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NOVEL BENZODIAZAPHOSPHININES WITH AN ENDOCYCLIC P–C BOND

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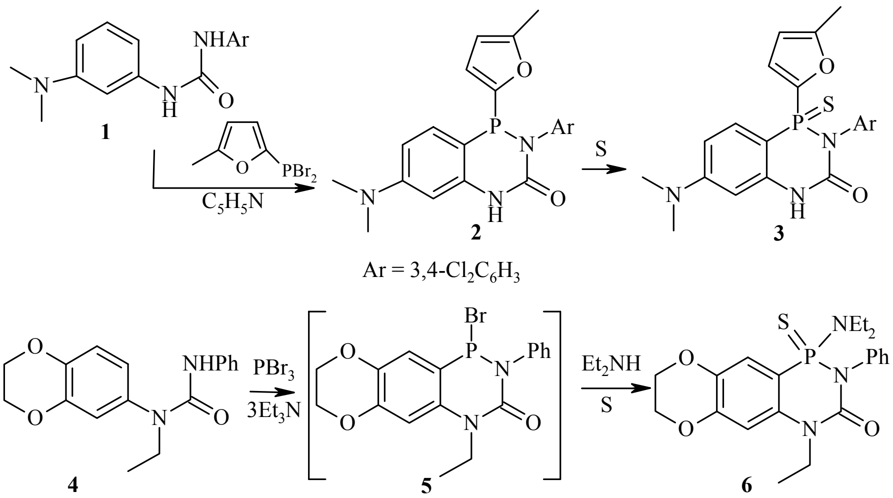
Phosphorylation of substituted ureas is a synthetic method for phosphorus-containing heterocycles [1-4]. It was of interest to study the possibility of formation of condensed phosphorus-containing heterocyclic systems by C-phosphorylation of electron-enriched diarylureas containing a ureide group in the position *ortho* to the C-nucleophilic center of the benzene ring. By reaction of phosphorus(III) halides with ureas **1** and **2**, we synthesized novel types of condensed phosphorus-containing systems with a 2,4,1-benzodiazaphosphinine ring (**3-6**); we did not isolate compound **5** when the P-thioxide **6** was obtained.

The structure of the synthesized compounds was confirmed by ^{31}P and ^{1}H NMR. A characteristic sign that a ring was formed in the case of compound **3** is the presence in the ^{1}H NMR spectrum of only one signal from the NH proton, and also the absence of a signal from the proton in the 4 position of the phenylenediamine moiety and a change in the character of the spin–spin coupling of the protons in it; and in the case of compound **6**, the absence in the ^{1}H NMR spectrum of a signal from the NH proton and simplification (as compared with the starting urea **2**) of the part of the spectrum assigned to the aromatic protons of the benzodioxane moiety. In the latter case, the signals from protons at the $C_{(5)}$ and $C_{(10)}$ atoms appear as two doublets with spin–spin coupling constant at the phosphorus atom of 6.3 Hz and 13.8 Hz, respectively.



1 2 3

Ar = 3,4-$Cl_2C_6H_3$

4 5 6

δP = 103.4 ppm

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Ureas **1** and **2** were synthesized by a general procedure from the corresponding anilines and isocyanates in dioxane [5].

N-(3,4-Dichlorophenyl)-N'-[3-(dimethylamino)phenyl]urea (1). Mp 207-209°C. ^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm, *J*, Hz: 2.87 (6H, s, Me$_2$N); 6.39 (1H, dd, ^{1}J = 8.0, ^{2}J = 2); 6.70 (1H, dd, ^{1}J = 8.0, ^{2}J = 1.2); 6.91 (1H, t, ^{2}J = 1.6); 7.07 (1H, t, ^{1}J = 8.0); 7.32 (1H, dd, ^{1}J = 8.8, ^{2}J = 2.4); 7.5 (1H, d, ^{1}J = 8.8): 7.88 (1H, d, ^{2}J = 2.4); 8.62 (1H, s, NH); 8.90 (1H, s, NH). Found, %: C 55.67; H 4.54; N 12.96; Cl 21.37. $C_{15}H_{15}Cl_2N_3O$. Calculated, %: C 55.57; H 4.66; N 12.96; Cl 21.87.

N-Ethyl-N-(3,4-ethylenedioxyphenyl)-N'-phenylurea (2). Mp 90-92°C. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm, *J*, Hz: 1.15 (3H, t, $NCH_2\underline{CH}_3$); 3.72 (2H, q, $N\underline{CH}_2$); 4.30 (4H, s, OC_2H_4O); 6.18 (1H, br. s, NH); 6.76 (1H, dd); 6.83 (1H, d); 6.96 (1H, m); 6.99 (1H, t); 7.25 (4H, m). Found, %: N 9.2; P 7.42. $C_{20}H_{18}Cl_2N_3O_2P$. Calculated, %: N 9.68; P 7.13.

2-(3,4-Dichlorophenyl)-6-dimethylamino-1-(5-methyl-2-furyl)-1,4-dihydro-2,4,1-benzodiazaphosphinan-3-one (3). A solution of diarylurea **1** (1.9 g, 5.88 mmol) in pyridine (10 ml) was added with stirring to a solution of dibromo(5-methyl-2-furyl)phosphine (1.6 g, 5.88 mmol) in pyridine (10 ml). This was allowed to stand at ~20°C for 2 days. Then triethylamine (1.8 g, 17.64 mmol) was added and it was stirred for 0.5 h. Pyridine was evaporated under vacuum, and the product was extracted with hot toluene and reprecipitated with hexane. Yield 1.8 g (70.5%); mp 210-215°C (MeCN, with decomposition). ^{31}P NMR spectrum (CHCl$_3$): 11.3 ppm. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm, *J*, Hz: 2.28 (3H, s, Me); 2.87 (6H, s, Me$_2$N); 5.90 (1H, s); 6.18 (1H, s); 6.29 (1H, d, ^{2}J = 2.7); 6.46 (1H, d, ^{1}J = 8.1); 7.21 (1H, d); 7.26 (1H, dd); 7.42 (1H, d, ^{1}J = 8.1); 7.48 (1H, s); 8.75 (1H, br. s, NH). Found, %: N 8.61; P 6.83; S 7.2. $C_{20}H_{18}Cl_2N_3O_2PS$. Calculated, %: N 9.01; P 6.64; S 7.2.

2-(3,4-Dichlorophenyl)-6-dimethylamino-1-(5-methyl-2-furyl)-3-oxo-1,4-dihydro-2,4,1λ^{5}-benzodiazaphosphinine-1-thioxide (4). Elemental sulfur (0.034 g, 1.1 mmol) was added to a solution of benzodiazaphosphinane **3** (0.5 g, 1.1 mmol) in pyridine (10 ml). After the sulfur dissolved, the pyridine was evaporated under vacuum, the residue was recrystallized from 2-propanol. Yield 0.2 g (39%); mp 266°C. ^{31}P NMR spectrum (DMSO): 38 ppm. ^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm, *J*, Hz: 2.32 (3H, s, Me); 2.98 (6H, s, Me$_2$N); 6.23 (1H, br.); 6.35 (1H, br. d, *J* = 4.4); 6.60 (1H, d, *J* = 9.3); 6.95 (2H, m); 7.18 (1H, br.); 7.31 (1H, d, ^{1}J = 8.5); 7.65 (1H, d, ^{1}J = 8.5); 10.60 (1H, s, NH). Found, %: C 68.4; H 6.05; N 9.75. $C_{17}H_{18}N_2O_3$. Calculated, %: C 68.44; H 6.08; N 9.39.

1-Diethylamino-3-oxo-2-phenyl-4-ethyl-6,7-ethylenedioxy-1,4-dihydro-2,4,1λ^{5}-benzodiazaphosphinine-1-thioxide (6). Phosphorus tribromide (0.15 ml, 1.59 mmol) and triethylamine (0.67 ml, 4.78 mmol) were added with stirring to a solution of urea **2** (0.5 g, 1.59 mmol) in pyridine (50 ml). After 2 days, diethylamine (0.17 ml, 1.59 mmol) and elemental sulfur (0.051 g, 1.59 mmol) were added with stirring to the reaction mixture. After the sulfur dissolved, the pyridine was evaporated off under vacuum, and the residue was triturated with water and recrystallized from 2-propanol. Yield 0.35 g (51%); mp 170°C. ^{31}P NMR spectrum (acetone): 60.4 ppm. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm, *J*, Hz: 0.79 (6H, t, $PNCH_2\underline{CH}_3$); 1.33 (3H, t, 4-$NCH_2\underline{CH}_3$); 3.02 (2H, dt, $PN\underline{CH}_2$); 3.24 (2H, dt, $PN\underline{CH}_2$); 4.01 (2H, m, 4-$N\underline{CH}_2$); 4.28 (2H, t, OCH$_2$); 4.32 (2H, t, OCH$_2$); 6.67 (1H, d, $J_{m\text{-PCCH}}$ = 6.3, 5-CH); 7.24 (1H, $J_{o\text{-PCCH}}$ = 13.8, d, 10-CH); 7.39 (5H, m, NPh). Found, %: N 9.63; P 7.11; S 7.5. $C_{21}H_{26}N_3O_3PS$. Calculated, %: N 9.63; P 7.11; S 7.5.

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