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DIHETEROANNELATED AZAPHOSPHEPINES

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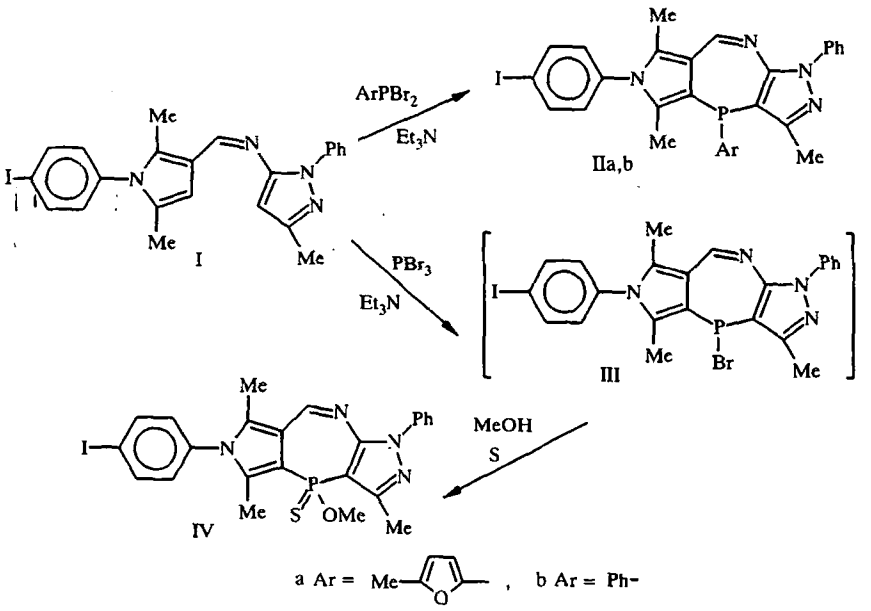
Tricyclic systems in which a seven membered, phosphorus containing ring is condensed with two heterocycles are unknown. We have obtained the first representatives of these systems (II, IV) by treating the Schiff base I with dibromoarylphosphines or with phosphorus tribromide in pyridine. The availability of Schiff bases of type I with electron rich heterocyclic residues gives us confidence that the method proposed will have general applicability.



The structure of compounds II, IV was confirmed using ^{31}P and ^{1}H NMR spectroscopy and also mass spectroscopy.

N-[1-(1-p-Iodophenyl-2,5-dimethyl-3-pyrrolyl)methylidene]-N-(3-methyl-1-phenyl-1H-5-pyrazolyl)amine (I). A solution of 5-amino-3-methyl-1-phenylpyrazole (6.26 g, 19.3 mmole), 1-p-iodophenyl-2,5-dimethylpyrrole-3-carboxaldehyde (3.4 g, 19.3 mmole), and p-toluenesulfonic acid (0.2 g) in propan-2-ol (50 ml) was refluxed until starting materials had disappeared (monitoring by TLC using propan-2-ol eluent). The reaction mixture was cooled and the precipitate filtered off. Yield 7.3 g (79%), mp 194-195°C as pale pink crystals. PMR spectrum (DMSO-D_6): 1.96 (3H, s, CH_3); 2.32 (6H, s, CH_3); 6.3 (1H, s, CH); 6.4 (1H, s, CH); 7.15 (2H, d, CH); 7.26 (1H, t, CH); 7.44 (2H, t, CH); 7.8 (2H, d, CH); 7.95 (2H, d, CH); 8.7 ppm (1H, s, CH).

6-p-Iodophenyl-3,5,7-trimethyl-4-(5-methyl-2-furyl)-1-phenyl-4,6-dihydro-1H-pyrazolo[3,4-b]pyrrolo[3,4-e][1.4]azaphosphepine (IIa). (5-Methyl-2-furyl)dibromophosphine (1.13 g, 4.2 mmole) was added to a solution of Schiff base I (2 g, 4.2 mmole) in pyridine (30 ml) followed by triethylamine (1.8 ml, 12.6 mmole). The mixture was held for one day, the pyridine evaporated, the residue extracted with hot toluene (≅ 30 ml), cooled, and the triethylamine hydrochloride filtered off. The mother liquor was decanted and evaporated to half volume. After cooling, the precipitate of IIa was separated. Yield

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1.54 g (63%), mp 223°C (colorless crystals). M^+ 590. ^{31}P NMR spectrum (CH_2Cl_2); $\delta P = -92$ ppm. PMR spectrum ($CDCl_3$); 2.18 (3H, s, CH_3); 2.21 (3H, s, CH_3); 2.24 (3H, s, CH_3); 2.47 (3H, s, CH_3); 5.8 (1H, m, CH); 6.3 (1H, m, CH): 6.9 (2H, d, CH); 7.3-7.6 (5H, m, CH); 7.8 (2H, d, CH); 8.33 ppm (1H, s, CH).

6-p-Iodophenyl-3,5,7-trimethyl-1,4-diphenyl-4,6-dihydro-1H-pyrazolo[3,4-b]pyrrolo[3,4-e][1.4]azaphosphepine (IIb). Obtained similarly. Yield 86%, mp 235°C (colorless crystals). M^+ 586. ^{31}P NMR spectrum (CH_2Cl_2): $\delta P = -69$ ppm. PMR spectrum (DMSO-D_6): 2.16 (3H, s, CH_3); 2.31 (3H, s, CH_3); 2.54 (3H, s, CH_3); 6.93 (2H, m, CH); 7.1-7.5 (8H, m, CH); 7.68 (2H, d, CH); 7.89 (2H, d, CH); 8.17 ppm (1H, s, CH).

6-p-Iodophenyl-4-methoxy-3,5,7-trimethyl-1-phenyl-4,6-dihydro-1H-4Δ^5-pyrazolo[3,4-b]pyrrolo[3,4-e][1,4]azaphosphepine-4-thione (IV). Phosphorus tribromide (0.2 ml, 2.1 mmole) was added to a solution of compound I (1 g, 2.1 mmole) in pyridine (20 ml). It was held for one day at 20°C. The ^{31}P NMR spectrum showed a single signal at δP = 38.7 ppm. Methanol (0.084 ml, 2.1 mmole) and sulfur (0.07 g, 2.1 mmole) were added to the solution. The product was held with stirring until the sulfur dissolved. Pyridine was evaporated off, the residue was dissolved in methylene chloride, and the salt extracted with water. The organic phase was dried with sodium sulfate and the solvent evaporated. The residue was recrystallized from propan-2-ol. Yield 0.4 g (34%), mp 268°C (colorless crystals). M^+ 572. ^{31}P NMR spectrum (CH_2Cl_2): δP = 52.7 ppm. PMR spectrum ($CDCl_3$): 2.16 (3H, s, CH_3); 2.51 (3H, s, CH_3); 2.74 (3H, s, CH_3); 3.5 (3H, d, J_{POCH3} = 14.76 Hz, OCH_3); 6.96 (2H, m, CH); 7.45 (3H, m, CH); 7.65 (2H, d, CH); 7.9 (2H, d, CH); 8.37 ppm (1H, s, CH).