TETRAHYDRODIPYRROLO-[3,4-*b*,*e*]-1,4-DIPHOSPHORINS

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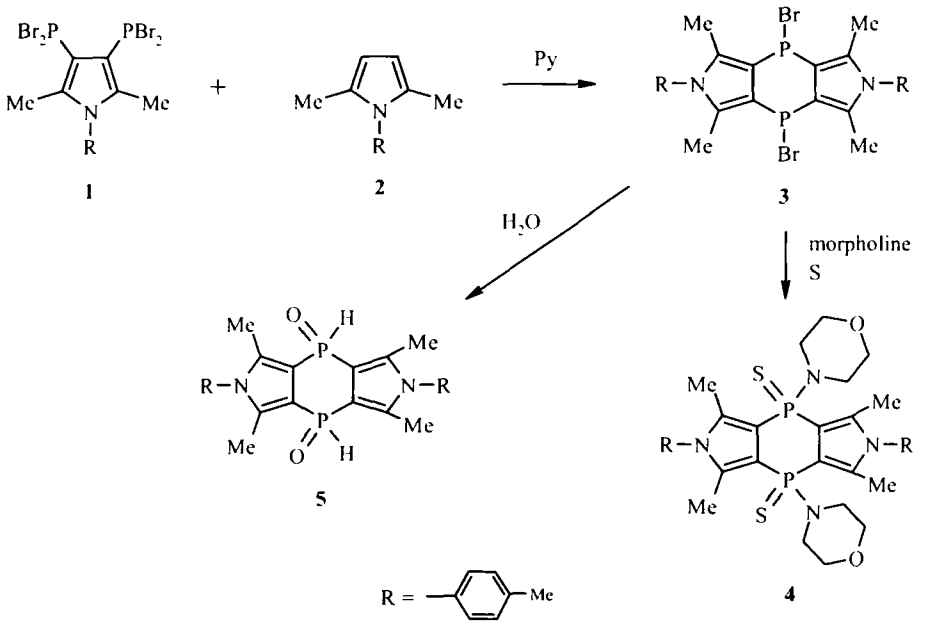
Keywords: bisdibromophosphine, bisthiomorpholide, bisphosphite, diphosphorin, tetrahydropyrrolo-[3,4-*b*,*e*]diphosphorins.

Dihydrobenzodiphosphorins are interesting as subjects for conformational analysis [1, 2]. Among their bisheterocyclic analogs only dithienodiphosphorins are well known [3]. We found that the reaction of bisdibromophosphine **1** with pyrrole **2** in pyridine under mild conditions led to the formation of diphosphorin **3**, from which good yields of bisthiomorpholide **4** and bisphosphite **5** were obtained.



1,8-Dibromo-1,3,5,7-tetramethyl-2,6-di(*p*-tolyl)-2,4,6,8-tetrahydrodipyrrolo[3,4-*b*,*e*]-1,4-diphosphorin (3). To a solution of bisdibromophosphine **1** [4] (0.01 mol) in pyridine (50 ml) we added with stirring a solution of pyrrole **2** (0.01 mol) in pyridine (10 ml). After 72 h the mixture was filtered, and the filtrate was evaporated under vacuum. The residue was dissolved in benzene (50 ml) and filtered. The filtrate was evaporated under vacuum, and the residue was boiled with hexane (50 ml). Yield 74%; mp 308°C. ^{31}P NMR spectrum (benzene), ppm: 39.1. ^{1}H NMR spectrum ($CDCl_3$, TMS), ppm: 2.20 (12H, s, Het–CH_3); 2.57 (6H, s, Ar–CH_3); 7.05 (4H, d, J_{HH} = 8.0 Hz, *m*-Ar). Found, %: N 4.69; P 10.57. $C_{36}H_{36}N_2P_2Br_2$. Calculated, %: N 4.76; P 10.53.

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 0009-3122/00/3604-0498$25.00©2000 KluwerAcademic/Plenum Publishers

1,3,5,7-Tetramethyl-1,4-dimorpholino-2,6-di(*p*-tolyl)-1,8-dithioxo-2,4,6,8-tetrahydrodipyrrolo[3,4-*b*,*e*]-1,4-diphosphorin (4). To a solution of diphosphorin **3** (0.01 mol) in benzene (50 ml) we added dropwise with stirring a solution of morpholine (0.02 mol) in benzene (50 ml). After 2 h sulfur (0.02 mol) was added to the reaction mixture, and the mixture was boiled for 1 h. The solution was filtered, and the filtrate was evaporated under vacuum. The product was crystallized from ethanol. Yield 73%; mp 335°C. ^{31}P NMR spectrum (CH_2Cl_2), ppm: 34.6. ^{1}H NMR spectrum ($CDCl_3$, TMS), ppm: 2.38 (12H, s, Het–CH_3); 2.46 (6H, s, Ar–CH_3); 3.20 (8H, m, CH_2–N); 3.60 (8H, m, CH_2–O); 7.10 (4H, d, J_{HH} = 7.8 Hz, *m*-Ar); 7.34 (4H, d, J_{HH} = 7.8 Hz, *o*-Ar). Found, %: N 9.42; P 10.29. $C_{34}H_{42}N_4O_2P_2$. Calculated, %: N 9.33; P 10.31.

1,3,5,7-Tetramethyl-1,8-dioxo-2,6-di(*p*-tolyl)-2,4,6,8-tetrahydrodipyrrolo[3,4-*b*,*e*]-1,4-diphosphorin (5). To a solution of diphosphorin **3** (0.01 mol) in methylene chloride (100 ml) we added water (20 ml). After 24 h the organic layer was separated and washed with water (2 × 20 ml), dried with sodium sulfate, and evaporated under vacuum. The residue was boiled with diethyl ether (20 ml). Yield 53%; mp 279°C. ^{31}P NMR spectrum (CH_2Cl_2), ppm: 47.0 (J_{HP} = 150 Hz). ^{1}H NMR spectrum ($CDCl_3$, TMS), ppm: 2.26 (12H, s, Het–CH_3); 2.46 (6H, s, Ar–CH_3); 7.11 (4H, d, J_{HH} = 8.1 Hz, *m*-Ar); 7.35 (4H, d, J_{HH} = 8.1 Hz, *o*-Ar); 7.37 (2H, d, J_{HP} = 150 Hz). Found, %: N 6.12; P 13.33. $C_{36}H_{38}N_2O_2P_2$. Calculated, %: N 6.06; P 13.39.

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