

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

6.* Reactions of halogenotetrafluorobenzenes RC_6F_4X ($X = Cl, Br, \text{ or } I$) with chlorotrimethylsilane

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The rate of replacement of the halogen atom in isomers of RC_6F_4X ($X = Cl, Br, \text{ or } I$) 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 ($X = Br \text{ or } I$) 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 $-20^\circ C$. Second, in the isolation of products, poorly soluble phosphonium salts that form are easily removed by filtration or washing with acid.

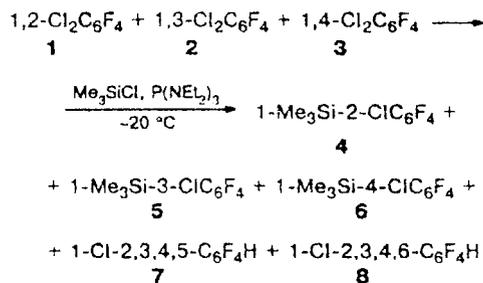
In this work, we studied the dependence of the reactivity of aryl halides RC_6F_4X ($X = Cl, Br, \text{ or } I$) in the model reaction with Me_3SiCl in the presence of $P(NEt_2)_3$ on the nature of the substituent R and its position in the ring.

Isomeric dichlorotetrafluorobenzenes (**1-3**) slowly react (Scheme 1) in hexane at $-20^\circ C$ to form "normal" products (**4-6**) and the reduction products (**7** and **8**).

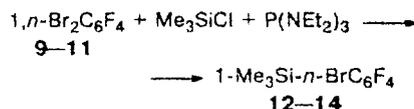
The reactions of isomeric dibromotetrafluorobenzenes (**9-11**) with equimolar amounts of the reagents in hexane are completed in 1 h to form products **12-14** in quantitative yields (Scheme 2) (Table 1).

The reactions of tetrafluorodiiodobenzenes with an excess of Me_3SiCl and $P(NEt_2)_3$ (Scheme 3) are completed in 24-65 h at $-20^\circ C$ and also yield products of

Scheme 1



Scheme 2



$$n = 2 (\mathbf{9}, \mathbf{12}), 3 (\mathbf{10}, \mathbf{13}), 4 (\mathbf{11}, \mathbf{14})$$

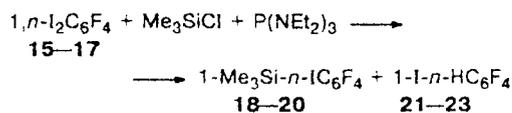
replacement of only one iodine atom (**18-20**) together with the monohydrodeiodination products (**21-23**) (see Table 1). The latter compounds are apparently formed independently because interconversion of the products does not occur in the course of the reaction: when conversion of diiodobenzene **17** 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).

* For Part 5, see Ref. 1.

Table 1. Reactions of polyfluoroaryl halides with Me₃SiCl and P(NEt₂)₃ in hexane

Substrate	Number of mmoles			Time /h	Reaction product (yield (%))
	Substrate	Me ₃ SiCl	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) ^e
23	1.2	1.4	1.6	20	29 (46), 20 (23), 30 (31) ^e
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 ₆ F 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 CH₂Cl₂. ^e The reaction did not occur. ^f C₆H₆. ^g At 50 °C.

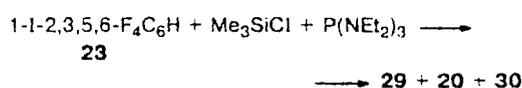
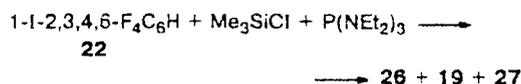
Scheme 3

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

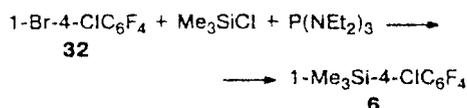
In the case of monohalogenotetrafluorobenzenes, the rate of silyldehalogenation decreases, and unexpected silyldeprotonation and protodehalogenation occur. 1-Bromo-2,3,4,5-tetrafluorobenzene (24) remained unchanged under the action of Me₃SiCl and P(NEt₂)₃ in hexane (36 h) or in CH₂Cl₂ (12 h). The isomeric 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 CH₂Cl₂, this reaction noticeably accelerated to give 1,3-bis(trimethylsilyl)tetrafluorobenzene instead of com-

pound 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

However, silyldeprotonation was not observed in the case of pentafluorobenzene (CH₂Cl₂, 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

In the polyfluoroaromatic ring, the replacement of the Cl atom by the Me₃Si group under the action of P(NEt₂)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 RC₆F₄X 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 ¹⁹F NMR, bromopentafluorobenzene (36) reacts with Me₃SiCl and P(NEt₂)₃ in CH₂Cl₂ or hexane faster than iodopentafluorobenzene (37) (see Table 2), which qualitatively agrees with the results of silyldehalogenation of other RC₆F₄X compounds (see Table 1). It is remarkable that the conversion of bromo- and iodopenta-

Table 2. Competitive reactions of ArX and Ar'X with Me₃SiCl and P(NEt₂)₃

ArX, Ar'X (number of mmoles)	Number of mmoles		Time /h	The ArX : Ar'X ratio after the reaction (%)
	Me ₃ SiCl	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 C₆F₅Br > C₆F₅I >> C₆F₅Cl >> C₆F₆.

When the positions of the substituent R and the halogen atom X in 2- and 3-RC₆F₄Br 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 ≥ Me₃Si and F > Br > H > Me₃Si for 2-R and 3-R, respectively. Note the absence of bis(trimethylsilyl)tetrafluorobenzenes in the products of the reaction of compounds C₆F₄X₂ (X = Cl, Br, or I), which indicates that the rate of silyldehalogenation of these compounds is higher than that of silyltetrafluorohalogenobenzenes C₆XF₄SiMe₃ regardless of the nature of X and its position relative to the Me₃Si 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-RC₆F₄Br, 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-RC₆F₄Br with Me₃SiCl and P(NEt₂)₃ varies in the series CN = CF₃ > F = Cl ≥ Br > H = OMe > SiMe₃. An analogous situation was observed for polyfluorinated aryl chlorides and aryl iodides. Thus, the rates of the reactions of C₆F₅Cl and

1,4-C₆Cl₂F₄ are identical and are higher than that of the reaction of 4-HC₆F₄Cl, whereas 4-iodoheptafluorotoluene (44) is consumed faster than iodopentafluorobenzene.

The rates of the reactions of compounds RC₆F₄X with Me₃SiCl and P(NEt₂)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-C₆F₄X₂ ≥ 1,3-C₆F₄X₂ >> 1,2-C₆F₄X₂ (X = Cl, Br, or I). It is interesting to note that all isomers of C₆F₄Cl₂ are transformed into ClC₆F₄Li under the action of BuLi. The reaction of ClC₆F₄Li with Me₃SiCl 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-Br-2,3,5,6-C₆F₄H > 1-Br-2,3,4,6-C₆F₄H >> 1-Br-2,3,4,5-C₆F₄H > 1-I-2,3,5,6-C₆F₄H > 1-I-2,3,4,6-C₆F₄H.

Therefore, the relative rate of the reaction of polyfluoroaryl halides RC₆F₄X with Me₃SiCl and P(NEt₂)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 C₆F₅R with MeONa in MeOH (50 °C) are 1, 5, 21, 20, 1.6 · 10⁴, 4.8 · 10⁵, and 3.2 · 10⁶ for R = H, F, Cl, Br, CF₃, CN, and NO₂, respectively,⁶ which qualitatively agrees with the results of the competitive reactions of 4-RC₆F₄X with Me₃SiCl and P(NEt₂)₃. However, the relative amount of the isomers of NuC₆F₄R decreases in the series 4-Nu > 2-Nu >> 3-Nu in the nucleophilic defluorination of compounds C₆F₅R (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 RC₆F₄X, 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(NEt₂)₃. In this case, the inductive effect of substituents at the C-2 and C-6 atoms of the RC₆F₄⁻ 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-RC₆F₄X 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	$^5J_{\text{H}-\text{CSiCC}-\text{F}} = 2.3, J_{3,4} = 20, J_{3,6} = 11, J_{4,5} = 19, J_{4,6} = 4, J_{5,6} = 22$
6	0.42	35.33	20.95		20.95	35.33	$^5J_{\text{H}-\text{CSiCC}-\text{F}} = 1.5^a$
10	0.46		35.61	10.21	6.24	38.69	$^5J_{\text{H}-\text{CSiCC}-\text{F}} = 2.5, J_{3,4} = 21.5, J_{3,5} = 3.5, J_{3,6} = 11, J_{4,5} = 19, J_{4,6} = 5, J_{5,6} = 22.5$
12	0.38	65.10		38.39	-0.16	40.36	$^5J_{\text{H}-\text{CSiCC}-\text{F}} = 1.5, J_{2,5} = 11, J_{4,5} = 20.5, J_{4,6} = 7.6, J_{5,6} = 23$
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 $\text{C}_6\text{F}_5\text{H} > 1,4\text{-C}_6\text{H}_2\text{F}_4 > 1,3\text{-C}_6\text{H}_2\text{F}_4 > 1,2\text{-C}_6\text{H}_2\text{F}_4$.⁸

However, the pathways of reduction of diiodotetrafluorobenzenes to iodotetrafluorobenzenes is still a question. Although the reduction of 4-I-C₆F₄CN⁹ and 4-iodotetrafluoropyridine¹⁰ by iodide anions in polar solvents has been previously reported, we demonstrated that a mixture of I-C₆F₅ and diiodotetrafluorobenzene **16** remained unchanged under the action of P(NEt₂)₃ClI (in CH₂Cl₂) 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 Me₃SiCl and P(NEt₂)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-pentafluorobiphenyl 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 C₆F₄H₂, C₆F₅H, and 4-ClC₆F₄H are inert with respect to Me₃SiCl and P(NEt₂)₃, it should be suggested that silyldeprotonation of halides RC₆F₄H (R = Br or I) is preceded by coordination of P(NEt₂)₃ to the Br or I atom.

Unlike silyldehalogenation of polyfluoroaryl halides, the replacement of the F atom by the Et₃Ge group under the action of Et₃GeCl and P(NEt₂)₃, which we have observed previously for fluorobenzenes C₆F₅R (R = CF₃, CO₂Me, CN, or NO₂), occurs according to the mechanism whose key stage is, apparently, the nucleophilic attack of P(NEt₂)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 gemyldefluorination on the nature of the substituent R is close to that for methoxydefluorination with sodium methoxide. Using competitive reactions of fluorobenzenes C₆F₅CN-C₆F₅NO₂ and C₆F₅CN-C₆F₅CF₃ with Me₃SiCl and P(NEt₂)₃ as an example, it was demonstrated that this dependence exists in the silyldefluorination. It should be noted that in the competitive reaction, C₆F₅CN reacts substantially faster than octafluorotoluene, whereas the rates of consumption of 4-BrC₆F₄CN and 4-BrC₆F₄CF₃ 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 previously¹² 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 KF¹³ 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 (Me₄Si and C₆F₆ as internal standards). The IR spectra were recorded on a Specord M-80 instrument in CCl₄ (3%).

Me₃SiCl was distilled over CaH₂ before use. P(NEt₂)₃ was purified according to the known procedure.⁴ Hexane and CH₂Cl₂ were dried with CaCl₂ and distilled over CaH₂. Compound **15** was synthesized according to the modified procedure¹⁶ 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 KIO₄ (3.9 g, 17 mmol) in concentrated H₂SO₄ (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 $\text{Na}_2\text{S}_2\text{O}_3$ 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 ($\sigma : m : p = 23 : 65 : 12$) (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 ethereal 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. $\text{C}_9\text{H}_9\text{ClF}_4\text{Si}$. Calculated (%): C, 42.1; H, 3.51; Cl, 13.8; F, 29.6.

Silyldehalogenation of tetrafluorobenzenes $\text{RC}_6\text{F}_4\text{X}$ (general procedure). Compound $\text{RC}_6\text{F}_4\text{X}$ (X = Cl, Br, or I) and Me_3SiCl were dissolved in hexane (dichloromethane). $\text{P}(\text{NEt}_2)_3$ 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 ($\sigma : m : p = 23 : 65 : 12$) (32 mmol) with Me_3SiCl (37 mmol) and $\text{P}(\text{NEt}_2)_3$ (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 $\text{P}(\text{NEt}_2)_3$ (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. $\text{C}_9\text{H}_9\text{BrF}_4\text{Si}$. 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. $\text{C}_9\text{H}_9\text{BrF}_4\text{Si}$. 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. $\text{C}_9\text{H}_9\text{F}_4\text{I}$. 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. $\text{C}_9\text{H}_9\text{ClF}_4\text{Si}$. 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' with Me_3SiCl and $\text{P}(\text{NEt}_2)_3$ (see Table 2). Me_3SiCl and $\text{P}(\text{NEt}_2)_3$ 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 $\text{RC}_6\text{F}_4\text{X}$ and $\text{C}_6\text{F}_5\text{X}_2$.

Competitive reaction of $\text{C}_6\text{F}_5\text{Br}$ and $\text{C}_6\text{F}_5\text{I}$ 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 $\text{C}_6\text{F}_5\text{Br}$ (5 mmol) and $\text{C}_6\text{F}_5\text{I}$ (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 $\text{C}_6\text{F}_5\text{Br}$, $\text{C}_6\text{F}_5\text{I}$, and $\text{C}_6\text{F}_5\text{MgX}$ in a ratio of 25 : 26 : 49 mol. %.

Reaction of polyfluoroaryl iodides with $\text{P}(\text{NEt}_2)_3\text{I}$. A solution of 1,3-diiodotetrafluorobenzene (1 mmol), iodo-pentafluorobenzene (1.4 mmol), and $\text{P}(\text{NEt}_2)_3\text{I}$ (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 $\text{C}_6\text{F}_5\text{X}$ and $\text{C}_6\text{F}_5\text{Y}$ with Me_3SiCl and $\text{P}(\text{NEt}_2)_3$. A. $\text{P}(\text{NEt}_2)_3$ (74 mg, 0.3 mmol) was added to a solution of $\text{C}_6\text{F}_5\text{CN}$ (85 mg, 0.44 mmol), $\text{C}_6\text{F}_5\text{NO}_2$ (93 mg, 0.436 mmol), and Me_3SiCl (60 mg, 0.55 mmol) in CH_2Cl_2 (0.8 mL). After 40 min, the $\text{C}_6\text{F}_5\text{CN} : \text{C}_6\text{F}_5\text{NO}_2$ ratio was 62 : 38, and it remained unchanged after 14 h (^{19}F NMR).

B. $\text{P}(\text{NEt}_2)_3$ (55 mg, 0.222 mmol) was added to a solution of $\text{C}_6\text{F}_5\text{CN}$ (70 mg, 0.362 mmol), $\text{C}_6\text{F}_5\text{CF}_3$ (96 mg, 0.408 mmol), and Me_3SiCl (62 mg, 0.568 mmol) in CH_2Cl_2 (0.8 mL). After 1 h, the $\text{C}_6\text{F}_5\text{CN} : \text{C}_6\text{F}_5\text{CF}_3$ ratio was 23 : 77. Products of conversion of octafluorotoluene were not observed (^{19}F NMR).

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