Chem. Rev. **1996,** *96,* 1779–1808 **1779**

Fluorinated Peroxides

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Received November 9, 1995 (Revised Manuscript Received March 21, 1996)

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I. Introduction

Recently, there has been considerable interest in organofluorine compounds which exhibit various properties such as biological activity, low surface energy, excellent chemical and thermal stability, low refractive index, and dielectric constants which cannot be achieved in the corresponding nonfluorinated compounds.[1] Fluorinated organic peroxides are also expected to show different chemical reactivities from the corresponding nonfluorinated organic peroxides. In general, nonfluorinated organic peroxides have been classified according to their structure into hydroperoxides (ROOH), percarboxylic acid [RC(=O)OOH], dialkyl peroxides (ROOR), peroxy esters [RC(=O)OOR′], and diacyl peroxides [RC(=O)OO(O=)CR], and numerous reviews of the chemistry and applications of these peroxides have been published.[2] Fluorinated organic peroxides can be similarly classified into dialkyl peroxides (R_FOOR_F), percarboxylic acids [$R_FC(=O)OOH$], hydroperoxides (R_FOOH), peroxy esters [$R_FC(=O)OOR_F$], and diacyl peroxides [$R_FC(=O)OOC(O=)CR_F$]. Fluorinated peroxides, in particular, reviews of fluorinated inorganic peroxides, were reported in 1974 and 1976 by Shreeve et al.[3] However, because studies on fluorinated organic peroxides have been very limited compared with nonfluorinated organic peroxides there have been few reviews of their chemistry and applications except for our recent account of fluorinated organic peroxides[4] and Rakhimov's recent review of fluorinated peroxides. The latter are prepared by using fluorinated aldehydes and ketones as the main starting materials.[5]

Hideo Sawada was born in Gunma, Japan, on February 9, 1956. He received his B.S. degree in 1978 from Gunma University and M.S. degree in 1980 from Tokyo Metropolitan University. He was associated with NOF Corporation from 1980 and received his Ph.D. degree in 1986 from Tokyo Metropolitan University. In 1993, he accepted a position as Associate Professor at Nara National College of Technology. His current research interests concern the decomposition behavior of fluorinated organic peroxides and the synthesis and properties of novel fluorinated compounds using fluorinated organic peroxides. He received the Progress Award of the Japan Oil Chemists' Society in 1992, the Award of the Japan Society of Colour Material in 1994, and the Award of the Japan Research Institute of Material Technology in 1996.

Fluorinated peroxides, especially, fluorinated alkanoyl peroxides, are expected to exhibit quite different decomposition behaviors from the corresponding nonfluorinated alkanoyl peroxides, owing to the strong electron-withdrawing properties of the fluoroalkyl groups. In fact, the presence of two strong electron-withdrawing groups in alkanoyl peroxides can greatly weaken the O−O bond in addition to lowering the energy level of the antibonding O−O bond compared to the corresponding nonfluorinated peroxides. These unique properties of fluorinated organic peroxides were applied to the introduction

S0009-2665(94)01148-9 CCC: $25.00

of fluoroalkyl groups into various substrates via either a radical process or a single electron transfer. Usually, the introduction of perfluoroalkyl groups is not easy since the usual alkylation methods cannot be applied to perfluoroalkylation due to the strong electronegativity of fluorine. Perfluoroalkyl groups are, therefore, introduced through the ester bond, and these materials are in general unstable under acid or alkaline conditions, owing to the ester moieties. The development of a novel synthetic method for direct fluoroalkylation has been long sought. In general, perfluoroalkylations with perfluoroalkyl iodides provide a convenient method for introducing perfluoroalkyl groups, since these starting materials can be handled easily and are commercially available. In particular, copper-induced Ullmann-type reactions with perfluoroalkyl iodides are well-known in the preparation of perfluoroalkylated compounds with carbon−carbon bond formation.[6] Since fluoroalkanoyl peroxides are a convenient tool for the introduction of the corresponding fluoroalkyl groups into various organic molecules via a radical or a single electron-transfer process, such novel fluoroalkylated organofluorine compounds are strongly expected to have greater application in a variety of fields.

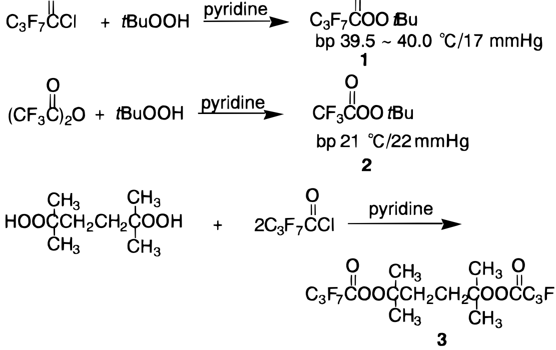
In the present review, we would like to survey the synthesis and reactions of a series of fluorinated peroxides in accordance with the above structural classification of peroxides with particular emphasis on the fluorinated alkanoyl peroxides which exhibit nontypical decomposition behaviors and reactivities from the corresponding nonfluorinated peroxides.

II. Mono- and Bifunctional Fluorinated Peroxy Esters

A. Synthesis of Mono- and Bifunctional Fluorinated Peroxy Esters

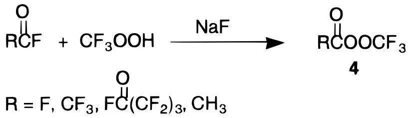
It is generally well-known that peroxy esters can be prepared by the reaction of hydroperoxides with acid anhydrides under basic conditions.[7] Similarly fluorinated peroxy esters (**1** and **2**) can be prepared by the reaction of the hydroperoxides with fluorinated acyl chlorides or fluorinated acid anhydrides in the presence of pyridine as the base. Recently, this method was applied to the synthesis of the bifunctional fluorinated peroxy ester 2,5-dimethyl-2,5-bis(heptafluorobutyrylperoxy)hexane (**3**).[8] However, there have been only a few reports of the synthesis of these fluorinated peroxy esters as shown in Scheme 1.[9,10]

Scheme 1



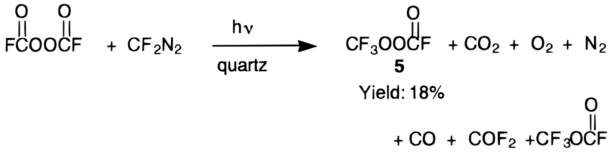
DesMarteau et al. demonstrated that a series of trifluoromethyl peroxy esters (**4**) can be prepared by the reaction of acyl fluorides with trifluoromethyl hydroperoxide in the presence of NaF[11] (Scheme 2).

Scheme 2



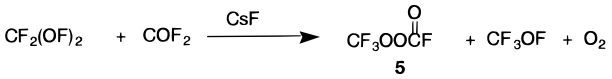
Talbott et al. reported that perfluoroperoxy ester [$FC({=}O)OOCF_3$] is obtained in low yields by the photolysis of fluoroformyl peroxide and difluorodiazirine[12] (Scheme 3).

Scheme 3



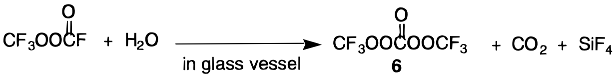
Trifluoromethyl peroxy ester **5** was also prepared in excellent to moderate yields by the reaction of $CF_2(OF)_2$ with COF_2 in the presence of CsF[12] (Scheme 4).

Scheme 4



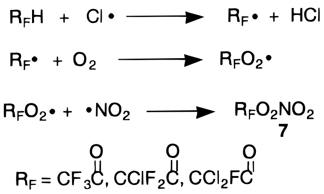
Bis(trifluoromethyl) peroxycarbonate (**6**) was obtained by the hydrolysis of trifluoromethyl peroxy ester **5**[13] (Scheme 5).

Scheme 5



Very recently, a series of fluorinated peroxynitrates **7** were prepared in situ by the photolysis of $R_FH/Cl_2/O_2/N_2$ mixtures[14] (Scheme 6).

Scheme 6



The fluorinated peroxy ester of phosphorus, trifluoromethyl peroxyphosphoryl difluoride **8**, $F_2P({=}O)OOCF_3$], is prepared in 87% yield by condensing *μ*-oxo-bis(phosphonyl difluoride) and trifluoromethyl hydroperoxide in the absence of solvent[15] (Scheme 7).

Scheme 7

$$P_2O_3F_4 + CF_3OOH \rightarrow \underset{\mathbf{8}}{F_2P({=}O)OOCF_3} + F_2P({=}O)OH$$

Table 1. Rate Constants for the Thermal Decomposition of *tert*-Butyl Peroxy Esters in Various Solvents

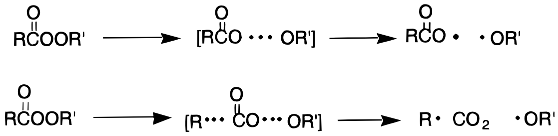
peroxy ester	T (°C)	$k_d \times 10^5$ (s^{-1})	solvent
$CH_3CO_2OC(CH_3)_3$	130	0.57	benzene
	130	0.51	hexane
$CH_3(CH_2)_8CO_2OC(CH_3)_3$	110	5.41	propionic acid
	110	8.30	chlorobenzene
	110	6.58	nitrobenzene
	110	6.39	diphenylether

This peroxy ester can be purified by distillation in vacuo, and was extensively studied as a synthetic intermediate.

B. Reactions of Mono- and Bifunctional Fluorinated Peroxy Esters

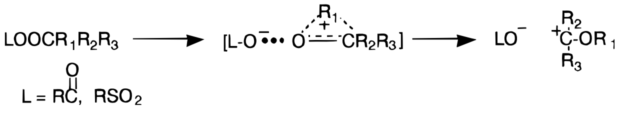
It is well-known that peroxy esters [RC(=O)OOR′] decompose with a homolytic or ionic cleavage of the O−O bond.[15] Radical decomposition of peroxy esters has been shown to involve only oxygen−oxygen bond breaking or a concerted (two-bond) homolysis in the rate-determining step as shown in Scheme 8.[16]

Scheme 8



Pryor et al. reported that the most restrictive differentiation of one-bond vs multibond homolysis of *tert*-butyl peroxy esters is highly dependent on the enthalpy of activation ($\Delta H^\ddagger$). Peroxy esters with $\Delta H^\ddagger$ greater than 33 kcal/mol decompose via a one-bond homolysis, while those with $\Delta H^\ddagger$ less than 27 kcal/mol decompose via a multibond (concerted) homolysis.[17] On the other hand, Winstein, Bartlett, and Leffler et al. independently reported that *tert*-butyl peroxy esters derived from strong organic acids such as *p*-nitrobenzoic acid and *p*-toluenesulfonic acid, or cumyl peroxy esters such as cumyl peracetate might well undergo an ionic cleavage accompanied by a Criegee rearrangement[18] (Scheme 9).

Scheme 9



Although the mechanism for the thermolysis of a series of peroxy esters has been extensively investigated studies using fluorinated peroxy esters are very limited. Fluorinated peroxy esters are expected to exhibit a different decomposition character from the corresponding aliphatic peroxy esters due to the strong electron-withdrawing properties of fluorine.

In general, it is well-known that thermal decomposition rates of *tert*-butyl peroxy esters to afford a homolytic cleavage as shown in Table 1 are not affected by solvent polarity.[19]

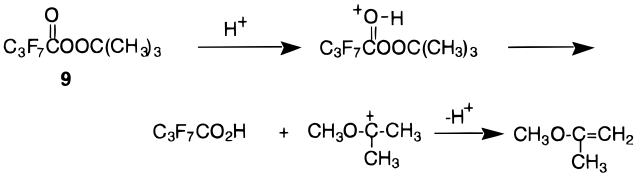
On the other hand, as listed in Table 2, the decomposition of fluorinated peroxy esters $C_3F_7C(=O)OOC(CH_3)_3$ was reported to be considerably affected by solvent polarity. The decomposition proceeded homolytically in nonpolar solvents such as octane and benzene, whereas ionic decomposition with a Criegge rearrangement became dominant in polar solvents such as nitrobenzene and pyridine. As listed in Scheme 10, the fluorinated peroxy ester **9** was shown to undergo acid-catalyzed decomposition. The anomalous behavior regarding the thermal decomposition of highly acid-sensitive peroxy esters is well-known, and pyridine has usually been used to prevent autocatalysis as shown in Table 2.[20,21]

Table 2. Thermal Decomposition of $C_3F_7C(=O)OOC(CH_3)_3$ in the Presence of Equivalent Molar Pyridine in Various Solvents

solvent	$k_d \times 10^5$ (s^{-1}, 65 °C)	$\Delta H^\ddagger$ (kcal/mol)
benzene	1.61	26.0
toluene	1.88	21.4
methoxybenzene	13.78	22.8
nitrobenzene[a]	41.97	19.9
pyridine[a]	68.75	18.3
methanol[a,b]	177.33	10.6
octane[c]	0.03	32.7

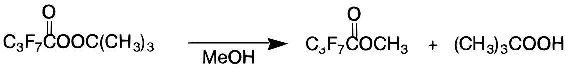
[a] Calculated from rates at lower temperatures. [b] In the absence of pyridine. [c] Calculated from rates at higher temperatures.

Scheme 10



In contrast, in methoxybenzene, the decomposition is characteristic of mixed ionic and radical cleavages. In methanol, this peroxy ester underwent the transesterification shown in Scheme 11.[18,19]

Scheme 11



9

The value of the activation energy ($\Delta E_a = 22.6$ kcal/mol) of the bulk polymerization of styrene initiated by $C_3F_7C(=O)OOC(CH_3)_3$ showed that this peroxy ester decomposed homolytically.[22]

Trifluoromethyl peroxyphosphoryl difluoride (**10**) decomposed slowly at 22 °C and rapidly at 115 °C to afford difluorocarbonyl, phosphorus oxyfluoride, and oxygen as shown in Scheme 12.[23]

Scheme 12

$$F_2P(=O)OOCF_3 \rightarrow COF_2 + POF_3 + 1/2O_2$$

10

Interestingly, the reaction of this fluorinated peroxy ester with CF_3OF gives the fluorinated trioxide (**11**)[23] (Scheme 13).

Scheme 13

$$F_2P(=O)OOCF_3 + CF_3OF \rightarrow CF_3OOOCF_3 + POF_3$$

10 **11**

The reaction of **10** with methyl alcohol gives a similar methanolysis to $C_3F_7C(=O)OOC(CH_3)_3$ (Scheme 14).

Scheme 14

$$\underset{\mathbf{10}}{F_2P(=O)OOCF_3} + MeOH \rightarrow F_2P(=O)OMe + CF_3OOH$$

On the other hand, the photochemical decomposition of this fluorinated peroxy ester in the presence of oxygen affords bis(trifluoromethyl) peroxide and bis(trifluoromethyl) trioxide via a reaction involving the tetraoxide which is derived from the trifluoromethylperoxy radical ($CF_3OO^\bullet$) intermediate rather than the trifluoromethoxy radical ($CF_3O^\bullet$)[23] (Scheme 15).

Scheme 15

$$\underset{\mathbf{10}}{F_2P(=O)OOCF_3} + O_2 \xrightarrow{h\nu} P_2O_3F_4 + [CF_3OOOOCF_3]$$

$$[CF_3OOOOCF_3] + O_2 \xrightarrow{h\nu} CF_3OOCF_3 + CF_3OOOCF_3 + {}^1\!/_2 O_2$$

It has been suggested that partly halogenated chlorofluorocarbons may contribute to the greenhouse effect. The environmental impact of these chemicals depends on their tropospheric lifetime and the formation of long-lived intermediates.[24a] Therefore, there is considerable interest in the degradation mechanism of these compounds, especially their NO_2 derivatives. The atmospheric degradation of CCl_3CH_3 is believed to proceed via the peroxy radicals $CCl_3CH_2O_2$ and $CCl_3C(=O)OO$.[24b]

From these species, the peroxynitrates $CCl_3CH_2O_2NO_2$ and $CCl_3(C=O)O_2NO_2$ can be formed by the addition of NO_2. Similarly, peroxynitrate may form in the same way from the precursors CCl_3FCH_3, $CClF_2CH_3$, and CF_3CH_3.[14] The thermal lifetimes of a series of fluorinated peroxynitrates, $CF_3C(=O)O_2NO_2$, $CClF_2C(=O)O_2NO_2$, and $CCl_2F(C=O)O_2NO_2$, are reported as >4000 years in the upper troposphere.[14]

Similarly, the thermal stability of $FC(=O)OONO_2$ was investigated using a long-path Fourier transform IR spectrometer.[25]

Recently, the conformational properties of numerous peroxy esters including $CF_3C(=O)O_2Me$ were studied using a theoretical ab initio MO approach.[26]

Bifunctional fluorinated peroxy ester 2,5-dimethyl-2,5-bis(heptafluorobutyrylperoxy)hexane (**3**) was found to decompose faster than a monofunctional fluorinated peroxy ester such as $C_3F_7C(=O)OOC(CH_3)_3$.[8] This bifunctional peroxy ester was also found to be a useful radical initiator for the styrene monomer.

III. Fluorinated Dialkyl Peroxides

A. Synthesis of Fluorinated Dialkyl Peroxides

In general, it is well-known that dialkyl peroxides are prepared by the nucleophilic replacement of hydroperoxides in the presence of acid or base catalysts.[27,28]

However, the synthesis of fluorinated dialkyl peroxides has hitherto been limited. The following specific methods have been reported:

(a) Trifluoromethyl peroxide (**12**) can be synthesized by the reaction of CF_3OF and COF_2 at 275 °C for 3 h at 100 atm in 93% yield[29] (Scheme 16).

Scheme 16

$$CF_3OF + COF_2 \rightarrow \underset{\mathbf{12}\,:\ \text{bp}\ -37\,^\circ\text{C}}{CF_3OOCF_3}$$

This peroxide was also prepared by the fluorination of CO in the presence of AgF_2[30] (Scheme 17).

Scheme 17

$$2CO + 3F_2 \xrightarrow{AgF_2} \underset{\mathbf{12}}{CF_3OOCF_3}$$

The photolysis of trifluoromethyl hypochlorites afforded trifluoromethyl peroxide in good yield[31] (Scheme 18).

Scheme 18

$$CF_3OCl \xrightarrow[\text{100W}]{\text{Pyrex}} CF_3OOCF_3$$

Cady et al. reported that trifluoromethyl peroxide was prepared by the fluorination of xenon with CF_3OF[32] (Scheme 19).

Scheme 19

$$2CF_3OF + Xe \rightarrow CF_3OOCF_3$$

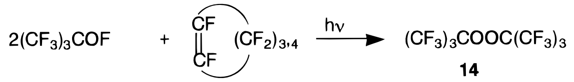
Xenon difluoride was used in the synthesis of bis(pentafluorophenyl) peroxide (**13**)[33] (Scheme 20).

Scheme 20

$$C_6F_5OH + XeF_2 \rightarrow \underset{\mathbf{13}}{C_6F_5OOC_6F_5} + Xe + HF$$

Perfluoro-*tert*-butyl peroxide (**14**) was prepared by the photolysis of $(CF_3)_3COF$ with perfluorocycloolefins[34] (Scheme 21) or the reaction of N_2F_2 with $(CF_3)_3COF$[35] (Scheme 22).

Scheme 21



14

Scheme 22

$$2(CF_3)_3COF + N_2F_4 \rightarrow \underset{\mathbf{14}}{(CF_3)_3COOC(CF_3)_3}$$

ClF_3 is a convenient reagent for the synthesis of fluorinated alkyl peroxides as shown in Scheme 23.[36]

Scheme 23

$$2(CF_3)_3COH + ClF_3 \rightarrow \underset{\mathbf{14}}{(CF_3)_3COOC(CF_3)_3}$$

Unsymmetrical fluorinated dialkyl peroxides [R_F-OOR_F'] such as pentafluoroethyl trifluoromethyl peroxide (**15**) were prepared by the fluorination of trifluoroacetate salts[37] (Scheme 24).

Scheme 24

$$CF_3CO_2M + F_2 \rightarrow \underset{\mathbf{15}}{C_2F_5\text{-}OO\text{-}CF_3}$$

Similarly, F_2O is a useful reagent for preparing unsymmetrical fluorinated dialkyl peroxides[38] (Scheme 25).

Scheme 25

$$F_2O + C_2F_5OCs \rightarrow C_2F_5\text{-OO-}CF_3$$

15

Bis[difluoro(fluorooxy)methyl] peroxide (**16**) was prepared by the fluorination of bis(fluoroformyl) peroxide in the presence of KF[39] (Scheme 26).

Scheme 26

$$F(C{=}O)OOC({=}O)F + F_2 \xrightarrow{KF} FOCF_2OOCF_2OF$$

16

The structure of CF_3OOCF_3 was evaluated by the ab initio gradient method, and the structure of CH_3OOCH_3 was also computed for comparison.[40]

Fluoroperoxytrifluoromethane [CF_3OOF] was first prepared by Thompson,[41] and the improved preparative methods of this peroxide were reported by Solomon and DesMarteau.[42,43]

DesMarteau et al. reported that $(CF_3)_3COOF$ can be prepared by the reaction of F_2 with $(CF_3)_3COO^-$.[44]

A series of sulfur fluoride and oxyfluoride peroxides (**17**−**19**) are prepared in good yields using SOF_4, SF_5OCl, and $ClOSO_3F$ as shown in Scheme 27.[45]

Scheme 27

$$SOF_4 + S_2O_6F_2 \rightarrow SF_5OOSO_2F \text{ (Yield: 81\%)}$$

17

$$SF_5OCl \xrightarrow{h\nu} SF_5OOSF_5 \text{ (Yield: 85\%)}$$

18

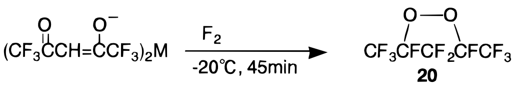
$$2ClOSO_3F \xrightarrow{h\nu} S_2O_6F_2 \text{ (Yield: 94\%)}$$

19

SF_5OOH, SF_5OOF, and SF_5OOCl were prepared by DesMarteau et al., and the formation of the trioxide (SF_5OOOSF_5) was postulated.[46]

Talbott reported that perfluoro-3,5-dimethyl-1,2-dioxolane (**20**) is obtained by the fluorination of copper(II) or nickel(II) hexafluoroacetylacetonate[47] (Scheme 28).

Scheme 28

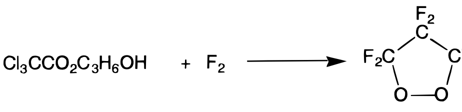


20

cis-trans isomer

Prager reported the fluorination of 1-hydroxy-3-trichloroacetoxypropane to afford the hexafluoro-1,2-dioxolane (**21**)[48] (Scheme 29).

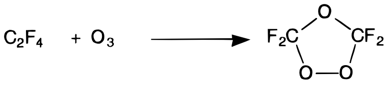
Scheme 29



21

A fluorinated trioxolane tetrafluoro-1,2,4-trioxolane (**22**) was prepared by the reaction of C_2F_4 with ozone[49] (Scheme 30).

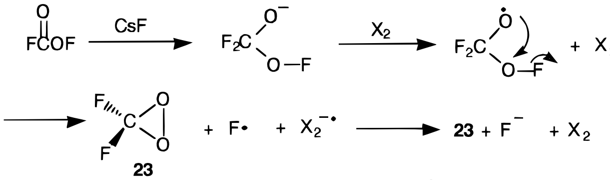
Scheme 30



22

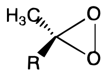
Fluoroformyl hypofluorite (FC=O)OF was reported to be an important precursor in the synthesis of difluorodioxirane (**23**) as shown in Scheme 31.[50]

Scheme 31



X = Cl$_2$, ClF, F_2

Methyl(trifluoromethyl)dioxirane(**24a**) was isolated by the reaction of CF_3COMe with potassium peroxomonosulfate and fully characterized spectroscopically.



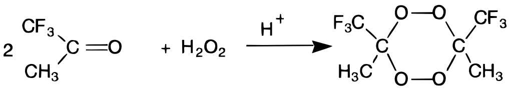
24-a R = CF_3
24-b R = CH_3

The yellow solutions of this peroxide could be stored at −20 °C with only minor loss of dioxirane content (~6%, 48 h), while a half-life of ~20 h was estimated at 15 °C. Thus, not only this fluorinated dioxirane (**24a**) but also dimethyldioxirane (**24b**)[51] are moderately stable in solution at room temperature, but cannot be isolated as pure compounds.[52]

In contrast, Sander et al. reported that dimesityldioxirane is isolable at room temperature both in solution and pure by the oxidation of the corresponding diazo compound.[53]

Recently, Adam et al. reported that fluorinated cyclic ketone diperoxides such as 3,6-bis(trifluoromethyl)-3,6-dimethyl-1,2,4,5-tetraoxane (trifluoroacetone diperoxide, **25**) can be prepared by the reaction of trifluoroacetone with 30% hydrogen peroxide in the presence of concentrated sulfuric acid in good yield[54] (Scheme 32).

Scheme 32



25

The synthesis and reactivities of fluorinated trioxides such as CF_3OOOCF_3 was studied by Fox and DesMarteau et al.[55−62]

B. Reactions of Fluorinated Dialkyl Peroxides

Roberts showed that a series of telomers [$CF_3O(C_3F)_nOCF_3$] (**26**) were obtained by the reaction of bis(trifluoromethyl) peroxide with hexafluoropropene[28] (Scheme 33).

Scheme 33

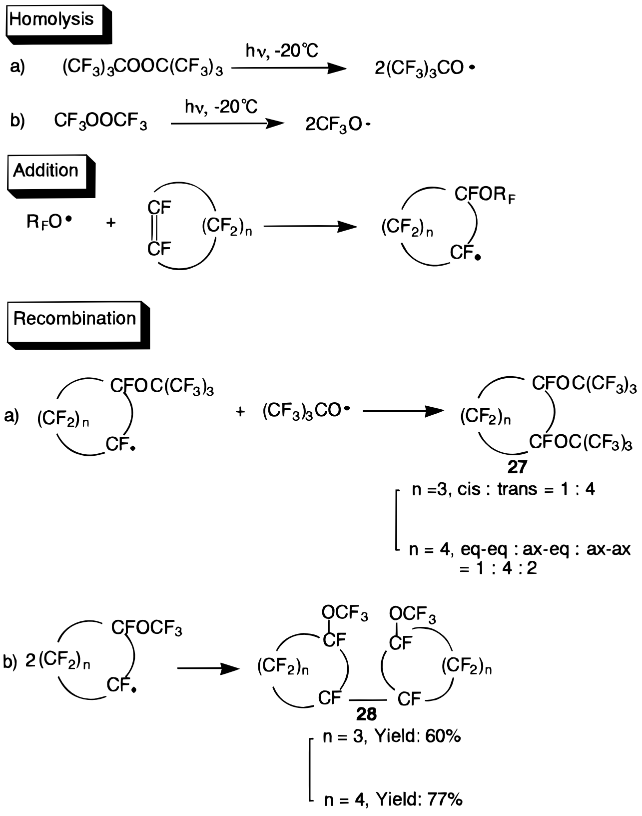
$$CF_3OOCF_3 + CF_3CF{=}CF_2 \rightarrow CF_3O(C_3F_6)_nOCF_3$$

12 **26**

The thermal decomposition of perfluoro-*tert*-butyl peroxide was studied in the gas phase. The decomposition of this peroxide was found to follow a first-order equation to give $(CF_3)_3CO^\bullet$ radical as the product, which decomposes with β-scission to afford perfluoroacetone and trifluoromethyl radical.[63]

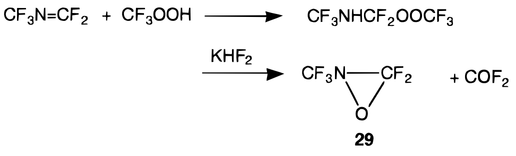
The photolysis of perfluorocycloolefins (c-C_5H_8, c-C_6F_{10}) with perfluoro-*tert*-butyl peroxide and trifluoromethyl peroxide afforded 1:1 adducts **27** and dimeric products **28**, respectively (Scheme 34). In the reaction with perfluoro-*tert*-butyl peroxide, the formation of 1:1 adducts **27** and not dimeric products is due to the steric hindrance of the perfluoro-*tert*-butoxy radical. On the other hand, it was reported that β-fission of the $(CF_3)_3CO^\bullet$ radical is unlikely since only the decomposition products derived from the perfluoro-*tert*-butoxy radical were obtained.[35]

Scheme 34



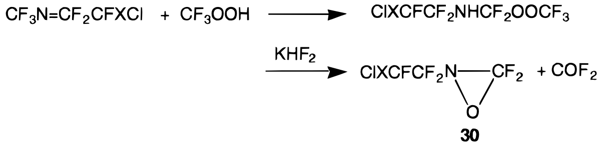
Addition of CF_3OOH to perfluoro-2-azapropene ($CF_3N{=}CF_2$) affords the fluorinated dialkyl-type peroxide ($CF_3NHCF_2OOCF_3$). The reactions of $CF_3OOCF_2NHCF_3$ with various metal fluorides such as LiF, NaF, KF, CsF, KHF_2, and PbF_2 were studied by DesMarteau et al., and this peroxide was proposed as being useful in preparing fluorinated oxaziridine **29**[64] (Scheme 35).

Scheme 35



Similarly, $CF_3OOCF_2NHCF_2CFXCl$ (X = F, Cl, Br) was prepared by the reaction of $CF_2{=}NCF_2CFXCl$ (X = F, Cl, Br) with trifluoromethyl hydroperoxide (CF_3OOH) and subsequent treatment with KHF_2, giving the corresponding oxaziridine (**30**) in excellent yields[65] (Scheme 36).

Scheme 36



Bis(perfluoroalkyl) trioxides are well-documented as being stable, three oxygen atom species similar to ozone.[66] For example, the decomposition behavior of CF_3OOOCF_3 and CF_3OOF were studied in detail. Photolysis of an argon matrix sample of CF_3OOF at 8 K affords CF_4 and the CF_3OO radical. The formation of CF_4 is believed to occur by a concerted intramolecular process in which the O−F and C−O bonds are broken along with the simultaneous formation of a C−F bond and molecular oxygen.[67]

Bis(trifluoromethyl) trioxide photodissociates to produce CF_3OCF_3, CF_4, COF_2, and the CF_3OO radical as the predominant infrared observable products.[67]

ESR analyses of the radical produced by the photolysis in solution at −196 °C of CF_3OOCF_3 in the presence of small amounts of oxygen showed the presence of a trioxy radical ($CF_3OOO^\bullet$).[67−69]

Fox et al. measured the gas-phase core-level binding energies for CF_3OOOCF_3 and CF_3OOCF_3.[70]

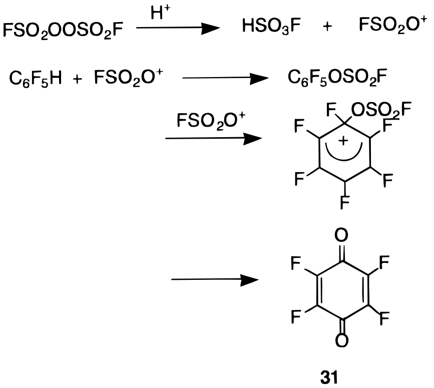
Recently, the 248 nm photolysis of CF_3OOCF_3 was also investigated in detail.[71]

The $CF_3OO^\bullet$ radical has been postulated as a chemical intermediate in various reactions of fluoroperoxy compounds.[72]

Very recently, photolysis of CF_3OOCF_3 at 245 nm in the presence of O_3 in oxygen has been shown to afford CF_2O and CF_3OOOCF_3 as products.[73]

Fluorosulfonyl peroxide decomposes smoothly in the presence of strong acid to afford the fluorosulfonyl cation. This fluorosulfonyl cation reacts with pentafluorobenzene to give fluoranil (**31**)[74] (Scheme 37).

Scheme 37



Fluoroalkyl radicals which are obtained by the thermal decomposition of fluoroalkyl peroxide [$ROCF_2OCF_2CF_2OOCF_2CF_2OCF_2OR'$] were directly observed by ESR[75] (Scheme 38).

Kevan et al. used ESR to demonstrate the presence of two different peroxy radicals [the midchain peroxy radical $-CF_2CF(OO^\bullet)CF_2-$ and the end-chain peroxy

Scheme 38

$$ROCF_2OCF_2CF_2OOCF_2CF_2OCF_2OR' \rightarrow [ROCF_2OCF_2CF_2O\bullet]$$
$$\rightarrow ROCF_2OCF_2\bullet + CF_2{=}O$$

radical $-CF_2CF_2CF_2OO^\bullet$] formed in the oxidation of poly(tetrafluoroethylene).[76]

Bis(trifluoromethanesulfonyl) peroxide (**32**) decomposes smoothly at the room temperature to afford trifluoromethyl trifluoromethanesulfonate as the main product[77] (Scheme 39).

Scheme 39

$$\underset{\mathbf{32}}{CF_3SO_2OOSO_2CF_3} \rightarrow \underset{\mathbf{33}\ \text{(Yield: 63\%)}}{CF_3SO_3CF_3} + CF_3CF_3 + SO_3$$

The synthesis and applications of a series of fluorosulfur peroxides such as $SF_5OSF_4OOSF_4OSF_5$, FSO_2OOSO_2F, $SF_5OSF_4OOSF_5$, and SF_5OOSF_5 were reported. For example, it was demonstrated that SF_5OOSF_5 (**34**) reacts with SO_2 to give $SF_5OSO_2OSF_5$ (**35**)[78] (Scheme 40).

Scheme 40

$$\underset{\mathbf{34}}{SF_5OOSF_5} + SO_2 \rightarrow \underset{\mathbf{35}}{SF_5OSO_2OSF_5}$$

Bis(pentafluorosulfur) peroxide (SF_5OOSF_5) decomposes in the presence of carbon monoxide to afford CO_2 and S_2F_{10} as the final products.[79]

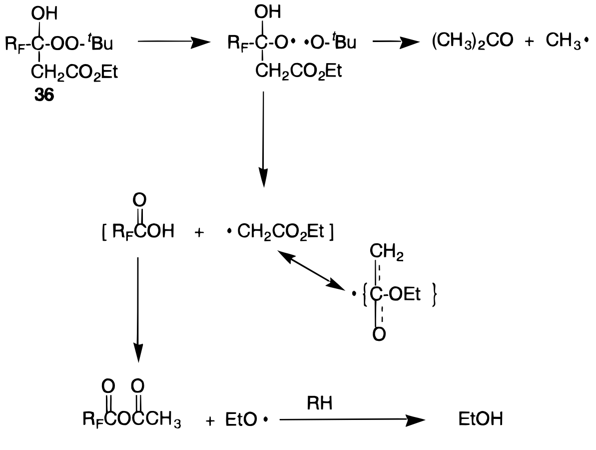
Peroxodisulfuryl difluoride was applied to a general synthesis of lactones from the corresponding carboxylic acids.[80]

The thermal decomposition of dialkyl peroxides containing perfluoroalkyl and polyfluoroalkyl groups [$R_FC(OO^tBu)(OH)CHXCO_2Et$ (**36**)] was studied and the decomposition rates (k_d) for these peroxides at 70 °C are as follows:

R_F	X	k_d (s^{-1})
$H(CF_2)_4$	Cl	0.47×10^{-3}
$H(CF_2)_4$	H	0.73×10^{-3}
$H(CF_2)$	H	0.47×10^{-3}
CF_3	H	0.67×10^{-3}

The decomposition behavior of these fluorinated dialkyl peroxides are considered to proceed with initial O−O bond homolysis[81] (Scheme 41).

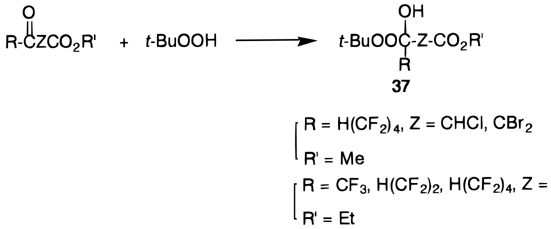
Scheme 41



In some fluorinated peroxides containing a nitro group [$ROONO_2$], the introduction of fluorine strengthens the oxygen−nitrogen bond: [bond energy kcal/mol)] 23.9 (R = CCl_3), 24.6 (R = CCl_2F), 24.9 (R = $CClF_2$).[82]

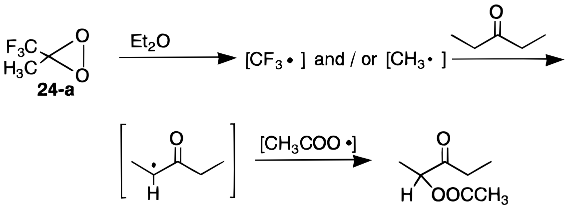
Fluorinated *β*-keto esters react with *tert*-butyl hydroperoxide to afford α-hydroxyalkyl peroxides (**37**)[83] (Scheme 42).

Scheme 42



Thermal decomposition of methyl(trifluoromethyl)dioxirane (**24a**) induced by dialkyl ethers was investigated by Messeguer et al. The decomposition products shown in Scheme 43 support the hypothesis of an acetyloxy radical generation during this peroxide decomposition process.[84]

Scheme 43

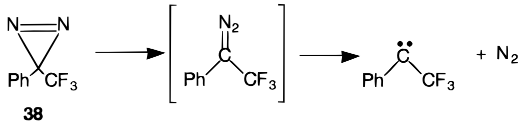


Similarly, Adam et al. reported the hypothesis of a radical chain process initiated by the attack of the CH_3 and CF_3 radicals on methyl(trifluoromethyl)dioxirane (**24**) to give α-alkoxy-α-alkoxy radical intermediates, which would afford ester derivatives by *β*-alkyl fragmentation.[85]

Furthermore, Adam et al. established the structure of methyl(trifluoromethyl)dioxirane (**24a**) induced by catalytic amounts of iodide anion.[86]

In contrast, 3-phenyl-3-(trifluoromethyl)diazirine (**38**) decomposes to afford its diazo isomer and a free carbene[87] (Scheme 44).

Scheme 44

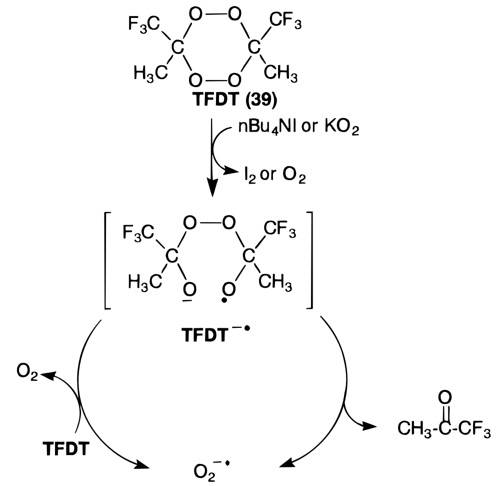


Methyl(trifluoromethyl)dioxirane (**24a**) is also applicable to both the epoxidation of olefins[88] and the enantioselective oxidation of sulfides to give sulfoxides[89] by using this peroxide generated in situ.

3,6-Bis(trifluoromethyl)-3,6-dimethyl-1,2,4,5-tetroxane (TFDT) (**39**) was shown to be quantitatively converted into trifluoroacetone and dioxygen by a catalytic amount of tetrabutylammonium iodide through a reductive electron-transfer chain reaction via the superoxide ion[54] (Scheme 45).

Fluorinated dialkyl peroxides such as $CF_3O(CF_2O)_nCF_2OO(CF_2CF_2O)_mCF_3$ (average molecular weight 3000) were used as radical initiators for the copolymerization of methyl methacrylate and sty-

Scheme 45



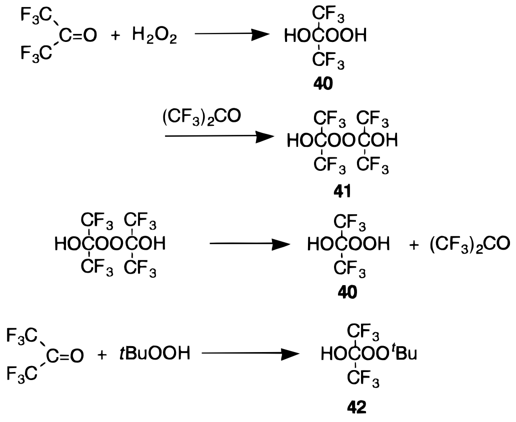
rene. The copolymers obtained exhibited higher stability than polymers which were prepared in the presence of conventional radical initiators. This is suggested as being dependent upon the introduction of fluoroalkyl end groups into such polymers.[90]

IV. Fluorinated Percarboxylic Acids and Hydroperoxides

Much attention has been focused on hexafluoroacetone, which is seen as a useful precursor in the synthesis of novel organofluorine compounds due to its unique reactivity toward numerous nucleophiles.[91]

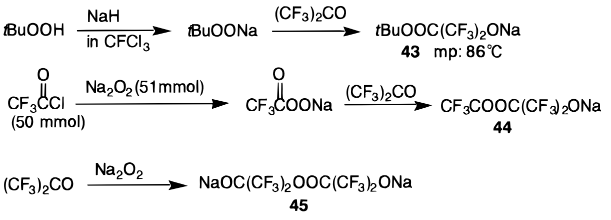
In the synthesis of fluorinated organic peroxides, the peroxides (**40**−**42**) shown in Scheme 46 are prepared by the reaction of hexafluoroacetone with nucleophiles such as hydrogen peroxide and *tert*-butyl hydroperoxide[92]

Scheme 46



Fluorinated organic peroxides (**43**−**45**) which are soluble in water and polar solvents are prepared by the reaction of hexafluoroacetone with the sodium salts of hydroperoxides[93] (Scheme 47).

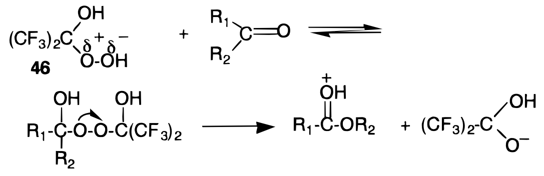
Scheme 47



These fluorinated peroxides are less flammable and less explosive than the corresponding hydrocarbon analogs.

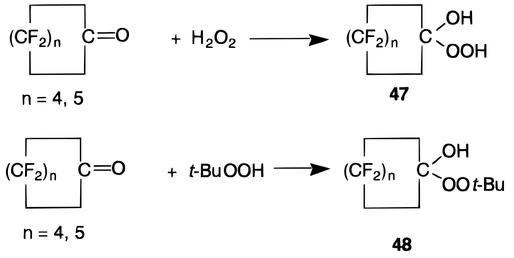
Fluorinated peroxy acid [$(CF_3)_2C(OH)OOH$] (**46**), which is formed by the reaction of hexafluoroacetone with hydrogen peroxide, can be used as a Baeyer−Villiger-type oxidizing reagent[94] (Scheme 48).

Scheme 48



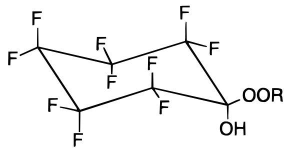
In addition, the reaction of hydrogen peroxide (or *tert*-butyl hydroperoxide) with perfluorocyclohexanone or perfluorocyclopentanone was studied, and similar products (**47** and **48**) to the reactions with hexafluoroacetone were obtained[95] (Scheme 49).

Scheme 49



The structural characteristics of fluorinated peroxides which are obtained by the reaction of hydrogen peroxides (or *tert*-butyl hydroperoxide) with perfluorocyclohexanone or perfluorocyclopentanone were studied by IR spectroscopy, ^{19}F NMR spectroscopy, and quantum-chemical calculations. It was demonstrated that the peroxide group is in the equatorial position (Scheme 50), and the introduction of fluorine atoms promotes opening of the ring.[96]

Scheme 50



49 (R = H, *t*-Bu)

DesMarteau et al. showed that trifluoromethyl hydroperoxide is obtained by the hydrolysis of $CF_3OOC(=O)F$ in good yield[97] (Scheme 51).

Scheme 51

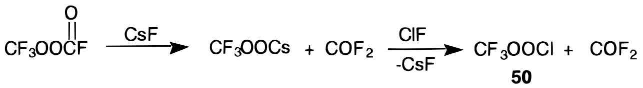
$$\underset{\mathbf{5}}{CF_3OOC(=O)F} + H_2O \rightarrow \underset{\sim 80\%}{CF_3OOH} + CO_2 + HF$$

Trifluoromethyl hydroperoxide is soluble in water without decomposition, and a freshly prepared 0.5 M solution has a pH of about 4. The reaction of trifluoromethyl hydroperoxide with chlorine monofluoride (ClF) affords chloroperoxytrifluoromethane (CF_3OOCl) (**50**).[97a] A superior method for synthesis of **50** from $CF_3OOC(=O)F$ was reported by DesMarteau et al.[97b] (Scheme 52).

Scheme 52

$$CF_3OOH + ClF \longrightarrow CF_3OOCl + HF$$

50



$$CF_3OOC(=O)F \xrightarrow{CsF} CF_3OOCs + COF_2 \xrightarrow[-CsF]{ClF} CF_3OOCl + COF_2$$

50

It was demonstrated that this peroxide is a stable yellow gas at room temperature and is the first stable compound containing an OOCl linkage.[97a] However, DesMarteau et al. showed that this peroxide has only limited stability at room temperature, decomposing readily to CF_3OCl and O_2.[97b]

Interestingly, this peroxide exhibited quite a different reactivity from those of the perfluoroalkyl hypochlorites.[98] Thus, although CF_3OCl readily adds CO, SO_2, or C_2F_4 to yield $CF_3OC(=O)Cl$, CF_3OSO_2Cl, and $CF_3OC_2F_4Cl$, respectively,[99] CF_3OOCl does not add under similar reaction conditions. This finding is due to a stronger Cl−O linkage in CF_3OOCl. The products obtained from photolysis of CF_3OOCl can be explained by primary cleavage of the O−O bond[97a] (Scheme 53).

Scheme 53

$$CF_3OOCl \xrightarrow{h\nu} CF_3O\cdot + \cdot OCl$$

50

$$2CF_3O\cdot \rightarrow CF_3OOCF_3$$

$$ClO\cdot \rightarrow [ClOOCl] \rightarrow ClO_2 + Cl\cdot$$

Compound **50** is a useful precursor for the preparation of fluorinated dialkyl peroxides ($CF_3OOCH_2CH_2Cl$, $CF_3OOC_2F_4Cl$, $CF_3OOCF_2CH_2Cl$, etc.) since **50** adds readily to olefins such as $CH_2{=}CH_2$, $CF_2{=}CF_2$, and $CF_2{=}CH_2$ to give high yield of these fluorinated peroxides.[97b]

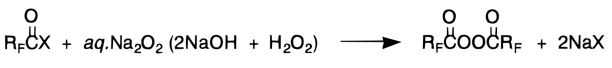
V. Fluorinated Diacyl Peroxides

The attachment of fluoroacyl groups [$R_FC(=O)$] to oxygen-forming diacyl peroxides are expected to exhibit quite different decomposition behavior from that of the nonfluorinated analogs owing to the strong electron-withdrawing properties of the fluoroalkyl groups. In particular, two strong electron-withdrawing groups in diacyl peroxide [$R_FC(=O)OOC(=O)R_F$] are not only able to greatly weaken the O−O bond but also to effectively lower the energy level of the antibonding ($2p\sigma^*$) oxygen−oxygen bond compared with other peroxides. From this point of view, numerous interesting reports on fluorinated diacyl peroxides have been published.[4]

A. Synthesis of Fluorinated Diacyl Peroxides

In general, fluorinated diacyl peroxides **51** as well as nonfluorinated diacyl peroxides can be prepared by the reaction of acyl halides with not only sodium (or potassium) peroxide but also aqueous solutions of NaOH and H_2O_2[100] (Scheme 54).

Scheme 54

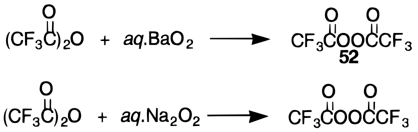


$$R_FC(=O)X + aq.Na_2O_2\,(2NaOH + H_2O_2) \longrightarrow R_FC(=O)OOC(=O)R_F + 2NaX$$

51

In addition, acyl chlorides can be replaced by acid anhydrides[101,102] (Scheme 55).

Scheme 55



$$(CF_3C(=O))_2O + aq.BaO_2 \longrightarrow CF_3C(=O)OOC(=O)CF_3$$

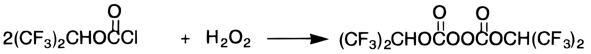
52

$$(CF_3C(=O))_2O + aq.Na_2O_2 \longrightarrow CF_3C(=O)OOC(=O)CF_3$$

52

Fluorinated peroxydicarbonates **53** can also be prepared by the reaction of the corresponding chloroformates with hydrogen peroxides under alkaline conditions as well as the preparation of fluorinated diacyl peroxides[103] (Scheme 56).

Scheme 56

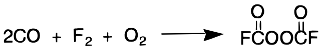


$$2(CF_3)_2CHOC(=O)Cl + H_2O_2 \longrightarrow (CF_3)_2CHOC(=O)OOC(=O)OCH(CF_3)_2$$

53

Bis(fluoroformyl) peroxide (**54**) was obtained in excellent to moderate isolated yields by the reaction of CO, F_2, and O_2 at room temperature for 6 h (Scheme 57). However, this peroxide decomposes easily above room temperature.[104]

Scheme 57



$$2CO + F_2 + O_2 \longrightarrow FC(=O)OOC(=O)F$$

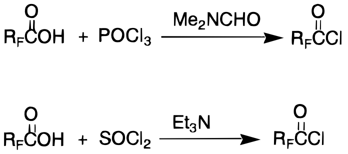
54

In view of the shock sensitivity and thermal instability of fluorinated alkanoyl peroxides, it is advantageous to both store and use these peroxides in dilute halogenated alkane solutions such as 1,1,2-trichloro-1,2,2-trifluoroethane.[105]

However, chlorofluorocarbons such as 1,1,2-trichloro-1,2,2-trifluoroethane are believed to contribute to the stratospheric burden of chlorine and the greenhouse effect. Therefore, the exploration of alternative fluorocarbon solvents for use with fluorinated peroxides was highly desirable. Hydrochlorofluorocarbons such as 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane have been recently reported as useful alternative chlorofluorocarbons for fluorinated peroxides.[106]

Fluorinated acyl halides **55**, which are in general used as starting materials for the preparation of diacyl peroxides, can be easily synthesized by the halogenation of the corresponding carboxylic acids (Scheme 58). The common halogenated reagents such as PCl_3, PCl_5, $SOCl_2$, and $POCl_3$ for carboxylic acids are convenient for these halogenations.[107]

Scheme 58



$$R_FC(=O)OH + POCl_3 \xrightarrow{Me_2NCHO} R_FC(=O)Cl$$

$$R_FC(=O)OH + SOCl_2 \xrightarrow{Et_3N} R_FC(=O)Cl$$

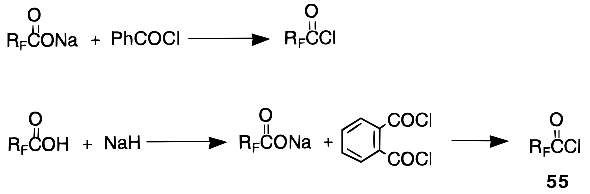
55

Table 3. Physical Data of a Series of Fluoroalkanoic Acids, Fluoroalkanoyl Halides, and Fluoroalkanoyl Peroxides

	R_FCOOH			R_FCOX		$(R_FCOO)_2$	
R_F	bp (°C)	mp (°C)	d_4^{20}	bp (°C)	d_4^{20}	bp (°C)	mp (°C)
CF_3	74	−15.4		X = Cl: −18 = F: −59			
CF_3CF_2	96−98		1.561	X = Cl: 7−9 = F: −30			
$CF_3CF_2CF_2$	119−121		1.651	X = Cl: 38−9 = Br: 52−3 = I: 75−6	1.55 1.735 2.00	19/6mm	−15
$CF_3(CF_2)_3$	139/749mm		1.713	X = Cl: 67.5−68.0			
$CF_3(CF_2)_4$	156		1.762	X = Cl: 85.8−86.0	1.66		
$CF_3(CF_2)_5$	175/742mm		1.792				
$CF_3(CF_2)_6$	190/740mm	53		X = Cl: 129−130 = F: 104			
$CF_3(CF_2)_8$	218/740mm			X = Cl: 173			
$CF_3(CF_2)_{12}$	270/740mm						
$CF_3CF_2CF_2O$-$[CF(CF_3)CF_2$-$O]_{n-2}CF(CF_3)$							
$n = 2$				X = F: 52−56/760mm			
$n = 3$				X = F: 112−116/760mm			
$n = 4$				X = F: 93−96/80mm			
$n = 5$				X = F: 126−131/80mm			
$n = 6$				X = F: 110−114/10mm			

Tiers and Ishikawa independently reported the chlorination of sodium fluorocarboxylates[108,109] (Scheme 59).

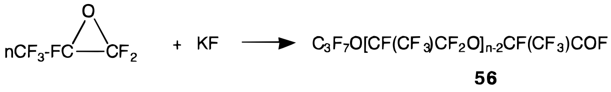
Scheme 59



Fluorinated acyl halides can be also prepared by the reaction of polyfluoroalkanes with $AlCl_3$ and H_2SO_4, and by the telomerization of $CF_2{=}CF_2$ and $CF_2{=}CFCl$ with CF_3I.[110]

Fluorinated acyl fluorides are also applicable to the preparation of the peroxides, and a series of perfluorooxaalkanoyl fluorides (**56**) such as perfluoro-2-methyl-3-oxahexanoyl fluoride ($n = 2$) are obtained by the oligomerization of perfluoropropylene oxide with anhydrous potassium fluoride[111−114] (Scheme 60).

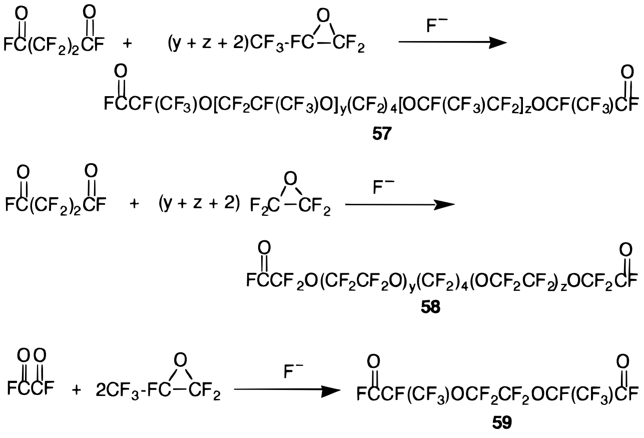
Scheme 60



Similarly, perfluoro-2,4-dimethyl-3-oxapentanoyl fluoride $[(CF_3)_2CFOCF(CF_3)COF]$ can be prepared by the reaction of perfluoropropylene oxide with hexafluoroacetone in the presence of CsF.[115]

Perfluorooxaalkane diacid fluorides (**57**−**59**) are convenient precursors for the preparation of polymeric fluorinated acyl peroxides, and these acid fluorides can be isolated by the oligomerization of perfluoroalkylene oxides[116] (Scheme 61).

Scheme 61



Physical data of a series of fluoroalkanoic acids, fluoroalkanoyl halides, and fluoroalkanoyl peroxides are shown in Table 3.[117]

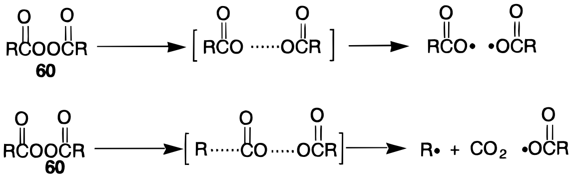
B. Thermal Decomposition of Fluorinated Aroyl Peroxides

In general, it is well-known that diacyl peroxides $[RC({=}O)OOC({=}O)R]$ (**60**) decompose via a radical mechanism (Scheme 62). The radical path usually competes with an ionic mechanism, depending on the ionizing power of the solvent, the structure of the

Table 4. Thermal Decomposition of Alkanoyl Peroxides

peroxide	$k_d \times 10^5$ (10 °C)	ref
$(CH_3)_3CC(=O)OOC(=O)C(CH_3)_3$	19000	122
$(CH_3)_2CHC(=O)OOC(=O)CH(CH_3)_2$	135	123
$CH_3CH_2CH_2C(=O)OOC(=O)CH_2CH_2CH_3$	0.19	124

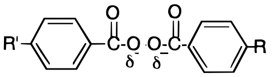
Scheme 62



diacyl peroxide, etc. In the radical decomposition of diacyl peroxides [RC(=O)OOC(=O)R], the following one-bond radical fission and the concerted two-bond fission have been established.

The concerted two-bond fission of diacyl peroxides [RC(=O)OOC(=O)R] depends mainly upon the formation of the stable R radical.[118,119]

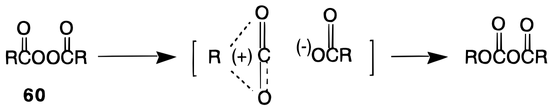
In the thermal decomposition of substituted diaroyl peroxides (**61**), the introduction of electron-donating groups into the phenyl moiety enhances the rate of decomposition of the peroxide. This finding is due to the increase in electrostatic repulsion between the peroxidic oxygen−oxygen atoms.[120]



61

Not only unsymmetrical diacyl peroxides in which one ring bears an electron-withdrawing group and the other an electron-donating substituent but also alkanoyl peroxides possessing secondary and tertiary alkyl groups, generally decompose heterolytically with carboxy inversion[121] (Scheme 63).

Scheme 63



For example, pivaloyl peroxide decomposes more rapidly than isobutyryl peroxide or *n*-butyryl peroxide as shown in Table 4.

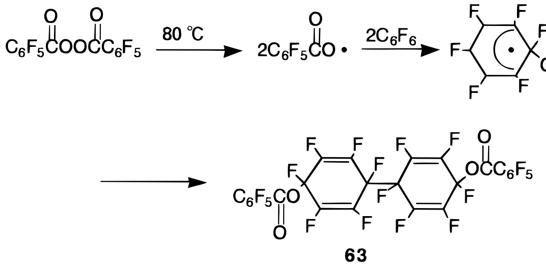
The thermal decomposition of diacyl peroxides, in particular, fluorinated diaroyl peroxides in which the hydrogen atom is replaced by a fluorine atom are expected to have quite different decompositional behavior from the corresponding nonfluorinated peroxides. In fact, pentafluorobenzoyl peroxide [$C_6F_5C(=O)OOC(=O)C_6F_5$] (**62**) was shown to exhibit unique decompositional behavior. For example, pentafluorobenzoyl peroxide decomposes in hexafluorobenzene to give $C_6F_5C_6F_5$ and $C_6F_5C(=O)OC_6F_5$ as the decomposition products[125] (Scheme 64).

Scheme 64

$$\underset{\mathbf{62}}{C_6F_5C(=O)OOC(=O)C_6F_5} \xrightarrow[\text{reflux}]{C_6F_6} \underset{2\%}{C_6F_5\text{-}C_6F_5} + \underset{7\%}{C_6F_5C(=O)OC_6F_5}$$

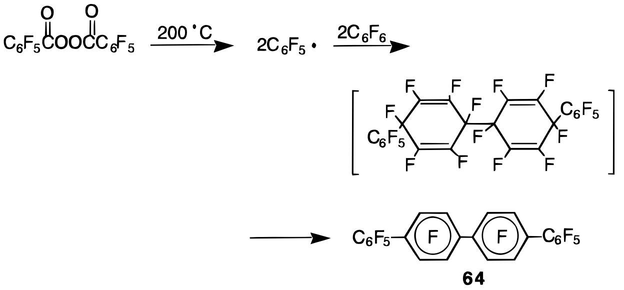
In the thermal decomposition of pentafluorobenzoyl peroxide in hexafluorobenzene at 80 °C, the dimer of the [$C_6F_5C(=O)O^{\bullet}-C_6F_6$] σ-complex (**63**) is isolated in 70% yield[126] (Scheme 65).

Scheme 65



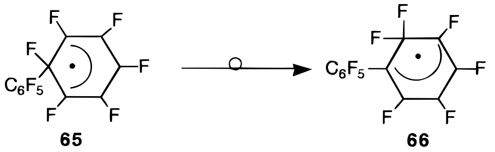
On the other hand, on thermal decomposition at 200 °C, the dimer of the [$C_6F_5^{\bullet}-C_6F_6$] σ-complex (**64**) is obtained[127] (Scheme 66).

Scheme 66



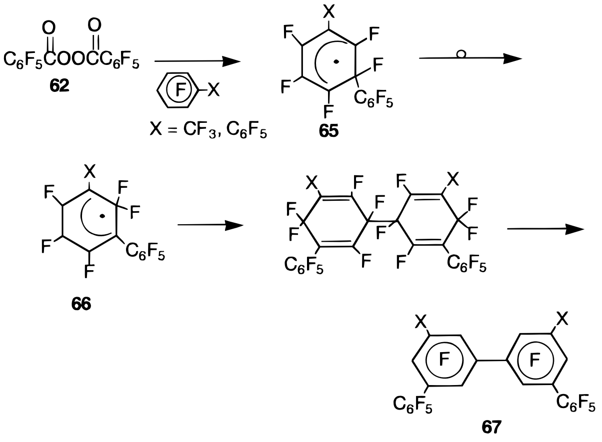
Interestingly, a fluorine atom rearrangement (**66**) was in part observed in the [$C_6F_5^{\bullet}-C_6F_6$] σ-complex (**65**)[128] (Scheme 67).

Scheme 67



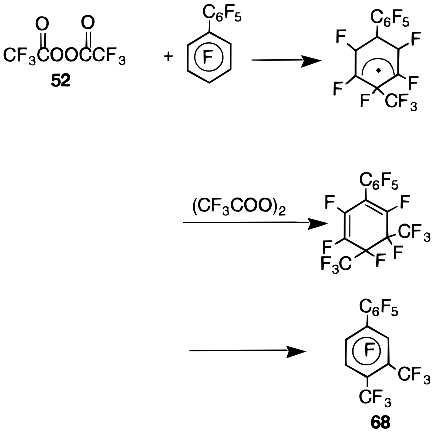
In octafluorotoluene or decafluorobiphenyl, pentafluorobenzoyl peroxide decomposes to afford the σ-complex (**65** in Scheme 68) by C_6F_5 radical and then to give the dimeric compound **67** in good yields.[129]

Scheme 68



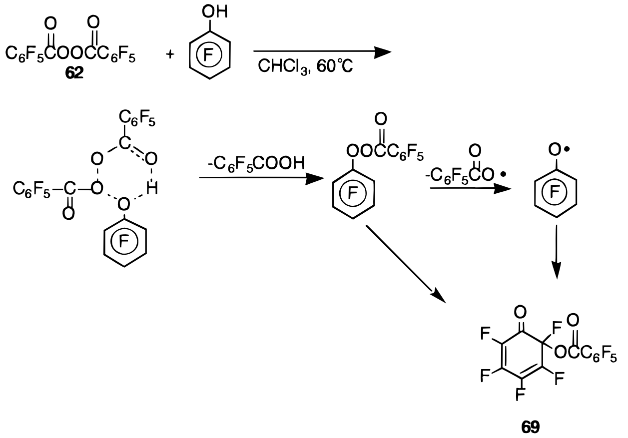
In contrast, the thermal decomposition of fluorinated alkanoyl peroxides such as trifluoroacetyl peroxide (**52**) does not afford the rearrangement of a fluorine atom. However, the addition of a trifluoromethyl radical is observed[130] (Scheme 69).

Scheme 69



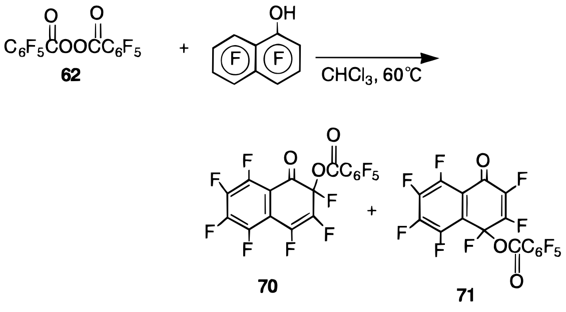
Pentafluorobenzoyl peroxide (**62**) reacts with pentafluorophenol to afford mainly perfluoro-6-(benzoyloxy)-2,4-cyclohexadien-1-one (**69**)[131] (Scheme 70).

Scheme 70



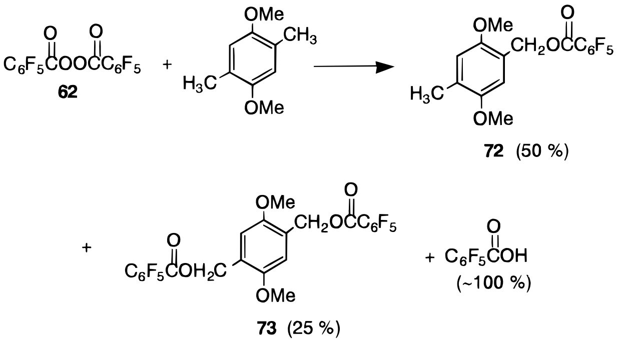
In the reaction of pentafluorobenzoyl peroxide with heptafluoro-1-naphthol, perfluoro-1-oxo-2-(benzoyloxy)-1,2-dihydronaphthalene (**70**) is obtained as the main product, and perfluoro-1-oxo-4-(benzoyloxy)-1,4-dihydronaphthalene (**71**) as the minor product[132] (Scheme 71).

Scheme 71



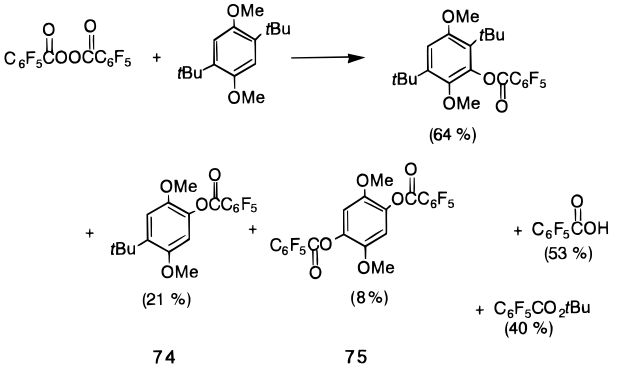
In the reaction of pentafluorobenzoyl peroxide with 2,5-dimethyl-1,4-dimethoxybenzene, the side chain-substituted (benzylic-substituted) esters (**72** and **73**) are obtained as the main products[133] (Scheme 72).

Scheme 72

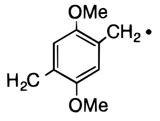


On the other hand, in the reaction of 2,5-di-*tert*-butyl-1,4-dimethoxybenzene, esters involving ring substitution with elimination of a *t*-Bu group, (*ipso*-substituted esters) (**74** and **75**) are also obtained (Scheme 73).

Scheme 73

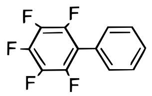


It is suggested that the different reactivities are due to the stability of the benzyl radical **76**.[133]



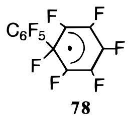
76

In the thermal decomposition of pentafluorobenzoyl peroxide in benzene, 2,3,4,5,6-pentafluorobiphenyl (**77**) is obtained as the main product. The decomposition is believed to proceed with a mechanism similar to that of benzoyl peroxide.[134]



77

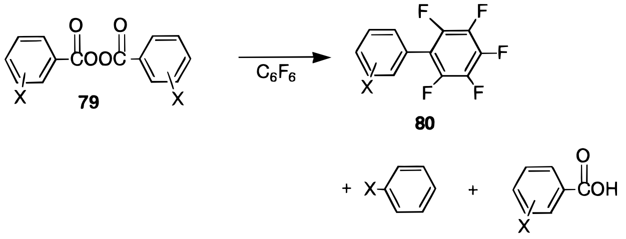
In contrast, the reaction in hexafluorobenzene gave very little decafluorobiphenyl. This is due to the relative unreactivity of the electron-deficient nuclear carbon atoms of hexafluorobenzene toward the pentafluorophenyl radical, which would be expected to be fairly electrophilic, and also to the lack of an easy route for the defluorination of the σ-complexes **78**.[125b]



78

In the thermal decomposition of nonfluorinated aroyl peroxides (**79**) in hexafluorobenzene, 2,3,4,5-pentafluorobiphenyls **80** are the main products. Benzenes and aromatic carboxylic acids are also obtained as minor products[135] (Scheme 74).

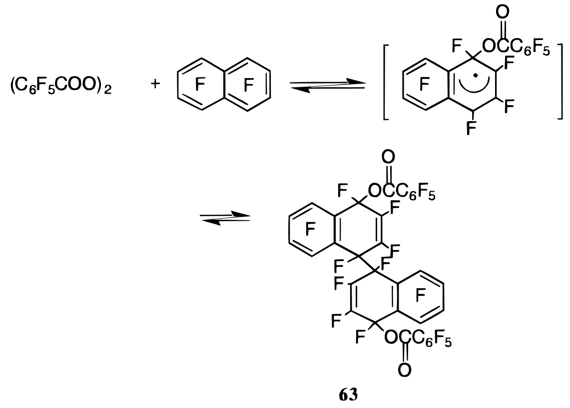
Scheme 74



The thermal decomposition mechanism for pentafluorobenzoyl peroxide was also studied in detail by CIDNP (chemically induced dynamic nuclear polarization) with ^{19}F NMR and ^{1}H NMR,[136] and a similar decomposition behavior to the nonfluorinated benzoyl peroxide was proposed.[137]

In the reaction of pentafluorobenzoyl peroxide with octafluoronaphthalene, the dimerization of the σ-complex on addition of the pentafluorobenzoyloxy radical to octafluoronaphthalene (**63**) occurred[138,139] (Scheme 75).

Scheme 75

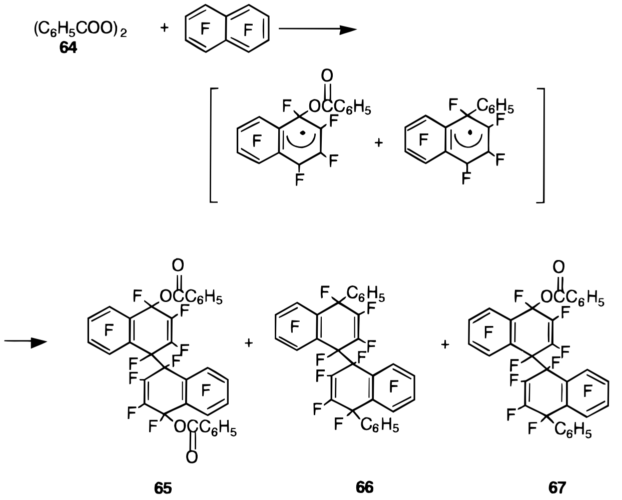


In contrast, the reaction of octafluoronaphthalene with nonfluorinated benzoyl peroxide (**64**) afforded a mixture of the dimers (**65**–**67**)[138,139] (Scheme 76).

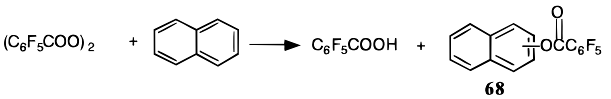
On the other hand, the reaction of pentafluorobenzoyl peroxide with naphthalene gave pentafluorobenzoic acid and a mixture of isomeric naphthyl pentafluorobenzoates (96% of the α-isomer) (**68**)[138,139] (Scheme 77).

In addition, the reaction behavior of pentafluorobenzoyl peroxide has been recently reviewed by Kobrina.[140]

Scheme 76



Scheme 77



C. Thermal Decomposition of Fluoroalkanoyl Peroxides

There are more reports on the thermal decomposition of perfluoroalkanoyl peroxides than for those of fluorinated aroyl peroxides. This is due to the fact that perfluoroalkanoyl peroxides decompose differently from the corresponding nonfluorinated peroxides. In contrast, fluorinated aroyl peroxides exhibit similar reactivities to nonfluorinated aroyl peroxides.

Swain et al. demonstrated that the introduction of electron-donating groups enhances the decomposition rates of aroyl peroxides.[120] The electron-donating group on the benzene ring suppresses the electron-withdrawing influence of the carbonyl group. Therefore, the attachment of fluoroalkanoyl groups [$R_FC(=O)$] at the ends of the oxygen–oxygen bond is expected to enhance the thermal stability of the peroxide link. However, Zhao et al. and Sawada et al. individually reported that large rate enhancements were observed in the thermal decomposition of perfluoroalkanoyl peroxides such as perfluorobutyryl peroxide [$(C_3F_7COO)_2$] and trifluoroacetyl peroxide [$(CF_3COO)_2$].[141,142]

Furthermore, the activation enthalpy for the decomposition of fluoroalkanoyl peroxides is lower than that of the corresponding nonfluorinated alkanoyl peroxide by 3–8 kcal/mol, as shown in Table 7. Zhao et al. and Sawada et al. independently proposed that the acceleration of the decomposition rate or decrease in activation enthalpy arises from the stability of perfluoroalkyl radicals in perfluoroalkanoyl peroxides leading to a concerted dissociation with a three-bond fission such as suggested by Bartlett and Leffler for the thermal decomposition of phenylacetyl peroxides[143] (Scheme 78).

Scheme 78

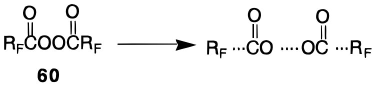
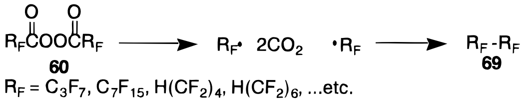


Table 5. Relative Rate Constants (k_2/k_1) for Rates (k_2) of Addition of Radicals to Olefins in Relation to Rates (k_1) of Abstraction of a Hydrogen Atom from Heptane at 50 °C

olefin	$CF_3^\bullet$	$C_2F_5^\bullet$	$C_3F_7^\bullet$
$CH_2{=}CH_2$	132 ± 4	340 ± 20	290 ± 10
$CH_2{=}CHF$	30 ± 2	108 ± 3	40 ± 2
$CH_2{=}CF_2$	9 ± 1	13 ± 1	
$CHF{=}CF_2$	6 ± 1	9 ± 1	
$CF_2{=}CF_2$	8 ± 1	7 ± 1	<0.3
$CF_2{=}CFCF_3$		0.33 ± 0.08	
$CF_2{=}CFOCF_3$		1.1 ± 0.2	

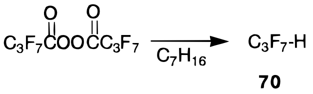
In fact, the decomposition of perfluoroalkanoyl peroxides selectively affords the corresponding coupling products **69** in good yields[141] (Scheme 79).

Scheme 79



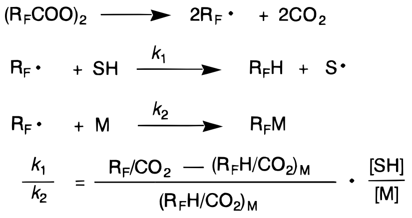
On the other hand, decomposition in hydrocarbon solvents affords monohydroperfluoroalkanes [$CF_3(CF_2)_nH$] (**70**) as the products[144,145] (Scheme 80).

Scheme 80



The thermal decomposition of perfluoroalkanoyl peroxides in heptane was applied to the source of the free radicals $CF_3^\bullet$, $C_2F_5^\bullet$, and $C_3F_7^\bullet$. The rate constants for the addition of perfluoroalkyl radicals to various monomers were determined at 50 °C in relation to the rate constants for the abstraction of a hydrogen atom from heptane using the equations shown in Scheme 81 where R_F is $CF_3^\bullet$, $C_2F_5^\bullet$, or $C_3F_7^\bullet$,

Scheme 81



SH is heptane, R_FH/CO_2 is the molar ratio between the corresponding monohydroperfluoroalkane, and carbon dioxide formed during decomposition of the peroxide in the absence of the unsaturated compound M, and $(R_FH/CO_2)_M$ is the same in its presence.

Table 5 indicates a decrease in reactivity with increase in the number of fluorine atoms in ethylene molecules. Such a relationship indicates a dominate electrostatic interaction effect, and the resonance stabilization of the radical adduct is not predominant in the addition of perfluorinated radical to fluorine-substituted ethylenes.[146] In particular, the C_2F_5 radical is more reactive for addition to $CH_2{=}CF_2$, $CHF{=}CF_2$, and $CF_2{=}CF_2$ than the CF_3 radical.[146]

The relative rate constants $k_1(CF_3)/k_1(C_2F_5)$ for the abstraction of a hydrogen atom from heptane by CF_3 and C_2F_5 radicals were reported as follows:[147]

$$k_1(CF_3)/k_1(C_2F_5) = 3.6 \pm 0.4$$

From this value and the data given in Table 5, the relative rate constants $k_2(CF_3)/k_2(C_2F_5)$ for the addition to ethylene and its fluorine-substituted derivatives can be calculated, and these results are shown in Table 6.

Table 6. Relative Rate Constants for Addition of CF_3 and C_2C_5 Radicals to Ethylene and Its Fluorine-Substituted Derivatives

olefin	$k_2(CF_3)/k_2(C_2F_5)$
$CH_2{=}CH_2$	1.36
$CH_2{=}CHF$	0.97
$CH_2{=}CF_2$	2.42
$CHF{=}CF_2$	2.33
$CF_2{=}CF_2$	4.0

The relative rate constants (k_2^E/k_2^{TFE}) for the addition of CF_3, CH_3CF_2, and CH_3 radicals, which are obtained by the thermal decomposition of $(CF_3COO)_2$, $(CH_3CF_2COO)_2$, and $(CH_3COO)_2$ in heptane and isooctane, to ethylene (k_2^E) and tetrafluoroethylene (k_2^{TFE}) were determined as follows:[148] (k_2^E/k_2^{TFE}) 16.5 ($CF_3^\bullet$); 1.6 ($CH_3CF_2^\bullet$); 0.1 ($CH_3^\bullet$).

In addition, the relative rate constants (k_2/k_1) for the rates (k_2) of the addition of these radicals to C_6F_6, $C_6F_5CF_3$, $C_6F_5O(CF_2)_4OC_6F_5$, p-$(CF_3)_2C_6H_4$, and C_6H_6 in relation to the rates (k_1) of abstraction of a hydrogen atom from heptane and isooctane were studied. It was shown that the value of k_2/k_1 increases for nucleophilic radicals (CH_3 radical), but decreases for electrophilic radicals.[149]

Table 7. Thermal Decomposition of Perfluoroalkanoyl and Alkanoyl Peroxides [$(RCOO)_2$]

R in peroxide	solvent	$k_d \times 10^5$ (s^{-1}, 85 °C)	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ [kcal/(mol deg)]
CF_3	$CF_2ClCFCl_2$	174	25.8	0.7
C_3F_7	$CF_2ClCFCl_2$	3596	23.9	1.7
C_7F_{15}	$CF_2ClCFCl_2$	9225	23.4	0.4
$H(CF_2)_4$	$CF_2ClCFCl_2$	7123	20.6	−6.1
$H(CF_2)_6$	$CF_2ClCFCl_2$	9463	24.0	3.0
CH_3	$PhCH_3$	17.3		
C_3H_7	$PhCH_3$	30.2	29.1	10.1
C_7H_{15}	$PhCH_3$	37.8	29.2	9.7

Table 7 shows that the introduction of fluorine atoms into the alkyl group in a diacyl peroxide increases the rate of decomposition of the diacyl peroxide. The activation enthalpy for the decomposition of a perfluoroalkanoyl peroxide is lower than that of the corresponding nonfluorinated alkanoyl peroxide by 5−8 kcal/mol.[141,142,150] These results suggest that a more stable perfluoroalkyl radical is likely to form by the concerted three-bond radical fission of perfluoroalkanoyl peroxides compared to the corresponding nonfluorinated alkanoyl peroxides.

Interestingly, in the thermal decomposition of a series of perfluoroalkanoyl peroxides, it was found that the rate of decomposition (k_d; s^{-1} at 20 °C) of perfluoroalkanoyl peroxides such as perfluorooctanoyl peroxide [$(C_7F_{15}COO)_2$], perfluorobutyryl peroxide [$(C_3F_7COO)_2$], perfluoropropionyl peroxide [$(C_2F_5COO)_2$], and trifluoroacetyl peroxide [$(CF_3COO)_2$] lies in the following order:[150] $(C_7F_{15}COO)_2$ 5.9×10^{-5} >

Table 8. Thermal Decomposition of Fluorinated and Nonfluorinated Alkanoyl Peroxides [$(RCOO)_2$]

solvent	R	T (°C)	ΔE_a (kcal/mol)	$k_d \times 10^3$ (s^{-1}, 30 °C)	$k_d \times 10^5$ (s^{-1}, 65 °C)	ref
isooctane						
	CH_3	50−85	32.2		0.84	153
	CH_3CH_2	65−85	31.2		0.79	124
	$CH_3CH_2CH_2$	65−85	31.9		0.82	124
	$(CH_3)_2CH$	25−55	27.3	0.007	74.6	154
	CF_3CH_2	65−95	28.5		0.74	155
heptane						
	CF_3CH_2	65−95	29.0		0.37	155
	$(CF_3)_2CH$	65−95	28.1		0.50	155
	CH_3CF_2	5−30	21.8	1.85		149
	CF_3	25−65	27.0	0.04	370	156
	CF_3CF_2	25−65	28.4	1.05		156
	$CF_3CF_2CF_2$	25−65	22.0	0.78		156

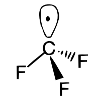
Table 9. Decomposition Rates (s^{-1}, 25 °C) and Some Electronic Properties (in eV) of Alkanoyl Peroxides $(RCOO)_2$

R in peroxide	$k_d \times 10^8$ (s^{-1})	E_R^{1-5}	E_R^{2-4}	σ*(O−O)
$(CH_3)_3COCH_2CF_2$	100000[a]	−17.939	−12.650	0.050
CH_3CF_2	96000[b]	−17.953	−12.682	0.121
$CF_3(CF_2)_6$	5860[c]	−17.962	−12.821	−1.963
$CF_3(CF_2)_2$	3320[d]	−17.965	−12.833	−1.614
CH_3CH_2Cl	2970[a]	−18.063	−14.094	0.653
CF_3CF_2	1160[a]	−17.980	−12.885	−1.385
CF_3	100[c]	−17.996	−12.881	−0.978
$CH_3(CH_2)_6$	6[e]	−18.112	−14.122	1.390
$CH_3(CH_2)_2$	4[f]	−18.111	−14.122	1.387
CH_3CH_2	3[e]	−18.096	−14.183	1.393
CH_3	2[e]	−18.087	−14.351	1.438
CF_3CH_2	1[g]	−18.113	−14.275	0.062

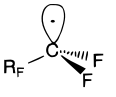
[a] H. Sawada, unpublished results. [b] Reference 149. [c] Reference 142. [d] Reference 163. [e] Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*, 2nd ed., Wiley-Interscience: New York: 1975. [f] Reference 124. [g] Reference 155.

$(C_3F_7COO)_2$ 3.3×10^{-5} > $(C_2F_5COO)_2$ 1.2×10^{-5} ≫ $(CF_3COO)_2$ 0.1×10^{-5}.

This finding suggests that the stabilizing effect of the perfluoroalkyl radical will be in the order of $CF_3 < C_2F_5 < C_3F_7 < C_7F_{15}$. In particular, perfluoroalkyl radical which is longer in chain length than the trifluoromethyl group is known to indicate s-character rather than p-character in the hybridization at carbon.[151,152]



p-character



s-character

Thus, it was suggested that longer perfluoroalkyl chains in the peroxides weaken the bonds between the carbonyl carbon and perfluoroalkyl group, and these peroxides undergo a faster homolytic cleavage in contrast to $(CF_3COO)_2$.

Furthermore, the decomposition of α-fluorinated alkanoyl peroxides [$(CH_3CF_2COO)_2$] is much faster than that of β-fluorinated peroxides [$(CF_3CH_2COO)_2$ and $((CF_3)_2CHCOO)_2$] or the corresponding nonfluorinated peroxides as listed in Table 8. In contrast, the decomposition of β-fluorinated peroxides [$(CF_3CH_2COO)_2$] is almost the same as that of $(CH_3CH_2COO)_2$, and [$((CF_3)_2CHCOO)_2$] decomposes more slowly than the nonfluorinated peroxide [$((CH_3)_2CHCOO)_2$].

In order to elucidate the unique decomposition behavior of fluoroalkanoyl peroxides, the electronic structure of a series of these peroxides based on MNDO molecular orbital calculations were studied in detail.[150]

From the lowest energy conformations of acetyl peroxide and trifluoroacetyl peroxide, it was determined that the introduction of a fluorine atom to the α-carbon atom makes the peroxy O−O bond long and the dihedral angle between the two COO planes large. Table 9 shows that the rate of the O−O cleavage correlates well with the destabilization of the resonance energy of both the O−O bond (E_R^{1-5}) and C_2-C_4 bond [carbonyl carbon−fluoroalkyl carbon (E_R^{2-4})], but not with the electrostatic energy of these bonds. In general, the total energy of a molecule can be partitioned into one-atom and two-atom terms

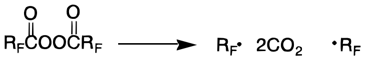
$$E_{\text{total}} = \sum_{A} E_A + \sum_{A>B} E_{A,B}$$

$$E_{AB} = E_R^{A,B} + E_K^{A,B} + E_{ES}^{A,B}$$

where $E_R^{A,B}$, $E_K^{A,B}$, and $E_{ES}^{A,B}$ are resonance, exchange, and electrostatic energies, respectively.[150] It was demonstrated that the O−O bond and C_2-C_4 bonds of fluoroalkanoyl peroxides are weaker than those of the corresponding nonfluorinated alkanoyl peroxides.

As shown in Table 9, the introduction of fluorine or chlorine atoms into the α-position weakens the O−O peroxy bond as well as the C_2-C_4 bond, whereas the introduction of fluorine atoms into the β-position does not weaken these bonds to the same extent. Fluorination at the α-carbon atom makes both the O−O and C_2-C_4 bonds weaker than those of the corresponding nonfluorinated peroxide. This should accelerate decarboxylation and O−O cleavage in a homolytic fashion to afford the corresponding fluoroalkyl radical as illustrated in Scheme 82.

Scheme 82

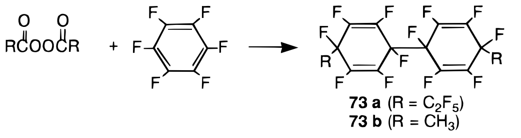


60

Another specific fluoroalkanoyl peroxide characteristic is that perfluoroalkanoyl peroxides lower the 2pσ*(O−O) antibonding orbital considerably compared to that of nonfluorinated molecules. Therefore, the perfluoroalkanoyl peroxide is expected to become a useful electron acceptor via single-electron transfer from various substrates.

In hexafluorobenzene (**72**), perfluoropropionyl peroxide (**71a**) decomposes to afford perfluoro-4,4′-diethyl-1,1′,4,4′-tetrahydrobiphenyl (**73a**) as the main product. In addition, the decomposition of acetyl peroxide (**71b**) affords a similar dimeric product[157] (Scheme 83).

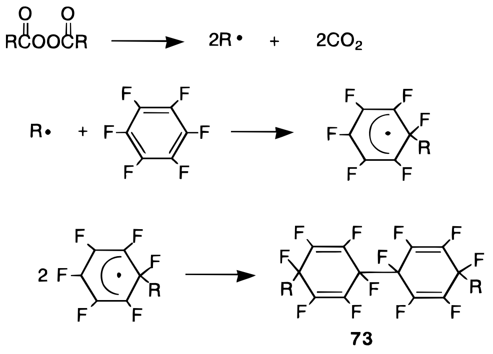
Scheme 83



71 72 **71-a**: R = C_2F_5, 26% (**71-a/72** (mol/mol) = 1/40)
71-b: R = CH_3, 42% (**71-b/72** (mol/mol) = 1/40)

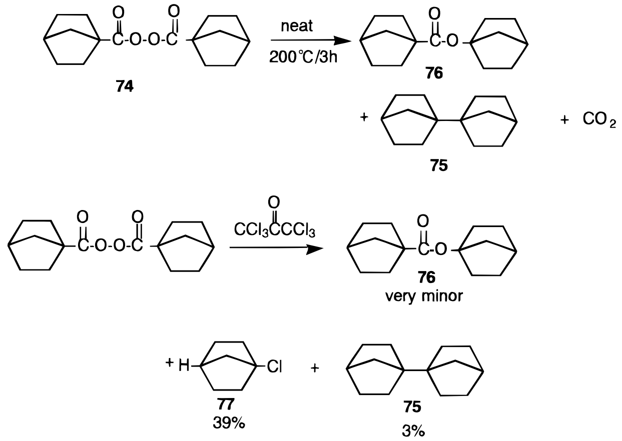
The yields of the dimeric products obtained by the decomposition of $(CH_3COO)_2$ are higher than that of $(C_2F_5COO)_2$. This result is due to the fact that the C_2F_5 radical is more electrophilic than the CH_3 radical. The reaction mechanism shown in Scheme 84 is proposed.[157]

Scheme 84



The thermal decomposition of fluorinated cyclic peroxides such as bis(4*H*-decafluorobicyclo[2.2.1]-heptyl-1-carbonyl) peroxide (**74**) affords not only the coupling product (4*H*,4*H*′-eicosafluoro-1,1′-spirobi-(bicyclo[2.2.1]heptane) (**75**) but also the ester 4*H*-decafluorobicyclo[2.2.1]hept-1-yl 4*H*-decafluorobicyclo-[2.2.1]heptane-1-carboxylate (**76**). In hexachloroacetone, this peroxide decomposes to give 4*H*-1-chloro-decafluorobicyclo[2.2.1]heptane (**77**) as the main product[158] (Scheme 85).

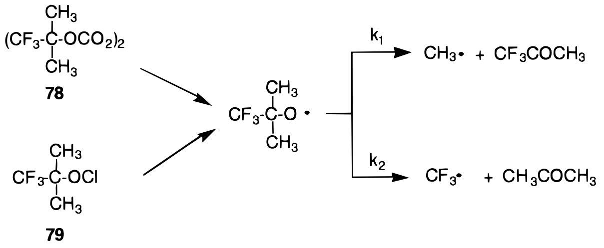
Scheme 85



[All unmarked bonds bonded to fluorine]

The precursor radicals [$CF_3CMe_2O^\bullet$] were generated from two different compounds: the fluorinated peroxydicarbonate (**78**) and the hypochlorite (**79**) (Scheme 86). In the thermolytic reaction of the

Scheme 86

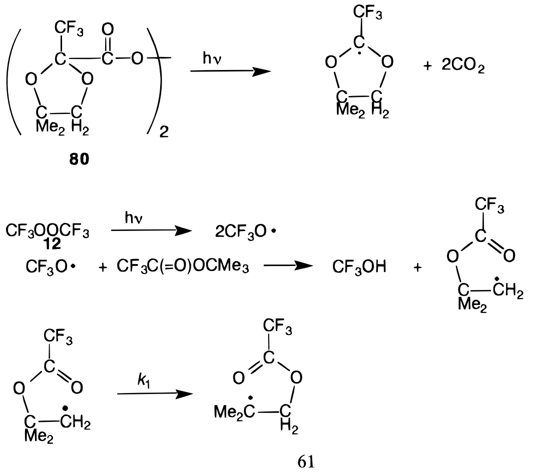


fluorinated peroxy dicarbonate at 140 °C, 50% of CF_3COCH_3 and 1.6% of CH_3COCH_3 were produced. On the other hand, the thermolysis of the hypochlorite at 160 °C afforded 74% of CF_3COCH_3 and 0.6% of CH_3COCH_3. The k_1/k_2 ratio evaluated in the β-scission of the CF_3CMe_2O radical produced by the decomposition of the peroxide is approximately 13. This is in good qualitative agreement with the hypochlorite experiments (k_1/k_2 = 10.5).

These results suggest that the trifluoromethyl radical is disfavored compared to the methyl radical in the β-scission of the CF_3CMe_2O radical.[159]

Trifluoromethylated alkanoyl peroxide (**80**) and trifluoromethyl peroxide (**12**) were used in a mechanism study of the 1,2 migration of acyloxy groups in β-(acyloxy)alkyl radicals[160] (Scheme 87).

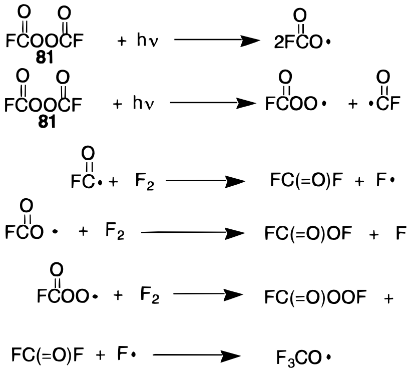
Scheme 87



Photolysis of bis(fluoroformyl) peroxide [FC(=O)OOC(=O)F] (**81**) in the presence of fluorine yields FC(=O)OF in addition to CO_2, FC(=O)F, CF_3OF, SiF_4, CF_3OOCF_3, $FC(=O)OOCF_3$, and CF_3OOOCF_3.[161]

It was demonstrated that F(C=O)OOF is formed during the formation of FC(=O)F with the photodecomposition of bis(fluoroformyl) peroxide and decomposes rapidly into FC(=O)F with O_2[162] (Scheme 88).

Scheme 88



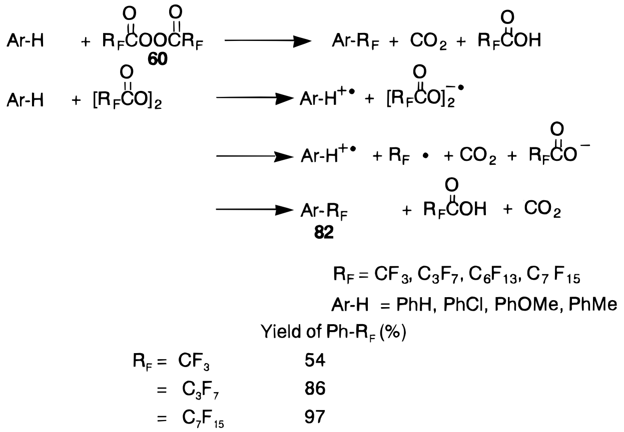
VI. Reactions of Fluoroalkanoyl Peroxides with Nucleophiles

A. Reactions with Aromatic and Heteroaromatic Compounds—Perfluoroalkylation with Perfluoroalkanoyl Peroxide

As shown in Table 9, a MNDO molecular orbital study for perfluoroalkanoyl peroxides showed that the energy levels of the unoccupied 2pσ*(O−O) orbital in these fluorinated peroxides are much lower than those in the corresponding nonfluorinated alkanoyl peroxides. Therefore, a perfluoroalkanoyl peroxide is expected to become a useful electron acceptor even from well-known poor electron-donor aromatic compounds such as benzene and chlorobenzene.

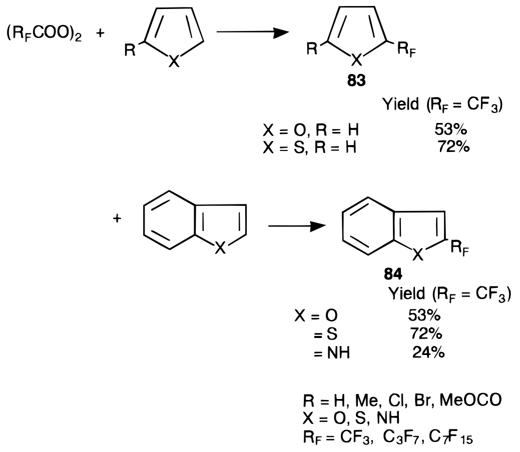
In fact, it was demonstrated that perfluoroalkanoyl peroxides [$(R_FCOO)_2$, $R_F = CF_3, C_3F_7, C_6F_{13}, C_7F_{15}$] are useful reagents for the introduction of the corresponding perfluoroalkyl groups into aromatic compounds such as benzene, chlorobenzene, toluene, and anisole via a single electron-transfer process under very mild conditions[142,163] (Scheme 89).

Scheme 89



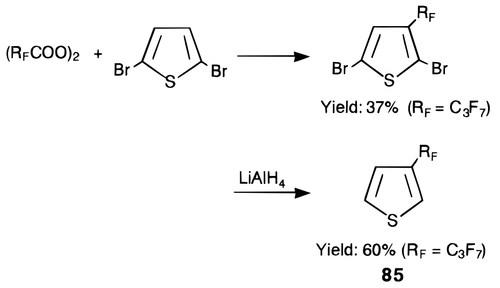
Similarly, perfluoroalkanoyl peroxides react with heteroaromatic compounds such as thiophenes, furans, benzofuran, and benzothiophene to afford the corresponding perfluoroalkylated heteroaromatic compounds (**83** and **84**) in good yields under very mild conditions[164] (Scheme 90).

Scheme 90



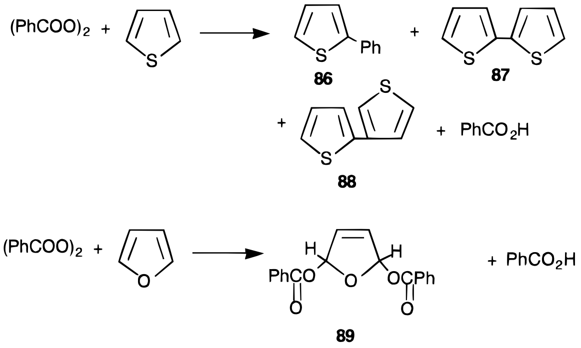
3-Perfluoroalkylated thiophenes (**85**) were prepared using 2,5-dibromothiophene[165] (Scheme 91).

Scheme 91



On the other hand, in the reaction of a nonfluorinated diacyl peroxide such as benzoyl peroxide with thiophene, not only 2-phenylthiophene (**86**) but also the dimeric products of the thiophenes **87** and **88** were obtained. In addition, the reaction of furan with benzoyl peroxide gave 2,5-dibenzoyl-2,5-dihydrofuran (**89**) as the main product[166−168] (Scheme 92).

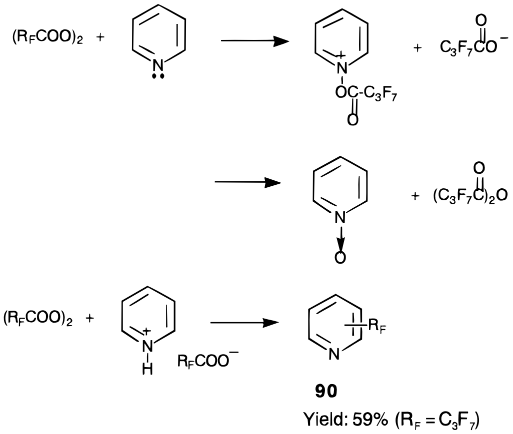
Scheme 92



In the reaction with pyridine, perfluoroalkylated pyridines were not obtained, and pyridine *N*-oxide was obtained by the usual nucleophilic attack of the pyridine *N*-lone pair at the peroxide O−O bond. A similar nucleophilic attack of an *N*-lone pair at the O−O bond in nonfluorinated diacyl peroxides such as benzoyl peroxide is well-known.[169]

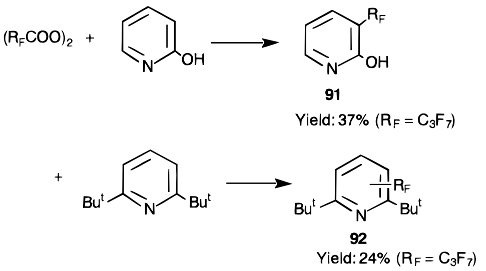
However, the reaction of perfluoroalkanoyl peroxides with pyridinium perfluoroalkanoates which have no lone pair on the nitrogen atom gave the expected perfluoroalkylated pyridines (**90**). This reaction mechanism is believed to proceed by a radical process rather than electron transfer[164] (Scheme 93).

Scheme 93



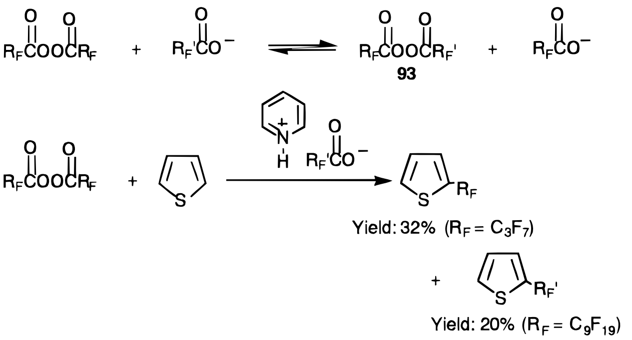
2-Hydroxypyridine and 2,6-di-*tert*-butylpyridine, in which the nucleophilicity of the *N*-lone pair was suppressed, reacted directly with perfluoroalkanoyl peroxides to afford the corresponding perfluoroalkylated pyridine derivatives **91** and **92**[170] (Scheme 94).

Scheme 94



Interestingly, perfluoroalkanoyl peroxide [$(R_F\text{-}COO)_2$] was shown to undergo a nucleophilic displacement with perfluoroalkanoate ion [$R_F'COO^-$] to afford new mixed diacyl peroxides [$R_FC(=O)OOC(=O)R_F'$] (**93**). Thus, it was demonstrated that both the perfluoroalkyl (R_F) of the peroxide and the perfluoroalkyl (R_F') of perfluoroalkanoate are introduced into thiophene[171] (Scheme 95).

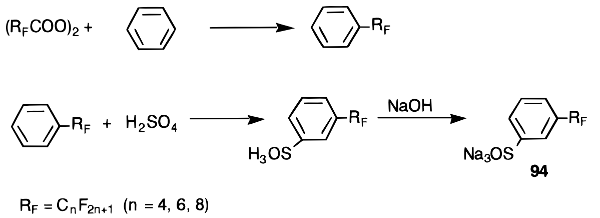
Scheme 95



Recently, fluoroalkanoyl peroxides have been used in the preparation of fluoroalkylated lactone derivatives.[172]

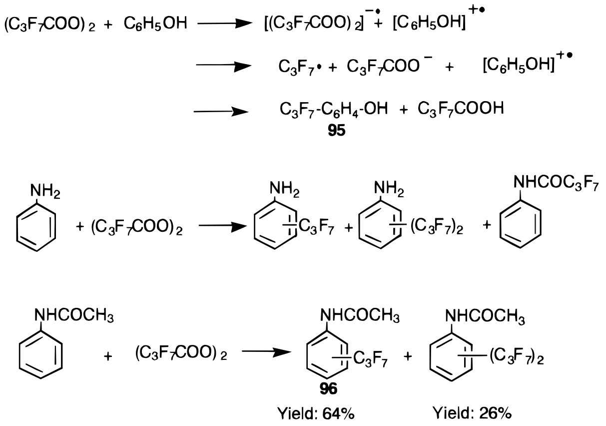
Perfluoroalkanoyl peroxides were also used in the preparation of perfluoproalkylated aromatic surfactants containing the sulfo group (**94**)[173] (Scheme 96).

Scheme 96



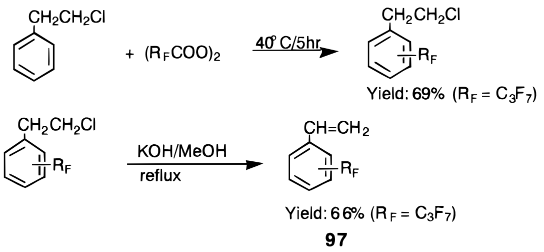
The aromatic perfluoroalkylation of phenol was found to proceed smoothly with perfluoroalkanoyl peroxides to afford perfluoroalkylated phenols **95** via single electron transfer (Scheme 97). On the other hand, in the reaction of aniline, some nucleophilic attack of the *N*-lone pair on the peroxide occurred. However, aromatic perfluoroalkylation of aniline (**96**) with peroxide was found to proceed preferentially in good yield by protecting the amino group in aniline. This method was applied to the aromatic perfluoroalkylation of diamines.[174]

Scheme 97

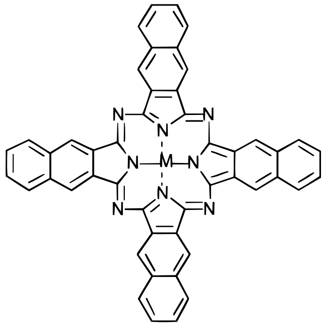


Perfluoroalkanoyl peroxides were also shown to be useful in the preparation of fluoroalkylated styrene monomers (**97**)[175] (Scheme 98).

Scheme 98



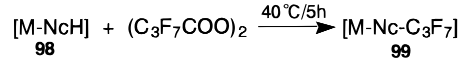
Direct perfluoroalkylation of aromatic rings in metal-free naphthalocyanine, and its copper or silicon complexes including dihydroxy and bis(trialkylsiloxy)silicon ligands, (**98**) with perfluoroalkanoyl peroxide was found to proceed in good yield under mild conditions. Perfluoroalkylation of naphthalocyanines with peroxide was shown to lead to a drastic improvement of solubility in common organic solvents[176] (Scheme 99).



98

M	abbreviation
H_2	H_2-NcH
Cu	Cu-NcH
$Si[OSi(C_6H_{13})_3]_2$	$(Hex_3SiO)_2Si$-NcH
$Si[OSi(C_3H_7)_3]_2$	$(Pr_3SiO)_2Si$-NcH
$Si[OSi(C_2H_5)_3]_2$	$(Et_3SiO)_2Si$-NcH
$Si(OH)_2$	$(HO)_2Si$-NcH

Scheme 99

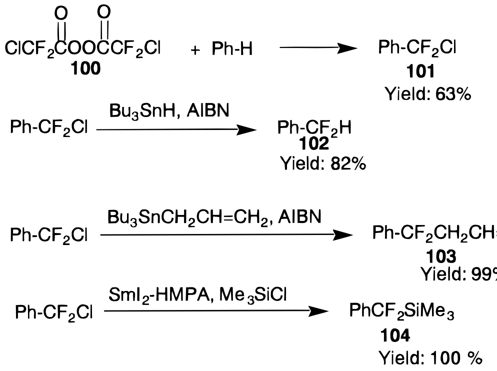


$$\underset{\textbf{98}}{[\text{M-NcH}]} + (C_3F_7COO)_2 \xrightarrow{40℃/5h} \underset{\textbf{99}}{[\text{M-Nc-}C_3F_7]}$$

M = H_2, Cu, $(Hex_3SiO)_2Si$, $(Pr_3SiO)_2Si$, $(Et_3SiO)_2Si$, $(HO)_2Si$.

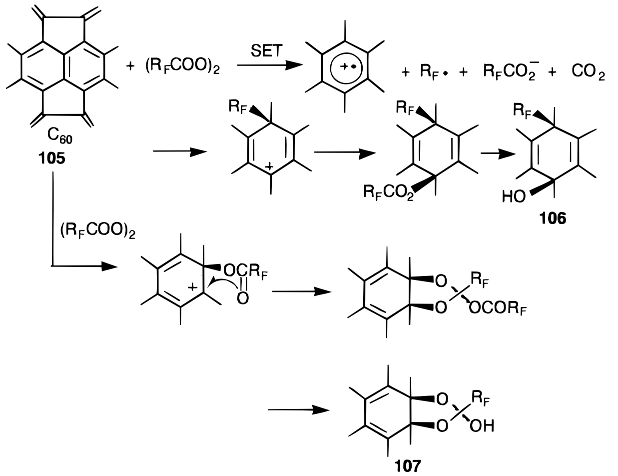
Chlorodifluoromethylation of aromatic compounds was achieved by using chlorodifluoroacetyl peroxide (**100**). Chlorodifluoromethylated aromatic compounds in particular are expected to become useful precursors for the synthesis of $ArCF_2$ derivatives (**100**–**104**)[177,178] (Scheme 100).

Scheme 100



Very recently, the perfluoroalkylation of buckminsterfullerene (C_{60} (**105**)) with perfluoroalkanoyl peroxide has been reported, and a reaction mechanism involving a C_{60} cation radical was proposed[179] (Scheme 101).

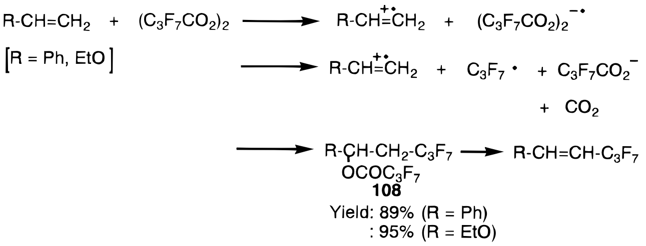
Scheme 101



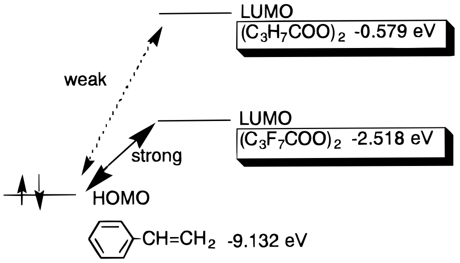
Furthermore, the radical species R_F–$C_{60}^{\bullet}$ formed by the addition to C_{60} of a single fluoroalkyl radical, which is produced by the thermal or photochemical decomposition of perfluoroalkanoyl peroxide, was detected by ESR.[180]

It is well-known that styrene is a useful radical polymerizable monomer, and diacyl peroxides such as benzoyl peroxide are widely used as convenient radical initiators. However, it was demonstrated that styrene reacts with fluoroalkanoyl peroxides to afford not the radical polymerizable products but 1:1 adducts $[PhCH(OCOR_F)CH_2R_F]$ via a single electron transfer from styrene to peroxide. Similarly, in the reactions of electron-rich olefins such as ethyl vinyl ether, perfluoroalkylated 1:1 adducts (**108**) were obtained in good yields under very mild conditions[181] (Scheme 102).

Scheme 102

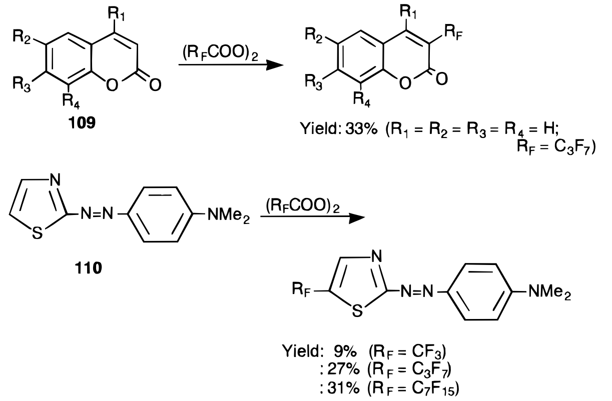


This finding indicates that a stronger interaction between the HOMO energy level of styrene (−9.132 eV, value calculated with MNDO-PM3 semiempirical MO method; Stewart, J. J. P. and Fujitsu Limited MOPAC 93, Tokyo, Japan) and LUMO (peroxide; for example, $(C_3F_7COO)_2$ −2.518 eV) does not give the usual radical polymerization as found for nonfluorinated diacyl peroxides but an electron transfer from styrene to the 2pσ* (O−O) antibonding orbital of peroxide.



Direct perfluoroalkylation with perfluoroalkanoyl peroxides was applied to dye molecules such as coumarins **109**[182] and azo compounds **110**[183] (Scheme 103).

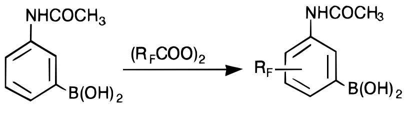
Scheme 103



The absorption and emission maxima of 3-(perfluoroalkyl)coumarins show bathochromic shifts compared with the unsubstituted coumarins. Furthermore, the photostabilities of these fluoroalkylated coumarins are higher than those of the unsubstituted compounds.

The perfluoroalkylated phenylboronic acid (**111**) was prepared by using perfluoroalkanoyl peroxides (Scheme 104). The lower pK_a (6.6) of the fluoroalkylated boronic acid compared with that (8.3) of the parent boronic acid suggests that this material has the potential to bind with polyols under physiological pH conditions, thus opening up wide application in the field of biological science.[184]

Scheme 104

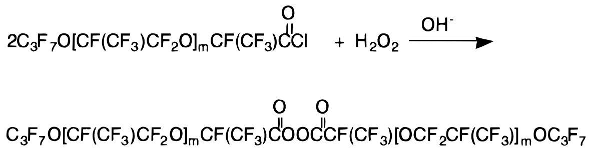


111

B. Synthesis and Applications of Perfluorooxaalkylated Aromatic Compounds with Perfluorooxaalkanoyl Peroxides

In addition to the synthesis of perfluoroalkanoyl peroxide, a series of perfluorooxaalkanoyl peroxides (**112**) can be synthesized by the reaction of the corresponding acid fluorides with hydrogen peroxide under alkaline conditions[185] (Scheme 105).

Scheme 105



$$2C_3F_7O[CF(CF_3)CF_2O]_mCF(CF_3)\overset{O}{\overset{\|}{C}}Cl + H_2O_2 \xrightarrow{OH^-}$$

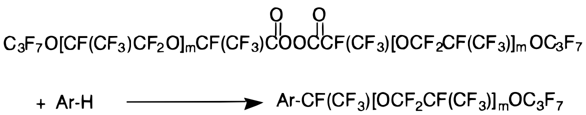
$$C_3F_7O[CF(CF_3)CF_2O]_mCF(CF_3)\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}CF(CF_3)[OCF_2CF(CF_3)]_mOC_3F_7$$

112

m = 0, 1, 2, 3

Perfluorooxaalkanoyl peroxides were found to be effective reagents for the introduction of perfluorooxaalkyl groups into aromatic and heteroaromatic compounds via single electron-transfer reactions analogous to these for perfluoroalkanoyl peroxides.[185] Thus, it was shown that perfluorooxaalkanoyl peroxides are convenient tools for the synthesis of new functional materials containing perfluorooxaalkyl groups with carbon−carbon bond formation (Scheme 106).

Scheme 106



$$C_3F_7O[CF(CF_3)CF_2O]_mCF(CF_3)\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}CF(CF_3)[OCF_2CF(CF_3)]_mOC_3F_7$$

$$+ \ Ar\text{-}H \longrightarrow Ar\text{-}CF(CF_3)[OCF_2CF(CF_3)]_mOC_3F_7$$

113

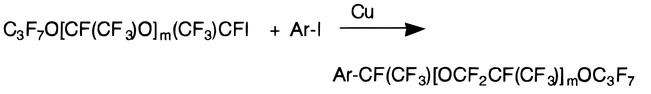
Ar- = phenyl, 2-thienyl, 2-furyl, 2-pyrrolyl
m = 0, 1, 2

	Yield of **113** (Ar = phenyl)
m = 0	62
= 1	65
= 2	94

Long-chain perfluoroalkanoic and perfluoroalkanesulfonic acids are widely used as fluorinated surfactants. These surfactants possess straight perfluorinated carbon chains which are known to be hard and inflexible, giving a low solubility in various solvents. Hence, it is highly desirable to develop surfactants bearing other fluoroalkyl groups such as the perfluorooxaalkyl group. In fact, it was demonstrated that perfluorooxaalkylated benzenes [PhCF(CF$_3$)[OCF$_2$CF(CF$_3$)]OC$_3$F$_7$; *m* = 0, 1] are capable of reducing the surface tension of *m*-xylene by around 10 mN/m effectively compared with those of perfluoroalkylated ones (around 25 mN/m). The behavior of surfactants possessing perfluorooxaalkyl groups are of particular interest because they exhibit a surface activity not shown by either ordinary hydrocarbon surfactants or other fluoroalkylated surfactants. This unique surface tension reduction is associated with a surfactant having a particular number of trifluoromethyl groups and ether linkages.[186]

Very recently, Eapen's group reported that perfluorooxaalkylated benzenes (**114**) can be prepared by the copper-induced Ullmann-type reactions with perfluorooxaalkyl iodides[187] (Scheme 107).

Scheme 107



$$C_3F_7O[CF(CF_3)O]_m(CF_3)CFI \ + \ Ar\text{-}I \xrightarrow{Cu} Ar\text{-}CF(CF_3)[OCF_2CF(CF_3)]_mOC_3F_7$$

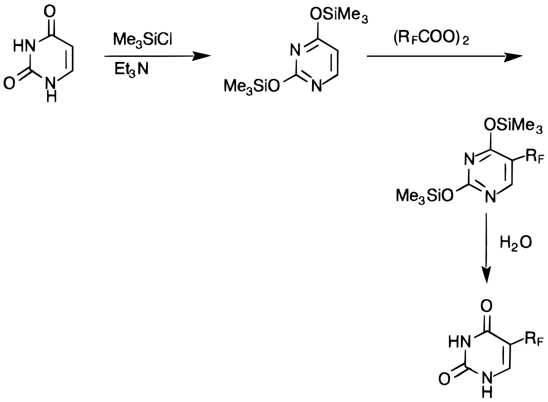
114

m = 0, 1, 2

Fluorine-containing molecules such as 5-fluorouracil have attracted increasing attention because of their unique biological activities, and numerious fluorinated, trifluoromethylated, and perfluoroalkylated uracil derivatives have been synthesized and tested for their biological properties.[188]

Perfluoroalkanoyl peroxides [(R$_F$COO)$_2$; R$_F$ = CF$_3$, C$_3$F$_7$, C$_6$F$_{13}$] were applied to the perfluoroalkylations of uracils **115** (Scheme 108), uridines **116** (Scheme 109), and purines.[189,190]

Scheme 108

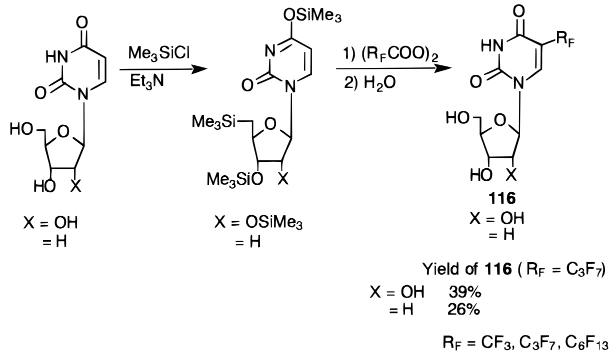


115

Yield: 13% (R$_F$ = CF$_3$); 57% (R$_F$ = C$_3$F$_7$); 38% (R$_F$ = C$_6$F$_{13}$)

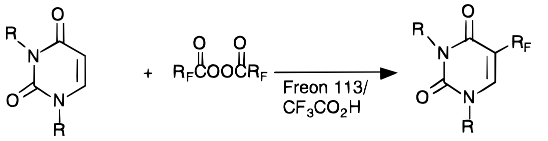
Furthermore, it was demonstrated that not only a perfluoropropyluracil (7F-DU) but also a new 5-(perfluoro-1-methyl-2-oxapentyl)-1,3-dimethyluracil (5-PFDU) can be prepared by the reaction of the corresponding peroxide with 1,3-dimethyluracil in

Scheme 109



1,1,2-trifluoro-1,2,2-trichloroethane under mild conditions in the presence of trifluoroacetic acid as a cosolvent[191] (Scheme 110).

Scheme 110



	Yield(%)
7F-UR : R = H, $R_F = C_3F_7$	5
7F-DU : R = CH_3, $R_F = C_3F_7$	70
5-PFDU : R = CH_3, $R_F = CF(CF_3)OC_3F_7$	63

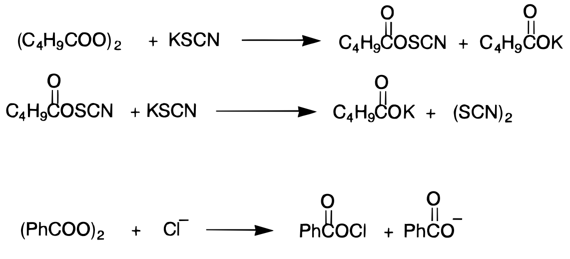
Interestingly, 5-PFDU displayed cytotoxicities as potent as 5-FU for both MT-4 cells and KB cells. A different pharmacological mechanism to that of 5-fluorouracil would be expected since 5-PFDU has a perfluoro-1-methyl-2-oxapentyl group at C-5 instead of a fluorine atom.[191]

The EI mass spectral fragmentation of a series of perfluorooxaalkylated aromatic compounds [$ArCF(CF_3)[OCF_2CF(CF_3)]_mOC_3F_7$; $m = 0, 1, 2$; Ar = phenyl, 2-furyl, 2-thienyl, 2-pyrrolyl], which were prepared by using the corresponding perfluorooxaalkanoyl peroxides, have been studied relative to those of nonfluorinated compounds [$PhCH(CH_3)OC_3H_7$] and of perfluoroalkylated benzenes [$Ph(CF_2)_nCF_3$; $n = 2, 6$].[192]

C. Reactions with Carbanions, Thiolate Anions, and Other Nucleophiles

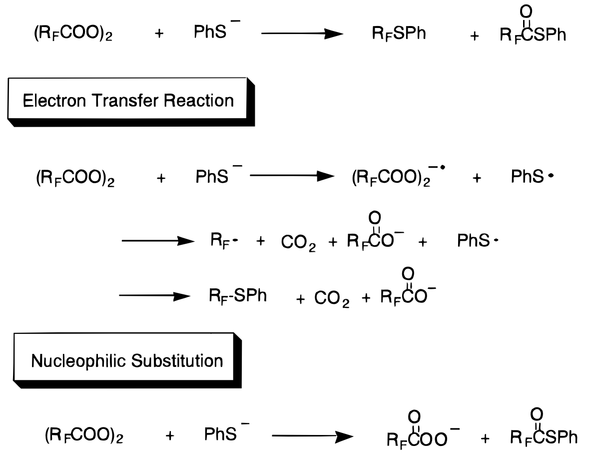
In general, it is well-known that diacyl peroxides such as pentanoyl peroxide and benzoyl peroxide react with nucleophiles such as SCN^- and Cl^- as illustrated in Scheme 111.[193−195]

Scheme 111



On the other hand, two types of reactions (one is an electron transfer and the other is a nucleophilic substitution) have been observed in the reactions of perfluoroalkanoyl peroxides with carbanions and thiolate anions[196] (Scheme 112).

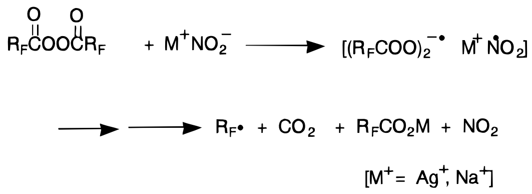
Scheme 112



ESR analyses showed the generation of bis(polyfluoroalkyl) nitroxides [$R_FN(O)R_F$] and polyfluoroalkyl nitroalkyl nitroxides [$R_FN(O)CR^1R^2(NO_2)$] by making use of the spontaneous electron-transfer-initiated reactions between polyfluoroalkanoyl peroxide [$(R_FCOO)_2$] and carbanions [$R^1R^2C^-NO_2\ Na^+$] derived from nitroalkanes.[197]

The single electron-transfer reactions of NO_2^- with fluoroalkanoyl peroxides were studied by ESR[198,199] (Scheme 113).

Scheme 113



In hexamethylphosphoric triamide, the decomposition of trifluoroacetyl peroxide was found to proceed via a single electron transfer. However, nonfluorinated alkanoyl peroxides such as lauroyl peroxide decompose similarly via a single electron-transfer reaction.[200]

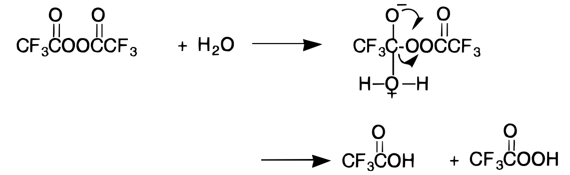
On the other hand, in the reaction of 2-nitro-2-nitrosopropane [$Me_2C(NO_2)NO$], the decomposition of fluoroalkanoyl peroxides were shown to proceed via a radical reaction rather than a single electron-transfer reaction.[201]

In the reaction of fluoroalkanoyl peroxides with di-*tert*-butyl nitroxide [t-Bu_2NO] or *tert*-butyl nitroxide [t-$BuNO^•$], similar radical decomposition mechanisms were proposed.[202,203]

Polyfluoroalkyl radicals generated by a one-electron reduction of polyfluoroalkanoyl peroxides by copper(0) were trapped by 2-nitro-2-nitrosopropane to yield polyfluoroalkyl nitroalkyl nitroxide $R_FN(O)CMe_2NO_2$.[204] Very recently, the reaction mechanism of ω-hydroperfluoroalkanoyl peroxides [$H((CF_2CF_2)_nCOO)_2$] with 2-aminopyrimidines has been studied in detail by Zhao et al.[205]

The thermal decomposition of perfluoroalkanoyl peroxides in the presence of water was studied (Scheme 114). Kinetic studies showed that the

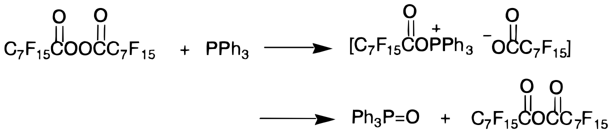
Scheme 114



decomposition of trifluoroacetyl peroxide is greatly accelerated by the addition of water to give trifluoroacetic acid and trifluoroacetyl peracid via a nucleophilic attack of water on a carbonyl carbon (hard acid moiety) in the peroxide, whereas that of perfluorooctanoyl peroxide is only slightly accelerated. Therefore, a strong repulsion for water, owing to the high surface-active property of the long chain perfluoroalkyl group (perfluoroheptyl group), was suggested as affecting the hydrolysis of perfluorooctanoyl peroxide.

On the other hand, in the reaction of a soft base such as triphenylphosphine with perfluorooctanoyl peroxide, a nucleophilic attack of triphenylphosphine on the O−O bond (soft acid moiety in the peroxide) afforded triphenylphosphine oxide and perfluorooctanoic anhydride[206] (Scheme 115).

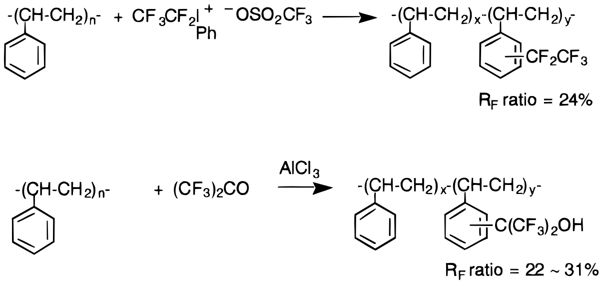
Scheme 115



D. Aromatic Fluoroalkylation of Polymeric Compounds with Fluoroalkanoyl Peroxides

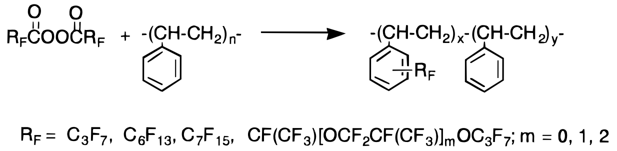
It has been well-known that acrylated or methacrylated polymers containing perfluoroalkyl groups exhibit excellent properties imparted by the presence of fluorine.[207] Usually, perfluoroalkyl groups are introduced into polymers through the ester or amide bond. Yet these materials are in general unstable under acid or alkaline conditions, owing to the ester or the amide moieties. Therefore, it has been highly desirable to explore novel synthetic methods for the direct fluoroalkylation of these compounds. It is of particular interest to explore the direct aromatic fluoroalkylation of polymers and to examine their properties from the material science viewpoint. However, there have been few synthetic reports except for the direct aromatic fluoroalkylations of polystyrene with FITS (perfluoroalkyl phenyliodonium trifluoromethane sulfonate) or hexafluoroacetone[208,209] (Scheme 116).

Scheme 116



Recently, it has been demonstrated that perfluoroalkanoyl and perfluorooxaalkanoyl peroxides are useful reagents for the direct aromatic fluoroalkylation (perfluoroalkylation and perfluorooxaalkylation) of polymers such as polystyrenes, polydiphenylsilane, polydiphenylsiloxane, polyimides, and polyamic acids[185,210] (Scheme 117).

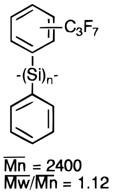
Scheme 117



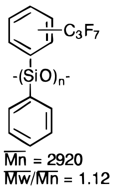
In the reaction of polystyrenes with fluoroalkanoyl peroxides, it was found that the molecular weights of the perfluoroalkylated and perfluorooxaalkylated polystyrenes (PStR$_F$) were increased by the perfluoroalkylations and perfluorooxaalkylations of the parent polystyrenes. The $\bar{M}_w/\bar{M}_n$ of perfluoroalkylated and perfluorooxaalkylated polystyrenes were comparable to those of the parent polystyrenes. This finding indicates that degradation of the polymer did not occur under the fluoroalkylation conditions. The fluoroalkylation of polystyrenes with fluoroalkanoyl peroxides can be accounted for by a single electron-transfer mechanism from the substrate to the antibonding (2pσ*) O−O bond of the peroxide such as was proposed for perfluoroalkylation with perfluoroalkanoyl peroxides.

It was found that the T_g of the PStR$_F$ was increased from 89 °C to about 106 °C by the perfluoroalkylation. Moreover, the n_D of the PStR$_F$ was drastically lowered compared with that of the parent polystyrene. For example, the n_D of the PStC$_3$F$_7$ [1.39 (R$_F$ ratio = 69%)] is close to that of polytetrafluoroethylene (1.35).

Furthermore, under similar reaction conditions direct aromatic perfluoropropylation of polydiphenylsilane **117** and polydiphenylsiloxane **118** with perfluorobutyryl peroxide proceeded in yields of 78% and 51% perfluoroalkylation, respectively.



117



118

The critical surface tensions of the perfluorooxaalkylated polystyrenes are compared to those of the perfluoroalkylated analogs in Table 10.[211−213]

The critical surface tensions (γ_c) of the perfluorooxaalkylated polystyrene films are diminished dramatically in comparison with those of perfluoroalkylated polystyrenes. The γ_c of both perfluorooxaalkylated and perfluoroalkylated polystyrene films were found to decrease with an increase in the R_F ratio, and to remain constant above a specific R_F ratio value. The surface behavior of the polystyrenes possessing perfluorooxaalkyl groups is of particular interest because they exhibit a surface activity not shown either by ordinary hydrocarbon polymers or

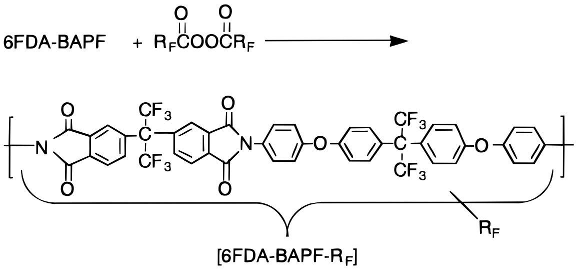
Table 10. Critical Surface Tensions (γ_c) of $C_3F_7O[CF(CF_3)CF_2O]_mCF(CF_3)PSt$ and $CF_3(CF_2)_nPSt$ Films

polymer	R_F ratio (%)	γ_c (mN/m)
$C_3F_7O[CF(CF_3)CF_2O]_mCF(CF_3)PSt$		
$m = 0$	0	35.7
	2	27.2
	5	24.6
	10	22.7
$m = 1$	4	25.4
	6	24.0
	13	16.2
	43	16.2
$CF_3(CF_2)_nPSt$		
$n = 2$	4	28.7
	12	26.4
	26	25.2
	40	24.7
	69	24.6
$n = 5$	2	27.0
	3	26.2
	7	25.5
	16	23.5
	30	23.4
	60	23.4
$n = 6$	67	23.3

other fluoroalkylated polymers (perfluoroalkylated polystyrenes). This unique critical surface tension reduction could be associated with a polystyrene having a particular number of trifluoromethyl groups and ether linkages. In particular, the γ_c values (16.2 mN/m) of perfluorooxaalkylated polystyrenes ($m = 1$, R_F ratio = 13%, 43%) were shown to be superior to that of polytetrafluoroethylene (18.5 mN/m).

In the direct aromatic fluoroalkylations of polyimides such as 6FDA-BAPF, the perfluoroalkylated polyimides were obtained using of fluoroalkanoyl peroxides under similar reaction conditions as shown in Scheme 118.[214]

Scheme 118

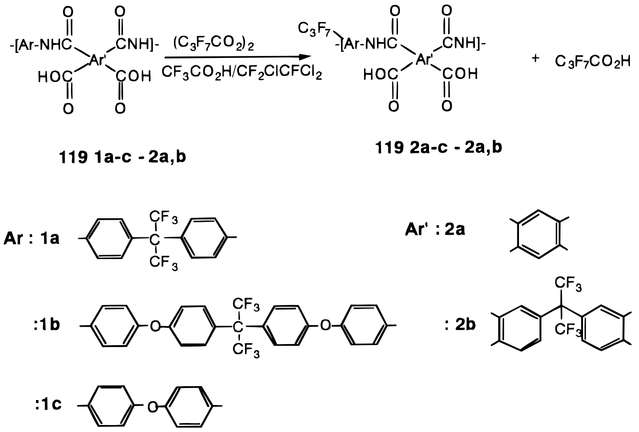


However, a reduction in molecular weight of fluoroalkylated 6FDA-BAPF [6FDA-BAPF-R_F] was observed. This finding suggests that the imide groups in the polymer were hydrolyzed with fluoroalkanoic acids which are produced as fluoroalkylation byproducts.

It was found that the T_g values of 6FDA-BAPF-R_F are decreased, whereas the dielectric constants of 6FDA-BAPF-R_F are increased by the fluoroalkylation. Usually, it is well-known that the dielectric constants of polyimides are decreased by the fluorination of the parent polyimides.[215] On the other hand, the dielectric constants of these fluoroalkylated polyimides, 6FDA-BAPF-R_F were found to increase compared with that of the parent polyimide. This finding would be dependent upon that the polymer chains becoming more polarizable, owing to the introduction of longer fluoroalkyl chains such as perfluoropropyl, perfluorohexyl, and perfluoroheptyl groups into the aromatic moieties in polyimides.

Furthermore, polyamic acids containing a perfluoropropyl group (**119-2**) were obtained by the reactions of perfluorobutyryl peroxide with the corresponding polyamic acids (**119-1**) under similar mild conditions (Scheme 119). However, the molecular weights of the perfluoropropylated polyamic acids obtained were lower than those of the parent polyamic acids, owing to the degradation of polyamic acid through hydrolysis with perfluorobutyric acids which is produced as perfluoropropylation byproducts.[216]

Scheme 119



Recently, these fluoroalkanoyl peroxides were used in the direct aromatic fluoroalkylations of the surface only of polyester film and to the surface modification of silk fabric.[217,218]

Polymers bearing benzene rings such as polystyrene, poly(2,6-dimethyl-*p*-phenylene oxide), and poly(diphenylacetylene) were chemically modified using fluoroalkanoyl peroxides. These fluoroalkylated polymers were shown to have higher gas permeabilities than the parent polymers.[219]

VII. Synthesis of Fluoroalkylated Compounds with Fluoroalkanoyl Peroxides via a Radical Process

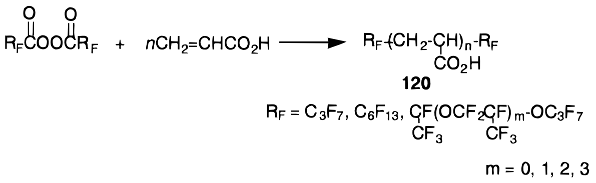
A. Synthesis and Properties of Fluoroalkylated Oligomers Using Fluoroalkanoyl Peroxides

It is well-known that perfluoropolymers such as poly(tetrafluoroethylene) exhibit some excellent properties imparted by the presence of fluorine. However, in general these materials have an extremely low solubility in organic solvents. In contrast, it has been reported that cyclic fluoropolymers lead to an increased solubility in selected fluorinated solvents.[220,221]

Very recently, partially protonated ring-containing fluoropolymers have been reported as being soluble in polar aprotic solvents such as DMF, THF, acetone, and acetonitrile although these polymers are insoluble in benzene, chloroform, and methanol.[222]

Fluoroalkanoyl peroxide is a useful tool for the direct introduction of the corresponding fluoroalkyl group into organic molecules via a radical process. From this point of view, it is of much interest to develop fluoroalkylated polymeric materials which are easily soluble in various solvents by using fluoroalkanoyl peroxides. In fact, acrylic acid oligomers containing two fluoroalkylated end groups **120** are prepared via a radical process by using fluoroalkanoyl peroxides[223] (Scheme 120).

Scheme 120



Elemental analyses for fluorine confirmed that these oligomers contain two fluoroalkylated end groups in one molecule.[224]

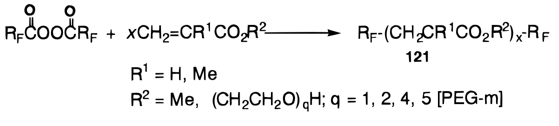
These fluoroalkylated acrylic acid oligomers were shown to be soluble in both water and polar organic solvents such as methanol, ethanol, and tetrahydrofuran. Additionally, these oligomers were found to be effective in reducing the surface tension of water by around 10 m/Nm although these compounds are oligomeric (high molecular mass) materials.

Acrylic acid oligomers containing two fluoroalkyl end groups obtained by using fluoroalkanoyl peroxides are expected to become novel polymeric inhibitors of HIV-1 with high stability and low toxicity due to their high solubility in water.[225] Fluorinated oligomers containing shorter fluoroalkyl groups such as perfluoropropyl, perfluorohexyl, and perfluoro-1-methyl-2-oxapentyl groups were found to be inactive. However, although acrylic and methacrylic acid oligomers containing longer fluoroalkyl groups such as perfluoro-1,4-dimethyl-2,5-dioxaoctyl group were potent inhibitors in HIV-1 replication, these compounds did not affect the growth and viability of mock-infected MT-4 cells at concentrations $\leq 100\ \mu g/mL$. These fluoroalkylated oligomers have a similar activity against HIV-1 as that of dextran sulfate, which is considered to be both a potent and selective polymeric inhibitor of HIV-1 replication in cell culture.[226]

It has been suggested that dextran sulfate is easily degraded into inactive fragments by glycosidic cleavage owing to the polysaccharide,[227] and might be desulfated by sulfatase enzyme in vivo. In contrast, since these fluorinated oligomers are structurally stable, these new oligomers are expected to have advantage over dextran sulfate.

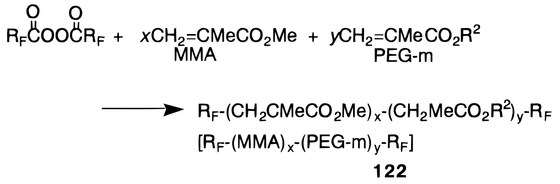
Fluoroalkylated methyl methacrylate and hydroxylated ethylene oxide units containing methacrylate or acrylate oligomers **121** were prepared using fluoroalkanoyl peroxides as shown in Scheme 121.[228]

Scheme 121



Furthermore, it was found that fluoroalkylated methyl methacrylate–ethylene oxide units containing methacrylate cooligomers **122** are also obtained under similar conditions[229] (Scheme 122).

Scheme 122

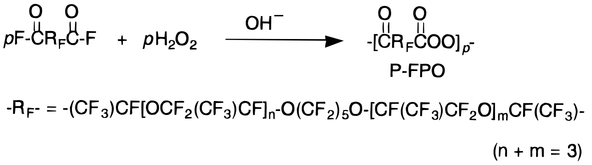


Perfluorooxaalkylated oligomers containing hydroxylated ethylene oxide units $[R_F[CH_2CRCO_2(CH_2CH_2O)_qH]_xR_F]$ exhibit surface properties typical of amphiphiles. The surface behavior of perfluorooxaalkylated oligomers containing hydroxylated ethylene oxide units is of great interest because the contact angles of such oligomers, especially those of oligomers bearing long ethylene oxide chains, exhibit strong hydrophilic properties despite the fact that these oligomers possess perfluorooxaalkyl groups.[229]

The fluoroalkylated acrylic acid oligomers $[R_F(CH_2CHCO_2H)_nR_F]$ and methacrylate oligomers containing ethylene oxide units $[R_F[CH_2CMeCO_2(CH_2CH_2O)_qH]R_F]$ were found to be soluble in hydrocarbon oligomer solutions. Furthermore, these acrylic acid and methacrylate oligomers reacted with the usual epoxy and melamine curing agents, respectively, to afford the cured films. These films were found to exhibit surface properties typical of the amphiphiles.[230]

The polymeric perfluorooxaalkane diacyl peroxide (P-FPO) was prepared by the reaction of the corresponding diacid fluoride and hydrogen peroxide under alkaline conditions in moderate isolated yields (about 50%)[231] (Scheme 123).

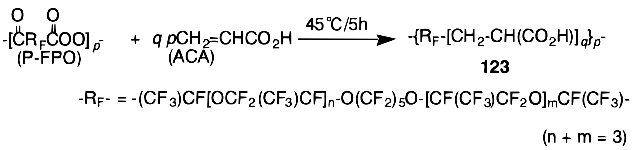
Scheme 123



The activation energy ($\Delta E_a = 21.9$ kcal/mol) for the decomposition of P-FPO is quite similar to those for fluoroalkanoyl peroxides such as $(C_7F_{15}CO_2)_2$ ($\Delta E_a = 23.5$ kcal/mol) and $[C_3F_7OCF(CF_3)CO_2]_2$ ($\Delta E_a = 23.9$ kcal/mol), leading to a concerted dissociation with the three-bond homolytic fissions. This suggests that P-FPO decomposes with homolysis of the C–C (carbonyl carbon–fluoroalkyl carbon) and O–O peroxy bonds and provides a useful tool for the introduction of the perfluorooxaalkylene unit ($-R_F-$) into oligomers by a radical process.

In fact, it was demonstrated that the reactions of P-FPO with acrylic acid proceed smoothly to afford acrylic acid oligomers containing perfluorooxaalkylene unit **123** in good yields (Scheme 124).

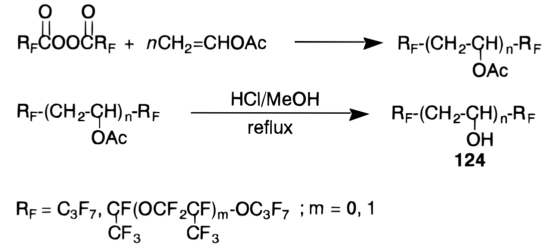
Scheme 124



In addition to acrylic acid oligomers containing two perfluorooxaalkyl end groups, acrylic acid oligomers containing the perfluorooxaalkylene unit obtained using P-FPO were found to be easily soluble not only in water but also in water-soluble organic solvents such as methanol, ethanol, and tetrahydrofuran. Thus, it has been demonstrated that such oligomers are potential new fluorinated surfactants, as well as potent and selective inhibitors of HIV-1 in vitro.[232]

Fluoroalkanoyl peroxides were also used in the preparation of fluoroalkylated vinyl alcohol oligomers (**124**) (Scheme 125). In general, poly(vinyl alcohol)s are known to be soluble in water but not in organic solvents. These fluoroalkylated vinyl alcohol oligomers **124** were found to be completely insoluble in water and to exhibit good solubility in common organic solvents such as chloroform, methanol, ethanol, tetrahydrofuran, and ethyl acetate. Furthermore, these oligomers possess good water- and oil-repellent properties.[233,234]

Scheme 125

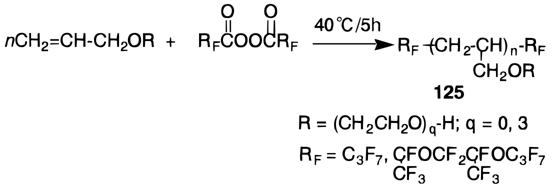


124

$R_F = C_3F_7$, $CF(CF_3)(OCF_2CF(CF_3))_m$-$OC_3F_7$; m = 0, 1

In the reactions of allylic compounds such as allyl alcohol and allyl alcohol containing the polyoxyethylene unit, fluororoalkylated allyl alcohol oligomers **125** are obtained under very mild conditions (Scheme 126). In particular, fluoroalkylated allyl alcohol oligomers containing the polyoxyethylene unit (*q* = 3) were shown to be effective in reducing the surface tension of water and to have potential as new nonionic fluorinated amphiphiles.[235]

Scheme 126



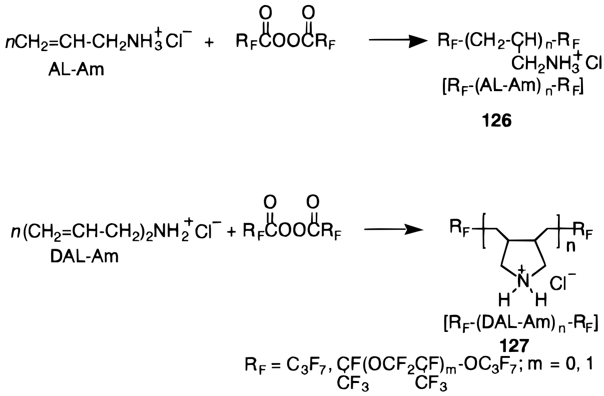
125

R = $(CH_2CH_2O)_q$-H; q = 0, 3

$R_F = C_3F_7$, $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$

Similarly, fluoroalkylated allyl- and diallylammonium chloride oligomers (**126** and **127**) are obtained by the oligomerization of allyl ammonium chloride and the cyclooligomerization of diallylammonium chloride using fluoroalkanoyl peroxides (Scheme 127).

Scheme 127



126

127

$R_F = C_3F_7$, $CF(CF_3)(OCF_2CF(CF_3))_m$-$OC_3F_7$; m = 0, 1

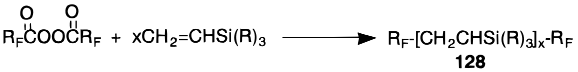
These fluoroalkylated cationic oligomers were able to reduce the surface tension of water to around 10 m/Nm and thus are new cationic oligosurfactants containing fluoroalkyl groups.[236]

B. Synthesis and Properties of Fluorosilicon Oligomers Using Fluoroalkanoyl Peroxides

In general, organosilicon compounds are well-known to exhibit good hydrophobic properties but not oleophobic properties. In contrast, organofluorine compounds bearing long perfluoroalkyl chains have not only hydrophobic but also oleophobic properties owing to the long perfluoroalkyl chains. Hence, there has been a great demand for the development of new functional materials possessing the excellent properties imparted by the presence of both silicon and fluorine.

Recently, it has been demonstrated that perfluoroalkylated and perfluorooxaalkylated organosilicon oligomers **128** are obtained in excellent to moderate yields under very mild conditions[237] (Scheme 128).

Scheme 128



128

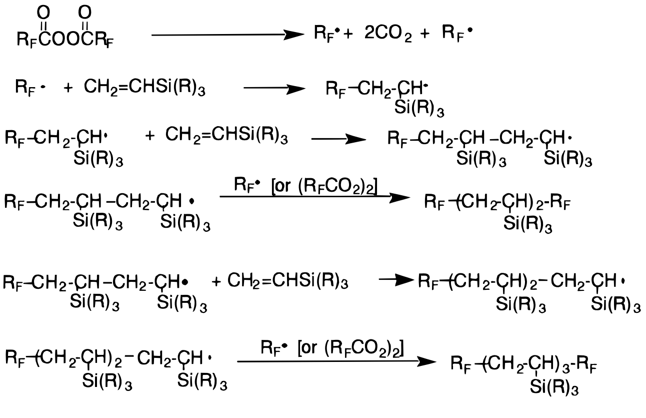
x = 2 or 3

R_F = $-C_3F_7$ or $-CF(CF_3)[OCF_2CF(CF_3)]_mOC_3F_7$; m = 0 or 1

R = OMe or Me

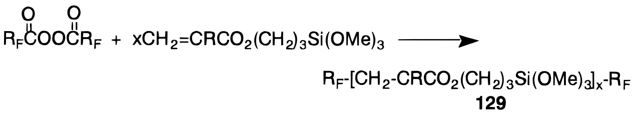
These products suggest that reaction proceeds by the usual free radical addition to vinylsilanes of fluoroalkyl radicals produced by the homolytic decomposition of peroxide and by chain transfer to the peroxide[237] (Scheme 129).

Scheme 129



Furthermore, [3-(methacryloxy)propyl]trimethoxysilane (MMA−Si) and [3-(acryloxy)propyl]trimethoxysilane (AC−Si) were shown to react smoothly with the peroxides under mild condition to give fluorine-containing silicon oligomers **129** in good yields via a radical process as shown in Scheme 130.[238]

Scheme 130



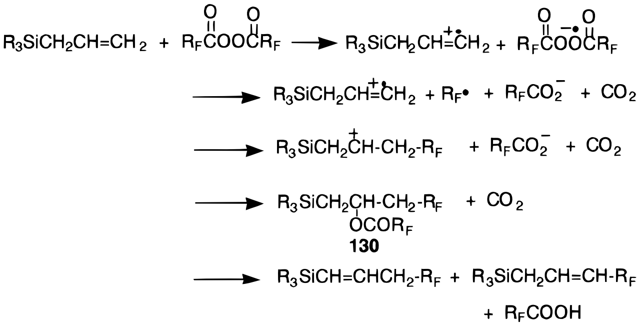
129

R_F = $-C_3F_7$ or $-CF(CF_3)[OCF_2CF(CF_3)]_mOC_3F_7$; m = 0, 1

R = H, Me

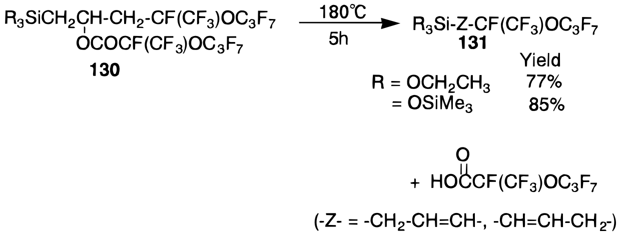
In contrast, allylsilanes such as trimethoxyallylsilane and trimethylallylsilane were found to react with fluoroalkanoyl peroxides to afford 1:1 adducts [$R_FCH_2CH(OCOR_F)CH_2Si(R)_3$] (**130**) in good yields without oligomer formation[239] (Scheme 131).

Scheme 131



The olefinic compounds [$R_FZSi(R)_3$, $-Z- = -CH{=}CHCH_2-$, $-CH_2CH{=}CH-$] were formed as byproducts in each of the above reactions. From the thermolysis of the 1:1 adducts, it was suggested that the formation of $R_FZSi(R)_3$ is dependent on the following elimination of fluorocarboxylic acid as shown in Scheme 132.[239]

Scheme 132

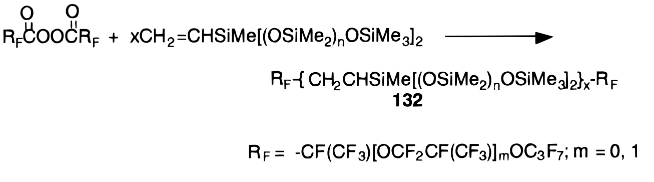


The different reactivities of vinylsilanes and allylsilanes may depend on the different HOMO energy levels between these silicon compounds.[239]

Organosilicon compounds containing perfluoroalkyl and perfluorooxaalkyl groups obtained by the reaction of VM−Si, MMA−Si, and AC−Si with fluoroalkanoyl peroxides were shown to be useful as surface-active materials.[237−239]

New fluorosilicone oligomers having different perfluorooxaalkyl and siloxane chain lengths (**132**) were obtained by the oligomeric reaction with fluoroalkanoyl peroxides[240] (Scheme 133).

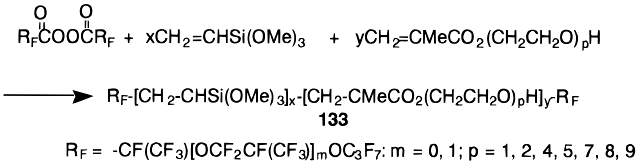
Scheme 133



Fluorosilicone oligomers possessing dimethylsilicone segments [$R_F\{CH_2CHSiMe[(OSiMe_2)_nOSiMe_3]_2\}_nR_F$] (**132**) were found to reduce the friction coefficient of liquid paraffin from 0.086 to 0.015 (about an 86% reduction). On the other hand, nonfluorinated dimethylsilicones were found to be ineffective in reducing the friction coefficient of liquid paraffin.[240]

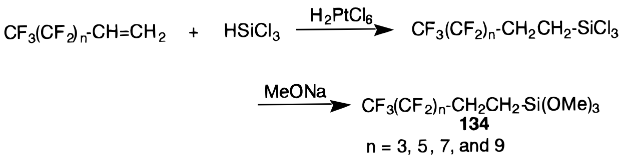
Furthermore, fluorosilicon cooligomers (**133**) are obtained by the reaction of fluoroalkanoyl peroxides with trimethoxyvinylsilane and methacrylate monomers containing poly(oxyethylene) units[241] (Scheme 134). Not only have these fluorosilicon cooligomers (**133**) been predicted to be new amphiphilic fluorosilane coupling agents, they have been shown to have good surface activity and to be active as a new type of an amphiphilic fluorosilane coupling agent.[241]

Scheme 134



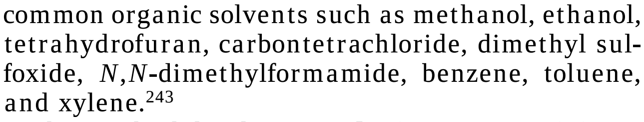
Recently, the hydrosilylation of fluorine-containing alkenes promoted by a platinum catalyst has been applied to the preparation of silane coupling agents containing one perfluoroalkyl group (**134**)[242] (Scheme 135).

Scheme 135



Usually, fluorinated surfactants, such as perfluoroalkanoic and perfluoroalkanesulfonic acids, and perfluoroalkyl acrylate polymers are well-known to have a poor solubility in most solvents except for fluorinated solvents. The exploration of fluoroalkylated materials leading to relatively high solubility in both water and common organic solvents will open a new route to the development of new functional materials, particularly new amphiphilic fluorinated materials. Interestingly, it was found that fluoroalkylated acrylic acid−trimethylvinylsilane cooligomers (**135**) obtained by the reaction of a series of fluoroalkanoyl peroxides with acrylic acid and trimethylvinylsilane leads to a new series of fluorinated amphiphilic materials (Scheme 136). These fluorosilicon cooligomers are soluble both in water and in common organic solvents such as methanol, ethanol, tetrahydrofuran, carbontetrachloride, dimethyl sulfoxide, *N*,*N*-dimethylformamide, benzene, toluene, and xylene.[243]

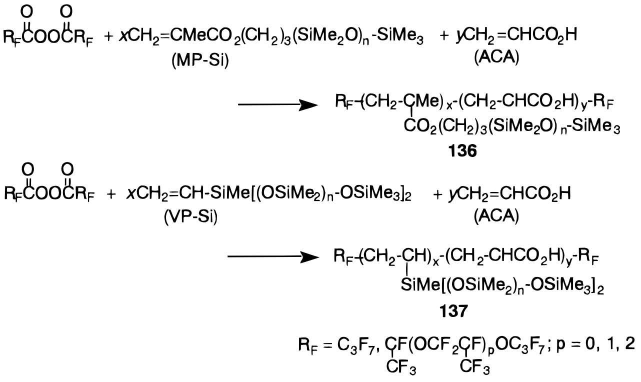
Scheme 136



The amphiphilic oligomers, [$R_F(CH_2CHCO_2H)_x(CH_2CHSiMe_3)_yR_F$] (**135**) were shown to decrease the surface tension of both water and *m*-xylene effectively.

Similarly, fluoroalkylated acrylic acid cooligomers containing dimethylsilicone segments (**136** and **137**) have been prepared by the reaction of fluoroalkanoyl peroxides with acrylic acid and dimethylsilicones possessing one vinyl or one methacryloxypropyl end group under very mild conditions (Scheme 137).

Scheme 137



These fluorinated silicone cooligomers were soluble in both water and in common organic solvents. In addition they were found to be potent and selective inhibitors of HIV-1 in vitro.[244,245]

Acknowledgments

Our work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

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