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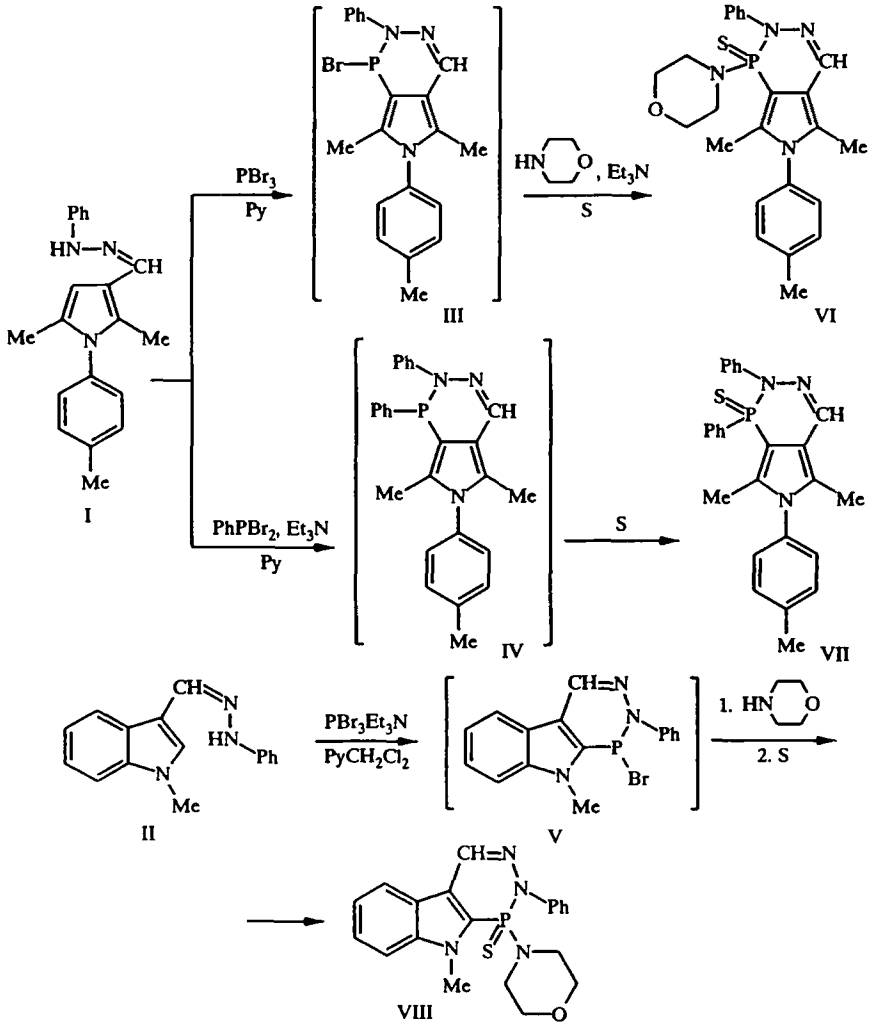
HETEROCONDENSED 1,2,3-DIAZOPHOSPHORINES

S. P. Ivonin, A. A. Chaikovskaya, T. N. Kudrya,
T. E. Terikovskaya, and A. A. Tolmachev

It is has been shown that the interaction of phenylhydrazones of pyrrolecarbaldehydes and indolecarbaldehydes with trivalent phosphorus halides results in annelation of the 1,2,3-diazophosphorine ring.

Up to the present time, only one example has been reported for the synthesis of the 1,2,3-diazophosphorine ring by reaction of the difficulty accessible phosphine of nitriloimine with the dimethyl ester of acetylene dicarboxylic acid [1-3].



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We have found that the phenylhydrazones of the pyrrolecarbaldehyde I and the indolecarbaldehyde II interact with trivalent phosphorus halides to form a 1,2,3-diazophosphorine ring. The bromophosphines III and V and the phosphine IV were identified on the basis of their ^{31}P NMR spectra, and were characterized after conversion to the amidophosphine thioxides VI and VIII and the phosphine thioxide VII. The hydrazone I is more active in this reaction, as indicated by the synthesis of the phosphine IV. We were not able to carry out the analogous reaction with the hydrazone II.

EXPERIMENTAL

5,7-Dimethyl-2-phenyl-6-(p-tolyl)-1-(N-morpholino)-1-thio-1,2-dihydropyrrolo[3,4-d][1,2,3]diazophosphorine (VI). To a solution of 0.01 mole of phosphorus tribromide in 10 ml of pyridine, a solution of 0.1 mole of the phenylhydrazone I in 10 ml of pyridine was added dropwise, with cooling and stirring. The reaction mixture was held 24 h (^{31}P NMR 96.4 ppm). Then, a solution of 0.01 mole of morpholine and 0.03 mole of triethylamine in 30 ml of benzene was added with cooling and stirring. After 2 h, 0.01 mole of sulfur was added, and the mixture was refluxed for 1 h. The precipitate was filtered off, the filtrate was evaporated down, and the residue was treated with ethanol. Yield 55%, mp 191-195°C (from ethanol). ^{31}P NMR spectrum ($CHCl_3$), ppm: 47.1. PMR spectrum ($CDCl_3$, TMS), ppm: 2.15 (3H, s, 1-CH_3); 2.26 (3H, d, J_{HP} = 1.0 Hz, 2-CH_3); 2.46 (3H, s, Ph−CH_3); 3.00, 3.30 (4H, m, N−CH_2); 3.48 (4H, t, J_{HH} = 4.8 Hz, O−CH_2); 7.25 (7H, m, m-H tolyl + Ph); 7.64 (1H, s, CH=N); 7.70 (2H, d, J_{HH} = 8.1 Hz, o-H tolyl). Found, %: N 12.03; P 6.84. $C_{12}H_{27}N_4OPS$. Calculated, %: N 12.44; P 6.88.

5,7-Dimethyl-1,2-diphenyl-6-(p-tolyl)-1-thio-1,2-dihydropyrrolo[3,4-d][1,2,3]diazophosphorine (VII). To a solution of 0.01 mole of phenyldibromophosphine in 20 ml of pyridine, a solution of 0.01 mole of the phenylhydrazone I and 0.02 mole of triethylamine in 20 ml of pyridine was added. After 48 h (^{31}P NMR 1.14 ppm), 0.01 mole of sulfur was added, and the mixture was refluxed 1 h. The precipitate of salts was filtered off, and the filtrate was evaporated to dryness. Yield 29%, mp 210-212°C (from acetone). ^{31}P NMR spectrum ($CHCl_3$), ppm: 40.30. PMR spectrum ($CDCl_3$, TMS), ppm: 2.00 (3H, s, 7-CH_3); 2.18 (3H, s, 2-CH_3); 2.43 (3H, s, Ph−CH_3); 7.25 (12H, m, m-H tolyl + Ph); 7.77 (1H, s, CH=N); 7.85 (2H, d, J_{HH} = 8.1 Hz, o-H tolyl). Found, %: N 10.01; P 7.00. $C_{26}H_{24}N_3PS$. Calculated, %: N 9.52; P 7.03.

9-Methyl-2-phenyl-1-(N-morpholino)-1-thio-1,2-dihydroindolo[3,4-d][1,2,3]dihydrophosphine (VIII). To a solution of 0.01 mole of phosphorus tribromide in 30 ml of pyridine, a solution of 0.01 mole of the phenylhydrazone VI and 0.03 mole of triethylamine in 10 ml of pyridine and 20 ml of methylene chloride was added. The reaction mixture was held for 2 h at 60°C and then cooled (^{31}P NMR 82.07 ppm). A solution of 0.01 mole of morpholine in 10 ml of benzene was added; and after 30 min, 0.01 mole of sulfur was added. The reaction mixture was refluxed 1 h, the precipitate was filtered off, the filtrate was evaporated down, and the residue was treated with ethanol. Yield 57%, mp 192-193°C (from alcohol). ^{31}P NMR spectrum (CH_2Cl_2), ppm: 41.01. PMR spectrum ($CDCl_3$), ppm: 2.90, 3.30 (4H, m, N−CH_2); 3.41 (4H, t, J_{HH} = 4.0 Hz, O−CH_2); 4.06 (3H, s, N−CH_3); 7.38 (7H, m, 5H Ph + 2H Ind.); 7.75 (1H, d, J_{HH} = 7.8 Hz, H Ind.); 7.89 (1H, d, J_{HH} = 7.8 Hz, H Ind.); 8.05 (1H, s, CH=N). Found, %: N 14.03; P 7.85. $C_{20}H_{21}N_4OPS$. Calculated, %: N 14.1; P 7.81.

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