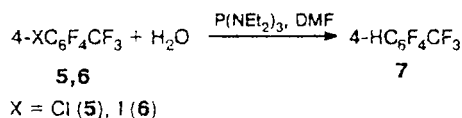


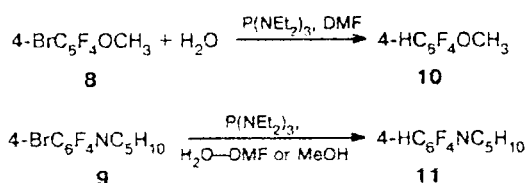
(5) and 4-bromoheptafluorotoluene (6) were reduced to 4-H-heptafluorotoluene (7) at 20 °C in 15–30 min (Scheme 2). However, unlike bromoheptafluorotoluene 6, conversion of chlorine analog 5 under the action of 1 equiv. of $P(NEt_2)_3$ did not exceed 40%, and an excess of $P(NEt_2)_3$ was required for complete conversion.

Scheme 2



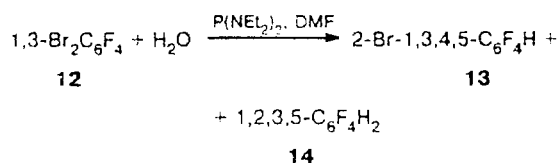
In spite of the presence of electron-donor substituents, 4-bromo-2,3,5,6-tetrafluoroanisole (8) and 4-bromo-2,3,5,6-tetrafluoro-1-piperidinobenzene (9) also undergo protodebromination under the action of $P(NEt_2)_3$ in methanol or aqueous DMF to form 2,3,5,6-tetrafluoroanisole (10) and 2,3,5,6-tetrafluoro-1-piperidinobenzene (11), respectively (Scheme 3).

Scheme 3



If a polyfluoroarene molecule contains more than one bromine (iodine) atom, one would expect the consecutive replacement of these atoms by hydrogen. Actually, when 1,3-dibromotetrafluorobenzene (12) was treated with 1 equiv. of $P(NEt_2)_3$, 2-bromo-1,3,4,5-tetrafluorobenzene (13) and 1,2,3,5-tetrafluorobenzene (14) formed (Scheme 4). In the presence of an excess of $P(NEt_2)_3$, both bromine atoms were replaced by hydrogen.

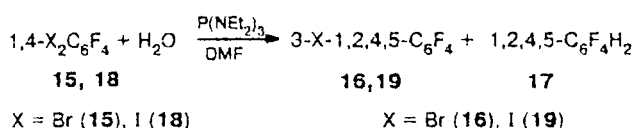
Scheme 4



Under analogous conditions (1.2 equiv. of $P(NEt_2)_3$), 1,4-dibromotetrafluorobenzene (15) was transformed partially into 3-bromo-1,2,4,5-tetrafluorobenzene (16) and 1,2,4,5-tetrafluorobenzene (17). Analogously, 3-iodo-1,2,4,5-tetrafluorobenzene (19) and tetrafluoro-

benzene 17 formed from 1,4-diiodotetrafluorobenzene (18) (conversion of compound 18 was 82%). In the presence of an excess of $P(NEt_2)_3$, both compounds, 15 and 18, were reduced rapidly to tetrafluorobenzene 17 (Scheme 5).

Scheme 5



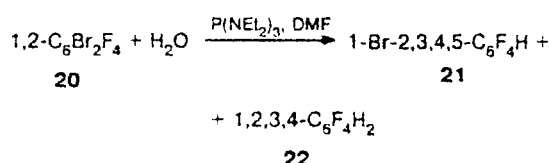
Reduction of dihalotetrafluorobenzenes 12, 15, and 18 with water and 1 equiv. of $P(NEt_2)_3$ yields tetrafluorobenzenes 14 and 17, which is indicative of a slight difference in the rates of the reaction of $X_2C_6F_4$ and HC_6F_4X compounds with identical mutual arrangement of the substituents other than fluorine. However, this difference becomes more pronounced in the reduction of 1,2-dibromotetrafluorobenzene (20). Treatment of the latter with 1 equiv. of $P(NEt_2)_3$ in aqueous DMF or with 1 equiv. of tris(piperidino)phosphine in a MeOH—CH₂Cl₂ mixture affords 1-bromo-2,3,4,5-tetrafluorobenzene (21) and a small amount of 1,2,3,4-tetrafluorobenzene (22) (Scheme 6). Further replacement of bromine in bromobenzene 21 occurs slowly. Thus, treatment of 1,2-dibromotetrafluorobenzene 20 with H₂O and 2 equiv. of $P(NEt_2)_3$ for 84 h yields compounds 21 and 22 in a ratio of 23 : 77.

Table 1. Protodehalogenation of halopolyfluorobenzenes Ar_FX

Ar _F X	Number of moles		V/mL		Time /min	Products (yield, %)
	Ar _F X	$P(NEt_2)_3$	H ₂ O	DMF		
2	4.8	6.5		5 ^a	10	4 (100) ^b
2	10	10	0.2	7.5	15	4 (72)
3	6.5	8	0.15	6	10	4 (94)
5	2	7	0.2	3	30	7 (100) ^b
6	6.0	21	0.6	8	15	7 (77)
8	10	10	0.25	10	120	10 (67)
9	3.2	4.8	0.32	6	80	11 (81)
9	3.2	4.8		5 ^a	20	11 (92)
12	0.9	0.9	0.04	2.5	30	13 (41), 14 (22) ^{b,c}
12	1.0	2.5	0.1	2.5	30	14 (100) ^b
15	0.6	0.7	0.03	2	30	16 (33), 17 (39) ^{b,c}
15	2.9	11	0.45	3	40	17 (93)
18	1.2	1.4	0.1	3	20	19 (55), 17 (27) ^{b,c}
18	1.2	3.5	0.2	5	15	17 (72)
20	1.6	1.6	0.04	3	30	21 (96), 22 (4) ^b
20	1.6	3.4	0.04	3	84 h	21 (50), 22 (50) ^b

^a MeOH. ^b The yield according to the data of ¹⁹F NMR spectroscopy. ^c Conversions of compounds 12, 15, and 18 were 63%, 72%, and 82%, respectively.

Scheme 6



It is noteworthy that in 1-bromotetrafluorobenzene **21**, the replacement of bromine by a trimethylsilyl group does not occur under the action of ClSiMe_3 and $\text{P(NEt}_2)_3$ in less polar solvents (hexane or dichloromethane).¹

The dependence of the rate of replacement of a halogen atom by an electrophile under the action of $\text{P(NEt}_2)_3$ on the mutual arrangement of the halogen atom and the CF_3 group was observed in the competitive reduction of 3-chloroheptafluorotoluene (**23**) and 4-chloro isomer **5** in aqueous ether by the successive addition of 0.45 and 1.0 equiv. of $\text{P(NEt}_2)_3$. As a result, 5-H-heptafluorotoluene (**24**) and the 4-H-isomer **7** form, and *para* isomer **5** is predominantly consumed.

A comparison of our results with the data¹ on silyldehalogenation of tetrafluorobenzene derivatives $\text{RC}_6\text{F}_4\text{X}$ by chlorotrimethylsilane and $\text{P(NEt}_2)_3$ allows one to conclude that there exist general regularities for the replacement of chlorine, bromine, and iodine atoms by electrophiles in halopolyfluoroaromatic compounds. This fact is confirmed also by the fact that the decrease in the rate of protodehalogenation in the series $\text{C}_6\text{F}_5\text{Br} > \text{C}_6\text{F}_5\text{I} \gg \text{C}_6\text{F}_5\text{Cl}$, coincides with that for silyldehalogenation,¹ which has been demonstrated in a competitive reaction of bromo- and iodopentafluorobenzenes. The treatment of an equimolar mixture of **2** and **3** with 1 equiv. of $\text{P(NEt}_2)_3$ in aqueous DMF yielded pentafluorobenzene. The ratio of unconsumed compounds **2** and **3** was ~1 : 4.

The ^1H and ^{19}F NMR spectra of the compounds obtained agree with those of compounds reported in the literature.

Experimental

The ^1H (200 MHz) and ^{19}F (188.28 MHz) spectra were recorded on a Bruker WP 200 SY spectrometer (Me_4Si and C_6F_6 as internal standards).

Protodehalogenation of halopolyfluoroaromatic compounds (general procedure). $\text{P(NEt}_2)_3$ was added dropwise to a stirred solution of halopolyfluoroarene in MeOH or aqueous DMF cooled with cold water. The mixture was stirred at -20°C and diluted with 3–4 volumes of water. The product was steam distilled. The organic layer was separated and dried with CaCl_2 (Table 1).

Reduction of dibromotetrafluorobenzene **20** (2.92 mmol) in MeOH (0.5 mL) and CH_2Cl_2 (1 mL) was carried out by adding $\text{P(NEt}_2)_3$ (2.92 mmol) in CH_2Cl_2 (1 mL). After 30 min, the reaction mixture was washed with water, dilute H_2SO_4 , and water, and dried with CaCl_2 . Bromotetrafluorobenzene **21** was isolated by distillation (yield 42%).

Competitive reaction of $\text{C}_6\text{F}_5\text{Br}$ and $\text{C}_6\text{F}_5\text{I}$ with H_2O and $\text{P(NEt}_2)_3$. $\text{P(NEt}_2)_3$ (2 mmol) was added dropwise to a stirred solution of $\text{C}_6\text{F}_5\text{Br}$ (2 mmol), $\text{C}_6\text{F}_5\text{I}$ (2 mmol), and water (0.1 mL) in DMF (4 mL). After 10 min, the contents of $\text{C}_6\text{F}_5\text{Br}$, $\text{C}_6\text{F}_5\text{I}$, and $\text{C}_6\text{F}_5\text{H}$ were 12, 46, and 42%, respectively (^{19}F NMR).

Reaction of chloroheptafluorotoluenes $\text{ClC}_6\text{F}_4\text{CF}_3$ with H_2O and $\text{P(NEt}_2)_3$. Tris(diethylamino)phosphine was added in two portions to a stirred solution of chloroheptafluorotoluenes **23** and **5** (3 : 1) (0.61 g, 2.4 mmol)* and water (0.1 mL) in ether (3 mL). After each addition, the reaction mixture was stirred for 1 h, and the composition of the mixture was analyzed by ^{19}F NMR spectroscopy. The ratios of compounds **23** : **5** were 84 : 16 (0.45 equiv. of $\text{P(NEt}_2)_3$) and 90 : 10 (1 equiv. of $\text{P(NEt}_2)_3$).

This work was supported by the International Science Foundation (Grant NQM 000) and the International Science Foundation and the Russian Government (Grant NQM 300).

* The mixture also contained 10 mol.% of 2- $\text{ClC}_6\text{F}_4\text{CF}_3$. Products of the conversion of 2- $\text{ClC}_6\text{F}_4\text{CF}_3$ were not analyzed.

References

1. V. V. Bardin, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 813 [*Russ. Chem. Bull.*, 1997, 780 (Engl. Transl.)].
2. *Sintezy fluororganicheskikh soedinenii* [Syntheses of Fluoroorganic Compounds], Eds. I. L. Knunyants and G. G. Yakobson, Khimiya, Moscow, 1973, 86 pp. (in Russian).
3. G. G. Yakobson, in *Reaktsionnaya sposobnost' polifluoroaromaticheskikh soedinenii* [Reactivity of Polyfluoroaromatic Compounds], Nauka, Novosibirsk, 1983, 5 (in Russian).
4. L. S. Kobrina, in *Fluorine Chem. Revs.*, Ed. P. Tarrant, Dekker, New York, 1974, 7, 1.
5. V. I. Krasnov and V. E. Platonov, *Zh. Org. Khim.*, 1993, 29, 1078 [*Russ. J. Org. Chem.*, 1993, 29 (Engl. Transl.)]; V. I. Krasnov and V. E. Platonov, *Zh. Org. Khim.*, 1994, 30, 1271 [*Russ. J. Org. Chem.*, 1994, 30 (Engl. Transl.)].
6. H. Kobayashi, T. Sonoda, K. Takuma, N. Honda, and T. Nakata, *J. Fluorine Chem.*, 1985, 27, 1.
7. B. J. Grady and D. C. Dittmer, *J. Fluorine Chem.*, 1990, 50, 151.
8. V. V. Bardin, L. N. Aparina, L. S. Pressman, and G. G. Furin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2153 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, 38, 1983 (Engl. Transl.)].
9. V. V. Bardin, L. N. Aparina, L. S. Pressman, and G. G. Furin, *Zh. Obshch. Khim.*, 1992, 62, 2342 [*Russ. J. Gen. Chem. USSR*, 1992, 62, 1931 (Engl. Transl.)].
10. V. V. Bardin, L. S. Pressman, L. N. Rogozha, and G. G. Furin, *J. Fluorine Chem.*, 1991, 53, 213.
11. V. V. Bardin, L. S. Pressman, and G. G. Furin, *Sib. Khim. Zh. [Siberian Chem. J.]*, 1992, No. 3, 52 (in Russian).
12. V. V. Bardin, L. S. Pressman, and G. G. Furin, *J. Organometal. Chem.*, 1993, 448, 55.
13. V. V. Bardin and L. S. Pressman, *Main Group Met. Chem.*, 1995, 18, 333.
14. R. Appel, *Angew. Chem. Int. Ed. Engl.*, 1975, 14, 801.