# AN EFFICIENT SYNTHESIS OF 5-PHOSPHORYLATED 1,3,2-DIAZAPHOSPHININES FROM β-FUNCTIONALIZED ENAMINES DERIVED FROM PHOSPHINE OXIDES AND PHOSPHONATES

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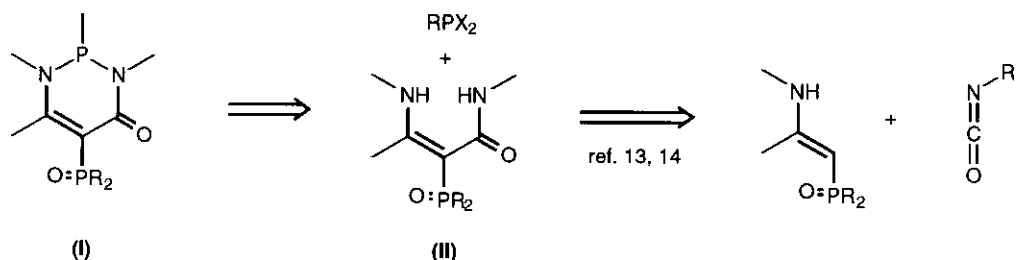
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*Abstract-* An easy and efficient synthesis of 1,3,2-$P^{III}$-diazaphosphininones (**3, 4**) substituted with a phosphine oxide or a phosphonate group in the 5-position is described. The key step is a cyclocondensation reaction of substituted β-enamino amides (**1**) to phosphorus trichloride and phenylphosphonous dichloride. Subsequent treatment of 1,3,2-$P^{III}$-diazaphosphininones (**3**) with elemental sulfur, water or hydrogen peroxide afforded the substituted 2-thio- (**7, 8**) and 2-oxo-1,3,2-$P^{V}$-diazaphosphininones (**5, 6, 9**).

Diazaphosphinine[1] ring systems represent an important class of compounds[2] and have attracted an attention in recent years for their biological activities.[3] Likewise, 1,3,2-diazaphosphinine derivatives have been used in the preparation of malonic acid receptors with decarboxylative activity[4] and as versatile precursors of 1,2-azaphosphinines,[5a] polyfunctional phosphinines[5b] and bicyclic heterocycles.[5c] In this context, we are interested in the design of new 1,3,2-diazaphosphinine derivatives substituted with a phosphine oxide or a phosphonate group in the 5 position of the heterocyclic system. This substituent could regulate important biological functions and could increase the biological activity of these type of compounds, in a similar way to that reported for other pharmaceuticals.[6] Classical approaches[2] to 1,3,2-diazaphosphinine involving cyclocondensation reactions of acyclic precursors such as phosphorodiamidates and diacyl chlorides[7] as well as from 4-aminoazabutadienes[8] or diazatitanacycles[5a] with phosphorus halides have been reported. However, to the best of our knowledge, the synthesis of phosphorus substituted 1,3,2-diazaphosphininones has not been reported.
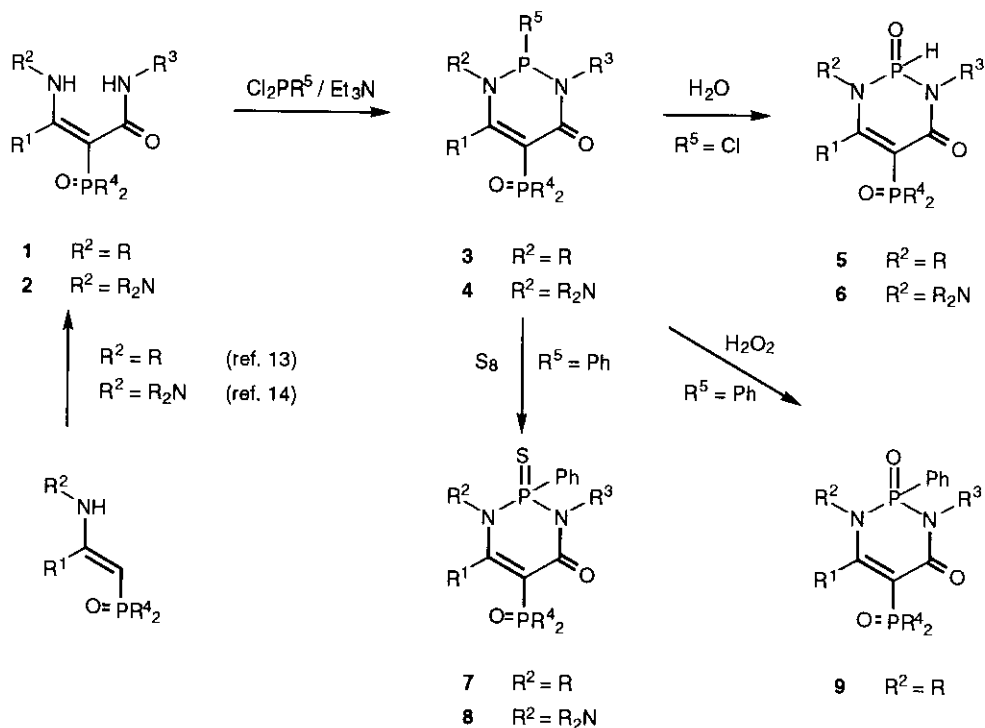
In connection with our interest in the synthesis of five[9] and six[10] membered phosphorylated nitrogen heterocycles we have used β-functionalized enamines derived from phosphazenes, phosphonium salts, phosphine oxides and phosphonates as synthetic intermediates in the synthesis of acyclic derivatives such as oximes[11a] allylamines,[11b] hydrazones,[11c] azadienes,[11d] aminodienes,[11e] and β-amino functionalized compounds[11f,g] as well as of phosphorus containing heterocycles.[12] Continuing with our interest in the synthesis of new phosphorus substituted heterocycles we report here an easy and high yielding synthesis of 1,3,2-diazaphosphininone derivatives (**I**) from phosphorus halides and amido-enamines containing a

phosphoryl or a phosphonyl group (**II**), prepared from functionalized enamines[13] or ene hydrazines.[14] (Scheme 1).



Scheme 1

Functionalized β-enamino ($R^2$=Alk or Ar) (**1**) and β-ene hydrazino amides ($R^2$=$R_2$N) (**2**) were easily prepared by reaction of β-enamines[13] and β-ene hydrazines[14] derived from phosphine oxides and phosphonates with isocyanates. The reaction of enamino-amides derived from phosphine oxides (**1**, $R^4$ = Ph) with phosphorus trichloride in the presence of triethylamine and aqueous work-up gave high yields of substituted 2-oxo-1,3,2-$P^V$-diazaphosphinin-4-ones (**5**) (see Table 1, entries 5-10).



Scheme 2

The formation of these heterocycles (5) can be explained by cyclocondensation reaction of the phosphorus halide with compounds (1) and insertion of the phosphorus atom between both nitrogen atoms to give 1,3,2-$P^{III}$-diazaphosphinin-4-ones (3), followed by oxidation with water (Scheme 2). Compounds (5) were characterized on the basis of their spectroscopic data. Thus, the ^{31}P-NMR spectrum of compound (5a) showed two well resolved doublets with the long-range coupling constant $^4J_{PP} = 29.8$ Hz for the diphosphoryl group ($\delta_P = 36.8$ ppm) and for the heterocyclic phosphorus atom ($\delta_P = 3.8$ ppm) while in the ^{13}C-NMR spectrum of this compound (5a) C-5 resonates at $\delta_C = 89.0$ ppm as a double doublet with coupling constants $^1J_{PC} = 116.6$ and $^3J_{PC} = 19.4$ Hz.

**Table 1.** 1,3,2-$P^{III}$-Diazaphosphinin-4-ones **3**, 2-oxo-1,3,2-$P^V$-Diazaphosphinin-4-ones (**5, 6** and **9**) and 2-thio-1,3,2-$P^V$-Diazaphosphinin-4-ones (**7** and **8**).

| Entry | Compound | R$^1$ | R$^2$ | R$^3$ | R$^4$ | Yield (%) | mp (°C) |
|-------|----------|-------|-------|-------|-------|-----------|---------|
| 1 | **3a** | H | p-Me-Ph | Ph | Ph | a | a |
| 2 | **3b** | H | p-Me-Ph | Et | Ph | a | a |
| 3 | **3c** | Me | Ph | Ph | Ph | a | a |
| 4 | **3d** | H | CH$_2$=CH-CH$_2$ | Ph | OEt | a | a |
| 5 | **5a** | H | p-Me-Ph | Ph | Ph | 77[b] | 238-239[d] |
| 6 | **5b** | H | p-Me-Ph | Et | Ph | 71[b] | 176-177[d] |
| 7 | **5c** | H | Ph-CH$_2$ | Ph | Ph | 85[b] | 142-143[d] |
| 8 | **5d** | Me | p-Me-Ph | Ph | Ph | 82[b] | 242-243[d] |
| 9 | **5e** | Me | Ph-CH$_2$ | Ph | Ph | 74[b] | 138-139[d] |
| 10 | **5f** | p-Me-Ph | p-Me-Ph | Ph | Ph | 77[b] | 130-131 |
| 11 | **5g** | H | CH$_2$=CH-CH$_2$ | Ph | OEt | 90[b] | oil[e] |
| 12 | **6** | H | Me$_2$N | $^t$Bu | Ph | 85[c] | 244-245 |
| 13 | **7a** | H | p-Me-Ph | Ph | Ph | 82[b] | 140-142 |
| 14 | **7b** | H | p-Me-Ph | Et | Ph | 74[b] | 158-160 |
| 15 | **7c** | Me | Ph | Ph | Ph | 79[b] | 168-169[d] |
| 16 | **7d** | H | CH$_2$=CH-CH$_2$ | Ph | OEt | 90[b] | 150-151 |
| 17 | **8** | Me | Me$_2$N | Ph | Ph | 79[c] | 95-97 |
| 18 | **9a** | H | p-Me-Ph | Ph | Ph | 77[b] | 135-137 |
| 19 | **9b** | H | p-Me-Ph | Et | Ph | 71[b] | 150-151 |
| 20 | **9c** | Me | Ph | Ph | Ph | 85[b] | 155-156 |
| 21 | **9d** | H | CH$_2$=CH-CH$_2$ | Ph | OEt | 77[b] | 135-136 |

[a] The crude products (**3**) were characterized (^{1}H, ^{13}C and ^{31}P NMR) without isolation. [b] Yield of isolated purified compounds (**5, 7** and **9**) from functionalized amides (**1**). [c] Yield of isolated purified compounds (**6**) and (**8**) from functionalized amides (**2**). [d] Decomposition. [e] Purified by flash chromatography.

**Table 2.** Selected spectral data for compounds (**3**, **5**, **6**, **7**, **8** and **9**).

| Com-pound | $^{31}$P-NMR (CDCl$_3$)[a] δ (ppm) | $^1$H-NMR (CDCl$_3$)[a] δ (ppm) | $^{13}$C-NMR (CDCl$_3$)[a] δ (ppm) | IR[b] ν (cm$^{-1}$) | MS[c] (m/z) |
|---|---|---|---|---|---|
| **3 a** | 31.9 (POPh$_2$), 83.5 (N-P-N) | 2.21 (s, 3H, CH$_3$), 2.32 (s, 3H, CH$_3$), 7.01-7.82 (m, 24H, Ar) | 20.4 (CH$_3$), 21.0 (CH$_3$), 107.0 (d, $^1J_{PC}$ = 112.8 Hz, C-P), 118.0-137.5 (C$_{Ar}$), 162.8 (d, $^2J_{PC}$ = 12.8 Hz), 165.9 | d | d |
| **3 b** | 27.9 (POPh$_2$), 81.3 (N-P-N) | 1.13 (t, 3H, $^3J_{HH}$ = 7.2 Hz, CH$_3$), 2.05 (s, 3H, CH$_3$), 2.24 (s, 3H, CH$_3$), 3.84 (q, 2H, $^3J_{HH}$ = 7.2 Hz, CH$_2$), 7.02-7.80 (m, 19H, Ar) | 12.6 (CH$_3$), 20.4 (CH$_3$), 20.7 (CH$_3$), 37.5 (CH$_2$), 109.6 (d, $^1J_{PC}$ = 119.3 Hz, C-P), 117.7-137.0 (C$_{Ar}$), 163.5, 164.3 | d | d |
| **3 c** | 28.8 (POPh$_2$), 84.7 (N-P-N) | 0.64 (t, 3H, $^3J_{HH}$ = 7.2 Hz, CH$_3$), 2.57-2.83 (m, 2H, CH$_2$), 6.83-7.85 (m, 25H, Ar) | 11.9 (CH$_3$), 25.7 (CH$_2$), 101.3 (d, $^1J_{PC}$ = 114.8 Hz, C-P), 118.4-142.9 (C$_{Ar}$), 169.0, 169.7 | d | d |
| **3 d** | 15.1 (PO(OEt)$_2$), 22.1 (N-P-N) | 1.29 (m, 6H, CH$_3$), 2.47 (s, 3H, CH$_3$), 3.75 (m, 2H, CH$_2$-N), 3.98 (m, 4H, CH$_2$-O), 5.21 (m, 2H, =CH$_2$), 5.85 (m, 1H, =CH), 7.16-7.58 (m, 10H, Ar) | 16.1 (CH$_3$), 19.8 (CH$_3$), 44.8 (CH$_2$-N), 61.1 and 62.2 (CH$_2$-O), 80.1 (d, $^1J_{PC}$ = 196.4 Hz, C-P), 116.5-139.9 (C$_{Ar}$, =CH$_2$ and CH), 165.3, 166.0 | d | d |
| **5 a** | 3.8 (d, $^4J_{PP}$ = 29.8 Hz, P=O), 36.8 (d, $^4J_{PP}$ = 29.8 Hz, POPh$_2$) | 1.71 (s, 3H, CH$_3$), 2.38 (s, 3H, CH$_3$), 7.15-7.95 (m, 19H, Ar) | 19.0 (d, $^3J_{PC}$ = 2.5 Hz, CH$_3$), 21.2 (CH$_3$), 89.0 (dd, $^1J_{PC}$ = 116.6 Hz, $^3J_{PC}$ = 19.4 Hz, C-P), 120.2-137.2 (C$_{Ar}$), 172.0, 173.1 | 1514, 1182, 1129 | 512 (M$^+$, 25%) |
| **5 b** | 2.8 (d, $^4J_{PP}$ = 30.9 Hz, P=O), 35.7 (d, $^4J_{PP}$ = 30.9 Hz, POPh$_2$) | 1.47 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH$_3$), 1.64 (s, 3H, CH$_3$), 2.37 (s, 3H, CH$_3$), 4.10 (q, 2H, $^3J_{HH}$ = 7.1 Hz, CH$_2$), 7.25-7.82 (m, 14H, Ar) | 15.4 (CH$_3$), 18.7 (CH$_3$), 21.1 (CH$_3$), 43.9 (d, $^2J_{PC}$ = 6.1 Hz, CH$_2$-N), 87.3 (dd, $^1J_{PC}$ = 116.8 Hz, $^3J_{PC}$ = 18.6 Hz, C-P), 127.4-139.2 (C$_{Ar}$), 172.3, 174.4 | 1597, 1103 | 464 (M$^+$, 23%) |
| **5 c** | 6.8 (d, $^4J_{PP}$ = 31.1 Hz, P=O), 36.4 (d, $^4J_{PP}$ = 31.1 Hz, POPh$_2$) | 1.65 (s, 3H, CH$_3$), 4.78 (d, 2H, $^3J_{PH}$ = 7.2 Hz, CH$_2$), 7.15-7.92 (m, 20H, Ar) | 18.6 (CH$_3$), 47.1 (CH$_2$), 89.3 (dd, $^1J_{PC}$ = 113.3 Hz, $^3J_{PC}$ = 19.1 Hz, C-P), 115.3-145.7 (C$_{Ar}$), 170.4, 174.4 | 1567, 1182, 1122 | 512 (M$^+$, 54%) |
| **5 d** | 4.9 (d, $^4J_{PP}$ = 29.6 Hz, P=O), 37.1 (d, $^4J_{PP}$ = 29.6 Hz, POPh$_2$) | 1.07 (t, 3H, $^3J_{HH}$ = 7.5 Hz, CH$_3$), 2.35 (s, 3H, CH$_3$), 3.25 (q, 3H, $^3J_{HH}$ = 7.5 Hz, CH$_2$), 7.02-7.87 (m, 19H, Ar) | 19.8 (CH$_3$), 21.3 (CH$_3$), 27.6 (CH$_2$), 89.7 (dd, $^1J_{PC}$ = 116.1 Hz, $^3J_{PC}$ = 19.0 Hz, C-P), 119.0-138.5 (C$_{Ar}$), 166.3, 171.4 | 1571, 1110 | 526 (M$^+$, 55%) |
| **5 e** | 7.4 (d, $^4J_{PP}$ = 31.7 Hz, P=O), 37.2 (d, $^4J_{PP}$ = 31.7 Hz, POPh$_2$) | 0.38 (t, 3H, $^3J_{HH}$ = 7.1 Hz, CH$_3$), 2.15 (q, 2H, $^3J_{HH}$ = 7.1 Hz, CH$_2$), 5.02 (m, 2H, CH$_2$), 7.24-8.15 (m, 20H, Ar) | 9.4 (CH$_3$), 24.9 (CH$_2$), 46.8 (CH$_2$-N), 87.8 (dd, $^1J_{PC}$ = 114.3 Hz, $^3J_{PC}$ = 19.6 Hz, C-P), 122.5-137.4 (C$_{Ar}$), 171.1, 172.9 | 1445, 1188 | 526 (M$^+$, 34%) |
| **5 f** | 3.7 (d, $^4J_{PP}$ = 29.6 Hz, P=O), 37.6 (d, $^4J_{PP}$ = 29.6 Hz, POPh$_2$) | 2.08 (s, 3H, CH$_3$), 2.14 (s, 3H, CH$_3$), 3.48 (s, 3H, CH$_2$), 6.90-7.88 (m, 23H, Ar) | 20.9 (CH$_3$), 21.0 (CH$_3$), 51.6 (CH$_2$), 88.3 (dd, $^1J_{PC}$ = 115.3 Hz, $^3J_{PC}$ = 19.1 Hz, C-P), 120.1-140.5 (C$_{Ar}$), 162.1, 173.0 | 1567, 1182, 1109 | 602 (M$^+$, 100%) |

**Table 2.** (continuation)

| Compound | $^{31}$P-NMR (CDCl$_3$)$^a$ δ (ppm) | $^1$H-NMR (CDCl$_3$)$^a$ δ (ppm) | $^{13}$C-NMR (CDCl$_3$)$^a$ δ (ppm) | IR$^b$ ν (cm$^{-1}$) | MS$^c$ (m/z) |
|---|---|---|---|---|---|
| 5 g | 8.1 (d, $^4$J$_{PP}$ = 50.0 Hz, P=O), 17.3 (d, $^4$J$_{PP}$ = 50.0 Hz, PO(OEt)$_2$) | 1.31 (t, 6H, $^3$J$_{HH}$ = 7.1 Hz, CH$_3$), 2.32 (s, 3H, CH$_3$), 4.03 (m, 4H, CH$_2$), 4.42 (m, 2H, CH$_2$), 5.28 (m, 2H, =CH$_2$), 5.94 (m, 1H, =CH), 7.21-7.78 (m, 5H, Ar) | 16.2 (CH$_3$), 16.5 (d, $^3$J$_{PC}$ = 4.0 Hz, CH$_3$), 46.1 (CH$_2$-N), 62.8 (CH$_2$-O), 89.9 (dd, $^1$J$_{PC}$ = 202.9 Hz, $^3$J$_{PC}$ = 20.6 Hz, C-P), 119.3 (=CH$_2$), 122.3 (=CH), 127.9-137.1 (C$_{Ar}$), 167.7, 174.3 | 1548, 1179, 1038 | 383 (M$^+$ - 15, 100%) |
| 6 | 1.8 (d, $^4$J$_{PP}$ = 32.3 Hz, P=O), 36.8 (d, $^4$J$_{PP}$ = 32.3 Hz, POPh$_2$) | 1.67 (s, 9H, CH$_3$), 1.82 (s, 3H, CH$_3$), 2.99 (s, 6H, CH$_3$N), 7.27-7.76 (m, 10H, Ar) | 17.2 (CH$_3$), 30.6 (CH$_3$), 46.5 (CH$_3$N), 58.4 (C), 84.4 (dd, $^1$J$_{PC}$ = 116.8 Hz, $^3$J$_{PC}$ = 17.6 Hz, C-P), 128.5-133.1 (C$_{Ar}$), 171.3, 173.0 | 1580, 1104 | 445 (M$^+$, 1%) |
| 7 a | 30.7 (POPh$_2$), 66.7 (P=S) | 2.26 (s, 3H, CH$_3$), 2.38 (s, 3H, CH$_3$), 6.89-7.93 (m, 24H, Ar) | 23.3 (CH$_3$), 25.7 (CH$_3$), 105.1 (d, $^1$J$_{PC}$ = 120.9 Hz, C-P), 118.7-139.5 (C$_{Ar}$), 169.8, 170.1 (d, $^2$J$_{PC}$ = 12.1 Hz) | 1548, 1202, 685 | 604 (M$^+$, 15%) |
| 7 b | 31.1 (POPh$_2$), 67.8 (P=S) | 1.01 (t, 3H, $^3$J$_{HH}$ = 6.9 Hz, CH$_3$), 2.28 (s, 3H, CH$_3$), 2.33 (s, 3H, CH$_3$), 3.46 (q, 2H, $^3$J$_{HH}$ = 6.9 Hz, CH$_2$), 7.10-7.92 (m, 19H, Ar) | 14.3 (CH$_3$), 20.9 (CH$_3$), 21.1 (CH$_3$), 39.3 (CH$_2$), 104.1 (d, $^1$J$_{PC}$ = 120.7 Hz, C-P), 124.8-139.2 (C$_{Ar}$), 163.5, 165.0 | 1642, 1170, 692 | 556 (M$^+$, 55%) |
| 7 c | 30.9 (POPh$_2$), 66.6 (P=S) | 0.99 (t, 3H, $^3$J$_{HH}$ = 7.2 Hz, CH$_3$), 2.97 (q, 2H, $^3$J$_{HH}$ = 7.2 Hz, CH$_2$), 6.92-7.97 (m, 25H, Ar) | 14.8 (CH$_3$), 25.7 (CH$_2$), 105.0 (d, $^1$J$_{PC}$ = 117.1 Hz, C-P), 118.6-139.7 (C$_{Ar}$), 169.9, 170.1 | 1540, 1104, 698 | 604 (M$^+$, 62%) |
| 7 d | 22.0 (PO(OEt)$_2$), 55.6 (P=S) | 1.37 (m, 6H, CH$_3$), 1.60 (s, 3H, CH$_3$), 3.89 (m, 2H, CH$_2$-N), 4.20 (m, 4H, CH$_2$-O), 5.14 (m, 2H, =CH$_2$), 5.80 (m, 1H, =CH), 7.09-7.97 (m, 10H, Ar) | 16.3 (CH$_3$), 34.9 (d, $^3$J$_{PC}$ = 15.6 Hz, CH$_3$), 45.2 (CH$_2$-N), 62.7 and 63.2 (CH$_2$-O), 85.1 (d, $^1$J$_{PC}$ = 193.4 Hz, C-P), 117.1 (=CH$_2$), 127.6-135.6 (C$_{Ar}$ and =CH), 162.5, 165.4 | 1575, 1036 | 490 (M$^+$, 51%) |
| 8 | 29.6 (POPh$_2$), 55.6 (P=S) | 1.05 (t, 3H, $^3$J$_{HH}$ = 7.2 Hz, CH$_3$), 2.83-2.90 (m, 1H, CH$_2$), 3.17 (s, 3H, CH$_3$N), 3.20 (s, 3H, CH$_3$N), 3.63-3.69 (m, 1H, CH$_2$), 6.91-7.89 (m, 20H, Ar) | 13.9 (CH$_3$), 24.2 (CH$_2$), 46.1 (CH$_3$N), 46.7 (CH$_3$N), 104.7 (d, $^1$J$_{PC}$ = 115.3 Hz, C-P), 127.1-135.2 (C$_{Ar}$), 163.0 (dd, $^2$J$_{PC}$ = 12.1 Hz, $^2$J$_{PC}$ = 4.0 Hz), 173.7 (dd, $^2$J$_{PC}$ = 12.1 Hz, $^2$J$_{PC}$ = 23.2 Hz) | 1652, 1513, 1114, 727 | 571 (M$^+$, 23%) |
| 9 a | 12.0 (P=O), 32.1 (POPh$_2$) | 2.28 (s, 3H, CH$_3$), 2.52 (s, 3H, CH$_3$), 7.01-7.93 (m, 24H, Ar) | 19.7 (CH$_3$), 20.9 (CH$_3$), 100.9 (d, $^1$J$_{PC}$ = 119.4 Hz, C-P), 118.5-139.5 (C$_{Ar}$), 163.0 (d, $^2$J$_{PC}$ = 8.6 Hz), 165.8 (d, $^2$J$_{PC}$ = 14.1 Hz) | 1669, 1360, 1103 | 588 (M$^+$, 100%) |
| 9 b | 12.1 (P=O), 32.1 (POPh$_2$) | 0.89 (t, 3H, $^3$J$_{HH}$ = 6.1 Hz, CH$_3$), 2.27 (s, 3H, CH$_3$), 2.32 (s, 3H, CH$_3$), 3.63 (q, 2H, $^3$J$_{HH}$ = 6.1 Hz, CH$_2$), 6.90-7.92 (m, 19H, Ar) | 14.3 (CH$_3$), 20.9 (CH$_3$), 21.2 (CH$_3$), 39.1 (CH$_2$), 104.0 (d, $^1$J$_{PC}$ = 120.0 Hz, C-P), 124.8-139.2 (C$_{Ar}$), 163.2, 164.8 | 1611, 1219, 1110 | 572 (M$^+$, 65%) |
| 9 c | 12.6 (P=O), 32.4 (POPh$_2$) | 1.11 (t, 3H, $^3$J$_{HH}$ = 6.9 Hz, CH$_3$), 3.10 (q, 2H, $^3$J$_{HH}$ = 6.9 Hz, CH$_2$), 7.07-7.99 (m, 25H, Ar) | 14.7 (CH$_3$), 23.8 (CH$_2$), 101.2 (d, $^1$J$_{PC}$ = 115.8 Hz, C-P), 126.8-135.1 (C$_{Ar}$), 163.7, 170.7 | 1641, 1228, 1170 | 588 (M$^+$, 65%) |

**Table 2.** (continuation)

| Com-pound | $^{31}$P-NMR (CDCl$_3$)[a] δ (ppm) | $^1$H-NMR (CDCl$_3$)[a] δ (ppm) | $^{13}$C-NMR (CDCl$_3$)[a] δ (ppm) | IR[b] ν (cm$^{-1}$) | MS[c] (m/z) |
|---|---|---|---|---|---|
| 9 d | 15.1 (P=O), 22.1 (PO(OEt)$_2$) | 1.43 (m, 6H, CH$_3$), 2.87 (s, 3H, CH$_3$), 3.98 (m, 2H, CH$_2$-N), 4.34 (m, 4H, CH$_2$-O), 5.27 (m, 2H, =CH$_2$), 5.93 (m, 1H, =CH), 7.21-7.88 (m, 10H, Ar) | 13.2 (CH$_3$), 28.9 (d, $^3J_{PC}$ = 15.0 Hz, CH$_3$), 45.3 (CH$_2$-N), 62.4 and 62.7 (CH$_2$-O), 85.2 (d, $^1J_{PC}$ = 194.4 Hz, C-P), 117.3 (=CH$_2$), 118.6 (=CH), 127.6-134.7 (C$_{Ar}$), 162.2, 165.4 | 1680, 1260, 1036 | 474 (M$^+$, 51%) |

[a] Obtained on a Varian VXR 300 Spectrometer. [b] Recorded in a Nicolet FTIR Magna 550. [c] Obtained on a Hewlett Packard 5890 Spectrometer. [d] The crude products (3) were characterized ($^1$H, $^{13}$C and $^{31}$P NMR) without isolation.

In order to enhance the scope and the synthetic use of this reaction, the reaction of polifunctionalized derivatives (1) with phosphorus dihalide was explored. Treatment of enamino-amides (1) with phenylphosphonous dichloride in the presence of triethylamine led to the formation of 1,3,2-*P$^{III}$*-diazaphosphinin-4-ones (3, R$^5$ = Ph) in excellent yields (Table 1, entries 1-3 ). Spectroscopic data were in agreement with the assigned structure. $^{31}$P-NMR spectrum of compound (3a) showed two absorptions at δ$_P$ = 83.5 and 31.9 ppm for the heterocyclic phosphorus atom and for the diphosphoryl group. However, these phosphorus derivatives (3) which proved to be unstable to distillation or chromatography, were therefore not isolated, and crude reaction mixtures without purification were oxidized to the thio- and oxo-derivatives with sulfur and hydrogen peroxide. Treatment of 1,3,2-*P$^{III}$*-diazaphosphinin-4-ones (3a-c) with elemental sulfur in THF yielded 2-thio-1,3,2-*P$^V$*-diazaphosphinin-4-ones (7) (Table 1, entries 13-15), while these compounds (3a-c) underwent oxidation with hydrogen peroxide to give the corresponding 2-oxo-1,3,2-*P$^V$*-diazaphosphinin-4-ones (9) (Table 1, entries 18-20). This methodology used for the preparation of heterocyles derived from phosphine oxides (3), (5), (7) and (9) can also be applied not only to phosphonate derivatives (Table 1, entries 4, 11, 16 and 21) but also to hydrazino (R$^2$ = R$_2$N) compounds (6) and (8) (Table 1, entries 12 and 17).

In conclusion, the synthesis described in this paper provides an efficient and easy access to 1,3,2-diazaphosphinin-4-ones (3) and the corresponding 2-thio (7, 8) and 2-oxo (5, 6, 9) derivatives substituted with a phosphine oxide or a phosphonate group in 5 position, making use of readily available starting materials.

## ACKNOWLEDGMENTS

## REFERENCES AND NOTES

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