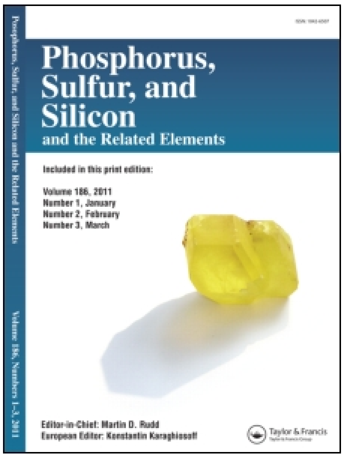

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Organosulphur Phosphorus Acid Compounds. Part 7. Preparation and Analytical Identification of Difluorobenzylphosphono-Sulfonic Acids

E. Montoneri; P. Savarino; P. Quagliotto; F. Adani; G. Ricca

To cite this Article Montoneri, E. , Savarino, P. , Quagliotto, P. , Adani, F. and Ricca, G.(1998) 'Organosulphur Phosphorus Acid Compounds. Part 7. Preparation and Analytical Identification of Difluorobenzylphosphono-Sulfonic Acids', Phosphorus, Sulfur, and Silicon and the Related Elements, 134: 1, 99 — 108

To link to this Article: DOI: 10.1080/10426509808545455

URL: http://dx.doi.org/10.1080/10426509808545455

Phosphorus, Sulfur and Silicon, 1998, Vol. 134/135, pp. 99-108
Reprints available directly from the publisher
Photocopying permitted by license only

ORGANOSULPHUR PHOSPHORUS ACID COMPOUNDS. PART 7. PREPARATION AND ANALYTICAL IDENTIFICATION OF DIFLUOROBENZYLPHOSPHONO-SULFONIC ACIDS

E. MONTONERI[a]*, P. SAVARINO[a], P. QUAGLIOTTO[a], F. ADANI[b] and G. RICCA[c]

[a]*Dipartimento di Chimica Generale ed Organica Applicata Universitá di Torino, Corso Massimo D'Azeglio 48–10125 Torino, Italy,* [b]*Dipartimento di Fisiologia delle Piante Coltivate e Chimica Agraria, Universitá di Milano, Via Celoria 2–20133 Milano, Italy and* [c]*Dipartimento di Chimica Organica e Industriale, Universitá di Milano, Via Venezian 21–20133 Milano, Italy*

(Received 6 November, 1997)

Fifteen new difluorinated phosphonic and sulfophosphonic acids have been synthesized and characterized by ^{1}H, ^{13}C, ^{31}P and ^{19}F n.m.r. spectroscopy. The results are discussed in relation to previous work on monofluorinated acids.

Keywords: Sulphonation; difluorobenzylphosphonic acid; difluorobenzylphosphono-sulfonic acid

Fluorobenzylphosphono-sulfonic acids have been proven to be useful intermediates for the synthesis of layered metal salts with good solid state proton conductivity.[1] In this context, the availability of difluorobenzylphosphono-sulfonic acids is desirable in order to synthesize perfluorinated salts and investigate the full potential of fluorine on conductivity properties. The present work therefore reports the synthesis and characterization of several difluorobenzylphosphono-sulfonic acids and of parent difluorobenzylphosphonic acids.

---

* To whom correspondence should be addressed.

RESULTS AND DISCUSSION

The synthesis and identification of the title products was accomplished as described in the Experimental Part. Previous work[2] on sulfonation of fluorobenzylphosphonic acids by liquid SO_3 at room temperature showed that the reaction is selectively ruled by the ortho-para mesomeric effect of fluorine. The same reaction with diflurobenzylphosphonic acids did not occur as selectively, yielding in most cases a mixture of isomeric products as shown in Figure 1. Sulfonation by concentrated H_2SO_4 required higher temperature (140–150 °C). The results showed that, regardless of the sulfonating agent, the reaction occurs selectively with formation of one compound only starting from II24 and II26 isomers (Fig. 1). These compounds have a carbon atom available for substitution in ortho to one CF carbon and in para to the other CF carbon and, in addition, this available carbon is in ortho to a third CH carbon. Thus, each of these two phosphonic acids have one carbon bearing the highest electron charge density, and not being sterically hindered. The other difluorobenzylphosphonic acid isomers do not have this feature, and yield mixtures of isomeric products upon sulfonation. Specifically, compound II35 has the C2 carbon in ortho to F3 and in para to F5, but this carbon is sterically hindered by the $CH_2PO_3H_2$ substituent. In compounds II23, II34, and II25 the electron charge density is likely to be more evenly distributed over the ring. In this case, the favoured reaction site appears the one being in para to the fluorine atom and, at the same time, the least sterically hindered. Sulfonation by sulphuric acid gave similar results, but some changes of the products yield ratio starting from II23, II25, II34 and II35.

N.m.r. spectroscopy for products and reagents confirmed previous findings obtained for fluorobenzylphosphonic acids[2,3] on the effect of SO_3H functional group on chemical shifts and coupling constants. Ranges of values for deshielding of aromatic and CH_2P protons by SO_3H in difluorobenzylphosphonic acids (Table I) are $0.37 \leq d\delta \leq 0.73$ for ring protons in ortho to SO_3H, $d\delta \leq 0.37$ for farther ring protons, and $0.61 \leq d\delta \leq 0.77$ or $d\delta \leq 0.16$ for protons in CH_2P bonded to ring carbon, being respectively in ortho to or farther from SO_3H. Effects on ^{31}P chemical shift were none or small. SO_3H moves upfield the chemical shift of ^{19}F resonance by 0.9–8.4 p.p.m., but the effect does not readily appear to be correlated with the relative position of the sulfonic and fluorine substituents.

TABLE I ^1H magnetic resonance data for difluorobenzylphosphonic acids (II) and sulfonated derivatives (III): chemical shift (δ, p.p.m.),[a] coupling constant (J, Hz)[b] and deshielding effect of SO_3H substituent ($d\delta$, p.p.m.)[c]

Cpd[d]		CH_2		*ring protons*				
				H2	*H3*	*H4*	*H5*	*H6*
II26	δ^e	3.24	δ^f		7.00	7.33	7.00	
II26	J^g	21.32	J^h		7.86	7.22	7.86	
II26			J^i			7.22		
II26			J^j			2.20		
III263	δ^e	3.40	δ^k			7.80	7.15	
III263	J^g	21.05	J^h			8.57	8.86	
III263			J^i			7.36		
III263			J^j			2.50		
III263	$d\delta$	0.16				0.47	0.15	
II34	δ^e	3.16	δ^l	7.15			7.15	7.15
II34	J^g	21.00						
III346	δ^e	3.77	δ^m	7.52			7.88	
III346	J^g	22.08	J^h	11.3			9.41	
III346			J^i	7.49			8.38	
III346			J^j	2.85				
III346	$d\delta$	0.61		0.37			0.73	
II24	δ^e	3.18	δ^n		6.97		6.97	7.47
II24	J^g	21.5	J^h		8.71		8.71	
II24			J^o					8.00
II24			J^j		2.70		2.70	2.76
III245	δ^e	3.33	δ^p		7.19			7.84
III245	J^g	21.04	J^h		9.80			
III245			J^i					8.04
III245			J^j					2.75
III245	$d\delta$	0.15			0.22			0.37
II23	δ^e	3.26	δ^q			7.19	7.19	7.19
II23	J^g	21.70						
III235	δ^e	3.41	δ^r			7.67		7.67
III235	J^g	21.43						
III235	$d\delta$	0.15				0.48		0.48
III236	δ^e	3.90	δ^s			7.35	7.81	
III236	J^g	22.10	J^t			9.73		
III236			J^o			8.11		
III236			J^j			2.16		
III236	$d\delta$	0.64				0.16	0.62	

Cpd[d]		CH_2		ring protons				
				H2	H3	H4	H5	H6
II35	δ[e]	3.20	δ[u]	6.97		6.84		
II35	J[g]	21.9	J[h]	8.5		9.25		
III352	δ[e]	3.97	δ[v]			7.09		7.12
III352	J[g]	22.56	J[h]			9.49		9.49
III352			J[w]					2.68
III352	dδ	0.77				0.25		0.15
III354[x]	δ[e]	3.35						
III354[x]	J[g]	22.56						
III25	δ[e]	3.22			7.14[y]	7.14[y]		7.14[y]
III25	J[g]	21.86						
III254	δ[e]	3.35	δ[z]		7.59			7.32
III254	J[g]	21.72	J[h]		8.97			10.07
III254			J[i]		5.86			5.67
III254			J[j]					2.75
III254	dδ	0.13			0.45			0.18

[a] CH_2/Hi signal area ratios = 2 for $2 \le i \le 6$ in each compound n.m.r. spectrum; ring protons numbered as the bonded carbons in Figure 1.

[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] $d\delta = \delta_{III} - \delta_{II}$, δ_{III} and δ_{II} are chemical shifts for the same proton, respectively in the product and in the parent compound shown in Figure 1.

[d] Compound; key to legends in Figure 1.

[e] Doublet.

[f] False triplet for H3 and H5, multiplet of five lines, each split into a doublet for H4.

[g] $^2J(PH)$.

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

[i] Meta FH coupling constant.

[j] PH coupling constant.

[k] False triplet for H5; doublet of triplets, each signal further split into doublet, for H4.

[l] Very complex multiplet from 7.13 to 7.33 p.p.m. containing over 22 lines.

[m] Doublet of doublets for H2 and H5, but each signal further split into doublet for H5.

[n] Triplet showing further splitting for H3 and H5, complex multiplet for H6.

[o] ^3JHH and ^4JFH.

[p] Triplet for H3; triplet of doublets for H6.

[q] Complex multiplet of over 17 lines from 7.12 to 7.26 p.p.m.

[r] Overlapping multiplets due to H4 and H6 resonances covering the 7.61–7.73 p.p.m. range.

[s] Broad multiplets.

[t] ^3JFH.

[u] Broad multiplet containing at least seven lines for H2 and H6, and triplet showing further splitting for H4; $J \le 3$ Hz omitted.

[v] Broad triplet for H4, and broad doublet of doublets for H6.

[w] ^4JHH and/or ^4JPH.

[x] Ring proton signals masked by main isomer pattern.

[y] Complex multiplet of over 20 lines from 7.0 to 7.3 p.p.m.

[z] Doublet of doublets for H3; doublet of doublets of doublets for H6.

TABLE II Chemical shifts (δ, p.p.m.) and coupling constants (J, Hz) from ^1H noise-decoupled ^{31}P and ^{19}F resonance spectra[a] of difluorobenzylphosphonic acids (II) and sulfonated derivatives (III)

Cpdb		^{31}*pc*	*F2*	*F3*	*F4*	*F5*	*F6*
II23	δ	23.5	-143.9	-140.7			
II23	J(PF)			4.8			
II23	J(FF)		20.1	20.1			
III235	δ	23.2	-137.5	-136.0			
	J(PF)		2.7	5.0			
	J(FF)		20.0	20.0			
III236	δ	23.4	-135.6	-133.1			
	J(PF)		2.7	5.0			
	J(FF)		20.0	20.0			
II35	δ	21.8		-112.1		-112.1	
III352	δ	25.0		-103.7		-106.7	
	J(PF)			2.6		2.6	
	J(FF)			11.7		11.7	
III354	δ	23.6		-110.9		-110.9	
II34	δ	24.3		-140.6	-143.6		
	J(FF)			20.6	20.6		
III346	δ	24.8		-134.2	-139.1		
	J(PF)			1.8	5.0		
	J(FF)			23.0	23.0		
II24	δ	24.0	-115.0		-115.0		
III245	δ	24.1	-107.6		-114.0		
	J(PF)		4.4		6.0		
	J(FF)		11.6		11.6		
II25	δ	23.4	-121.0			-124.5	
III254	δ	23.2	-121.5			-118.8	
III254	J(PF)		4.5			2.3	
III254	J(FF)		18.0			18.0	
III253	δ	23.5	-122.7			-117.6	
III253	J(PF)		4.5			2.3	
	J(FF)		18.0			18.0	
II26	δ	22.9	-114.65				-114.6

Cpdb		$^{31}P^{c}$	*F2*	*F3*	*F4*	*F5*	*F6*
II26	J(PF)		4.3				4.3
II26	J(FF)		18.8				18.8
III263	δ	23.0	-108.1				-112.0
III263	J(PF)		4.4				4.4
III263	J(FF)		9.4				9.4

[a] Omitted J values could not be picked out due to low resolution; other legends as in Table I.

EXPERIMENTAL

Physical Measurements. ^{1}H (at 200 MHz) and ^{13}C (at 50.288 MHz) n.m.r. spectra were recorded on Bruker AC 200 spectrometer. ^{31}P (at 80.961 MHz) and ^{19}F (at 188.154 MHz) n.m.r. spectra were recorded on Gemini 200 Varian Aerograph spectrometer. Solvents were D_2O for III and MeOD for II at room temperature. Sample concentration was ca. 10 % w/w. ^{1}H and ^{13}C chemical shifts 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 ^{1}H and ^{13}C values, 1.29 and 31.30 p.p.m. respectively for the ^{1}H and ^{13}C chemical shifts of the methyl group in MP from TMS. ^{31}P chemical shifts are in p.p.m. from external 85 % w/w H_3PO_4 in D_2O. ^{19}F chemical shifts were measured in p.p.m. from external fluorobenzene and converted to values from $CFCl_3$, the difference in chemical shifts between these two reference compounds being 113.6. $CFCl_3$ could not be used as reference due to overlap of its resonance chemical shift with that of the investigated compounds. Conversion of chemical shifts from fluorobenzene to chemical shifts from $CFCl_3$ was performed in order to be able to compare experimental data from this work with data from previous work.[2]

Preparation and characterization of II and III. The phosphonic acids (II) and the sulfonated products (III) were obtained respectively from parent difluorobenzylbromides (Aldrich reagents) and by sulfonation of II with liquid SO_3 under similar conditions reported for other phosphonic acids and sulfophosphonic acids.[3] Both II and III were shown to decompose or melt with decomposition at 180–300 °C. All products were characterized by N.m.r. Chemical shifts assignments and product identification was per-

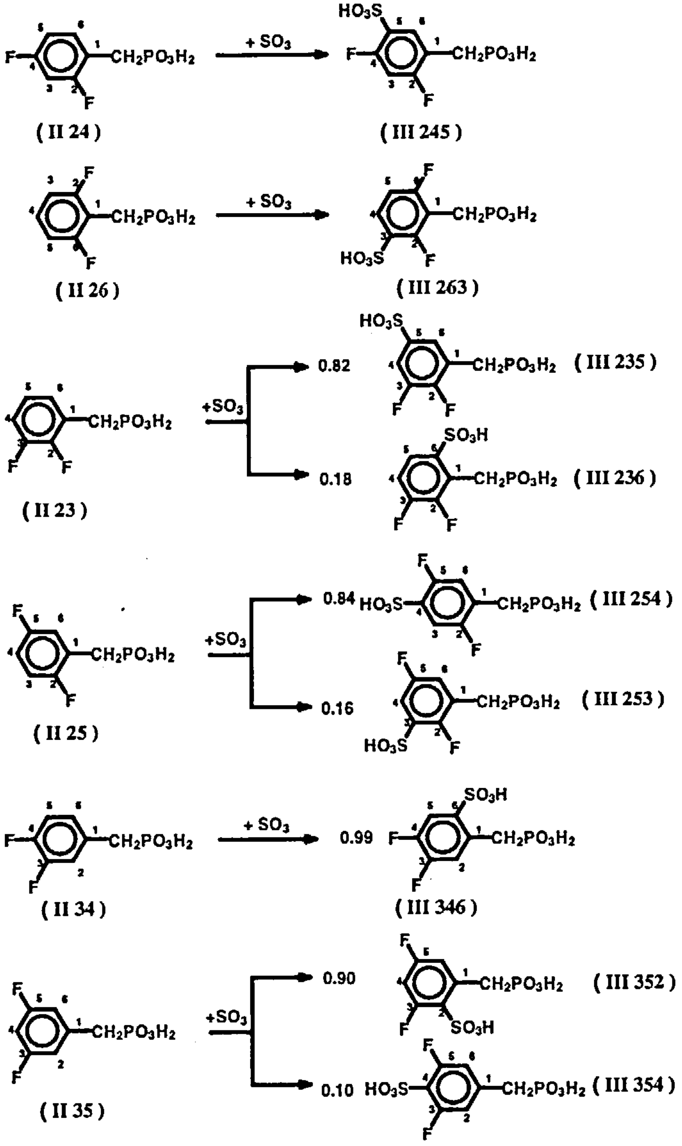

FIGURE 1 Structure and distribution of product isomers in the synthesis of difluorobenzylphosphono-sulfonic acid. Reagents and product isomers throughout the paper are identified by the Roman numeral corresponding to the empirical formula, followed by two or three digit Arabic numerals identifying respectively the two fluorine bearing carbons and the carbon bonded to sulphur

formed as reported previously.[2] Calculated ^{13}C chemical shifts for III were obtained on the basis of the additivity of substituent effects, starting from the experimental values of the parent II 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.[2]

Missing experimental details are as previously reported.[2,3]

TABLE III ^{13}C magnetic resonance data for difluorobenzylphosphonic (II) acids and sulfonated derivatives (III):[a] experimental chemical shifts (δf, p.p.m.) and coupling constants (J, Hz) from ^1H noise-decoupled spectra, and calculated chemical shifts (δc, p.p.m.)

		^{13}C magnetic resonance data						
		ring carbons						*PCH_2*
		C1	*C2*	*C3*	*C4*	*C5*	*C6*	
II23	δ_f	124.6	150.4	152.1	116.3	125.3	128.1	28.7
II23	J(PC)	8.8	8.5					136.5
II23	^1J(FC)		241.3	246.4				
II23	^2J(FC)	14.0	12.8	12.8	17.1			
III235	δ_f	124.9	152.0	151.4	115.5	140.6	125.7	29.2
III235	δ_c	125.7	154.0	153.2	113.9	140.2	125.7	
III235	J(PC)	11.0						132.5
III235	^1J(FC)		255.7	250.6				
III235	^2J(CF)	11.0	11.0	12.3	19.6			
III236	δ_f				117.3			27.6
III236	δ_c	122.2	151.5	155.7	117.4	123.1	143.0	
III236	^2J(FC)				16.9			
II35	δ_f	139.0	113.9	164.3	102.8	164.3	113.9	35.8
II35	J(PC)	8.5	7.2				7.2	135.0
II35	^1J(CF)			246.2		246.2		
II35	^2J(FC)		25.8		25.6		25.8	
II35	^3J(FC)	8.32		12.7		12.7		
III352	δ_f	136.4	127.6	162.4	105.8	164.5	116.6	32.9
III352	δ_c		136.6	128.8	161.9	103.9	167.9	115.0
III352	J(PC)							131.0
III352	^1J(CF)				253.6		253.6	
III352	^2J(FC)					27.0		21.8
III352	^3J(CF)				13.2		12.9	
III354	δ_f	141.1	115.6				115.6	33.2
III354	δ_c	143.0	115.0	161.9	117.7	162.1	115.0	

		^{13}C magnetic resonance data						
		ring carbons						*PCH_2*
		C1	*C2*	*C3*	*C4*	*C5*	*C6*	
III354	J(PC)							130.8
III354	$^2J(FC)$		24.8				24.8	
II26	δ_f	111.1	162.8	112.2	129.7	112.2	162.8	23.3
II26	J(PC)	8.7	8.5				8.5	
II26	$^1J(CF)$		247.5				247.5	
II26	$^2J(CF)$	20.0		24.0		24.0		
II26	$^3J(CF)$		8.5		9.5		8.5	
III263	δ_f	112.0^f	158.9^f	128.2^f	129.7	113.0	164.4^f	23.6
III263	δ_c	112.2	160.4	127.1	127.3	113.3	166.4	
III263	J(PC)	10.6						134.6
III263	$^1J(CF)$		249.1				254.2	
III263	$^2J(FC)$	20.6		16.4		25.2		
III263	$^3J(CF)$				10.6			
II25	δ_f	123.8	158.5	119.2	117.5	160.0	115.9	28.7
II25	J(PC)	8.7	6.8				8.8	137.0
II25	$^1J(CF)$		241.6			241.1		
II25	$^2J(CF)$	17.8			26.3		21.6	
II25	$^3J(CF)$	8.7			8.5		8.8	
III254	δ_f	127.3	155.9	121.2	131.4	157.4	116.9	29.3
III254	δ_c	127.4	159.6	116.8	132.4	157.6	117.0	
III254	J(PC)	9.9						131.6
III254	$^1J(FC)$		246.8			244.1		
III254	$^2J(CF)$	26.4		25.4	18.1		27.3	
III254	$^3J(CF)$	9.9						
III253	δ_f		154.5		115.8	158.8	123.0	
III253	δ_c	124.9	156.1	134.1	115.0	161.1	119.5	
III253	J(CF)		244.5		25.4	248.0	26.8	
II24	δ_f	117.8	163.5	104.5	162.5	112.2	134.0	28.0
II24	J(PC)	10.0			11.3			138.2
II24	$^1J(CF)$		245.5		245.5			
II24	$^2J(CF)$	18.9		26.2		22.4	5.2	
II24	$^3J(CF)$		11.4		11.3			
III245	δ_f	117.9	164.0	107.0	160.1	128.1	132.8	28.5
III245	δ_c	118.9	167.2	105.5	160.1	127.3	131.6	
III245	J(CP)		7.5					134.5
III245	$^1J(CF)$		251.8		252.7			
III245	$^2J(CF)$	21.9		26.6		14.6		

		^{13}C magnetic resonance data						
		ring carbons						*PCH_2*
		C1	*C2*	*C3*	*C4*	*C5*	*C6*	
III245	$^3J(CF)$		12.3		12.3			
II34	δ_f	127.4	118.1	153.0	150.6	119.8	132.1	35.1
II34	J(CP)							135.4
II34	$^1J(CF)$			245.4	243.7			
II34	$^2J(CF)$		16.8	10.1	10.1	17.3		
II34	$^3J(CF)$					5.2		
III346	δ_f	129.4	118.9	152.6	149.6	122.1	140.0	32.2
III346	δ_c	125.0	119.2	156.6	151.7	117.4	147.0	
III346	J(CP)							133.8
III346	$^1J(CF)$			250.9	248.7			
III346	$^2J(CF)$		19.7	12.0	12.3	19.1		

[a] Compounds legend and carbon atoms numbered as in Figure 1; quaternary carbon atoms identified from ^1H noise-coupled ^{13}C spectra.

References

[1] G. Alberti, L. Boccali, M. Casciola, L. Massinelli and E. Montoneri, Solid Sate Ionics **84**, 7, 1996.

[2] E. Montoneri, P. Savarino, F. Adani and G. Ricca, Phosphorus, Sulfur, and Silicon, **106**, 37 (1995)

[3] E. Montoneri, P. Savarino, G. Viscardi and M. C. Gallazzi, Phosphorus, Sulfur, and Silicon, **86**, 145 (1994).