

Reactions of pentafluorophenylxenon(II) hexafluoroarsenate $[\text{C}_6\text{F}_5\text{Xe}]^+[\text{AsF}_6]^-$ with aromatic compounds

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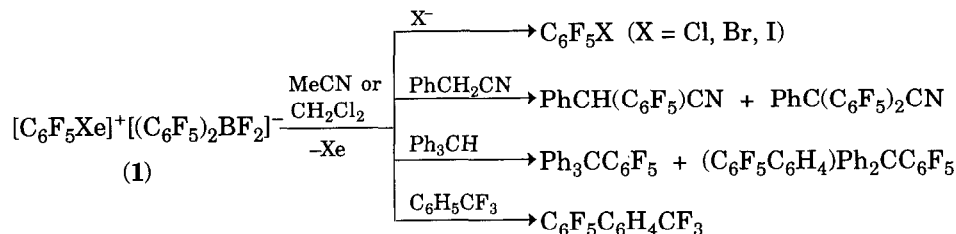
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Abstract

Pentafluorophenylxenon(II) hexafluoroarsenate $[\text{C}_6\text{F}_5\text{Xe}]^+[\text{AsF}_6]^-$ reacts (MeCN, 20 °C) with aromatic compounds $\text{C}_6\text{H}_5\text{X}$ ($\text{X} = \text{CH}_3, \text{F}, \text{CF}_3, \text{NO}_2$ and CN), yielding isomeric mixtures of polyfluorinated biphenyls $\text{XC}_6\text{H}_4\text{C}_6\text{F}_5$. When $\text{X} = \text{I}$, iodopentafluorobenzene is formed in addition, whereas trimethylsilylbenzene ($\text{X} = \text{SiMe}_3$) is only converted to $\text{C}_6\text{H}_5\text{C}_6\text{F}_5$ and $\text{C}_6\text{F}_5\text{H}$. These results are compared with the data for the radical pentafluorophenylation and fluorination reactions of the corresponding aromatic compounds with XeF_2 . Polyfluoroaromatic compounds C_6F_6 , $\text{C}_6\text{F}_5\text{H}$, $\text{C}_6\text{F}_5\text{I}$, $\text{C}_6\text{F}_5\text{CN}$ and $\text{C}_6\text{F}_5\text{SiMe}_3$ do not react with $[\text{C}_6\text{F}_5\text{Xe}]^+[\text{AsF}_6]^-$ under the same conditions.

Introduction

Since the first communications on the synthesis of $[\text{C}_6\text{F}_5\text{Xe}]^+[\text{Y}]^-$ $\{\text{Y} = \text{C}_6\text{F}_5\text{BF}_3$ [1, 2], $(\text{C}_6\text{F}_5)_3\text{BF}$ [3] and $(\text{C}_6\text{F}_5)_2\text{BF}_2$ **1** [4], only a few data have been available about their reactivity [1–7]. The reaction of **1** with nucleophiles X^- ($\text{X} = \text{Cl}, \text{Br}$ and I) leads to halogenopentafluorobenzenes $\text{C}_6\text{F}_5\text{X}$ [1, 2]. Interaction of salt **1** with C–H acids results in the replacement of the acidic proton by the C_6F_5 group. Substitution of the aromatically bonded hydrogen by the C_6F_5 group proceeds to a small extent, but the structure of the products has not yet been investigated [5–7].



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However, the $[\text{C}_6\text{F}_5\text{Xe}]^+$ cation is able to arylate aromatic compounds. The information on isomer distribution in the pentafluorophenylated products could suggest the mechanism of the reaction. Unfortunately, thermal instability of $[\text{C}_6\text{F}_5\text{Xe}]^+[(\text{C}_6\text{F}_5)_2\text{BF}_2]^-$ [4] did not allow us to study the reactivity of the $[\text{C}_6\text{F}_5\text{Xe}]^+$ cation at room or elevated temperatures.

Hence, we have studied the interaction of aromatic compounds with $[\text{C}_6\text{F}_5\text{Xe}]^+[\text{AsF}_6]^-$ (**2**). This salt can easily be prepared from salt **1** [4] (details of the preparation are described elsewhere). Its solution in MeCN was stable at room temperature for c. 1 d, but quickly decomposed at 70–80 °C (3–4 h) to yield pentafluorobenzene and decafluorobiphenyl (~10:1, mol).

Results and discussion

Pentafluorophenylxenon(II) hexafluoroarsenate (**2**) reacts readily with toluene at room temperature in acetonitrile to yield xenon and a mixture of 2'-, 3'- and 4'- $\text{CH}_3\text{C}_6\text{H}_4\text{C}_6\text{F}_5$ (**3a**, **3b**, **3c**). No pentafluorobenzene or benzyl derivatives such as $\text{C}_6\text{H}_5\text{CH}_2\text{C}_6\text{F}_5$ were detected among the reaction products (Table 1). Interaction of salt **2** with fluorobenzene proceeds more slowly and gives isomeric hexafluorobiphenyls $\text{FC}_6\text{H}_4\text{C}_6\text{F}_5$ (**4a**, **4b**, **4c**). Very similar

TABLE 1

Reactions of $[\text{C}_6\text{F}_5\text{Xe}]^+[\text{AsF}_6]^-$ (**2**) with $\text{C}_6\text{H}_5\text{X}$ (CH_3CN , RT)

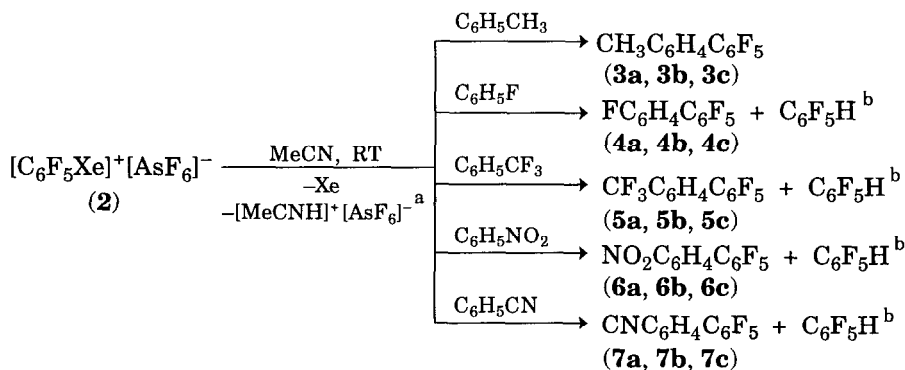
2 (μmol)	$\text{C}_6\text{H}_5\text{X}$ (μmol)	Time (h)	Yield of $\text{C}_6\text{F}_5\text{H}$ (%)	$\text{XC}_6\text{H}_4\text{C}_6\text{F}_5$ isomers (%)					
				Yield			Relative ratio ^a		
				2'-	3'-	4'-	2'-	3'-	4'-
45	$\text{C}_6\text{H}_5\text{CH}_3$ (76)	1.25	—	50	21	21	44	19	37
51	$\text{C}_6\text{H}_5\text{F}$ (62)	14	5	35	20	24	37	19	44
12	$\text{C}_6\text{H}_5\text{CF}_3$ (25)	30	5	18	40	20	18	41	41
55	$\text{C}_6\text{H}_5\text{NO}_2$ (65)	42	trace	27	22.5	22.5	28	24	48
45	$\text{C}_6\text{H}_5\text{CN}$ (62)	24	trace	35	31	26	30	26	44
55 ^b	$\text{C}_6\text{H}_5\text{I}$ (60)	1	6.3	11.1	7.5	11.6	26	18	56
53 ^c	$\text{C}_6\text{H}_5\text{SiMe}_3$ (53)	1	29						

^aCorrected for two *ortho* and two *meta* positions.

^bIodopentafluorobenzene (50% yield) and $\text{C}_6\text{F}_5\text{C}_6\text{H}_5$ (6.5% yield) were obtained.

^c $\text{C}_6\text{F}_5\text{C}_6\text{H}_5$ (57% yield) and FSiMe_3 were obtained.

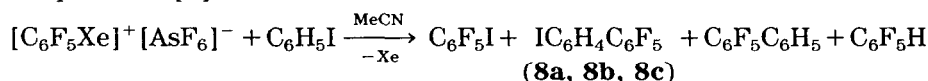
results were obtained in the reactions of salt **2** with benzotrifluoride, nitrobenzene and benzonitrile, but here the conversion was complete only after 24–42 h and small amounts of C_6F_5H were formed in addition to the corresponding isomeric biphenyls.



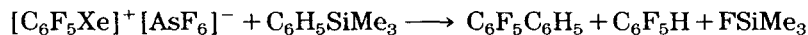
^aDuring the reaction, the concentration of $[AsF_6]^-$ remained virtually unchanged.

^bTraces or minor amounts.

The reaction of iodobenzene with salt **2** leads to a mixture of isomeric $IC_6H_4C_6F_5$ (**8a**, **8b**, **8c**). Small amounts of $C_6F_5C_6H_5$ and C_6F_5H are obtained, as well, but the main product is iodopentafluorobenzene. Examination of this process by ^{19}F NMR spectroscopy immediately after addition of C_6H_5I to the MeCN solution of **2** showed no formation of phenyl-(pentafluorophenyl)iodonium salts as possible precursors of C_6F_5I . It should be emphasized that $[C_6F_5IC_6H_5]^+$ is relatively stable in MeCN at room temperature [8].



Interaction of salt **2** with trimethylsilylbenzene proceeds immediately after addition of the aromatic compound to the solution of salt **2**. 2,3,4,5,6-Pentafluorobiphenyl is the main product in addition to pentafluorobenzene, fluorotrimethylsilane and xenon.



This regiospecificity of the pentafluorophenylation of $C_6H_5SiMe_3$ is not attributed to other trimethylsilylarenes: treatment of salt **2** with 1-trimethylsilyl-2-fluorobenzene or 1-trimethylsilyl-3-trifluoromethylbenzene leads to the formation of a mixture of pentafluorophenylated aromatics.

Comparison of the reactions of $[C_6F_5Xe]^+[AsF_6]^-$ in acetonitrile and of XeF_2/HF in CH_2Cl_2 or CCl_4 [9] with aromatic compounds indicates formally similar results: transfer of group Z from $[Z-Xe]$ ($Z=C_6F_5$ or F) to C_6H_5X and generation of $Z-C_6H_4X$ and xenon. But the isomer ratio of $XC_6H_4C_6F_5$ ($X=CH_3$, F, CF_3 and NO_2) differs substantially from that of aryl fluorides

which were obtained by the fluorination of C_6H_5X with XeF_2 [9]. In the latter case, the relative ratio of isomeric aryl fluorides FC_6H_4X demonstrates the preferential formation of *ortho*- and *para*-disubstituted benzenes ($X = CH_3$, F), whereas predominantly *meta* isomers were obtained from $C_6H_5CF_3$ and $C_6H_5NO_2$ (Table 2). (Unfortunately, our attempts to perform the reaction of salt **2** with fluorobenzene or benzotrifluoride in dichloromethane suspension failed, but in our opinion the observed difference between $XeF_2/HF-CH_2Cl_2$ (CCl_4) and $[C_6F_5Xe]^+[AsF_6]^-$ -MeCN cannot be explained by the different solvent.) On the other hand, the composition of our products and the relative ratio of isomeric biphenyls $XC_6H_4C_6F_5$ ($X = CH_3$, F, NO_2 , CF_3 , CN) are in accordance with the products obtained in the pentafluorophenylation of C_6H_5X with C_6F_5 radicals (Table 3). At the same time, the different composition of the reaction mixtures derived from $[C_6F_5Xe]^+[AsF_6]^-$ and C_6H_5X ($X = CH_3$, F, CF_3 , NO_2 and CN) on the one hand, and iodobenzene and trimethylsilyl-

TABLE 2

Reactions of C_6H_5X with XeF_2 [9]

C_6H_5X	FC_6H_4X (relative ratio, %) ^a					
	In CH_2Cl_2-HF			In CCl_4-HF		
	2-F	3-F	4-F	2-F	3-F	4-F
$C_6H_5CH_3$				35	6	59
C_6H_5F	16	4	80	15	4	81
$C_6H_5CF_3$	28	48	24	0	91	9
$C_6H_5NO_2$	20	55	25	18	53	29

^aCorrected for two *ortho* and two *meta* positions.

TABLE 3

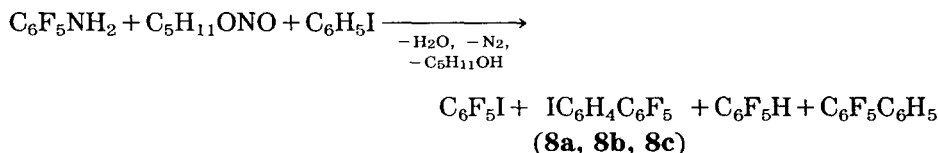
Reactions of C_6H_5X with C_6F_5 radicals

C_6H_5X	$XC_6H_4C_6F_5$ (relative ratio, %) ^a			Ref.
	2'-X	3'-X	4'-X	
$C_6H_5CH_3$	53	19	28	10
$C_6H_5CH_3$	49	25	26	11
$C_6H_5CH_3$	44	19	37	13
C_6H_5F	33	24	43	12
C_6H_5F	28	13	59	13
$C_6H_5CF_3$	18	46	36	^b
C_6H_5CN	29	35	37	^b
C_6H_5I	26	18	56	^b
$C_6H_5NO_2$	17	42	41	10

^aCorrected for two *ortho* and two *meta* positions.^bThis work.

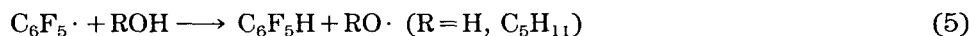
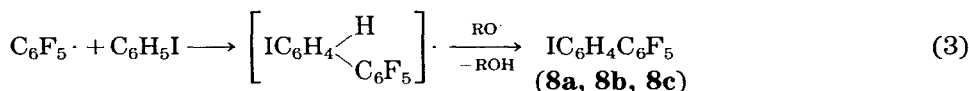
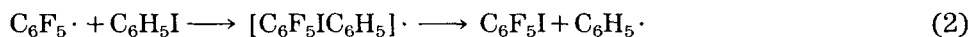
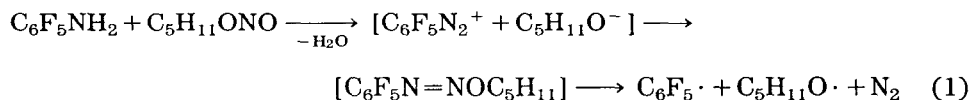
benzene on the other hand, has prompted us to study the unknown interaction of pentafluorophenyl radicals with C_6H_5I and $C_6H_5SiMe_3$.

Following the authors of refs. 10, 12 and 13, we used the reaction of pentafluoroaniline with pentyl nitrite for the generation of the C_6F_5 radical. Treatment of $C_6F_5NH_2$ with $C_5H_{11}ONO$ in an excess of iodobenzene causes spontaneous heating of the solution up to 70–80 °C and gas evolution. Analysis of the reaction mixture by ^{19}F NMR spectroscopy showed the presence of the same products as obtained earlier in the reaction of iodobenzene with pentafluorophenylxenon(II) hexafluoroarsenate.

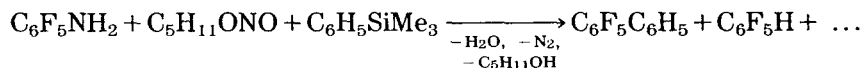


It should be noted that the isomer ratio of $IC_6H_4C_6F_5$ (**8a**, **8b**, **8c**) obtained here is the same as for the reaction of $[C_6F_5Xe]^+[AsF_6]^-$ with C_6H_5I .

The predominant formation of iodopentafluorobenzene may be explained by the attack of the electrophilic pentafluorophenyl radical [13] on C_6H_5I and subsequent decomposition of the unstable diaryliodonium radical [eqn. (2)]. The transfer of iodine to the more electronegative aryl group during decomposition of the unsymmetric radical $[RR'I]\cdot$ has been discussed in ref. 14. Furthermore, addition to the iodine atom of iodobenzene is the preferable direction of electrophilic attack under the kinetically controlled conditions [15]. The formation of other products may be represented by eqns. (3)–(5).



Generation of the $C_6F_5\cdot$ radical from $C_6F_5NH_2$ and $C_5H_{11}ONO$ in excess trimethylsilylbenzene leads to the formation of 2,3,4,5,6-pentafluorobiphenyl and pentafluorobenzene, together with some pentafluoroaniline derivatives.

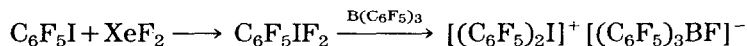


In order to fill in the gap in the literature, we have also carried out the radical pentafluorophenylation of $C_6H_5CF_3$ and C_6H_5CN . The results (Table

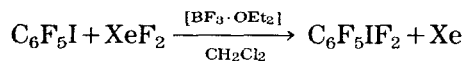
3) are in a good agreement with our data on the pentafluorophenylation of these aromatics with salt **2** (Table 1).

It is known that hexafluorobenzene does not react with pentafluorophenyl radicals produced from pentafluoroaniline and pentyl nitrite at 80 °C [10], whereas pentafluorobenzene [11] or 1,2,4,5-tetrafluorobenzene [16] are very slowly converted to deca- and nona-fluorobiphenyls, respectively.

To complete the investigation of the reaction of $[\text{C}_6\text{F}_5\text{Xe}]^+[\text{AsF}_6]^-$ with aromatic compounds, we have studied the interaction of salt **2** with polyfluoroaromatics. We have found that C_6F_6 , $\text{C}_6\text{F}_5\text{H}$, $\text{C}_6\text{F}_5\text{CN}$, $\text{C}_6\text{F}_5\text{SiMe}_3$ and $\text{C}_6\text{F}_5\text{I}$ are inert towards $[\text{C}_6\text{F}_5\text{Xe}]^+[\text{AsF}_6]^-$. No reaction was observed between $[\text{C}_6\text{F}_5\text{Xe}]^+[\text{BF}_4]^-$ and $\text{C}_6\text{F}_5\text{I}$ in boiling acetonitrile, as well. This result contradicts that in ref. 3 which reports formation of the $[(\text{C}_6\text{F}_5)_2\text{I}]^+$ salt on treatment of $\text{C}_6\text{F}_5\text{I}$ with $[\text{C}_6\text{F}_5\text{Xe-MeCN}]^+[(\text{C}_6\text{F}_5)_3\text{BF}]^-$. It should be noted that the salt $[\text{C}_6\text{F}_5\text{Xe}]^+[(\text{C}_6\text{F}_5)_3\text{BF}]^-$ was not isolated as an individual substance [3]. Hence, the formation of the iodonium salt $[(\text{C}_6\text{F}_5)_2\text{I}]^+$ may possibly be explained by the reaction of $\text{C}_6\text{F}_5\text{I}$ with the initial XeF_2 which remains in the reaction mixture. Actually, we have found out that XeF_2 can convert iodopentafluorobenzene via $\text{C}_6\text{F}_5\text{IF}_2$ in the presence of acidic $\text{C}_6\text{F}_5\text{BXY}$ compounds to the corresponding iodonium salt. (The conversion of $\text{C}_6\text{F}_5\text{IF}_2$ to $[(\text{C}_6\text{F}_5)_2\text{I}]^+$ has also been demonstrated in ref. 3.)

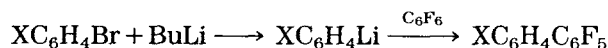


The inertness of the pentafluorobenzene derivatives $\text{C}_6\text{F}_5\text{X}$ towards salt **2** is contrary to the easy fluorination of these compounds by $\text{XeF}_2\text{-BF}_3\cdot\text{OEt}_2$ which produces 1-X-heptafluoro-1,4-cyclohexadienes ($\text{X}=\text{F}$, H [17], SiMe_3 [18]). We have found that XeF_2 reacts with iodopentafluorobenzene in CH_2Cl_2 in the presence of catalytic amounts of $\text{BF}_3\cdot\text{OEt}_2$ in the same manner as in the absence of a Lewis acid or a solvent [19].



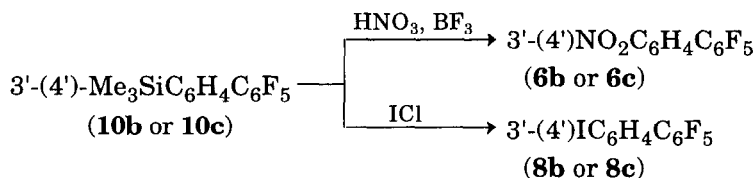
The results obtained have encouraged us to the conclusion that the pentafluorophenyl radical is a reactive key intermediate which participates in the reaction of $[\text{C}_6\text{F}_5\text{Xe}]^+[\text{AsF}_6]^-$ with aromatic compounds. The mechanism of the generation of this species from salt **2** is being examined at present.

The synthesis of individual fluorinated biphenyls for identification of the products produced in the reaction of $[\text{C}_6\text{F}_5\text{Xe}]^+[\text{AsF}_6]^-$ with $\text{C}_6\text{H}_5\text{X}$ was performed by the following principal methods:



[$\text{X}=2\text{-CH}_3$ (**3a**), 3-CH_3 (**3b**), 4-CH_3 (**3c**), 3-CF_3 (**5b**), 4-CF_3 (**5c**), 3-Br (**9b**), 3-SiMe_3 (**10b**), 4-SiMe_3 (**10c**)]

Nitro- and iodo-pentafluorobiphenyls were prepared by electrophilic desilylation of the corresponding trimethylsilyl-containing pentafluorobiphenyls:



2,3,4,5,6-Pentafluoro-2'- and 4'-cyanobiphenyls (**7a** and **7c**) were obtained by the Ullmann reaction from $\text{C}_6\text{F}_5\text{Br}$, $\text{IC}_6\text{H}_4\text{CN}$ and copper powder. 2,3,4,5,6-Pentafluoro-3'-cyanobiphenyl (**7b**) was prepared by the reaction of 2,3,4,5,6-pentafluoro-3'-bromobiphenyl (**9b**) with CuCN in DMF. The identification of 2'- $\text{NO}_2\text{C}_6\text{H}_4\text{C}_6\text{F}_5$ (**6a**) was performed by using a mixture of 2'-, 3'- and 4'- $\text{NO}_2\text{C}_6\text{H}_4\text{C}_6\text{F}_5$ isomers (**6a**, **6b** and **6c**) produced by nitration of 2,3,4,5,6-pentafluorobiphenyl [20]. It should be noted that the ^{19}F NMR spectrum of 4'- $\text{NO}_2\text{C}_6\text{H}_4\text{C}_6\text{F}_5$ (**6c**) which we have obtained differs from the one published earlier { -137.8 ppm (F-2,6), -147.8 ppm (F-4), -156.1 ppm (F-3,5) [21]} (cf. Table 4), probably due to the use of C_6F_6 as the external reference by the authors of ref. 21. The syntheses of 2,3,4,5,6-pentafluoro-2'-trifluoromethylbiphenyl (**5a**) and 2,3,4,5,6-pentafluoro-2'-iodo-biphenyl (**8a**) will be described elsewhere. Hexafluorobiphenyls $\text{FC}_6\text{H}_4\text{C}_6\text{F}_5$ (**4a**, **4b** and **4c**) were identified via their ^{19}F NMR spectra [12, 22].

Experimental

The ^1H and ^{19}F NMR spectra were recorded on a Varian EM 360 L (^1H at 60 MHz and ^{19}F at 56.4 MHz), a Bruker WP 80 SY (^{19}F at 75.4 MHz) and a WP 200 SY (^1H at 200 MHz, ^{19}F at 188.3 MHz) spectrometer (TMS and C_6F_6 as internal references). The chemical shifts $\delta(\text{F})$ were assigned to CFCl_3 using a $\delta(\text{F})$ value for C_6F_6 of -162.9 ppm. The IR spectra were recorded on a Specord M 80 instrument in KBr and the high-resolution mass spectra on a Finnigan MAT 8200 spectrometer.

Acetonitrile was refluxed over KMnO_4 , dried with P_4O_{10} and CaH_2 and stored over 3 Å molecular sieves.

Moisture-sensitive solids were handled in a Braun glovebox MB 100 G. All experiments with $[\text{C}_6\text{F}_5\text{Xe}]^+[\text{AsF}_6]^-$ were performed under a dry argon atmosphere in PTFE-FEP tube reactors. Tables 4-6 list the NMR, IR and analytical data for the new compounds.

Reactions of $[\text{C}_6\text{F}_5\text{Xe}]^+[\text{AsF}_6]^-$ (2) with aromatic compounds

Acetonitrile (0.10-0.15 ml) was added to a known weight of salt **2**. To the light yellow solution formed, an aromatic compound was added with a syringe. The reaction mixture was kept at room temperature until the $[\text{C}_6\text{F}_5\text{Xe}]^+$ signals disappeared from the ^{19}F NMR spectrum. The yields of products were determined by ^{19}F NMR methods using benzonitrile as a quantitative internal reference. The compounds were identified by adding samples prepared independently. The results are given in Table 1.

TABLE 4

Nuclear magnetic resonance spectral data

Compound	Solvent	¹ H NMR δ (ppm)	¹⁹ F NMR δ (ppm)		
			F-2,6	F-4	F-3,5
2'-CH ₃ C ₆ H ₄ C ₆ F ₅ (3a)	CD ₃ OD	7.25 (C ₆ H ₄); 1.13 (CH ₃)	-140.8	-156.4	-163.1
3'-CH ₃ C ₆ H ₄ C ₆ F ₅ (3b)	CD ₃ OD	7.42-7.20 (C ₆ H ₄); 2.40 (CH ₃)	-143.0	-157.0	-163.2
4'-CH ₃ C ₆ H ₄ C ₆ F ₅ (3c)	C ₆ D ₆	7.04 (AA'BB') (C ₆ H ₄); 1.09 (CH ₃)	-144.0	-157.0	-163.0
3'-Me ₃ SiC ₆ H ₄ C ₆ F ₅ (10b)	CD ₃ OD	7.62-7.38 (C ₆ H ₄); 0.28 (SiMe ₃)	-143.1	-156.7	-163.1
4'-Me ₃ SiC ₆ H ₄ C ₆ F ₅ (10c)	CD ₃ OD	7.52 (AA'BB') (C ₆ H ₄); 0.30 (SiMe ₃)	-143.0	-156.8	-163.1
3'-NO ₂ C ₆ H ₄ C ₆ F ₅ (6b)	CD ₃ OD	7.90-7.50 (C ₆ H ₄)	-143.0	-154.6	-162.3
4'-NO ₂ C ₆ H ₄ C ₆ F ₅ (6c)	CD ₃ OD	8.10 (AA'BB') (C ₆ H ₄)	-142.6	-154.4	-162.3
4'-NO ₂ C ₆ H ₄ C ₆ F ₅ (6c)	CDCl ₃	8.07 (AA'BB') (C ₆ H ₄)	-143.5	-153.6	-161.9
2'-CF ₃ C ₆ H ₄ C ₆ F ₅ (5a) ^a	CDCl ₃		-139.8	-153.1	-163.2
3'-CF ₃ C ₆ H ₄ C ₆ F ₅ (5b) ^b	CD ₃ OD	7.85-7.45 (C ₆ H ₄)	-143.3	-155.1	-162.5
4'-CF ₃ C ₆ H ₄ C ₆ F ₅ (5c) ^c	CD ₃ OD	7.75 (AA'BB') (C ₆ H ₄)	-142.9	-155.1	-162.6
4'-CF ₃ C ₆ H ₄ C ₆ F ₅ (5c)	CDCl ₃		-143.9	-154.9	-162.6
2'-CNC ₆ H ₄ C ₆ F ₅ (7a)	CD ₃ OD	8.00-7.64 (C ₆ H ₄)	-140.4	-153.2	-162.0
3'-CNC ₆ H ₄ C ₆ F ₅ (7b)	CD ₃ OD	7.93-7.74 (C ₆ H ₄)	-143.0	-154.9	-162.5
4'-CNC ₆ H ₄ C ₆ F ₅ (7c)	CDCl ₃	7.66 (AA'BB') (C ₆ H ₄)	-143.8	-154.0	-162.0
3'-BrC ₆ H ₄ C ₆ F ₅ (9b)	CD ₃ OD	7.69-7.44 (C ₆ H ₄)	-142.9	-155.6	-162.7
3'-IC ₆ H ₄ C ₆ F ₅ (8b)	CD ₃ OD	7.87-7.29 (C ₆ H ₄)	-142.9	-155.7	-162.7
4'-IC ₆ H ₄ C ₆ F ₅ (8c)	CD ₃ OD + C ₆ D ₆	7.19 (AA'BB') (C ₆ H ₄)	-143.5	-155.8	-162.6
11b ^d	C ₆ D ₆	7.70-6.97 (C ₆ H ₄)	-143.9		-143.9
11c ^e	C ₆ D ₆	7.47 (AA'BB') (C ₆ H ₄)	-144.2		-144.2
1-C ₆ H ₁₁ OC ₆ F ₄ H (12)	CD ₃ OD	6.99 (C ₆ F ₄ H); 4.21 (OCH ₂); 1.77-1.39 (CH ₂) ₅ ; 0.95 (CH ₃)	-157.2		-140.3

^aIn CF₃C₆H₄C₆F₅ isomer mixture.^bδ(CF₃), -62.5 ppm.^cδ(CF₃), -62.2 ppm.^d1,4-(3'-CF₃C₆H₄)₂C₆F₄; δ(CF₃), -62.6 ppm.^e1,4-(4'-CF₃C₆H₄)₂C₆F₄; δ(CF₃), -63.7 ppm.

TABLE 5
Infrared spectral data

Compound	Wavenumber (cm ⁻¹)
3'-Me ₃ SiC ₆ H ₄ C ₆ F ₅ (10b)	3032; 2956; 2896; 1652; 1522; 1498; 1480; 1388; 1340; 1324; 1252; 1120; 1068; 990; 892; 840; 806; 754; 736; 708; 692; 648; 620.
4'-Me ₃ SiC ₆ H ₄ C ₆ F ₅ (10c)	3068; 3028; 2956; 2900; 1654; 1600; 1550; 1526; 1504; 1496; 1488; 1392; 1340; 1324; 1252; 1118; 1108; 1062; 990; 842; 828; 736; 700; 624; 516.
3'-NO ₂ C ₆ H ₄ C ₆ F ₅ (6b)	3100; 2964; 1652; 1544; 1526; 1496; 1434; 1108; 1090; 1074; 990; 920; 904; 836; 812; 744; 724; 700; 680; 644.
4'-NO ₂ C ₆ H ₄ C ₆ F ₅ (6c)	3104; 1658; 1604; 1524; 1508; 1494; 1404; 1396; 1350; 1312; 1288; 1200; 1108; 1064; 1012; 988; 864; 840; 748; 740; 728; 688; 438.
3'-CF ₃ C ₆ H ₄ C ₆ F ₅ (5b) ^a	3080; 1654; 1526; 1502; 1490; 1446; 1420; 1388; 1338; 1310; 1284; 1198; 1172; 1134; 1100; 1080; 1068; 990; 908; 896; 812; 780; 768; 700; 676; 664; 644.
4'-CF ₃ C ₆ H ₄ C ₆ F ₅ (5c)	1656; 1620; 1580; 1534; 1516; 1490; 1432; 1408; 1326; 1178; 1164; 1146; 1126; 1108; 1062; 1020; 988; 956; 860; 848; 768; 720; 600; 508; 404.
2'-CNC ₆ H ₄ C ₆ F ₅ (7a)	3084; 2236; 1654; 1596; 1572; 1526; 1500; 1484; 1448; 1324; 1284; 1188; 1108; 1062; 1032; 990; 968; 864; 800; 774; 716; 644; 556; 492.
3'-CNC ₆ H ₄ C ₆ F ₅ (7b)	3084; 2932; 2236; 1652; 1580; 1528; 1498; 1480; 1436; 1410; 1332; 1232; 1164; 1080; 990; 920; 900; 808; 780; 758; 688; 656; 584.
4'-CNC ₆ H ₄ C ₆ F ₅ (7c)	3000; 2240; 1722; 1654; 1562; 1530; 1510; 1488; 1408; 1280; 1188; 1112; 1076; 1066; 988; 860; 780; 756; 554.
3'-BrC ₆ H ₄ C ₆ F ₅ (9b)	3064; 1654; 1596; 1562; 1522; 1496; 1480; 1432; 1404; 1380; 1320; 1096; 1080; 1064; 988; 912; 892; 879; 804; 770; 736; 698; 684.
3'-IC ₆ H ₄ C ₆ F ₅ (8b)	1652; 1564; 1524; 1496; 1476; 1428; 1396; 1096; 1076; 1062; 988; 912; 876; 800; 764; 736; 688; 680.
4'-IC ₆ H ₄ C ₆ F ₅ (8c)	3060; 1656; 1592; 1560; 1524; 1490; 1392; 1322; 1200; 1068; 1060; 1008; 1000; 986; 944; 852; 828; 806; 772; 500.
1,4-(3'-CF ₃ C ₆ H ₄) ₂ C ₆ F ₄ (11b)	3084; 1524; 1496; 1480; 1434; 1408; 1342; 1330; 1320; 1300; 1282; 1186; 1176; 1128; 1096; 1078; 978; 950; 908; 816; 804; 772; 760; 752; 704; 692; 672; 644.
1,4-(4'-CF ₃ C ₆ H ₄) ₂ C ₆ F ₄ (11c)	1622; 1472; 1406; 1336; 1320; 1170; 1132; 1108; 1070; 1020; 978; 954; 840; 766; 676; 600.
1-C ₅ H ₁₁ OC ₆ F ₄ H (12) ^a	3088; 2960; 2935; 2870; 1638; 1514; 1489; 1470; 1400; 1383; 1266; 1215; 1170; 1120; 1087; 966; 937; 871; 822; 733; 707.

^aNeat liquid.

TABLE 6
Analytical data

Compound	Found (%)			Empirical formula
	Calculated (%)			
	C	H	F	
3'-Me ₃ SiC ₆ H ₄ C ₆ F ₅ (10b)	57.2	4.37	30.0	C ₁₅ H ₁₃ F ₅ Si
	56.9	4.11	30.1	
4'-Me ₃ SiC ₆ H ₄ C ₆ F ₅ (10c)	56.7	4.32	29.8	C ₁₅ H ₁₃ F ₅ Si
	56.9	4.11	30.1	
3'-NO ₂ C ₆ H ₄ C ₆ F ₅ (6b) ^a	50.5	1.52	32.5	C ₁₂ H ₄ F ₅ NO ₂
	49.8	1.38	32.9	
3'-CF ₃ C ₆ H ₄ C ₆ F ₅ (5b)	50.3	1.41	48.6	C ₁₃ H ₄ F ₈
	50.0	1.28	48.7	
1,4-(3'-CF ₃ C ₆ H ₄) ₂ C ₆ F ₄ (11b)	55.2	1.96	43.6	C ₂₀ H ₈ F ₁₀
	54.8	1.82	43.4	
1,4-(4'-CF ₃ C ₆ H ₄) ₂ C ₆ F ₄ (11c)	54.7	1.96	43.4	C ₂₀ H ₈ F ₁₀
	54.8	1.82	43.4	
1-C ₅ H ₁₁ OC ₆ F ₄ H (12)	55.9	5.00	31.9	C ₁₁ H ₁₂ F ₄ O
	55.9	5.08	32.2	

^aFound: N, 4.94%; calculated: N, 4.84%.

No reaction occurred on treatment of a suspension of salt **2** in dichloromethane with fluorobenzene or benzotrifluoride for 122 h, or of an acetonitrile solution of salt **2** with the pentafluorobenzene derivatives C₆F₅X (X = H, F, I, CN, SiMe₃) (60–70 h).

Fluorination of iodopentafluorobenzene with xenon difluoride in the presence of BF₃·OEt₂

Xenon difluoride (0.199 g, 1.18 mmol) was added gradually to a stirred solution of iodopentafluorobenzene (0.294 g, 1.00 mmol) and BF₃·OEt₂ (20 μl, 0.16 mmol) in 1.5 ml of dichloromethane placed in an FEP reactor. When gas evolution stopped, the mixture was stirred for a further 30 min and the volatile components were removed *in vacuo* to produce 0.291 g (88%) of difluoriodopentafluorobenzene.

Reaction of C₆F₅IF₂ with B(C₆F₅)₃

A cool (–50 °C) solution of B(C₆F₅)₃ (77.1 mg, 0.15 mmol) in 0.4 ml of MeCN was added to a cool (–50 °C) solution of C₆F₅IF₂ (50 mg, 0.15 mmol) in acetonitrile (0.25 ml). After 4 d at –50 °C, all the borane had reacted. According to ¹⁹F NMR spectroscopy [(C₆F₅)₂I]⁺X[–] was formed in quantitative yield {X = BF₄ (37 mol%) and (C₆F₅)₃BF (63 mol%)} In dichloromethane (–50 °C), the reaction was faster (< 1 h) and gave a suspension. The solid when dissolved in MeCN contained a different mixture of anions X[–]: X = BF₄, C₆F₅BF₃, (C₆F₅)₂BF₂ and (C₆F₅)₃BF (6, 45, 37 and 12 mol%).

Preparation of 2,3,4,5,6-pentafluoro-2'-methylbiphenyl (3a)

A solution consisting of 3.42 g (20 mmol) 2-bromotoluene in 5 ml of ether was added to a cool (-25°C) solution of 23 mmol of BuLi in 14 ml of hexane and 10 ml of ether. The solution was stirred at $10-20^{\circ}\text{C}$ for 1 h and added gradually to a solution of 3.72 g (20 mmol) hexafluorobenzene in 45 ml of ether. The mixture was stirred at room temperature for 1 h, then poured into 5% HCl; the organic layer was separated and the aqueous layer extracted with ether. The combined extracts were washed with water and dried over CaCl_2 . The solvent was distilled off. The residue was distilled *in vacuo* to give 3.75 g (70%) of the product **3a**, b.p. $78-80^{\circ}\text{C}/6\text{ mmHg}$ ($200-203^{\circ}\text{C}$ [11]). The IR spectrum was correct [23].

Preparation of 2,3,4,5,6-pentafluoro-3'-methylbiphenyl (3b)

This was obtained in a similar manner from 4.28 g (25 mmol) 3-bromotoluene, 30 ml of 1.1 M BuLi in pentane and 9 g (48 mmol) hexafluorobenzene in 55 ml of ether. Vacuum distillation gave 4.20 g (65%) of the product **3b**, b.p. $83-85^{\circ}\text{C}/2\text{ mmHg}$ ($236-238^{\circ}\text{C}$ [11]). The IR spectrum was correct [23].

Preparation of 2,3,4,5,6-pentafluoro-4'-methylbiphenyl (3c)

This was obtained in a similar manner from 4.28 g (25 mmol) 4-bromotoluene, 30 ml of 1.6 M BuLi in hexane and 4.65 g (25 mmol) hexafluorobenzene in 55 ml of ether. Crystallization from hexane gave 4.06 g (63%) of the product **3c**, m.p. $116-118^{\circ}\text{C}$ ($117-118^{\circ}\text{C}$ [24], $119-120^{\circ}\text{C}$ [11]). The IR spectrum was correct [23].

Preparation of 2,3,4,5,6-pentafluoro-3'-bromobiphenyl (9b) (nc)

This compound was prepared similarly from 4.7 g (20 mmol) 1,3-dibromobenzene, 31 ml of 1.1 M BuLi in pentane and 9 g (48 mmol) hexafluorobenzene in 61 ml of ether. Crystallization from MeOH gave 2.9 g (48%) of the product **9b**, m.p. $60-61^{\circ}\text{C}$. Analysis: Found: M^+ 321.9413 (by mass spectrum). $\text{C}_{12}\text{H}_4\text{BrF}_5$ requires: M^+ 321.9417.

Preparation of 2,3,4,5,6-pentafluoro-3'-trifluoromethylbiphenyl (5b) (nc)

This was obtained in a similar manner from 3.38 g (15 mmol) 3-bromobenzotrifluoride, 13 ml of 1.6 M BuLi in hexane and 2.80 g (15 mmol) hexafluorobenzene in 40 ml of ether. After the solvent had been distilled off and the residue crystallized from hexane, 0.74 g (11%) 1,4-bis(3'-trifluoromethylphenyl)tetrafluorobenzene (**11b**) (nc) was isolated, m.p. $126-128^{\circ}\text{C}$. From the mother liquor, 2,3,4,5,6-pentafluoro-3'-trifluoromethylbiphenyl (**5b**) was isolated by preparative GLC methods, b.p. $85-87^{\circ}\text{C}/14\text{ mmHg}$.

Preparation of 2,3,4,5,6-pentafluoro-4'-trifluoromethylbiphenyl (5c) (nc)

This was obtained in a similar manner from 3.38 g (15 mmol) 4-bromobenzotrifluoride, 13 ml of 1.6 M BuLi in hexane and 2.80 g (15 mmol)

hexafluorobenzene in 50 ml of ether. After the solvent had been distilled off, the residue was crystallized from hexane to give 1.3 g (20%) of 1,4-bis(4'-trifluoromethylphenyl)tetrafluorobenzene (nc) (**11c**), m.p. 228–230 °C. The mother liquor was evaporated and the residue sublimed to give 0.93 g (20%) of 2,3,4,5,6-pentafluoro-4'-trifluoromethylbiphenyl (**5c**), m.p. 59–60 °C (from MeOH). Analysis: Found: M^+ 312.0185 (by mass spectrum). $C_{13}H_4F_8$ requires: M^+ 312.0185.

Preparation of 2,3,4,5,6-pentafluoro-3'-trimethylsilylbiphenyl (10b) (nc)

This was obtained in a similar manner from 7.43 g (32 mmol) 3-bromophenyltrimethylsilane, 22 ml of 1.6 M BuLi in hexane and 7.0 g (37 mmol) hexafluorobenzene in 55 ml of ether. Vacuum distillation gave 5.20 g (51%) of the product **10b**, b.p. 105–107 °C/8 mmHg.

Preparation of 2,3,4,5,6-pentafluoro-4'-trimethylsilylbiphenyl (10c) (nc)

This was obtained by a similar procedure from 5.47 g (24 mmol) 4-bromophenyltrimethylsilane, 15 ml of 1.6 M BuLi in hexane and 4.3 g (24 mmol) hexafluorobenzene in 60 ml of ether. Vacuum distillation gave 3.94 g (54%) of the product **10c**, b.p. 111–113 °C/6 mmHg.

Preparation of 2,3,4,5,6-pentafluoro-3'-iodobiphenyl (8b) (nc)

Iodine monochloride (0.7 g, 4.3 mmol) dissolved in 1 ml of $CHCl_3$ (0 °C) was added dropwise to a solution consisting of 0.52 g (1.57 mmol) 2,3,4,5,6-pentafluoro-3'-trimethylsilylbiphenyl (**10b**) in 1 ml of $CHCl_3$. The solution was stirred for 3 h at room temperature, then treated with an aqueous $Na_2S_2O_5$ solution. The solvent was distilled off and the residue crystallized from MeOH. This gave 0.42 g (72%) of the product **8b**, m.p. 48–49 °C. Analysis: Found: M^+ 369.9291 (by mass spectrum). $C_{12}H_4F_5I$ requires: M^+ 369.9280.

Preparation of 2,3,4,5,6-pentafluoro-4'-iodobiphenyl (8c) (nc)

This was obtained in a similar manner from 1.58 g (5 mmol) 2,3,4,5,6-pentafluoro-4'-trimethylsilylbiphenyl (**10c**) in 12 ml of CH_2Cl_2 and 0.98 g (6 mmol) ICl in 8 ml of CH_2Cl_2 (0 °C). Yield of product **8c**, 1.21 g (65%), m.p. 110–111 °C. Analysis: Found: M^+ 369.9264 (by mass spectrum). $C_{12}H_4F_5I$ requires: M^+ 369.9280.

Preparation of 2,3,4,5,6-pentafluoro-3'-nitrobiphenyl (6b)

A solution consisting of 0.35 g (5.6 mmol) 100% HNO_3 and 0.63 g (5.8 mmol) $BF_3 \cdot NMe_3$ in 10 ml of MeCN was added to a solution consisting of 0.8 g (2.53 mmol) 2,3,4,5,6-pentafluoro-3'-trimethylsilylbiphenyl (**10b**) in 5 ml of MeCN. The mixture was refluxed for 5 h, then poured on to ice, extracted with dichloromethane and dried over $CaCl_2$. The solvent was distilled off and the residue sublimed to give 0.35 g (48%) of the product **6b**, m.p. 110–112 °C (106–108 °C [22], 113–114 °C [20]).

Preparation of 2,3,4,5,6-pentafluoro-4'-nitrobiphenyl (6c)

This was obtained similarly from 0.45 g (7.0 mmol) 100% HNO_3 , 0.66 g (6.1 mmol) $\text{BF}_3 \cdot \text{NCMe}$ and 1.36 g (4.3 mmol) 2,3,4,5,6-pentafluoro-4'-trimethylsilylbiphenyl (**10c**) in 10 ml of MeCN. This gave 0.82 g (66%) of the product **6c**, m.p. 89–90 °C (87–89 °C [22], 92–93 °C [20], 93–94 °C [21]). Analysis: Found: M^+ 289.0166 (by mass spectrum). $\text{C}_{12}\text{H}_4\text{F}_5\text{NO}_2$ requires: M^+ 289.0162.

Preparation of 2,3,4,5,6-pentafluoro-2'-cyanobiphenyl (7a) (nc)

Bromopentafluorobenzene (1.1 g, 4.4 mmol), 2-iodobenzonitrile (1.0 g, 4.4 mmol) and copper powder (2.0 g, 31 mmol) were heated in a sealed glass tube for 18 h at 190–200 °C. The mixture was cooled, extracted with hot CHCl_3 and the solvent distilled off. The dark residue was extracted with hot hexane and the solvent again distilled off. Preparative TLC (silica gel, eluent CCl_4) gave 0.23 g (31%) decafluorobiphenyl, 0.1 g (22%) 2,2'-dicyanobiphenyl (both compounds identified by IR spectroscopy) and 0.50 g (42%) 2,3,4,5,6-pentafluoro-2'-cyanobiphenyl (**7a**), m.p. 73–74 °C (from pentane). Analysis: Found: M^+ 269.0264 (by mass spectrum). $\text{C}_{13}\text{H}_4\text{F}_5\text{N}$ requires: M^+ 269.0264.

Preparation of 2,3,4,5,6-pentafluoro-4'-cyanobiphenyl (7c) (nc)

This was obtained in a similar manner from bromopentafluorobenzene (1.1 g, 4.4 mmol), 4-iodobenzonitrile (1.0 g, 4.4 mmol) and copper powder (2.0 g, 31 mmol). Yield, 0.32 g (27%) **7c**, m.p. 112–113 °C (from MeOH). Analysis: Found: M^+ 269.0270 (by mass spectrum). $\text{C}_{13}\text{H}_4\text{F}_5\text{N}$ requires: M^+ 269.0264.

Preparation of 2,3,4,5,6-pentafluoro-3'-cyanobiphenyl (7b) (nc)

2,3,4,5,6-Pentafluoro-3'-bromobiphenyl (**9b**) (1.0 g, 3.1 mmol) and CuCN (0.38 g, 4.2 mmol) were refluxed in DMF (3 ml) for 8 h. Then a solution consisting of 0.7 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 7 ml of 1 N HCl was added. The mixture was refluxed for a further 30 min and stream distilled. Yield of product **7b**, 0.65 g (78%), m.p. 75–76 °C (from MeOH). Analysis: Found: M^+ 269.0267 (by mass spectrum). $\text{C}_{13}\text{H}_4\text{F}_5\text{N}$ requires: M^+ 269.0264.

Reaction of $\text{C}_6\text{F}_5\text{NH}_2$ and $\text{C}_5\text{H}_{11}\text{ONO}$ with $\text{C}_6\text{H}_5\text{I}$

Pentyl nitrite (2.5 ml, 19 mmol) was added dropwise to a stirred solution of $\text{C}_6\text{F}_5\text{NH}_2$ (3.0 g, 16 mmol) in iodobenzene (14.9 g, 73 mmol). After a few moments, a vigorous reaction started and the temperature of the reaction mixture spontaneously increased up to 80 °C. After 30 min, the solution was cooled and analyzed by ^{19}F NMR spectroscopy. Yields of compounds $\text{C}_6\text{F}_5\text{I}$, $\text{C}_6\text{F}_5\text{H}$, $\text{C}_6\text{F}_5\text{C}_6\text{H}_5$, 2'- $\text{IC}_6\text{H}_4\text{C}_6\text{F}_5$ (**8a**), 3'- $\text{IC}_6\text{H}_4\text{C}_6\text{F}_5$ (**8b**) and 4'- $\text{IC}_6\text{H}_4\text{C}_6\text{F}_5$ (**8c**) were 35.8, 8.4, 6.3, 11.5, 7.7 and 12.3%, respectively.

Reaction of $\text{C}_6\text{F}_5\text{NH}_2$ and $\text{C}_5\text{H}_{11}\text{ONO}$ with $\text{C}_6\text{H}_5\text{SiMe}_3$

The reaction of $\text{C}_6\text{F}_5\text{NH}_2$ (0.93 g, 5.2 mmol), pentyl nitrite (1.0 ml, 7.5 mmol) with trimethylsilylbenzene (2.9 g, 19.2 mmol) was conducted at 80

°C as described above (mixing of the reagents was not accompanied by any pronounced exothermal effect). The pentafluorobenzene and 2,3,4,5,6-pentafluorobiphenyl obtained were identified by ^{19}F NMR spectroscopy (yields, 32 and 39%, respectively).

Reaction of $\text{C}_6\text{F}_5\text{NH}_2$ and $\text{C}_5\text{H}_{11}\text{ONO}$ with $\text{C}_6\text{H}_5\text{CN}$

Pentyl nitrite (1.6 ml, 14 mmol) was added to a solution of $\text{C}_6\text{F}_5\text{NH}_2$ (2.0 g, 11 mmol) in benzonitrile (10 ml, 97 mmol) (80 °C). A mixture of 2'-, 3'- and 4'-CNC $_6\text{H}_4\text{C}_6\text{F}_5$ (**7a**, **7b** and **7c**) (yields, 20.4, 24.5 and 13.1%, respectively) resulted. The reaction mixture also contained pentafluorobenzene (yield, 18%) and some unidentified products resulting from the partial oxidation of pentafluoroaniline.

Reaction of $\text{C}_6\text{F}_5\text{NH}_2$ and $\text{C}_5\text{H}_{11}\text{ONO}$ with $\text{C}_6\text{H}_5\text{CF}_3$

A similar reaction between 7.0 g (38 mmol) $\text{C}_6\text{F}_5\text{NH}_2$, 5 ml (43 mmol) of pentyl nitrite with 20 ml (164 mmol) of benzotrifluoride gave a mixture of 2'-, 3'- and 4'-CF $_3\text{C}_6\text{H}_4\text{C}_6\text{F}_5$ (**5a**, **5b** and **5c**) (yields, 12.1, 31.0 and 12.1%, respectively) and 1-pentyloxy-2,3,5,6-tetrafluorobenzene (29%).

*Preparation of 1-pentyloxy-2,3,5,6-tetrafluorobenzene (**12**) (nc)*

BuLi in pentane (30 ml of a 1.1 M solution) was added via a syringe to 10 ml of pentanol. To the resulting suspension, 5.1 g (30 mmol) pentafluorobenzene were added with stirring. The mixture was heated at 60–70 °C for 6 h, then poured into 5% HCl. The organic layer was separated, diluted with CHCl_3 (10 ml), dried over CaCl_2 and distilled *in vacuo* to give 2.5 g (35%) of product **12**, b.p. 67–70 °C/7 mmHg.

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