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Nucleophilic Displacement of Bis(perfluoroalkanoyl) Peroxides with Perfluoroalkanoate

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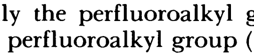
Synopsis. Bis(perfluoroalkanoyl) peroxide ($(R_FCO_2)_2$) suffered a nucleophilic displacement with perfluoroalkanoate ($R_F'CO_2^-$) to give new mixed peroxide ($R_F(CO)OO(CO)R_F'$). When thiophene was reacted with bis(perfluoroalkanoyl) peroxide in the presence of pyridinium perfluoroalkanoate, not only the perfluoroalkyl group (R_F) of the peroxide, but also perfluoroalkyl group (R_F') of perfluoroalkanoate, was introduced into thiophene.

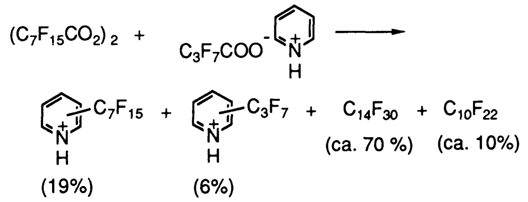
The O–O bonds of diacyl peroxides are usually weak and homolytic cleavages take place easily. On the other hand, diacyl peroxides, especially which have strong electron-withdrawing groups, also react as electrophiles in the presence of nucleophiles such as amines, sulfides, or electron-rich benzenes.[1] We have been studying the reactions of bis(perfluoroalkanoyl) peroxides (**1**) and found three types of reactions: (1) a homolytic cleavage of the O–O bond, (2) electron transfer from substrate to the peroxide, and (3) a nucleophilic reaction on the O–O bond of the peroxide.[2] Due to the strong electron-withdrawing fluoroalkyl groups peroxide **1** easily suffered electron transfers or nucleophilic attacks. In the course of the study we found that perfluoroalkanoate ($R_F'COO^-$) attacked bis(perfluoroalkanoyl) peroxide ($(R_FCOO)_2$) to give new mixed peroxide (R_F $(CO)OO(CO)R_F'$); the results will be described herein.



$$C_nF_{2n+1}\underset{O}{C}OO\underset{O}{C}C_nF_{2n+1}$$

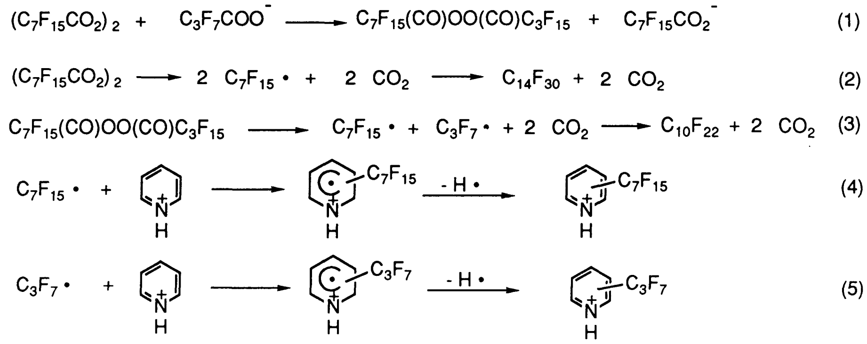
n = 1 (**1a**), n = 3 (**1b**), n = 7 (**1c**)

In the reaction of pyridinium perfluorobutyrate with **1c**, not only perfluoroheptylpyridines but also perfluoropropylpyridines were formed. Both perfluorodecane ($C_{10}F_{22}$) and perfluorotetradecane ($C_{14}F_{30}$) were also detected as coupling products of perfluoroalkyl radicals by GC-MS.



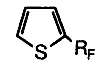
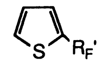
In order to explain these results, we propose the exchange of the perfluoroheptanoyloxy group in **1c** with perfluorobutyrate to give mixed diacyl peroxide and perfluoroheptanoate, as shown in Scheme 1 (Eq. 1). Peroxide **1c** decomposes homolytically to give perfluorotetradecane via a perfluoroheptyl radical (Eq. 2 in Scheme 1). The mixed peroxide also decomposes to perfluoroheptyl and perfluoropropyl radicals and perfluorododecane is produced as a coupling product (Eq. 3 in Scheme 1). The cage escaped perfluoroheptyl or perfluoropropyl radical attacks the pyridinium salt to give perfluoroheptyl- or perfluorpropylpyridine (Eqs. 4 and 5 in Scheme 1).[3] This is the first example of a nucleophilic displacement of the carboxy group in diacyl peroxide with another carboxylate to give new mixed peroxide (as far as we know,[4]), whereas a nucleophilic displacement with carbanions[5,6] or halide anions[7] has in general been well-investigated.

We have reported that peroxide **1** reacts with an electron-rich substrate to give a perfluoroalkylated compound via electron transfer from the substrate to **1**.[2,3] Thus, if a nucleophilic displacement of peroxide **1** with perfluoroalkanoate while affording mixed peroxide occurs, the perfluoroalkyl group of the pyridinium perfluoralkanoate should be introduced into the substrate when **1** reacts with an electron-rich substrate in the presence of pyridinium perfluoroalkanoate. Since we have thoroughly studied the perfluoroalkylation of thiophene,[3,8] we chose thiophene

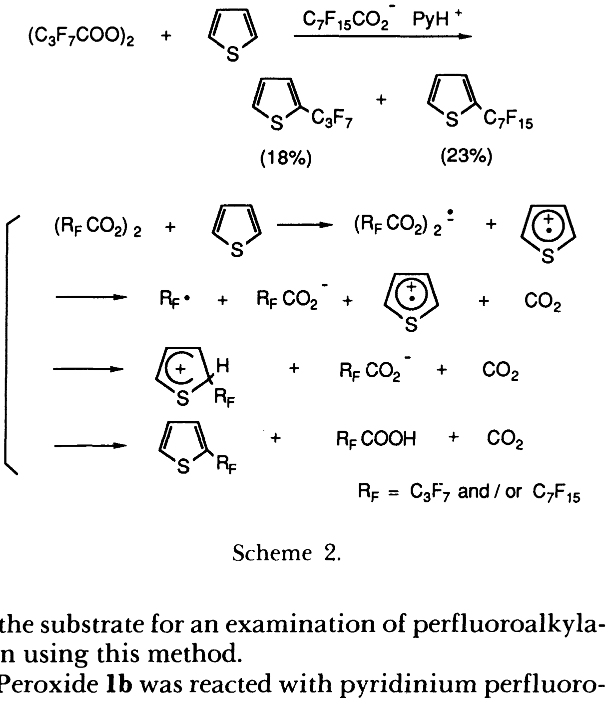


Scheme 1.

Table 1. Perfluoroalkylation of Thiophene with **1** in the Presence of Pyridinium Perfluoroalkanoate[a)]

Run	R_F of **1**	R_F' of pyridinium salt/mmol		Yields of products/%		
						Total yield
1	C_3F_7	C_7F_{15}	1.0	18	23	41
2	C_7F_{15}	C_3F_7	1.0	20	17	37
3	C_3F_7	C_7F_{15}	0.5	32	22	54
4	C_3F_7	C_7F_{15}	1.5	11	23	34
5[b)]	C_3F_7	None		98	—	98
6	C_7F_{15}	None		97	—	97
7	CF_3	C_7F_{15}	1.0	19	48	67
8	C_3F_7	C_9F_{19}	1.0	32	20	52

a) 0.5 mmol of peroxide was used. The yield was determined by GC based on peroxide. b) From Ref. 3.



Scheme 2.

as the substrate for an examination of perfluoroalkylation using this method.

Peroxide **1b** was reacted with pyridinium perfluorooctanoate at 0°C for 1 h and then thiophene was added. The resulting solution was further kept at 40 °C for an additional 3 h under vacuum conditions. As expected, 2-(perfluoroheptyl)thiophene was obtained in a yield of 23% in addition to 2-(perfluoropropyl)thiophene in 18% yield, as shown in Scheme 2. The ratio of perfluoropropylthiophene and perfluoroheptylthiophene remained unaltered, even when **1b** and pyridinium perfluorooctanoate was reacted for more than 1 h; then, thiophene was added. Similarly, reactions of **1** with thiophene in the presence of some pyridinium perfluoroalkanoate were performed under various conditions; the results are summarized in Table 1.

In the reaction of thiophene with **1c** in the presence of pyridinium perfluorobutyrate, the perfluoropropyl group was introduced into thiophene. The ratio of perfluoroheptylthiophene and perfluoropropylthiophene was almost the same as that obtained from a reaction system of **1b** and pyridinium perfluorooctanoate (Table 1, Runs **1** and **2**). This means that in the reaction systems of peroxide **1** and pyridinium perfluoroalkanoate, equilibrium as shown below must be attained:

$$(C_3F_7CO_2)_2 + C_7F_{15}CO_2^- \rightleftharpoons C_3F_7(CO)OO(CO)C_7F_{15} + C_3F_7CO_2^-$$

$$C_3F_7(CO)OO(CO)C_7F_{15} + C_7F_{15}CO_2^- \rightleftharpoons (C_7F_{15}CO_2)_2 + C_3F_7CO_2^-$$

Thus, perfluoroheptylthiophene is expected to be obtained selectively when a large excess of pyridinium perfluorooctanoate per **1b** is used. However, the total yield of perfluoroalkylated thiophenes decreased upon increasing the amounts of the pyridinium salt, whereas the ratio of perfluoroheptylthiophene per perfluoropropylthiophene increased (Table 1, Runs **1**, **3**, and **4**). Perfluoroalkylations of thiophene with **1b** or **1c** proceeded almost quantitatively (Table 1, Runs **5** and **6**); however, in the reaction of thiophene with **1** in the presence of pyridinium salt, the total yield of perfluoroalkylthiophenes was about 40%, as shown in Table 1, Runs **1** and **2**. The low yields of perfluoroalkylthiophenes in these reaction systems may not be attributed to the homolytic decomposition of **1** during the exchange reaction of **1** with perfluoroalkanoate, because the homolytic decomposition of **1b** or **1c** does not occur at 0 °C for 1 h. However, it was reported that a N-lone pair of amine attacked nucleophilically the O–O bond of **1b** to decompose the peroxide rapidly, even at 0 °C.[3)] Probably, peroxide **1** reacted with free pyridine which was liberated from the pyridinium salt during the exchange reaction; thus, the yield of perfluoroalkylated thiophene in the presence of pyridinium salt might have been decreased, especially when the amount of pyridinium salt was increased.

By choosing the peroxide, the ratio of perfluoroheptylthiophene per total yield of perfluoroalkylated thiophenes could be increased; the ratio of perfluoroheptylthiophene per total yield was larger in a reaction using **1a** as the peroxide than in one using **1b** (Table 1, Runs **1** and **7**). Peroxide **1a** might suffer a nucleophilic displacement with perfluoroalkanoate more easily than **1b**.

It is very interesting from the view of synthetic chemistry that the perfluoroalkyl group of pyridinium perfluoralkanoate is introduced into thiophene. We have been studying the synthesis of the diacyl peroxides which contain perfluoroalkyl groups. However, we have not succeeded in the synthesis of the diacyl peroxides which contain perfluoroalkyl chains longer than perfluoroheptyl. We therefore tried to prepare perfluorononylthiophene in a reaction of thiophene with pyridinium perfluorododecanoate in the presence of **1b** (Table 1, Run **8**). Although the yield of the perfluorononylthiophene was not sufficient, the perfluorononyl group could be introduced into thiophene without the synthesis of bis(perfluorododecanoyl) peroxide.

Perfluoroalkylation with peroxide **1** was shown to be a useful and effective method in our previous papers.[2,3,8] In this paper we show that the perfluoroalkyl group can be introduced into thiophene, even if the corresponding peroxide can not be synthesized.

Experimental

^{1}H NMR spectra were taken with a JEOL JNM PMX 60si (60MHz) spectrometer. ^{13}C NMR spectra were taken with a JEOL JNM Fx90Q FTNMR spectrometer. IR spectra were recorded on a Hitachi 260-10 spectrometer. Gas chromatography was performed by a Hitachi 163 or 263-30 gas chromatograph with a SE-30 (10%) 1 m stainless-steel column. Gel-permeation chromatography was performed by means of a JAI Model LC-08 liquid chromatograph equipped with JAIGEL-1H columns (20 ϕX600 mmX2) and using chloroform as an eluent. Mass spectra were obtained with JEOL JMS DX-300 spectrometer by an electron-impact (EI) ionization technique at 70 eV.

Materials. The syntheses of bis(perfluoroalkanoyl) peroxides were described in the literature.[3,9] These peroxides were used as solutions of Freon 113 without isolation. Pyridinium perfluoroalkanoates were prepared from pyridine with the corresponding perfluoroalkanoic acids. Pyridinium perfluorobutyrate (mp 56—58 °C (from ether)), pyridinium perfluorooctanoate (mp 69—70 °C (from ether)), and pyridinium perfluorododencanoate (mp 101—103 °C (from ether)).

Reaction of Pyridinium Perfluorobutyrate with Bis(perfluorooctanoyl) Peroxide. A solution containing 2 mmol of bis(perfluorooctanoyl) peroxide and 1 mmol of pyridinium perfluorobutyrate in 25 ml of Freon 113 in a degassed sealed tube was kept at 40 °C for 5 h. The solution was then washed with 20 ml of 5% NaOH and 20ml of water. The organic layer was analyzed by GC-MS.

Reaction of Thiophene with Pyridinium Perfluoroalkanoate in the Presence of Peroxide. The reaction was typically performed as follows. A solution containing 0.5 mmol of **1b** and 1.0 mmol of pyridinium perfluorooctanoate in 5 ml of Freon 113 was stirred for 1 h in an ice bath, and then 1.0 mmol of thiophene was added. The resulting mixture was degassed and kept at 40 °C for 3 h in a sealed tube. The reaction mixture was chromatographed over silica gel (Wakogel C-60) using ether as an eluent in order to remove the pyridinium salt and acid. The yields of the perfluoroalkylated thiophene were determined by GC using chlorobenzene as an internal standard. Perfluoropropylthiophene and perfluoroheptylthiophene were isolated using gel-permeation chromatography.

Reaction of Thiophene with 1c without Pyridinium Salt. A solution containing 2 mmol of **1c** and 4 mmol of thiophene in 25 ml Freon 113 was degassed and kept at 40 °C for 3 h in a sealed tube. The solution was washed with 20 ml of water and the organic layer was analyzed by GC-MS. The yield of perfluoroheptylthiophene was determined by GC using chlorobenzene as an internal standard.

2-Pentadecafluoroheptylthiophene; ^{1}H NMR($CDCl_3$) δ= 7.17 (1H), 7.4—7.6 (2H); ^{13}C NMR ($CDCl_3$) δ=127.5(C5), 130.3 (C4), 130.8 (C3); IR 1360 (CF_3), 1220 (CF_2) cm^{-1}; MS *m/z* 452 (M$^+$); Exact MS: *m/z* 451.9765, Calcd for $C_{11}H_3F_{15}S$: 451.9717.

2-(Nonadecafluorononyl)thiophene; ^{1}H NMR ($CDCl_3$) δ=7.00 (1H), 7.2—7.5 (2H); ^{13}C NMR ($CDCl_3$) δ=127.4 (C5), 130.2 (C4), 130.6 (C3); IR 1360 (CF_3), 1200 (CF_2) cm^{-1}; MS *m/z* 552 (M$^+$); Exact MS: *m/z* 551.9664, Calcd for $C_{13}H_3F_{19}S$: 551.9652.

The spectral data for 2-(heptafluoropropyl)thiophene was reported in the literature.[3]

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