Journal of Fluorine Chemistry, 51 (1991) 117–129

Received: June 29, 1990; accepted: October 19, 1990

SYNTHESIS OF AROMATIC COMPOUNDS CONTAINING PERFLUORO-OXA-ALKYL GROUPS

Hideo SAWADA* and Masaharu NAKAYAMA

Tsukuba Research Laboratory, Nippon Oil & Fats Co., Ltd., Tokodai,
Tsukuba-City, Ibaraki, 300-26 (Japan)

SUMMARY

Perfluoro-oxa-alkanoyl peroxides[[$C_3F_7O\{CF(CF_3)CF_2O\}_nCF(CF_3)CO_2]_2$, n= 0, 1, 2] smoothly reacted with thiophene and furan under mild conditions to afford 2-perfluoro-oxa-alkylthiophenes and furans in good yields. Perfluoro-oxa-alkylations of benzene and pyrrole were also found to proceed by the use of these peroxides. Furthermore, these peroxides were found to be applied to direct aromatic perfluoro-oxa-alkylations of polystyrene.

---

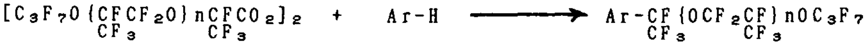
* Author to whom correspondence should be addressed.

0022-1139/91/$3.50

INTRODUCTION

Recently, there has been considerable interest in organofluorine compounds, due to their extraordinary biological, physical, and chemical properties[1]. In particular, perfluoroalkyl ether derivatives exhibit excellent thermal and oxidative stabilities compared with non-fluorinated ones [2]. However, little has been reported about the direct introduction of perfluoroalkyl groups bearing ether bonds (perfluoro-oxa-alkyl groups) into aromatic nuclei and the behavior of these perfluoro-oxa-alkylated compounds, though much effort has been devoted to the introduction of perfluoroalkyl groups themselves into such nuclei [3]. We have previously reported on the trifluoromethylation, perfluoropropylation and perfluoroheptylation of various aromatic compounds using trifluoroacetyl, perfluorobutyryl and perfluorooctanoyl peroxides [4]

In this paper, we wish to report on a novel synthesis of perfluoro-oxa-alkylthiophenes, furans, benzenes and pyrroles with perfluoro-oxa-alkanoyl peroxides; $[[C_3F_7O\{CF(CF_3)OCF_2\}nCF(CF_3)CO_2]_2$, n= 0(1a), 1(1b), 2(1c)] according to the following scheme.



$$[C_3F_7O\{\underset{CF_3}{CF}CF_2O\}n\underset{CF_3}{CF}CO_2]_2 \quad + \quad Ar\text{-}H \longrightarrow Ar\text{-}\underset{CF_3}{CF}\{OCF_2\underset{CF_3}{CF}\}nOC_3F_7$$

Ar-H = Aromatic Compounds

Scheme 1.

Furthermore, we tried to apply these peroxides for direct aromatic perfluoro-oxa-alkylations of polymers such as polystyrene.

RESULTS AND DISCUSSION

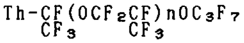
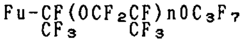
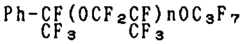
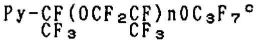
Perfluoro-oxa-alkanoyl peroxides 1a, 1b, 1c were prepared from the corresponding acyl fluorides and hydrogen peroxide in the presence of aqueous sodium hydroxide in 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113) according to our previous reported method [4]. The infrared spectra of 1 showed the characteristic diacyl peroxide carbonyl bands at 1825, 1860(1a), 1830, 1860(1b), and 1835, 1860 cm^{-1} (1c). The half-lives of 1 in Freon-113 at 20℃ were calculated to be 261(1a), 433(1b), and 261 minutes(1c) from the corresponding rate constants, so the decomposition of 1 was found to occur easily in comparison with those of perfluoroalkanoyl peroxides; for example, $(C_7F_{15}CO_2)_2$: 614 minutes [4].

Regioselectively 2-substituted thiophene carrying a perfluoro-1-methyl-2-oxapentyl group was obtained in 62% yield by the reaction of thiophene with 1a in Freon-113 at 40 ℃ for 5h. 2-(perfluoro-1',4'-dimethyl-2',5'-dioxaoctyl) and 2-(perfluoro-1',4',7'-trimethyl-2',5',8'-trioxaundecyl)-thiophenes were also obtained in 65% and 94% yields, respectively. Similarly, peroxides; 1a, 1b, 1c were treated with furan, benzene and pyrrole to give perfluoro-oxa-alkylfurans, benzenes , and pyrroles in moderate to high yields. The results are summarized in Table 1.

As shown in Table 1, the yields for perfluoro-oxa-alkylations of thiophene, furan, and pyrrole with the peroxides increased in the order of 1a < 1b <1c and 2-(perfluoro-1',4',7'-trimethyl-2',5',8'-trioxaundecyl)thiophene and furan was obtained in the highest yields.

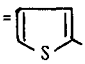
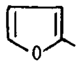
TABLE 1

The perfluoro-oxa-alkylations of aromatic compounds(Ar-H) with peroxides(1a, 1b, 1c)

Ar-H (mmol)	Peroxide (mmol)	Reaction temp/hr	Product % Yield[a]
ThH[b]			 $\text{Th-}\underset{CF_3}{CF}(OCF_2\underset{CF_3}{CF})nOC_3F_7$
(2,0mmol)	1a(2.5mmol)	40/5	(n = 0), 62
(2.0mmol)	1b(2.5mmol)	40/5	(n = 1), 65
(1.3mmol)	1c(1.0mmol)	40/5	(n = 2), 94
FuH[b]			 $\text{Fu-}\underset{CF_3}{CF}(OCF_2\underset{CF_3}{CF})nOC_3F_7$
(2.5mmol)	1a(2,0mmol)	40/5	(n = 0), 62
(2.5mmol)	1b(2.0mmol)	40/5	(n = 1), 71
(1.3mmol)	1c(1.0mmol)	40/5	(n = 2), 96
PhH			 $\text{Ph-}\underset{CF_3}{CF}(OCF_2\underset{CF_3}{CF})nOC_3F_7$
(2.5mmol)	1a(2,0mmol)	40/5	(n = 0), 59
(2.5mmol)	1b(2.0mmol)	40/5	(n = 1), 30
(1.3mmol)	1c(1.0mmol)	40/5	(n = 2), 42
Pyrrole			 $\text{Py-}\underset{CF_3}{CF}(OCF_2\underset{CF_3}{CF})nOC_3F_7$[c]
(2.5mmol)	1a(2,0mmol)	rt/1	(n = 0), 33
(2.5mmol)	1b(2.0mmol)	rt/1	(n = 1), 36
(1.3mmol)	1c(1.0mmol)	rt/1	(n = 2), 67

---

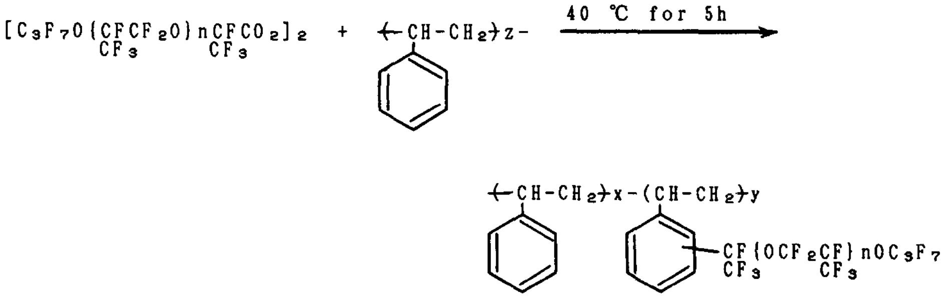
[a] The yields were determined by GC based on the peroxides used.

[b] Th- =  , Fu- = 

[c] Py indicates pyrrolyl group.

In the case of pyrrole, perfluoro-oxa-alkylations proceeded smoothly even at room temperature compared with that of thiophene or furan; however, considerable amounts of polymeric compounds were obtained. Furthermore, we succeeded in perfluoro-oxa-alkylations of benzene by the use of the peroxides, although the yields were not so high compared with those of thiophene and furan.

In the reactions of polystyrene with the peroxides 1a and 1b, the direct aromatic perfluoro-oxa-alkylations of polystyrene were found to proceed smoothly in moderate to high perfluoro-oxa-alkylated ratios (R_F-ratios) under mild conditions, even though the reactions were carried out in heterogeneous system as shown in Scheme 2.



n	R_F-ratio[y/(x+y)]	Mn	Mw/Mn
0	10%	1.5×10^5	1.59
1	43%	1.7×10^5	1.89
—	0%	1.0×10^5	2.18

Scheme 2.

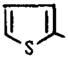
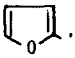
It was found that the molecular weights of perfluoro-oxa-alkylated polystyrenes were increased by the perfluoro-oxa-alkylations of parent polystyrene and the Mw/Mn of perfluoro-oxa-alkylated polystyrenes did not change to that of parent polystyrene. These results indicate that the degradation of the polymer chain did not occur under these reaction conditions.

The perfluoro-oxa-alkylation of thiophene, furan, benzene, pyrrole, and polystyrene with the peroxides 1a, 1b or 1c would be accounted for by Scheme 3 involving electron transfer reaction from the substrates to the antibonding(2pσ*) O-O bond of the peroxides as was proposed in perfluoroalkylations with perfluoroalkanoyl peroxides [4-a].

$$(R_FCO_2)_2 \ + \ Ar\text{-}H \longrightarrow [(Ar\text{-}H)^{+\cdot} \ + \ (R_FCO_2)^{-\cdot}]$$

$$\longrightarrow [(Ar\text{-}H)^{+\cdot} \ + \ R_F^{\cdot} + CO_2 + R_FCO_2^{-}]$$

$$\longrightarrow Ar\text{-}R_F + R_FCO_2H + CO_2$$

$R_F = -\underset{CF_3}{CF}(OCF_2\underset{CF_3}{CF})nOC_3F_7$, Ar- =  ,  , Ph , pyrrolyl

and phenyl group of polystyrene,

n = 0, 1, 2

Scheme 3.

In the perfluoro-oxa-alkylations with the peroxides(1a, 1b, 1c), it was clarified that the products yields increase in the following order;

1a < 1b < 1c

This would be dependent upon that the unoccupied 2pσ*(O-O) orbital levels of 1a, 1b and 1c lower in the order of 1a < 1b < 1c, and the lower unoccupied molecular orbital can accept an electron more easily from each aromatic compound.

EXPERIMENTAL

NMR spectra were taken with a JEOL JNM FX 90Q FT-NMR spectrometer IR spectra were recorded on a JASCO IR-810 spectrophotometer. Mass spectra were taken on a JEOL JMS-DX303 spectrometer by an electron-impact(EI) ionization technique at 70eV. Gas chromatography was performed by Shimadzu GC-8A gas chromatography with 2m glass column(SE-30, 20%). Kugelrohr distillation was performed with a Sibata glass tube oven GTO-350RD. Molecular weights and polydispersities for polystyrenes were calculated by using a Toyo Soda HLC-802A gel permeation chromatography (calibration was based on polystyrene standards).

Typical Procedure

A solution containing 2 mmol of 1b and 2.5 mmol of benzene in 30g of Freon-113 was degassed and kept at 40℃ for 5h in a sealed tube.

The solution was then washed with 20 ml of 5% $NaHCO_3$ and 20 ml of water. The organic layer was analyzed by GC using internal standard. Perfluoro-1,4-dimethyl-2,5-dioxaoctylbenzene was isolated by distillation(bp 108 - 110 ℃/32 mmHg), which was identified by IR, ^1H-NMR, ^{13}C-NMR, and MS. The other products were isolated by Kugelrohr distillation.

Perfluoro-1,4-dimethyl-2,5-dioxaoctylbenzene

IR(cm^{-1}) 1335, 1310(CF_3), 1240(CF_2); ^1H-NMR($CDCl_3$) δ 7.6(5H, m); ^{13}C-NMR($CDCl_3$) δ 126.9(t, J_{CCCF} = 6.3 Hz), 128.8, 132.0; ^{19}F-NMR($CDCl_3$, ext. CF_3CO_2H) δ -4.0 ~ -9.2(13F), -54.1(2F), -56.5(1F), -70.0(1F); MS m/z 528(M^+), 459, 177, 169(base), 127; Exact MS: 527.9951, Calcd for $C_{14}H_5F_{17}O_2$: 528.0018.

Perfluoro-1-methyl-2-oxapentylbenzene

IR(cm^{-1}) 1330, 1315(CF_3), 1240(CF_2); ^1H-NMR($CDCl_3$) δ 7.5(5H, m); ^{13}C-NMR($CDCl_3$) δ 126.5(t, J_{CCCF} = 7.4 Hz), 128.7, 131.8; ^{19}F-NMR($CDCl_3$, ext. CF_3CO_2H) δ -2.8 ~ -8.9(8F), -54.5(2F), -55.0(1F); MS m/z 362(M^+), 293, 177, 127, 105(base); Exact MS: 362.0245, Calcd for $C_{11}H_5F_{11}O$: 362.0325.

Perfluoro-1,4,7-trimethyl-2,5,8-trioxaundecylbenzene

IR(cm^{-1}) 1330(CF_3), 1240(CF_2); ^1H-NMR($CDCl_3$) δ 7.5(5H, m); ^{19}F-NMR($CDCl_3$, ext. CF_3CO_2H) δ -3.2 ~ -9.1(18F), -54.1(2F), -56.0(1F)

, -69.8(2F); MS m/z 694(M^+), 625, 177, 169(base); Exact MS: 693.9933, Calcd for $C_{17}H_5F_{23}O_3$: 693.9872.

2-(Perfluoro-1'-methyl-2'-oxapentyl)thiophene

IR(cm^{-1}) 1340, 1320(CF_3), 1230(CF_2); ^{1}H-NMR($CDCl_3$) δ 7.1(1H, m), 7.4(1H, m), 7.6(1H, m); ^{13}C-NMR($CDCl_3$) δ 127.7, 130.2, 130.8; ^{19}F-NMR($CDCl_3$, ext. CF_3CO_2H) δ -2.8 ~ -9.0(8F), -54.2(2F), -56.0(1F); MS m/z 368(M^+), 299, 183, 133, 111(base); Exact MS: 367.9734, Calcd for $C_9H_3F_{11}OS$: 367.9729.

2-(Perfluoro-1',4'-trimethyl-2',5'-dioxaoctyl)thiophene

IR(cm^{-1}) 1335(CF_3), 1240(CF_2); ^{1}H-NMR($CDCl_3$) δ 7.1(1H, m), 7.4(1H, m), 7.6(1H, m); ^{13}C-NMR($CDCl_3$) δ 128.0, 130.5, 130.9; ^{19}F-NMR($CDCl_3$, ext. CF_3CO_2H) δ -3.8 ~ -9.8(13F), -53.9(2F), -56.1(1F), -69.6(1F); MS m/z 534(M^+), 465, 183(base), 133, 169, 111 ; Exact MS: 533.9546, Calcd for $C_{12}H_3F_{17}O_2S$: 533.9583.

2-(Perfluoro-1',4',7'-dimethyl-2',5',8'-trioxaundecyl)thiophene

IR(cm^{-1}) 1335(CF_3), 1240(CF_2); ^{1}H-NMR($CDCl_3$) δ 7.1(1H, m), 7.4(1H, m), 7.5(1H, m); ^{13}C-NMR($CDCl_3$) δ 128.0, 130.5, 131.0; ^{19}F-NMR($CDCl_3$, ext. CF_3CO_2H) δ -3.5 ~ -9.5(18F), -54.0(2F), -56.2(1F), -69.5(2F); MS m/z 700(M^+), 631, 183(base), 133, 169, 111 ; Exact MS: 699.9483, Calcd for $C_{15}H_3F_{23}O_3S$: 699.9435.

2-(Perfluoro-1'-methyl-2'-oxapentyl)furan

IR(cm^{-1}) 1340, 1320(CF$_3$), 1240(CF$_2$); ^{1}H-NMR(CDCl$_3$) δ 6.5(1H, m), 6.8(1H, m), 7.6(1H, m); ^{13}C-NMR(CDCl$_3$) δ 111.6, 114.2, 146.0; ^{19}F-NMR(CDCl$_3$, ext. CF$_3$CO$_2$H) δ -2.9 ~ -9.0(8F), -54.2(2F), -56.1(1F) MS m/z 352(M$^+$), 283(base), 167, 117; Exact MS: 351.9858, Calcd for $C_9H_3F_{11}O_2$: 351.9958.

2-(Perfluoro-1',4'-dimethyl-2',5'-dioxaoctyl)furan

IR(cm^{-1}) 1335(CF$_3$), 1240(CF$_2$); ^{1}H-NMR(CDCl$_3$) δ 6.5(1H, m), 6.8(1H, m), 7.5(1H, m); ^{13}C-NMR(CDCl$_3$) δ 111.6, 114.5, 146.3; ^{19}F-NMR(CDCl$_3$, ext. CF$_3$CO$_2$H) δ -3.5 ~ -9.0 (13F), -54.2(2F), -56.4(1F), -69.8(1F); MS m/z 518(M$^+$), 449, 169, 167(base), 117; Exact MS: 517.9883, Calcd for $C_{12}H_3F_{17}O_3$: 517.9811.

2-(Perfluoro-1',4', 7'-trimethyl-2',5',8'-trioxaundecyl)furan

IR(cm^{-1}) 1335(CF$_3$), 1240(CF$_2$); ^{1}H-NMR(CDCl$_3$) δ 6.5(1H, m), 6.8(1H, m), 7.5(1H, m); ^{13}C-NMR(CDCl$_3$) δ 111.7, 114.7, 146.4; ^{19}F-NMR(CDCl$_3$, ext. CF$_3$CO$_2$H) δ -3.8 ~ -9.2 (18F), -54.2(2F), -56.2(1F), -69.8(2F); MS m/z 684(M$^+$), 615, 169, 167(base), 117 ; Exact MS: 683.9608, Calcd for $C_{15}H_3F_{23}O_4$: 683.9664.

Perfluoro-1-methyl-2-oxapentylpyrrole [5]

MS m/z 351(M$^+$, base), 282, 169, 166, 113, 94; Exact MS: 351.0136, Calcd for $C_9H_4F_{11}ON$: 351.0117.

Perfluoro-1,4-dimethyl-2,5-dioxaoctylpyrrole*

MS m/z 517(M^+), 448(base), 169, 166, 113, 94; Exact MS: 516.9696, Calcd for $C_{12}H_4F_{17}O_2N$: 516.9971.

Perfluoro-1,4,7-trimethyl-2,5,8-tri-oxaundecylpyrrole*

MS m/z 683(M^+), 614, 169(base), 166, 116, 113, 94; Exact MS: 682.9856, Calcd for $C_{15}H_4F_{23}O_3N$: 682.9824.

Reaction of Polystyrene with 1b

1b (25 mmol) in Freon-113 solution (300g) was added into the mixture of polystyrene [Mn = 1.0 x 10^5, Mw/Mn = 2.18, 4.0g (38 mmol; calculated from styrene monomer units) and Freon-113 (50g). The heterogeneous solution was stirred vigorously at 40℃ for 5h under nitrogen. Chloroform (500 ml) was added to the reaction mixture and the solution was stirred for 10 min, then washed with 1% NaOH (500 ml) and water (500 ml). After drying over anhydrous magnesium sulphate, and removal of the solvent, the obtained polymer was reprecipitated from chloroform-methanol and dried over in vacuo to

---

* The formation of perfluoro-oxa-alkylpyrroles (probably, 2-perfluoro-oxa-alkylpyrroles) was confirmed by only GC-MS information, because these compounds could not be isolated owing to their instability.

give perfluoro-1,4-dimethyl-2,5-dioxaoctyl polystyrene (11.2g; R_F-ratio = 43%). R_F-ratio {(y/x+y) x 100; perfluoro-oxa-alkylated ratio} was determined by ^{19}F-NMR in comparision with the peak area of the perfluoro-oxa-alkyl group of polymer with trifluoromethyl group of benzotrifluoride as the internal standard.

Perfluoro-1,4-dimethyl-2,5-dioxaoctyl Polystyrene:

IR(cm^{-1}) 1335(CF_3), 1240(CF_2); ^{19}F-NMR($CDCl_3$, ext. CF_3CO_2H) δ -3.9 ~ -9.2(13F), -56.4(3F).

Perfluoro-1-methyl-2-oxapentyl Polystyrene:

IR(cm^{-1}) 1315(CF_3), 1235(CF_2); ^{19}F-NMR($CDCl_3$, ext. CF_3CO_2H) δ -2.5 ~ -9.1(8F), -54.7(3F).

REFERENCES

1 a) J. F. Liebman, A. Greenberg, and W. R. Dolbier, Jr., 'Fluorine-Containing Molecules, Structure, Reactivity, Synthesis, and Applications', VCH, New York, 1988.

b) R. Filler and Y. Kobayashi, 'Biomedical Aspects of Fluorine Chemistry', Kodansha, Tokyo, 1982. c) R. E. Banks, 'Organofluorine Chemicals and their Industrial Applications',Ellis Horwood, Chichester 1979.

2 W. R. Jones, Jr., T. R. Bierschenk, T. J. Juhlke, H. Kawa and R. J. Lagow, Ind. Eng. Chem. Res., 27 (1988) 1497.

3 a) Trifluoromethylation: Y. Kobayashi and I. Kumadaki, Tetrahedron Lett., (1969) 4095 ; G. K. S. Prakash, R. Krishnamurti and G. A. Olah, J. Am. Chem. Soc., 111 (1989) 393 and references cited there in. b) Perfluoroalkylation: H. Sawada and M. Nakayama, J. Jpn. Oil Chem. Soc., 38 (1989) 985 ; V. C. R. McLoughlin and J. Thrower, Tetrahedron, 25 (1969) 5921 ; J. Leroy, M. Rubinstein and C. Wakselman, J. Fluorine Chem., 27 (1985) 291; T. Fuchikami and I. Ojima, J. Fluorine Chem., 22 (1983) 541.

4 a) M. Yoshida, H. Amemiya, M. Kobayashi, H. Sawada, H. Hagii and K. Aoshima, J. Chem. Soc., Chem. Commun., (1985) 234; b) H. Sawada , M. Yoshida, H. Hagii, K. Aoshima and M. Kobayashi, Bull. Chem. Soc. Jpn., 59 (1986) 215; c) M. Yoshida, T. Yoshida, N. Kamigata, and M. Kobayashi, Bull. Chem. Soc. Jpn., 61, (1988) 3549; d) M. Yoshida, T. Yoshida, M. Kobayashi and N. Kamigata, J. Chem. Soc. Perkin Trans. I, (1989) 909; e) M. Yoshida, S. Sasage, N. Kamigata, H. Sawada and M. Nakayama, Bull. Chem. Soc. Jpn., 62 (1989) 2416 ; f) H. Sawada, M. Mitani, M. Nakayama, M. Yoshida and N. Kamigata, Poly. Commun., 31 (1990) 63; g) H. Sawada, M. Nakayama, M. Yoshida and N. Kamigata, J. Fluorine Chem., 46, (1990) 423; h) M. Yoshida, N. Kamigata, H. Sawada and M. Nakayama, J. Fluorine Chem., 49 (1990) 1.