Studies on sulfinatodehalogenation. XXVI. Perfluoroalkylation of nitrogen-containing heteroaromatic compounds with perfluoroalkyl halides and Rongalite

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Abstract

Perfluoroalkylation of some nitrogen-containing heteroaromatic compounds such as pyrrole, pyridines, quinoline and isoquinoline has been achieved by reacting with perfluoroalkyl iodides or bromides in the presence of Rongalite under mild conditions. The distribution of isomers formed was consistent with a radical reaction mechanism.

Introduction

Recently, a remarkable amount of attention has been focused on perfluoroalkyl-containing compounds due to their unique properties and use as starting materials for the preparation of fluorine-containing dyes, drugs, insecticides, etc., with the introduction of perfluoroalkyl groups being the subject of much research in organofluorine chemistry. Over the past few years, much work has been undertaken with electron-rich aromatic compounds such as pyrrole [1], anilines [2] and phenols [3], but there are few reports on the perfluoroalkylation of pyridine and its derivatives. Pyridine is very stable to many alkylating reagents and can even be used as a solvent in some perfluoroalkylation reactions [4]. Cowell and Tamborski [5] have reported the perfluoroalkylation of pyridine with perfluoroalkyl iodides through a thermolysis reaction, but a high temperature and long reaction time (200 °C over 20 h) were needed. Yoshida *et al.* [6] have recently found that some nitrogen-containing heteroaromatic compounds may be perfluoroalkylated by bis(perfluoroalkanoyl)peroxides; however, in the reaction, only some substituted pyridines gave alkylation products with the perfluoroalkylation of pyridine itself being not achieved. Herein we report a new and facile method for the direct perfluoroalkylation of nitrogen-containing heteroaromatics with perfluoroalkyl halides initiated by Rongalite.

Rongalite, sodium hydroxymethane sulfinate, is a useful reducing agent in industry. As a new sulfinatodehalogenation reagent, it has been shown to

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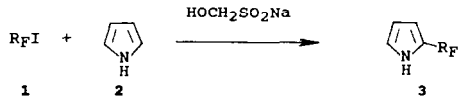
convert perfluoroalkyl iodides or bromides to the corresponding sodium sulfinate [7]. The conversion was thought to be a free-radical process and the expected addition products were obtained when olefins were added to trap the perfluoroalkyl radicals generated in the reaction system [8]. On further study, however, we have found that the R_FI/Rongalite system can also react with pyrrole, pyridine and its derivatives, giving the corresponding perfluoroalkylated products.

Results and discussion

With acetonitrile being used as cosolvent, perfluoroalkyl iodides reacted with pyrrole in an aqueous solution of Rongalite to give the α-substituted perfluoroalkylated pyrroles (Scheme 1). The reaction proceeded readily at 60–70 °C, and $NaHCO_3$ was added to keep the medium slightly basic to prevent dissociation of Rongalite. The yields and reaction conditions are shown in Table 1.

It is interesting to find that a similar reaction occurred when pyridine was used as a substrate. The reaction was performed at 70–75 °C, affording the corresponding perfluoroalkylated products as a mixture of 2-, 3- and 4-isomers, with a small amount of byproducts such as R_FH and R_FSO_2Na. On prolonged reaction time, the reaction also occurred when perfluoroalkyl bromides were used as reagents (Scheme 2). The results obtained are listed in Table 2.

Some derivatives of pyridine such as 4-methylpyridine (**9**), 3-methylpyridine (**10**), 3,5-dimethylpyridine (**11**), quinoline (**12**) and isoquinoline (**13**) were examined. They all reacted readily with perfluoroalkyl iodides in



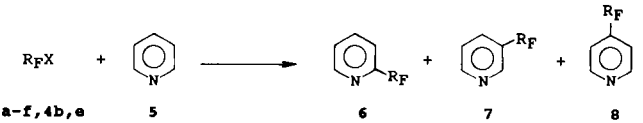
R_F = $Cl(CF_2)_4$, **1a**; $Cl(CF_2)_6$, **1b**; $Cl(CF_2)_8$, **1c**;
$FO_2S(CF_2)_2O(CF_2)_2$, **1g**

Scheme 1.

TABLE 1

Reaction of R_FI with pyrrole

R_FI	Temperature (°C)	Time (h)	Product	Yield (%)
1a	60	5	**3a**	68
1b	65	4	**3b**	65
1c	65	4	**3c**	60
1g	60	4	**3g**	58



1a-f,4b,e 5 6 7 8

X = I, R_F = $F(CF_2)_6$, 1d; $F(CF_2)_7$, 1e; $F(CF_2)_8$, 1f
X = Br, R_F = $Cl(CF_2)_6$, 4b; $F(CF_2)_7$, 4e

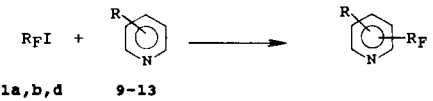
Scheme 2.

TABLE 2

Reaction of R_FX with pyridine

R_FX	Time (h)	Yield (%)	Isomer composition (%)[a]		
			6	**7**	**8**
1a	6	58	47	44	9
1b	5	65	48	44	8
1c	6	63	47	45	8
1d	5	57	46	47	7
1e	5	62	46	45	9
1f	6	68	47	45	8
4b	24	48	45	45	10
4e	25	52	48	43	9

[a]Determined by ^{19}F NMR spectroscopy.



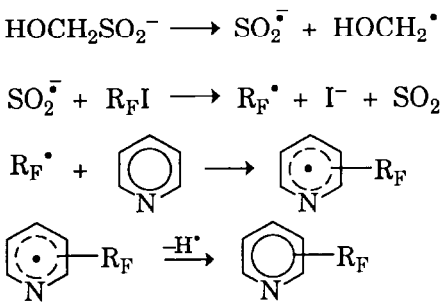
1a,b,d 9-13

Scheme 3.

a similar manner to form the perfluoroalkylated products (Scheme 3), but no regioselectivity was observed in these reactions. The results are summarized in Table 3.

Other substances examined such as pyrazine (**14**) and imidazole were difficult to perfluoroalkylate. Their reaction with perfluoralkyl iodides under similar conditions gave predominantly R_FSO_2Na and R_FH.

The reaction of perfluoroalkyl iodides and Rongalite can result in the formation of perfluoroalkyl free radicals [8]. The presence of $R_F^{\cdot}$ was again likely in the present reactions. The thermolysis perfluoroalkylation of pyridine reported by Cowell and Tamborski gave a mixture of 2-, 3- and 4-isomers in a ratio of about 5:5:1, which was consistent with our results (Table 2). Thus a free-radical mechanism is proposed for the reaction.



Scheme 4.

TABLE 3

Reaction of R_FI with derivatives of pyridine

R_FI	Aromatics	Time (h)	Yield (%)	Isomer composition (%)[a]		
				2	**3**	**4**
1a	9	7	55	49	51	
1b	9	8	42	44	56	
1d	9	8	52	48	52	
1a	10	6	42	60	27	13
1b	10	6	46	62	26	12
1d	11	6	38	95		5
1a	12	10	44[b]			
1a	13	8	57[b]			
1a	14	8	27			

[a]Determined by ^{19}F NMR spectroscopy.
[b]Mixture of regioisomers.

The reason why pyridine and its derivatives can be perfluoroalkylated under such mild conditions is not yet clear.

Experimental

Temperatures are uncorrected. IR spectra were recorded on Perkin-Elmer 983 and Carl Diatomite IR-440 spectrometers. ^1H NMR spectra were recorded on a Varian EM-360A spectrometer at 60 MHz. ^{19}F NMR spectra were recorded on a Varian EM-360L spectrometer at 54.6 MHz, chemical shifts in ppm being positive upfield using TFA as an external standard. The

values reported were $\delta_F = \delta_{TFA} + 76.8$ ppm. MS spectra were obtained on a Finnigan 4021 spectrometer. All reagents and solvents were used directly without further purification.

Reaction of R_FI with pyrrole

A mixture consisting of 5.44 g (15 mmol) ClC_4F_8I, 1.58 g (24 mmol) pyrrole, 3.08 g (20 mmol) Rongalite and 1.68 g (20 mmol) $NaHCO_3$ in 10 ml MeCN and 15 ml H_2O was stirred for 5 h at 60–65 °C under an N_2 atmosphere. After the ClC_4F_8I had been consumed completely, the mixture was extracted with ether, washed with water and dried over anhydrous Na_2SO_4. Distillation under reduced pressure gave 3.07 g (68% yield) of 2-(4-chloro-octafluorobutyl)pyrrole (**3a**), b.p. 57–58 °C/8 mmHg (62 °C/ 10 mmHg [1]). IR (cm^{-1}): 3500; 1565; 1460; 1420; 1190. ^1H NMR (CCl_4) δ: 8.40 (1H, s, NH); 6.85 (1H, s); 6.58 (1H, m); 6.25 (1H, m) ppm. ^{19}F NMR (CCl_4) δ: 67.8 (2F, t, CF_2Cl); 107.4 (2F, t, CF_2Ar); 119.6 (2F, m); 121.7 (2F, m) ppm.

Compounds **1b**, **1c** and **1g** reacted similarly with pyrrole to give the corresponding products **3b**, **3c** and **3g**, which were identified by comparison of their spectra with authentic specimens.

Reaction of R_FI with pyridine

A mixture consisting of 8.92 g (20 mmol) $C_6F_{13}I$, 3.16 g (40 mmol) pyridine, 4.62 g (30 mmol) Rongalite, 2.94 g (35 mmol) $NaHCO_3$, 12 ml MeCN and 24 ml H_2O was stirred at 70–75 °C for 6 h. The product was extracted with ether (25 ml × 3), washed with water and dried over anhydrous Na_2SO_4. Distillation under reduced pressure gave 4.5 g (57% yield) of a colorless liquid, b.p. 66–68 °C/5 mmHg. The 2- and 3-tridecafluorohexyl-pyridines were isolated by column chromatography on silica gel with petroleum ether/ benzene (1:1) as eluent. The formation of the 4-isomer was indicated by ^{19}F NMR spectroscopy.

2-Tridecafluorohexylpyridine (**6d**): Analysis: $C_{11}H_4F_{13}N$ requires: C, 33.27; H, 1.02; N, 3.53; F, 62.19%. Found: C, 32.92; H, 0.93; N, 3.64; F, 62.55%. MS (*m/z*): 399; 398; 397 (M); 128 ($ArCF_2$, 100); 78 (Ar). IR (cm^{-1}): 3070; 1590; 1472; 1439; 1240–1200. ^1H NMR ($CDCl_3$) δ: 8.82 (1H, d); 8.15–7.35 (3H, m) ppm. ^{19}F NMR ($CDCl_3$) δ: 80.6 (3F, t, CF_3); 113.4 (2F, t, CF_2Ar); 121.4 (4F, m); 122.5 (2F, m); 125.9 (2F, m) ppm.

3-Tridecafluorohexylpyridine (**7d**): Analysis: $C_{11}H_4F_{13}N$ requires: C, 33.27; H, 1.02; N, 3.53; F, 62.19%. Found: C, 33.48; H, 0.88; N, 3.75; F, 62.08%. MS (*m/z*): 399; 398; 397 (M); 128 ($ArCF_2$, 100); 78 (Ar). IR (cm^{-1}) 3060; 1594; 1482; 1426; 1240–1200. ^1H NMR ($CDCl_3$) δ: 8.95 (2H, m); 8.02 (1H, d); 7.65–7.40 (1H, m) ppm. ^{19}F NMR ($CDCl_3$) δ: 81.2 (3F, t, CF_3); 111.7 (2F, t, CF_2Ar); 121.7 (4F, m); 122.8 (2F, m); 126.2 (2f, m) ppm.

The reaction of other perfluoroalkyl iodides with pyridine was performed as above. All products, except for **7c** and **7f**, were colorless liquids; **7c** and **7f** are white solids.

2-(4-Chloro-octafluorobutyl)pyridine (**6a**): Analysis: $C_9H_4ClF_8N$ requires: C, 34.47; H, 1.28; N, 4.47; F, 48.47%. Found: C, 34.60; H, 1.18; N, 4.60; F, 48.38%. MS (*m/z*): 315; 314; 313 (M); 128 ($ArCF_2$, 100); 78 (Ar). IR (cm^{-1}) 3050; 1590; 1472; 1440; 1190. ^1H NMR ($CDCl_3$) δ: 8.78 (1H, d); 8.10–7.30 (3H, m) ppm. ^{19}F NMR ($CDCl_3$) δ: 67.8 (2F, t, CF_2Cl); 113.7 (2F, t, CF_2Ar); 119.2 (2F, m); 120.8 (2F, m) ppm.

3-(4-Chloro-octafluorobutyl)pyridine (**7a**): Analysis: $C_9H_4ClF_8N$ requires: C, 34.47; H, 1.28; N, 4.47; F, 48.47%. Found: C, 34.30; H, 1.31; N, 4.24; F, 48.32%. MS (*m/z*): 315; 314; 313 (M); 128 ($ArCF_2$, 100); 78 (Ar). IR (cm^{-1}): 3040; 1595; 1480; 1428; 1190. ^1H NMR ($CDCl_3$) δ: 8.90 (2H, m); 8.00 (1H, d); 7.65–7.40 (1H, m) ppm. ^{19}F NMR ($CDCl_3$) δ: 68.0 (2F, t, CF_2Cl); 111.4 (2F, t, CF_2Ar); 119.2 (2F, m); 120.9 (2F, m) ppm.

2-(6-Chlorododecafluorohexyl)pyridine (**6b**): Analysis: $C_{11}H_4ClF_{12}N$ requires: C, 31.94; H, 0.97; N, 3.39; F, 55.12%. Found: C, 31.81; H, 0.84; N, 3.62; F, 55.86%. MS (*m/z*): 415; 414; 413 (M); 128 ($ArCF_2$, 100); 78 (Ar). IR (cm^{-1}): 3064; 1590; 1472; 1440; 1210. ^1H NMR ($CDCl_3$) δ: 8.75 (1H, d); 8.05–7.30 (3H, m) ppm. ^{19}F NMR ($CDCl_3$) δ: 68.2 (2F, t, CF_2Cl); 113.6 (2F, t, CF_2Ar); 121.0 (8F, m) ppm.

3-(6-Chlorododecafluorohexyl)pyridine (**7b**): Analysis: $C_{11}H_4ClF_{12}N$ requires: C, 31.94; H, 0.97; N, 3.39; F, 55.12%. Found: C, 31.94; H, 0.90; N, 3.45; F, 55.54%. MS (*m/z*): 415; 414; 413 (M); 128 ($ArCF_2$, 100); 78 (Ar). IR (cm^{-1}): 3048; 1594; 1481; 1426; 1200. ^1H NMR ($CDCl_3$) δ: 8.88 (2H, m); 7.98 (1H, d); 7.60–7.40 (1H, m) ppm. ^{19}F NMR ($CDCl_3$) δ: 68.2 (2F, t, CF_2Cl); 111.8 (2F, t, CF_2Ar); 121.2 (8F, m) ppm.

2-(8-Chlorohexadecafluoro-octyl)pyridine (**6c**): Analysis: $C_{13}H_4ClF_{16}N$ requires: C, 30.40; H, 0.78; N, 2.73; F, 59.18%. Found: C, 30.14; H, 0.69; N, 2.84; F, 59.85%. MS (*m/z*): 515; 514; 513 (M); 128 ($ArCF_2$, 100); 78 (Ar). IR (cm^{-1}) 3065; 1590; 1472; 1439; 1210. ^1H NMR ($CDCl_3$) δ: 8.83 (1H, d); 8.10–7.30 (3H, m) ppm. ^{19}F NMR ($CDCl_3$) δ: 68.2 (2F, t, CF_2Cl); 114.0 (2F, t, CF_2Ar); 120.2 (2F, m); 121.6 (10F, m) ppm.

3-(8-Chlorohexadecafluoro-octyl)pyridine (**7c**), m.p. 39–40 °C: Analysis: $C_{13}H_4ClF_{16}N$ requires: C, 30.40; H, 0.78; N, 2.73; F, 59.18%. Found: C, 30.26; H, 0.69; N, 2.87; F, 59.18%. MS (*m/z*): 515; 514; 513 (M); 128 ($ArCF_2$, 100); 78 (Ar). IR (cm^{-1}): 3050; 1595; 1480; 1435; 1210. ^1H NMR ($CDCl_3$) δ: 8.88 (2H, m); 7.92 (1H, d); 7.55–7.35 (1H, m) ppm. ^{19}F NMR ($CDCl_3$) δ: 68.2 (2F, t, CF_2Cl); 111.7 (2F, t, CF_2Ar); 120.2 (2F, m); 121.6 (10F, m) ppm.

2-Pentadecafluoroheptylpyridine (**6e**): Analysis: $C_{12}H_4F_{15}N$ requires: C, 32.23; H, 0.90; N, 3.13; F, 63.73%. Found: C, 32.35; H, 0.77; N, 3.36; F, 63.37%. MS (*m/z*): 449; 448; 447 (M); 128 ($ArCF_2$, 100); 78 (Ar). IR (cm^{-1}): 3060; 1590; 1470; 1440; 1200. ^1H NMR ($CDCl_3$) δ: 8.75 (1H, d); 8.05–7.30 (3H, m) ppm. ^{19}F NMR ($CDCl_3$) δ: 81.0 (3F, t, CF_3); 113.8 (2F, t, CF_2Ar); 121.5 (8F, m); 126.0 (2F, m) ppm.

3-Pentadecafluoroheptylpyridine (**7e**): Analysis: $C_{12}H_4F_{15}N$ requires: C, 32.23; H, 0.90; N, 3.13; F, 63.73%. Found: C, 32.11; H, 0.64; N, 3.27; F, 63.58%. MS (*m/z*): 449; 448; 447 (M); 128 ($ArCF_2$, 100); 78 (Ar). IR (cm^{-1}):

3050; 1594; 1580; 1480; 1425; 1200. ^{1}H NMR ($CDCl_3$) δ: 8.90 (2H, m); 8.02 (1H, d); 7.70–7.50 (1H, m) ppm. ^{19}F NMR ($CDCl_3$) δ: 81.0 (3F, t, CF_3); 111.6 (2F, t, CF_2Ar); 121.5 (8F, m); 126.0 (2F, m) ppm.

2-Heptadecafluoro-octylpyridine (**6f**): Analysis: $C_{13}H_4F_{17}N$ requires: C, 31.41; H, 0.81; N, 2.82; F, 64.96%. Found: C, 31.30; H, 0.72; N, 2.96; F, 64.93%. MS (*m/z*): 499; 498; 497 (M); 128 ($ArCF_2$, 100); 78 (Ar). IR (cm^{-1}): 3065; 1587; 1470; 1438; 1200. ^{1}H NMR ($CDCl_3$) δ: 8.82 (1H, d); 8.10–7.30 (3H, m) ppm. ^{19}F NMR ($CDCl_3$) δ: 81.1 (3F, t, CF_3); 114.0 (2F, t, CF_2Ar); 121.6 (8F, m); 126.0 (2F, m) ppm.

3-Heptadecafluoro-octylpyridine (**7f**), m.p. 43–44 °C: Analysis: $C_{13}H_4F_{17}N$ requires: C, 31.41; H, 0.81; N, 2.82; F, 64.96%. Found: C, 31.13; H, 0.63; N, 2.76; F, 65.38%. MS (*m/z*): 499; 498; 497 (M); 128 ($ArCF_2$, 100); 78 (Ar). IR (cm^{-1}): 3040; 1598; 1583; 1482; 1430; 1200. ^{1}H NMR ($CDCl_3$) δ: 8.95 (2H, m); 8.02 (1H, d); 7.68–7.45 (1H, m) ppm. ^{19}F NMR ($CDCl_3$) δ: 81.0 (3F, t, CF_3); 111.7 (2F, t, CF_2Ar); 121.7 (8F, m); 126.1 (2F, m) ppm.

Reaction of R_FI with derivatives of pyridine

A typical procedure is as follows. A mixture consisting of 3.63 g (10 mmol) ClC_4F_8I, 1.86 g (20 mmol) 4-methylpyridine, 2.3 g (15 mmol) Rongalite, 1.26 g (15 mmol) $NaHCO_3$, 5 ml MeCN and 10 ml H_2O was stirred at 70–75 °C for 8 h. The product was extracted with ether and chromatographed through a silica gel column to give 4-methyl-2-(4-chloro-octafluorobutyl)pyridine and 4-methyl-3-(4-chloro-octafluorobutyl)pyridine in 55% combined yield.

4-Methyl-2-(4-chloro-octafluorobutyl)pyridine: Analysis: $C_{10}H_6ClF_8N$ requires: C, 36.66; H, 1.85; N, 4.28; F, 46.39%. Found: C, 36.62; H, 1.94; N, 4.25; F, 46.45%. MS (*m/z*): 329; 328; 327 (M); 142 ($ArCF_2$, 100); 92 (Ar). IR (cm^{-1}): 3060; 1615; 1320; 1200. ^{1}H NMR ($CDCl_3$) δ: 8.68 (1H, d); 7.56 (1H, s); 7.36 (1H, d); 2.48 (3H, s) ppm. ^{19}F NMR ($CDCl_3$) δ: 67.8 (2F, t, CF_2Cl); 114.0 (2F, t, CF_2Ar); 119.7 (2F, m); 121.2 (2F, m) ppm.

4-Methyl-3-(4-chloro-octafluorobutyl)pyridine: Analysis: $C_{10}H_6ClF_8N$ requires: C, 36.66; H, 1.85; N, 4.28; F, 46.39%. Found: C, 36.42; H, 1.73; N, 4.44; F, 46.16%. MS (*m/z*): 329; 328; 327 (M); 142 ($ArCF_2$, 100); 92 (Ar). IR (cm^{-1}): 3050; 1600; 1365; 1200. ^{1}H NMR ($CDCl_3$) δ: 8.75 (2H, m); 7.26 (1H, d); 2.55 (3H, t) ppm. ^{19}F NMR ($CDCl_3$) δ: 67.7 (2F, t, CF_2Cl); 107.2 (2F, t, CF_2Ar); 120.0 (4F, m) ppm.

4-Methyl-2-(6-chlorododecafluorohexyl)pyridine: Analysis: $C_{12}H_6ClF_{12}N$ requires: C, 33.71; H, 1.41; N, 3.28; F, 53.31%. Found: C, 33.64; H, 1.25; N, 3.26; F, 53.64%. MS (*m/z*): 429; 428; 427 (M); 142 ($ArCF_2$, 100); 92 (Ar). IR (cm^{-1}): 3050; 1610; 1315; 1210. ^{1}H NMR ($CDCl_3$) δ: 8.72 (1H, d); 7.61 (1H, s); 7.41 (1H, d); 2.48 (3H, s) ppm. ^{19}F NMR ($CDCl_3$) δ: 68.0 (2F, t, CF_2Cl); 114.0 (2F, t, CF_2Ar); 120.3 (2F, m); 121.2 (6F, m) ppm.

4-Methyl-3-(6-chlorododecafluorohexyl)pyridine: Analysis: $C_{12}H_6ClF_{12}N$ requires: C, 33.71; H, 1.41; N, 3.28; F, 53.31%. Found: C, 33.66; H, 1.38; N, 3.51; F, 53.33%. MS (*m/z*): 429, 428; 427 (M); 142 ($ArCF_2$, 100); 92 (Ar). IR (cm^{-1}): 3040; 1600; 1420; 1200. ^{1}H NMR ($CDCl_3$) δ: 8.72 (2H,

m); 7.30 (1H, d); 2.53 (3H, t) ppm. ^{19}F NMR ($CDCl_3$) δ: 68.0 (2F, t, CF_2Cl); 107.2 (2F, t, CF_2Ar); 120.3 (2F, m); 121.2 (6F, m) ppm.

4-Methyl-2-tridecafluorohexylpyridine: Analysis: $C_{12}H_6F_{13}N$ requires: C, 35.05; H, 1.47; N, 3.41; F, 60.07%. Found: C, 35.03; H, 1.40; N, 3.45; F, 59.82%. MS (*m/z*): 413; 412; 411 (M); 142 ($ArCF_2$, 100); 92 (Ar). IR (cm^{-1}): 3060; 1615; 1320; 1200. ^1H NMR ($CDCl_3$) δ: 8.70 (1H, d); 7.57 (1H, s); 7.36 (1H, d); 2.48 (3H, s) ppm. ^{19}F NMR ($CDCl_3$) δ: 81.1 (3F, t, CF_3); 114.0 (2F, t, CF_2Ar); 121.8 (6F, m); 126.3 (2F, m) ppm.

4-Methyl-3-tridecafluorohexylpyridine: Analysis: $C_{12}H_6F_{13}N$ requires: C, 35.05; H, 1.47; N, 3.41; F, 60.07%. Found: C, 34.72; H, 1.44; N, 3.53; F, 59.84%. MS (*m/z*): 413; 412; 411 (M); 142 ($ArCF_2$, 100); 92 (Ar). IR (cm^{-1}): 3050; 1600; 1364; 1200. ^1H NMR ($CDCl_3$) δ: 8.77 (2H, m); 7.27 (1H, d); 2.52 (3H, t) ppm. ^{19}F NMR ($CDCl_3$) δ: 81.3 (3F, t, CF_3); 107.3 (2F, t, CF_2Ar); 122.1 (6F, m); 126.3 (2F, m) ppm.

The mixture of 3-methyl-2-(4-chloro-octafluorobutyl)pyridine and 5-methyl-2-(4-chloro-octafluorobutyl)pyridine: Analysis: $C_{10}H_6ClF_8N$ requires: C, 36.66; H, 1.85; N, 4.28; F, 46.39%. Found: C, 36.25; H, 1.65; N, 4.39; F, 46.89%. MS (*m/z*): 329; 328; 327 (M); 142; 92. IR (cm^{-1}): 3040; 1580; 1455; 1320; 1190. ^1H NMR ($CDCl_3$) δ: 8.62 (1H, m); 7.65–7.30 (2H, m); 2.52–2.45 (3H, m) ppm. ^{19}F NMR ($CDCl_3$) δ: 68.0 (2F, t, CF_2Cl); 108.8; 113.5 (2F, t, CF_2Ar); 119.2–121.0 (4F, m) ppm.

3-Methyl-4-(4-chloro-octafluorobutyl)pyridine: Analysis: $C_{10}H_6ClF_8N$ requires: C, 36.66; H, 1.85; N, 4.28; F, 46.39%. Found: C, 36.48; H, 1.78; N, 4.38; F, 46.37%. MS (*m/z*): 329; 328; 327 (M); 143; 92. IR (cm^{-1}): 3020; 1582; 1445; 1320; 1200. ^1H NMR ($CDCl_3$) δ: 8.75 (2H, m); 7.46 (1H, d); 2.54 (3H, t) ppm. ^{19}F NMR ($CDCl_3$) δ: 68.2 (2F, t, CF_2Cl); 109.3 (2F, t, CF_2Ar); 120.2 (4F, m) ppm.

5-Methyl-3-(4-chloro-octafluorobutyl)pyridine: Analysis: $C_{10}H_6ClF_8N$ requires: C, 36.66; H, 1.85; N, 4.28; F, 46.39%. Found: C, 36.73; H, 1.70; N, 4.41; F, 46.87%. MS (*m/z*): 329; 328; 327 (M); 143; 92. IR (cm^{-1}): 3040; 1580; 1455; 1320; 1190. ^1H NMR ($CDCl_3$) δ: 8.70 (2H, s); 7.75 (1H, s); 2.43 (3H, s) ppm. ^{19}F NMR ($CDCl_3$) δ: 68.0 (2F, t, CF_2Cl); 111.5 (2F, t, CF_2Ar); 119.4 (2F, m); 121.0 (4F, m) ppm.

The mixture of 3-methyl-2-(6-chlorododecafluorohexyl)pyridine and 5-methyl-2-(6-chlorododecafluorohexyl)pyridine: Analysis: $C_{12}H_6ClF_{12}N$ requires: C, 33.70; H, 1.41; N, 3.28; F, 53.31%. Found: C, 33.45; H, 1.20; N, 3.30; F, 54.21%. MS (*m/z*): 429; 428; 427 (M); 143; 92. IR (cm^{-1}): 3050; 1580; 1455; 1300; 1200. ^1H NMR ($CDCl_3$) δ: 8.55 (1H, m); 7.60–7.30 (2H, m); 2.45 (3H, m) ppm. ^{19}F NMR ($CDCl_3$) δ: 68.2 (2F, t, CF_2Cl); 108.8; 113.6 (2F, t, CF_2Ar); 121.2 (8F, m) ppm.

3-Methyl-4-(6-chlorododecafluorohexyl)pyridine: Analysis: $C_{12}H_6ClF_{12}N$ requires: C, 33.70; H, 1.41; N, 3.28; F, 53.31%. Found: C, 33.41; H, 1.28; N, 3.46; F, 54.10%. MS (*m/z*): 429; 428; 427 (M); 143; 92. IR (cm^{-1}): 3040; 1580; 1450; 1305; 1200. ^1H NMR ($CDCl_3$) δ: 8.62 (2H, m); 7.36 (1H, d); 2.42 (3H, s) ppm. ^{19}F NMR ($CDCl_3$) δ: 68.2 (2F, t, CF_2Cl); 109.2 (2F, t, CF_2Ar); 121.2 (8F, m) ppm.

5-Methyl-3-(6-chlorododecafluorohexyl)pyridine: Analysis: $C_{12}H_6ClF_{12}N$ requires: C, 33.70; H, 1.41; N, 3.28; F, 53.31%. Found: C, 33.78; H, 1.33; N, 3.52; F, 53.71%. MS (*m/z*): 429; 428; 427 (M); 143; 92. IR (cm^{-1}): 3040; 1580; 1458; 1305; 1200. ^1H NMR ($CDCl_3$) δ: 8.62 (2H, s); 7.65 (1H, s); 2.42 (3H, s) ppm. ^{19}F NMR ($CDCl_3$) δ: 68.2 (2F, t, CF_2Cl); 111.6 (2F, t, CF_2Ar); 121.0 (8F, m) ppm.

3,5-Dimethyl-2-tridecafluorohexylpyridine: Analysis: $C_{13}H_8F_{13}N$ requires: C, 36.72; H, 1.90; N, 3.29; F, 58.09%. Found: C, 36.38; H, 1.65; N, 3.24; F, 58.85%. MS (*m/z*): 426; 425 (M); 157 ($ArCF_2$); 107 (Ar). IR (cm^{-1}) 3040–2900; 1602; 1460; 1362; 1200. ^1H NMR ($CDCl_3$) δ: 8.38 (1H, s); 7.42 (1H, s); 2.44 (3H, t); 2.36 (3H, s) ppm. ^{19}F NMR ($CDCl_3$) δ: 81.2 (3F, t, CF_3); 109.0 (2F, t, CF_2Ar); 121.3 (4F, m); 122.8 (2F, m); 126.2 (2F, m) ppm.

2-(4-Chloro-octafluorobutyl)pyrazine: Analysis: $C_8H_3ClF_8N_2$ requires: C, 30.55; H, 0.96; N, 8.90; F, 48.32%. Found: C, 30.35; H, 0.79; N, 9.15; F, 48.66%. MS (*m/z*): 316; 315; 314 (M); 129 ($ArCF_2$, 100); 79 (Ar). IR (cm^{-1}): 3050; 1470; 1410; 1320; 1200. ^1H NMR (CCl_4) δ: 8.63 (2H, s); 8.84 (1H, s) ppm. ^{19}F NMR (CCl_4) δ: 68.8 (2F, t, CF_2Cl); 115.0 (2F, t, CF_2Ar); 120.0 (2F, m); 121.8 (2F, m) ppm.

*Reaction of **1b** with quinoline*

A mixture consisting of 7.25 g (20 mmol) **1b**, 4.5 g (35 mmol) quinoline, 4.62 g (30 mmol) Rongalite, 2.52 g (30 mmol) $NaHCO_3$, 10 ml MeCN and 20 ml H_2O was stirred at 75 °C for 8 h. The product was extracted with ether, washed with water and dried over anhydrous Na_2SO_4. Distillation under reduced pressure gave 3.2 g (44% yield) of colorless liquid, b.p. 98–102 °C/ 2 mmHg. Analysis: $C_{13}H_6ClF_8N$ requires: C, 42.94; H, 1.66; N, 3.85; F, 41.80%. Found: C, 42.81; H, 1.63; N, 3.82; F, 42.64%. MS (*m/z*): 365; 364; 363 (M); 178 ($ArCF_2$, 100); 128 (Ar). IR (cm^{-1}): 3040; 1625; 1595; 1498; 1190. ^1H NMR (CCl_4) δ: 8.9–7.1 ppm. ^{19}F NMR (CCl_4) δ: 68.0 (2F, s, CF_2Cl); 104.8–115.2 (2F, m, CF_2Ar); 119.6 (4F, m) ppm.

*Reaction of **1b** with isoquinoline*

Isoquinoline (4.5 g, 35 mmol) and **1b** (20 mmol) were reacted in a similar way to give 4.15 g (57% yield) of colorless liquid, b.p. 98–100 °C/ 2 mmHg. Analysis: $C_{13}H_6ClF_8N$ requires: C, 42.94; H, 1.66; N, 3.85; F, 41.80%. Found: C, 42.47; H, 1.67; N, 4.03; F, 42.96%. MS (*m/z*): 365; 364; 363 (M); 178 ($ArCF_2$, 100); 128 (Ar). IR (cm^{-1}): 3050; 1605; 1580; 1508; 1190. ^1H NMR (CCl_4) δ: 9.4–7.7 ppm. ^{19}F NMR (CCl_4) δ: 68.0 (2F, t, CF_2Cl); 104.0–115.5 (2F, m, CF_2Ar); 119.6 (4F, m) ppm.

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