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

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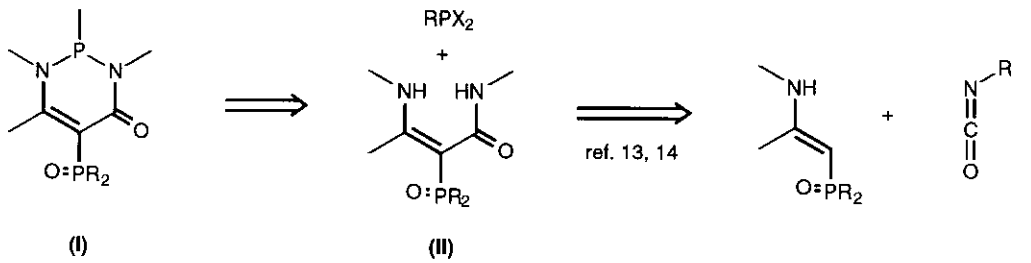
***Abstract***- An easy and efficient synthesis of 1,3,2-$P^{III}$-diazaphosphininones (**3**, **4**) substituted with a phosphine oxide or a phosphonate group in the 5-position is described. The key step is a cyclocondensation reaction of substituted β-enamino amides (**1**) to phosphorus trichloride 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.

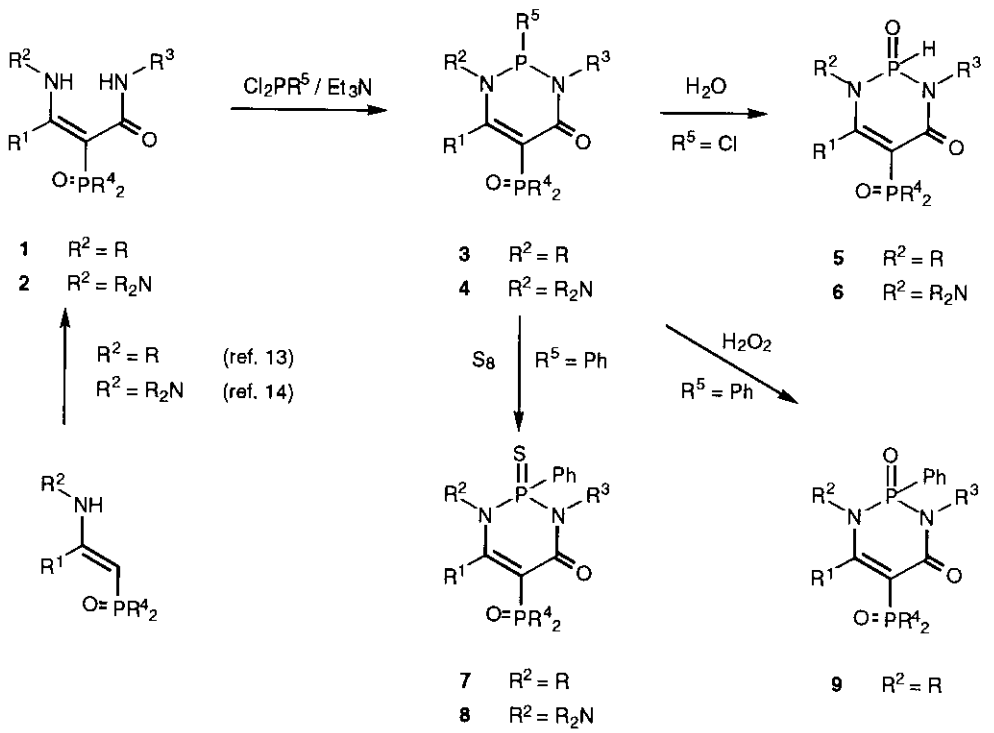
In connection with our interest in the synthesis of five[9] and six[10] membered phosphorylated nitrogen heterocycles we have used β-functionalized enamines derived from phosphazenes, phosphonium salts, phosphine oxides and phosphonates as synthetic intermediates in the synthesis of acyclic derivatives 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 ($R^2$=$R_2N$) (**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 $^{4}J_{PP}$ = 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 $^{1}J_{PC}$ = 116.6 and $^{3}J_{PC}$ = 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 | $Me_2N$ | $^t$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 | $Me_2N$ | 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**).

| 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) |
|---|---|---|---|---|---|
| **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, $^{1}J_{PC}$ = 112.8 Hz, C-P), 118.0-137.5 ($C_{Ar}$), 162.8 (d, $^{2}J_{PC}$ = 12.8 Hz), 165.9 | d | d |
| **3 b** | 27.9 ($POPh_2$), 81.3 (N-P-N) | 1.13 (t, 3H, $^{3}J_{HH}$ = 7.2 Hz, $CH_3$), 2.05 (s, 3H, $CH_3$), 2.24 (s, 3H, $CH_3$), 3.84 (q, 2H, $^{3}J_{HH}$ = 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, $^{1}J_{PC}$ = 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, $^{3}J_{HH}$ = 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, $^{1}J_{PC}$ = 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, $^{1}J_{PC}$ = 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, $^{4}J_{PP}$ = 29.8 Hz, P=O), 36.8 (d, $^{4}J_{PP}$ = 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, $^{3}J_{PC}$ = 2.5 Hz, $CH_3$), 21.2 ($CH_3$), 89.0 (dd, $^{1}J_{PC}$ = 116.6 Hz, $^{3}J_{PC}$ = 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, $^{4}J_{PP}$ = 30.9 Hz, P=O), 35.7 (d, $^{4}J_{PP}$ = 30.9 Hz, $POPh_2$) | 1.47 (t, 3H, $^{3}J_{HH}$ = 7.1 Hz, $CH_3$), 1.64 (s, 3H, $CH_3$), 2.37 (s, 3H, $CH_3$), 4.10 (q, 2H, $^{3}J_{HH}$ = 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, $^{2}J_{PC}$ = 6.1 Hz, $CH_2$-N), 87.3 (dd, $^{1}J_{PC}$ = 116.8 Hz, $^{3}J_{PC}$ = 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, $^{4}J_{PP}$ = 31.1 Hz, P=O), 36.4 (d, $^{4}J_{PP}$ = 31.1 Hz, $POPh_2$) | 1.65 (s, 3H, $CH_3$), 4.78 (d, 2H, $^{3}J_{PH}$ = 7.2 Hz, $CH_2$), 7.15-7.92 (m, 20H, Ar) | 18.6 ($CH_3$), 47.1 ($CH_2$), 89.3 (dd, $^{1}J_{PC}$ = 113.3 Hz, $^{3}J_{PC}$ = 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, $^{4}J_{PP}$ = 29.6 Hz, P=O), 37.1 (d, $^{4}J_{PP}$ = 29.6 Hz, $POPh_2$) | 1.07 (t, 3H, $^{3}J_{HH}$ = 7.5 Hz, $CH_3$), 2.35 (s, 3H, $CH_3$), 3.25 (q, 3H, $^{3}J_{HH}$ = 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, $^{1}J_{PC}$ = 116.1 Hz, $^{3}J_{PC}$ = 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, $^{4}J_{PP}$ = 31.7 Hz, P=O), 37.2 (d, $^{4}J_{PP}$ = 31.7 Hz, $POPh_2$) | 0.38 (t, 3H, $^{3}J_{HH}$ = 7.1 Hz, $CH_3$), 2.15 (q, 2H, $^{3}J_{HH}$ = 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, $^{1}J_{PC}$ = 114.3 Hz, $^{3}J_{PC}$ = 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, $^{4}J_{PP}$ = 29.6 Hz, P=O), 37.6 (d, $^{4}J_{PP}$ = 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, $^{1}J_{PC}$ = 115.3 Hz, $^{3}J_{PC}$ = 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, $CH_3N$), 7.27-7.76 (m, 10H, Ar) | 17.2 ($CH_3$), 30.6 ($CH_3$), 46.5 ($CH_3N$), 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, $CH_3N$), 3.20 (s, 3H, $CH_3N$), 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 ($CH_3N$), 46.7 ($CH_3N$), 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)

| 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) |
|---|---|---|---|---|---|
| **9d** | 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, $^{3}J_{PC}$ = 15.0 Hz, $CH_3$), 45.3 ($CH_2$-N), 62.4 and 62.7 ($CH_2$-O), 85.2 (d, $^{1}J_{PC}$ = 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 $\delta_P$ = 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 ($R^2 = R_2N$) 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

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## REFERENCES AND NOTES


1. These compounds are also very often named as 1,3,2-diazaphosphorines.
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