ELSEVIER

Journal of Fluorine Chemistry 76 (1996) 193–200

JOURNAL OF FLUORINE CHEMISTRY

Synthesis of new phosphonic derivatives with fluorinated chains

C. Brondino [a], B. Boutevin [a,*], Y. Hervaud [a], N. Pelaprat [a], A. Manséri [b]

[a] *Ecole Nationale Supérieure de Chimie de Montpellier, URA CNRS 1193, 8 rue Ecole Normale, F 34053 Montpellier Cedex 1, France*

[b] *Institut de Biologie, Université de Tlemcen, Tlemcen, Algeria*

Received 26 July 1995; accepted 28 September 1995

Abstract

The synthesis of phosphonic derivatives (phosphonates and phosphonic acids) bearing fluorinated chains is presented. Such compounds with different spacers between these groups have been produced mainly by the telomerization of ω-unsaturated phosphonic derivatives with fluorinated transfer agents such as mercaptans. The fluorinated phosphonates were quantitatively hydrolyzed to fluorinated phosphonic acids via two pathways: a classical one involving acids and another via silylation. Most products have been characterized by NMR and mass spectroscopy.

Keywords: Dialkyl fluorophosphonates; Allyl phosphonate; Vinyl phosphonate; Fluoromercaptans; Telomerization; Adhesion on steel

1. Introduction

Fluorinated derivatives containing phosphorus atoms are known for applications such as surfactants [1,2], additives for lubricants, impregnation agents [3] for increasing oleophoby, flame-retardant materials, defoaming agents for pesticide [4] or insecticide [5] formulations, mold-release agents [6], biological chelating agents [7,8] and electrolytes [9]. They may be used either as additives [10,11] or chemically linked to polymers [12,13]. However, most products exhibit the fluorinated group linked to the phosphorus atom by a C–O–P bond which is labile and hydrolyzable.

The literature describes several ways to prepare fluoroalkyl phosphonic derivatives of the type R_F–P(O)$(OR)_2$.

(1) By fluorination of alkyl phosphonic compounds with $FClO_3$ [14] or Et_2NSF_3 [15,16].

(2) By reaction of perfluoroalkyl iodides R_FI with phosphorus, followed by oxidative saponification [17].

(3) Via the Michaelis–Arbuzov reaction [18] between halogenated derivatives and trialkyl phosphites. This reaction was often successful with fluorinated derivatives [19,20], but it was not the case with, for example, $CFCl_2CF_2CCl_3$ [21] or $C_6F_{13}C_2H_4I$, $CFCl_2CF_2Cl$, $CFCl_2CFCl_2$ and with $CFCl_2CF_2CH_2R$ (R = OTs or I) [22]. α-Monofluoro (alkyl or vinyl) phosphonates have been described by Blackburn and Parratt [23,24].

(4) By telomerization with the phosphonic group present either in the monomers (taxogens) [25–31] or in the telogen [32–34]. In Table 1, we have recorded the different results reported in the literature on fluorophosphonic compounds obtained by telomerization.

To prepare fluorophosphonic derivatives, we chose to telomerize allyl and vinyl phosphonates with fluoroalkyl thiols. No work has been published on these reactions, but thiols are good telogens [35–40]. Since we were interested in the hydrolysis of our new fluorophosphonates, we have applied two methods for such reaction: a classic one [41] involving acids and another based on silylation [42].

2. Results and discussion

2.1. Starting materials

We first attempted to add a phosphonate group on to the allyl-fluorinated olefins.

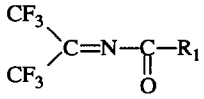
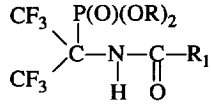
2.1.1. Synthesis of allyl-fluorinated olefins

Two different olefins were synthesized, i.e. with the 1,1,2,2-tetrahydroperfluorinated group and the allyl function linked either through an oxygen or a sulphur atom. In both cases, the Williamson reaction between allyl chloride and 1,1,2,2-tetrahydroperfluoro-octanol or the homologous fluorinated mercaptan was carried out in an alkaline medium at 42 °C in the presence of a phase-transfer catalyst [e.g. a quaternary ammonium salt such as tetrabutylammonium hydrogen sulphate (TBAH)] [43,44] as follows:

* Corresponding author.

Elsevier Science S.A.
SSDI 0022-1139(95)03362-9

Table 1
Fluorophosphonate compounds obtained by telomerization

Monomer	Telogen	Catalysis	Telomers	Reference
$CF_2=CF_2$	$HP(O)(OR)_2$	radical	$H-(CF_2-CF_2)_n-P(O)(OR)_2$	[25,26]
$CF_2=CF_2$	$HP(O)(OEt)_2$	γ-ray	$H-(CF_2-CF_2)_n-P(O)(OEt)_2$	[26,27]
$CF_2=CFCl$	$HP(O)(OR)_2$ (R = Me, Et, ^{n}Bu)	radical	$H-(CFCl-CF_2)_n-P(O)(OR)_2$ (R = Me, Et, ^{n}Bu)	[28]
$CFX=CX_2$ (X = Cl, F)	$HP(O)(OR)_2$ (R = Me, ^{t}Bu)	γ-ray	$H-(CX_2-CFX)_n-P(O)(OR)_2$ (R = Me, Et, ^{n}Bu)	[27]
$CF_3-(CF_2)_n-CH=CH_2$ (n = 5, 7, 9)	$HP(O)(OR)_2$ (R = Me, Et, ^{n}Bu)	radical	$CF_3-(CF_2)_n-CH_2-CH_2-P(O)(OR)_2$	[29]
$CF_2=CFCl$	$CCl_3-P(O)(Cl)_2$	redox	$Cl-(CFCl-CF_2)_n-CCl_2-P(O)(Cl)_2$	[30]
$CF_2=CFCl$	$POCl_3$	radical	$Cl-(CFCl-CF_2)_n-P(O)Cl_2$	[31]
	$HP(O)(OR)_2$	enzymatic		[32]
$CH_2=CH-P(O)(OEt)_2$	R_F-I	radical	$R_F-(CH_2-CH)_n-I$ $P(O)(OEt)_2$	[33]
$CH_2=CH-P(O)(OEt)_2$	$R-CCl_3$ (R = CF_3, $-(CF_2-CFCl)_n-Cl$)	redox	$RCCl_2-(CH_2-CH)_m-Cl$ $P(O)(OEt)_2$	[34]
$CH_2=CH-CH_2-P(O)(OEt)_2$	$R-CCl_3$ (R = CF_3, $-(CF_2-CFCl)_n-Cl$)	redox	$RCCl_2-(CH_2-CH)_m-Cl$ $CH_2-P(O)(OEt)_2$	[34]

$$C_6F_{13}C_2H_4XH + ClCH_2CH=CH_2 \xrightarrow{TBAH}$$
(X = O or S)

$$C_6F_{13}C_2H_4XCH_2CH=CH_2$$
X = O: **1**
X = S: **2**

The fluoroallyl ether derivative was obtained in 95% yield and the corresponding thioether in 80% yield. The difference in yields may be explained by the electronegativities of the X heteroatoms which allow the proton of the OH end-group to react more easily with the chlorine atom of the olefin.

The fluorinated thioether compounds was characterized by IR and NMR spectroscopies, and by mass spectrometry. The IR spectrum does not show bands attributable to the mercaptan group at 1700 cm^{-1} nor the presence of unsaturation at 1620 cm^{-1}. The ^1H NMR spectrum exhibits signals at 5.1 ppm and in the 5.7–5.9 ppm range, characteristic of the ethylenic protons of the allyl group. A doublet at 3.2 ppm is assigned to the methylene group adjacent to the double bond and to the sulphur atom. Finally, complex signals centred at 2.4 and 2.7 ppm correspond to the methylene groups adjacent to the sulphur atom and to the fluorinated chain, respectively.

The ^{13}C NMR spectrum shows signals similar to those of the fluorinated allyl ether homologue, except that the signals of both the methylene groups adjacent to the sulphur atom are high-field shifted: 35.40 and 21.67 ppm (thioether) to 72.96 and 62.74 ppm (ether) for methylenes adjacent to unsaturated groups and in the β position to the fluorinated chain, respectively.

2.1.2. Preparation of phosphonic products

Synthesis of the allyl phosphonate monomer was performed by the Michaelis–Arbuzov reaction from an equimolar amount of allyl bromide or chloride and triethyl phosphite stirred at about 125 °C. The product was obtained in 95% yield [41]. The main signals in its ^1H NMR spectrum may be attributed to the ethylenic protons in the 5.0–6.1 ppm range and the methylene of the allyl group at 2.46 ppm as a doublet of doublets.

$$CH_2=CH-CH_2Br + P(OEt)_3 \longrightarrow CH_2=CH-CH_2-P(O)(OEt)_2 + EtCl \quad (3)$$

2.2. Attempts at $HP(O)(OEt)_2$ addition on to allylic fluoro monomers

We sought to perform the following reactions:

$$R_FC_2H_4XCH_2-CH=CH_2 + HP(O)(OEt)_2 \longrightarrow$$
(X = O or S)

$$R_FC_2H_4XC_3H_6P(O)(OEt)_2$$

Table 2
Addition of $C_6F_{13}C_2H_4SH$ to $CH_2=CH-CH_2P(O)(OEt)_2$

Run No.	Initiator	Solvent	Temp. (°C)	Time (h)	Process [b]	Yield (%) [c]
1	AIBN	acetonitrile	70	18	A	0
2	AIBN	acetonitrile	100	18	A	0
3	perkadox [a]	acetonitrile	60	18	A	0
4	AIBN	heptane	100	3	B	100
5	UV	acetonitrile	20	18	A	0
6	UV	heptane	20	18	D	20
7	UV + $\phi CO\phi$	heptane	20	3	C	100
8	UV + $\phi CO\phi$	acetonitrile	20	3	C	100
9	UV + $\phi CO\phi$	heptane	20	3	D	100
10	sunlight	heptane	20	18	D	0
11	sunlight + Ph_2O	heptane	20	3	D	85

[a] Perkadox 16S bis(4-t-butylcyclohexyl)peroxydicarbonate.
[b] Processes: A: sealed tube; B: under continuous N_2 flow; C: under continuous vacuum (20 mmHg); D: under vacuum (20 mmHg).
[c] Yields calculated from GC results.

Table 3
Addition of $C_6F_{13}C_2H_4SH$ to $CH_2=CH-P(O)(OEt)_2$

Run No.	Initiator	Solvent	Temp. (°C)	Time (h)	Process [a]	Yield (%) [b]
12	AIBN	heptane	70	3	A	100
13	AIBN	heptane	70	3	B	100
14	UV + $\phi CO\phi$	heptane	20	3	D	100
15	UV + $\phi CO\phi$	–	20	3	D	100
16	UV	–	20	18	D	20
17	sunlight	heptane	20	18	D	0
18	sunlight + Ph_2CO	heptane	20	3	D	90

[a] Processes: A: sealed tube; B: under continuous N_2 flow; D: under vacuum (20 mmHg).
[b] Yields calculated from GC results.

The reactions were attempted with classic initiators (peroxides, azo compounds) or photochemically (using UV radiation with different photosensitizers such as acetophenone or benzophenone); we also changed the other experimental conditions [temperature, solvent (acetonitrile or heptane), reaction time] but were not successful with the initial reagents always being recovered unchanged. With fluoro monomers such as $R_F-CH=CH_2$; $R_F=CF_3-(CF_2)_n-$, $n=5, 7, 9$, Block [29] has described the formation of the corresponding mono adducts with $HP(O)(OR)_2$ using peroxide initiators. However, with our allylic monomers there was no reaction. Despite these results, we tried another method of synthesis starting from phosphonic monomers.

2.3. Telomerization of allyl and vinyl phosphonates with fluoromercaptans

The synthesis of fluorinated phosphonated telomers can be achieved via a one-step reaction by the radical addition of the fluorinated mercaptan on to vinyl or allyl phosphonate according to the following scheme:

$$C_6F_{13}C_2H_4SH + H_2C=CH(CH_2)_xP(O)(OEt)_2 \longrightarrow$$
$$(x=0 \text{ or } 1)$$
$$C_6F_{13}C_2H_4S(CH_2)_{x+2}P(O)(OEt)_2$$
$$x=0: \mathbf{6}$$
$$x=1: \mathbf{7}$$

The radical additions were performed in the presence of initiators (AIBN or peroxides) or photochemically initiated. The results are summarized in Tables 2 and 3.

2.3.1. Telomerization of allyl phosphonate 3

Four different experimental processes have been used as shown in Table 2, either under nitrogen flow or vacuum, in sealed tubes or in round-bottomed flasks. The main conclusions are as follows.

(i) Attempts 1–3 using radical initiators under classic conditions were unsuccessful whereas operating in heptane and under a continuous flow of nitrogen as in attempt 4, addition was achieved quantitatively. This difference may be explained in terms of solvent polarity. The best results were achieved with hexane (non-polar).

(ii) With UV radiation, no reaction was observed in acetonitrile (attempt 5) and only a 20% yield was achieved in heptane (attempt 6), both after 18 h exposure.

(iii) The presence of benzophenone (attempts 7–9) leads to quantitative yields.

(iv) Using sunlight (attempts 10 and 11) led to a good yield (85%) in the presence of benzophenone.

In attempts 4, 6–9 and 11, only one product, i.e. $C_6F_{13}C_2H_4SC_3H_6P(O)(OEt)_2$, was obtained.

GC and SEC chromatograms indicated only one product, although two isomers could be envisaged; thus $RS–CH_2–CH_2–CH_2–P(O)(OEt)_2$ (**7a**) and $RS–\underset{\displaystyle CH_3}{\underset{|}{CH}}–CH_2–P(O)(OEt)_2$ (**7b**).

In the corresponding ^{13}C NMR spectra (in a *J*-mode system), only one peak was observed at 15.7 ppm (a doublet with $J_{C-P}=6$ Hz) in the primary and tertiary carbon area. That proves that only one CH_3 arising from the ethoxy groups is present, and thus the correct structure is **7a**.

We also prepared the fluorophosphonate $C_8F_{17}C_2H_4S-C_3H_6P(O)(OEt)_2$ (**8**) starting from the thiol $C_8F_{17}C_2H_4SH$.

2.3.2. Telomerization of vinyl phosphonate 4

Several attempts were made under conditions similar to those for the allyl phosphonate. The results are given in Table 3. Same conclusions were reached for both monomers and the yields were in the same order of magnitude.

With phosphonate **4**, addition of thiols is also selective and leads to $C_6F_{13}C_2H_4SC_2H_4–P(O)(OEt)_2$ (**6**). After distillation, fluorinated phosphonates **6** and **7** were mainly characterized by NMR (^1H, ^{19}F, ^{13}C and ^{31}P) spectroscopy. For example, using ^{31}P NMR spectroscopy, it is possible to observe good selectivity for the reactions because in each case only one peak exists. Moreover, a greater influence of the fluorine chain was observed on the chemical shift of the phosphorus atom in the case of vinyl phosphonate **6** ($\delta=31.73$ ppm) than with the allyl product **7** ($\delta=28.63$ ppm).

2.4. Synthesis of fluorinated phosphonic acids

Hydrolysis of fluorophosphonates **7** and **8** has been attempted via several pathways:

$$R–P(O)(OEt)_2 \longrightarrow R–P(O)(OH)_2$$

Sulphuric acid (96%) and hydrochloric acid (35%) did not lead to the corresponding phosphonic acids. However, hydrolysis effected by the reaction of oleum or by silylation resulted in good yields.

2.4.1. Hydrolysis of fluorophosphonates by oleum

The reaction of 30% oleum on phosphonates **7** and **8** at about 50 °C gave the corresponding phosphonic acids. Above 100 °C degradations as noted by Brace [26] were observed. The fluorophosphonic acids obtained were surfactants making them difficult to purify. In contrast, the disodium salt obtained by neutralization of the acids with NaOH was easier to control and analyze.

$$R–P(O)(OH)_2 \xrightarrow{NaOH} R–P(O)(ONa)_2$$

The main products synthesized and analyzed were $C_6F_{13}C_2H_4–S–C_3H_6P(O)(OH)_2$ (**9**) and $C_6F_{13}C_2H_4–S–C_2H_4P(O)(OH)_2$ (**10**).

We also prepared the fluorophosphonic acid **11** starting from the thiol $C_8F_{17}C_2H_4SH$ to give **8** which was hydrolyzed to $C_8F_{17}C_2H_4–S–C_3H_6P(O)(OH)_2$ (**11**).

2.4.2. Hydrolysis of fluorophosphonates via a silylation reaction

Synthesis of phosphonic acids by this method was performed in two steps, i.e. silylation of the fluorophosphonates by $XSi(CH_3)_3$, with X = Cl or Br, and then hydrolysis with an excess of methanol. The silylation step was more efficient with $BrSi(CH_3)_3$ than with $ClSi(CH_3)_3$ as expected from previous results [45].

It is very difficult to obtain the disilylated product **12** with the chlorinated reagent whatever the stoichiometry of the reaction

$$R–P(O)(OEt)_2 \xrightarrow{ClSi(CH_3)_3} R–P(O)(OEt)[OSi(CH_3)_3] \quad (\mathbf{13})$$

In contrast, using the brominated silane it was possible to stop the reaction at the monosilylated product **13** by using an equivalent amount of reactants. However, with excess $BrSi(CH_3)_3$ (1:2.1), the disilylated compound **12** was obtained:

$$R–P(O)(OEt)_2 \xrightarrow{BrSi(CH_3)_3} R–P(O)[OSi(CH_3)_3]_2 \quad (\mathbf{12})$$

Hydrolysis was accomplished using water [46] or methanol. In the latter case, the reaction was more efficient and it is easier to remove the solvent.

$$R–P(O)(OEt)_x[OSi(CH_3)_3]_{2-x} \xrightarrow{CH_3OH}$$

$$R–P(O)(OEt)_x(OH)_{2-x} + (CH_3)_3SiOSi(CH_3)_3$$

$R=C_nF_{2n+1}C_2H_4SC_3H_6–$; $n=6$, $x=0$: **9**
$n=6$, $x=1$:**14**
$n=8$, $x=0$:**11**

The acids could be titrated with sodium hydroxide and showed good equivalence.

2.5. Application of the fluoro compounds

These new fluorinated phosphonates (diester, diacid or monoacid) were applied to steel surfaces in order to evaluate their adhesive properties on to metal.

The products **7a, 8, 9** and **11** were spread in solution using a bar coater and, after evaporation, the coated surface was extracted using a Soxhlet apparatus (THF) in order to remove the molecular excess and those molecules not linked to the surface.

Table 4
Contact angles of water on galvanized steel before and after coating

Compound	Angle before coating (°)	Angle after coating (°)
$C_6F_{13}C_2H_4SC_3H_6P(O)(OEt)_2$ (**7a**)	54	40
$C_6F_{13}C_2H_4SC_3H_6P(O)(OH)_2$ (**9**)	45	120
$C_8F_{17}C_2H_4SC_3H_6P(O)(OEt)_2$ (**8**)	54	96
$C_8F_{17}C_2H_4SC_3H_6P(O)(OH)_2$ (**11**)	66	130
Teflon	119	119

The properties were evaluated by measuring the contact angle of a drop of water on the surface before and after coating. The results are listed in Table 4. These clearly show that the molecules were strongly linked to the surface and resulted in very good surface properties, with the C_8F_{17} group exhibiting the best behaviour as expected. Soxhlet extraction is a very drastic process and indicates a strong reaction between steel and the phosphonic acid group.

3. Experimental details

3.1. Materials

Vinyl phosphonate, CH_2=CH–P(O)$(OEt)_2$ (**4**), and diethyl hydrogen phosphonate, HP(O)$(OEt)_2$ (**5**), were purchased from Sigma-Aldrich Chimie, 38299 Saint Quentin-Fallavier, France.

3.2. Instrumentation

Telomerizations of monomers were carried out either in Carius tubes (CT) or at atmospheric pressure in a two-necked round-bottom Pyrex flask equipped with a condenser and a device for the introduction of nitrogen. The Carius tubes were first saturated with nitrogen and then filled with the reactants under nitrogen, cooled in liquid nitrogen/acetone mixture (−80 °C), sealed and placed into the cavity of an aluminium block of a shaken autoclave equipped with a thermoregulator. At the end of the reaction, the tube was left at room temperature then cooled with liquid nitrogen and opened.

For photochemistry, the CTs or flasks were irradiated with a HPW 125 Philips UV lamp under conditions described previously (Tables 2 and 3). These reactions were monitored by SEC using a Trivector Trilab apparatus equipped with a Knauer HPLC (model 64) pump. THF was used as the eluent (flow 1.5 ml min^{-1} at 30 °C). Separation was carried out with a set of three Polymer Lab columns. The diameters of the pores were 1000, 500 and 50 Å. Detection was performed using a differential refractometer.

The different pure telomers were characterized by ^1H, ^{13}C, ^{19}F and ^{31}P NMR spectroscopy at room temperature. Spectra were recorded on a Bruker CW 60 apparatus or, for a higher resolution, on Bruker WM 360 or Bruker AC 250 instruments, using deuterated chloroforms as solvent and TMS as reference for ^1H and ^{13}C nuclei. References for ^{19}F and ^{31}P NMR were $CFCl_3$ and H_3PO_4, respectively. The letters s, d, t, q and m stand for singlet, doublet, triplet, quartet and multiplet, respectively.

IR spectra were recorded with a Perkin-Elmer 398 spectrophotometer. The position of the bands are given in cm^{-1} with an error of ± 2.5 cm^{-1}. The letters vs, s, m and w designate very strong, strong, medium or weak intensities.

Mass spectra were obtained on a CEC 21-110C double beam apparatus equipped with a flame ionization source and a system of direct introduction. The m/z values are given for main peaks with their relative abundances to the base peak in brackets. The formulae of some important fragment ions are also given: M is the mass peak.

Contact angle measurements were obtained using the contact angle meter G1 (Krûss). A 25 μm thickness coating was effected with a bar coater from RK Print-Coat Instruments Ltd.

3.3. Synthesis of starting materials

3.3.1. Preparation of fluorinated olefins

Synthesis of $C_6F_{13}C_2H_4OCH_2CH$=CH_2 (1)

Into a three-necked round-bottomed flask, equipped with a condenser, a mechanical stirrer and a dropping funnel, was introduced a mixture of 0.154 mol (56.0 g) of 1,1,2,2-tetrahydro-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroalcohol, 80 ml of 20 N aqueous sodium hydroxide and 15.4 mol (5.23 g) of tetrabutylammonium hydrogen sulphate, while 0.77 mol (60.0 g) of allyl chloride were added dropwise with stirring at 30 °C. The mixture was heated to 45 °C and stirred for 6 h. After reaction, it was cooled to room temperature, diluted with 40 ml of methylene chloride and washed three times with water. After evaporation of the solvent and volatile compounds, the residue was distilled under vacuum when 58.5 g of a colourless liquid was obtained (yield, 94%), b.p. 75–76 °C/20 mmHg.

IR (KBr) (cm^{-1}): 2940–2860 (m); 1645 (w); 1320 (m); 1260–1140 (broad); 1000 (m); 950 (m); 930 (m); 720 (m); 710 (s); 695 (m); 650 (m); 560 (w); 530 (m). ^{19}F NMR ($CDCl_3$) δ: −82.8 (t, CF_3, 3F); −114.2 (t, CH_2CF_2, 2F); −123.6 (m, $CH_2CF_2CF_2$, 2F); −124.3 (m, $C_3F_7CF_2$, 2F); −125.5 (m, $C_2F_5CF_2$, 2F); −127.2 (m, CF_3CF_2, 2F); −127.2 (m, CF_3CF_2, 2F) ppm.

3.3.2. Synthesis of fluorinated allyl thioether 2

In a similar manner, 0.039 mol (15.0 g) of $C_6F_{13}C_2H_4SH$, 35 ml of 20 N aqueous NaOH, 0.003947 mol (1.34 g) of TBAH and 0.197 mol (15.1 g) of allyl chloride were successively introduced. The mixture was stirred at 500 rpm at 40 °C for 6 h. After a similar work-up as above, 13.1 g of a colourless liquid were obtained by distillation (yield, 80%), b.p. 90–91 °C/20 mmHg.

IR (KBr) (cm^{-1}): 3100–2920 (w, broad); 1640 (w); 1440 (m); 1360 (m); 1250–1170 (s, broad); 1140 (s); 990 (w); 960 (w); 920 (m); 845 (w); 810 (w); 745 (m); 735 (m); 725 (m); 705 (m); 650 (m); 530 (w). ^{1}H NMR ($CDCl_3$) δ: 2.4 (m, 2H, CF_2CH_2); 2.7 (m, 2H, $CF_2CH_2CH_2$); 3.15 (d, CH_2–CH=, 2H, J=5.5 Hz); 5.15 (m, H_2C=CH, 1H); 5.8 (m, CH=CH_2, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 21.67 (t, $R_FCH_2CH_2$, J=4.6 Hz, 1C); 32.67 (t, R_FCH_2, J=22.0 Hz, 1C); 35.40 (s, CH_2CH=CH_2, 1C); 117.95 (s, CH=CH_2, 1C); 134.51 (s, CH=CH_2, 1C); 110–150 (m, C_6F_{13}, 6C) ppm. ^{19}F NMR ($CDCl_3$) δ: −83.1 (t,t,t, CF_3, 3F); −115.7 (t, CF_2CH_2, 2F); −123.3 (m, $CH_2CF_2CF_2$, 2F); −124.3 (m, $C_3F_7CF_2$, 2F); −124.6 (m, $CF_3CF_2CF_2$, 2F); −127.6 (m, CF_3CF_2, 2F); −127.2 (m, CF_3CF_2, 2F) ppm. Analysis: Calc. for 7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-4-thiadodecene (**2**), $C_{11}H_9F_{13}S$ (420.24): C, 31.44; H, 2.16; F, 58.77; S, 7.63%. Found: C, 31.79; H, 2.32; F, 58.19; S, 7.40%.

3.4. Synthesis of fluorophosphonates

3.4.1. Synthesis of $C_6F_{13}C_2H_4SC_3H_6P(O)(OEt)_2$ (7)

In a Pyrex Carius tube was placed a mixture of 0.025 mol (9.5 g) of 1,1,2,2-tetrahydro-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octanethiol, 0.025 mol (4.45 g) of allyl diethyl phosphonate and 0.25 mmol (45.5 mg) of benzophenone and this was stirred with a magnetic bar whilst being maintained under vacuum (40 mbar). The tube was then irradiated for 2 h with a HPW 125 Philips lamp at a distance of 5 cm, being cooled with an air flow throughout the reaction. After reaction, the mixture was filtered over silica and eluted with hexane in order to remove benzophenone and residual monomer. After evaporation of the solvent, the thiol was recovered by distillation. The product was 13.6 g of an oily orange residue and shown to be diethyl-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-4-thiadodecanyl phosphonate (yield, 97%), b.p. 135–139 °C/0.2 mbar.

IR (KBr) (cm^{-1}): 2980 (s); 2850 (w); 1460 (w); 1440 (m); 1380 (w); 1240 (vs); 1170 (s); 1025 (s); 950 (s); 800 (w); 750 (w); 700 (w); 650 (m); 550 (w). ^{1}H NMR ($CDCl_3$) δ: 1.3 (t, J=7.0 Hz, OCH_2CH_3, 6H); 1.9 (m, CH_2CH_2P, 4H); 2.4 (m, R_FCH_2, 2H); 2.9 (m, CH_2SCH_2, 4H); 4.1 (dq, OCH_2CH_3, J=7.0 Hz, J_{CH_2OP}=8.2 Hz, 4H) ppm. ^{19}F NMR ($CDCl_3$) δ: 82.5 (t, CF_3, 3F); −114.5 (t, CH_2CF_2, 2F); −123.2 (m, $CH_2CF_2CF_2$, 2F); −124.3 (m, $C_3F_7CF_2$, 2F); −125.8 (m, $C_2F_5CF_2$, 2F); −127.5 (m, CF_3CF_2, 2F) ppm. ^{31}P NMR ($CDCl_3$) δ: 31.73 (s) ppm. MS (m/z): 558 (46) M; 513 (25) M−OEt; 421 (17) $C_6F_{13}C_2H_4SC_3H_6^{+\bullet}$; 379 (71) $C_6F_{13}C_2H_4S^{+\bullet}$; 239 (13); 225 (13); 219 (13); 211 (91) $^{\bullet+}SC_3H_6P(O)(OEt)_2$; 183 (21) $^{\bullet+}SC_3H_6P(O)(OH)(OEt)$; 182 (33); 181 (17); 180 (50) $^{\bullet+}SC_3H_3P(O)(OH)(OEt)$; 179 (21); 166 (30); 165 (21); 152 (42) CH_2=$P^{+\bullet}(O)(OH)(OEt)$; 151 (17); 149 (17); 139 (54); 138 (50) $P^{+\bullet}(OH)(OEt)_2$; 137 (33) $^{\bullet+}P(O)(OEt)_2$; 119 (17); 110 (100) $^{\bullet+}P(OH)_2(OEt)$; 109 (33) $^{\bullet+}P(O)(OH)(OEt)$; 108 (42); 83 (63); 82 (50) $^{\bullet+}P(OH)_3$; 81 (67) $^{\bullet+}P(O)(OH)_2$; 69 (30). Analysis: Calc. for 7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-4-thiadodecanyl diethyl phosphonate (**7**), $C_{15}H_{20}F_{13}O_3SP$ (558.32): C, 32.27; H, 3.61; F, 44.23; S, 5.74; P, 5.55%. Found: C, 31.71; H, 3.85; F, 44.15; S, 5.52; P, 6.02%.

3.4.2. Synthesis of $C_6F_{13}C_2H_4SC_2H_4P(O)(OEt)_2$ (6)

As in the previous experiment, a Carius tube containing a mixture composed of 0.022 mol (8.47 g) of 1,1,2,2-tetrahydro-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octanethiol, 0.022 mol (3.66 g) of vinyl diethyl phosphonate and 0.25 mmol (45 mg) of benzophenone was exposed to UV light. GC analyses of samples showed the conversion rate was about 40% after 2 h exposure and 100% after 8 h. After work-up, the product was distilled under vacuum when 11.3 g of diethyl-6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-3-thia-undecanyl phosphonate were obtained (yield, 95%), b.p. 134–136 °C/0.3 mbar.

IR (KBr) (cm^{-1}): 2990 (m); 2940 (w); 2920 (w); 1445 (w); 1390 (w); 1360 (w); 1300 (m); 1240 (vs); 1200 (s); 1150 (s); 1060 (s); 1030 (s); 960 (s); 710 (w); 650 (w). ^{1}H NMR ($CDCl_3$) δ: 1.3 (t, J=7.0 Hz, OCH_2CH_3, 6H); 2.1 (m, 4H); 2.8 (m, 4H); 4.1 (dq, OCH_2CH_3, J=7.0 Hz, J_{CH_2OP}=8.2 Hz, 4H) ppm. ^{31}P NMR ($CDCl_3$) δ: 28.63 (s) ppm. The ^{19}F NMR spectrum was similar to that for the fluorinated mercaptan. Analysis: Calc. for 6,6,7,7,8,8,9,9,10,10,11,11,11-tridecafluoro-3-thia-undecanyl diethyl phosphonate (**6**), $C_{14}H_{18}F_{13}OSP$ (544.29): C, 30.89; H, 3.31; F, 45.38; S, 5.89; P, 5.69%. Found: C, 30.92; H, 3.40; F, 45.64; S, 6.21; P, 5.47%.

The phosphonated derivatives were synthetized in the same manner as with $C_8F_{17}C_2H_4SH$ as the precursor. Analogous results were obtained after addition to monomers **3** and **4** with a fluorinated chain.

3.5. Synthesis of fluorinated phosphonic acid

3.5.1. Hydrolysis by oleum

Synthesis of acid $C_6F_{13}C_2H_4SC_3H_6P(O)(OH)_2$ (9)

To a solution composed of 8.94 mmol (5.0 g) of diethyl-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-4-thiadodecanyl phosphonate in 50 g of tetrachloromethane were added 4 g of 30% oleum. The mixture was stirred at 50 °C for 14 h. After cooling to room temperature, the mixture was poured dropwise into ice. The phosphonic acid was extracted with diethyl ether and precipitated from pentane when 4.1 g of 7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-4-thiadodecanyl phosphonic acid were obtained (yield, 91%).

IR (KBr) (cm^{-1}): very broad band in the 2500–3000 cm^{-1} range. The other bands were similar to those for the fluorinated phosphonate. Neutralization: titration of 80.3 mg of acid **9** with NaOH (solution containing 4.1 g l^{-1}). Calculated volume of NaOH: 3.19 ml (found: 3.08 ml). The ^{19}F NMR spectrum of the compound was similar to that for the corresponding fluorinated phosphonate. MS (m/z): 502 (35); 485 (18); 452 (59); 425 (53); 421 (18); 412 (53);

411 (18); 407 (53); 406 (47); 393 (100); 379 (29); 359 (18); 327 (41); 283 (12); 233 (18); 186 (18); 169 (24); 157 (12); 156 (18); 155 (53); 124 (35); 123 (47); 121 (53); 109 (41); 96 (59); 95 (29); 82 (47); 81 (35); 69 (65). ^{31}P NMR (CD_3COCD_3) δ: 32 (s) ppm. Analysis: Calc. for $C_{11}H_{12}F_{13}O_3SP$ (502.23): C, 26.30; H, 2.40; F, 49.20; S, 6.37; P, 6.17%. Found: C, 25.00; H, 2.51; F, 46.49; S, 8.03; P, 7.90%.

Synthesis of $C_6F_{13}C_2H_4SC_2H_4P(O)(OH)_2$ (10)

Using similar conditions as for phosphonic acid **9**, 10 mmol (5.44 g) of the diethyl phosphonate $C_6F_{13}C_2H_4SC_2H_4P(O)(OEt)_2$ were converted into 4.88 g of the corresponding phosphonic acid **10** (yield, 89%).

Neutralization: titration of 95.2 mg of acid **10** with NaOH (solution containing 4 g l^{-1}). Calculated volume of NaOH: 3.90 ml (found: 3.78 ml). The ^{19}F NMR spectrum of the compound was similar to that for the corresponding phosphonate **7**. Analysis: Calc. for $C_{10}H_{10}F_{13}O_3SP$: C, 24.59; H, 2.05; F, 50.61; S, 6.56; P, 6.35%. Found: C, 24.10; H, 1.82; F, 48.90; S, 6.95; P, 7.14%.

3.5.2. Hydrolysis after silylation

The first step (silylation) was successfully performed in a three-necked flask equipped with a condenser and a dropping funnel. On to 10.0 g of phosphonate **6** (0.0179 mol) in 10 ml of dichloromethane, 5.79 g or 2.75 g (0.0378 mol for the synthesis of **9** or 0.018 mol for the synthesis of **14**) of bromotrimethylsilane were added dropwise under nitrogen. In the case of **9**, after 90 min at 25 °C the solvent was evaporated and 11.32 g (100%) of $C_6F_{13}C_2H_4SC_3H_6P(O)[OSi(CH_3)_3]_2$ (**12a**) was obtained. The ^{1}H NMR spectrum of **12a** showed a new peak at 0.3 ppm corresponding to $Si(CH_3)_3$, the disappearance of the triplet at 1.3 ppm showing that all the OEt groups had been converted.

The second step (hydrolysis) was performed in methanol at 25 °C for 1 h. Phosphonic acid **9** was purified by evaporating the methanol under vacuum initially at 40 °C/20 mmHg and then at 25 °C 2×10^{-2} mbar. Product **9** was obtained as a white powder (8.18 g; 91% yield). All analyses were in good agreement with those described above.

We also prepared $C_8F_{17}C_2H_4SC_3H_6P(O)(OH)_2$ (**11**) by this method starting from 34 g (0.052 mol) of the phosphonate $C_8F_{17}C_2H_4SC_3H_6P(O)(OEt)_2$ (**8**). After dropwise addition of 17.40 g (0.11 mol) of $(CH_3)_3SiBr$ and methanol hydrolysis, we obtained 29.7 g (95% yield) of phosphonic acid **11**. The ^{1}H NMR spectrum of **11** showed a new peak at 9–10 ppm corresponding to $-P(O)(OH)_2$ and the disappearance of the peak at 0.3 ppm showing that all the $Si(CH_3)_3$ groups had been hydrolyzed. Analysis: Calc. for $C_{13}H_{12}O_3SP$ (601.83): C, 25.91; H, 1.99; F, 53.65; S, 5.32; P, 5.15%. Found: C, 25.30; H, 2.16; F, 51.05; S, 6.83; P, 5.71%.

3.6. Application of fluoro compounds

Before each coating, the galvanized steel surfaces were washed with ether in order to improve their hydrophobicity. Products **7a, 8, 9** and **11** in solvent solution (50% by weight) were applied using a bar coater. The samples obtained were heated at 150 °C over 1 h.

4. Conclusions

The synthesis of new fluorinated phosphonates can be achieved by monoaddition of fluorinated mercaptans on to unsaturated phosphonates using UV initiation. The fluorophosphonates were hydrolyzed quantitatively into the corresponding diacids by the use of oleum or silylation followed by methanol hydrolysis. Such simple methods produce a wide range of compounds possessing different spacers between the fluorinated chain and the phosphonate end-group.

References

[1] C. Heid, D. Hoffmann and J. Polster, Ger. Pat. 2 233 941, 1974; [*Chem. Abs., 81* (1974) 79 674b].

[2] J. Mondt (Hoechst AG), Ger. Pat. 3 128 143, 1983; [*Chem. Abs., 98* (1983) 145 138j].

[3] W. Bloech, Ger. Pat. 1 254 150, 1967; [*Chem. Abs., 68* (1967) 49 763u].

[4] K. Albrecht and J. Kocur (Hoechst AG), Eur. Pat. Appl. EP 407 874, 1991; [*Chem. Abs., 115* (1991) 108 588e].

[5] Sagami Chemical, Jpn. Pat. 57 142 926, 1982; [*Chem. Abs., 98* (1983) 34 296q].

[6] Nippon Mektron Co. Ltd., Jpn. Pat. 59 66 496, 1984; [*Chem. Abs., 101* (1984) 193 060e].

[7] E.S. Percec and F.N. Popescu, Romanian Pat. 71 010, 1981.

[8] R.W. Stackman, *Ind. Eng. Chem., Prod. Res. Dev., 21* (1982) 328.

[9] T. Mahmood and J.M. Shreeve, *Inorg. Chem., 25* (1986) 3128, and references therein.

[10] D.J. Burton, D.J. Pietrzyk, T. Ishihara, T. Fonong and R.M. Flynn, *J. Fluorine Chem., 20* (1982) 617.

[11] T. Fonong, D.J. Burton and D.J. Pietrzyk, *Anal. Chem., 55* (1986) 1089.

[12] A. Chiotis, G. Clouet and J. Brossas, *Polym. Bull., 7* (1982) 303.

[13] M. Shimada and Y. Nakamura, *ACS Symp. Ser., No. 212,* Am. Chem. Soc., Washington, DC, 1983, p. 237.

[14] C.R. Hall, T.D. Inch and N.E. Williams, *J. Chem. Soc., Perkin Trans. 1* (1985) 233.

[15] G.M. Blackburn and D.E. Kent, *J. Chem. Soc., Perkin Trans., 1* (1986) 6.

[16] G.M. Blackburn and D.E. Kent, *J. Chem. Soc., Chem. Commun.,* (1981) 511.

[17] S. Billenstein, H. Brecht, E. Schuierer and Tr. Mezhduanar, *Kongr. Poverkhn. Akt. Veshchestvam., 7th,* 1976, Vol. 1, p. 54 [*Chem. Abs., 91* (1976) 22 785r].

[18] A. Michaelis and B.A. Arbuzov, *J. Russ. Phys. Chem. Soc., 38* (1906) 687.

[19] D.J. Burton, R. Guneratne, W. Cen, R.L. Kirchmeier, A.S. Modak, W.A. Sanderson, J.M. Shreeve and D. Su (Gas Res. Inst.), PCT Int. Pat. WO 90 07 513, 1990; [*Chem. Abs., 114* (1990) 122 2704a].

[20] A.E. Platt and B. Tittle, *J. Chem. Soc. C,* (1967) 1150.

[21] B. Boutevin, Y. Hervaud and Y. Pietrasanta, *Phosphorus Sulfur, 11* (1981) 373.

[22] B. Boutevin, Y. Hervaud and Y. Pietrasanta, *Phosphorus Sulfur, 20* (1984) 197.

[23] G.M. Blackburn and M.J. Parratt, *J. Chem. Soc., Chem. Commun.,* (1983) 886.

[24] G.M. Blackburn and M.J. Parratt, *J. Chem. Soc., Chem. Commun.*, (1982) 1270.
[25] J.A. Bittles and A.M. Joyce, US Pat. 2 559 754, 1951; [*Chem. Abs., 46* (1952) 1026].
[26] N.O. Brace, *J. Chem. Soc.*, (1961) 3, 3197.
[27] K. Inukai, T. Ueda and H. Maramatsu, *J. Org. Chem., 29* (1964) 2224.
[28] R.N. Haszeldine, D.L. Hobson and D.R. Taylor, *J. Fluorine Chem., 8* (1976) 115.
[29] H.D. Block (Bayer AG), Ger. Pat. 2 514 640, 1976; [*Chem. Abs., 86* (1976) 72 867m].
[30] M. Asscher and H. Rosin, Fr. Pat. 7 209 144, 1972.
[31] W.S. Barnhart, US Pat. 2 786 827, 1957.
[32] O.V. Korenchenko, Yu.Y. Ivanov, A.Y. Aksinenko, V.A. Sokolov and I.V. Martinov, *Khim. Farm. Zh., 26* (1992) 21; [*Chem. Abs., 118* (1992) 59 786u].
[33] L.H. Chance and J.P Moreau, US Pat. 3 910 886, 1976.
[34] B. Boutevin, Y. Hervaud and Y. Pietrasanta, *Phosphorus Sulfur, 20* (1984) 189.
[35] N.O. Brace, *J. Fluorine Chem., 62* (1993) 217.
[36] B. Boutevin, Y. Furet, Y. Hervaud and G. Rigal, *J. Fluorine Chem., 69* (1994) 11.
[37] B. Boutevin, Y. Furet, Y. Hervaud and G. Rigal, *J. Fluorine Chem., 74* (1995) 37.
[38] B. Boutevin and Y. Pietrasanta, in J.C. Bevington (ed.), *Comprehensive Polymer Science*, Pergamon Press, Oxford, 1989, Vol. 3, p. 185.
[39] A. Duda and S. Percec, in R.E. Kirk and D.F. Othmer (eds.), *Encyclopedia of Polymer Science and Technology*, 2nd edn., John Wiley & Sons, New York, 1989, Vol. 16, p. 268.
[40] E.K. Kleiner, T.W. Cooke and R.A. Falk (Ciba Geigy), Eur. Pat. Appl. 19 584, 26.11.80; [*Chem. Abs., 94* (1981) 104 115y].
[41] K.H. Worms and M. Schmidt-Dunker, in G.M. Kosolapoff and L. Maier (eds.), *Organic Phosphorus Compounds*, J. Wiley & Sons, New York, 1976, Vol. 7.
[42] Y. Machida, S. Nomoto and I. Saito, *Synth. Commun.*, (1979) 97.
[43] B. Boutevin, S. Boileau, Y. Pietrasanta and A. Lantz, Fr. Pat. 2 566 401, 27.12.85; [*Chem. Abs., 105* (1985) 62 676v].
[44] B. Boutevin, B. Youssef, S. Boileau and A.M. Garnaud, *J. Fluorine Chem., 35* (1987) 399.
[45] J. Chojnowski, M. Cypryk and J. Michalski, *Synthesis, 10* (1978) 777.
[46] T. Morita, Y. Okamoto and H. Sakurai, *Tetrahedron Lett.*, (1978) 2523.