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α-Branched-perfluorodiacyl peroxides: preparation and characterization

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This paper is dedicated to Prof. R.D. Chambers on his 70th birthday.

Abstract

New perfluorodiacyl peroxides substituted at the α position have been synthesized and characterized. This class of peroxides shows good hydrolytic stability.

Keywords: Perfluorodiacyl peroxides; Preparation; Characterization; Hydrolysis; Thermolysis

1. Introduction

Perfluoro diacyl peroxides are an interesting and useful source of perfluoroalkyl radicals [1].

Their utility as initiators in the free radical polymerization of fluoromonomers has been recognized since the early 1950s [2]. Recently, perfluoroalkyl free radical chemistry has raised considerable interest, as demonstrated by many important articles and reviews which appeared in the specialized literature [1–6].

Along with the increasing importance of perfluoroalkyl radical chemistry the number of initiation methods has also increased, but the thermal decomposition of perfluorodiacyl peroxides remains the method of choice for free radical polymerization.

This is due to the mild thermal conditions required and the clean reaction which generates perfluoroalkyl radical. In addition, thermal homolytic peroxide decomposition is monomolecular and auto-induced decomposition is not observed in the range of peroxide concentrations used in the polymerization initiation [6]. This initiation system cannot act as a free radical transfer reagent and allows a better control of the polymer molecular weight. Perfluoroalkyl radicals are directly introduced at the extremity of the polymer chain, allowing the preparation of fluoropolymers with excellent thermal and optical properties [7], as well as pharmaceutical properties [8]. The industrial research in this area has been very active since the early discoveries [9–11].

However, there are a few drawbacks in the preparation, purification and utilization of these peroxides. Perfluoroacyl halides, chlorides, fluorides and perfluoro anhydrides are generally utilized as starting materials for the preparation of acyl peroxides with H_2O_2 in alkaline conditions. The low to medium yields in their preparation are due to diacyl peroxide and starting material hydrolysis. In fact the two strong electron withdrawing perfluoro alkyl groups enhance the rate of hydrolysis as compared to the hydrogenated diacyl peroxide [1]. Wlassics found that the rate of hydrolysis increases with increasing MW of the perfluorooxyalkyl radical bonded to the carbonyl of the diacyl peroxide [12]. According to Diffendall et al. the higher the molecular weight of the peroxide used in a dispersion, the longer the peroxide survives before significant hydrolysis takes place, although no specific data were reported [13].

The presence of electron withdrawing groups, like fluorine or perfluoroalkyl radicals bonded to the carbonyl of the diacyl peroxide, also enhance their thermal homolytic decomposition rates compared to hydrogenated diacyl peroxides [1].

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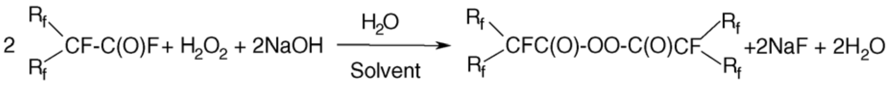
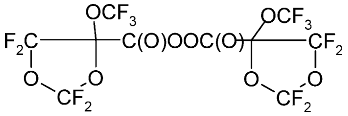
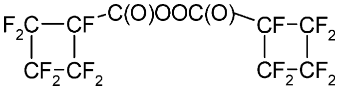


Scheme 1.

Table 1
Thermolysis and hydrolysis data for peroxides **1–6** in $CF_2ClCFCl_2$ as solvent

Peroxide	*T* (C°)	Thermolysis, k_d ($\times 10^5$ s^{-1})	Hydrolysis, k_d ($\times 10^5$ s^{-1})
(**1**) Perfluoroisobutyrylperoxide, $(CF_3)_2CFC(O)OOC(O)CF(CF_3)_2$	70	17.3	21.1
(**2**) Perfluoro-2-methoxy-propionylperoxide, $CF_3(CF_3O)CFC(O)OOC(O)CF(OCF_3)CF_3$	20	1.8	1.5
(**3**) Perfluoro-2,2-dimethoxy-propionylperoxide, $(CF_3O)_2CF_3CC(O)OOC(O)CCF_3(OCF_3)_2$	15	7.6	7.3
(**4**) bis(perfluoro-5-methoxy-2,3-dioxolane-5-carbonyl)peroxide, 	30	11.7	13.9
(**5**) bis(perfluorocyclobutane carbonyl)peroxide, 	70	10.8	13.3
(**6**) Perfluorobutyrylperoxide, $CF_3CF_2CF_2C(O)OOC(O)CF_2CF_2CF_3$	15	1.5	4.5
(**7**) Fomblin *Z*-diacylperoxides (Mw = 529) [12], $[CF_3O(CF_2O)_r(CF_2CF_2O)_sC(O)O]_2$	20	0.25	467

This behavior may give limitations in the choice of polymerization conditions, particularly in the case of slow reacting monomers for which high polymerization temperatures are preferred [9]. Low polymerization temperatures are instead chosen in the case of vinylidene fluoride (CF_2=CH_2) polymer, where the formation of $–CF_2CH_2–CH_2CF_2–$ segments in the polymer backbone needs to be controlled [10,14].

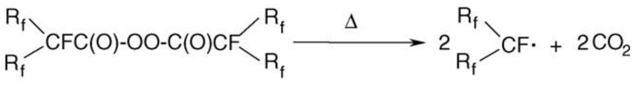
In order to overcome these limitations, we directed our study towards the preparation of perfluoro diacyl peroxides characterized by a good hydrolytic stability and by a wide range of thermal decomposition temperatures.

2. Results and discussion

Starting from low molecular weight perfluoroacyl fluorides substituted in the α position, we obtained good to medium yields in the preparation of α substituted dialkanoyl peroxides utilizing the described preparation method which employs hydrogen peroxide in aqueous NaOH in a biphasic system [1,9], as illustrated in Scheme 1.

The hydrolysis of the perfluoro diacyl peroxide end product has been minimized choosing the proper experimental conditions as shown in Section 4 and Table 4.

The presence of a bulky substituent α to the acylfluoride decreases the hydrolysis side reactions in the diacyl peroxide preparation, where highly hydrolytic conditions like aqueous NaOH are utilized.

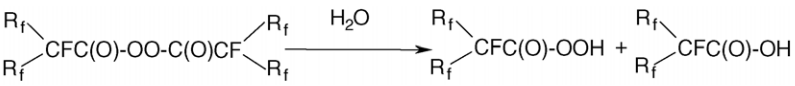


Scheme 2.

The low molecular weight of the starting acylfluoride also avoids the presence of annoying emulsions that are often the cause of a low preparation yield [12].

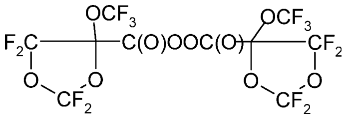
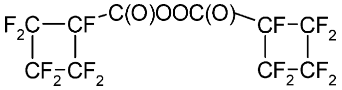
The hydrolytic decomposition of perfluoro diacyl peroxide substituted in the α position with respect to diacyl peroxide is very low in de-ionized water, see Table 1.

Schemes 2 and 3 illustrate the thermal and the hydrolytic decompositions, respectively, of this family of perfluoro diacyl peroxides. As can be seen in Table 1, the hydrolysis reaction of these peroxides does not substantially interfere with the homolytic thermal decomposition in de-ionized water. The hydrolysis is a heterogeneous reaction; therefore its rate is also a function of the stirring efficiency and of the presence of surfactants or cosolvents. The hydrolysis data shown in Table 1 are important as relative values, in particular in the case of linear di(perfluorobutyryl) peroxide **6** and perfluoro PFPE dialkanoyl peroxide **7**, whose "hydrolytic k_d" are three times and three orders of magnitude higher than the "thermolytic k_d", respectively. On the contrary, thermolytic k_d and hydrolytic k_d for the



Scheme 3.

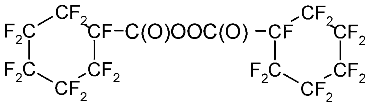
Table 2
Thermolysis, Arrhenius and Eyring data for peroxides **1**–**5** in $CF_2ClCFCl_2$ as solvent

Peroxide	T (°C)	Thermolysis, k_d ($\times 10^5$ s^{-1})	Arrhenius		Eyring	
			ln(A)	E_a (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (kJ mol^{-1})
(**1**) Perfluoroisobutyrylperoxide, $(CF_3)_2CFC(O)OOC(O)CF(CF_3)_2$	60	4.4	35.0	124.7	121.7	36.4
	70	17.3				
	80	56.5				
(**2**) Perfluoro-2-methoxy-propionylperoxide, $CF_3(CF_3O)CFC(O)OOC(O)CF(OCF_3)CF_3$	20	1.8	37.7	118.4	115.9	59.8
	30	9.9				
	40	40.8				
(**3**) Perfluoro-2,2-dimethoxy-propionylperoxide, $(CF_3O)_2CF_3CC(O)OOC(O)CCF_3(OCF_3)_2$	5	1.8	37.3	112.1	109.6	57.7
	10	7.6				
	15	46.2				
(**4**) bis(perfluoro-5-methoxy-2,3-dioxolane-5-carbonyl)peroxide, 	20	3.1	33.2	106.3	103.8	22.6
	30	11.7				
	40	50.2				
(**5**) bis(perfluorocyclobutane carbonyl)peroxide, 	60	3.0	34.5	124.7	121.7	33.0
	70	10.9				
	80	38.5				

α-branched peroxides **1**–**5**, although not identical, have the related values in the same range. It should be pointed out that the hydrolysis kinetic constants k_d of Table 1 are inclusive of the inherent homolytic decomposition, therefore these data should be considered as a computation of the homolytic and hydrolytic decomposition (see Section 4.4).

The thermal decomposition of peroxides **1**–**5** (Scheme 2) follows first-order kinetics (see Section 4.3). The decomposition rate constants k_d in $CF_2ClCFCl_2$ for peroxides **1**–**5**, calculated for three different temperatures, are reported in Table 2. The activation energy and the kinetic parameters calculated according to the Arrhenius and Eyring transition

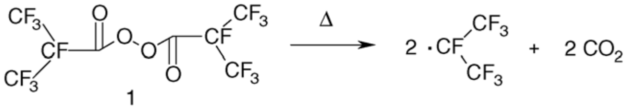
Table 3
Thermolysis, Arrhenius and Eyring data for peroxides **8**–**10**

Peroxide	T (°C)	Thermolysis, k_d ($\times 10^5$ s^{-1})	Arrhenius		Eyring	
			ln(A)	E_a (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (kJ mol^{-1})
(**8**) Perfluoroacetylperoxide [17], $CF_3C(O)OOC(O)CF_3$	45	1.6	30.9	110.9	108.4	2.9
	55	6.0				
	60	10.4				
(**9**) Perfluoroproprionylperoxide [1], $CF_3CF_2C(O)OOC(O)CF_2CF_3$	25	1.2		118.8		
(**10**) bis(perfluorocyclohexane carbonyl)peroxide [18], 	35	0.7	30.6	108.4	105.8	1.6
	40	1.7				
	45	3.1				

state equations are also reported in Table 2, whereas data derived from the literature of known peroxides are reported in Table 3 for comparison.

From Tables 2 and 3, it can be seen that the activation enthalpies for the decomposition of peroxides **1–5** are generally higher than enthalpies of peroxides **8–10**, with the exception of peroxide **4**. Activation entropies are also higher; particularly for peroxides **2** and **3**, probably indicating a disordered transition state. The enthalpic contribute for peroxides **1** and **5** prevails leading to high value of $\Delta G^{\#}$ and consequent high temperature of decomposition. The entropic contribute for peroxide **3** prevails, leading to low $\Delta G^{\#}$ value and consequent low temperature of decomposition and also the fact that the activated complex is more favorable than the reactants.

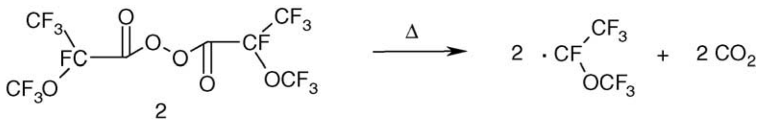
The thermal di(perfluoroalkanoyl) peroxide decomposition can be seen as a concerted process involving the simultaneous homolysis of the C_2–C_1 and O–O bonds, where the stability of the end perfluoroalkyl radical is an important variable to determine the decomposition rate of the starting diacyl peroxide [1,3,15–17]. The same reaction has also been recognized as one-bond homolytic decomposition process, depending on the nature and viscosity of the solvent [21].



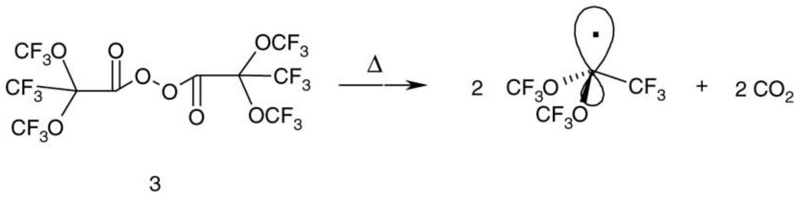
Scheme 4.

Although the data reported in Table 2 are not extrapolated to zero viscosity as suggested by DeSimone et al. [21], the nature of the substituents bonded to the carbonyl of the diacyl peroxide is an important variable in determining the homolytic decomposition rate of diacyl peroxide compounds.

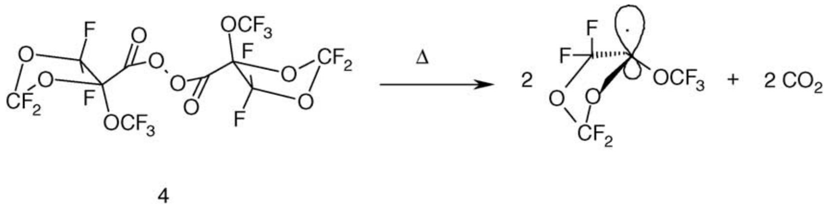
In Table 2 an increase in the decomposition rate from dialkanoyl peroxide **1** to peroxide **2** can be seen. The thermal decomposition reaction variation can be ascribed to a different substitution at the α carbon of the dialkanoyl



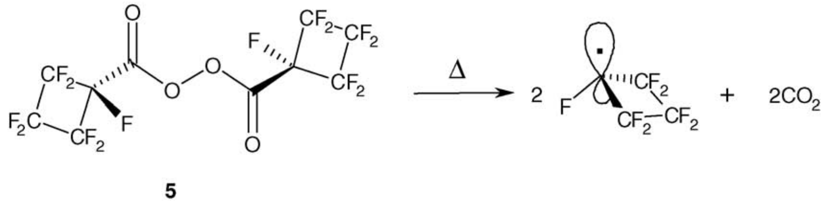
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

peroxide, trifluoromethyl radical and trifluoromethoxy radical for peroxides **1** and **2**, respectively, as shown in Schemes 4 and 5.

A further increase in the decomposition rate is observed from peroxide **2** to peroxide **3**; this may be due to the second trifluoromethyl group introduction at the α carbon of the dialkanoyl peroxide, as shown in Scheme 6.

The di(perfluoroalkanoyl) peroxides **4** and **5** undergo the formation of radicals centered on a secondary carbon atom on cyclic structures (Schemes 7 and 8). The effect of the destabilization of the peroxide due to the presence of two oxygen atoms α to the perfluorinated dialkanoyl peroxide observed for dialkanoyl peroxide **3** is not observed for peroxide **4**, this might be due to the strain of the five member ring of the perfluorodiooxolyl radical shown in Scheme 7.

In Scheme 8 the perfluorocyclobutyl radicals derive from the thermal decomposition of peroxide **5**. The strain of the four-member ring of perfluorocyclobutyl radical may be one the reasons of the moderate increase of the stabilization of this peroxide compared to peroxide **10** of Table 3.

The thermal behavior of peroxides **1**–**5** may be interpreted through the stabilization/destabilization effect of the substituents on the perfluoro radical formed by the decomposition of the di(perfluoroalkanoyl) peroxide.

EPR spectroscopic studies will give experimental information on the geometry and in particular on the degree of ‘‘bending’’ of the radicals derived from the decomposition of peroxides **1**–**5**. Concerning the geometry of perfluoroalkyl radical by EPR study, Corvaia and coworkers discovered a substantially planar perfluoroalkyl radical intermediate in the addition of hypofluorite to highly substituted perfluoro olefins [22], on the contrary Faucitano et al. noticed a pyramidal structure for radical substituted by a less bulky group in the photodecomposition of perfluoro oxyalkylperoxides [23].

3. Conclusions

In order to overcome the limitations of known perfluoro diacyl peroxides, we have identified a class of perfluorodiacyl peroxide characterized by a good hydrolytic stability and by a wide range of thermo decomposition temperatures ranging from 0 up to 90 °C with a half time of few hours. A class of peroxides so designed can be easily utilized as initiators in a variety of polymerization or oligomerization reactions [9].

4. Experimental

4.1. General methods, materials and safety precautions

4.1.1. General methods

Volatile compounds were handled in a glass and/or stainless-steel vacuum system equipped with glass/PTFE or stainless-steel valves. Pressures were measured with a Druck PDCR 110/W differential pressure gauge. Quantities of gaseous reactants and products were measured from fixed volumes assuming ideal gas behavior. ^{19}F NMR spectra were recorded on a Varian 200 MHz spectrometer; chemical shifts are expressed as δ values with neat $CFCl_3$ as an internal reference. IR spectra were obtained on a Perkin-Elmer FTIR 1600. Mass spectra were performed on a Varian Mat CH-A spectrometer in the electron impact mode at ionization energy of 70 eV.

4.1.2. Materials

Chemicals were obtained from commercial sources and directly utilized. Perfluoroacyl fluorides were prepared according to standard methods described in the literature [19,24].

4.1.3. Safety precautions

Perfluoroacyl fluorides react with moisture developing HF and perfluoro carboxylic acids, some toxicity information on these categories are available in Houben-Weyl [20]. Perfluorodiacyl peroxides may decompose very quickly through auto induced decomposition [6]; solutions having peroxides concentration as high as 15% have been prepared and stored at appropriate temperature for days. Pure peroxide samples were not prepared for safety reasons.

4.2. General peroxide preparation procedure

In a typical run, a 100 ml four-necked flask was equipped with a mechanical stirrer, a solid CO_2 condenser, a thermometer and a dropping funnel; the alkaline conditions were created dissolving NaOH in bi-distilled water, 40–50 ml of solvent ($CF_2ClCFCl_2$) were added, the temperature of the system was lowered by an external cooling bath to about 0 °C, then the hydrogen peroxide was slowly introduced. Finally, the acyl-fluoride was added drop by drop in about 1 min employing a dropping funnel. The exothermicity of the reaction was controlled by the cooling bath, maintaining the internal temperature at about 2 °C;

Table 4
Experimental conditions, yields and purity for the preparation of peroxides **1**–**5**

Peroxide	Acyl-F (mmol)	Na(OH) (mmol)	H_2O_2 (mmol)	Temperature (°C)	Reaction time (min)	Yield (%)	Purity (%)
1	47	49	94	2	10	70	99
2	44	49	90	0	12	69	95
3	26	35	62	0	90	46	95
4	23	25	43	2	10	56	99
5	30	33	60	0	25	55	96

Table 5
Perfluorinated impurities present in the peroxides **1**–**5** solutions

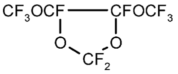
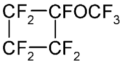
Peroxide	Impurities
1	$CF_3OCF_2CF_2CF_3$, $CF_3OCF(CF_3)_2$
2	$CF_3OCF_2CF_2OCF_3$, $(CF_3O)_2CFCF_3$
3	$(CF_3O)_2CFCF_2OCF_3$
4	
5	

Table 6
Observed kinetic constant values (k_{obs}) obtained at different initial peroxide concentrations

Initial peroxide **1** concentration (M)	k_{obs} ($\times 10^5$ s^{-1}) (at 64 °C)
0.367	5.38
0.209	5.52
0.117	5.63
0.066	5.63
0.036	5.47

when the IR analysis confirmed the disappearance of the typical band of the –C(O)F group of the acyl-fluoride, the flask content was transferred into a separatory funnel and the organic phase was washed with distilled water until a neutral pH was obtained, then it was anhydrified with anhydrous Na_2SO_4. The peroxide concentration was determined by iodometric titration.

The yields in peroxide with respect to the different acyl-fluorides, the amounts of the reagents, operative conditions and purity are reported in Table 4.

The purity of peroxides **1**–**5** was verified through ^{19}F NMR, ^{1}H NMR, GC–MS spectra. The purity values reported in Table 4 were estimated from the ^{19}F NMR spectra as the integral of fluorine signals of the peroxide divided by the integral of all fluorine signals present, excluding the solvent and multiplied by 100.

The ^{1}H NMR spectra showed no significant signals for all peroxides prepared. The GC–MS, excluding the signal of the solvent, gave signals of the product associated to the coupling of the radicals formed in the decomposition of the peroxides and signals associated to radical hydrogen abstraction. GC–MS spectra of previously decomposed peroxide samples gave signals associated to the coupling of the radicals formed in the decomposition of peroxides; no significant signals associated with radical hydrogen abstraction were present.

The perfluorinated impurities present in the peroxides **1**–**5** solutions were recognized as contamination already present in the perfluoroacyl fluorides starting materials. GC and NMR analysis allowed their identification; the nature of the impurities was strictly due to the peculiar preparation of the perfluoroacyl fluorides [24]. Table 5 shows the impurity present in the peroxides **1**–**5** solutions.

4.3. Kinetic measurements in the absence of water

4.3.1. Decomposition kinetics at different peroxide concentrations

Literature information suggests to work at low peroxide concentration (<0.05 M) for kinetics decomposition experiments to avoid possible peroxide auto-induced decomposition phenomena [6]. We utilized higher peroxide initial concentrations (0.2–0.4 M) in order to reduce the error in determining the turning point and improving the handling of the peroxide. However, in the case of peroxide **1** it has been experimentally verified that a high initial concentration does not invalidate the results. In Table 6 the k_{obs} values obtained at different initial peroxide concentrations are reported. Even increasing the initial concentration ten times, it is possible to notice that the k_{obs} shows a maximum variation of 3% compared to the mean value.

4.3.2. Decomposition kinetics methodology

In a typical kinetic measurement, about 1.5 ml of peroxide solution were put in a glass test tube with screw neck; a whole set of these tubes was placed in a thermostat (±0.1 °C), and they were taken out at specified times and immediately frozen to dry ice temperature. The tubes were opened while cool, and 1.0 ml of the peroxide solution was titrated by standard iodometry.

First-order rate constant at different temperatures (Table 2) and activation parameters (Table 3) were calculated by linear regression analysis.

4.4. Decomposition kinetics methodology in the presence of water

In a typical kinetic measurement, about 1.5 ml of peroxide solution and 2.0 ml of distilled water were put in a small glass bottle with screw neck and a magnetic stir bar; a whole set of these bottles was placed in a thermostated bath under vigorous stirring, and they were taken out at specified times and immediately frozen to ice temperature. The bottles were opened while cool, and 1.0 ml of peroxide solution was titrated by standard iodometry.

First-order rate constant at different temperatures (Table 1) were calculated by linear regression analysis.

*4.5. Characterization of peroxide **1** $[(CF_3{}^b)_2CF^aCOO]_2$*

^{19}F NMR (188 MHz, $CFCl_3$), δ (ppm): −184.7 (m, 2F, F^a, J = 8 Hz), −74.8 (d, 12F, F^b, J = 8Hz).

IR spectrum main bands (cm^{-1}, w: weak, m: mean, s: strong, vs: very strong): 1853 (m), 1824 (m), 1309 (m) and 1264.

Mass spectrum gave signals associated to the coupling of the radicals formed in the decomposition of the peroxides as follows: main peaks and respective intensities: 319 (3), 281 (3), 231 (5), 181 (5), 131 (5), 69 (100).

4.6. Characterization of peroxide **2** $[(CF_3{}^aO)(CF^b{}_3)CF^cCOO]_2$

Mixture of MESO and D,L form in 1/1 ratio. ^{19}F NMR (188 MHz, $CFCl_3$), δ (ppm): −53.0 (m, 6F, F^a, MESO), −53.5 (m, 6F, F^a, D,L), −77.6 (m, 6F, F^b, D,L) −78.8 (m, 6F, F^b, MESO), −141.8 (m, 2F, F^c, D,L), −144.0 (m, 2F, F^c, MESO).

IR spectrum main bands (cm^{-1}, w: weak, m: mean, s: strong, vs: very strong): 1857 (m), 1828 (s), 1284 (s) and 1232 (vs).

Mass spectrum gave signals associated to the coupling of the perfluoroalkyl radicals formed in the decomposition of the peroxides as follows: main peaks and respective intensities: 281 (4), 263 (13), 219 (18), 185 (26), 131 (25), 97 (45) and 69 (100).

4.7. Characterization of peroxide **3** $[(CF_3{}^aO)_2(CF_3{}^b)CCOO]_2$

^{19}F NMR (188 MHz, $CFCl_3$), δ (ppm): −55.2 (s, 12F, F^a) and −78.4 (s, 6F, F^b).

IR spectrum main bands (cm^{-1}, w: weak, m: mean, s: strong, vs: very strong): 1854 (m), 1828 (m), 1287 (s) and 1254 (s).

Mass spectrum gave signals associated to the coupling of the perfluoroalkyl radicals formed in the decomposition of the peroxides as follows: main peaks and respective intensities: 263 (6), 251 (3), 135 (2), 97 (4), 69 (100).

4.8. Characterization of peroxide **4** $[cyclo\text{-}O\text{–}CF^cF^d\text{–}OCF^aF^b\text{–}C(OCF^e{}_3)(COO)\text{–}]_2$

^{19}F NMR (188 MHz, $CFCl_3$), δ (ppm): −51.5 (dd, 2F, F^c, J = 70, 9 Hz), −52.3 (s, 6F, F^e), −56.4 (dd, 2F, F^d, J = 70, 7 Hz), −75.2 (dd, 2F, F^a, J = 135, 9 Hz) and −89.5 (dd, 2F, F^b, J = 135, 7 Hz).

IR spectrum main bands (cm^{-1}, w: weak, m: mean, s: strong, vs: very strong): 1857 (m), 1828 (m), 1349 (m) and 1236 (s).

Mass spectrum gave signals associated to the coupling of the perfluoroalkyl radicals formed in the decomposition of the peroxides as follows: main peaks and respective intensities: 229 (42), 163 (21), 135 (7), 116 (3), 97 (30), 78 (4), 69 (100) and 50 (6).

4.9. Characterization of peroxide **5** $[cyclo\text{-}CF^aF^b\text{–}CF^cF^d\text{–}CF^aF^b\text{–}CF^e(COO)\text{–}]_2$

^{19}F NMR (188 MHz, $CFCl_3$), δ (ppm): −126 (d, 4F, F^a, J = 230 N_2), −130 (d, 4F, F^b, J = 230 N_3), −130, 4(d, 2F, F^c, J = 230 N_2) −131, 2 (d, 2F, F^d, J = 230 N_2) and −188 (2F, F^e).

IR spectrum main bands (cm^{-1}, w: weak, m: mean, s: strong, vs: very strong): 1843 (m), 1817 (m), 1289 (s) and 1232 (s).

Mass spectrum gave signals associated to the coupling of the perfluoroalkyl radicals formed in the decomposition of the peroxides as follows: main peaks and respective intensities: 293 (25), 262 (12), 243 (20), 193 (29), 162 (47), 100 (100) and 69 (37).

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