

# Studies on organophosphorus compounds. Part 96.† Nucleophilicity of the isocyano carbon atom in diethyl isocyanomethylphosphonate. First generation of a phosphorylated nitrile ylide and new syntheses of pyrrolinephosphonates and pyrrolephosphonates

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Reactions of acyl chlorides with diethyl isocyanomethylphosphonate afford  $\alpha$ -ketoimidoyl chlorides which, when treated with triethylamine, provide a new class of nitrile ylides. These species react *in situ* with alkenes by a 1,3-dipolar cycloaddition mechanism to give phosphoryl pyrrolines or pyrroles.

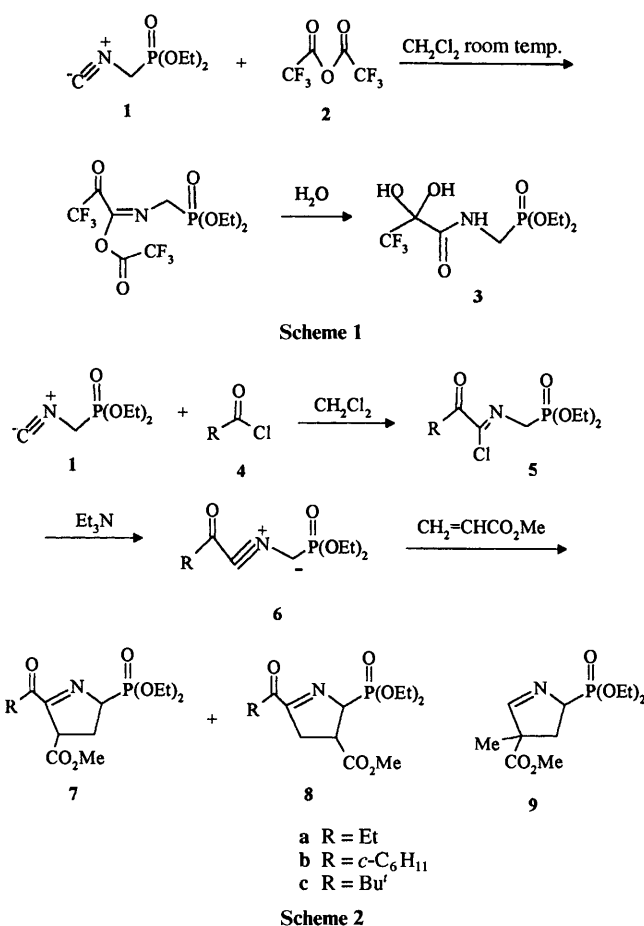
As demonstrated by Hückel, MNDO and *ab initio* MO calculations, the predominant contribution to the valence-bond description of alkyl isocyanides is made by the polar structure  $\text{RN}^+\equiv\text{C}^-$ , an iminocarbene resonance hybrid.<sup>1</sup> The isocyano carbon atom then carries a non-bonding (n) electron pair with a formal negative charge. A nucleophilic character is therefore not unexpected. Evidence for such a property is the [1 + 4] cycloaddition of alkyl isocyanides with conjugated nitroalkenes.<sup>2</sup> However, isocyanomethylphosphonate **1** does not react similarly with nitroalkenes,<sup>3</sup> which is attributed to the reduced nucleophilicity of its isocyano carbon atom caused by the electron withdrawing phosphoryl group. The weak nucleophilicity of isocyanomethylphosphonate **1** would be demonstrated by its reaction with a strong electrophile. Thus, we investigated the  $\alpha$ -addition reaction of trifluoroacetic anhydride and acyl chlorides with isocyanomethylphosphonate **1**.

We are also interested in the synthesis of heterocyclic compounds bearing a phosphoryl moiety, due to their potential biological importance. However, this class of compounds is difficult to obtain because the conventional methods for the formation of carbon-phosphorus bonds have proved to be impractical.<sup>4</sup> We considered preparing them *via* a cyclization since 1,3-dipolar cycloaddition of  $\alpha$ -phosphoryl nitrile oxide to alkenes has been reported;<sup>5</sup> nevertheless, phosphorylated nitrile ylides have not, to the best of our knowledge, been studied yet. In this paper we demonstrate that  $\alpha$ -ketoimidoyl chlorides generated from the  $\alpha$ -addition reaction of acyl chlorides to isocyanomethylphosphonate **1** may serve as precursors to phosphorylated nitrile ylides.

## Results and discussion

Isocyanomethylphosphonate **1** was first allowed to react with highly electrophilic trifluoroacetic anhydride **2**. As shown in Scheme 1, this exothermic reaction occurred at room temperature in dichloromethane, giving the trifluoropropanamide hydrate **3** after hydrolysis of the imine  $\alpha$ -adduct. Spectroscopic data [ $\delta_{\text{H}}$  3.24 (br, 3 H, NH and 20 H);  $\delta_{\text{F}}$  -6.3 (s)] and combustion microanalysis confirmed the structure of compound **3**.

We next examined the reaction of acyl chlorides **4** with isocyanomethylphosphonate **1**. As shown in Scheme 2, acyl chlorides derived from the corresponding primary, secondary



and tertiary alkanolic acids reacted with isocyanide **1** in refluxing dichloromethane over 20 h (TLC monitor). The  $\alpha$ -adduct with a  $\alpha$ -ketoimidoyl chloride structure can be easily distinguished from the starting materials on a TLC plate by its ultraviolet absorption due to the conjugation between the carbonyl and imine groups. The observed difference between trifluoroacetic anhydride **2** and acyl chlorides **4** when they reacted with isocyanomethylphosphonate **1**, was attributed to the weaker electrophilicity of acyl chlorides compared to that of trifluoroacetic anhydride.

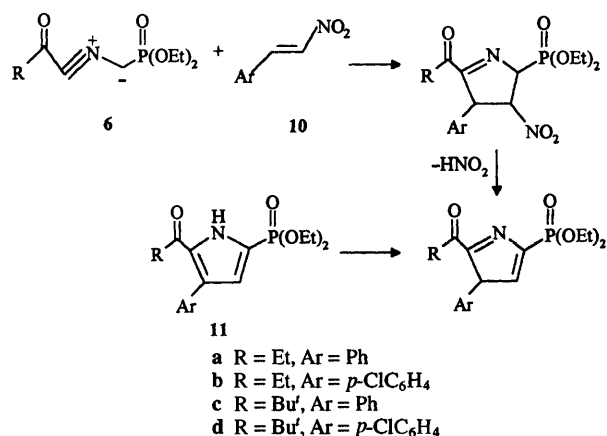
The  $\alpha$ -ketoimidoyl chlorides **5** formed in the above manner were treated with triethylamine without isolation, providing a 1,3-dipolar species upon 1,3-dehydrochlorination. This 1,3-

† For Part 95, see C. Yuan *et al.*, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1995, **106**, 163.

dipolar intermediate **6** was then trapped *in situ* with methyl acrylate to give a mixture of the cycloadducts **7** and **8**.

The regioisomers **7** and **8** are very difficult to separate by chromatography and their ratio is hard to determine by  $^1\text{H}$  NMR, due to overlap of absorption peaks even when measured at 300 MHz. We calculated the ratios based on  $^{31}\text{P}$  NMR by comparison with that of pyrroline **9**, prepared previously by us *via*  $\text{Cu}_2\text{O}$  catalysed reaction of isocyanomethylphosphonate **1** with methyl methacrylate.<sup>6</sup> Compound **9** resonates at  $\delta$  23.43 and 23.97 in the  $^{31}\text{P}$  NMR spectra due to the *cis* or *trans* configuration of substituents on C-2 and C-4. Thus, where R is *tert*-butyl, the compound with chemical shifts of  $\delta$  20.6 and 22.0 is assigned structure **7c**, similar to that of **9**; however, we could not decide which chemical shift corresponds to the *cis* configuration. The other two chemical shifts ( $\delta$  15.5 and 18.1) are, therefore, of regioisomer **8c**. The ratio of **7c** to **8c** is 89:11, calculated from integration values. Analogous determination derived the ratios of **7a** to **8a** and **7b** to **8b** as 1:4 and 1:3, respectively.

When nitroalkenes **10** were used as dipolarophiles to intercept the above 1,3-dipole intermediate **6**, pyrrole-2-phosphonates **11** were obtained in moderate yield, together with some unidentified components. The pyrrole structure was deduced from spectroscopic measurements. The resonances at  $\delta_{\text{p}}$  8.39–9.19 (singlets) are close to those of 3,4-disubstituted pyrrole-2-phosphonates synthesized previously by us,<sup>7</sup> and are further upfield than those of pyrroline **7** or **8** because the phosphoryl group is attached to an  $\text{sp}^2$  carbon. The peaks at  $\delta_{\text{H}}$  7.00 (dd) for **11a** and  $\delta_{\text{C}}$  118.8 (d), 119.7 (d) for **11d** clearly reveal the formation of 4,5-disubstituted pyrrole-2-phosphonates. As illustrated in Scheme 3, this pyrrole is produced *via*



Scheme 3

regioselective 1,3-dipolar cycloaddition followed by elimination of nitrous acid and subsequent aromatization.

The chemistry of the isocyanomethylphosphonate **1** has rarely been investigated, except for the studies on its Ugi-type<sup>8</sup> and Passerini-type<sup>9</sup> reactions. In our work, we have confirmed the weak nucleophilicity of isocyanomethylphosphonate **1** *via* its  $\alpha$ -addition reaction with trifluoroacetic anhydride or acyl chlorides. The adducts provided a new class of nitrile ylides upon dehydrochlorination. Moreover, we have developed a new approach to pyrroline- and pyrrole-phosphonates *via* 1,3-dipolar cycloaddition of these phosphorylated nitrile ylides with methyl acrylate or nitroalkenes.

## Experimental

### General

The melting points are uncorrected. IR spectra were taken on a Shimadzu-440 spectrophotometer.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker AM-300 spectrometer

in  $\text{CDCl}_3$  (if unspecified) at 300, 75.4 and 121.4 MHz, respectively. Chemical shifts ( $\delta$ ) were reported in ppm downfield from  $\text{Me}_4\text{Si}$  or 85%  $\text{H}_3\text{PO}_4$ ;  $J$  values are given in Hz.  $^{19}\text{F}$  NMR spectra were obtained on a Varian EM 360A spectrometer at 56.2 MHz using  $\text{CF}_3\text{CO}_2\text{H}$  as an external standard, positive for downfield shifts. EI-MS were measured on a HP5989A mass spectrometer. Microanalyses were done by the Analytical Department of this Institute.

Diethyl isocyanomethylphosphonate was prepared by the literature method<sup>10</sup> with some modification.<sup>11</sup> Nitroalkenes were synthesized *via* condensation of nitromethane with aromatic aldehydes.<sup>12</sup> Trifluoroacetic anhydride, cyclohexanecarbonyl chloride and pivaloyl chloride were purchased from Merck, Fluka and Tokyo Kasei, respectively. Other reagents were commercially available from a local source (Shanghai Chemical Co.).  $\text{CH}_2\text{Cl}_2$  was dried over  $\text{P}_2\text{O}_5$  and distilled prior to use. MeCN and  $\text{Et}_3\text{N}$  were dried with molecular sieves and sodium hydroxide pellets, respectively.

### *N*-(Diethoxyphosphonomethyl)-3,3,3-trifluoro-2,2-dihydroxypropanamide **3**

To a solution of  $(\text{CF}_3\text{CO})_2\text{O}$  (2  $\text{cm}^3$ ) in  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ) was added dropwise diethyl isocyanomethylphosphonate **1** (5 mmol, 0.8  $\text{cm}^3$ ). The mixture was stirred at room temp. for 6 h and  $\text{H}_2\text{O}$  (10  $\text{cm}^3$ ) was added. Vigorous stirring was continued for 2 h. The organic phase was separated and the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (2  $\times$  20  $\text{cm}^3$ ). The combined organic phase and extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and then filtered. The filtrates were concentrated to give a white fluffy solid which was recrystallized from  $\text{EtOH-H}_2\text{O}$  to provide pure **3** (1.21 g, 78%) as a white powder, mp 128–130 °C (Found: C, 31.4; H, 4.6; N, 4.45.  $\text{C}_8\text{H}_{15}\text{F}_3\text{NO}_6\text{P}$  requires C, 31.1; H, 4.85; N, 4.5%);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  3335 (br, O–H, N–H), 1680 (C=O), 1240 (P=O), 1180 (C–F) and 1025 (P–O–C);  $\delta_{\text{H}}(\text{CD}_3\text{COCD}_3)$  1.30 (6 H, t,  $J$  7.0, 2 Me), 3.24 (3 H, br, NH and 2 OH), 3.76 (2 H, d,  $J$  12.0,  $\text{CH}_2\text{P}$ ) and 4.11 (4 H, q,  $J$  7.0, 2  $\text{OCH}_2$ );  $\delta_{\text{F}}(\text{CD}_3\text{COCD}_3)$  –6.3 (s);  $\delta_{\text{p}}$  27.9 (s);  $m/z$  213 (27%), 194 [ $\text{M}^+ - \text{CF}_3\text{C}(\text{OH})_2$ , 47], 166 [ $\text{M}^+ - \text{CF}_3\text{C}(\text{OH})_2\text{C}(\text{O})$ , 31], 138 (100), 131 (22), 115 (19), 91 (18) and 69 (19).

### Diethyl 4-methoxycarbonyl-5-propionyl-3,4-dihydro-2H-pyrrole-2-phosphonate **7a** and diethyl 3-methoxycarbonyl-5-propionyl-3,4-dihydro-2H-pyrrole-2-phosphonate **8a**. Typical procedure

Freshly distilled propionyl chloride (5 mmol, 0.44  $\text{cm}^3$ ) and isocyanide **1** (5 mmol, 0.8  $\text{cm}^3$ ) were mixed in  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ). The resulting mixture was refluxed for 20 h under  $\text{N}_2$ . TLC (light petroleum– $\text{EtOAc}$ , 2:1, v/v) indicated the completion of  $\alpha$ -addition. The solvent was removed by distillation and the residue was dissolved in MeCN (5  $\text{cm}^3$ ). To another flask equipped with thermometer,  $\text{N}_2$  inlet and rubber septum was added MeCN (10  $\text{cm}^3$ ), methyl acrylate (20 mmol, 1.8  $\text{cm}^3$ ) and  $\text{Et}_3\text{N}$  (5.5 mmol, 0.77  $\text{cm}^3$ ). This mixture was cooled to –10 °C. The previously formed solution of  $\alpha$ -adduct in MeCN was then added dropwise to this cooled mixture. The precipitation of  $\text{Et}_3\text{N}\cdot\text{HCl}$  was observed and the temperature was kept below 0 °C. Stirring was continued at 0 °C for 5 h. Absolute  $\text{Et}_2\text{O}$  (10  $\text{cm}^3$ ) was added and the precipitate was filtered off. The filtrate was concentrated under reduced pressure to afford a brown residue which upon column chromatography on silica gel ( $\text{EtOAc}$ –light petroleum, 1:1, v/v) provided pyrrolines **7a** and **8a** (0.87 g, 55%) as a pale yellow liquid (Found: C, 49.0; H, 6.8; N, 4.3.  $\text{C}_{13}\text{H}_{22}\text{NO}_6\text{P}$  requires C, 48.9; H, 6.9; N, 4.4%);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  3000 (C–H), 1725 and 1720 (C=O), 1690 (C=N), 1240 (P=O) and 1020 (P–O–C);  $\delta_{\text{H}}$  1.08, 1.10 (3 H, 2 t,  $J$  7.2, 7.1,  $\text{CH}_3\text{CH}_2\text{CO}$ ), 1.39, 1.40 (6 H, 2 t,  $J$  7.0, 2  $\text{OCH}_2\text{CH}_3$ ), 2.20–2.73 (4 H, m,  $\text{CH}_2\text{CO}$  and ring  $\text{CH}_2$ ), 3.78, 3.79 (3 H, 2 s, OMe), 3.72–3.91 (2 H, m, CHP,  $\text{CHCO}_2$ ) and 4.19–4.31 (4 H, m, 2  $\text{OCH}_2\text{CH}_3$ );  $\delta_{\text{p}}$  16.0 and 23.3 (4:1);  $m/z$  320 ( $\text{MH}^+$ , 27%), 288

(21), 177 (20), 165 (100), 137 (24), 121 (25), 109 (27) and 57 ( $C_2H_5CO^+$ , 24).

**Diethyl 4-methoxycarbonyl-5-cyclohexylcarbonyl-3,4-dihydro-2H-pyrrole-2-phosphonate 7b and diethyl 3-methoxycarbonyl-5-cyclohexylcarbonyl-3,4-dihydro-2H-pyrrole-2-phosphonate 8b.** A colourless liquid (50%) (Found: C, 54.6; H, 7.6; N, 3.8.  $C_{17}H_{28}NO_6P$  requires C, 54.7; H, 7.5; N, 3.75%);  $\nu_{max}(\text{film})/\text{cm}^{-1}$  2900 (C–H), 1740 and 1710 (C=O), 1690 (C=N), 1240 (P=O) and 1020 (P–O–C);  $\delta_H$  1.21–1.42 (11 H, m), 1.55–2.68 (9 H, m), 3.71, 3.74, 3.76, 3.78 (3 H, 4 s, OMe) and 4.03–4.31 (5 H, m, 2  $OCH_2$ , CHP);  $\delta_P$  16.0, 16.9, 23.2 and 23.3 (the former two: the latter two 3:1);  $m/z$  374 ( $MH^+$ , 96%), 342 (35), 315 ( $MH^+ - CO_2Me$ , 31), 232 (23), 165 (100), 109 (21), 83 (67) and 55 (30).

**Diethyl 4-methoxycarbonyl-5-trimethylacetyl-3,4-dihydro-2H-pyrrole-2-phosphonate 7c and diethyl 3-methoxycarbonyl-5-trimethylacetyl-3,4-dihydro-2H-pyrrole-2-phosphonate 8c.** A colourless liquid (58%) (Found: C, 51.7; H, 7.5; N, 4.2.  $C_{15}H_{26}NO_6P$  requires C, 51.9; H, 7.5; N, 4.0%);  $\nu_{max}(\text{film})/\text{cm}^{-1}$  3000 (C–H), 1680–1760 (br, C=O, C=N), 1250 (P=O) and 1025 (P–O–C);  $\delta_H$  1.23–1.43 (15 H, m, 5 Me), 3.17–3.46 (3.1 H, m,  $CH_2$ ,  $CHCO_2$ , 0.1 CHP), 3.72, 3.74 (3 H, 2 s, OMe), 4.14–4.27 (4 H, m, 2  $OCH_2$ ) and 5.03 (0.9 H, ddd,  $J_{PH}$  2.1,  $J_{cis-HH}$  5.1,  $J_{trans-HH}$  2.6, 0.9, CHP);  $\delta_P$  15.5, 18.1, 20.6 and 22.0 (9:2:10:79);  $m/z$  348 ( $MH^+$ , 51%), 280 (27), 223 (100), 194 (38), 166 (24), 165 (24), 138 (54) and 57 (59).

#### Diethyl 4-phenyl-5-propionylpyrrole-2-phosphonate 11a.

##### Typical procedure

A mixture of freshly distilled propionyl chloride (5 mmol, 0.44  $\text{cm}^3$ ) and isocyanide **1** (5 mmol, 0.8  $\text{cm}^3$ ) in  $CH_2Cl_2$  (10  $\text{cm}^3$ ) was refluxed for 20 h under  $N_2$ . This mixture was then cooled to  $-10^\circ\text{C}$  and a solution of  $\beta$ -nitrostyrene (5 mmol, 0.75 g) and  $Et_3N$  (5.5 mmol, 0.77  $\text{cm}^3$ ) in  $CH_2Cl_2$  (10  $\text{cm}^3$ ) was added dropwise below  $0^\circ\text{C}$ . Stirring was continued at  $0^\circ\text{C}$  for 5 h. The mixture was concentrated under reduced pressure and the residue was dissolved in EtOAc. The undissolved component was filtered off. The filtrate was concentrated and then subjected to column chromatography on silica gel (EtOAc–light petroleum, 1:1, v/v) to afford pyrrole **11a** (0.74 g, 44%) as a pale yellow oil (Found: C, 61.1; H, 6.5; N, 4.15.  $C_{17}H_{22}NO_4P$  requires C, 60.9; H, 6.6; N, 4.2%);  $\nu_{max}(\text{film})/\text{cm}^{-1}$  2950 (C–H), 1670 (C=O), 1550 (C=C), 1240 (P=O), 1020 (P–O–C) and 910 and 730 (benzene);  $\delta_H$  1.16 (6 H, t,  $J$  7.1, 2  $OCH_2CH_3$ ), 1.23 (3 H, t,  $J$  7.4,  $CH_3CH_2CO$ ), 2.86 (2 H, q,  $J$  7.4,  $CH_2CO$ ), 4.07 (4 H, q,  $J$  7.1, 2  $OCH_2$ ), 7.00 (1 H, dd,  $J_{HH}$  2.8,  $J_{PH}$  4.2, 3-H), 7.35 (3 H, m, Ph), 7.59 (2 H, m, Ph) and 9.90 (1 H, br s, NH);  $\delta_P$  8.69 (s);  $m/z$  336 ( $MH^+$ , 27%), 335 ( $M^+$ , 100), 306 (57), 278 (51), 250 (75), 232 (29), 199 (25) and 166 (21).

**Diethyl 4-(*p*-chlorophenyl)-5-propionylpyrrole-2-phosphonate 11b.** A pale yellow oil (46%) (Found: C, 55.1; H, 5.55; N, 4.0.  $C_{17}H_{21}ClNO_4P$  requires C, 55.2; H, 5.7; N, 3.8%);  $\nu_{max}(\text{film})/\text{cm}^{-1}$  3400 (N–H), 2950 (C–H), 1670 (C=O), 1550 (C=C), 1240 (P=O), 1020 (P–O–C) and 910, 730 and 650 (benzene);  $\delta_H$  1.15–1.25 (9 H, m, 3 Me), 2.86 (2 H, q,  $J$  7.4,

$CH_2CO$ ), 4.08 (4 H, q,  $J$  7.2, 2  $OCH_2$ ), 6.97 (1 H, dd,  $J_{HH}$  2.8,  $J_{PH}$  4.0, 3-H), 7.19 (2 H, d,  $J$  8.5, Ar), 7.52 (2 H, d,  $J$  8.5, Ar) and 10.02 (1 H, br s, NH);  $\delta_P$  8.49 (s);  $m/z$  371 (37%), 369 ( $M^+$ , 100), 340 (48), 312 (46), 286 (27), 284 (78), 266 (28) and 233 (26).

**Diethyl 4-phenyl-5-trimethylacetylpyrrole-2-phosphonate 11c.** A white solid (52%), mp  $156^\circ\text{C}$  (Found: C, 63.1; H, 6.9; N, 3.7.  $C_{19}H_{26}NO_4P$  requires C, 62.8; H, 7.2; N, 3.85%);  $\nu_{max}(\text{film})/\text{cm}^{-1}$  2900 (C–H), 1670 (C=O), 1540 (C=C), 1240 (P=O), 1020 (P–O–C) and 910 and 730 (benzene);  $\delta_H$  1.18 (9 H, s,  $Me_3C$ ), 1.35 (6 H, t,  $J$  7.1, 2  $OCH_2CH_3$ ), 4.16 (4 H, q,  $J$  7.2, 2  $OCH_2$ ), 6.73 (1 H, dd,  $J_{HH}$  3.0,  $J_{PH}$  5.9, 3-H), 7.30–7.37 (5 H, m, Ph) and 9.91 (1 H, br s, NH);  $\delta_P$  9.19 (s);  $m/z$  363 ( $M^+$ , 9%), 307 (18), 306 ( $M^+ - Me_3C$ , 100), 278 (28), 250 (37), 232 (16), 140 (10) and 69 (10).

**Diethyl 4-(*p*-chlorophenyl)-5-trimethylacetylpyrrole-2-phosphonate 11d.** A pale yellow solid (46%), mp  $212^\circ\text{C}$  (Found: C, 57.6; H, 6.6; N, 3.7.  $C_{19}H_{25}ClNO_4P$  requires C, 57.4; H, 6.3; N, 3.5%);  $\nu_{max}(\text{film})/\text{cm}^{-1}$  3000 (C–H), 1660–1690 (C=O and C=N), 1550 (C=C), 1230 (P=O), 1020 (P–O–C) and 910 and 730 (benzene);  $\delta_H$  1.10 (9 H, s,  $Me_3C$ ), 1.38 (6 H, t,  $J$  7.1, 2  $OCH_2CH_3$ ), 4.17 (4 H, q,  $J$  7.2, 2  $OCH_2$ ), 6.69 (1 H, dd,  $J_{HH}$  2.9,  $J_{PH}$  5.8, 3-H), 7.26–7.37 (4 H, m, Ar) and 10.1 (1 H, br s, NH);  $\delta_C$  16.3 (d,  $J_{PC}$  6.3,  $OCH_2CH_3$ ), 27.3 (s,  $CH_3$ ), 44.4 (s,  $Me_3C$ ), 62.9 (d,  $J_{PC}$  4.9,  $OCH_2$ ), 118.8 (d,  $J_{PC}$  16.2, C-3), 119.7 (d,  $J_{PC}$  255.2, C-2), 128.5 (d,  $J_{PC}$  13.4, C-4), 131.3 (d,  $J_{PC}$  9.81, C-5), 128.4, 130.2, 133.0 and 134.0 (Ar) and 202.2 (C=O);  $\delta_P$  8.39 (s);  $m/z$  399 (6%), 397 ( $M^+$ , 16), 342 (37), 341 (20), 340 (100), 312 (29), 284 (39), 119 (22) and 57 (25).

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