Chemistry of phosphorus ylides: Part 44
Reaction of 1-trimethylsilyl-1*H*-imidazole with phosphorus reagents. A convenient synthesis of phosphorus silyl imidazoles

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The reaction of 1-trimethylsilyl-1*H*-imidazole with nucleophilic active phosphacumulenes afforded imidazole silyl phosphoranylidenes or imidazole phosphoranylidenes according to the reaction conditions. The reaction of hexaphenylcarbodiphosphorane with 1-trimethylsilyl-1*H*-imidazole resulted in the formation of silyl phosphoranylidene phosphoranyl imidazole, silyl phosphoranylidene imidazole and triphenylphosphane. Moreover, Lawesson and Japanese reagents afforded imidazole phosphinothioic thioanhydrides.

Keywords: 1-trimethylsilyl-1*H*-imidazole, phosphonium ylides, Lawesson's reagent, phosphoranylidenes, phosphinothioic thioanhydride

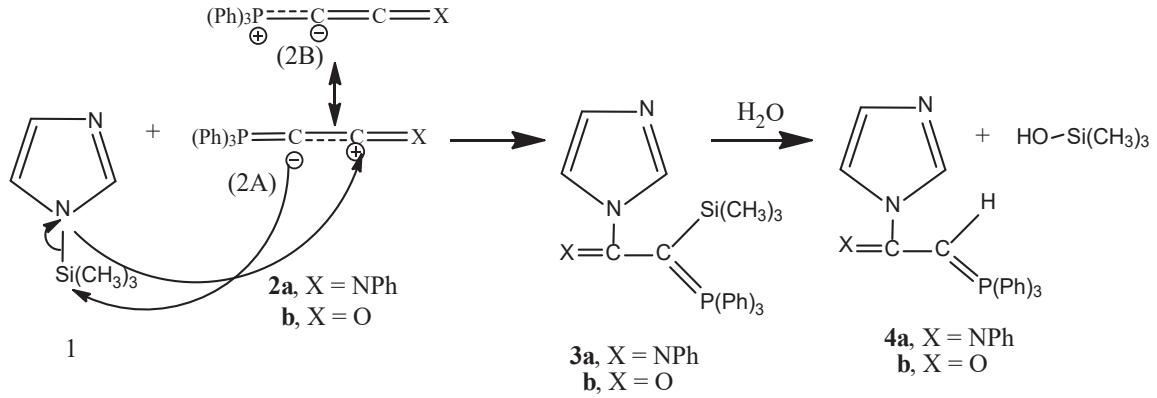
Trimethylsilylimidazoles have received much attention because of their synthetic and application challenges.[1,2] Moreover, the trimethylsilyl group is characterised by chemical inertness and a large molecular volume, which makes it useful in a number of applications.[3–5] Trimethylsilylimidazoles are used as silyl protecting and derivatisation reagents,[6,7] reducing agents,[8] in cross-coupling chemistry[9] and to stabilise α-carbanions and β-carbocations.[9]

Previously we studied the reactions of the active phosphacumulenes, phosphallenes, stabilised phosphonium ylides, Lawesson and Japanese reagents to prepare new heterocyclic and homocyclic compounds containing phosphorus moieties of industrial and biological interest.[10–19]

Results and discussion

We now report the reaction of 1-trimethylsilyl-1*H*-imidazole (**1**) with (*N*-phenyliminovinylidene)triphenylphosphorane (**2a**), (2-oxovinylidene)triphenylphosphorane (**2b**), hexaphenylcarbodiphosphorane (**5**), Lawesson's reagent (**8a**) and Japanese reagent **9a** (Schemes 1–4). The phosphacumulene ylides (**2a** and **2b**) can each be described by the resonance structures **2A** and **2B** (Scheme 1). Accordingly, treatment of **1** with 1 equiv. of **2a** in dry toluene led to the formation of imidazolesilylphosphoranylidene aniline **3a**. When the reaction was performed in hot THF and the product was chromatographed on silica gel, the new compound imidazolephosphoranylidene aniline **4a** was isolated. Adduct **3a** was formed by nucleophilic attack of **2a** on **1** and fast exchange of the trimethylsilyl group between N and phosphorane C, when the reaction was performed in dry toluene. Subsequently, a desilylation reaction of compound **3a** occurred with the formation of **4a** and trimethylsilanol when the reaction was carried out in THF and the product chromatographed on silica gel. The structures of compounds **3a** and **4a** were elucidated by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and mass spectrometry. The most important features in their NMR spectra are the appearance of the trimethylsilyl group at δ –0.026 and 16.11 in the ^{1}H NMR and ^{13}C NMR of compound **3a** respectively and their absence in compound **4a**. Also a doublet appeared at δ 3.18 ($^{2}J_{H\text{-}P}$ = 21), assigned to *H*–C=P(Ph)$_3$, in the ^{1}H NMR spectrum of **4a**. When **1** reacted with the active (2-oxovinylidene) triphenylphosphorane (**2b**) in dry boiling toluene, the corresponding imidazolesilanylphosphoranylidene ethanone **3b** was isolated. In addition, the reaction of **1** with **2b** in THF proceeded with the formation of imidazolephosphoranylidene ethanone **4b**. (Scheme 1).

The reaction of **1** with the phosphallene, hexaphenylcarbodiphosphorane (**5**), was also investigated. Compounds **1** and **5** react in equimolar ratio in boiling toluene to give two products, silylphosphoranylidenephosphoranyl imidazole **6** and silylphosphoranylidene imidazole **7**, together with triphenylphosphane. The reaction proceeds by nucleophilic reaction of compound **5** on 1, producing compound **6**. Since triphenylphosphane is a good leaving group, fragmentation and rearrangement of **6** occurs with the formation of compound **7**



Scheme 1

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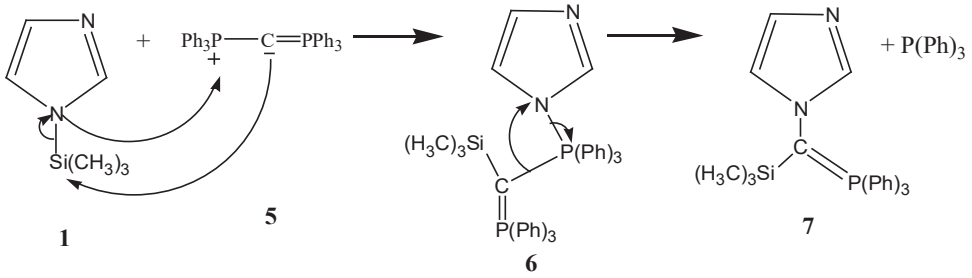
and triphenylphosphane. In the ^{31}P NMR spectrum of compound **6**, two signals were observed at δ 23.20 and 29.04 ppm, while compound **7** showed only one signal at δ 20.45 ppm (Scheme 2).

It is well-known that Lawesson's reagent, 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiaphosphetane-2,4-disulfide (**8a**) can be in equilibrium with a highly reactive thiophosphine ylide (**8b** ↔ **8c**). Compound **8b** ↔ **8c** which is depicted in Scheme 3,[20] can react with **1** in boiling toluene for 5 h to give an imidazole phosphinothioic thioanhydride **14**. When **1** reacted with 2,4-bisthiophenyl-1,3,2,4-dithiaphosphetane-2,4-disulfide (**9a**) in boiling toluene for 7 h, the corresponding imidazole phosphinothioic thioanhydride **15** was obtained. It is believed that **8b** or **9b** reacted first with **1** to form the intermediate **10** or **11**, which decomposed to the dithiol **12** or **13** and trimethylsilanol. Expulsion of hydrogen sulfide from two moles afforded the final products **14** or **15**. A signal at δ 93.28 ppm was observed in the ^{31}P NMR spectrum of compound **15** (Scheme 3).

In addition, the reaction of **1** with diphenyl hydrogen phosphate (**16**) was performed in boiling THF and diphenyl 1*H*-imidazol-1-ylphosphonate (**17**) was obtained, along with trimethylsilanol. The ^{31}P NMR spectrum of **17** showed a signal at δ –11.00 ppm and the mass spectrum showed an ion peak at *m/z* 301 $[M + H]^+$ (Scheme 4).

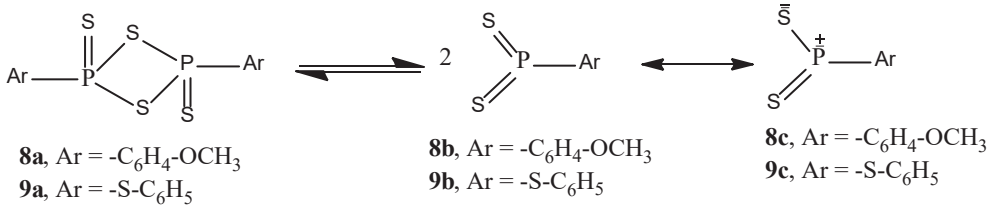
Conclusion

From the above results, the reaction of 1-trimethylsilyl-1*H*-imidazole (**1**) with active phosphacumulenes represents an interesting approach to the synthesis of phosphorus substances, coupled with desilylation due to the high nucleophilicity of phosphacumulene reagents. In contrast, the reaction with phosphallene ylide, which is less nucleophilic, afforded the silylated phosphorus compounds. The reaction of the Lawesson and Japanese reagents with **1** resulted in desilylation coupled with the formation of new compounds containing phosphorus and



1 **5** **6** **7**

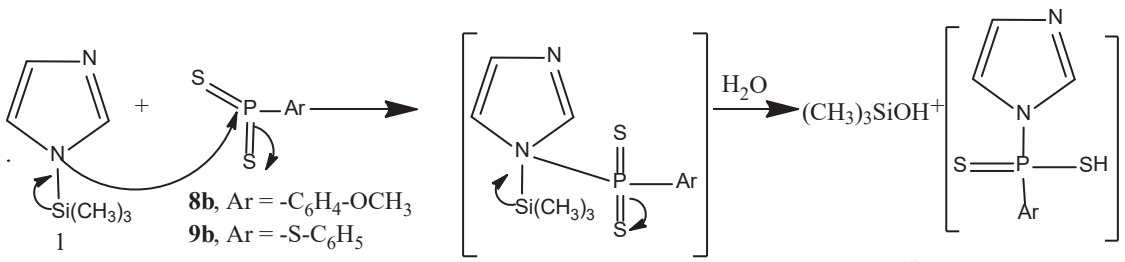
Scheme 2



8a, Ar = -C_6H_4-OCH_3
9a, Ar = -S-C_6H_5

8b, Ar = -C_6H_4-OCH_3
9b, Ar = -S-C_6H_5

8c, Ar = -C_6H_4-OCH_3
9c, Ar = -S-C_6H_5

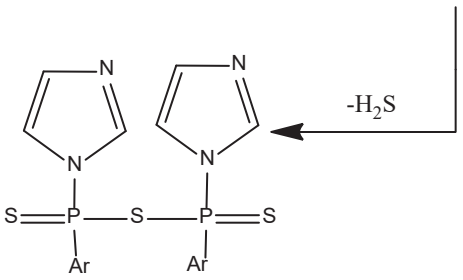


1

8b, Ar = -C_6H_4-OCH_3
9b, Ar = -S-C_6H_5

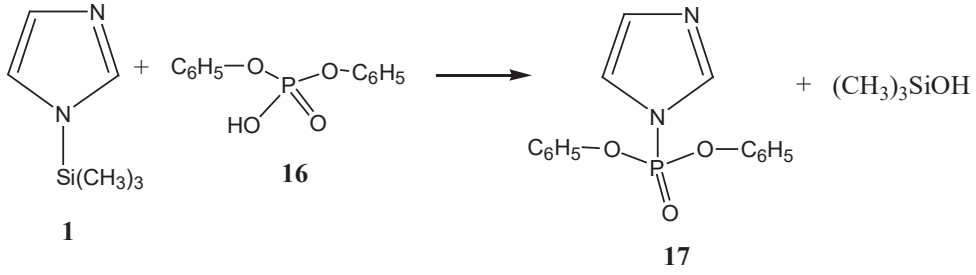
10, Ar = -C_6H_4-OCH_3
11, Ar = -S-C_6H_5

12, Ar = -C_6H_4-OCH_3
13, Ar = -S-C_6H_5



14, Ar = -C_6H_4-OCH_3
15, Ar = -S-C_6H_5

Scheme 3



Scheme 4

sulfur moieties. On the other hand, the reaction of **1** with diphenyl hydrogen phosphate (**16**) resulted in desilylation and formation of a new imidazole phosphonate. It is evident that this synthetic strategy has opened multifaceted preparative possibilities.

Experimental

Melting points were determined with an electrothermal digital melting point apparatus (Electro-Thermal Engineering Ltd., Essex, UK). The IR spectra were recorded in KBr disks on Pye Unicam SP 3300 and Shimadzu FT IR 8101 PC instruments. ^{1}H and ^{13}C NMR spectra were obtained with a Jeol ECA 500 MHz NMR spectrometer using deuterated dimethylsulphoxide (DMSO-d_6) as a solvent and TMS as an internal reference at 500 and 125 MHz respectively. ^{31}P NMR spectra were obtained at 200 MHz. Mass spectra (EI-MS) were obtained with an ISQ (Single Quadrupole MS, Thermo Scientific) instrument. Elemental analyses (C, H, N) were obtained with an Elementar Vario EL instrument and phosphorus was measured by spectrophotometric methods. Silicon was measured using micro-sample volume introduction into an atomic absorption spectrometer (Agilent technology 200 series AA). All data agreed satisfactory with the calculated values. The recorded yields are of pure isolated materials obtained by column chromatography using silica gel 60 (Merck) and thin layer chromatography (TLC), which was performed on Merck Kiesel gel F254 pre-coated plates. Solvents were dried/purified according to literature procedures**.** The starting material **1** was obtained from Aldrich.

Reaction of 1-trimethylsilyl-1H-imidazole (**1**) *with active phosphacumulene ylides* **2a** *and* **2b**

A solution of 1-trimethylsilyl-1*H*-imidazole (**1**) (0.14 g, 0.001 mol) in dry toluen*e* (20 mL) was added to a solution of (*N*-phenyliminovinylidene) triphenylphosphorane (**2a**)[21] (0.37 g, 0.001 mol) or (2-oxovinylidene) triphenylphosphorane (**2b**)[22] (0.30 g, 0.001 mol) in toluene (20 mL). The reaction mixture was refluxed for 5 h when using **2a** and for 7 h when using **2b**. The solvent was removed under reduced pressure and the residue was crystallised from ethyl acetate/petroleum ether (60–80 °C) to give **3a** or **3b.**

N-*[1-(1*H-*Imidazol-1-yl)-2-(trimethylsilyl)-2-(triphenylphosphoranylidene)ethylidene]aniline* (**3a**): Yellow crystals; yield 55%; m.p. 164 °C; IR (KBr) (ν cm^{-1}): 1626 (C=NPh), 1427 (C=P); ^{1}H NMR (500 MHz, DMSO-d_6, δ_{ppm}): –0.026 (s, 9H, Si(CH$_3$)$_3$), 6.87–8.40 (m, 23H, arom.); ^{13}C NMR (500 MHz, DMSO-d_6, δ_{ppm}): 16.11 (3CH$_3$), 117.03–136.80 (C–arom.), 148.00, 151.31 (2C=N); ^{31}P NMR (202.4 MHz, DMSO-d_6, δ_{ppm}): 20.67; MS *m/z*: 517 M$^+$. Anal. calcd for $C_{32}H_{32}N_3PSi$ (517.68): C, 74.24; H, 6.23; N, 8.12; P, 5.98; Si, 5.43; found: C, 74.18; H, 6.15; N, 8.00; P, 5.90; Si, 5.38%.

*1-(1*H-*Imidazol-1-yl)-2-(trimethylsilyl)-2-(triphenylphosphoranylidene)ethanone* (**3b**): Eluent: petroleum ether 60–80 °C/ ethyl acetate (2:8, v/v); colourless crystals; yield 65%; m.p. 100 °C; IR (KBr) (ν cm^{-1}): 1628 (br, C=O), 1431 (C=P); ^{1}H NMR (500 MHz, DMSO-d_6, δ_{ppm}): –0.0024 (s, 9H, Si(CH$_3$)$_3$), 7.70–8.19 (m, 18H, arom.); ^{31}P (202.4 MHz, DMSO-d_6, δ_{ppm}): 20.40 MS *m/z*: 441 [M – H]$^+$. Anal. calcd for $C_{26}H_{27}N_2OPSi$ (442.56): C, 70.56; H, 6.15; N, 6.33; P, 7.00; Si, 6.35; found: C, 70.50; H, 6.05; N, 6.21; P, 6.98; Si, 6.29%.

When the reaction of (*N*-phenyliminovinylidene)triphenylphosphorane (**2a**) (0.37 g, 0.001 mol) or (2-oxovinylidene) triphenylphosphorane (**2b**) (0.30 g, 0.001 mol) with **1** was performed in THF, the reaction mixture was refluxed for 5 h when using **2a** and for 6 h when using **2b**. THF was distilled off under reduced pressure and the residue was subjected to silica gel column chromatography using petroleum ether (60–80 °C)/acetone to give **4a** or **4b** together with trimethylsilanol.

N-*[1-(1*H-*Imidazol-1-yl)-2-(triphenylphosphoranylidene) ethylidene]aniline* (**4a**): Eluent: petroleum ether (60–80 °C)/ acetone (3:7, v/v); colourless crystals; yield 35%; m.p. 277 °C; IR (KBr) (ν cm^{-1}): 1626 (Ph–N=C), 1433 (C=P); ^{1}H NMR (500 MHz, DMSO-d_6, δ_{ppm}): 3.18 (d, 1H, H-C=P(Ph)$_3$), 6.90–7.75 (m, 23H, arom.); ^{13}C NMR (500 MHz, DMSO-d_6, δ_{ppm}): 122.46–150.28 (C–arom.), 151.29 (C=P), 166.70 (C=N); ^{31}P NMR (202.4 MHz, CDCl$_3$, δ ppm): 26.16; MS *m/z*: 445 M$^+$. Anal. calcd for $C_{29}H_{24}N_3P$ (445.49): C, 78.19; H, 5.43; N, 9.43; P, 6.95; found: C, 78.10; H, 5.42; N, 9.39; P, 6.86%.

*1-(1*H-*Imidazol-1-yl)-2-(triphenylphosphoranylidene)ethanone* (**4b**): Eluent: petroleum ether (60–80 °C)/acetone (4:6, v/v); colourless crystals; yield 30%; m.p. 110 °C; ^{1}H NMR (500 MHz, DMSO-d_6, δ_{ppm}): 2.06 (d, 1H, H–C=P(Ph)$_3$), 7.47–7.76 (m, 18H, arom.); ^{13}C NMR (500 MHz, DMSO-d_6, δ_{ppm}): 115.12–146.69 (C–arom.); 153.53 (C=P); 184.33 (C=O); ^{31}P NMR (202.4 MHz, DMSO-d_6, δ_{ppm}): 27.07. Anal. calcd for $C_{23}H_{19}N_2OP$ (370.38): C, 74.58; H, 5.17; N, 7.56; P, 8.36; found: C, 74.50; H, 5.12; N, 7.52; P, 8.31%.

Reaction of hexaphenylcarbodiphosphorane (**5**) *with 1-trimethylsilyl-1H-imidazole* (**1**)

A mixture of 1-trimethylsilyl-1*H*-imidazole (**1**) (0.14 g, 0.001 mol) in 20 mL of dry toluene was added dropwise to a solution of hexaphenylcarbodiphosphorane[23] (**5**) (0.53 g, 0.001 mol) in 20 mL of dry toluene. The reaction mixture was refluxed for 10 h until no more of the starting materials could be detected (TLC). Toluene was distilled off under reduced pressure and the remaining residue was chromatographed on silica gel using petroleum ether (60–80 °C)/ethyl acetate as an eluent to form compounds **6** and **7** together with triphenylphosphane.

*1-{Triphenyl[(trimethylsilyl)(triphenylphosphoranylidene)methyl] phosphoranyl}-1*H-*imidazole* (**6**): Eluent: petroleum ether (60–80 °C)/ ethyl acetate (6:4, v/v) as: Colourless crystals; m.p. 136 °C; yield 25%; IR (KBr) (ν cm^{-1}): 1429 (C=P); ^{1}H NMR (500 MHz, DMSO-d_6, δ_{ppm}): –0.038 (s, 9H, Si–(CH$_3$)$_3$), 6.77–7.52 (m, 33H, arom.); ^{31}P NMR (202.4 MHz, CDCl$_3$, δ_{ppm}): 23.20 and 29.04; MS *m/z*: 414 [M – Ph$_3$P]$^+$, 262 [Ph$_3$P]$^+$. Anal. calcd for $C_{43}H_{42}N_2P_2Si$ (676.84): C, 76.30; H, 6.25; N, 4.14; P, 9.15; Si, 4.15; found: C, 76.29; H, 6.20; N, 4.10; P, 9.08; Si, 4.10%.

*1-[(Trimethylsilyl)(triphenylphosphoranylidene)methyl]-1*H-*imidazole* (**7**): Eluent: petroleum ether (60–80 °C)/ethyl acetate (3:7, v/v); yellow crystals; m.p. 110 °C; yield 30%; IR (KBr) (ν cm^{-1}): 1429 (C=P); ^{1}H NMR (500 MHz, DMSO-d_6, δ_{ppm}): –0.038 (s, 9H, Si–(CH$_3$)$_3$), 7.43–7.50 (m, 18H, arom.); ^{31}P NMR (202.4 MHz, CDCl$_3$, δ_{ppm}): 20.45; MS *m/z*: 152 [M – Ph$_3$P]$^+$, 262 [Ph$_3$P]$^+$. Anal. calcd for $C_{25}H_{27}N_2PSi$ (414.55): C, 72.43; H, 6.56; N, 6.76; P, 7.47; Si, 6.77; found: C, 72.39; H, 6.53; N, 6.72; P, 7.42; Si, 6.70%.

Reaction of Lawesson's reagent (**8a**) *or 4-bisthiophenyl-1,3,2,4-dithiaphosphetane-2,4-disulfide* (**9a**) *with 1-trimethylsilyl-1H-imidazole* (**1**)

A solution of 1-trimethylsilyl-1*H*-imidazole (**1**) (0.14 g, 0.001 mol) in dry toluene (20 mL) was added to a solution of Lawesson's reagent[24]

(**8a**) (0.40 g, 0.001 mol) or the Japanese reagent[25] **9a** (0.40 g, 0.001 mol) in dry toluene (20 mL). The reaction mixture was refluxed for 10 h when using **8a** and for 7 h when using **9a**, during which H_2S gas was evolved. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel using petroleum ether 60–80 °C ethyl acetate as an eluent to give **14** or **15**.

*(1*H*-Imidazol-1-yl)(4-methoxyphenyl)phosphinothioic thioanhydride* (**14**): Eluent: petroleum ether (60–80 °C)/ethyl acetate (3:7, v/v); white crystals; yield 35%, m.p. 175–177 °C; IR (KBr) (ν cm^{-1}): 2923 (OCH_3), 1602 (C=N), 651 (P=S); ^{1}H NMR (500 MHz, DMSO-d_6, δ_{ppm}): 3.79 (s, 6H, $2OCH_3$), 6.98–7.74 (m, 14H, arom.); ^{13}C NMR (500 MHz, DMSO-d_6, δ_{ppm}): 55.64 (OCH_3), 113.87–133.00 (C–arom.), 161.61 (*C*–OCH_3); MS *m/z*: 508 $[M + 2]^+$. Anal. calcd for $C_{20}H_{20}N_4O_2P_2S_3$ (506.54): C, 47.42; H, 3.98; N, 11.06; P, 12.23; S, 18.99; found: C, 47.39; H, 3.95; N, 11.00; P, 12.21; S, 19.00%.

*(1*H*-Imidazol-1-yl)(thiophenyl)phosphinothioic thioanhydride* (**15**): Eluent: petroleum ether (60–80 °C)/ethyl acetate (4:6, v/v); white crystals; yield 55%, m.p. 88–91 °C; IR (KBr) (ν cm^{-1}): 1631 (C=N), 686 (P=S); ^{1}H NMR (500 MHz, DMSO-d_6, δ_{ppm}): 7.39–7.56 (m, 16H, arom.); ^{13}C NMR (500 MHz, DMSO-d_6, δ_{ppm}): 122.00–132.50 (C–arom.); ^{31}P NMR (202.4 MHz, DMSO-d_6, δ_{ppm}): 93.28. Anal. calcd for $C_{18}H_{16}N_4P_2S_5$ (510.62): C, 42.34; H, 3.16; N, 10.97; P, 12.13; S, 31.40; found: C, 42.30; H, 3.13; N, 10.95; P, 12.11; S, 31.35%.

Reaction of diphenyl hydrogen phosphate (**16***) with 1-trimethylsilyl-1H-imidazole* (**1**)

A mixture of 1-trimethylsilyl-1*H*-imidazole (**1**) (0.14 g, 0.001 mol) in dry THF (20 mL) was added dropwise to a solution of **16** (0.25 g, 0.001 mol) in dry THF (20 mL). The reaction mixture was refluxed for 8 h until no more of the starting materials could be detected (TLC). THF was distilled off under reduced pressure and the remaining residue was chromatographed on silica gel using petroleum ether (60–80 °C)/ethyl acetate as an eluent (4:6) to form compound **17**.

*Diphenyl 1*H*-imidazol-1-ylphosphonate* (**17**): White crystals; yield 50%; m.p. 98–100 °C; IR (KBr) (ν cm^{-1}): 1591 (C=N); ^{1}H NMR (500 MHz, $CDCl_3$, δ_{ppm}): 6.78–7.56 (m, 13H, arom.); ^{13}C NMR (500 MHz, DMSO-d_6, δ_{ppm}): 122.00–157.30 (C–arom.); ^{31}P NMR (202.4 MHz, $CDCl_3$, δ_{ppm}): –11.00; MS *m/z*: 301 $[M + H]^+$; Anal. calcd for $C_{15}H_{13}N_2O_3P$ (300.25): C, 60.00; H, 4.36; N, 9.33; P, 10.32; found: C, 59.89; H, 4.33; N, 9.30; P, 10.21%.

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