Journal of Fluorine Chemistry, *49* (1990) 1–20

REVIEW

RECENT PROGRESS IN PERFLUOROALKYLATION BY RADICAL SPECIES WITH SPECIAL REFERENCE TO THE USE OF BIS(PERFLUOROALKANOYL) PEROXIDES

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SUMMARY

Radical species play important roles in perfluoroalkylation, so recent advances in perfluoroalkylation with radical intermediates are reviewed from two aspects; one is thermal and photochemical generations of perfluoroalkyl radicals and the other is via electron transfer. Especially, in this article, perfluoroalkylations with bis(perfluoroalkanoyl) peroxides via electron transfer developed in our laboratory are discussed in detail and compared with methods using other reagents.

Organofluorine compounds often show unique properties [1], and are widely used as medicines, pesticides, dyes or surfactants. Especially the substitution by perfluoroalkyl group at particular positions of organic compounds may give rise to unique physical or biological properties which cannot be achieved by incorporating other functional groups. However, the methods for the introduction of perfluoroalkyl groups into organic compounds have not yet been well

0022-1139/90/$3.50

established. Although nucleophilic substitution via cationic intermediates is the most important and common reaction in hydrocarbon chemistry, the generation of perfluoroalkyl cationic intermediates is very difficult due to the strong electronegativity of fluorine [2] (Scheme 1).

$$C_nH_{2n+1}X \quad + \quad Nu^- \longrightarrow C_nH_{2n+1}Nu \quad + \quad X^-$$

$$C_nF_{2n+1}X \quad + \quad Nu^- \not\longrightarrow C_nF_{2n+1}Nu \quad + \quad X^-$$

electronegativity: F (4.0), CF_3 (3.46), C_2F_5 (3.40), Cl (3.0), I (2.5), CH_3 (2.27)

Scheme 1.

Anionic perfluoroalkylating reagents such as Grignard reagents, analogous to those commonly used as alkylating reagents, are generally unstable and decompose as shown in eq. 1 and 2. This problem has been gradually overcome by the choice of metals to be counter cations [3]. For example, Grignard type reactions were achieved by treating perfluoroalkyl iodides and substrates with zinc under irradiation by ultrasound (eq. 3) [3a]. As a method for perfluoroalkylation using anionic reagents, coupling reactions as shown in eq. 4 have been developed, and are frequently used [4,5].

$$R_FCF_2CF_2MgI \longrightarrow R_FCF{=}CF_2 \quad + \quad MgIF \tag{1}$$

$$CF_3MgI \longrightarrow :CF_2 \quad + \quad MgIF \tag{2}$$

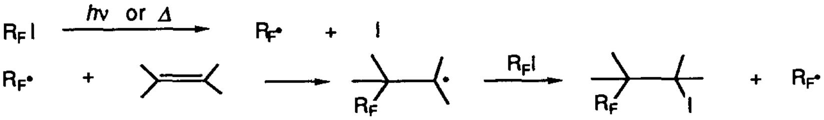
$$R_FI \quad + \quad Zn \longrightarrow [R_FZnI] \xrightarrow{>C=O} R_F-\overset{|}{\underset{|}{C}}-OH \tag{3}$$

$$R_FI \quad + \quad Cu \quad + \quad ArI \longrightarrow ArR_F \tag{4}$$

On the other hand, the generation of perfluoroalkyl radicals is relatively easy, so the significance of radical species in perfluoroalkylation has been increasingly recognized. There are two trends in the recent studies in this field; one is the development of novel reagents to generate perfluoroalkyl radicals more effectively under milder conditions, and the other is the exploitation of novel methods to generate the radical species from reagents which are already known. Especially, electron-transfer reactions are likely to play important roles as methods for the generation of perfluoroalkyl radicals. Thus, in this account we would like to review the recent advances in perfluoroalkylation with radical intermediates which are generated by thermal or photochemical homolysis and via electron transfer.

THERMAL AND PHOTOCHEMICAL GENERATION OF PERFLUOROALKYL RADICALS

The addition reactions of perfluoroalkyl iodides to olefins or acetylenes have long been known as one of the most important and general methods for the introduction of perfluoroalkyl groups. The reaction is initiated by light [6], heating [6], or radical initiators [7], and proceeds via a radical chain mechanism (Scheme 2).



Scheme 2.

The efficiency of homolytic cleavage of perfluoroalkyl iodides is not good. So the aromatic radical substitutions with perfluoroalkyl iodides require high temperatures or long irradiation times, and the yields and selectivities were generally poor [8]. However, the perfluoroalkylations of some heteroaromatic compounds such as imidazoles, which are good radical trapping reagents, by perfluoroalkyl iodides have been reported to proceed in good yields [9].

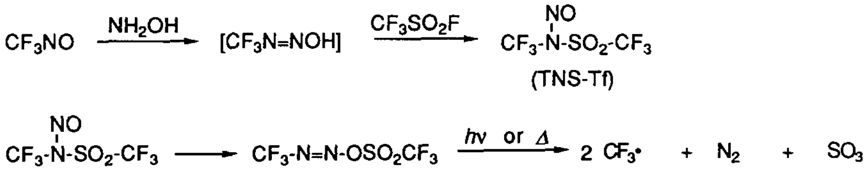
The perfluoroalkylazo derivatives [10], hexafluoroacetone [11], and perfluoroalkanesulfonyl chlorides [12] are known to give perfluoroalkyl radicals by homolysis (eq. 5 - 7). However, these also are not effective reagents for the generation of the trifluoromethyl radical, and applications to synthetic chemistry are little reported.

$$R_F\text{-}N{=}N\text{-}R_F \xrightarrow{h\nu} 2\ R_F\cdot + N_2 \tag{5}$$

$$CF_3COCF_3 \xrightarrow{h\nu} 2\ CF_3\cdot + CO \tag{6}$$

$$R_FSO_2Cl \xrightarrow{h\nu \text{ or } \Delta} R_F\cdot + SO_2 + Cl \tag{7}$$

Thus, the development of new reagents for the generation of perfluoroalkyl radicals effectively under mild conditions is desirable. Umemoto et al. have developed N-trifluoromethyl-N-nitrosomethanesulfonamide (TNS-Tf) as a novel type of trifluoromethylating reagent made from trifluoronitrosomethane [13](Scheme 3). Photochemical or thermal reactions of TNS-Tf effectively give two trifluoromethyl radicals and are used for trifluoromethylation of activated aromatics, mercaptans, disulfides or uridine derivatives. Also synthesized were N-trifluoromethyl-N-nitrosobenzenesulfonamide (TNS-B) [14] and derivatives [15]; however, these compounds were too stable to act as reagents for trifluoromethylation.

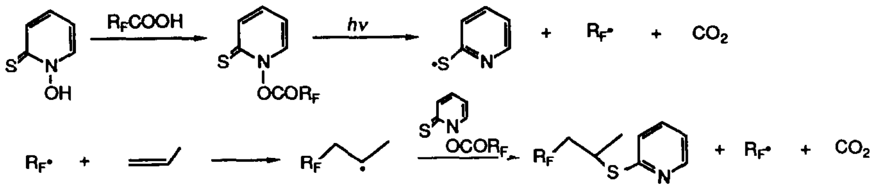


$$CF_3NO \xrightarrow{NH_2OH} [CF_3N{=}NOH] \xrightarrow{CF_3SO_2F} CF_3\text{-}\overset{NO}{N}\text{-}SO_2\text{-}CF_3 \ \text{(TNS-Tf)}$$

$$CF_3\text{-}\overset{NO}{N}\text{-}SO_2\text{-}CF_3 \longrightarrow CF_3\text{-}N{=}N\text{-}OSO_2CF_3 \xrightarrow{h\nu \text{ or } \Delta} 2\ CF_3\cdot + N_2 + SO_3$$

Scheme 3.

Lower members of the perfluoroalkyl iodide series and trifluoronitrosomethane are gases, so it is necessary to handle them in autoclaves, and further, they are very expensive. On the other hand, perfluoroalkanoic acids are readily available and easy to handle. Barton et al. synthesized the trifluoroacetic acid ester of N-hydroxypyridine 2-thione, which gave perfluoroalkyl radicals on irradiation [16]. Photoirradiation of this ester in the presence of an olefin affords adducts in a radical chain reaction (Scheme 4). As the ester of N-hydroxypyridine 2-thione is a very good radical acceptor, the radical chain reaction proceeds effectively.



Scheme 4.

The diacyl peroxides containing perfluoroalkyl groups (bis(perfluoroalkanoyl) peroxides) were synthesized from corresponding acid chlorides or acid anhydrides with hydrogen peroxide or sodium diperoxide [17, 18]. These peroxides are also known to decompose homolytically to give perfluoroalkyl radicals under mild conditions [17 - 20](Scheme 5), and they are often used as radical initiators for polymerizations of vinyl chloride or fluorine-substituted olefins.

$$R_FCOCl \xrightarrow{H_2O_2} (R_FCOO)_2$$

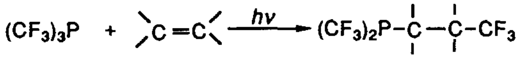
$$(R_FCO)_2O \xrightarrow{H_2O_2 \text{ or } Na_2O_2} (R_FCOO)_2$$

$$(R_FCOO)_2 \xrightarrow{\Delta} 2\ R_F\bullet + 2\ CO_2$$

Scheme 5.

Bis(trifluoromethyl)mercury [21], bis(trifluoromethyl)-telluride [21], and tris(trifluoromethyl)phosphine [22] also gave trifluoromethyl radicals (eq. 8, 9). The reactivities of bis(trifluoromethyl)mercury, and telluride were compared with that of trifluoromethyl iodide: they were found to increase in the series $(CF_3)_2Hg$ < CF_3I << $(CF_3)_2Te$ [21].

$$\underset{(M = Hg,\ Te)}{(CF_3)_2M} \xrightarrow{hv} CF_3\bullet + MCF_3 \xrightarrow{hv} 2\ CF_3\bullet + M \qquad (8)$$



$$(CF_3)_3P + \gt C{=}C\lt \xrightarrow{hv} (CF_3)_2P-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-CF_3 \qquad (9)$$

GENERATION OF PERFLUOROALKYL RADICALS VIA ELECTRON TRANSFER

Perfluoroalkyl radicals can be produced from perfluoroalkanoic acids by anodic oxidation and introduced into olefins [23], heteroaromatic compounds, such as uracil [24] or pyridine [25], and compounds containing activated methylenes [26]. Recently, the applications of electrochemistry to the synthesis of trifluoromethylated compounds have been studied by Muller [27] and Uneyama et al.[28].

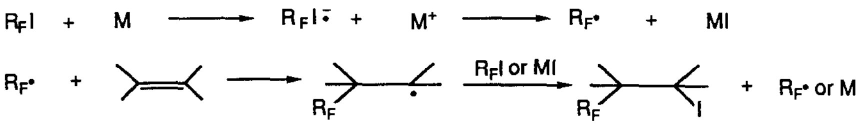
$$R_FCO_2H \xrightarrow{e^-} R_F\bullet + CO_2 + H^+ \qquad (10)$$

Perfluoroalkanoic acids also gave perfluoroalkyl radicals by electron transfer from xenon difluoride; perfluoroalkylation of electron-poor benzenes was reported in the reaction of benzenes with perfluoroalkanoic acids in the presence of xenon difluoride (eq. 11) [29]. It is postulated that the reaction is initiated by electron transfer from perfluoroalkanoate to xenon difluoride to produce a perfluoroalkyl radical.

$$R_FCO_2H + ArH + XeF_2 \longrightarrow ArR_F + CO_2 + Xe + 2\,HF \qquad (11)$$

Although the reduction potentials of perfluoroalkyl halides are predicted to be low due to the strong electronegativity of fluorine, there are few examples of the electroreductive generations of perfluoroalkyl radicals. Perfluoroalkylations with perfluoroalkyl iodides [30] or bromides [31] by electroreduction were reported. However, it is not certain what kind of active species are generated.

One electron reductions of perfluoroalkyl iodides affording perfluoroalkyl radicals can be promoted by metals. By the addition of catalytic amounts of metals or their complexes, the addition reactions of fluoroalkyl iodides to olefins or acetylenes proceed readily under mild conditions [32 - 38]. Most of these reactions may involve a radical chain process initiated by electron transfer from metal to iodide (Scheme 6). Many metals, Cu, Hg, Ru, Co, Ni, Pt, Fe, Zn, Mg, Al and Pd have been reported to catalyze the addition reactions of perfluoroalkyl iodides.



Scheme 6.

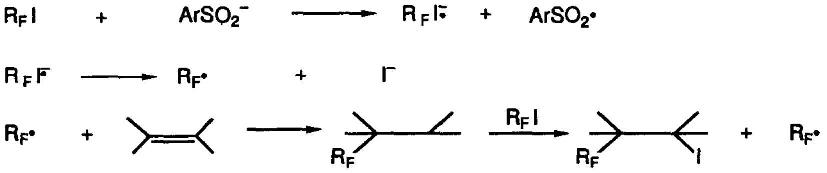
Perfluoroalkyl iodides are known to be very resistant to normal nucleophilic attack, because the electronegativities of perfluoroalkyl groups are larger than that of iodine. However, in the reactions of perfluoroalkyl iodides with nucleophiles, such as enamines [39], thiolates [40, 41], selenoates [42], sulfinates [43], enolates [44], nitronates [45], and nitrites [46], perfluoroalkyl groups were introduced into the nucleophilic centres. The reactions were reported to be initiated by electron transfer from the nucleophiles to the iodide ($S_{RN}1$ mechanism; Scheme 7). The electron-transfer reactions are accelerated by light. Recently, photoelectron transfer from aromatic compounds to trifluoromethyl bromide was reported to afford perfluoromethylarenes [47].

$$R_FI + Nu^- \longrightarrow R_FNu + I^-$$

$$\left[\begin{array}{l} R_FI + Nu^- \longrightarrow R_FI^{\cdot-} + Nu\cdot \\ R_FI^{\cdot-} \longrightarrow R_F\cdot + I^- \\ R_F\cdot + Nu^- \longrightarrow R_FNu^{\cdot-} \\ R_FNu^{\cdot-} + R_FI \longrightarrow R_FNu + R_FI^{\cdot-} \end{array}\right.$$

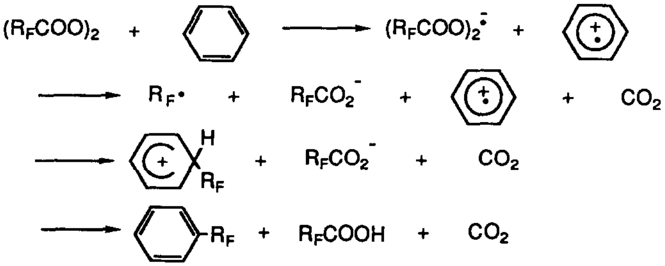
Scheme 7.

Sodium arene- or alkane- sulfinates were also used as initiators of the radical chain addition of perfluoroalkyl iodides to olefins [48](Scheme 8).



Scheme 8.

Bis(perfluoroalkanoyl) peroxides suffer electron transfer from copper [49], carbanions [50, 51], nitrites [46], or thiolates [51] to give perfluoroalkyl radicals. The peroxides also react with arenes to give perfluoroalkylated arenes and perfluoroalkanoic acids [52, 53]. The peroxides unimolecularly decompose to perfluoroalkyl radicals and carbon dioxide. However, the decays of the peroxides were accelerated by the addition of benzene, and the activation entropies in the presence of benzene had negative values. So the perfluoroalkylation of benzene is explained as an electron-transfer reaction as shown in Scheme 9. The electron transfer from benzene to the peroxide gives a radical cation of benzene and radical anion of the peroxide. The radical anion decomposes to a perfluoroalkyl radical, perfluoroalkanoate, and carbon dioxide. The perfluoroalkyl radical recombines with the radical cation of the benzene to give the perfluoroalkylbenzene via the cation intermediate. Since in this reaction the perfluoroalkyl radical is produced as a radical pair in close proximity with the radical cation of the substrate in a solvent cage, the perfluoroalkyl radical reacts with the radical cation selectively.



Scheme 9.

Perfluoroalkyl halides and bis(perfluoroalkanoyl) peroxides are likely to act as good electron acceptors and give effectively perfluoroalkyl radicals under mild conditions. The reduction potential of trifluoromethyl iodide is estimated to be less than -0.6 V vs SCE [30]. Although the reduction potentials of bis(perfluoroalkanoyl) peroxides have not yet been reported, peroxides are predicted to be better electron acceptors than are perfluoroalkyl iodides. The peroxides undergo electron transfer from benzene but perfluoroalkyl iodides do not; the iodides barely react with N-methylpyrrole for which the ionization potential is very low [39]. Therefore, we considered the electron-transfer reactions of peroxides as a general method for perfluoroalkylation of electron-rich substrates.

BIS(PERFLUOROALKANOYL) PEROXIDES (1) AS REAGENTS FOR PERFLUOROALKYLATION

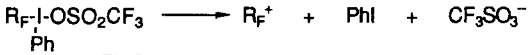
In the reactions of bis(perfluoroalkanoyl) peroxides (R_F = CF_3 1a, R_F = C_3F_7 1b, R_F = C_7F_{15} 1c) with several substituted benzenes, perfluoroalkylated benzenes were obtained in good yields under mild conditions [53, 54]. The results are shown in Table 1 together with those obtained from other reagents for perfluoroalkylation.

TABLE 1

Perfluoroalkylation of benzenes with various reagents

Substrate	Reagent for Perfluoroalkylation	Conditions	Yield	Ref.
benzene	1a	70 °C	54	54
benzene	1b	40 °C	86	53
benzene	1c	40 °C	97	54
benzene	CF_3I	hν	14	8e
benzene	TNS-Tf	hν	49	13
benzene	CF_3COOH + XeF_2	room temp.	33	29
benzene	FITS-6	benzene reflux	97	55
anisole	1a	70 °C	69	54
anisole	1b	40 °C	93	53
toluene	1a	70 °C	71	54
toluene	1b	40 °C	85	53
chlorobenzene	1a	70 °C	18	54
chlorobenzene	1b	40 °C	45	53

As the perfluoroalkylations with peroxides 1 are initiated by electron transfer from benzenes to 1 and proceed via benzenium cation intermediates as shown in Scheme 9, the process is superficially equivalent to cationic perfluoroalkylation. In fact, the yields of the perfluoroalkylations with 1 were high for electron-rich benzenes. Electrophilic perfluoroalkylations of benzenes are little reported. The method using (perfluoroalkyl)phenyliodonium trifluoromethanesulfonate (FITS) is the only example of electrophilic perfluoroalkylation of electron-rich benzenes via a perfluoroalkyl cation (eq. 12) [55]. Thus, perfluoroalkylation with 1 is a useful method for the introduction of various perfluoroalkyl groups, such as CF_3, C_3F_7, and C_7F_{15}, into electron-rich benzenes under mild conditions.



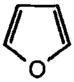
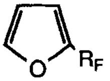
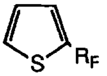
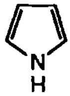
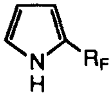
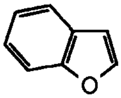
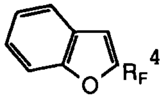
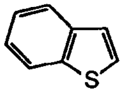
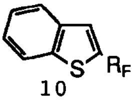
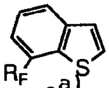
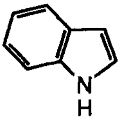
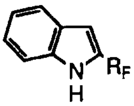
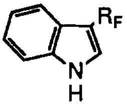
$$R_F\text{-}\underset{Ph}{I}\text{-}OSO_2CF_3 \longrightarrow R_F^+ + PhI + CF_3SO_3^- \qquad (12)$$

FITS-m ($R_F = C_mF_{2m+1}$)

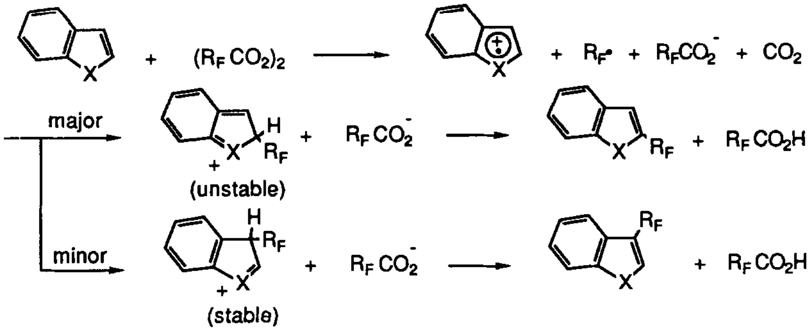
Perfluoroalkylations of heteroaromatic compounds, such as furan [56], thiophene [56], pyrrole [57], benzothiophene [58], or indole [57], were achieved with peroxides 1. The results are shown in Table 2. Perfluoroalkylations of furan, thiophene, and pyrrole proceeded in good yields and regioselectively. The reactions of pyrrole with 1 were very fast at room temperature and proceeded even at -80 ° C, while the reactions of thiophene or furan were performed at 40 ° C. The high reactivity of pyrrole should be due to its low ionization potential (IP 9.20 ev) compared with those of thiophene (8.87 ev) and furan (8.89 ev). The perfluoroalkylations of benzothiophene or indole occurred preferentially at the C-2 position. Usually, electrophilic substitution of benzothiophene or indole occurs at C-3; the selectivity should be due to the stability of the Wheland intermediates (Scheme 10). The observed orientations in the perfluoroalkylations with 1, therefore, cannot be explained by the stabilities of the cationic intermediates, but may be attributed to the spin density distributions in the radical cation intermediates (Scheme 10).

TABLE 2

Perfluoroalkylation of heteroaromatic compounds with 1

Substrate	Peroxide	Temp. / °C	Products / %			
	1a 1b 1c	60 40 40		53 98 99		
	1a 1b 1c	60 40 40		72 99 98		
	1a 1b 1c	-30 -30 -30		72 100 77		
	1a	60		47		
	1a 1b	60 40		10 54	 $9^{a)}$	 30
	1a 1b	-30 -30		24 63		11 13

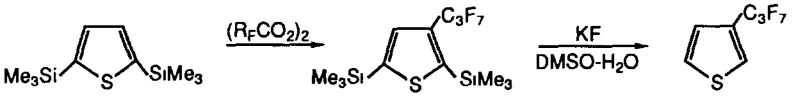
[a] 3-Trifluoromethylbenzothiophene was also obtained in 9% yield.



Scheme 10.

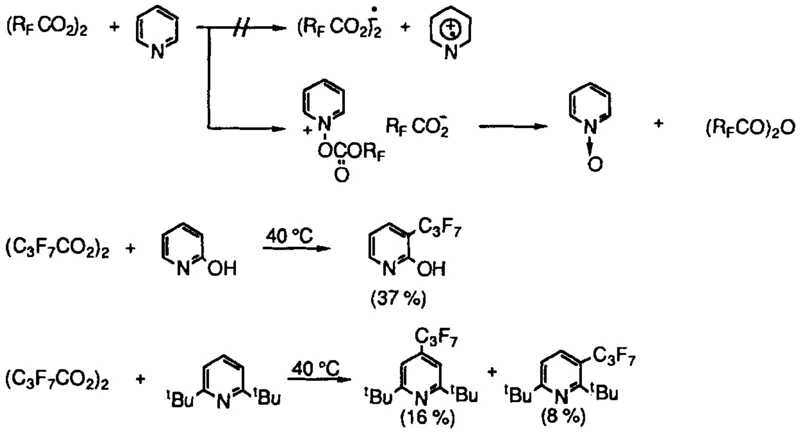
Electron-withdrawing groups deactivate the electron transfer; however, perfluoroalkylations of 2-formylpyrrole [57], 2-formylthiophene [58], or 2-bromothiophene [56] could be achieved with 1 affording 5-perfluoroalkylated derivatives in good yields. Formyl or halogen groups are important functional groups due to their extensive synthetic utility. Therefore, perfluoroalkylations of these compounds are very valuable in synthetic chemistry.

Examples of the preparation of 3-perfluoroalkylthiophene, which are important as starting materials for thiophene polymers, are rare. The reaction of a 3-halogenothiophene with a perfluoroalkyl iodide in the presence of copper-bronze in DMF was the only example to give a 3-perfluoroalkylthiophene [59]. Although perfluoroalkylations of thiophene by peroxides occurred at the C-2 position selectively, perfluoroalkyl groups were introduced into the C-3 position in 2,5-disubstituted thiophenes [58]. 3-Perfluoropropylthiophene was obtained as shown in eq. 13 from 2,5-bis(trimethylsilyl)thiophene [58].



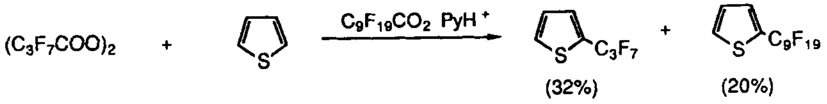
(13)

Perfluoroalkylation of pyridine, the most common heteroaromatic compound, with 1 could not be achieved. Peroxides 1 decomposed instantly when pyridine was added to solutions of them, but perfluoroalkylpyridines were not produced. Usually, two types of reactions are known to occur on treatment of peroxides with nucleophiles [60]; one is an S_N2 type nucleophilic displacement and the other is an electron-transfer reaction from the nucleophile to the peroxide. Electron transfer from the substrate to the peroxide is essential for perfluoroalkylation with 1; however nucleophilic attack of the N lone pair of pyridine on the O-O bond of the peroxide probably occurs in preference to the electron transfer from the π-orbital of pyridine (scheme 11). The perfluoroalkylations of 2-hydroxypyridine and 2,6-di-t-butylpyridine, in which the N lone pairs were not so nucleophilic, occurred (Scheme11) [57]. The nucleophilicity of the N lone pair of 2-hydroxypyridine was suppressed by tautomerism between the hydroxy form and amide form. The nucleophilic attack of the N lone pair of 2,6-di-t-butylpyridine may be prevented by steric hindrance of the 2,6-di-t-butyl groups.



Scheme 11.

Although various perfluoroalkyl groups can be introduced in principle, the synthesis of the diacyl peroxides which contain perfluoroalkyl chains longer than perfluoroheptyl are difficult and have not yet been developed sufficiently. However, the perfluorononyl group can be introduced into thiophene as follows. Peroxide 1b was reacted with pyridinium perfluorododecanoate, and then thiophene was added giving 2-perfluoropropylthiophene and 2-perfluorononylthiophene as products [61].



(14)

This reaction can be explained by the nucleophilic displacement of peroxide 1b with perfluorododecanoate to give mixed peroxide and then bis(perfluorododecanoyl) peroxide, which act as reagents for perfluorononylation of thiophene.

Thus, a perfluoroalkyl group can be introduced into thiophene, even if the corresponding peroxide cannot be synthesized.

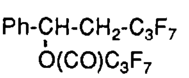
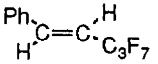
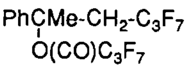
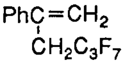
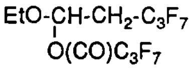
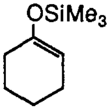
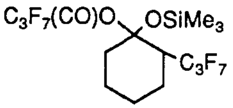
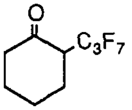
$$(C_3F_7CO_2)_2 + C_9F_{19}CO_2^- \rightleftharpoons C_3F_7(CO)OO(CO)C_9F_{19} + C_3F_7CO_2^- \qquad (15)$$

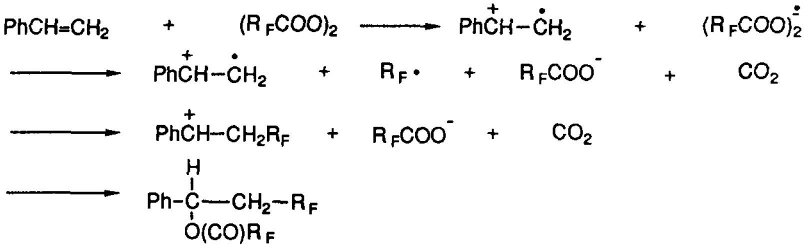
$$C_3F_7(CO)OO(CO)C_9F_{19} + C_9F_{19}CO_2^- \rightleftharpoons (C_9F_{19}CO_2)_2 + C_3F_7CO_2^- \qquad (16)$$

In the reaction of electron-rich olefins, such as styrene, α-methylstyrene, ethyl vinyl ether, or silyl enol ether, with 1, the adducts of perfluoroalkyl and perfluoroalkanoyloxy groups were obtained in good yields and regioselectively (Table 3) [62]. The mechanism in the reaction of styrene with 1b is shown in Scheme 12. Peroxide 1b has been widely used as an initiator for radical polymerization, however, it did not behave as an initiator for the polymerization of styrene. In the reaction of styrene with 1b, electron transfer from styrene to 1b occurs at first, and the following reaction may proceed in a solvent cage as a bimolecular reaction.

TABLE 3

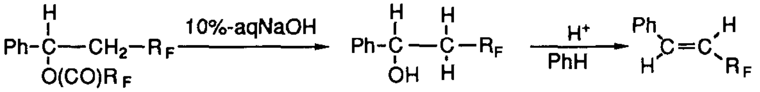
Reactions of various electron-rich olefins with 1b -

Olefin	Products / %	
$PhCH=CH_2$	 $\mathrm{Ph\text{-}\underset{O(CO)C_3F_7}{CH}\text{-}CH_2\text{-}C_3F_7}$ (89)	 (7)
$PhCMe=CH_2$	 $\mathrm{Ph\underset{O(CO)C_3F_7}{C}Me\text{-}CH_2\text{-}C_3F_7}$ (77)	 $\mathrm{Ph\underset{CH_2C_3F_7}{C}{=}CH_2}$ (21)
$EtOCH=CH_2$	 $\mathrm{EtO\text{-}\underset{O(CO)C_3F_7}{CH}\text{-}CH_2\text{-}C_3F_7}$ (95)	
	 (48)	 (27)



Scheme 12.

The hydrolysis of the adduct obtained by the reaction of styrene with 1b gave an alcohol under basic conditions. The alcohol can be converted into perfluoroalkylated olefin by refluxing in benzene in the presence of p-toluenesulfonic acid (eq.17). Thus, peroxides 1 can be also used as reagents for perfluoroalkylations of electron-rich olefins.



(17)

Peroxides 1 are synthesized from the commercially available and relatively cheap perfluoroalkanoic acid chloride or acid anhydride. These peroxides are thermally stable and easy to handle; the half-life of 1a, 1b, and 1c were 498 days at 0 °C, 490 days at -20 °C, and 425 days at -20 °C, respectively. Thus, the method for perfluoroalkylation with 1 has high potential as a general and practical electrophilic perfluoroalkylation of aromatic rings and olefins.

CONCLUSIONS

As was reviewed in this article, radical species play more important role in perfluoroalkylation than in alkylation. Perfluoroalkyl iodides have been used for a long time as reagents for the generation of perfluoroalkyl radicals. Recently, as effective reagents for the generation of perfluoroalkyl radicals, TNS-Tf, esters of N-hydroxypyridine

2-thione, and bis(perfluoroalkanoyl) peroxides have been developed. On the other hand, perfluoroalkyl iodides and bis(perfluoroalkanoyl) peroxides were found to suffer one electron reduction by metals, anions, or electron-rich substrates to give effectively perfluoroalkyl radicals under mild conditions Especially, the peroxides were found to be good electron acceptors, and by the use of the electron-transfer reactions from the substrates to the peroxides, perfluoroalkyl groups could be effectively introduced into various anions, olefins, and aromatic rings. Fluorine, due to its strong electronegativity, lowers the energy level of LUMO of the organofluorine compounds, so the electron-transfer reactions in organofluorine chemistry are expected to be of considerable value.

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