

Direct Perfluoroalkylation of Aromatic and Heteroaromatic Compounds with Perfluoroalkanesulfonyl Chlorides Catalysed by a Ruthenium(II) Phosphine Complex

Nobumasa Kamigata,* Takeshi Ohtsuka, Takamasa Fukushima, Masato Yoshida and Toshio Shimizu

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Minami-ohsawa, Hachioji, Tokyo 192-03, Japan

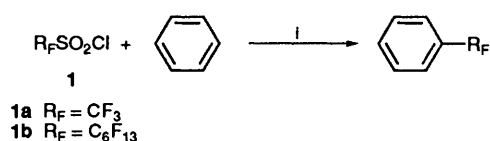
The perfluoroalkylation of aromatic and heteroaromatic compounds by perfluoroalkanesulfonyl chlorides **1** has been investigated in the presence of a ruthenium(II) phosphine complex. The reaction of compounds **1** with substituted benzenes or thiophenes proceeded smoothly with extrusion of sulfur dioxide at 120 °C to give corresponding perfluoroalkylated compounds in good yield. No expected perfluoroalkylated product was obtained in the reaction of compounds **1** with pyrrole; however, 1-trimethylsilyl- and 1-triisopropylsilyl-pyrrole were regioselectively perfluoroalkylated at their 2- and 3-position, respectively.

Recently, much attention has been focussed on fluorinated organic compounds due to the characteristic features of the fluorine atom, particularly in the field of medicinal and agricultural chemistry and materials science. The replacement of hydrogen in aromatic and heteroaromatic compounds by a perfluoroalkyl group may have a profound influence on the physical and biological properties of such molecules.¹ As a result, considerable efforts have been devoted to the introduction of perfluoroalkyl units in such systems, as exemplified by the reactions of the reactive perfluoroalkyl cationic or radical species.² However, these processes often required careful preparation of the reactive intermediates³ and were not available to conduct both perfluoroalkylation (>C₂) and trifluoromethylation. Previously, we reported a novel chloroperfluoroalkylation of alkenes with trifluoromethane- and tridecafluorohexane-sulfonyl chlorides catalysed by a ruthenium(II) complex.⁴ The reaction was found to be applicable to the trifluoromethylation or tridecafluorohexylation of aromatic compounds, and the results were reported as a preliminary communication.⁵ We now give a full account of this novel perfluoroalkylation of aromatic and heteroaromatic compounds with perfluoroalkanesulfonyl chlorides in the presence of a ruthenium(II) catalyst.

Results and Discussion

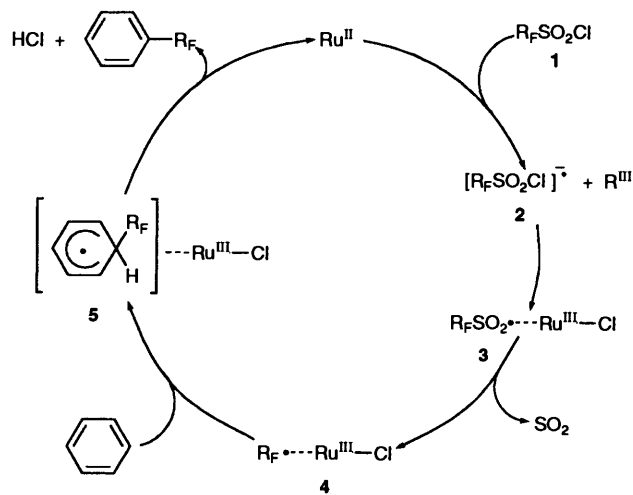
When a solution containing trifluoromethanesulfonyl chloride **1a** (2.0 mmol) and dichlorotris(triphenylphosphine)ruthenium(II) (0.02 mmol) in benzene (5.0 cm³) was degassed and heated at 120 °C in a sealed tube for 19 h, the reaction proceeded smoothly with extrusion of sulfur dioxide. Flash column chromatography on Florisil with benzene, followed by gel permeation chromatography using chloroform, gave benzotrifluoride in 41% yield. The reaction of tridecafluorohexanesulfonyl chloride **1b** with benzene in the presence of the ruthenium(II) catalyst under similar conditions afforded tridecafluorohexylbenzene in 44% yield.

Similarly, several aromatic compounds were treated with trifluoromethane- or tridecafluorohexane-sulfonyl chloride in the presence of the ruthenium(II) catalyst under similar conditions, and the results are summarized in Table 1. As shown in Table 1, benzene, toluene, anisole, bromobenzene, chlorobenzene, *p*-xylene, and *p*-dimethoxybenzene were perfluoroalkylated in moderate to good yields. However, benzonitrile was perfluoroalkylated to only a trace amount, and no



Reagent and conditions: i, RuCl₂(PPh₃)₃, 120 °C

perfluoroalkylated product was obtained in the reaction of chlorides **1** with nitrobenzene or diethyl phthalate under similar conditions. The results show that the present perfluoroalkylating method cannot be applied to such aromatic compounds possessing strongly electron-withdrawing groups. Anyway, it was demonstrated that our novel chloroperfluoroalkylation of alkenes by reaction with perfluoroalkanesulfonyl chloride catalysed by the ruthenium(II) complex⁴ is also applicable to the perfluoroalkylation of aromatic nuclei. Trifluoromethyl iodide has been widely employed as a trifluoromethylating reagent but the method is not convenient in most organic laboratories since trifluoromethyl iodide is a gas at atmospheric pressure (b.p. -23 °C). In contrast, trifluoromethanesulfonyl chloride **1a** has a boiling point of 32 °C and can be easily handled at room temperature. Therefore, the present reaction is a synthetically useful method for replacement of hydrogen of an aromatic nucleus by a perfluoroalkyl group.



Scheme 1

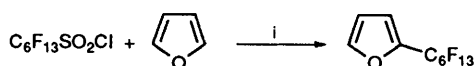
Table 1 Reaction of compounds **1** with aromatic compounds catalysed by dichlorotris(triphenylphosphine)ruthenium(II)

R _F in 1	Aromatic compound	Conditions	Product	Yield (%)
CF ₃	PhH	120 °C, 18 h	CF ₃ Ph	41
C ₆ F ₁₃	PhH	120 °C, 19 h	C ₆ F ₁₃ Ph	44
CF ₃	PhMe	120 °C, 18 h	CF ₃ C ₆ H ₄ Me ^a	36
C ₆ F ₁₃	PhMe	120 °C, 18 h	C ₆ F ₁₃ C ₆ H ₄ Me ^b	54
CF ₃	PhOMe	120 °C, 18 h	CF ₃ C ₆ H ₄ OMe ^c	58
C ₆ F ₁₃	PhOMe	120 °C, 18 h	C ₆ F ₁₃ C ₆ H ₄ OMe ^d	59
C ₆ F ₁₃	PhBr	120 °C, 24 h	C ₆ F ₁₃ C ₆ H ₄ Br ^e	39
C ₆ F ₁₃	PhCl	120 °C, 24 h	C ₆ F ₁₃ C ₆ H ₄ Cl ^f	40
C ₆ F ₁₃	PhCN	120 °C, 24 h	C ₆ F ₁₃ C ₆ H ₄ CN ^g	trace
CF ₃	<i>p</i> -MeC ₆ H ₄ Me	120 °C, 18 h	CF ₃ C ₆ H ₃ Me ₂	63
C ₆ F ₁₃	<i>p</i> -MeC ₆ H ₄ Me	120 °C, 24 h	C ₆ F ₁₃ C ₆ H ₃ Me ₂	41
CF ₃	<i>p</i> -MeOC ₆ H ₄ OMe	120 °C, 18 h	CF ₃ C ₆ H ₃ (OMe) ₂	71
C ₆ F ₁₃	<i>p</i> -MeOC ₆ H ₄ OMe	120 °C, 24 h	C ₆ F ₁₃ C ₆ H ₃ (OMe) ₂	63

^a The isomer proportions (*o*-, *m*- and *p*-isomer) were not determined. ^b Isomer distribution: *o*-, 32%; *m*-, 36%; *p*-, 32%. ^c Isomer distribution: *o*-, 53%; *m*-, 25%; *p*-, 22%. ^d Isomer distribution: *o*-, 49%; *m*-, 20%; *p*-, 31%. ^e Isomer distribution: *o*-, 36%; *m*-, 32%; *p*-, 32%. ^f Isomer distribution: *o*-, 40%; *m*-, 25%; *p*-, 35%. ^g Isomer distribution was estimated to be *o*-, 50%; *m*-, 25%; *p*-, 25% by GLC.

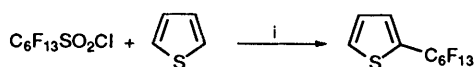
The reaction mechanism for these perfluoroalkylations is given in Scheme 1. The redox-transfer reaction between perfluoroalkanesulfonyl chloride **1** and the ruthenium(II) catalyst affords anion radical **2** of compound **1**, which cleaves homolytically to give perfluoroalkanesulfonyl radical **3** and Ru^{III}-Cl. Perfluoroalkyl radical **4**, formed from radical **3** by extrusion of sulfur dioxide, adds to the aromatic nucleus to give cyclohexadienyl radical **5**. The subsequent hydrogen-atom abstraction by Ru^{III}-Cl species from radical **5** affords perfluoroalkylbenzenes and hydrogen chloride, and the ruthenium(II) catalyst is regenerated. Radical intermediates **3**, **4** and **5** are considered to be confined in the coordination sphere of the ruthenium complex.⁶

The perfluoroalkylation of heteroaromatic compounds such as furan and thiophenes by the chloride **1b** was also investigated in the presence of the ruthenium(II) complex under similar conditions. When furan was treated with tridecafluorohexanesulfonyl chloride, the perfluoroalkylation occurred selectively at the 2-position and 2-(tridecafluorohexyl)furan was obtained in 30% yield; however, a lot of resinous black tar was also formed as a by-product.



Reagent and conditions: i, RuCl₂(PPh₃)₃, 120 °C

The reaction of tridecafluorohexanesulfonyl chloride with thiophene selectively afforded 2-(tridecafluorohexyl)thiophene in 77% yield.

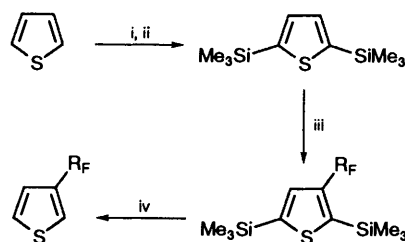


Reagent and conditions: i, RuCl₂(PPh₃)₃, 120 °C

Such regioselective perfluoroalkylations were observed in the reactions of compound **1b** with 2-methylthiophene, 2-(trimethylsilyl)thiophene, 2-bromothiophene, 2-chlorothiophene, and thiophene-2-carbaldehyde. It is noteworthy that thiophene-2-carbaldehyde was perfluoroalkylated selectively at the 5-position although the yield was low since substituted benzenes possessing electron-withdrawing groups such as cyano, ethoxycarbonyl, and nitro groups were not perfluoroalkylated under conditions similar to those mentioned above. In the reaction of compound **1b** with 3-methylthiophene, the tridecafluorohexyl group was introduced at both the 2- and the 5-position, and 4-methyl-2-(tridecafluorohexyl)thiophene and

3-methyl-2-(tridecafluorohexyl)thiophene were obtained in 44 and 36% yield, respectively. Similar results were observed in the reaction of compound **1b** with 3-bromothiophene. These results show that thiophene and monosubstituted thiophenes are selectively perfluoroalkylated at the 2-position and that no perfluoroalkylation occurs at the 3-position. However, 2,5-disubstituted thiophenes such as 2,5-dimethylthiophene, 2,5-bis(trimethylsilyl)thiophene, and 2,5-dichlorothiophene were perfluoroalkylated at the 3-position although the yields were moderate to low. The results are summarized in Table 2.

The trimethylsilyl groups of 2,5-bis(trimethylsilyl)-3-perfluoroalkylthiophene can be removed by treatment with fluoride anion as we have reported previously.⁷ Therefore, bistrimethylsilylation of thiophene at the 2- and 5-position, perfluoroalkylation of 2,5-bis(trimethylsilyl)thiophene, and subsequent desilylation will be an excellent method for the regioselective synthesis of 3-perfluoroalkylthiophenes since thiophene itself is regioselectively perfluoroalkylated at the 2-position and afforded only 2-(tridecafluorohexyl)thiophene and none of the 3-isomer.





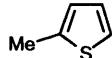
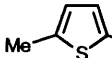
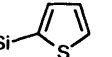
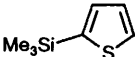
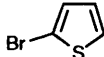
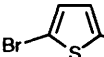
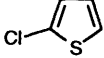
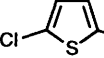
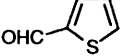
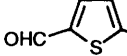

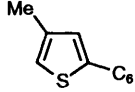
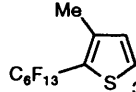

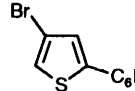
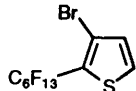
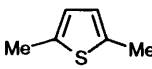

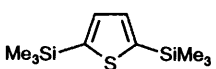
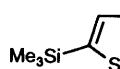
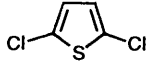



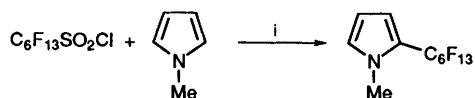
Reagents: i, BuLi, Me₂NCH₂CH₂NMe₂, Et₂O; ii, Me₃SiCl; iii, R_FSO₂Cl, RuCl₂(PPh₃)₃; iv, Bu₄N⁺F⁻

Perfluoroalkylation of pyrroles with tridecafluorohexanesulfonyl chloride catalysed by the ruthenium(II) complex was also studied under similar conditions. The results are summarized in Table 3.

When the reaction of tridecafluorohexanesulfonyl chloride **1b** with pyrrole was carried out in the presence of a catalytic amount of ruthenium(II) complex at 120 °C, no expected perfluoroalkylated pyrrole was found, and only black tar was obtained. Attempted perfluoroalkylation of 2-methylpyrrole or 2,6-dimethylpyrrole by compound **1b** under similar conditions also failed; however, 1-methylpyrrole was perfluoroalkylated and formed 1-methyl-2-(tridecafluorohexyl)pyrrole although the yield was very low. These results suggest that perfluoroalkylation of pyrroles can occur when the hydrogen atom on the

Table 2 Reaction of compound **1b** with furan and thiophenes catalysed by ruthenium(II) complex at 120 °C for 24 h



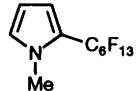
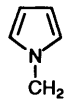
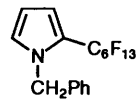
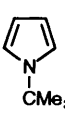
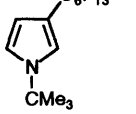
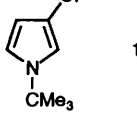
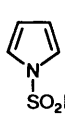
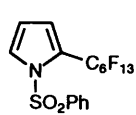
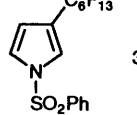
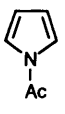
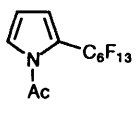
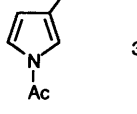
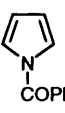
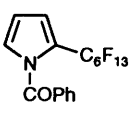
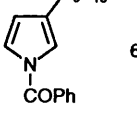
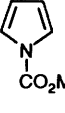
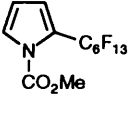
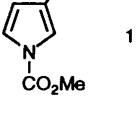
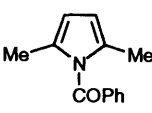
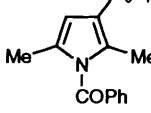
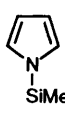
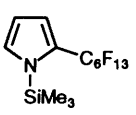
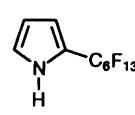
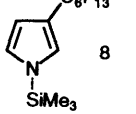
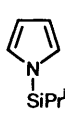
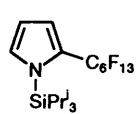
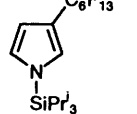
Entry	Substrate	Products [Yield (%)]
1		 30
2		 77
3		 73
4		 56
5		 50
6		 38
7		 26
8		 44  36
9		 34  31
10		 41
11		 23
12		 16 (30) ^a

^a The reaction time was 72 h.Reagent and conditions: i, RuCl₂(PPh₃)₃, 120 °C

pyrrole nitrogen has been previously replaced by an adequate substituent.

Thus, the treatment of compound **1b** with 1-benzylpyrrole in the presence of the ruthenium(II) catalyst under similar conditions afforded 1-benzyl-2-(tridecafluorohexyl)pyrrole in 53% yield. The results mean that the yield of perfluoroalkylation

Table 3 Reaction of compound **1b** with pyrroles catalysed by ruthenium(II) complex at 120 °C for 24 h

Entry	Substrate	Products [Yield (%)]
1		None
2		 4 (18) ^a
3		 53
4		 9  13
5		 35 (65) ^b  3 (17) ^b
6		 61 (80) ^b  3 (4) ^b
7		 92  6
8		 55  1
9		 52
10		 53  25  8
11		 25  59

^a The reaction time was 6 h. ^b The reaction time was 48 h.

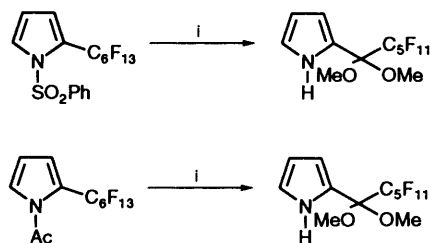
was significantly improved by replacing the hydrogen on the nitrogen of the pyrrole. However, the reaction of compound **1b** with 1-(*tert*-butyl)pyrrole gave 1-(*tert*-butyl)-3-(tridecafluorohexyl)pyrrole in only 9% yield together with a by-product, 1-(*tert*-butyl)-3-chloropyrrole (13% yield).^{*} Although the yield was low, it was of interest that the regioselectivity of the perfluoroalkylation was reversed and that perfluoroalkylation occurred regioselectively at the 3-position by replacing, with a *tert*-butyl group, the benzyl group on the nitrogen atom of the pyrrole ring. The reverse of regioselectivity is accounted for by the bulkiness of the *tert*-butyl group which sterically prevents the perfluoroalkylation at the 2-position. The reactions of compound **1b** with several pyrroles possessing an electron-withdrawing group on the nitrogen atom were also studied. These compounds were regioselectively perfluoroalkylated at the 2-position, and the yields were good to high [entries 5–8]. When the pyrrole has two substituents at the 2- and 5-position, perfluoroalkylation occurred at the 3-position. Namely, the reaction of compound **1b** with 1-benzoyl-2,5-dimethylpyrrole afforded 1-benzoyl-2,5-dimethyl-3-(tridecafluorohexyl)pyrrole in 52% yield.

The reaction of compound **1b** with 1-(trimethylsilyl)pyrrole in the presence of the ruthenium(II) catalyst afforded 2-tridecafluorohexyl-1-(trimethylsilyl)pyrrole (53%), 2-(tridecafluorohexyl)pyrrole (25%), and 3-tridecafluorohexyl-1-(trimethylsilyl)pyrrole (8%). 2-(Tridecafluorohexyl)pyrrole may be formed by desilylation from 2-tridecafluorohexyl-1-(trimethylsilyl)pyrrole once formed under the reaction conditions. The summation of the yields of 2-tridecafluorohexyl-1-(trimethylsilyl)pyrrole and 2-(tridecafluorohexyl)pyrrole is 78%. This means that the perfluoroalkylation of 1-(trimethylsilyl)pyrrole occurs regioselectively at the 2-position. In contrast, regioselective perfluoroalkylation at the 3-position was found in the reaction of compound **1b** with 1-(triisopropylsilyl)pyrrole catalysed by the ruthenium(II) complex, and 3-tridecafluorohexyl-1-(triisopropylsilyl)pyrrole was obtained in 59% yield together with 2-tridecafluorohexyl-1-(triisopropylsilyl)pyrrole (25%). The reverse of regioselectivity is accounted for by the bulkiness of the triisopropylsilyl group on the nitrogen atom, which prevents perfluoroalkylation at the 2-position by steric effects. Such reverse of regioselectivity by the bulkiness of the substituent on the nitrogen atom of pyrrole has been reported in the electrophilic formylation of pyrroles.⁹

Although attempted perfluoroalkylation of pyrrole itself failed by the present method as described above, perfluoroalkylation proceeded smoothly when the hydrogen on the nitrogen atom of the pyrrole was replaced by an adequate substituent. So, if the substituent could be replaced again with hydrogen, the substituent can be regarded as a protecting group for the perfluoroalkylation, and the method will provide an excellent synthetic method for perfluoroalkylpyrroles.

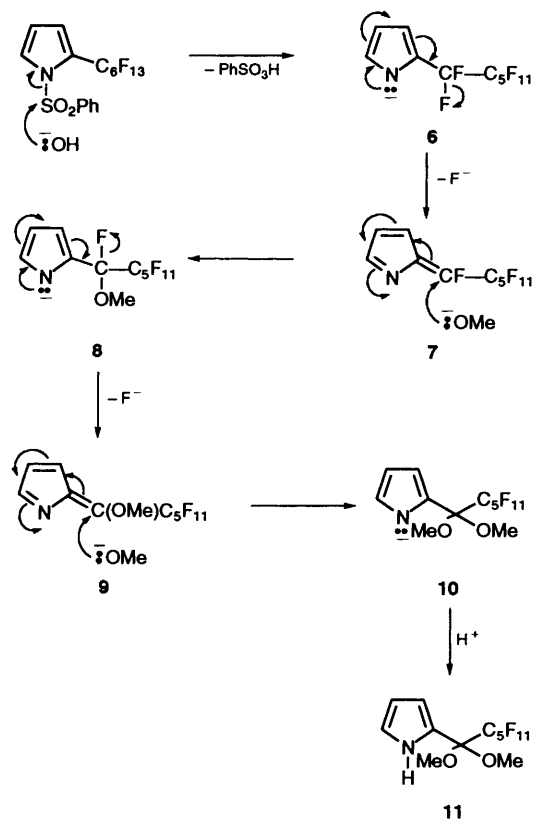
When the deprotection of 1-phenylsulfonyl-2-(tridecafluorohexyl)pyrrole with sodium hydroxide was carried out in methanol, the phenylsulfonyl group was readily replaced by hydrogen; however, the expected product, 2-(tridecafluorohexyl)pyrrole, was not obtained but the reaction afforded 2-(undecafluoro-1,1-dimethoxyhexyl)pyrrole in 84% yield. The same product was isolated in 75% yield in the reaction of 1-acetyl-2-(tridecafluorohexyl)pyrrole with sodium hydroxide in methanol.

The formation of 2-(undecafluoro-1,1-dimethoxyhexyl)pyrrole is accounted for by Scheme 2. Hydroxide ion attacks the sulfur atom of 1-phenylsulfonyl-2-(tridecafluorohexyl)pyrrole



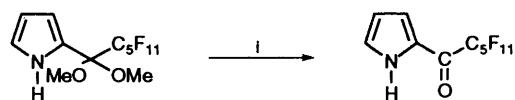
Reagents: i, NaOH, MeOH

to give anion **6**, which releases the α -fluorine atom of the tridecafluorohexyl group as fluoride ion to give enamine **7**, and subsequent addition of methoxide anion on the α -carbon of enamine **7** affords anion **8**. The remaining α -fluorine atom of anion **8** is eliminated to give the vinyl ether **9**, which reacts again with methoxide ion to give ketal **11** via anion **10**. A similar reaction mechanism is reported for the reaction of 2-(tri-fluoromethyl)indole with sodium ethoxide in ethanol.¹⁰



Scheme 2

The acid-catalysed hydrolysis of 2-(undecafluoro-1,1-dimethoxyhexyl)pyrrole afforded pyrrol-2-yl undecafluoropentyl ketone in 77% yield. This unexpected product may be a useful synthetic intermediate since the carbonyl group of this product can be converted into many other functional groups.

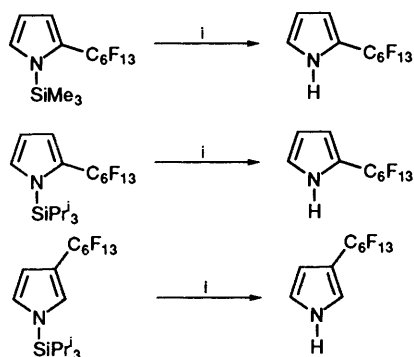


Reagent: i, H₃O⁺

The deprotection of 2-tridecafluorohexyl-1-(trimethylsilyl)pyrrole, 2-tridecafluorohexyl-1-(triisopropylsilyl)pyrrole, and 3-tridecafluorohexyl-1-(triisopropylsilyl)pyrrole was also investigated. When 2-tridecafluorohexyl-1-(trimethylsilyl)pyrrole was treated with tetrabutylammonium fluoride (TBAF) in

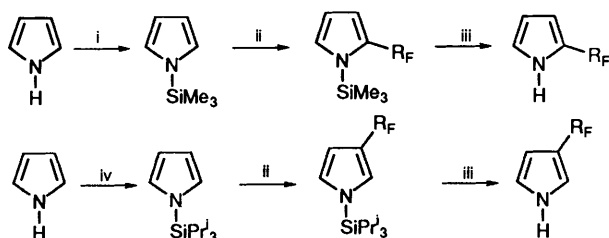
* Trifluoromethanesulfonyl chloride is known to act as a mild chlorination reagent of active methylene compounds such as dialkyl malonate (ref. 8). However, this is the first example of the chlorination of a pyrrole ring by this reagent.

diethyl ether, 2-(tridecafluorohexyl)pyrrole was isolated in 93% yield. Similarly, 2-tridecafluorohexyl-1-(triisopropylsilyl)pyrrole and 3-tridecafluorohexyl-1-(triisopropylsilyl)pyrrole were treated with TBAF in diethyl ether, and 2-(tridecafluorohexyl)pyrrole and 3-(tridecafluorohexyl)pyrrole were isolated in 92 and 95% yield, respectively.



Reagents: i. TBAF, Et₂O

Thus, protection of the hydrogen on the nitrogen atom of pyrrole by a silyl group, the reaction of tridecafluorohexanesulfonyl chloride with 1-trimethylsilyl- or 1-triisopropylsilylpyrrole catalysed by the ruthenium(II) complex, and deprotection of the silyl group is a very useful method for the regioselective introduction of a perfluoroalkyl group at the 2- or 3-position of pyrrole, respectively.



Reagents: i. BuLi, Me₃SiCl; ii. R_FSO₂Cl, RuCl₂(PPh₃)₃; iii. TBAF; iv. BuLi, Pr₃SiCl

In conclusion, the present reaction of perfluoroalkanesulfonyl chlorides with aromatic compounds or heteroaromatic compounds catalysed by a ruthenium(II) complex was found to be an excellent method for perfluoroalkylation. The method has the following characteristic features: (a) the yield is good to high, (b) the reaction can be achieved without use of special apparatus such as electrochemical equipment, (c) trifluoromethanesulfonyl chloride is a liquid (b.p. 32 °C) and can be easily handled at room temperature, whereas trifluoromethyl iodide, a well known trifluoromethylating reagent, is a gas (b.p. -23 °C) and troublesome to use in laboratories, (d) the ruthenium(II) catalyst is required in only catalytic amounts, in contrast to the situation in previously reported stoichiometric metal-activated reactions.

Experimental

M.p.s were determined on a Yamato MP21 apparatus and are uncorrected. IR spectra were determined on a Hitachi 260-10 spectrometer with samples as either neat liquids or KBr disks. ¹H NMR spectra were determined on JEOL JNM-PMX 60SI (60 MHz) and JEOL JNM-EX 400 FT NMR (400 MHz) spectrometers. ¹³C NMR spectra were measured on a JEOL JNM-FX 90Q FT NMR (22.5 MHz) and a JEOL JNM-EX 400 FT NMR (100 MHz) spectrometer. ¹H and ¹³C NMR signals were referenced to Me₄Si as internal standard, and *J*-values are given in Hz. Mass spectra were measured on a JEOL

JMS-DX300 and a JEOL JMS-AX 500 spectrometer by electron impact (EI) at 70 eV. Gas-liquid chromatography (GLC) was performed using an Hitachi 263-30 gas chromatograph with an SE-30 (10%) 1 m stainless steel column and an Hitachi G-3000 gas chromatograph with an OV-1 (10%) 25 m capillary column. Gel-permeation chromatography (GPC) was performed using a JAI LC-08 and a JAI LC-908 liquid chromatograph with two JAIGEL-1H columns (20 mm × 600 mm) with chloroform as eluent.

All solvents were distilled and stored under nitrogen. Dichlorotris(triphenylphosphine)ruthenium(II) was prepared by the method described in the literature.¹¹ Trifluoromethanesulfonyl chloride **1a** and tridecafluorohexanesulfonyl chloride **1b** (Fluorochem) were used without further purification. Substituted benzenes, furan, thiophene, 2-methylthiophene, 2-(trimethylsilyl)thiophene, 2-bromothiophene, 2-chlorothiophene, thiophene-2-carbaldehyde, 3-methylthiophene, 3-bromothiophene, 2,5-dimethylthiophene, 2,5-dichlorothiophene, pyrrole, 1-methyl pyrrole, and 2,5-dimethylpyrrole of Tokyo Kasei Chemicals were purified by distillation prior to use and were stored under nitrogen. 2,5-Bis(trimethylsilyl)thiophene,¹² 2-methylpyrrole,¹³ 1-benzylpyrrole,¹⁴ 1-(*tert*-butyl)pyrrole,¹⁵ 1-(phenylsulfonyl)pyrrole,¹⁶ 1-acetylpyrrole,¹⁷ 1-benzoylpyrrole,¹⁷ methyl pyrrole-1-carboxylate,¹⁸ 1-(trimethylsilyl)pyrrole,¹⁹ and 1-(triisopropylsilyl)pyrrole²⁰ were prepared by the methods recorded in the literature. The physical and spectral data of 1-(trimethylsilyl)pyrrole and 1-(triisopropylsilyl)pyrrole are as follows: 1-(Trimethylsilyl)pyrrole: oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2950, 1460, 1250, 1210, 1180, 1080 and 1040; $\delta_{\text{H}}(\text{CDCl}_3)$; 400 MHz) 0.41 (9 H, s), 6.28–6.34 (2 H, m) and 6.77–6.83 (2 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$; 100 MHz) 0.3, 111.1 and 123.2; *m/z* 139 (M⁺) and 124. 1-(Triisopropylsilyl)pyrrole: oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2940, 2860, 1560, 1460, 1390, 1370, 1260, 1220, 1190, 1080, 1050 and 1020; $\delta_{\text{H}}(\text{CDCl}_3)$; 400 MHz) 1.10 (18 H, d, *J* 7.3), 1.45 (3 H, septet, *J* 7.3), 6.29–6.33 (2 H, m) and 6.77–6.82 (2 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$; 100 MHz) 11.7, 17.8, 110.1 and 124.0; *m/z* 223 (M⁺), 1380 and 152.

General Procedure for the Reaction of Perfluoroalkanesulfonyl Chlorides **1 with Aromatic Compounds.**—A solution containing a perfluoroalkanesulfonyl chloride **1** (2.0 mmol), an aromatic compound (4–10 mmol), and dichlorotris(triphenylphosphine)ruthenium(II) (0.02 mmol) in dry pentane (4 cm³) was degassed by a freeze–pump–thaw cycle, sealed in an ampoule, and heated at 120 °C for 24 h. The reaction mixture was subjected to short-column chromatography on Florisil with benzene as eluent to remove the metal complex. The products were isolated from the reaction mixture by the use of GPC and/or column chromatography over silica gel (Wakogel C-60), and were identified by IR, NMR and MS spectroscopy. The yields of the products were determined based on the initial sulfonyl chlorides by GLC with undecane as internal standard. The physical and spectral data for new compounds are as follows.

(Tridecafluorohexyl)benzene. Pale yellow oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 1420, 1360, 1280, 1230, 1190 and 1140; $\delta_{\text{H}}(\text{CDCl}_3)$; 60 MHz) 7.47 (5 H, s); $\delta_{\text{C}}(\text{CDCl}_3)$; 22.5 MHz) 127.0 (t, *J* 6.7), 128.8 and 132.1; *m/z* 396 (M⁺), 377, 158, 127 and 77 (Found: M⁺, 396.0179. C₁₂H₅F₁₃ requires M, 396.0183).

o-(Tridecafluorohexyl)toluene. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 1295, 1230, 1190 and 1140; $\delta_{\text{H}}(\text{CDCl}_3)$; 60 MHz) 2.48 (3 H, t, *J* 3.0) and 7.03–7.70 (4 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$; 22.5 MHz) 20.4, 126.0, 128.5 (t, *J* 8.5), 131.8 and 132.6; *m/z* 410 (M⁺), 141, and 91 (Found: M⁺, 410.0272. C₁₃H₇F₁₃ requires M, 410.0340).

m-(Tridecafluorohexyl)toluene. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 1360, 1290, 1240, 1200 and 1150; $\delta_{\text{H}}(\text{CDCl}_3)$; 60 MHz) 2.30 (3 H, s) and 7.10–7.60 (4 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$; 22.5 MHz) 21.4, 124.1 (t, *J* 7.4), 127.4 (t, *J* 6.1), 128.6, 132.7 and 138.7; *m/z* 410 (M⁺), 141 and 91 (Found: M⁺, 410.0323).

$\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2950, 1510, 1410, 1360, 1250, 1200 and 1140; $\delta_{\text{H}}(\text{CDCl}_3; 60 \text{ MHz})$ 0.33 (18 H, s) and 7.23–7.39 (1 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 22.5 \text{ MHz})$ -0.42, 0.33, 135.2, 135.6 (t, J 25.7, C-C₆F₁₃), 147.2 and 150.2; m/z 546 (M⁺) and 531 (Found: M⁺, 546.0543. C₁₆H₁₉F₁₃SSi₂ requires M, 546.0538).

2,5-Dichloro-3-(tridecafluorohexyl)thiophene. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 1550, 1450, 1370, 1250, 1200, 1150, 1070 and 1040; $\delta_{\text{H}}(\text{CDCl}_3; 60 \text{ MHz})$ 6.79 (1 H, s); $\delta_{\text{C}}(\text{CDCl}_3; 22.5 \text{ MHz})$ 125.4 (t, J 5.5), 125.7 (t, J 5.5) and 128.4; m/z 470 (M⁺: ³⁵Cl), 451 and 435 (Found: M⁺, 469.8952. C₁₀H³⁵Cl₂F₁₃S requires M, 469.8968).

1-Methyl-2-(tridecafluorohexyl)pyrrole. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2960, 1540, 1485, 1430, 1360, 1320, 1230, 1190 and 1145; $\delta_{\text{H}}(\text{CDCl}_3; 60 \text{ MHz})$ 3.69 (3 H, s) and 6.04–6.24 (3 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 22.5 \text{ MHz})$ 35.7, 108.1, 114.7 (t, J 5.5) and 128.2; m/z 399 (M⁺), 380, 360 and 330 (Found: M⁺, 399.0280. C₁₁H₆F₁₃N requires M, 399.0292).

1-Benzyl-2-(tridecafluorohexyl)pyrrole. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3030, 1540, 1500, 1480, 1430, 1360, 1330, 1250, 1210, 1150 and 1080; $\delta_{\text{H}}(\text{CDCl}_3; 400 \text{ MHz})$ 5.16 (2 H, s), 6.18–6.24 (1 H, m), 6.59–6.66 (1 H, m), 6.69–6.76 (1 H, m), 7.02–7.13 (2 H, m) and 7.23–7.38 (3 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 100 \text{ MHz})$ 52.2, 108.8, 114.7, 127.0, 127.5, 128.0, 128.9 and 137.4; m/z 475 (M⁺), 456 and 437 (Found: M⁺, 475.0560. C₁₇H₁₀F₁₃N requires M, 475.0605).

1-(tert-Butyl)-3-(tridecafluorohexyl)pyrrole. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2980, 1560, 1500, 1460, 1370, 1230 and 1140; $\delta_{\text{H}}(\text{CDCl}_3; 60 \text{ MHz})$ 1.51 (9 H, s), 6.13–6.32 (1 H, m), 6.64–6.84 (1 H, m) and 6.89–7.07 (1 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 22.5 \text{ MHz})$ 30.6, 55.8, 107.0, 118.5 (t, J 7.3) and 119.0; m/z 442 (M⁺) and 426 (Found: M⁺, 441.0758. C₁₄H₁₂F₁₃N requires M, 441.0758).

1-(tert-Butyl)-3-chloropyrrole. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2980, 1480, 1460, 1370, 1280, 1230, 1100, 930 and 750; $\delta_{\text{H}}(\text{CDCl}_3; 60 \text{ MHz})$ 1.46 (9 H, s), 5.89–6.00 (1 H, m) and 6.51–6.76 (2 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 22.5 \text{ MHz})$ 30.5, 55.4, 107.7, 110.9, 115.0 and 117.3; m/z 159 (M⁺: ³⁵Cl), 157 and 122 (Found: M⁺, 157.0745. C₈H₁₂³⁵ClN requires M, 157.0658).

1-Phenylsulfonyl-2-(tridecafluorohexyl)pyrrole. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3160, 3080, 1580, 1560, 1460, 1450, 1380, 1210, 1190, 1090 and 1060; $\delta_{\text{H}}(\text{CDCl}_3; 400 \text{ MHz})$ 6.37–6.41 (1 H, m), 6.77–6.80 (1 H, m), 7.47–7.53 (2 H, m), 7.58–7.64 (1 H, m), 7.66–7.70 (1 H, m) and 7.79–7.84 (2 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 100 \text{ MHz})$ 111.4, 121.9, 127.4, 129.5, 129.7, 134.5 and 138.8; m/z 525 (M⁺), 506 and 384 (Found: M⁺, 524.9985. C₁₆H₈F₁₃NO₂S requires M, 525.0068).

1-Phenylsulfonyl-3-(tridecafluorohexyl)pyrrole. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3150, 3080, 1590, 1480, 1450, 1380, 1240, 1180, 1140 and 1070; $\delta_{\text{H}}(\text{CDCl}_3; 400 \text{ MHz})$ 6.53–6.57 (1 H, m), 7.20–7.24 (1 H, m), 7.48–7.51 (1 H, m), 7.53–7.59 (2 H, m), 7.64–7.69 (1 H, m) and 7.88–7.93 (2 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 100 \text{ MHz})$ 111.5, 121.4 (t, J 7.4), 121.8, 127.2, 129.8, 134.7 and 138.1; m/z 525 (M⁺), 506 and 456 (Found: M⁺, 525.0128).

1-Acetyl-2-(tridecafluorohexyl)pyrrole. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3150, 1750, 1560, 1470, 1420, 1370, 1340, 1270, 1220, 1140 and 1100; $\delta_{\text{H}}(\text{CDCl}_3; 400 \text{ MHz})$ 2.60 (3 H, s), 6.32–6.37 (1 H, m), 6.82–6.86 (1 H, m) and 7.31–7.36 (1 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 100 \text{ MHz})$ 23.9, 111.5, 120.8, 126.5 and 166.4; m/z 427 (M⁺), 408, 386 and 366 (Found: M⁺, 427.0272. C₁₂H₆F₁₃NO requires M, 427.0241).

1-Acetyl-3-(tridecafluorohexyl)pyrrole. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3150, 1740, 1580, 1490, 1400, 1380, 1350, 1330, 1230, 1140 and 1070; $\delta_{\text{H}}(\text{CDCl}_3; 400 \text{ MHz})$ 2.59 (3 H, s), 6.48–6.55 (1 H, m), 7.26–7.35 (1 H, m) and 7.58–7.67 (1 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 100 \text{ MHz})$ 22.2, 111.0, 120.1, 120.5 and 167.2; m/z 427 (M⁺), 385 and 366 (Found: M⁺, 427.0239).

1-Benzoyl-2-(tridecafluorohexyl)pyrrole. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3150, 3070, 1730, 1600, 1560, 1470, 1450, 1410, 1350, 1280, 1210, 1140 and 1090; $\delta_{\text{H}}(\text{CDCl}_3; 400 \text{ MHz})$ 6.39–6.44 (1 H, m), 6.90–6.95 (1 H, m), 7.03–7.07 (1 H, m), 7.48–7.55 (2 H, m), 7.62–7.68

(1 H, m) and 7.75–7.80 (2 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 100 \text{ MHz})$ 110.3, 120.2, 128.7, 128.9, 130.5, 132.7, 133.8 and 167.1; m/z 489 (M⁺) and 470 (Found: M⁺, 489.0453. C₁₇H₈F₁₃NO requires M, 489.0398).

1-Benzoyl-3-(tridecafluorohexyl)pyrrole. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3150, 1710, 1600, 1580, 1490, 1440, 1350, 1320, 1270, 1230, 1200, 1140, 1120 and 1090; $\delta_{\text{H}}(\text{CDCl}_3; 400 \text{ MHz})$ 6.49–6.53 (1 H, m), 7.34–7.38 (1 H, m), 7.53–7.59 (2 H, m), 7.59–7.62 (1 H, m), 7.65–7.70 (1 H, m) and 7.74–7.81 (2 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 100 \text{ MHz})$ 110.8, 122.1, 122.5, 128.9, 129.8, 131.8, 133.3 and 167.2; m/z 489 (M⁺) and 470 (Found: M⁺, 489.0372).

Methyl 2-(tridecafluorohexyl)pyrrole-1-carboxylate. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3150, 2950, 1780, 1560, 1460, 1440, 1410, 1360, 1290, 1210, 1140, 1090 and 1070; $\delta_{\text{H}}(\text{CDCl}_3; 400 \text{ MHz})$ 3.98 (3 H, s), 6.25–6.32 (1 H, m), 6.78–6.85 (1 H, m) and 7.52–7.58 (1 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 100 \text{ MHz})$ 54.8, 110.8, 120.8 (t, J 7.4), 127.6 and 149.6; m/z 443 (M⁺), 425 and 413 (Found: M⁺, 443.0192. C₁₂H₆F₁₃NO₂ requires M, 443.0191).

Methyl 3-(tridecafluorohexyl)pyrrole-1-carboxylate. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3150, 1740, 1580, 1490, 1400, 1380, 1350, 1330, 1230, 1140 and 1070; $\delta_{\text{H}}(\text{CDCl}_3; 400 \text{ MHz})$ 4.03 (3 H, s), 6.40–6.43 (1 H, m), 7.32–7.35 (1 H, m) and 7.59–7.62 (1 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 100 \text{ MHz})$ 54.8, 110.4, 121.1 (t, J 7.4), 121.3 and 150.0; m/z 443 (M⁺), 424 and 412 [Found: M⁺ + 1, 444.0274. C₁₂H₆F₁₃NO₂ (M⁺ + 1) requires M⁺ 444.0269].

1-Benzoyl-2,5-dimethyl-3-(tridecafluorohexyl)pyrrole. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2930, 1710, 1600, 1550, 1450, 1410, 1340, 1240, 1200, 1150, 1100 and 1070; $\delta_{\text{H}}(\text{CDCl}_3; 400 \text{ MHz})$; 2.05 (3 H, s), 2.16 (3 H, s), 6.02–6.10 (1 H, s), 7.43–7.57 (2 H, m) and 7.61–7.77 (3 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 100 \text{ MHz})$ 12.4, 13.7, 108.4, 129.2, 129.7, 130.5, 131.1, 134.2, 134.6 and 170.8; m/z 517 (M⁺), 498, 412 and 394 (Found: M⁺, 517.0680. C₁₉H₁₂F₁₃NO requires M, 517.0711).

2-Tridecafluorohexyl-1-(trimethylsilyl)pyrrole. Light purple oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2970, 1550, 1450, 1340, 1240, 1210 and 1150; $\delta_{\text{H}}(\text{CDCl}_3; 60 \text{ MHz})$ 0.45 (9 H, s), 6.13–6.37 (1 H, m), 6.59–6.80 (1 H, m) and 6.86–7.01 (1 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 22.5 \text{ MHz})$ 1.1, 110.9, 117.7 (t, J 3.7) and 129.6; m/z 457 (M⁺), 442 and 388 (Found: M⁺, 457.0540. C₁₃H₁₂F₁₃NSi requires M, 457.0531).

3-Tridecafluorohexyl-1-(trimethylsilyl)pyrrole. Pale yellow oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2960, 1570, 1550, 1350, 1240, 1210 and 1140; $\delta_{\text{H}}(\text{CDCl}_3; 60 \text{ MHz})$ 0.45 (9 H, s), 6.33–6.53 (1 H, m), 6.67–6.85 (1 H, m) and 6.93–7.11 (1 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 22.5 \text{ MHz})$ -0.44, 109.8, 124.0 (t, J 7.3) and 124.2; m/z 457 (M⁺), 442 and 388 (Found: M⁺, 457.0488).

2-Tridecafluorohexyl-1-(triisopropylsilyl)pyrrole. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2950, 2870, 1540, 1460, 1440, 1360, 1330, 1270, 1240, 1210, 1150, 1120, 1070, 1050 and 1020; $\delta_{\text{H}}(\text{CDCl}_3; 400 \text{ MHz})$ 1.13 (18 H, d, J 7.3), 1.56 (3 H, septet, J 7.3), 6.27–6.36 (1 H, m), 6.74–6.83 (1 H, m) and 7.01–7.11 (1 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 100 \text{ MHz})$ 13.8, 18.3, 110.7, 117.6 and 130.8; m/z 541 (M⁺), 522 and 498 (Found: M⁺, 541.1471. C₁₉H₂₄F₁₃NSi requires M, 541.1470).

3-Tridecafluorohexyl-1-(triisopropylsilyl)pyrrole. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 2940, 2860, 1570, 1550, 1480, 1460, 1360, 1340, 1230, 1200, 1140 and 1090; $\delta_{\text{H}}(\text{CDCl}_3; 400 \text{ MHz})$ 1.10 (18 H, d, J 7.3), 1.46 (3 H, septet, J 7.3), 6.41–6.49 (1 H, m), 6.74–6.81 (1 H, m) and 6.99–7.05 (1 H, m); $\delta_{\text{C}}(\text{CDCl}_3; 100 \text{ MHz})$ 11.7, 17.6, 109.4, 125.1 (t, J 7.4) and 125.4; m/z 541 (M⁺), 522 and 498 (Found: M⁺, 541.1513).

Attempted Deprotection of 1-Acetyl- or 1-Phenyl-sulfonyl-2-(tridecafluorohexyl)pyrrole using Methanolic Sodium Hydroxide.—A solution of 1-acetyl-2-(tridecafluorohexyl)pyrrole (400 mg, 0.93 mmol) and sodium hydroxide (196 mg, 4.65 mmol) in methanol (8 cm³) was stirred at room temperature for 24 h. Methanol was removed under reduced pressure, and the residue

was purified by Florisil column chromatography using diethyl ether as eluent, followed by GPC to give pure 2-(undecafluoro-1,1-dimethoxyhexyl)pyrrole (286 mg, 75%). The same product was obtained in 84% yield from 1-phenylsulfonyl-2-(tridecafluorohexyl)pyrrole by a similar procedure.

2-(Undecafluoro-1,1-dimethoxyhexyl)pyrrole. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3500, 2950, 1405, 1355, 1235, 1200, 1140, 1105, 1060 and 1010; $\delta_{\text{H}}(\text{CDCl}_3; 400 \text{ MHz})$ 3.36 (6 H, s), 6.20–6.24 (1 H, m), 6.32–6.36 (1 H, m), 6.78–6.82 (1 H, m) and 8.57 (1 H, br s); $\delta_{\text{C}}(\text{CDCl}_3; 100 \text{ MHz})$ 50.8, 97.7 [t, *J* 22.1, $\text{C}(\text{OME})_2\text{C}_5\text{F}_{11}$], 109.2, 110.1, 118.6 and 123.4; *m/z* 409 (M^+), 390 and 378 (Found: M^+ , 409.0589. $\text{C}_{12}\text{H}_{10}\text{F}_{11}\text{NO}_2$ requires *M*, 409.0536).

Hydrolysis of 2-(Undecafluoro-1,1-dimethoxyhexyl)pyrrole.—A mixture of 2-(undecafluoro-1,1-dimethoxyhexyl)pyrrole (100 mg, 0.24 mmol), water (0.5 cm^3), conc. sulfuric acid (2 drops), and tetrahydrofuran (THF) (3 cm^3) was heated at reflux for 24 h. The reaction mixture was washed with water and extracted with diethyl ether, and the ethereal solution was dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, the residual oil was subjected to GPC. Pyrrol-2-yl undecafluoropentyl ketone (63 mg, 77%) was isolated.

Pyrrol-2-yl undecafluoropentyl ketone. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3320, 1650, 1630, 1540, 1420, 1390, 1350, 1300, 1230, 1190, 1140, 1110, 1100, 1080 and 1060; $\delta_{\text{H}}(\text{CDCl}_3; 400 \text{ MHz})$ 6.38–6.46 (1 H, m), 7.20–7.32 (2 H, m) and 10.09 (1 H, br s); $\delta_{\text{C}}(\text{CDCl}_3; 100 \text{ MHz})$ 113.1, 126.6 (t, *J* 5.5), 127.6, 130.0 and 172.1 [t, *J* 26.7, $\text{C}(\text{O})\text{C}_5\text{F}_{11}$]; *m/z* 363 (M^+), 344 and 316 (Found: M^+ , 363.0111. $\text{C}_{10}\text{H}_4\text{F}_{11}\text{NO}$ requires *M*, 363.0117).

Typical Example of the Desilylation of 1-Trialkylsilyl-2-(tridecafluorohexyl)pyrroles by Tetrabutylammonium Fluoride.—To a solution of 2-tridecafluorohexyl-1-(trimethylsilyl)pyrrole (100 mg, 0.22 mmol) in diethyl ether (2 cm^3) was added a 1 mol dm^{-3} solution of TBAF in THF (0.44 cm^3 , 0.44 mmol) and the mixture was stirred at room temperature for 14 h. Water (1 cm^3) was added to the reaction mixture, and the organic layer was extracted with diethyl ether four times. The combined ethereal solution was dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. Purification of the residue by GPC afforded pure 2-(tridecafluorohexyl)pyrrole (78 mg, 93%).

2-(Tridecafluorohexyl)pyrrole. Pale yellow oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3500, 3420, 1570, 1460, 1420, 1360, 1310, 1240, 1200, 1150, 1120, 1080 and 1040; $\delta_{\text{H}}(\text{CDCl}_3; 400 \text{ MHz})$ 6.14–6.43 (1 H, m), 6.43–6.73 (1 H, m), 6.82–7.03 (1 H, m) and 8.58 (1 H, br s); $\delta_{\text{C}}(\text{CDCl}_3; 100 \text{ MHz})$ 110.0, 112.3 (t, *J* 4.9) and 121.6; *m/z* 385 (M^+), 366 and 346 (Found: M^+ , 385.0169. $\text{C}_{10}\text{H}_4\text{F}_{13}\text{N}$ requires *M*, 385.0136).

3-(Tridecafluorohexyl)pyrrole. Oil; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3500, 3430, 1570, 1500, 1430, 1360, 1350, 1240, 1200, 1150, 1080 and 1060; $\delta_{\text{H}}(\text{CDCl}_3; 400 \text{ MHz})$ 6.36–6.44 (1 H, m), 6.78–6.87 (1 H, m), 7.03–7.11 (1 H, m) and 8.51 (1 H, br s); $\delta_{\text{C}}(\text{CDCl}_3; 100 \text{ MHz})$ 107.6, 119.0 (t, *J* 7.4) and 119.1; *m/z* 385 (M^+) and 366 (Found: M^+ , 385.0104).

References

- R. Filler and Y. Kobayashi, *Biomedical Aspects of Fluorine Chemistry*, Elsevier Biomedical Press and Kodansha Ltd., 1982; J. T. Welch, *Tetrahedron*, 1987, **43**, 3123; M. Hudlicky, *Chemistry of Organic Fluorine Compounds*, Ellis Horwood, New York, 1976; R. E. Bancs, *Organo Fluorine Compounds and Their Applications*, Ellis Horwood, Chichester, 1979; T. Fuchikami, *Yuki Gosei Kagaku Kyokai-shi*, 1984, **42**, 775 (*Chem. Abstr.*, 1984, **101**, 190623e); H. Yoshioka, C. Takayama and N. Matsuo, *Yuki Gosei Kagaku Kyokai-shi*, 1984, **42**, 809 (*Chem. Abstr.*, 1984, **101**, 2059117); K. Uneyama, *Yuki Gosei Kagaku Kyokai-shi*, 1991, **49**, 612 (*Chem. Abstr.*, 1991, **115**, 1137258).
- T. Fuchikami and I. Ojima, *Tetrahedron Lett.*, 1984, **25**, 303; D. M. Wiemers and D. J. Burton, *J. Am. Chem. Soc.*, 1986, **108**, 832; Y. Tanabe, N. Matsuo and N. Ohno, *J. Org. Chem.*, 1988, **53**, 4582; W.-Y. Huang, W.-W. Ying, H.-Z. Zhang and J.-T. Liu, *Chin. J. Chem.*, 1993, **11**, 272.
- T. Umemoto, Y. Kuriu and H. Shuyama, *Chem. Lett.*, 1981, 1663; T. Umemoto and O. Miyano, *Tetrahedron Lett.*, 1982, **23**, 2939; T. Umemoto and A. Ando, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 447; M. Yoshida, H. Amemiya, M. Kobayashi, H. Sawada, H. Hagii and A. Aoyama, *J. Chem. Soc., Chem. Commun.*, 1985, 234; M. Yoshida, T. Yoshida, M. Kobayashi and N. Kamigata, *J. Chem. Soc., Perkin Trans. 1*, 1989, 909; H. Sawada, M. Nakayama, M. Yoshida, T. Yoshida and N. Kamigata, *J. Fluorine Chem.*, 1990, **46**, 423.
- N. Kamigata, T. Fukushima and M. Yoshida, *J. Chem. Soc., Chem. Commun.*, 1989, 1559; N. Kamigata, T. Fukushima, T. Terakawa, M. Yoshida and H. Sawada, *J. Chem. Soc., Perkin Trans. 1*, 1991, 627.
- N. Kamigata, T. Fukushima and M. Yoshida, *Chem. Lett.*, 1990, 649.
- M. Kameyama, N. Kamigata and M. Kobayashi, *J. Org. Chem.*, 1987, **52**, 3312, and references cited therein.
- M. Yoshida, T. Yoshida, N. Kamigata and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 3459.
- G. H. Hakimelahi and G. Just, *Tetrahedron Lett.*, 1979, 3643.
- C. F. Candy, R. A. Jones and P. H. Wright, *J. Chem. Soc. C*, 1970, 2653; S. Clementi, P. Linda and G. Marino, *J. Chem. Soc. B*, 1970, 1153.
- Y. Kobayashi, I. Kumadaki, Y. Hirose and Y. Hanzawa, *J. Org. Chem.*, 1974, **39**, 1836.
- T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 945; P. S. Hallman, T. A. Stephenson and G. Wilkinson, *Inorg. Synth.*, 1972, **12**, 238; T. A. Stephenson and G. Wilkinson, *J. Chem. Soc. A*, 1970, 2497.
- D. J. Chadwick and C. Willbe, *J. Chem. Soc., Perkin Trans. 1*, 1977, 887.
- R. L. Hinman and S. Theodoropoulos, *J. Org. Chem.*, 1963, **28**, 3052.
- H. Heaney and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, 1973, 499.
- N. Elming and N. Clauson-Kaas, *Acta Chem. Scand.*, 1952, **6**, 867.
- E. P. Papadopoulos and N. F. Haider, *Tetrahedron Lett.*, 1968, 1721.
- P. Linda and G. Marino, *Ric. Sci.*, 1967, 424 (*Chem. Abstr.*, 1968, **68**, 39570q).
- M. A. Acheson and J. M. Vernon, *J. Chem. Soc.*, 1961, 457.
- R. Fessenden and D. F. Crowe, *J. Org. Chem.*, 1960, **25**, 598.
- B. L. Bray, P. H. Mathies, R. Naef, D. R. Solas, T. T. Tidwell, D. R. Artis and J. M. Muchowski, *J. Org. Chem.*, 1990, **55**, 6317.

Paper 3/06773D

Received 11th November 1993

Accepted 20th January 1994