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NEW APPROACH TO THE SYNTHESIS OF 3H-1,3-BENZAZAPHOSPHOLES

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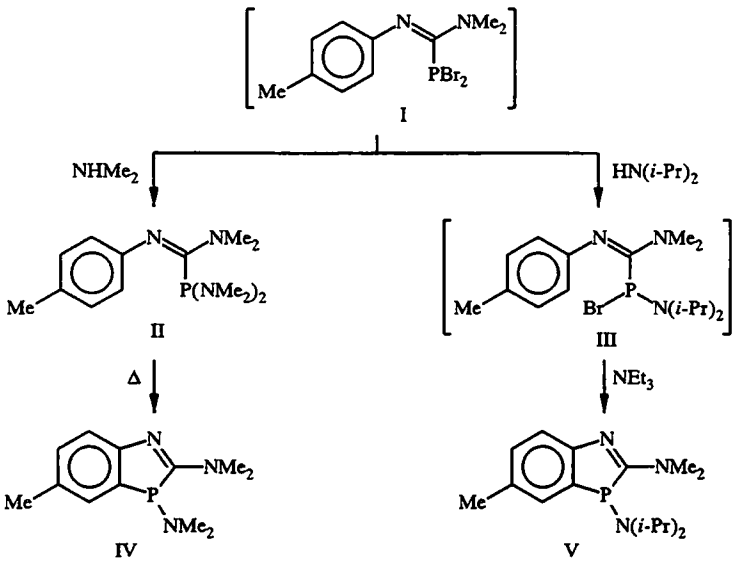
In contrast to 1H-1,3-benzazaphospholes [1], the isomeric 3H-1,3-benzazaphospholes are compounds which are not easily accessible and little studied [2, 3].

We found that the previously unknown 2,3-tetraalkyldiamino derivatives of benzazaphospholes, (IV) and (V), can be synthesized by the thermal cyclization of the diamidophosphonite (II) or the cyclization of the bromamidophosphonite (III), which occurs in the presence of a base at room temperature for 1 day. The synthesis of compounds (II) and (III) is accomplished *in situ* by the action of excess dimethylamine or diisopropylamine correspondingly on the dibromophosphine (I), previously described [4].

Solution of the Dibromophosphine (I). This is obtained as follows. To the mixture of 50 ml of pyridine, 50 ml of methylene chloride, 0.1 mole of N,N-dimethyl-N′-p-tolylformamidine, and 0.3 mole of triethylamine at 0°C is added, dropwise, 0.1 mole of phosphorus tribromide. The reaction mixture is left for 15 h, and is utilized without purification for further conversions.

Compound (IV). To the solution of the dibromophosphine (I), cooled to −30°C, is added 0.5 mole of dimethylamine, and the mixture is left at room temperature for 1 h. (All further operations for the purification of the diamidophosphonite (II) are conducted at a temperature not exceeding 20°C). The solvent is evaporated prior to the addition of 50 ml of benzene. The residue is separated, and the filtrate is concentrated to dryness. The residue is primed with pentane, and the solution is separated from the oil, and is concentrated. In the residue is the diamidophosphonite (II). Compound (IV) is obtained by the distillation of the diamidophosphonite (II) *in vacuo*.



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Compound (V). To the solution of the dibromophosphine (I) is added 0.5 mole of diisopropylamine with cooling to 0°C. The signal at 65.1 ppm, which we assign to the bromamidophosphonite (III), appears initially in the ^{31}P NMR spectra. After stirring the sample at room temperature for 24 h, it is completely converted to the signal with the δ_P = 35.7 ppm. The solvent is evaporated. The residue is primed with 50 ml of benzene, and the solution is filtered. The solvent is distilled off. The substance is purified by distillation *in vacuo*.

(N,N-Dimethyl-N'-p-tolylformamidino)tetramethyldiamidophosphonite (II). ($C_{14}H_{25}N_4P$). The ^{31}P NMR spectrum (benzene) is characterized at 97.0. The PMR spectrum (C_6D_6) is as follows: 2.19 ppm (3H, s, 4-Me), 2.48 ppm [12H, d, $^3J_{PH}$ = 8.7 Hz, $P(NMe_2)_2$], 2.73 ppm (6H, s, NMe_2), 6.82 ppm (2H, d, $^3J_{HH}$ = 7.8 Hz, ortho-H), and 6.99 ppm (2H, d, $^3J_{HH}$ = 7.8 Hz, meta-H).

2,3-Bis(dimethylamino)-5-methyl-1,3-benzazaphosphole (IV). ($C_{12}H_{18}N_3P$). The yield is 36%. The bp is 123-125°C (0.03 mm Hg). The mp is 101-102°C. The ^{31}P NMR spectrum (benzene) is characterized at 60.1. The PMR spectrum (C_6D_6) is as follows: 2.15 ppm (3H, s, 5-Me), 2.35 ppm (6H, d, $^3J_{PH}$ = 9.3 Hz, 3-NMe_2), 2.69 ppm (3H, s, 2-NMe), 2.95 ppm (3H, s, 2-NMe), 7.02 ppm (1H, d, $^3J_{HH}$ = 7.8 Hz, 7-H), 7.34 ppm (1H, broad s, 4-H), and 7.55 ppm (1H, d, $^3J_{HH}$ = 7.8 Hz, 6-H). The ^{13}C NMR spectrum (C_6D_6) is as follows: 20.97 ppm (d, $^4J_{PC}$ = 1.1 Hz, 5-Me), 37.4 ppm (s, 2-NMe), 40.4 ppm (s, 2-NMe), 41.67 ppm (d, $^2J_{PC}$ = 12 Hz, 3-NMe), 119.57 ppm (s, 7-C), 129.28 ppm (d, $^1J_{PC}$ = 7.9 Hz, 3a-C), 129.80 ppm (d, $^2J_{PC}$ = 24.0 Hz, 4-C), 130.41 ppm (d, $^3J_{PC}$ = 6.6 Hz, 5-C), 131.98 ppm (s, 6-C), 157.30 ppm (d, $^2J_{PC}$ = 8.9 Hz, 7a-C), and 175.52 ppm (d, $^1J_{PC}$ = 21.5 Hz, 2-C).

3-Diisopropylamino-2-dimethylamino-5-methyl-1,3-benzazaphosphole (V). ($C_{16}H_{26}N_3P$). The yield is 25%. The bp is 145-150°C (0.02 mm of Hg). The mp is 122-124°C. The ^{31}P NMR spectrum (benzene) is as follows: 35.77 s and 35.63 s (1:1). The PMR spectrum (C_6D_6) is as follows: 0.66 ppm, 0.72 ppm, 1.19 ppm, 1.32 ppm [4 × 3H, d, $^3J_{HH}$ = 6.3 Hz, 3-$N(CH\underline{Me}_2)_2$], 2.19 ppm (3H, s, 5-Me), 2.97 ppm [8H, m, 2-NMe_2, 3-$N(\underline{CH}Me_2)_2$], 7.02 ppm (1H, d, $^3J_{HH}$ = 7.8 Hz, 7-H), 7.38 ppm (1H, broad s, 4-H), and 7.59 ppm (1H, d, $^3J_{HH}$ = 7.8 Hz, 6-H).

The data of the elemental analysis for the compounds (IV) and (V) correspond with the calculated data.

The ^1H, ^{31}P, and ^{13}C NMR spectra were taken on the Varian VXR-300 instrument at 300, 121, and 75 MHz correspondingly.

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