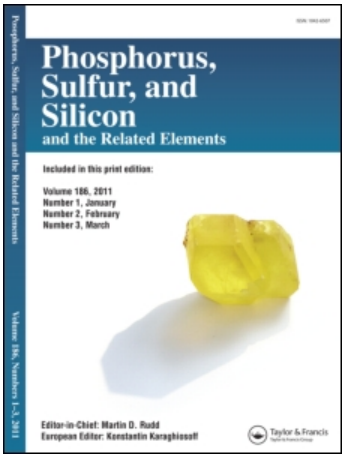

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STEREOCHEMISTRY OF 1,2-OXAPHOSPHOLANES. V. Phosphorus Shifts as a Probe of Configuration of Substituted 1,2-Oxaphospholan-3-ols

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STEREOCHEMISTRY OF 1,2-OXAPHOSPHOLANES. V. Phosphorus Shifts as a Probe of Configuration of Substituted 1,2-Oxaphospholan-3-ols*

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The ^{31}P NMR spectra of a series of diastereomeric 2-methoxy-2-oxo-1,2-oxaphospholan-3-ols are analyzed. A downfield shift $\Delta\delta(^{31}P) > 1$ ppm is specific for the isomer with the P=O and HO—C-3 groups in the *cis* configuration with respect to the *trans* isomer.

INTRODUCTION

Stereochemistry of organophosphorus heterocycles is conveniently studied by NMR spectroscopy.[1,2] The deshielding effect of the phosphoryl oxygen[1c] and the shielding effect of aromatic substituents,[1c,3] as well as the angular dependence of $^{2}J_{PH}$[1c,2,4a] are generally employed to establish the configuration at phosphorus by ^{1}H NMR. γ-Effects and/or $^{1-3}J_{PC}$ in ^{13}C NMR are also successfully applied.[1b,2,4a,5] Standard methods, however, cannot be easily used in assignments of configuration of some 1,2-oxaphospholanes,[6] and particularly of carbohydrates having phosphorus in the anomeric position[7] due to the complexity of the ^{1}H NMR spectra and overlap of the ^{13}C NMR signals of these compounds in the 3.5–5.0 ppm and 68–77 ppm regions. This note will describe a correlation of the ^{31}P NMR chemical shifts of diastereomeric 2-methoxy-2-oxo-1,2-oxaphospholan-3-ols and the relative configurations at P and C-3. Numerous examples of similar correlations are reported in the literature.[1a,4b]

RESULTS AND DISCUSSION

Recently, we have established the relative configurations at P and C-3 in the diastereomeric 2-methoxy-2-oxo-3,5,5-trimethyl-1,2-oxaphospholan-3-ols (**8A** and **8B**) (Figure 1 and Table I) based on the deshielding effect of the phosphoryl oxygen observed in the ^{1}H NMR spectrum of **8B**, and upfield shifts of both $\underline{C}H_3$—C-3 and $\underline{C}H_3OP$ signals found in the ^{13}C NMR spectrum of **8A**.[8] X-ray investigations[9] of **8A** confirmed the conclusions drawn from the NMR spectra as well as earlier ones from

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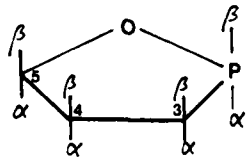

FIGURE 1 A general formula of the 1,2-oxaphospholanes.

the H-bond studies by IR.[10,11] The comparison of the ^{31}P NMR chemical shifts of **8A** and **8B** revealed the 2.7 ppm in chloroform and 1.5 ppm in methanol (Table II) downfield shifts of the diastereomer with the C-3—OH and P=O groups in the *cis* configuration. In the ^{31}P NMR spectra of the corresponding methyl esters **9A** and **9B** a negligible downfield shift was noticed in chloroform for **9A**, and a much larger one was observed in methanol (Table II). However, *p*-nitrobenzoylation of **8A** and **8B** caused the 1.5 ppm upfield shifts of the **10A** signals as compared with those of **10B** (Table II).

These results could not be rationalized in terms of the O—P—O angle—and/or (R)O—P—R dihedral angle—^{31}P NMR chemical shift relationships[4b] because of the insufficient crystal structure data for the O—P—O angles in diastereomeric pairs **8** and **10**, but mostly by the conformational mobility[8] of the 1,2-oxaphospholane ring, in which (R)O—P—O—R dihedral angles of only about 110—140° can be attained, as measured from the Dreiding models. The latter relationship is well documented for the six-membered phosphate triesters in the rigid envelope conformation[4b] where (R)O—P—O—C dihedral angles of about 60° and 180° are allowed for axially and equatorially oriented ester functions.

To explain the downfield shift of the ^{31}P NMR signal of **8A** in comparison with that of **8B**, we suggest that the intramolecular hydrogen bond in **8A** causes a decrease of the electron density around the phosphorus nucleus and therefore produces deshielding. Consequently, only minor differentiation of the ^{31}P NMR shifts is expected after the hydroxy groups have been protected.

In order to study the scope and limitations of the stereochemical dependence between the ^{31}P NMR chemical shifts and the relative configurations at P and C-3 a series of substituted 2-methoxy-2-oxo-1,2-oxaphospholan-3-ols (Figure 2) and some of their 3-O-protected derivatives were synthesized. Selected ^{1}H and ^{13}C parameters (Table I) were analyzed to assign the configurations at P and C-3 in the diastereoisomeric pairs **1**, **2**, **4** and **11**. In the ^{31}P NMR spectra of these pairs downfield shifts in chloroform of 1.3 to 4.2 ppm (Table II) are found for the **A** diastereomers having the *cis* arrangements of the C-3—OH and P=O groups. Furthermore, the same rule holds for the pairs **12** and **13** where the hydroxy group is replaced by the 3-(β,β-dimethylhydrazino) group,[12] although $\Delta\delta(^{31}P)$ drops to *ca.* 1 ppm (Table II). As it could be expected for the solutions of 3-hydroxy and 3-(β,β-dimethylhydrazino) derivatives in methanol a decrease of $\Delta\delta(^{31}P)$ is observed (Table II). It seems, that a downfield shift of the ^{31}P NMR signals of the **A** diastereomers occurs also in the spectra of ethers (Table II). On the other hand, in the examined esters there is no correlation between ^{31}P NMR shifts and the relative configurations (Table II). However, some reversed relationships can be found for **4** and **14** (Table II), and for this reason we propose to limit the applicability of the rule to these pairs

TABLE I

Structures of the studied 1,2-oxaphospholanes, ^{31}P NMR shifts,[a] ^{1}H and/or ^{13}C shifts[b] and $^{2}J_{HP}$[c] of selected groups important for stereochemical assignments

	Substituents of the 1,2-oxaphospholane ring								δ (^{31}P)				
Cpd.	5α	5β	4α	4β	3α	3β	2α	2β	$CHCl_3$	MeOH	δ(^{1}H)	δ(^{13}C)	$^{2}J_{HP}$
1A	H	Me	H	H	OH	H	O	OMe	45.2	44.8	H—C-3 4.18;		$^{2}J_{P,H\text{-}3}$ 7.5
1B	H	Me	H	H	OH	H	MeO	O	41.5	42.1	H—C-3 4.35;		$^{2}J_{P,H\text{-}3}$ 4.0
2A	Me	H	H	H	OH	H	O	OMe	42.7	42.4	H—C-3 4.26;		$^{2}J_{P,H\text{-}3}$ 1.6
2B	Me	H	H	H	OH	H	MeO	O	38.5	38.6	H—C-3 4.46;		$^{2}J_{P,H\text{-}3}$ 0
3A	Me	H	H	H	OR[d]	H	O	OMe	34.8	36.2	H—C-3 5.22;		$^{2}J_{P,H\text{-}3}$ 3.7
3B	Me	H	H	H	OR[d]	H	MeO	O	34.0	35.2	H—C-3 5.38;		$^{2}J_{P,H\text{-}3}$ 3.3
4A	H	H	Me	Me	OH	H	O	OMe	45.4	43.3	H—C-3 3.65;		$^{2}J_{P,H\text{-}3}$ 8.1
4B	H	H	Me	Me	OH	H	MeO	O	43.3	44.0	H—C-3 3.86;		$^{2}J_{P,H\text{-}3}$ < 2
5A	H	H	Me	Me	OR[d]	H	O	OMe	36.6	37.2	H—C-3 4.80;		$^{2}J_{P,H\text{-}3}$ 4.2
5B	H	H	Me	Me	OR[d]	H	MeO	O	38.1	39.1	H—C-3 4.92;		$^{2}J_{P,H\text{-}3}$ 0
6A	H	CH_2O	H	OCHPh	H	OR′[e]	MeO	O	35.3	—	H—C-3 4.41;		$^{2}J_{P,H\text{-}3}$ −8.6
6B	H	CH_2O	H	OCHPh	H	OR′[e]	O	OMe	34.0	—	H—C-3 4.57;		$^{2}J_{P,H\text{-}3}$ −9.9
7A	H	H	Me	H	OH	Me	O	OMe	45.8	45.5	$C\underline{H}_3$—C-3 1.44;	$\underline{C}H_3$—C-3 18.67;	$\underline{C}H_3OP$ 53.15
7B	H	H	Me	H	OH	Me	MeO	O	44.5	44.4	$C\underline{H}_3$—C-3 1.50;	$\underline{C}H_3$—C-3 20.16;	$\underline{C}H_3OP$ 54.94
8A	Me	Me	H	H	OH	Me	O	OMe	42.8	42.3	$C\underline{H}_3$—C-3 1.50;	$\underline{C}H_3$—C-3 22.52;	$\underline{C}H_3OP$ 52.88
8B	Me	Me	H	H	OH	Me	MeO	O	40.1	40.8	$C\underline{H}_3$—C-3 1.60;	$\underline{C}H_3$—C-3 24.28;	$\underline{C}H_3OP$ 54.83
9A	Me	Me	H	H	OMe	Me	O	OMe	38.9	39.6	$C\underline{H}_3$—C-3 1.48;	$\underline{C}H_3$—C-3 17.25;	$\underline{C}H_3OP$ 52.29
9B	Me	Me	H	H	OMe	Me	MeO	O	38.7	37.4	$C\underline{H}_3$—C-3 1.58;	$\underline{C}H_3$—C-3 19.75;	$\underline{C}H_3OP$ 54.58
10A	Me	Me	H	H	OR[d]	Me	O	OMe	33.9	34.8	$C\underline{H}_3$—C-3 1.87;		
10B	Me	Me	H	H	OR[d]	Me	MeO	O	35.4	36.3	$C\underline{H}_3$—C-3 1.96;		
11A	Me	Me	H	H	OH	Ph	O	OMe	39.6	39.5	$C\underline{H}_3OP$ 3.43;	$\underline{C}H_3OP$ 52.07	
11B	Me	Me	H	H	OH	Ph	MeO	O	36.4	37.3	$C\underline{H}_3OP$ 3.82;	$\underline{C}H_3OP$ 53.23	
12A	Me	Me	H	H	$NHNMe_2$	Me	O	OMe	42.9	43.5	$C\underline{H}_3$—C-3 1.45;	$\underline{C}H_3$—C-3 20.54;	$\underline{C}H_3OP$ 52.00
12B	Me	Me	H	H	$NHNMe_2$	Me	MeO	O	41.7	43.2	$C\underline{H}_3$—C-3 1.59;	$\underline{C}H_3$—C-3 22.10;	$\underline{C}H_3OP$ 52.64
13A	Me	Me	H	H	$NHNMe_2$	Ph	O	OMe	39.4	—	$C\underline{H}_3OP$ 3.50		
13B	Me	Me	H	H	$NHNMe_2$	Ph	MeO	O	38.9	—	$C\underline{H}_3OP$ 4.00		
14A	Ph	Ph	H	H	$NHNMe_2$	Ph	O	OMe	38.1	38.9	$C\underline{H}_3OP$ 3.43		
14B	Ph	Ph	H	H	$NHNMe_2$	Ph	MeO	O	39.0	39.4	$C\underline{H}_3OP$ 4.06		

[a] In parts per million from 85% H_3PO_4.
[b] In parts per million from Me_4Si; solvent $CDCl_3$.
[c] In Hz.
[d] R = $COC_6H_4NO_2$-*p*.
[e] R′ = Si^tBuMe_2.

TABLE II

^{31}P shift differences[a] $\Delta\delta(^{31}P)$ between the **A** and **B** diastereomers

	$CHCl_3$	CH_3OH		$CHCl_3$	CH_3OH
3-hydroxy derivatives			ethers		
1	3.7	2.7	**6**	1.3	—
2	4.2	3.8	**9**	0.2	2.2
4	2.1	−0.7	esters		
7	1.3	1.1	**3**	0.8	1.0
8	1.7	1.5	**5**	−1.5	−1.9
11	3.2	2.2	**10**	−1.5	−1.5
3-(β,β-dimethylhydrazino) derivatives					
12	1.2	0.3			
13	0.5	—			
14	−0.9	−0.5			

[a]In parts per million. $\Delta\delta(^{31}P) = \delta(^{31}P)_A - \delta(^{31}P)_B$.

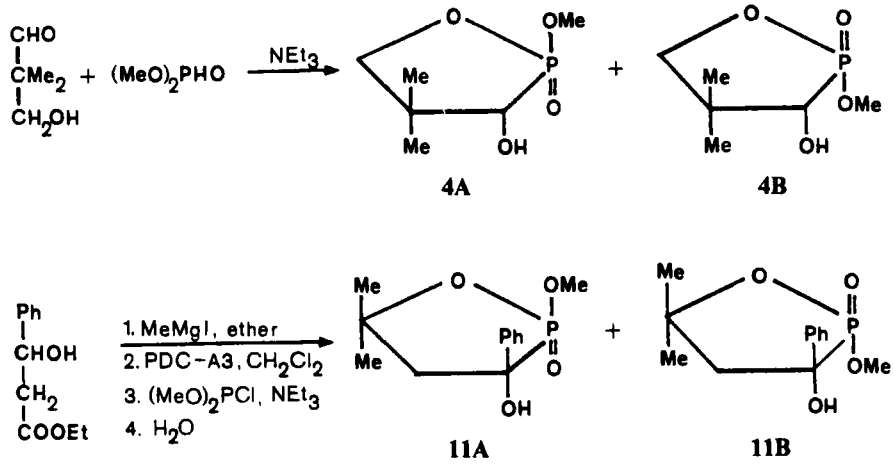

FIGURE 2 Synthetic pathways to diastereomeric mixtures of **4A/4B** and **11A/11B**.

of diastereomers where $\Delta\delta(^{31}P) > 1.0$ ppm is noticed. Actually, it becomes clear that a detailed discussion of the ^{31}P NMR chemical shifts of substituted 1,2-oxaphospholan-3-ols requires more sophisticated treatment.

Our interest in the synthesis of P-analogues of ribose and arabinose[13] has prompted us to examine the scope of application of the angular dependence of $^2J_{PH}$ in the 1,2-oxaphospholan-3-ols with the H—C-3 group. The two-bond P—H coupling constants for the pairs of **2, 3** and **6** (Table I) are too close to each other to be of diagnostic value. Surprisingly, for the O=P—C—H moiety of the *cis* configuration in **1B, 4B** and **5B** smaller $^2J_{PH}$ are found than in the *trans* isomers, although the reverse is generally observed.[1c] We believe that the conformational behaviour of the 1,2-oxaphospholane ring accounts for these discrepancies.

EXPERIMENTAL

Phosphorus NMR spectra were recorded at room temperature on a JEOL JNM FX 60 spectrometer at 24.3 MHz operating in the pulsed Fourier transform mode using 85% H_3PO_4 as an external standard. The computer resolution was 2.4 Hz, thus the accuracy of chemical shift measurements was ± 0.1 ppm. Samples were prepared as *ca.* 0.3 M solutions in chloroform or methanol. Proton as well as ^{13}C NMR spectra were taken on Bruker HX72 at 90 and 22.63 MHz, respectively by operating in the FT mode with TMS as the internal standard. Chemical shifts are expressed with positive sign when downfield from the reference substances. Other instrumentation and general procedures were the same as described earlier.[8]

Syntheses. Syntheses of **6**,[7] **7**,[6] **8–10**,[8] **12–14**[12] have been published in earlier papers. Compounds **1** and **2** were prepared by the base-catalyzed cyclization of *O,O*-dimethyl (1S*,3R*)- and (1R*,3R*)-1,3-dihydroxybutylphosphonates, respectively and synthesis and reactivity of these compounds will be presented elsewhere.

(2S, 3S*)- and (2R*, 3S*)-4,4-Dimethyl-2-methoxy-2-oxo-1,2-oxaphospholan-3-ols* (**4A** *and* **4B**, *respectively*). To 2,2-dimethyl-3-hydroxypropionaldehyde dimer[14] (3.47 g, 34 mmol) dimethyl phosphite (3.74 ml, 40.8 mmol) and triethylamine (0.65 ml, 20 mol%) were added. The mixture was stirred at 50°C for 5 h. The isomeric products were separated by column chromatography, on silica gel (75 g) to give **4A** (2.37 g, 39%), a mixture of **4A** and **4B** (1.37 g, 23%) and **4B** (0.66 g, 11%) as slightly yellowish oils which after distillation afforded colorless very viscous oils. A 67:33 mixture of **4A** and **4B** had b.p. 110–115°C/0.1 torr. Anal. Calcd. for $C_6H_{13}O_4P$: C, 40.00; H, 7.27; P, 17.20. Found: C, 39.95; H, 7.20; P, 16.72.

(2S, 3S*)-4,4-Dimethyl-2-methoxy-2-oxo-1,2-oxaphospholan-3-ol* (**4A**). B.p. 110°C/0.1 torr; ^1H NMR ($CDCl_3$): δ 1.16 and 1.17 (2s, CH_3—$C_{(4)}$—CH_3, 6 H), 3.65 (d, $^2J_{PH}$ = 8.1 Hz, 1 H), 3.72 (dAB, $^2J_{gem}$ = 9.1 Hz, $^3J_{PH}$ = 12.9 Hz), 3.83 (d, $^3J_{PH}$ = 11.0 Hz), 4.02 (dAB, $^2J_{gem}$ = 9.1 Hz, $^3J_{PH}$ = 9.4 Hz); ^1H NMR (C_6D_6): δ 0.81 and 1.07 (2s, CH_3—$C_{(4)}$—CH_3, 6 H), 3.25 (dAB, $^2J_{gem}$ = 9.1 Hz, $^3J_{PH}$ = 13.2 Hz, 1 H), 3.45 (d, $^3J_{PH}$ = 11.0 Hz, 3 H), 3.63 (d, $^2J_{PH}$ = 1.8 Hz, 1 H); 3.73 (dAB, $^2J_{gem}$ = 9.1 Hz, $^3J_{PH}$ = 10.3 Hz, 1H). IR (neat) 3500–3000 (s), 1240 (vs), 1045 (s) and 1000 (m) cm^{-1}.

(2R, 3S*)-4,4-Dimethyl-2-methoxy-2-oxo-1,2-oxaphospholan-3-ol* (**4B**). B.p. 125–130°C/0.1 torr; ^1H NMR ($CDCl_3$): δ 1.14 and 1.21 (2s, 6 H), 3.86 (d, $^2J_{PH}$ < 2 Hz), 3.90 (d, $^3J_{PH}$ = 10.6 Hz), 3.8–4.0 (m); ^1H NMR (C_6D_6): δ 0.95 and 1.03 (2s, 6 H), 3.44 (dAB, $^2J_{gem}$ = 9.1 Hz, $^3J_{PH}$ = 11.3 Hz, 1 H), 3.57 (dAB, $^2J_{gem}$ = 9.1 Hz, $^3J_{PH}$ = 10.4 Hz, 1 H), 3.68 (d, $^3J_{PH}$ = 10.7 Hz, 3 H). IR (neat) 3500–3000 (s), 1225 (vs), 1050 (s) and 1000 (m) cm^{-1}.

(2S, 3R*)-5,5-Dimethyl-2-methoxy-2-oxo-3-phenyl-1,2-oxaphospholan-3-ol* (**11A**). To a well stirred suspension of a molecular sieve (A3) powder (11.2 g) in methylene chloride (25 ml),[15] 3-methyl-1-phenylbutanediol-1,3 (2.0 g, 11.1 mmol) was added followed by pyridinium dichromate[16] (8.3 g, 22.2 mmol). After 1 h ether (75 ml) was added and solids were removed by filtration and washed thoroughly with ether. The filtrate and washings were concentrated to leave a crude 3-hydroxy-3-methyl-1-phenylbutanone-1 (1.9 g, 96%) as a brownish oil of *ca.* 95% purity based on ^1H NMR. ^1H NMR ($CDCl_3$): δ 1.25 (s, 6 H), 3.05 (s, 2 H), 3.75 (s, 1 H), 7.25–8.1 (m, 5 H). IR (neat) 3450 (s), 1670 (s) cm^{-1}.

To a solution of the crude β-hydroxyketone (1.9 g, 10.7 mmol) and triethylamine (1.5 ml, 11.7 mmol) in benzene (10 ml) dimethyl phosphorochloridite[17] (1.9 g, 14.8 mmol) was added dropwise below 10°C under argon atmosphere. The suspension was additionally stirred at room temperature for 1 h and solids were filtrated and washed with benzene. The filtrate and washings were evaporated to give a crude dimethyl-(1,1-dimethyl-3-oxo-3-phenylpropyl) phosphite (2.1 g, 73%). To the crude phosphite (2.1 g, 7.0 mmol) cooled in an ice-water bath, water (0.15 ml, 8.3 mmol) was added. When the slightly exothermic reaction ceased methanol and other volatile impurities were removed *in vacuo* to give the crude mixture (1.8 g, 70%) of isomeric 1,2-oxaphospholanes as the major components in a ratio of 8 : 2. This mixture was subjected to purification on the silica gel column to give a crystalline material (0.985 g, 55%) from which **11A** (0.375 g, 21%) was obtained after crystallization from chloroform/hexane; m.p. 158–159°C. ^1H NMR ($CDCl_3$): δ 1.51 and 1.67 (2s, 6 H), 2.2–2.7 (m, 2 H), 3.43 (d, $^3J_{PH}$ = 10.8 Hz, 3 H), 4.3 (s, 1 H), 7.3–7.6 (m, 5 H). IR (KBr) 3250 (s), 1250 (vs), 1140 (s) and 1070 (m) cm^{-1} Anal. Calcd. for $C_{12}H_{17}O_4P$: C, 56.25; H, 6.69; P, 12.09. Found: C, 56.09; H, 6.91; P, 11.80.

(2R, 3R*)-5,5-Dimethyl-2-methoxy-2-oxo-3-phenyl-1,2-oxaphospholan-3-ol* (**11B**). A solution of **11A** (0.845 g, 3.3 mmol) in methanol (20 ml) was treated with methanolic sodium methoxide (0.33 mmol, 10 mol%) at room temperature. The progress of equilibration[6,8] was monitored by ^{31}P NMR. The removal of methanol afforded an oil, which was purified by column chromatography on silica gel with a 2 : 1

hexane-ethyl acetate mixture to give **11A** (0.578 g, 68%) and **11B** (0.220 g, 26%) as colorless crystals; m.p. 152.5–153°C. ^{1}H NMR ($CDCl_3$): δ 1.53 and 1.62 (2s, 6 H), 2.2–2.7 (m, 2 H), 2.77 (d, $^3J_{POH}$ = 11.1 Hz, 1 H), 3.83 (d, $^3J_{PH}$ = 10.6 Hz, 3 H), 7.3–7.7 (m, 5 H). IR (KBr) 3200 (s), 1250 (vs), 1130 (s) and 1080 (m) cm^{-1}.

3-Methyl-1-phenylbutanediol-1,3. This compound was obtained from ethyl 3-hydroxy-3-phenylpropionate[18] and an excess of methyl magnesium iodide in 24% yield. M.p. 68–70°C (chloroform-hexane). ^{1}H NMR ($CDCl_3$): δ 1.20 and 1.31 (2s, 6 H), 1.5–2.2 (m, 2 H), 4.3 (s, 1 H), 4.9 (s, 1 H), 4.95–5.1 (m, 1 H), 7.0–7.5 (m, 5 H). IR (KBr) 3200 (s), 755 (w), 740 (m) and 700 (m) cm^{-1}.

Preparation of compounds **3A, 3B, 5A** *and* **5B**. Conventional *p*-nitrobenzoylation of **2A, 2B, 4A** and **4B** [1.2 eq. of *p*-nitrobenzoyl chloride, 1.2 eq. of triethylamine, a few crystals of 4-(*N*,*N*-dimethylamino)pyridine, chloroform] gave the corresponding esters.

(*2S**, *3S**, *5S**)-*2-Methoxy-5-methyl-3-(p-nitrobenzoyloxy)-2-oxo-1,2-oxaphospholane* (**3A**). M.p. 123–125°C (chloroform-hexane). ^{1}H NMR ($CDCl_3$): δ 1.54 (dd, $^3J_{HH}$ = 6.2 Hz; $^4J_{PH}$ = 1.3 Hz, 3 H), 2.31 (dddd ≈ ddt, $^2J_{gem}$ = 13.4 Hz, $^3J_{HH}$ = 8.8 Hz ≈ 9.2 Hz, $^3J_{PH}$ = 5.9 Hz, 1 H), 2.82 (dddd, $^2J_{gem}$ = 13.4 Hz, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 5.1 Hz, $^3J_{PH}$ = 25.1 Hz, 1 H), 3.96 (d, $^3J_{PH}$ = 11.2 Hz, 3 H), 4.40 (m, 1 H), 5.22 (ddd ≈ dt, $^2J_{PH}$ = 3.7 Hz, $^3J_{HH}$ = 8.8 Hz ≈ 8.4 Hz, 1 H), 8.3 (m, 4 H). IR (KBr) 1720 (s), 1285 (s), 1030 (m) cm^{-1}. Anal. Calcd. for $C_{12}H_{14}NO_7P$: C, 45.72; H, 4.48; N, 4.44; P, 9.83. Found: C, 45.33; H, 4.31; N, 4.09; P, 9.64.

(*2R**, *3S**, *5S**)-*2-Methoxy-5-methyl-3-(p-nitrobenzoyloxy)-2-oxo-1,2-oxaphospholane* (**3B**). Yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.52 (dd, $^3J_{HH}$ = 6.4 Hz, $^4J_{PH}$ = 0.9 Hz, 3 H), 2.16 (dddd ≈ ddt, $^2J_{gem}$ = 13.9 Hz, $^3J_{HH}$ = 6.8 Hz = 6.8 Hz, $^3J_{PH}$ = 11.9 Hz, 1 H), 2.94 (dddd, $^2J_{gem}$ = 13.9 Hz, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 6.2 Hz, $^3J_{PH}$ = 18.0 Hz, 1 H), 3.87 (d, $^3J_{PH}$ = 11.0 Hz, 3 H), 4.67 (dddq ≈ septet, $^3J_{HH}$ = 6.8 Hz ≈ 6.4 Hz ≈ 6.2 Hz, $^3J_{PH}$ = 6.6 Hz, 1 H), 5.38 (ddd ≈ dt, $^2J_{PH}$ = 3.3 Hz, $^3J_{HH}$ = 7.5 Hz ≈ 6.8 Hz, 1 H), 8.2–8.4 (m, 4 H). IR (neat) 1720 (s), 1270 (s), 1100 (s) and 1040 (m) cm^{-1}.

(*2S**, *3S**)-*4,4-Dimethyl-2-methoxy-3-(p-nitrobenzoyloxy-2-oxo-1,2-oxaphospholane* (**5A**). M.p. 113–114°C (chloroform-hexane). ^{1}H NMR ($CDCl_3$): δ 1.28 and 1.39 (2s, 6 H), 3.86 (dAB, $^2J_{gem}$ = 9.5 Hz, $^3J_{PH}$ = 8.6 Hz, 1 H), 3.95 (d, $^3J_{PH}$ = 11.4 Hz, 3 H), 4.06 (dAB, $^2J_{gem}$ = 9.5 Hz, $^3J_{PH}$ = 16.3 Hz, 1 H), 4.80 (d, $^2J_{PH}$ = 4.2 Hz, 1 H), 8.3 (s, 4 H); ^{1}H NMR (C_6D_6): δ 0.66 and 1.07 (2s, 6 H), 3.27 (dAB, $^2J_{gem}$ = 9.4 Hz, $^3J_{PH}$ = 8.2 Hz, 1 H), 3.50 (dAB, $^2J_{gem}$ = 9.4 Hz, $^3J_{PH}$ = 17.4 Hz, 1 H), 3.70 (d, $^3J_{PH}$ = 11.4 Hz, 3 H), 4.55 (d, $^2J_{PH}$ = 4.4 Hz, 1 H), 8.27 (s, 4 H). IR (KBr) 1720 (s), 1290 (s), 1070 (s), 1050 (m), 1015 (m) cm^{-1}.

(*2R**, *3S**)-*4,4-Dimethyl-2-methoxy-3-(p-nitrobenzoyloxy)-2-oxo-1,2-oxaphospholane* (**5B**). M.p. 94.0–94.5°C (ether-hexane).^{1}H NMR ($CDCl_3$): δ 1.23 and 1.43 (2s, 6 H), 3.75 (d, $^3J_{PH}$ = 11.2 Hz, 3 H), 3.9–4.1 (m, 2 H), 4.92 (s, 1 H), 8.1–8.4 (AA'BB', 4 H); ^{1}H NMR (C_6D_6): δ 0.67 and 1.04 (2s, 6 H), 3.43 (dAB, $^2J_{gem}$ = 9.1 Hz, $^3J_{PH}$ = 19.1 Hz, 1 H), 3.47 (d, $^3J_{PH}$ = 11.1 Hz, 3 H), 3.58 (dAB, $^2J_{gem}$ = 9.1 Hz, $^3J_{PH}$ = 6.1 Hz, 1 H), 4.80 (s, 1 H), 8.1–8.4 (AA'BB', 4 H), IR (KBr) 1720 (s), 1280 (s), 1050 (m), 1005 (m) cm^{-1}. Anal. Calcd. for $C_{13}H_{16}NO_7P$: C, 47.42; H, 4.90; N, 4.25; P, 9.41. Found: C, 47.05; H, 4.99; N, 3.97; P, 9.36.

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