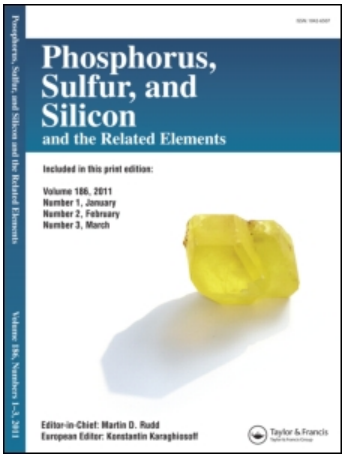

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ORGANOSULPHUR PHOSPHORUS ACID COMPOUNDS. PART 6. PREPARATION AND ANALYTICAL IDENTIFICATION OF FLUOROBENZYLPHOSPHONO-DISULPHONIC ACIDS

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To cite this Article Montoner, E. , Savarino, P. , Adani, F. and Ricca, G.(1995) 'ORGANOSULPHUR PHOSPHORUS ACID COMPOUNDS. PART 6. PREPARATION AND ANALYTICAL IDENTIFICATION OF FLUOROBENZYLPHOSPHONO-DISULPHONIC ACIDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 106: 1, 37 — 45
To link to this Article: DOI: 10.1080/10426509508027887
URL: http://dx.doi.org/10.1080/10426509508027887

Phosphorus, Sulfur, and Silicon, 1995, Vol. 106, pp. 37–45
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ORGANOSULPHUR PHOSPHORUS ACID COMPOUNDS. PART 6. PREPARATION AND ANALYTICAL IDENTIFICATION OF FLUOROBENZYLPHOSPHONO-DISULPHONIC ACIDS

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(Received March 28, 1995)

Three new organosulphur phosphorus acid compounds have been obtained by sulphonation with liquid SO_3: 2-fluorobenzylphosphonic gave 2-fluorobenzylphosphono-3,5-disulphonic, 3-fluorobenzylphosphonic acid gave 3-fluorobenzylphosphono-4,6-disulphonic acid, and 4-fluorobenzylphosphonic acid gave 4-fluorobenzylphosphono-3,5-disulphonic acid in nearly quantitative yields. The products analysis is based on n.m.r. spectroscopy.

Key words: Sulphonation, fluorobenzylphosphonic acid, fluorobenzylphosphono-sulphonic acid, fluorobenzylphosphono-disulphonic acid.

Fluorobenzylphosphono-sulphonic acids, $FC_6H_3(SO_3H)CH_2PO_3H_2$,[1] have been recently obtained (Figure 1) starting from diethylfluorobenzylphosphonates. Reactions (2, 4 and 6), shown in Figure 1, occur readily at room temperature upon mixing the reagents, and are well shifted to the right at a SO_3/II molar ratio of 3.2. The quantitative conversion of the fluorobenzylphosphonic acids (II) into the phosphono-sulphonic acids (III) allows to isolate easily the products from the reaction mixture, whereas separation of III from unconverted II would be very difficult. These results have encouraged the present investigation on the synthesis of fluorobenzylphosphono-disulphonic acids, $FC_6H_2(SO_3H)_2CH_2PO_3H_2$ (IV).

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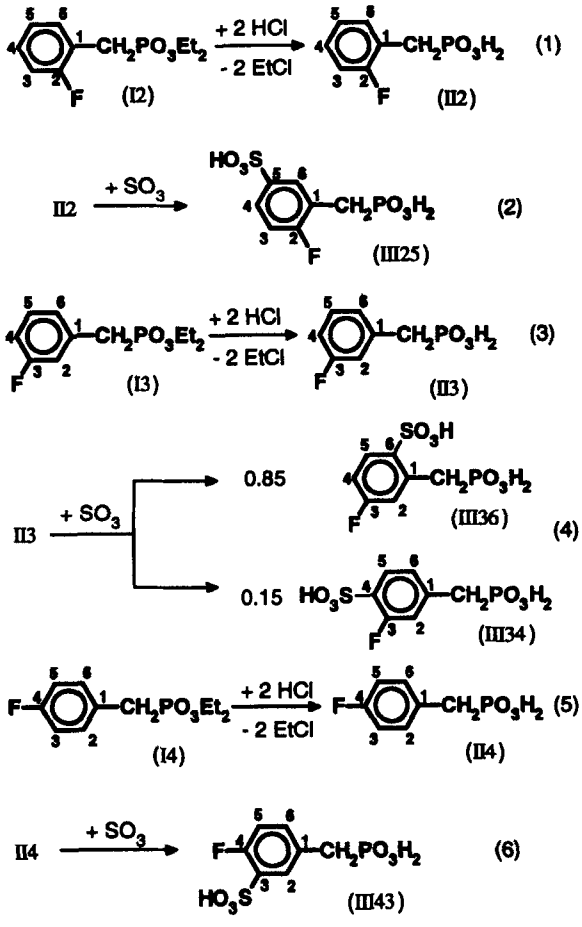

FIGURE 1 Structure and distribution of product isomers in the synthesis of fluorobenzylphosphono-sulphonic acids. Reagents and product isomers throughout the paper are identified by the Roman numeral corresponding to the empirical formula, followed by one to three digits Arabic numerals identifying respectively the carbon bonded to fluorine and the carbon or carbons bonded to sulphur.

RESULTS AND DISCUSSION

Several fluorobenzylphosphono-disulphonic acids isomers were obtained (Figure 2) starting from fluorobenzylphosphonic acids (see Experimental). The reactions, shown in Figure 2, were performed at 80°C and a SO_3/II molar ratio of 9.1, without prior isolation of the intermediates III. Complete conversion of II to IV was obtained in 8–12 days starting from II4 and II3, and in ca. 42 days starting from II2. The results showed that, while sulphonation of II to III is a fast reaction at room temperature,[1] further sulphonation requires higher temperature and is significantly slower. The effect is likely due to ring deactivation by the first SO_3H group, as observed in the sulphonation of phenylphosphonic acid under similar conditions.[2]

Elemental analyses and acid equivalent concentration (H^+ meq/g) measurements for the crude products of the reactions in Figure 2 (see Experimental) supported the trihydrated fluorobenzylphosphono-disulphonic acid formula. In principle how-

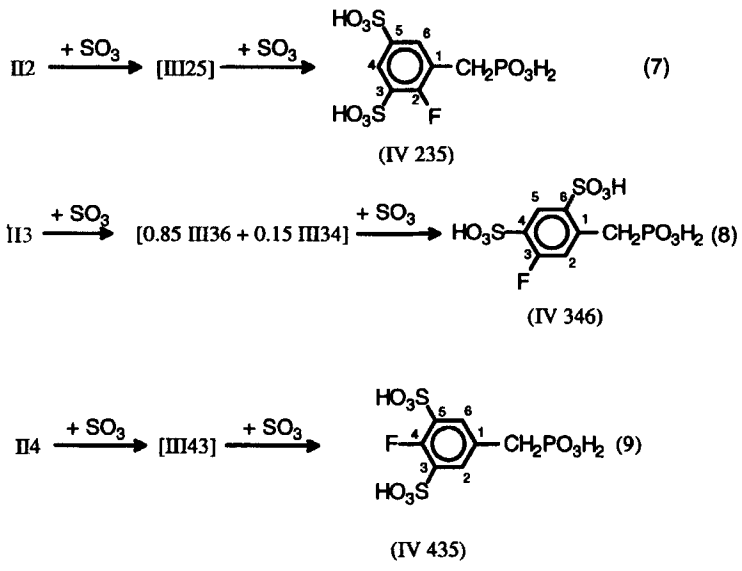

FIGURE 2 Reactions and structure of product isomers in the synthesis of fluorobenzylphosphono-disulphonic acids.

ever, each product could contain more than one isomer: i.e. IV235, IV245 and IV256 in reaction (7); IV326, IV346, IV356, IV324 and IV345 in reaction (8); IV435, IV423 and IV436 in reaction (9). N.m.r. spectra however supported formation of one compound in each reaction: i.e. signals equivalent to the presence of two ring protons and of two methylene protons in ^{1}H spectra (Table I); one resonance signal in ^{31}P and ^{19}F spectra (Table II); four quaternary carbon, two aromatic (H)C and one (P)$C(H)_2$ resonance signals in the ^{13}C spectra (Table III) of the products obtained from II2 and II3, and three signals due to the resonance of four quaternary carbons, one signal due to the resonance of two aromatic (H)C and one (P)$C(H)_2$ resonance signal in the ^{13}C spectrum (Table III) of the product obtained from II4 (see discussion below). In reaction (8), the only possibility for the mixture of parent intermediates (III36 and III34 in Figure 2) to yield one disulphonated isomer is the formation of IV346.

Structures were easily assessed based on analysis of ^{1}H resonance signals splitting pattern[3,4] (Table I). For the product of reaction (7), splitting of aromatic proton absorptions appeared at two levels, i.e. 6.1 Hz due to meta FH coupling and $\leq$ 3.1 Hz due to PH and/or meta HH coupling. The spectrum could arise only from compound IV235. The absence of splitting (J = 8–10 Hz) due to ortho HH and/or ortho FH coupling excludes the presence of the other possible isomers. The observed resonance splitting for the two ring protons in IV235 is indeed identical to that reported[1] for H6 in the parent intermediate III25, and is consistent with removal of the H3H4 coupling in this compound following substitution of H3 by a second SO_3H function. The assignment of the chemical shifts to H4 and H6 in IV235 is based on the chemical shifts reported for the same protons in III25, and on assuming stronger deshielding on H4 due to the ortho effect[1] of the SO_3H function.

TABLE I

[1]H magnetic resonance data for fluorobenzylphosphono-disulphonic acids (IV) and for fluorobenzylphosphono-sulphonic acids (III)[1]: chemical shift (δ, p.p.m.),[a] coupling constant (J, Hz)[b] and deshielding effect of SO_3H substituent ($\Delta\delta$, p.p.m.)[c]

				ring protons				
Cpd[d]		CH_2		H2	H3	H4	H5	H6
IV235	δ[e]	3.50	δ[g]			8.21		8.06
IV235	J[f]	21.4	J[h]			6.10		6.10
IV235			J[i]			≤3.10		≤3.10
III25	δ[e]	3.36	δ[j]		7.28	7.76		7.80
III25	J[f]	21.2	J[k]		9.03	8.53		
III25			J[h]			5.45		7.10
IV235	$\Delta\delta$	0.14				0.45		0.26
IV346	δ[e]	3.81	δ[l]	7.51			8.33	
IV346	J[f]	22.6	J[m]	10.69				
IV346			J[n]	2.00				
IV346			J[h]				6.84	
III36	δ[e]	3.71	δ[o]	7.23		7.07	7.88	
III36	J[f]	22.4	J[k]	9.83		8.55	8.76	
III36			J[h]				6.00	
III34	δ[e]	3.26	δ[p]	7.16			7.68	7.30
III34	J[f]	22.0	J[k]	9.83			9.82	9.82
IV346	$\Delta\delta$[q]	0.10		0.28			0.45	
IV346	$\Delta\delta$[r]	0.55		0.35			0.65	
IV435	δ[e]	3.39	δ[s]	7.95				7.95
IV435	J[f]	21.5	J[h]	5.86				5.86
IV435			J[i]	≤3.10				≤3.10
III43	δ[e]	3.30	δ[t]	7.74			7.25	7.46
III43	J[f]	20.5	J[k]				9.40	8.79
III43			J[h]	6.84				5.87
IV435	$\Delta\delta$	0.09		0.21				0.49

[a]CH_2/Hi signal area ratios = 2 for i = 2, 3, 4, 5 or 6 in each compound n.m.r. spectrum; ring protons numbered as the bonded carbons in Figures 1 and 2.

[b]Omitted coupling constants could not be picked out or assigned due to the complex multiplicity and/or overlap of signals arising from the resonance of different protons.

[c]$\Delta\delta = \delta_{IVijk} - \delta_{IIIij}$, δ_{IVijk} and δ_{IIIij} are chemical shifts for the same proton, respectively in the product and in the parent intermediate shown in Figure 2.

[d]Compound; key to legends in Figures 1 and 2.

[e]Doublet.

[f]^2J (PH).

[g]Two doublets of triplets.

[h]Meta FH coupling constant.

[i]PH and/or meta HH coupling constants.

[j]Triplet for H3, multiplet containing c. 9 lines for H4, and doublet of triplets for H6; $J \leq 3$ Hz omitted.

[k]Ortho HH and/or FH coupling constant.

[l]Doublet of doublets for H2 and doublet for H5.

[m]Ortho FH coupling constant.

[n]^4J (PH).

[o]Triplet of triplets for H4, doublet of triplets for H2, doublet of doublets for H5.

[p]Broad doublet showing additional splitting for H2, broad doublet of triplets for H6 with upfield outer peak covered by the H2 signal from III36, broad triplet for H5; $J \leq 3$ Hz omitted.

[q]III36 taken as parent intermediate to obtain $\Delta\delta$.[c]

[r]III34 taken as parent intermediate to obtain $\Delta\delta$.[c]

[s]Doublets (J^h) with further splitting (J^i).

[t]Triplet for H5, multiplet of eight lines for H6 and doublet of triplet for H2; $J \leq 3$ Hz omitted.

TABLE II

Chemical shifts (δ, p.p.m.) and coupling constants (J, Hz) from ^{31}P and ^{19}F resonance spectra of fluorobenzylphosphonic acids (II),[a] and of their sulphonated derivatives (III)[a] and (IV)

Cpd[b]	$\delta^{31}P$	$\delta^{19}F$	J(PF)[c]	^3J(FH)	^4J(FH)
II2	24.6	−120.3[d]	4.6		
III25	24.0	−115.4[e]	4.9		
IV235	23.4	−114.5[f]	4.4		6.1
II3	24.6	−116.6[g]			
III36	24.6	−111.7[f]		8.1	6.4
III34	24.2	−115.2[g]			
IV346	23.9	−111.2[h]	2.4	10.9	7.2
II4	25.6	−119.3[i]	5.7	9.9	6.8
III43	25.2	−118.3[e]	5.6	10.3	6.1
IV435	24.7	−117.8[j]	6.1		6.1

[a]Unpublished data from previous work[1]; omitted J values are not available or could not be picked out due to signal broadness.

[b]Compound; key to legends in Figures 1 and 2.

[c]Measured from ^1H noise-decoupled ^{31}P spectra. By comparison, J(PF) values reported in literature[5] for compounds I in Figure 1 are 4.6 Hz for I2, 2.2 Hz for I3, and 5.5 Hz for I4.

[d]Broad multiplet containing at least 10 lines.

[e]Broad multiplet containing at least 6 lines.

[f]Triplet of doublets.

[g]Poorly resolved multiplet.

[h]Multiplet showing 7 lines.

[i]Multiplet showing 8 lines.

[j]Quartet.

The ^1H spectrum of the product of reaction (8) was consistent with the presence of the expected compound IV346, i.e. a doublet of doublets for H2 due to FH2 (J = 10.69 Hz) and to PH2 (J = 2 Hz) coupling, and a doublet for H5 due to FH5 coupling (J = 6.84 Hz). Chemical shifts for this compound were assigned based on J constants.

The ^1H spectrum of the product of reaction (9) could arise only from IV435: i.e. one doublet with signal area equivalent to two protons and J = 5.86 Hz due to meta FH coupling, showing further splitting ($J \leq 3.1$ Hz) because of PH and meta HH coupling. For the other possible isomer products in reaction (9), two signals and splitting at higher level (J = 8–10 Hz) due to ortho HH or FH coupling were expected.

Comparison of chemical shifts for the protons in IV with the chemical shifts for the same protons in the parent intermediate III allowed to calculate the effect ($\Delta\delta$) of the second —SO_3H group over the ring. The results (Table I) confirm previous data obtained for the first —SO_3H group[1] on comparing III with parent II: i.e. the deshielding effect per sulphonic function is equivalent to 0.44–0.65 p.p.m. at the protons in ortho to SO_3H, and to ≤0.35 p.p.m. at the farther protons.

The ^{19}F n.m.r. spectra (Table II) gave J(FH) values in agreement with those measured in the ^1H resonance spectra. Analysis of ^1H noise-decoupled ^{31}P spectra (Table II) did not supply any further information, but assessing that sulphonation does not affect much $\delta^{31}P$ and J(PF) values in fluorobenzylphosphonates.

^{13}C resonance signal assignments (see Experimental) were based on identification of quaternary carbon signals, calculation of expected chemical shifts (δ_{cld}) and of FC and PC coupling constants (J_{cx}) for each of the above product isomers, and

TABLE III

^{13}C magnetic resonance data for fluorobenzylphosphono-disulphonic acids (IV) obtained in reactions (7–9), and for the parent intermediates[1] (III in Figure 2): experimental chemical shifts (δ_f, p.p.m.) and coupling constants (J, Hz)[a] from ^1H noise-decoupled spectra, and calculated chemical shifts (δ_{cld}, p.p.m.), expected coupling constants (J_{ex}, Hz) and standard deviation of J_{ex} (s_{jex})[1]

Cpd[c]		ring carbons[b]						
		C1	C2	C3	C4	C5	C6	PCH_2
IV[d]	$J(PC)_{ex}$	9.1	7.1	3.1	3.7	3.2	6.1	
IV[d]	$s_{J(PC)ex}$	0.5	1.0	0.4	0.3	0.4	0.7	
IV2[e]	$J(FC)_{ex}$	20.5	244.2	20.5	7.2	3.2	7.2	
IV2[e]	$s_{J(FC)ex}$	2.8	0.9	2.8	2.0	0.4	2.0	
IV235	δ_{cld}	123.5	161.4	132.7	125.9	141.5	134.6	
IV235	δ_f	124.5[f]	159.8[f]	132.5[f]	126.7	140.5[f]	134.0	29.1
IV235	$J(PC)_f$	9.1	7.6				4.6	134.3
IV235	$J(FC)_f$	17.5	256.3	17.1	≤8.0		5.6	
III25	δ_f	122.4[f]	163.8[f]	117.8	128.3	140.4[f]	131.0	29.1
III25	$J(PC)_f$	9.1	7.6			≤3.1	≤3.1	134.0
III25	$J(FC)_f$	16.8	250.2	22.4	9.2	≤3.1	≤3.1	
IV3[g]	$J(FC)_{ex}$	7.2	20.5	244.2	20.5	7.2	3.2	
IV3[g]	$s_{J(FC)ex}$	2.0	2.8	0.9	2.8	2.0	0.4	
IV346	δ_{cld}	138.4	116.8	162.8	135.1	129.4	140.4	
IV346	δ_f	138.8[f]	121.7	160.9[f]	130.2[f]	130.0	139.6[f]	33.0
IV346	$J(PC)_f$	9.1	4.6	3.3			6.3	129.7
IV346	$J(FC)_f$	9.1	24.4	257.8	13.4		3.3	
III36	δ_f	134.8[f]	115.7	165.2[f]	120.2	131.8	139.3[f]	32.9
III36	$J(PC)_f$	9.1	3.1	3.2	4.6	8.6	8.5	131.0
III36	$J(FC)_f$	9.1	22.9	253.3	22.9	11.4	5.7	
III34	δ_f	140.6[f]	119.7	160.6[f]	134.1[f]	130.2	127.2	35.7
III34	$J(PC)_f$	9.1				≤6.1	≤6.1	134.3
III34	$J(FC)_f$	9.1	26.0	250.2	13.0	≤6.1	≤6.1	
IV4[h]	$J(FC)_{ex}$	3.2	7.2	20.5	244.2	20.5	7.2	
IV4[h]	$s_{J(FC)ex}$	0.4	2.0	2.8	0.9	2.8	2.0	
IV435	δ_{cld}	131.6	134.5	132.5	157.0	133.6	134.1	
IV435	δ_f	130.9[f]	134.2	133.0[f]	155.8[f]	133.0[f]	134.2	
IV435	$J(PC)_f$	9.1	≤7.3		4.5	≤4.0	≤7.3	
IV435	$J(FC)_f$	4.5	≤7.3	16.8	256.6	16.8	≤7.3	
III43	δ_f	130.5[f]	130.9	131.4[f]	159.4[f]	118.7	136.5	34.9
III43	$J(PC)_f$	9.1	≤6.1	2.3	4.5		≤2.1	133.0
III43	$J(FC)_f$	3.1	≤6.1	15.2	250.2	22.9	≤2.1	

[a]Resonance bands appeared as follows: a doublet of doublets, when both J(PC) and J(FC) are given, and for $J(PC)=J(CF)$; a triplet, for $J(PC)=J(CF)$; a doublet, for J values preceded by ≤ to indicate that the measured value is assigned either to PC or to FC coupling and that the other coupling constant is equal or lower; a doublet, and no further splitting being observed, when only J(CF) is given.

[b]Carbons numbered as in Figures 1 and 2.

[c]Compound; key to legends in Figures 1 and 2.

[d]All compounds IV.

[e]All compounds IV2jk (j or k = 3–6).

[f]Quaternary carbons identified from ^1H noise-coupled ^{13}C spectra.

[g]All compounds IV3jk (j or k = 2, 4–6).

[h]All compounds IV4jk (j or k = 2, 3, 5, 6).

fitting of experimental (δ_f and J_f) to expected resonance data (Table III). For the products obtained in reactions (7) and (9), respectively, the data (J_f and δ_f in Table III) fit structures IV235 and IV435 only. The comparison of experimental to expected J(FC) constants established that the signals with splitting due to ortho FC coupling arise exclusively from the resonance of quaternary carbons. These carbons

TABLE IV

Effects ($\Delta^i J$)[a–i] of substitution of aromatic protons by SO_3H on ^1J(FC) and ^3J(FC) in fluorobenzylphosphonic acids

Compound[j]	$^1J(FC)_f$	$\Delta^1J(FC)^{a-d}$	^2J(FCi)	$\Delta^2J(FCi)^{e-i}$
II2	244.0		^2J(FC3) 21.3	
III25	250.2	6.2[a]	^2J(FC3) 22.4	
IV235	256.3	6.1[b]	^2J(FC)3 17.1	−5.3[e]
II3	244.1		^2J(FC4) 26.0	
III36	253.3	9.2[a]	^2J(FC4) 22.9	
III34	250.2	6.1[a]	^2J(FC4) 13.0	−8.4[f]
IV346	257.8	4.5[c]	^2J(FC4) 13.4	−9.5[g]
IV346	257.8	7.6[d]		
II4	243.0		^2J(FC3) 21.0	
II4			^2J(FC5) 22.9	
III43	250.2	7.2[a]	^2J(FC3) 15.2	−5.8[h]
III43			^2J(FC5) 22.9	
IV435	256.6	6.4[b]	^2J(FC5) 16.8	−4.2[i]
		$\frac{^1J(FC)^k}{6.7 \pm 1.4}$		$\frac{^2J(FC)^k}{6.6 \pm 2.2}$

[a]$\Delta^1 J(FC) = {}^1J(FC)_{III} - {}^1J(FC)_{II}$; J constants referred, respectively, to the compound III and to the parent compound II shown in Figure 1.

[b]$\Delta^1 J(FC) = {}^1J(FC)_{IV} - {}^1J(FC)_{III}$; J constants referred, respectively, to the compound IV and to the parent intermediate III shown in Figure 2.

[c]$\Delta^1 J(FC) = {}^1J(FC)_{IV346} - {}^1J(FC)_{III36}$; J constants referred to compound IV346 and III36, respectively.

[d]$\Delta^1 J(FC) = {}^1J(FC)_{IV346} - {}^1J(FC)_{III34}$; J constants referred to compound IV346 and III34, respectively.

[e]$\Delta^2 J(FC3) = {}^2J(FC3)_{IV235} - {}^2J(FC3)_{III25}$; C3 identifies the carbon (see Figures 1 and 2) in IV235 and III25, respectively.

[f]$\Delta^2 J(FC4) = {}^2J(FC4)_{III34} - {}^2J(FC4)_{II3}$; C4 identifies the carbon (see Figure 1) in III34 and II3.

[g]$\Delta^2 J(FC4) = {}^2J(FC4)_{IV346} - {}^2J(FC4)_{III36}$; C4 identifies the carbon (see Figures 1 and 2) in IV346 and III36.

[h]$\Delta^2 J(FC3) = {}^2J(FC3)_{III43} - {}^2J(FC3)_{II4}$; C3 identifies the carbon (see Figure 1) in III43 and II4.

[i]$\Delta^2 J(FC5) = {}^2J(FC5)_{IV435} - {}^2J(FC5)_{III43}$, C5 identifies the carbon (see Figures 1 and 2) in IV235 and III43.

[j]Key to legends as in Figures 1 and 2; data for compounds II reported in previous work[1]; data for III and IV selected from Table III.

[k]Average and standard deviation of the values shown above it in the same column.

could only be C1 and C3 in IV235, and C3 and C5 in IV435. The other isomers, which could possibly be obtained in the reactions under consideration, have H bonded carbons in ortho to (F)C and are therefore ruled out. The ^{13}C resonance spectrum of the product obtained in reaction (8) fit well the expected isomer structure IV346.

One may observe from the above data that sulphonation affects significantly the FC coupling constants over one bond and over two bonds. This effect is better evidenced in Table IV containing ^1J(FC) and ^2J(FC) values selected from Table III and the same coupling constants for fluorobenzylphosphonic acids (II) reported in previous work.[1] For ^1J(FC), the effect appears to be directly related to the number of sulphonic functions in the molecule: i.e. ^1J(FC) increases on the average by 6.7 ± 1.4 Hz per sulphonic function, regardless of its position in the ring. There is also a significant decrease of ^2J(FC) amounting to 6.6 ± 2.2 Hz, but this occurs only for the sulphonated carbon being in ortho to the fluorine bonded carbon.

EXPERIMENTAL

Physical Measurements. ^1H (at 399.8 MHz), ^{13}C (at 100.5 MHz), ^{31}P (at 161.8 MHz) and ^{19}F (at 376.2 MHz) n.m.r. spectra were recorded in D_2O at room temperature on Jeol EX 400 spectrometer. The sample concentration in D_2O was ca. 10% w/w. ^1H and ^{13}C chemical shifts (δ^1H and $\delta^{13}C$) were measured in p.p.m. from internal 1% w/w 2-methyl-2-propanol (MP) and converted into values referred to TMS by adding, to the measured ^1H and ^{13}C values, 1.29 and 31.30 p.p.m., respectively for the ^1H and ^{13}C chemical shifts of the methyl group in MP from TMS. ^{31}P chemical shifts ($\delta^{31}P$) are in p.p.m. from external 85% w/w H_3PO_4 in D_2O. ^{19}F chemical shifts ($\delta^{19}F$) are in p.p.m. from external $CFCl_3$.

Chemical Analyses. C, H, S and O concentrations were obtained by C. Erba 1108 elemental analyzer. Acid equivalent concentrations in solid product (H^+ meq/g) were obtained by titration to phenolphtalein end point with 0.1 N NaOH in water half saturated with NaCl.

Calculation of ^{13}C Chemical Shifts. The chemical shifts (δ_{cld}) of the ^{13}C resonance signals for compounds IV were calculated on the basis of the additivity of substituents effects,[1] starting from the experimental δ values of the parent intermediates III (Table III) and adding the SO_3H effect at each carbon, i.e. 14.9 p.p.m. at the carbon bearing the C—S bond, and −2.4, 1.1 and 3.6 at the ortho-, meta- and para-carbon, respectively.

^{13}C Resonance Signals Assignment. Quarternary carbons, $(PCH_2)C$, (F)C and (S)C, and carbons bonded to hydrogen, (H)C, were identified from both ^1H noise-coupled and ^1H noise-decoupled ^{13}C resonance spectra. Assignments of experimental signals for aromatic carbons to carbons in the structure under consideration (Table III) were accomplished by fitting first the experimental (J_f) to the expected[1] (J_{ex}) phosphorus-carbon and fluorine-carbon coupling constants. For both $J(PC)_{ex}$ and $J(FC)_{ex}$ the estimated standard deviations $S_{J(PC)ex}$ and $S_{J(FC)ex}$ (Table III) show that $J(FC)$ values may allow unequivocal identification of some carbon signals: i.e. due to the resonance of the F bonded carbon and of the carbons in ortho to it. In the cases where J values did not allow unambiguous assignment, signals were assigned based on fitting[1] the experimental (δ_f) to the closest calculated (δ_{cld}) chemical shift.

Preparation of IV. Authentic II (8 g) and liquid SO_3 were mixed as previously described.[1] The reactions shown in Figure 2 were performed in a glass bottle under autogenous pressure at 80°C and at SO_3/II, mole/mole ~9.1. The course of the reactions was followed up by sampling the viscous liquid reaction mix, quenching it in D_2O and analyzing the solution by ^{31}P n.m.r. spectroscopy. The initial samples were taken after 10 days for reaction (7), 8 days for reaction (8) and 24 h for reaction (9). The spectra contained resonance signals corresponding to those found (Table II) for the authentic monosulphonated intermediate (III) and disulphonated product (IV). The conversion of II to IV was calculated from the area ratio of ^{31}P resonance signals and from the equation $n_{II} = n_{III} + n_{IV}$, where n_{II} are the initial moles of compound II, and n_{III} and n_{IV} are moles of III and IV present in the reaction mix. Product isolation was carried out when the ^{31}P spectrum of the reaction mix contained only the signal assigned to IV: i.e. after 8 days starting from II4, 12 days starting from II3, and 42 days starting from II2. Thus, the reaction mixture was allowed to equilibrate with the room temperature, evaporated under vacuum to eliminate unreacted SO_3, and quenched with water to convert residual SO_3 to diluted sulphuric acid. The sulphonic acids were separated from H_2SO_4 by a previously established procedure[1]: i.e. addition of $HCl/BaCl_2$, filtration of insoluble $BaSO_4$, removal of soluble excess Ba^{2+} by ion exchange, and drying under vacuum at 60°C. The raw products were viscous liquids which crystallized upon long standing over P_2O_5. Elemental analysis for the solid products gave the following results: for the product obtained from II2 and identified as IV235, C 21.35, H 3.50, O 50.77, S 15.92% w/w, corresponding to C 7.00, H 13.6, O 12.5, S 1.95 relative atom/atom ratios; for the product obtained from II3 and identified as IV346, C 21.62, H 3.35, O 50.27, S 16.26% w/w, corresponding to C 7.00, H 12.9, O 12.2, S 1.97 atom/atom; for the product obtained from II4 and identified as IV435, C 21.43, H 3.50, O 52.22, S 16.05% w/w, corresponding to C 7.00, H 13.7, O 12.8, S 1.97 atom/atom. The products acid equivalent concentrations (H^+ meq/g) were found 9.80 for IV235, 9.84 for IV346 and 9.76 for IV435. The best theoretical formula fitting the experimental data is that for trihydrated fluorobenzylphosphono-disulphonic acid, $C_7H_{14}FO_{12}PS_2$: C 20.80, H 3.49, O 47.49, S 15.86% w/w, 9.89 H^+ meq/g. Yields for the recovered solid products, based on the above empirical formula, were ca. 86% mole/mole, relatively to initial II.

Missing experimental details are as previously reported.[1]

REFERENCES

1. E. Montoneri, P. Savarino, G. Viscardi and M. C. Gallazzi, *Phosphorus, Sulfur, and Silicon*, **86,** 145 (1994). (Corrigenda in this reference: at lines 3, 6, 9, 12, 15, 18, 21, 24, 27, 30 of second column in Table II, "*J*(PC)" should read "*J*(FC)"; compound III25 in Figure 1 should appear as the phosphonic acid, and not as the diethylphosphonate; line 16 at page 152 should read "signals at -111.7 and -115.2 p.p.m. from external $CFCl_3$" instead of "signals at -41.18 and -35.3 p.p.m.")
2. E. Montoneri, *Phosphorus, Sulfur, and Silicon*, **55,** 201 (1991).
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5. L. Ernst, *Org. Magn. Reson.*, **9,** 35 (1977).