Wittig–Horner Reagents: Structural and Conformational Study of Five- and Six-membered Cyclic Phosphonates and their Carbanions. Evidence of Anomeric Effect in Anionic Species

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A structural and conformational study of the electron-withdrawing substituted phosphonates 2-oxo-1,3,2-dioxaphosphorinanes (**1**) and (**2**) and of the related anionic species (**3**, K^+) and (**4**, K^+) in dimethyl sulphoxide has been made. Phosphonates (**1**) and (**2**) exist predominantly in the chair form with the P=O bond equatorial. The anion (**3**, K^+) gives rise to three rapidly interconverting species, in the chair form, and (**4**, K^+) to two interconverting chairs, chelated to K^+. In each anionic species (**3**) and (**4**), the P$\cdots$O axially substituted conformer is significantly populated, due to an anomeric effect. The 2-oxo-1,3,2-dioxaphospholane (**5**) is very sensitive to moisture, and open-chain compounds can be found in solutions of (**5**), if the solvent is not carefully dried. The related anionic species (**6**, K^+) is not very stable; however, its ^{1}H and ^{31}P n.m.r. data show some similarities with those of the related acyclic compound.

The stereoselective formation of *cis*-αβ-unsaturated nitriles and esters is a challenge in organic synthesis. A few years ago,[1] the use of five-membered-ring cyclic phosphonates, Wittig–Horner reagents, was proposed for this purpose by one of us. The high propensity of the phosphorus atom to suffer nucleophilic attack, when included in a five-membered ring, justified this choice.[1]

It therefore seemed interesting to examine the structure of such reagents in comparison with the cyclic six-membered analogues and with the related acyclic compounds (**7**), which have been previously studied.[2,3] We report here an i.r. and n.m.r. study (^{1}H, ^{13}C, ^{31}P) of the 2-oxo-1,3,2-dioxa-phosphorinanes (**1**) and (**2**) and -phospholane (**5**), as well as of their related anionic species (**3**, K^+), (**4**, K^+), and (**6**, K^+) formed by action of KOBu^t in dimethyl sulphoxide (DMSO). Related species associated with K^+ or Li^+ are insoluble in tetrahydrofuran or pyridine.

Results

The various compounds were prepared according to previously published methods.[1] The anionic species (**3**, K^+), (**4**, K^+), and (**6**, K^+) were generated under argon by addition of 1.2 equiv. KOBu^t to a 0.5M solution of (**1**), (**2**), or (**5**) in DMSO. If the DMSO was not carefully dried, (**5**) suffered hydrolysis.

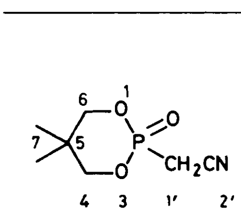
The characteristic i.r. features of (**1**), (**2**), (**3**, K^+), and (**4**, K^+) in DMSO solution are in Table 1. The spectrum of (**1**) shows a strong, sharp band at 2 250 cm^{-1} which is attributed to $\nu_{C\equiv N}$; this band is replaced by a strong, broad absorption at 2 120 cm^{-1} in (**3**, K^+). In the $\nu_{P=O}$ region a strong band at 1 280 and a shoulder at 1 265 cm^{-1} as well as weak bands at 1 235, 1 212, and 1 185 cm^{-1} can be seen in the spectrum of (**1**). That of (**3**, K^+) has three strong absorptions at 1 280, 1 210, and 1 180 cm^{-1} of similar intensities. The spectrum of (**2**) exhibits a strong band at 1 732 cm^{-1} ($\nu_{C=O}$) which is replaced by another at 1 605 cm^{-1} in that of (**4**, K^+). In the $\nu_{P=O}$ region, a strong band at 1 280 and a shoulder at 1 265 cm^{-1} are observed in the spectrum of (**2**) while two bands of unequal intensity at 1 212 and 1 190 cm^{-1} are observed for (**4**, K^+).

The chemical shifts of (**1**), (**2**), (**3**, K^+), (**4**, K^+), (**5**), and (**6**, K^+)

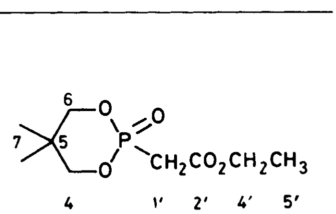
Table 1. Characteristic stretching frequencies[a] of phosphonates (**1**), (**2**) and their anions (**3**, K^+), (**4**, K^+)

Compounds	ν_{CN}	ν_{CO}	ν_{PO}
(**1**)	2 250 (vs)		1 280 (vs) 1 265 (sh) 1 235 (w) 1 212 (w) 1 185 (w)
(**3**)	2 120 (vs)		1 280 (s) 1 210 (s) 1 180 (s)
(**2**)		1 732 (s)	1 280 (s) 1 265 (sh)
(**4**)		1 605 (vs)	1 212 (vs) 1 190 (s)

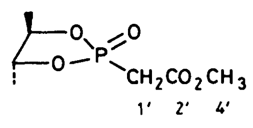
[a] ν values in cm^{-1}. Solvent DMSO.



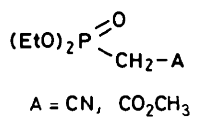
(**1**)



(**2**)



(**5**)



(**7**)

Table 2. Chemical shifts (^1H, ^{13}C, ^{31}P)[a] of phosphonates (**1**), (**2**), and (**5**) and their anions (**3**, K^+), (**4**, K^+), and (**6**, K^+) in DMSO

Compounds	1′-H	4′-H	5′-H	H_A	H_B	Me_A	Me_B	C(1′)	C(2′)	C(4′)	C(5′)	C(4)	C(5)	C(7A)	C(7B)	^{31}P
(**1**)	3.72			4.25	4.01	1.13^b	0.87^b	12.7_5	114.1_5			76.6_4	31.8_8	$20.8_9{}^b$	$19.3_7{}^b$	8.3
(**3**)	0.82			3.89	3.50	1.03^b	0.78^b	5.7_2	130.1_8			73.3_9	31.1_6	$21.5_4{}^b$	$20.9_0{}^b$	37.4
(**2**)	3.28	4.11	1.19	4.17	3.93	1.11^b	0.86^b	30.9_4	165.5_2	60.7_8	13.9_0	76.0_6	31.8_8	$21.1_6{}^b$	$19.5_7{}^b$	12.3
(**4**)	2.36	3.74	1.04	3.84	3.58	0.98^b	0.86^b	39.7_6	170.2_1	55.3_5	15.3_4	73.2_5	31.4_6	$21.4_3{}^b$	$21.2_6{}^b$	33.1
(**5**)	3.37	3.67				1.35	1.29	32.9	164.7	50.9		80.6	79.4	16.2	16.1_5	33.3
(**6**)	2.23	3.58														49.4

[a] $\delta_{^1H}$ and $\delta_{^{13}C}$ relative to internal Me_4Si. $\delta_{^{31}P}$ relative to external H_3PO_4 (85%). Positive δ values are in the direction of increasing frequency. [b] From $^{13}C\{^1H\}$ selective irradiation experiments; the deshielded methyl protons Me_A are bonded to the deshielded methyl carbon C(7A) and the shielded methyl protons Me_B are bonded to the shielded methyl carbon C(7B).

Table 3. Coupling constants[a] of phosphonates (**1**), (**2**), and (**5**) and their anions (**3**, K^+), (**4**, K^+), and (**6**, K^+) in DMSO

Compounds	$^2J_{P,1'-H}$	$^3J_{P,H_A}$	$^3J_{P,H_B}$	$^2J_{H_A,H_B}$	$^1J_{C(1'),1'-H}$	$^1J_{P,C(1')}$	$^2J_{P,C(2')}$	$^4J_{P,C(4')}$	$^2J_{P,C(4)}$	$^3J_{P,C(5)}$
(**1**)	-20.1^b	4.4	19.4	(−) 11.0	135.5	130.1^b	11.0		6.8	7.3^d
(**3**)	$+4.9^c$	6.6	17.2	(−) 10.6	162.9	250.0^c	10.6		6.7	4.7
(**2**)	-20.6^b	4.0	19.2	(−) 11.2	130.0	122.5^b	6.3	<0.7	6.2	6.9
(**4**)	$+16.1^c$	8.8	14.2	(−) 11.0	153.5	228.3^c	22.6	3.3	6.0	5.3
(**5**)	21.2					126.0	6.0			*e*
(**6**)	17.3									

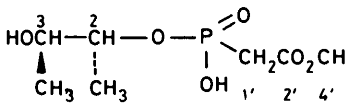
[a] *J* values in Hz. [b] From $^{13}C\{^1H\}$off-resonance experiments, $^1J_{P,C(1')}$ and $^2J_{P,1'-H}$ are of opposite signs, *i.e.* $^2J_{P,1'-H}$ is negative. [c] From $^{13}C\{^1H\}$off-resonance experiments, $^1J_{P,C(1')}$ and $^2J_{P,1'-H}$ bear the same sign, *i.e.* $^2J_{P,1'-H}$ is positive. [d] A long-range $^4J_{P,C(7B)}$ 0.7 Hz is observed for the upfield methyl carbon (C-7B). [e] Me_A, $^3J_{P,C}$ 6.9; Me_B $^3J_{P,C}$ 7.2 Hz.

are in Table 2 and the coupling constants are in Table 3. The lack of stability of (**6**, K^+) did not allow its ^{13}C spectrum to be obtained.

The ^1H n.m.r. spectra were recorded with and without ^{31}P noise decoupling, in order to distinguish between the $J_{H,H}$ and $J_{P,H}$ coupling constants. From experiments with (**1**), it appears that the 4- and 6-methylene protons in the ^{31}P noise-decoupled spectrum appear as an AA′BB′ system, the A part of which is broadened as is the 7-CH_3 low-field signal. This broadening is due to a long-range $^4J_{H,H}$ coupling, which can be shown by $^1H\{^1H\}$ double-resonance experiments. Therefore, H_A and the low-field CH_3 adopt a W geometry and are preferentially axially oriented. Similar broadening is observed in ester (**2**) and anionic species (**3**, K^+) and (**4**, K^+). The spectra without ^{31}P irradiation show that the deshielded 4- and 6-H exhibit smaller $^3J_{P,H}$ values than the shielded ones. Note that in (**2**), the 5′- and 7-methyl and the 4-,4′-, and 6-methylene signals partly overlap, so that the spectrum analysis is not so good.

The ^{13}C spectra were recorded with and without ^1H noise decoupling: while in (**1**) and (**2**) C(1′) appears as a triplet of doublets in the coupled spectra, this carbon gives a doublet of doublets in (**3**, K^+) and (**4**, K^+), confirming that deprotonation takes place on this site. From the off-resonance $^{13}C\{^1H\}$ spectra,[4] $^1J_{P,C}$ and $^2J_{P,H}$ bear opposite signs in (**1**) and (**2**), but the same sign in (**3**, K^+) and (**4**, K^+) *i.e.* $^2J_{P,H}$ is negative in (**1**) and (**2**) but positive in the related anionic species.

The ^1H spectrum of (**5**), when recorded in carefully dried DMSO, shows only one set of signals. However, in the presence of moisture, a new set of signals appears; this progressively increases in intensity with time, all the protons being shifted upfield. The ^{31}P spectrum shows the same phenomenon. This observation is reminiscent of that of Pudovik and his co-workers:[5] we therefore took the spectrum of (**5**) in dry $CDCl_3$ or DMSO and in the presence of increasing amounts of water. In addition to the signals due to (**5**), we observed the spectrum of another compound (see Experimental section), which was the only species present after a sufficient quantity of water was added. On the basis of ^1H, ^{31}P, and ^{13}C data as well as the mass spectrum (*m/z* 226), this compound is assigned structure (**8**).



(**8**)

The ^{31}P chemical shift of (**8**) in DMSO (δ 15.5) is within the range of that observed for linear phosphonates.[6] It is very close to the ^{31}P shift of $(EtO)_2P(O)CH_2CO_2CH_3$ in the same solvent.[3] This comparison is valid as literature data[7,8] indicate a small difference in ^{31}P chemical shifts of ethyl esters and the related phosphonic acids (*ca.* 2 p.p.m.). The mass spectrum also shows the presence of some dimeric material next to (**8**) which cannot be differentiated from (**8**) by n.m.r.

Discussion

1. *Six-membered-ring Systems.*—Previous results[9-11] indicate that 2-oxo-1,3,2-dioxaphosphorinanes can adopt two rapidly interconverting chair conformations: the angular dependence of the $^3J_{P-O-C-H}$ couplings, which fit a Karplus-like relationship, implies that $^3J_{P,H_{eq}}$ is larger than $^3J_{P,H_{ax}}$. If both chairs are equally populated, the two experimental coupling constants are equal, while if one chair form is predominant, they are different. However, the n.m.r. data do not permit a decision of whether the preferred conformer has an axial or an equatorial phosphoryl bond. This information can be deduced from P=O i.r. stretching frequencies, by comparing compounds having the same substituents at phosphorus, in the same medium:[12] equatorial P=O has a higher stretching frequency than does axial P=O.[9-13]

Neutral molecules. The inequality of the two experimental $^3J_{P,H_A}$ and $^3J_{P,H_B}$ values in (**1**) and (**2**) (4.4 and 4 *versus* 19.4 and 19.2 Hz) indicates that these molecules exist as biased equilibrium mixtures of two rapidly interconverting chair conformations, the P=O equatorial conformer predominating in DMSO as deduced from the i.r. stretching frequencies (strong band at 1 280, shoulder at 1 265 cm^{-1}), in agreement with previous results for other six-membered cyclic phosphonates.[9,10]

The sum $^3J_{P.H_A}$ + $^3J_{P.H_B}$ (23.8 and 23.2) is very close to those previously reported for similar compounds in the chair conformation.[9,10] The ^{31}P chemical shifts are also in the range for those reported for such molecules.[6,14]

Anionic species. When going from the neutral precursors (**1**) and (**2**) to the anionic species (**3**, K$^+$) and (**4**, K$^+$), the n.m.r. data indicate a large increase in $^1J_{P.C(1')}$ and $^1J_{C(1')H(1')}$, a change in sign of $^2J_{P.H(1')}$, and a lowfield shift of ^{31}P. These modifications, parallel to those observed in acyclic series,[2,3] show the great structural similarity in these species and indicate flattening of the anionic carbon which becomes planar or nearly so.[15]

Comparison of the sum $^3J_{P.H_A}$ + $^3J_{P.H_B}$ in the neutral precursors (**1**) and (**2**) and in the anionic moieties (**3**) and (**4**) shows virtually no change. However, in (**3**) and (**4**) one of these coupling constants increases ($^3J_{P.H_A}$ 6.6 and 8.8 Hz) while the other decreases ($^3J_{P.H_B}$ 17.2 and 14.2 Hz). This indicates that, in anionic species, two interconverting chairs do coexist, but the conformational preference between them is not so high as in (**1**) and (**2**).

Nitrile (**3**, K$^+$) *in DMSO.* The P$\overset{\cdots}{-}$O stretching frequencies appear as strong bands at 1 280, 1 210, and 1 180 cm^{-1}, showing that at least three species coexist. These species are different from the neutral precursor as the $\nu_{C\equiv N}$ band in (**1**) at 2 250 cm^{-1} totally disappears and is replaced by a new absorption band at 2 120 cm^{-1}.

The higher frequency band (1 280 cm^{-1}) is similar to the one observed in the acyclic analogue from (**7**; A = CN):[16] as there is no vibrational change for the same absorption in the neutral precursor, it implies that the phosphoryl oxygen–cation interaction should be very weak, *i.e.* K$^+$ should be either located in the vicinity of the C$\overset{\cdots}{\equiv}$N group or poorly associated with the anion. It is likely that, as in the neutral precursor (**1**), the P$\overset{\cdots}{-}$O bond should be equatorially oriented [(**3a**, K$^+$)].

The lower frequency bands at 1 210 and 1 180 cm^{-1} are assigned to longer P$\overset{\cdots}{-}$O bonds, the oxygen of which is associated to K$^+$. The 1 210 cm^{-1} bond should correspond to an equatorially oriented P$\overset{\cdots}{-}$O bond in (**3b**, K$^+$) and the 1 180 cm^{-1} one to an axially oriented one in (**3c**, K$^+$) which should be lengthened by operation of the anomeric effect involving the O(1) and O(3) lone pairs. Such an interaction is in agreement with the frequency differences between P$\overset{\cdots}{-}$O$_{ax}$ and P$\overset{\cdots}{-}$O$_{eq}$ in (**3**, K$^+$) ($\Delta\nu$ 30 cm^{-1}) which is larger than in (**1**) ($\Delta\nu$ 15 cm^{-1}).

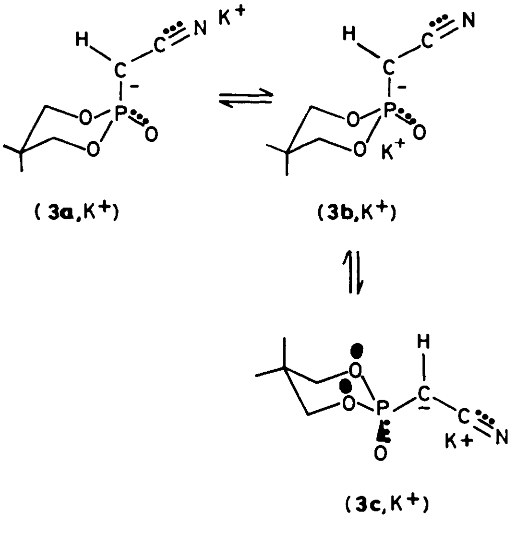
Therefore, the lengthening of the P$\overset{\cdots}{-}$O bond in the anionic species (**3**, K$^+$), relative to the neutral precursor (**1**), induces an increase in the population of the axially substituted P$\overset{\cdots}{-}$O bond conformer (**3c**). This result can be compared with the conformational equilibrium in phosphoric esters[9,10,12,14,17] for which the longer P–OR bond is axially oriented while the shorter P=O one is equatorial. In six-membered-ring phosphate anions, preferential association of Li$^+$ takes place with the axial P$\overset{\cdots}{-}$O oxygen,[18] in a similar way.

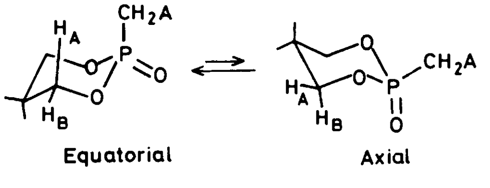
Furthermore, the hybridization change of C(1′) from sp^3 to sp^2 induces a shortening of the P–C(1′) bond in (**3**, K$^+$) relative to (**1**). This should decrease the populations of the conformers of (**3**, K$^+$) having an axial P–C(1′) bond by a reverse anomeric effect. Should this effect be the most important one, a fourth conformer, structurally related to (**3a**, K$^+$) but with an axial P$\overset{\cdots}{-}$O bond, absorbing around 1 260 cm^{-1}, should be expected.

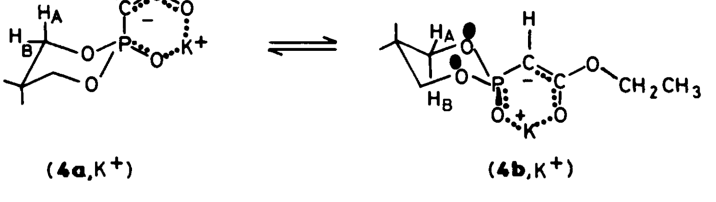
Ester (**4**, K$^+$) *in DMSO.* The existence of a long-range $^4J_{P\text{-}C\text{-}C\text{-}O\text{-}C(4)}$ coupling constant in (**4**, K$^+$) which does not exist in (**2**) is indicative of a W arrangement of these bonds in the anionic moiety.[19] The stretching frequencies appear at 1 605 cm^{-1} for C$\overset{\cdots}{-}$O and 1 212, 1 190 cm^{-1} for P$\overset{\cdots}{-}$O. Thus both interconverting chairs exist as chelates (**4a**, K$^+$) and (**4b**, K$^+$), as in acyclic analogues.[3]

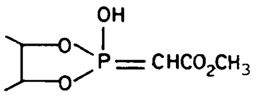
The values of $^3J_{P.H_A}$ and $^3J_{P.H_B}$ are in line with an unequal population of the two conformers; in so far as both extinction coefficients in $\nu_{P\cdots O}$ were similar, the i.r. data should suggest (**4a**, K$^+$) is favoured. The manifestation of the anomeric effect induces an increase in population of the axially substituted P$\overset{\cdots}{-}$O conformer in (**4a**, K$^+$) relative to (**2**). However, this effect seems to be weaker than in the nitrile case as the $\Delta\nu_{P\cdots O}$ between (**4a** and **b**) (22 cm^{-1}) is smaller than between (**3b** and **c**) (30 cm^{-1}). A smaller lengthening of the axial P$\overset{\cdots}{-}$O bond in (**4b**) (ν 1 190 cm^{-1}) than in (**3c**) (ν 1 180 cm^{-1}) can be ascribed to the interaction of the cation with two negatively charged oxygen atoms in (**4**, K$^+$) instead of one in (**3**, K$^+$).

2. *Five-membered-ring System.—Structural study of* (**5**) *and* (**6**, K$^+$). In (**5**), which is a single isomer, the structural parameters are in agreement with the expected ones: the ^{31}P signal is shifted to low field (δ 33.3 p.p.m.) relative to acyclic analogue,[3] in agreement with the literature.[6] Owing to its


(**3a**,K$^+$) (**3b**,K$^+$) (**3c**,K$^+$)




(**4a**,K$^+$) (**4b**,K$^+$)



(9)

instability, we could not obtain the ^{13}C n.m.r. spectrum of the related anionic species (6, K^+) in DMSO. The ^{1}H and ^{31}P n.m.r. data do not show any significant difference, when compared with the acyclic series:[3] the ^{31}P signal is shifted to low field by 16.1 p.p.m. and the ^{1}H signals are shifted upfield relative to those for the neutral precursor (5).

Hydrolysis of (5). It is well known that five-membered-ring phosphonates and phosphates suffer a very fast hydrolysis,[6,20] by far more rapid than the acyclic or six-membered-ring analogues. This explains why signals corresponding to compound (8) were observed in addition to those of 1,3,2-dioxaphospholane (5) in the presence of moisture. This questions the validity of the recent report of an ylide species (9) coexisting in CCl_4 or in aqueous EtOH with (5),[5] which is probably the open-chain compound (8). Furthermore, the pK_a determined for this ylide (9)[5] is close to the expected figure for a phosphonic acid such as (8).[21]

The mass spectrum shows the presence of a dimeric species along with (8). From literature data,[22] it appears that the ^{31}P, ^{1}H, and ^{13}C n.m.r. spectra of polymers from 2-alkoxy-2-oxo-1,3,2-dioxaphospholanes, which are easily formed at room temperature in basic medium, do not differ significantly from the spectra of the open-chain monomers. That is the reason why such species cannot be characterized in the n.m.r. spectra.

Conclusions.—The formation of anionic species from cyclic phosphonates (1), (2), and (5) induces ^{1}H and ^{31}P spectral modifications similar to those observed in the acyclic analogues (7).[2,3] In the six-membered series, the same observations hold for ^{13}C spectra, thus showing that the anionic carbon is planar.

The 2-oxo-1,3,2-dioxaphosphorinane ring in (1), (2), (3, K^+) and (4, K^+) has rapidly interconverting chair conformers. While in the neutral molecules (1) and (2) the P$\overset{\dots}{=}$O axially substituted conformer is weakly populated, the weight of this form becomes more important in the anionic species (3, K^+) and (4, K^+), due to the intervention of an anomeric effect.

Experimental

Materials.—The various cyclic phosphonates (1), (2), and (5) were obtained according to previously described procedures.[1] Compound (5), (4*R*,5*R*)-4,5-dimethyl-2-methoxycarbonylmethyl-2-oxo-1,3,2-dioxaphospholane, was prepared from D-(−)-butane-2,3-diol (Burdick and Jackson), b.p. 134—143 °C at 0.3 mmHg; $[\alpha]_D^{20}$ +21° ($CHCl_3$, *c* 0.05 g ml^{-1}). The anionic species (3, K^+), (4, K^+), and (6 K^+) were generated under strictly moisture- and oxygen-free conditions by addition of 1.2 equiv. of sublimated KOBu^t to a 0.5M solution of (1), (2), and (5) in DMSO.[2]

I.r. Spectra.—I.r. spectra were scanned on a Perkin-Elmer 457 spectrometer equipped with a double beam which allows the elimination of the solvent absorptions. The anion solution (*c* 0.25M) was introduced into an NaCl cell (fixed thickness 0.01 cm) and the solvent DMSO into an NaCl cell of variable thickness. The cells were filled in a dry-box.

Mass Spectra.—These were determined on a Nermag R-10-10 apparatus (electronic-impact ionisation at 70 eV or chemical ionisation by NH_3).

N.m.r. Spectra.—^{1}H Spectra were recorded on a Varian XL-100-12 W.G. spectrometer, using the continuous-wave mode, and the ^{1}H resonance of Me_4Si was used to provide the field frequency lock. Heteronuclear double-resonance experiments ^{1}H-{^{31}P} were performed by irradiating ^{31}P at 40.5 MHz using the gyrocode decoupler. The ^{31}P irradiating frequency was determined using an Eldorado-Varian frequency counter and ^{31}P chemical shifts relative to H_3PO_4 were calculated as previously described.[23] ^{13}C Spectra with ^{1}H noise decoupling were recorded at 25.17 (Varian XL-100), 15.08 (Bruker WP-60), or 125.76 MHz (Bruker WM-500) using the Fourier transform mode. The ^{2}H resonance of [$^2H_6$]DMSO or D_2O (in a capillary) was used to provide the field frequency lock. Proton-coupled ^{13}C spectra were obtained with gated proton decoupling.

Identification of Compound (8).—The structure of (8) was determined on the basis of its ^{1}H, ^{13}C, ^{31}P, and mass spectra: δ_H (DMSO–H_2O 99:1 v/v) 4.23 (2 H, m, 2- and 3-H), 3.61 (3 H, s, 4′-Me), 2.91 (2 H, d, $^2J_{P-H}$ 21.2 Hz, 1′-H), and 1.15 and 1.00 (3 H, and 3 H, d and d, $^3J_{HH}$ 6.6, $^3J_{HH}$ 6.6 Hz, 2- and 3-Me); δ_P (DMSO–H_2O 99:1 v/v) 15.5 p.p.m.; δ_C (DMSO + H_2O 99:1 v/v) 164.9 [C(2′)], 75.2 and 67.4 [J_{PC} 7.3 and J_{PC} 5.5 Hz, C(2) and C(3)], 51 [C(4′)], 33.6 [$^1J_{PC}$ 110.8 Hz, C(1′)], 16.6 (3-Me), and 15.5 p.p.m. ($^3J_{PC}$ 1.8 Hz, 2-Me); *m/z* 227 (*M* + 1) and 244 (*M* + NH_4^+), dimer at 416 (208 × 2), 417 (*M* + 1), and 434 (*M* + NH_4^+); *m/z* of (5) 208, 167 (100), 151, and 109.

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