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NOVEL APPROACH TO SYNTHESIS OF 1,2-DIHYDROBENZ[*c*]-[1,2]AZAPHOSPHOL-3-ONES

A. A. Chekotilo, A. A. Yurchenko, and A. A. Tolmachev

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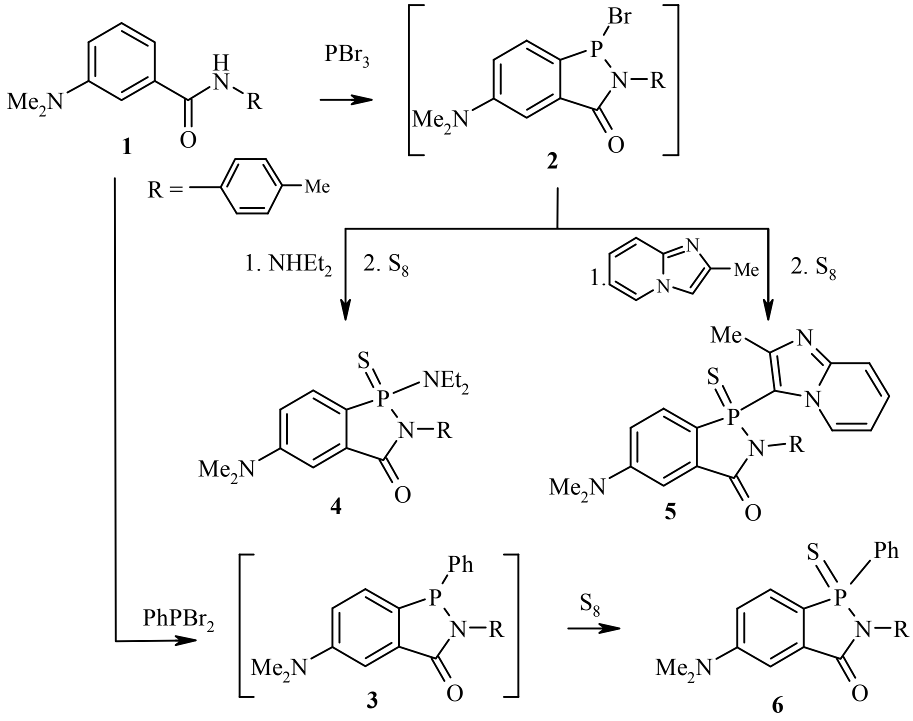
1,2-Dihydrobenz[*c*][1,2]azaphosphol-3-ones, which can be considered as the phosphorus analogs of phthalimides, have been little studied [1,2].

We have found that 2-aryl-5-dimethylamino-1,2-dihydrobenz[*c*][1,2]azaphosphol-3-ones **2** and **3** are formed on reaction of amides of *m*-dimethylaminobenzoic acid **1** with phosphorus(III) bromides in pyridine in the presence of triethylamine at room temperature. The reaction of benzazaphosphole **2** with secondary amines or 2-substituted imidazo[1,2-*a*]pyridines followed by addition of elemental sulfur leads to benzazophospholes **4** and **5**, respectively. Compound **6** is obtained similarly from benzazaphosphole **3**.



Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kiev 02056; e-mail: hetfos@ukrpack.net Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 569-570, April, 2001. Original article submitted December 9, 2000.

Solution of Bromobenzophosphole 2. Phosphorus tribromide (4.2 mmol) was added dropwise to a solution of amide **1** (4.2 mmol) [3] and triethylamine (12.6 mmol) in pyridine at 0°C (15 ml). The reaction mixture was held for 3 h at room temperature, and used without purification for further conversions. We observe a signal at 110.5 ppm in the ^{31}P NMR spectrum of the reaction mixture.

1-Diethylamino-5-dimethylamino-2-(4-methylphenyl)-1-thiooxo-1,2-dihydro-1λ^5-benzo[*c*][1,2]-azaphosphol-3-one (4). Diethylamine (4.2 mmol) and then 30 min later elemental sulfur (5 mmol) were added to the solution of bromobenzphosphole **2**. After 12 h, benzene (50 ml) was added and the mixture was stirred, then the precipitate was filtered off and the filtrate was evaporated down. The residue was chromatographed on silica gel with toluene as the eluent. Yield 67%; mp 201-203°C (ethanol). ^{31}P NMR spectrum (CDCl$_3$): 63.9 ppm. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm, *J*, Hz: 0.83 (6H, t, N(CH$_2\underline{CH_3}$)$_2$); 2.38 (3H, s, CH$_3$; 3.02 (2H, m, N$\underline{CH_2}$CH$_3$); 3.10 (6H, s, N(CH$_3$)$_2$); 3.22 (2H, m, N$\underline{CH_2}$CH$_3$); 6.95 (1H, m, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.1, $^4J_{HP}$ = 3.9, 6-H); 7.3 (5H, m, 4-H, NC$_6\underline{H}_4$CH$_3$); 7.6 (1H, dd, $^3J_{HH}$ = 8.7, $^3J_{HP}$ = 11.7, 7-H). Found, %: N 10.73, 10.82; P 7.93, 7.95. C$_{20}$H$_{26}$N$_3$OPS. Calculated, %: N 10.84; P 7.99.

5-Dimethylamino-1-(2-methylimidazo[1,2-*a*]pyridin-3-yl)-2-(4-methylphenyl)-1-thiooxo-1,2-dihydro-1λ^5-benz[*c*][1,2]azaphosphol-3-one (5). 2-Methylimidazo[1,2-*a*]pyridine (4.2 mmol) and then 30 min later elemental sulfur (5 mmol) were added to the solution of bromobenzphosphole **2**. After 12 h, benzene (50 ml) was added to the reaction mixture and the mixture was stirred, then the precipitate was filtered off and the filtrate was evaporated down, and the residue was recrystallized from toluene. Yield 35%; mp 251-253°C (toluene). ^{31}P NMR spectrum (CDCl$_3$); 37.6 ppm. ^{1}H NMR spectrum (CDCl$_3$), δ, ppm, *J*, Hz: 2.16 (3H, s, 2'-CH$_3$); 2.30 (3H, s, NC$_6\underline{H}_4$CH$_3$); 3.16 (6H, s, N(CH$_3$)$_2$); 6.74 (1H, t, $^3J_{HH}$ = 7.1, 6'-H); 6.96 (2H, d, $^3J_{HH}$ = 7.9, *o*-CH$_3$C$_6\underline{H}_4$); 7.00 (1H, m, 6-H); 7.10 (2H, d, $^3J_{HH}$ = 7.9, *m*-CH$_3$C$_6\underline{H}_4$); 7.32 (1H, dd, $^3J_{HH}$ = 7.1, $^3J_{HH}$ = 8.5, 7'-H); 7.38 (3H, br. s, 4-H); 7.61 (1-H, br. d, $^3J_{HH}$ = 8.5, 8'-H); 7.67 (1H, dd, $^3J_{HH}$ = 8.7, $^3J_{HP}$ = 11.7, 7-H); 9.1 (1-H, br. d, $^3J_{HH}$ = 7.1, 5'-H). Found, %: N 12.46, 12.51; P 6.87, 6.91. C$_{24}$H$_{25}$N$_4$OPS. Calculated, %: N 12.55; P 6.94.

5-Dimethylamino-2-(4-methylphenyl)-1-phenyl-1-thiooxo-1,2-dihydro-1λ^5-benzo[*c*][1,2]-azaphosphol-3-one (6). Dibromophenylphosphine (4.2 mmol) was added dropwise to a solution of amide **1** (4.2 mmol) [3] and triethylamine (12.6 mmol) in pyridine (15 ml) at 0°C, and then the mixture was allowed to stand for 4.5 h at room temperature. Then elemental sulfur (5 mmol) was added. After 12 h, the precipitate was filtered off, washed with water, and recrystallized from acetonitrile. Yield 54%; mp 235-236°C (acetonitrile). ^{31}P NMR spectrum (dioxane): 56.6 ppm. ^{1}H NMR spectrum (CF$_3$COOD), δ, ppm, *J*, Hz: 2.58 (3H, s, CH$_3$); 3.87 (6H, s, N(CH$_3$)$_2$); 7.2 (2H, d, $^3J_{HH}$ = 7.8, *o*-CH$_3$C$_6\underline{H}_4$); 7.43 (2H, d, $^3J_{HH}$ = 7.8, *m*-CH$_3$-C$_6\underline{H}_4$); 7.9 (5H, br. s+m, 6,7,3',4',5'-H); 8.43 (2H, m, 2',6'-H); 8.87 (1H, s, 4-H). Found, %: N 7.06, 7.11; P 7.75, 7.82. C$_{22}$H$_{21}$N$_2$OPS. Calculated, %: N 7.14; P 7.89.

The ^{1}H and ^{31}P NMR spectra were obtained on a Varian VXR-300.

REFERENCES

1. J. A. Miles and R. W. Street, *J. Org. Chem.*, **43**, 4668 (1978).
2. O. Nir, M. Fridkin, and Y. Segall, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **109**, 241 (1996).
3. V. Kmonicek, E. Svatek, J. Holubek, M. Ryska, M. Valchar, and M. Protiva, *Collect. Czech. Chem. Commun.*, **55**, 1817 (1990).