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1,2-DIHYDROPYRAZOLO- AND 1,2-DIHYDROTHIENO-1λ^5-[2,4,1]-DIAZAPHOSPHININES

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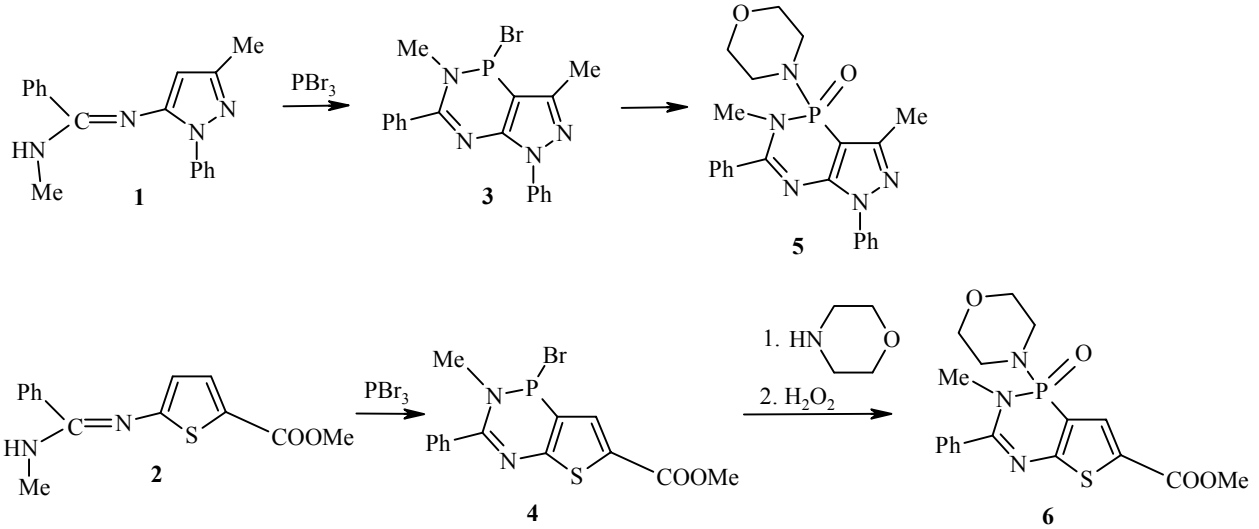
In previous work [1], we showed that the reaction of N^1,N^1-dimethyl-N^2-5-pyrazolyl- and N^1,N^1-dimethyl-N^2-5-thienylforamidines with trivalent phosphorus halides permits the introduction of a dihalophosphine group into the hetaryl residue at the position adjacent to the amidine function and opens broad possibilities for the modification of heterocycles by introducing various substituents at the phosphorus atom and by means of intramolecular heterocyclization [1, 2].

We have found that 3-methyl-5-(α-methylaminobenzylidene)amino-1-phenylpyrazole (**1**) and 5-(α-methylaminobenzylidene)amino-2-methoxycarbonylthiophene (**2**), which contain an NH function in the amidine fragment, react with phosphorus tribromide at two nucleophilic sites, namely, the nitrogen atom of the NH group and a heteroaromatic carbon atom to give 1-bromo-1,2-dihydro-1λ^3-[2,4,1]-diazaphosphinines **3** and **4**, which were characterized by ^{31}P NMR spectroscopy. Products **3** and **4** were used to synthesize tetracoordinated phosphorus derivatives **5** and **6**, whose structures were confirmed using ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy.



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The X-ray diffraction structural analysis data of **6** will be published in a subsequent communication.

The NMR spectra were taken on a Varian 300 spectrometer at 300 MHz for the ^{1}H NMR spectra and at 75 MHz for the ^{13}C NMR spectra with TMS as the intermal standard and at 121 MHz for the ^{31}P NMR spectra with 85% H_3PO_4 as the external standard. All the operations with the trivalent phosphorus derivatives were carried out using dry solvents in an argon atmosphere.

2-Methoxycarbonyl-5-(α-methylaminobenzylidene)aminothiophene (2). A sample of (N-methyl)-benzimidoyl chloride (0.01 mol) was added with stirring to a solution of (0.01 mol) 5-amino-2-methoxycarbonylthiophene (0.01 mol) and triethylamine (0.011 mol) in benzene (30 ml) cooled to 10°C. The reaction mixture was maintained for 12 h at 25°C. The precipitate was filtered off and the mother liquor was evaporated. The solid oily residue was recrystallized to give **2** in 47% yield; mp 133-134°C (ethanol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J* (Hz): 3.65 (3H, s, C$\underline{H}_3$–O); 2.88 (3H, d, J_{HH} = 4.5, C$\underline{H}_3$–N); 6.61 (1H, d, J_{HH} = 3.9, C$\underline{H}$=C–N, hetaryl); 7.29-7.48 (6H, m, $C_6\underline{H}_5$ + C$\underline{H}$=C–C, hetaryl); 7.88 (1H, br. s, N$\underline{H}$). Found, %: C 61.25, 61.27; H 5.11, 5.14; N 10.19, 10.22. $C_{14}H_{14}N_2O_2S$. Calculated, %: C 61.29; H 5.14; N 10.21.

3-Methyl-5-(α-methylaminobenzylidene)amino-1-phenylpyrazole (1) was synthesized in 80% yield analogously to **2** from 5-amino-3-methyl-1-phenylpyrazole; mp 203-204°C (ethanol–water). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 2.09 (3H, s, C$\underline{H}_3$–C); 3.03 (3H, br. s, C$\underline{H}_3$–N); 4.89 (1H, s, hetaryl); 4.82 (1H, br. s, N$\underline{H}$); 7.72 (2H, d, $^{3}J_{HH}$ = 7.8, *o*-$C_6\underline{H}_5$–N); 7.13-7.39 (8H, m, *m,p*-$C_6\underline{H}_5$N + C–$C_6\underline{H}_5$). Found, %: C 74.44, 74.48; H 6.24, 6.27; N 19.35, 19.31. $C_{18}H_{18}N_4$. Calculated, %: C 74.46; H 6.25, N 19.29.

6-Methoxycarbonyl-2-methyl-1-morpholino-1-oxo-3-phenyl-1,2-dihydro-1λ^5-thieno[3,2-*e*]-2,4,1-diazaphosphinine (6). A sample of phosphorus tribromide (0.01 mol) was added with stirring to a solution of compound **2** (0.01 mol) in pyridine (10 ml) cooled to 10°C and maintained at 25°C for 3 h. ^{31}P NMR spectrum of 1-bromo-1,2-dihydro-1λ^3-thieno[3,2-*e*]-2,4,1-diazaphosphinine **4** δP: 107 ppm. The mixture was cooled to 10°C and morpholine (0.04 mol) was added with stirring. After 2 h, pyridine was evaporated in vacuum. The residue was dissolved in benzene (20 ml) and 30% aq. hydrogen peroxide (5 ml) was added with stirring and cooling. The reaction mixture was stirred for 5 h. Then, the organic layer was separated, washed with two 30-ml water portions, and evaporated in vacuum. The oily residue was crystallized; mp 193-194°C (2-propanol). Yield of **6** 40%. ^{31}P NMR spectrum ($CHCl_3$), δP: 9 ppm. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 3.92 (3H, s, C$\underline{H}_3$–O); 3.15 (3H, d, $^{3}J_{HP}$ = 6.6, C$\underline{H}_3$–N); 2.99 and 3.26 (4H, m, C$\underline{H}_2$–N); 3.64 (4H, m, C$\underline{H}_2$–O); 7.43-7.52 (5H, m, C_{Ar}); 7.94 (1H, d, $^{3}J_{HP}$ = 5.7, hetaryl). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 32.79 (d, $^{2}J_{CP}$ = 5.7, $\underline{C}H_3N$), 44.70 (s, –$\underline{C}H_2N$), 52.77 (s, $\underline{C}H_3OC(O)$), 67.54 (d, $^{3}J_{CP}$ = 5.3, $\underline{C}H_2O$), 111.15 (d, $^{1}J_{CP}$ = 169, C–P), 127.97 (s, *m*-C_{Ar}), 129.18 (s, *o*-C_{Ar}), 129.53 (d, $^{3}J_{CP}$ = 19.7, $C_{(6)}$), 130.51 (s, *p*-C_{Ar}), 131.27 (d, $^{2}J_{CP}$ = 13.7, $C_{(7)}$), 135.59 (d, $^{3}J_{CP}$ = 5.7, *i*-C_{Ar}), 160.54 (s, $C_{(3)}$), 162.45 (s, $\underline{C}$=O), 167.51 (d, $^{3}J_{CP}$ = 10.9, S–$\underline{C}$–N). Found, %: P 7.59, 7.61; N 10.40; 10.37. $C_{18}H_{20}N_3O_4PS$. Calculated, %: P 7.64; N 10.36.

2,7-Dimethyl-1-(morpholino)-1-oxo-3,5-diphenyl-5H-1λ^5-pyrazolo[4,5-*e*]-2,4,1-diazaphosphinine (5) was synthesized in 60% yield analogously to **6** from pyrazole **1**. ^{31}P NMR spectrum of intermediate 1-bromo-2,7-dimethyl-3,5-diphenyl-1,2-dihydro-5H-1λ^3-pyrazolo[4,5-*e*]-2,4,1-diazaphosphinine (**3**), δP: 120 ppm. The mp of **5** 210-211°C (2-propanol). ^{31}P NMR spectrum ($CHCl_3$), δP: 11.6 ppm. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 2.58 (3H, s, C$\underline{H}_3$–C); 3.14 (3H, d, $^{3}J_{HP}$ = 6.6, C$\underline{H}_3$–N); 3.05 and 3.30 (4H, m, C$\underline{H}_2$–N); 3.68 (4H, t, $^{3}J_{HH}$ = 4.5, C$\underline{H}_2$–O); 7.94 (2H, d, $^{3}J_{HH}$ = 7.5, *o*-$C_{Ph\text{-}N}$); 7.22-7.55 (8H, m, *m,p*-$C_{Ph\text{-}N}$ + $C_{Ph\text{-}C}$). Found, %: P 7.40, 7.38; N 16.65, 16.68. $C_{22}H_{24}N_5O_2P$. Calculated, %: P 7.35; N 16.62.

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