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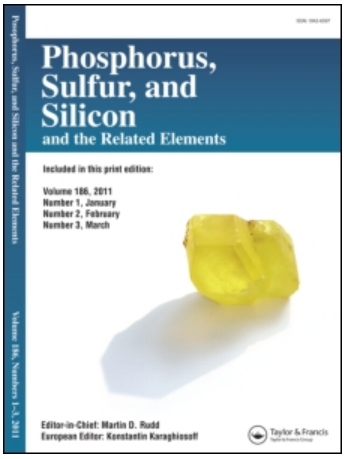

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Synthesis and Biological Activity of *O,O*-Dimethyl-2,6-Pyridinyl Diformyloxy Alkyl Phosphonates

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Synthesis and Biological Activity of *O,O*-Dimethyl-2,6-Pyridinyl Diformyloxy Alkyl Phosphonates

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In an attempt to discover novel compounds with high activity and low toxicity, a series of new O,O*-dimethyl-2,6-pyridinyl diformyloxy alkyl phosphonates* ***4a–4p*** *has been designed and synthesized by the reaction of 2,6-pyridinyl diformyloxy chloride with α-hydroxyalkyl phosphonate. The structures of all new compounds were characterized by elementary analysis, IR,* ^{1}*H NMR, and MS spectroscopies. The results of a preliminary bioassay indicate that some of the target compounds have obviously promotive action for plant growth against the stalk of barnyard grass.*

Keywords Biological activities; *O,O*-dimethyl-2,6-pyridinyl diformyloxy alkyl phosphonates; synthesis

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INTRODUCTION

We have reported the synthesis of a series of substituted phenoxy acetoxy alkyl phosphonates.[1–3] He and Wang[1–3] have demonstrated that some phosphonates and their derivatives exhibit notable herbicidal activity due to their inhibition against pyruvate dehydrogenase complex (PDHC). In order to find new phosphonates with better pesticide activity, the pyridine structural unit was introduced into their molecules, so *O,O*-dimethyl-2,6-pyridinyl diformyloxy alkyl phosphonates were synthesized by the reaction of 2,6-pyridinyl diformyloxy chloride with α-hydroxyalkyl phosphonate under mild conditions. The synthetic route is shown in Scheme 1.

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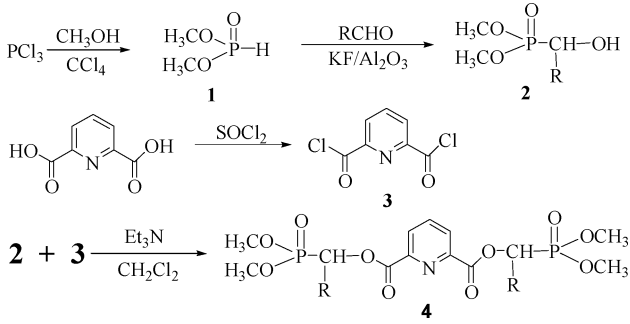

SCHEME 1 R: 4a: H; 4b: CH_3; 4c: CCl_3; 4d: CH_3CH_2; 4e: $CH_3CH_2CH_2$; 4f: $(CH_3)_2CH$; 4g: Ph; 4h: 2-ClPh; 4i: 4-ClPh; 4j: 2,4-2ClPh; 4k: 3-NO_2Ph; 4l: 4-CH_3OPh; 4m: 4-CH_3Ph; 4n: 3,4-OCH_2OPh; 4o: 2-Furyl; 4p: 2-Thiophenyl.

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RESULTS AND DISCUSSION

Preparation of α-Hydroxyalkylphosphonates 2 and *O,O*-Dimethyl-2,6-pyridinyl Diformyloxy Alkyl Phosphonates 4

The reaction of dialkyl phosphates **1** with aldehydes is a convenient method used to synthesize α-hydroxyphosphonates **2**. There are some reports on the synthesis of α-hydroxyphosphonates.[4, 5] However, there are few reports on the reaction of dimethylphosphonate with 2-thiophenecarboxaldehyde. Herein we report the reaction of dimethylphosphonate with 2-thiophenecarboxaldehyde to produce α-hydroxy phosphonates **2p**. The reaction under mild conditions (room temperature) resulted in high yields of the products as shown in Scheme 1.

However, the addition of a base (triethylamine) was essential to the addition reaction. Without the use of the triethylamine as a catalyst, the reaction rate was greatly slowed and the yields were very low. We tried to synthesize compound **2p** by the addition reaction of dimethylphosphonate with 2-thiophene-carboxaldehyde in the presence of KF/Al_2O_3, but only byproducts were found. Therefore we obtained the title compound **2p** by the reaction of compound **1** with 2-thiophenecarboxaldehyde in the presence of the triethylamine.

The compounds **4** were prepared from the compounds **2** and 2,6-pyridinyl diformyloxy chloride **3** in the presence of triethylamine. As the target phosphonate derivatives contain groups sensitive to acid, base, or water, such as carboxylic esters, so the reaction required conditions near room temperature and the use of anhydrous solvents.

The Structures of *O,O*-Dimethyl-2,6-pyridinyl Diformyloxy Alkyl Phosphonates 4

The molecular structures of all new compounds obtained were confirmed by ^{1}H NMR, IR spectra, MS, and elemental analyses. In the ^{1}H NMR spectra of **4**, the proton in the P—C moiety exhibits a doublet, while the proton in the P-OCH_3 moiety displays a doublet of doublets. The IR spectra of all compounds showed normal stretching absorption bands, indicating the existence of the Ph—H (–2950 cm^{-1}), C=O (–1730 cm^{-1}), C=C (–1620, –1450 cm^{-1}), P=O (–1260 cm^{-1}), P—O—C (–1050 cm^{-1}), and P—C (–750 cm^{-1}). The EI mass spectra of compounds **4a–p** gave the anticipated molecular ion peaks.

Herbicidal Activities

As seen from Table I, the compound **4c** exhibited notable herbicidal activity on the root of barnyard grass and rape at 100 ppm, while the compounds **4b, 4e, 4f, 4h, 4i, 4k, 4l, 4n, 4o**, and **4p** have an obviously promotive action for plant growth against a stalk of barnyard grass at 100 ppm.

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EXPERIMENTAL

Melting points are uncorrected. MS were measured with a Finnigan Trace MS spectrometer. IR were recorded with a PE-983 infrared spectrometer as KBr pellets. NMR were recorded in $CDCl_3$ or [d_6]DMSO with a Varian Mercury 400 spectrometer and resonances relative to TMS. Elementary analyses were taken with a Vario EL III elementary analysis instrument. The reagents and solvents were available commercially and purified according to conventional methods before use. Compounds **1**, **2**, and **3** were prepared according to the literature.[6–10]

Synthesis of *O,O*-Dimethyl-2,6-pyridinyl Diformyloxy Alkyl Phosphonates General Procedure

A solution of 2,6-pyridinyl diformyloxy chloride **3** (0.022 mol) in dichloromethane (10 mL) was added to a stirred mixture of α-hydroxy alkyl phosphonate **2** (0.01 mol) and triethylamine (0.022 mol) in dichloromethane (25 mL) at 20–25°C. The mixture was stirred at ambient temperature for 4 h, and then at 40°C for 1 h, and was washed with 0.1 M hydrochloric acid, saturated sodium hydrogen carbonate solution, and brine in that order. The resulting mixture was dried, and the solvent used was evaporated. The residue was chromatographed on

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TABLE I The Inhibition Percentage of Compounds 4 to Barnyard Grass and Rape*

		Barnyard grass				Rape			
		Stalk		Root		Stalk		Root	
Compound	R	10 ppm	100 ppm	10 ppm	100 ppm	10 ppm	100 ppm	10 ppm	100 ppm
4a	H	−29.4	−8.7	14.8	33.3	−2.2	17.0	17.6	55.9
4b	CH_3	−23.0	−58.8	8.5	16.7	1.8	−3.1	25.7	34.1
4c	CCl_3	33.3	42.0	78.3	87.9	34.4	59.7	77.5	93.4
4d	CH_3CH_2	−6.2	18.6	31.5	50.0	14.8	29.5	3.7	59.6
4e	$CH_3CH_2CH_2$	−6.0	−61.2	35.2	40.7	16.4	12.5	30.1	27.4
4f	$(CH_3)_2CH$	10.0	−70.0	29.6	51.9	20.7	14.3	−16.0	11.8
4g	Ph	−18.7	−21.9	18.5	64.8	15.4	−31.6	−4.4	−12.5
4h	2-ClPh	−38.1	−40.6	−30.4	−14.4	14.8	20.5	34.6	78.1
4i	4-ClPh	−22.5	−46.2	37.0	48.1	1.0	27.3	34.4	58.2
4j	2,4−2ClPh	−15.0	−15.6	45.2	−17.4	21.6	22.7	14.7	52.2
4k	3-NO_2Ph	−11.2	−51.9	0	14.8	−3.1	31.2	34.6	16.9
4l	4-CH_3OPh	11.9	−51.9	42.6	48.5	5.7	14.8	−11.6	0.6
4m	4-CH_3Ph	−15.0	−31.2	5.6	55.6	36.4	37.5	22.8	55.9
4n	3,4-OCH_2OPh	0	−70.0	−37.0	22.2	18.4	27.3	2.9	48.5
4o	2-Furyl	−2.5	−59.4	−5.5	22.2	6.8	−8.6	35.4	44.1
4p	2-Thiophenyl	−36.9	−58.1	−4.4	34.4	1.8	−21.0	18.2	6.0

*Negative inhibition percentage shows promotive action for plant growth.

silica with 20% acetone in petroleum ether as eluent to give the title compounds **4**.

O,O-*Dimethyl-2,6-pyridinyl Diformyloxy Methyl Phosphonate (4a)*

Light yellow liquid (yield 38%); n_D^{20}: 1.4619; IR (KBr)υ: 3095 (w, Ph−H), 2953, 2854 (m, C−H), 1739 (s, C=O), 1583, 1478, 1437 (s, Ph), 1246 (s, P=O), 1182 (s, C−O−C), 1042, 898 (s, P−O−C), 756 (s, P−C) cm^{-1}; ^1H NMR($CHCl_3$, 400Hz)δ: 3.88 (dd, 4 × 3H, 2 × ($-OCH_3$), J = 10.4 Hz), 4.74 (d, 2 × 2H, $-OCH_2P$, J = 5.28 Hz), 8.02–8.34 (m, 3H, $-C_5H_3N$). ^{31}P NMR($CHCl_3$, 400 Hz)δ: 15.77 ppm. MS (70 eV) m/z (%): 411 (M^+ +1 12); Anal. Calcd. (%) for $C_{13}H_{19}NO_{10}P_2$: C 37.97, H 4.66, N 3.41; Found C 37.73, H 4.57, N 3.70.

O,O-*Dimethyl-2,6-pyridinyl Diformyloxy Ethyl Phosphonate (4b)*

Light yellow liquid (yield 39%); n_D^{20}: 1.4687; IR (KBr)υ: 3091 (w, Ph−H), 2956, 2852 (m, C−H), 1736 (s, C=O), 1584, 1473, 1433 (s, Ph), 1243 (s, P=O), 1182 (s, C−O−C), 1044, 894 (s, P−O−C), 754 (s, P−C) cm^{-1}; ^1H NMR($CHCl_3$, 400Hz)δ: 1.63 (q, 2 × 3H, 2 × ($-CH_3$), J = 5.40 Hz), 3.90 (dd, 4 × 3H, 2 × ($-OCH_3$), J = 7.60 Hz), 5.58 (q, 2 × H, −OCHP, J = 2.80 Hz), 8.01–8.33 (m, 3H, $-C_5H_3N$). ^{31}P NMR ($CHCl_3$, 400Hz) δ: 16.32 ppm. MS (70eV) m/z (%): 439 (M^+ +1 22); Anal. Calcd. (%) for $C_{15}H_{23}NO_{10}P_2$: C 41.01, H 5.28, N 3.19; Found C 41.22, H 5.51, N 3.42.

O,O-*Dimethyl-2,6-pyridinyl Diformyloxy Trichloromethylmethyl Phosphonate (4c)*

White crystal (yield 73%); mp: 144–146; IR (KBr)υ: 3092 (w, Ph−H), 2962, 2851 (m, C−H), 1733 (s, C=O), 1583, 1473, 1432 (s, Ph), 1242 (s, P=O), 1184 (s, C−O−C), 1044, 895 (s, P−O−C), 754 (s, P−C) cm^{-1}; ^1H NMR ($CHCl_3$, 400Hz) δ: 3.92 (dd, 4 × 3H, 2 × ($-OCH_3$), J = 4.58 Hz), 6.21 (d, 2 × H, −OCHP, J = 7.78 Hz), 8.12–8.49 (m, 3H, $-C_5H_3N$). ^{31}P NMR ($CHCl_3$, 400 Hz) δ: 12.39 ppm. MS (70 eV) m/z (%): 645 (M^+ +1 14); Anal. Calcd. (%) for $C_{15}H_{17}Cl_6NO_{10}P_2$: C 27.89, H 2.65, N 2.17; Found C 27.65, H 2.74, N 2.42.

O,O-*Dimethyl-2,6-pyridinyl Diformyloxy Ethylmethyl Phosphonate (4d)*

Light yellow liquid (yield 65%); n_D^{20}: 1.4710; IR (KBr)υ: 3112 (w, Ph−H), 2959, 2855 (m, C−H), 1732 (s, C=O), 1586, 1476, 1436 (s, Ph), 1245 (s, P=O), 1185 (s, C−O−C), 1045, 895 (s, P−O−C), 755 (s, P−C) cm^{-1}; ^1H NMR($CHCl_3$, 400Hz) δ: 1.07 (t, 2 × 3H, 2 × ($-CH_3$),

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J = 6.80 Hz), 1.97–2.11 (m, 2 × 2H, 2 × (−$\underline{CH_2}CH_3$)), 3.87 (dd, 4 × 3H, 2 × (−OCH_3), J = 6.20 Hz), 5.51 (q, 2 × H, −OCHP, J = 2.82 Hz), 8.01–8.33 (m, 3H, −C_5H_3N). ^{31}P NMR ($CHCl_3$, 400 Hz) δ: 16.46 ppm. MS (70 eV) m/z (%): 467 (M^+ +1 13); Anal. Calcd. (%) for $C_{17}H_{27}NO_{10}P_2$: C 43.69, H 5.82, N 3.00; Found C 43.43, H 5.98, N 3.27.

O,O-*Dimethyl-2,6-pyridinyl Diformyloxy* n-*Propylmethyl Phosphonate (4e)*

Light yellow liquid (yield 43%); n_D^{20}: 1.4564; IR (KBr)υ: 3098 (w, Ph−H), 2960, 2850 (m, C−H), 1735 (s, C=O), 1580, 1477, 1439 (s, Ph), 1246 (s, P=O), 1162 (s, C−O−C), 1044, 894 (s, P−O−C), 753 (s, P−C) cm^{-1}; ^{1}H NMR($CHCl_3$, 400Hz)δ: 0.98 (t, 2 × 3H, 2 × (−CH_3), J = 6.80 Hz), 1.39–1.54 (m, 2 × 2H, 2 × (−$CH_2\underline{CH_2}CH_3$)), 1.93–2.16 (m, 2 × 2H, 2 × (-$\underline{CH_2}CH_2CH_3$)), 3.87 (dd, 4 × 3H, 2 × (−OCH_3), J = 6.20Hz), 5.59 (q, 2 × H, −OCHP, J = 2.80Hz), 8.00–8.32 (m, 3H, −C_5H_3N). ^{31}P NMR ($CHCl_3$, 400Hz) δ: 16.62 ppm. MS (70eV) m/z (%): 495 (M^+ +1 17); Anal. Calcd. (%) for $C_{19}H_{31}NO_{10}P_2$: C 46.06, H 6.31, N 2.83; Found C 46.38, H 6.60, N 3.07.

O,O-*Dimethyl-2,6-pyridinyl Diformyloxy* i-*Propylmethyl Phosphonate (4f)*

Light yellow liquid (yield 43%); n_D^{20}: 1.4604; IR (KBr)υ: 3089 (w, Ph−H), 2960, 2856 (m, C−H), 1737 (s, C=O), 1587, 1475, 1436 (s, Ph), 1247 (s, P=O), 1182 (s, C−O−C), 1046, 897 (s, P−O−C), 755 (s, P−C) cm^{-1}; ^{1}H NMR($CHCl_3$, 400 Hz)δ: 1.06 (d, 4 × 3H, 4 × (−CH_3), J = 4.27 Hz), 1.08–1.51 (m, 2 × H, 2 × (-$\underline{CH}(CH_3)_2$), 3.86 (dd, 4 × 3H, 2 × (−OCH_3), J = 6.80Hz), 5.43 (q, 2 × H, −OCHP, J = 2.80 Hz), 8.02–8.34 (m, 3H, −C_5H_3N). ^{31}P NMR ($CHCl_3$, 400Hz) δ: 16.95 ppm. MS (70eV) m/z (%): 495 (M^+ +1 19); Anal. Calcd. (%) for $C_{19}H_{31}NO_{10}P_2$: C 46.06, H 6.31, N 2.83; Found C 46.22, H 6.55, N 3.11.

O,O-*Dimethyl-2,6-pyridinyl Diformyloxy Benzyl Phosphonate (4g)*

White crystal (yield 73%); mp: 102–105; IR (KBr)υ: 3074 (w, Ph−H), 2959, 2857 (m, C−H), 1737 (s, C=O), 1587, 1476, 1457 (s, Ph), 1267 (s, P=O), 1156 (s, C−O−C), 1037, 835 (s, P−O−C), 757 (s, P−C) cm^{-1}; ^{1}H NMR ($CHCl_3$, 400Hz) δ: 3.81 (dd, 4 × 3H, 2 × (−OCH_3), J = 3.20 Hz), 6.47 (d, 2 × H, −OCHP, J = 5.00 Hz), 7.36–7.66 (m, 2 × 5H, 2 × (−C_6H_5)), 8.02–8.37 (m, 3H, −C_5H_3N). ^{31}P NMR ($CHCl_3$, 400 Hz) δ: 18.56 ppm. MS (70eV) m/z(%): 563 (M^+ +1 26); Anal. Calcd. (%) for $C_{25}H_{27}NO_{10}P_2$: C 53.29, H 4.83, N 2.49; Found C 53.08, H 4.96, N 2.66.

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O,O-*Dimethyl-2,6-pyridinyl Diformyloxy 2-Chlorobenzyl Phosphonate (4h)*

White crystal (yield 48%); mp: 119–122; IR (KBr)υ: 3087 (w, Ph−H), 2956, 2856 (m, C−H), 1736 (s, C=O), 1585, 1498, 1457 (s, Ph), 1267 (s, P=O), 1157 (s, C−O−C), 1069, 836 (s, P−O−C), 754 (s, P−C) cm^{-1}; ^1H NMR($CHCl_3$, 400 Hz)δ: 3.84 (dd, 4 × 3H, 2 × ($-OCH_3$), J = 4.00 Hz), 6.94 (d, 2 × H, −OCHP, J = 5.50Hz), 7.30–7.86 (m, 2 × 4H, 2 × ($-C_6H_4$)), 8.02–8.34 (m, 3H, $-C_5H_3N$). ^{31}P NMR ($CHCl_3$, 400 Hz) δ: 18.26 ppm. MS (70eV) m/z (%): 632 (M^+ +1 20); Anal. Calcd. (%) for $C_{25}H_{25}Cl_2NO_{10}P_2$: C 47.49, H 3.99, N 2.22; Found C 47.58, H 4.18, N 2.51.

O,O-*Dimethyl-2,6-pyridinyl Diformyloxy 4-Chlorobenzyl Phosphonate (4i)*

Light yellow liquid (yield 80%); n_D^{20}: 1.4855; IR (KBr)υ: 3089 (w, Ph−H), 2959, 2853 (m, C−H), 1736 (s, C=O), 1584, 1494, 1457(s, Ph), 1266 (s, P=O), 1154 (s, C−O−C), 1035, 835 (s, P−O−C), 755 (s, P−C) cm^{-1}; ^1H NMR ($CHCl_3$, 400 Hz) δ: 3.82 (dd, 4 × 3H, 2 × ($-OCH_3$), J = 2.80 Hz), 6.40 (q, 2 × H, −OCHP, J = 5.25 Hz), 7.34–7.59 (m, 2 × 4H, 2 × ($-C_6H_4$)), 8.03–8.35 (m, 3H, $-C_5H_3N$). ^{31}P NMR ($CHCl_3$, 400 Hz) δ: 18.34ppm. MS (70 eV) m/z(%): 632 (M^+ +1 13); Anal. Calcd. (%) for $C_{25}H_{25}Cl_2NO_{10}P_2$: C 47.49, H 3.99, N 2.22; Found C 47.60, H 4.21, N 2.45.

O,O-*Dimethyl-2,6-pyridinyl Diformyloxy 2,4-Dichlorobenzyl Phosphonate (4j)*

White crystal (yield 38%); mp: 199–201; IR (KBr)υ: 3088 (w, Ph−H), 2959, 2857 (m, C−H), 1734 (s, C=O), 1585, 1496, 1455 (s, Ph), 1268 (s, P=O), 1151 (s, C−O−C), 1051, 832 (s, P−O−C), 754 (s, P−C) cm^{-1}; ^1H NMR ($CHCl_3$, 400 Hz) δ: 3.87 (dd, 4 × 3H, 2 × ($-OCH_3$), J = 4.80 Hz), 6.83 (d, 2 × H, −OCHP, J = 6.00 Hz), 7.31–7.76 (m, 2 × 3H, 2 × ($-C_6H_3$)), 8.01–8.34 (m, 3H, $-C_5H_3N$). ^{31}P NMR ($CHCl_3$, 400 Hz) δ: 17.76 ppm. MS (70eV) m/z (%): 701 (M^+ +1 14); Anal.Calcd.(%) for $C_{25}H_{23}Cl_4NO_{10}P_2$: C 42.82, H 3.31, N 2.00; Found C 42.88, H 3.53, N 2.28.

O,O-*Dimethyl-2,6-pyridinyl Diformyloxy 3-Nitrobenzyl Phosphonate (4k)*

Light yellow crystal (yield 56%); mp: 127–128; IR (KBr)υ: 3124 (w, Ph−H), 2959, 2855 (m, C−H), 1732 (s, C=O), 1586, 1496, 1454 (s, Ph), 1268 (s, P=O), 1151 (s, C−O−C), 1039, 831 (s, P−O−C), 753 (s, P−C) cm^{-1}; ^1H NMR ($CHCl_3$, 400 Hz)δ: 3.88 (dd, 4 × 3H, 2 × ($-OCH_3$), J = 6.75 Hz), 6.52 (d, 2 × H, −OCHP, J = 7.25 Hz), 7.60–8.47 (m, 2 × 4H,

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2 × (−C_6H_4)), 8.08–8.38 (m, 3H, −C_5H_3N). ^{31}P NMR ($CHCl_3$, 400 Hz) δ: 17.31 ppm. MS (70 eV) m/z (%): 653 (M^+ +1 24); Anal.Calcd.(%) for $C_{25}H_{25}N_3O_{14}P_2$: C 45.95, H 3.86, N 6.43; Found C 46.16, H 4.03, N 6.61.

O,O-*Dimethyl-2,6-pyridinyl Diformyloxy 4-Methyloxybenzyl Phosphonate (4l)*

Light yellow liquid (yield 46%); n_D^{20}: 1.4740; IR (KBr)υ: 3084 (w, Ph−H), 2956, 2856 (m, C−H), 1737 (s, C=O), 1588, 1498, 1455 (s, Ph), 1263 (s, P=O), 1154 (s, C−O−C), 1036, 834 (s, P−O−C), 757 (s, P−C) cm^{-1}; ^{1}H NMR ($CHCl_3$, 400 Hz)δ: 3.73 (s, 2 × 3H, 2 × CH_3OPh), 3.82 (dd, 4 × 3H, 2 × (−OCH_3), J = 4.50 Hz), 6.40 (d, 2 × H, −OCHP, J = 4.00 Hz), 6.91–7.59 (m, 2 × 4H, 2 × (−C_6H_4)), 7.99–8.32 (m, 3H, −C_5H_3N). ^{31}P NMR ($CHCl_3$, 400Hz) δ: 18.76 ppm. MS (70eV) m/z (%): 623 (M^+ +1 21); Anal. Calcd. (%) for $C_{27}H_{31}NO_{12}P_2$: C 52.01, H 5.01, N 2.25; Found C 52.25, H 5.22, N 2.38.

O,O-*Dimethyl-2,6-pyridinyl Diformyloxy 4-Methyl Benzyl Phosphonate (4m)*

Light yellow liquid (yield 79%); n_D^{20}: 1.4985; IR (KBr)υ: 3099 (w, Ph−H), 2949, 2854 (m, C−H), 1736 (s, C=O), 1584, 1494, 1455 (s, Ph), 1264 (s, P=O), 1154 (s, C−O−C), 1036, 832 (s, P−O−C), 752(s, P−C) cm^{-1}; ^{1}H NMR($CHCl_3$, 400 Hz) δ: 2.32 (s, 2 × 3H, 2 × CH_3Ph), 3.80 (dd, 4 × 3H, 2 × (−OCH_3), J = 4.80 Hz), 6.42 (d, 2 × H, −OCHP, J = 6.50 Hz), 7.06–7.54 (m, 2 × 4H, 2 × (−C_6H_4)), 8.00–8.32 (m, 3H, −C_5H_3N). ^{31}P NMR ($CHCl_3$, 400Hz) δ: 18.62 ppm. MS (70 eV) m/z(%): 591 (M^+ +1 17); Anal.Calcd. (%) for $C_{27}H_{31}NO_{10}P_2$: C 54.83, H 5.28, N 2.37; Found C 54.99, H 5.47, N 2.43.

O,O-*Dimethyl-2,6-pyridinyl Diformyloxy 3,4-Methylenedioxy Benzyl Phosphonate (4n)*

Light yellow liquid (yield 61%); n_D^{20}: 1.4971; IR (KBr)υ: 3124 (w, Ph−H), 2959, 2855 (m, C−H), 1732 (s, C=O), 1586, 1496, 1454 (s, Ph), 1268 (s, P=O), 1151 (s, C−O−C), 1039, 831 (s, P−O−C), 753 (s, P−C) cm^{-1}; ^{1}H NMR($CHCl_3$, 400 Hz) δ: 3.82 (dd, 4 × 3H, 2 × (−OCH_3), J = 4.25 Hz), 5.98 (s, 2 × 2H, 2 × (−OCH_2OPh)), 6.35 (d, 2 × H, −OCHP, J = 4.50 Hz), 6.81–7.16 (m, 2 × 3H, 2 × (−C_6H_3)), 8.00–8.34 (m, 3H, −C_5H_3N). ^{31}P NMR ($CHCl_3$, 400 Hz) δ: 18.64 ppm. MS (70 eV) m/z (%): 651 (M^+ +1 15); Anal. Calcd. (%) for $C_{27}H_{27}NO_{14}P_2$: C 49.78, H 4.18, N 2.15; Found C 49.89, H 4.32, N 2.33.

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O,O-*Dimethyl-2,6-pyridinyl Diformyloxy 2-Furyl Methyl Phosphonate (4o)*

Yellow crystal (yield 54%); mp: 92–94; IR (KBr)υ: 3124 (w, Ph−H), 2959, 2855 (m, C−H), 1732 (s, C=O), 1586, 1496, 1454 (s, Ph), 1268 (s, P=O), 1151 (s, C−O−C), 1039, 831 (s, P−O−C), 753 (s, P−C) cm^{-1}; ^1H NMR ($CHCl_3$, 400Hz) δ: 3.92 (dd, 4 × 3H, 2 × ($-OCH_3$), J = 4.80 Hz), 6.57 (q, 2 × H, −OCHP, J = 9.50 Hz), 6.41–7.48 (m, 2 × 3H, $-C_4H_3O$), 8.00–8.33 (m, 3H, $-C_5H_3N$). ^{31}P NMR ($CHCl_3$, 400 Hz) δ: 17.44 ppm. MS (70 eV) m/z (%): 543 (M^+ +1 23); Anal. Calcd. (%) for $C_{21}H_{23}NO_{12}P_2$: C 46.42, H 4.27, N 2.58; Found C 46.31, H 4.53, N 2.76.

O,O-*Dimethyl-2,6-pyridinyl Diformyloxy 2-Thiophenyl Methyl Phosphonate (4p)*

Light yellow crystal (yield 57%); mp: 93–95; IR (KBr)υ: 3091 (w, Ph−H), 2956, 2853 (m, C−H), 1729 (s, C=O), 1585, 1452, 1423 (s, Ph), 1248 (s, P=O), 1185 (s, C−O−C), 1039, 842 (s, P−O−C), 757 (s, P−C) cm^{-1}; ^1H NMR($CHCl_3$, 400 Hz) δ: 3.85 (dd, 4 × 3H, 2 × ($-OCH_3$), J = 4.50 Hz), 6.70 (q, 2 × H, −OCHP, J = 6.50 Hz), 6.99–7.37 (m, 2 × 3H, $-C_4H_3S$), 7.98–8.31 (m, 3H, $-C_5H_3N$). ^{31}P NMR ($CHCl_3$, 400 Hz) δ: 17.84 ppm. MS (70 eV) m/z(%): 575 (M^+ +1 19); Anal. Calcd. (%) for $C_{21}H_{23}NO_{10}P_2$ S_2: C 43.83, H 4.03, N 2.43; Found C 43.99, H 4.33, N 2.62.

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REFERENCES

[1] H. W. He and T. Wang, *J. Organomet. Chem.*, **690,** 2608 (2005).
[2] T. Wang and H. W. He, *Phosphorus, Sulfur, and Silicon*, **178,** 2081 (2004).
[3] T. Wang and H. W. He, *Synth. Commun.*, **34**(8), 1415 (2004).
[4] F. Fexier-Bullet and A. Foucaud, *Synthesis*, 165 (1982).
[5] A. F. Janzen and R. Pollitt, *Can J. Chem*, **48,** 1987 (1970).
[6] M. A. Ruveda and S. A. Delicastro, *Tetrahedron*, **28,** 6013 (1972).
[7] B. Springs and P. Healbe, *J. Org. Chem.*, **14**(7), 1165 (1976).
[8] F. Fexier-Bullet and A. Foucaud, *Synthesis*, 916 (1982).
[9] F. Fexier-Bullet and M. Lequitte, *Tetrahedron Lett.*, **27**(30), 3515 (1986).
[10] P. Coutrot and A. Ghribi, *Synthesis*, 661 (1986).