3.10; Br, 26.9; F, 25.3. $C_9H_9BrF_4Si$. Calculated (%): C, 35.9; H, 2.99; Br, 26.6; F, 25.2. IR, ν/cm^{-1}: 2963, 2907, 1630, 1617, 1600, 1475, 1428, 1266, 1255, 1237, 1230, 1075, 1055, 895.

3-Iodo-1-trimethylsilyltetrafluorobenzene (19). B.p. 83—84 °C (1 Torr). Found (%): C, 31.1; H, 2.62; F, 22.0; I, 36.2. $C_9H_9F_4ISi$. Calculated (%): C, 31.0; H, 2.59; F, 21.8; I, 36.5. IR, ν/cm^{-1}: 2975, 2956, 2905, 1625, 1594, 1467, 1424, 1256, 1227, 1077, 1048, 886, 845.

4-Chloro-1-trimethylsilyltetrafluorobenzene (6). B.p. 203—206 °C. Found (%): C, 42.5; H, 3.51; Cl, 14.1; F, 29.6. $C_9H_9ClF_4Si$. Calculated (%): C, 42.1; H, 3.51; Cl, 13.8; F, 29.6. IR, ν/cm^{-1}: 2963, 2907, 1627, 1512, 1490, 1465, 1453, 1413, 1377, 1367, 1255, 1244, 954, 944, 850.

Competitive reactions of polyfluoroaryl halides ArX and Ar'X (Ar'Y) with Me_3SiCl and $P(NEt_2)_3$ (see Table 2). Me_3SiCl and $P(NEt_2)_3$ were added successively to a stirred solution of polyfluoroaryl halides ArX and Ar'X in CH_2Cl_2 (0.8—1 mL). The course of the reaction was monitored by ^{19}F NMR spectroscopy. When the reaction was carried out in hexane, the reaction mixture was washed previously with a dilute HCl and water and dried with $CaCl_2$. The statistical factor was taken into account in the analysis of products of the reaction of RC_6F_4X and $C_6F_4X_2$.

Competitive reaction of C_6F_5Br and C_6F_5I with Mg. Magnesium turning (5.1 mg-at.) were activated with iodine. Then anhydrous ether (7 mL) was added, and several drops of a solution of C_6F_5Br (5 mmol) and C_6F_5I (5 mmol) in ether (3 mL) was added with stirring. After the beginning of the reaction, the remaining solution was added dropwise over a period of 10 min, and the reaction mixture was refluxed for 40 min. According to the ^{19}F NMR data, the reaction mixture contained C_6F_5Br, C_6F_5I, and C_6F_5MgX in a ratio of 25 : 26 : 49 mol. %.

Reaction of polyfluoroaryl iodides with $P(NEt_2)_3ClI$. A solution of 1,3-diiodotetrafluorobenzene (1 mmol), iodopentafluorobenzene (1.4 mmol), and $P(NEt_2)_3ClI$ (2.4 mmol) in CH_2Cl_2 (1.5 mL) was stirred at ~20 °C for 6 days. According to the ^{19}F NMR data, compounds **16** and **37** remained unchanged.

Competitive reactions of C_6F_5X and C_6F_5Y with Me_3SiCl and $P(NEt_2)_3$. ***A.*** $P(NEt_2)_3$ (74 mg, 0.3 mmol) was added to a solution of C_6F_5CN (85 mg, 0.44 mmol), $C_6F_5NO_2$ (93 mg, 0.436 mmol), and Me_3SiCl (60 mg, 0.55 mmol) in CH_2Cl_2 (0.8 mL). After 40 min, the C_6F_5CN : $C_6F_5NO_2$ ratio was 62 : 38, and it remained unchanged after 14 h (^{19}F NMR).

B. $P(NEt_2)_3$ (55 mg, 0.222 mmol) was added to a solution of C_6F_5CN (70 mg, 0.362 mmol), $C_6F_5CF_3$ (96 mg, 0.408 mmol), and Me_3SiCl (62 mg, 0.568 mmol) in CH_2Cl_2 (0.8 mL). After 1 h, the C_6F_5CN : $C_6F_5CF_3$ ratio was 23 : 77. Products of conversion of octafluorotoluene were not observed (^{19}F NMR).

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