Chemistry of Heterocyclic Compounds, Vol. 35, No. 9, 1999

PHOSPHORYLATION OF 2-PHENYL-1,3,4-OXADIAZOLE WITH PHOSPHORUS (III) HALIDES

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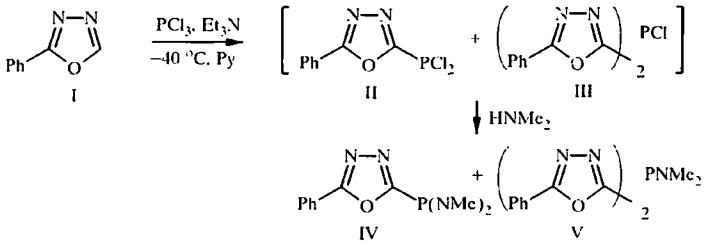
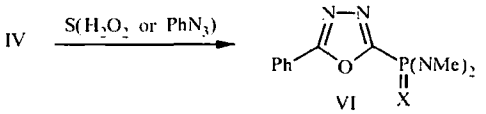
There is a single method in the literature for the preparation of phosphorylated 1,3,4-oxadiazoles: cyclization of bis(dialkylamino)phosphinodiazomethanes with acyl halides [1 - 3]. We have found that 2-phenyl-1,3,4-oxadiazole is phosphorylated by phosphorus (III) halides in basic media just as 1-alkylimidazoles [4].

The reaction of 2-phenyl-1,3,4-oxadiazole (I) with phosphorus trichloride in pyridine solution in the presence of triethylamine gave two compounds: dichlorophosphine II (δ_P 87.84 ppm) and chlorophosphine III (δ_P -34.66 ppm) even when a considerable excess of phosphorus trichloride was used. For example, in 3 h with 1.5 fold excess of phosphorus trichloride (a greater excess had little effect on the proportions of the products formed), at temperature of -40°C, the ratio of the reaction products II and III according to ^{31}P NMR spectroscopy data was 1:0.25, whereas when the reaction was run at room temperature the ratio was 1:0.6. The amides IV and V, which were isolated as pure compounds, were formed on addition of dimethylamine to the reaction mixture.



Various phosphorus (V) derivatives VIa-c were prepared from the tetramethyldiaminophosphonite IV by standard methods.



a X = S, b X = O, c X = NPh

2-Phenyl-1,3,4-oxadiazole I also interacts over 24 h with the less reactive chlorodiphenylphosphine and dichlorophenylphosphine at room temperature to give phosphines VII and VIII.

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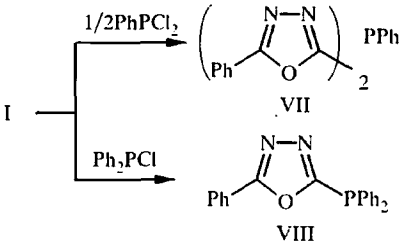

The structures and composition of the compounds synthesized were confirmed by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy and elemental analysis data.

Tetramethyldiamido(5-phenyl-1,3,4-oxadiazol-2-yl)phosphonite (IV, $C_{12}H_{17}N_4OP$) and Dimethylamidobis-(5-phenyl-1,3,4-oxadiazol-2-yl)phosphinite (V, $C_{18}H_{16}N_5O_2P$). Phosphorus trichloride (0.15 mol) was added to solution of 2-phenyl-1,3,4-oxadiazole (0.1 mol) in pyridine (100 ml). The reaction mixture was stirred for 3 h at -30 to -40°C, then diluted with cold toluene (100 ml) and dimethylamine (1.05 mol) was then added dropwise over 20 min. After 1 h the precipitate was filtered off and washed with toluene (50 ml), and the filtrate was evaporated to dryness in vacuum. The residue was washed with hexane (150 ml), the insoluble material was separated and recrystallized from benzene to give compound V, yield 13%; mp 144-145°C. ^{31}P NMR spectrum (pyridine): 18.00 ppm. ^{1}H NMR spectrum ($CDCl_3$): 8.08 (4H, d, J = 6.3 Hz, *o*-Ph); 7.53 (6H, m, *m*-,*p*-Ph); 3.02 ppm (6H, d, J = 10.2 Hz, NMe_2). The hexane solution was evaporated in vacuum and the residue distilled. to give compound IV, yield 51%; bp 139-142°C (0.08 mm Hg); mp 43-44°C. ^{31}P NMR spectrum (pyridine): 18.00 ppm. ^{1}H NMR spectrum (C_6D_6): 8.05 (2H, m, *o*-Ph); 7.14 (3H, m, *m*-, *p*-Ph); 2.69 ppm (12H, d, J = 9.9 Hz, NMe_2). ^{13}C NMR spectrum (C_6D_6): 168.62 (d, J = 18.5 Hz, 2-C); 166.04 (d, J = 1.3 Hz, 5-C); 131.44 (s, *ipso*-Ph); 129.14 (s, *m*-Ph); 127.13 (s, *o*-Ph); 124.88 (s, *p*-Ph); 41.71 ppm (d, J = 17.7 Hz, NMe_2).

Tetramethyldiamido(5-phenyl-1,3,4-oxadiazol-2-yl)thiophosphonate (VIa, $C_{12}H_{17}N_4OPS$). Finely ground sulfur (0.01 mol) was added to solution of compound IV (0.01 mol) in benzene (10 ml), the mixture was stirred for 1 h, then the solution was evaporated, the residue distilled and the fraction with bp 169-170°C (0.17 mm Hg) was collected. Yield 89%; mp 63-64°C. ^{31}P NMR spectrum (benzene): 59.9 ppm. ^{1}H NMR spectrum ($CDCl_3$): 8.13 (2H, dd, J_1 = 8.1, J_2 = 1.5 Hz, *o*-Ph); 7.54 (3H, m. *m*-,*p*-Ph); 2.79 ppm (12H, d, J = 12.9 Hz, NMe_2).

Tetramethyldiamido(5-phenyl-1,3,4-oxadiazol-2-yl)phosphonate (VIb, $C_{12}H_{17}N_4O_2P$). Hydrogen peroxide (30%, 3.4 ml, 0.03 mol) was added dropwise with intense stirring to solution of compound IV (0.01 mol) in methylene chloride (30 ml) upon cooling at 0°C. After 15 min water (40 ml) was added, stirring was continued for 5 min, the organic layer was separated, dried over sodium sulfate, evaporated in vacuum, and the residue distilled to give VIb as an oil. Yield 62%; bp 161-162°C. ^{31}P NMR spectrum ($CHCl_3$): 12.4 ppm. ^{1}H NMR spectrum ($CDCl_3$): 8.16 (2H, dd, J_1 = 7.7, J_2 = 0.9 Hz, *o*-Ph); 7.56 (3H, m, *m*-,*p*-Ph); 2.81 ppm (12H, d, J = 10.8 Hz, NMe_2).

Tetramethyldiamido(5-phenyl-1,3,4-oxadiazol-2-yl)phenylimidophosphonate (VIc, $C_{18}H_{22}N_5OP$). Phenylazide (0.01 mol) was added to solution of compound IV (0.01 mol) in benzene (30 ml) and the mixture was boiled for 3 h, the solvent was then evaporated, hexane (20 ml) was added to the residue, the mixture was heated to boiling, filtered, and hexane removed in vacuum to leave an oil. Yield 98%. The residue was distilled on necessity. Yield 91%; bp 202-204°C (0.16 mm Hg). ^{31}P NMR spectrum (benzene): 1.01 ppm. ^{1}H NMR spectrum ($(CD_3)_2CO$): 8.04 (2H, dd, J_1 = 8.0, J_2 = 1.6 Hz, *o*-Ph-Het); 7.59 (3H, m, *m*-,*p*-Ph-Het); 7.09 (2H, t, J = 7.0 Hz, *m*-Ph-N); 6.86 (2H, d, J = 8.4 Hz, *o*-Ph-N); 6.69 (1H, t, J = 7.4 Hz, *p*-Ph-N); 2.82 ppm (12H, d, J = 10.5 Hz, NMe_2).

Bis(5-phenyl-1,3,4-oxadiazol-2-yl)phenylphosphine (VII, $C_{22}H_{15}N_4O_2P$). Triethylamine (0.02 mol) and dichlorophenylphosphine (0.01 mol) were added successively to solution of compound I (0.02 mol) in pyridine (20 ml). After 24 h the solvent was evaporated, benzene (25 ml) was added, the mixture was brought to boiling, filtered, and the precipitate which separated on cooling was recrystallized from benzene; mp 110-111°C. ^{31}P NMR spectrum (pyridine): -51.58 ppm. ^{1}H NMR spectrum ($(CD_3)_2CO$): 8.05 (6H, m, *o*-Ph-Het + *o*-Ph-P); 7.62 ppm (9H, m, *m*-,*p*-Ph-Het + *m*-,*p*-Ph-P).

(5-Phenyl-1,3,4-oxadiazol-2-yl)diphenylphosphine (VIII, $C_{20}H_{15}N_2OP$). Triethylamine (0.02 mol) and chlorodiphenylphosphine (0.02 mol) were added to solution of compound I (0.02 mol) in pyridine (25 ml). After 24 h the reaction mass was evaporated, benzene (30 ml) was added, the solution was filtered, benzene was evaporated in vacuum and the residue recrystallized from methanol; mp 79-80°C. ^{31}P NMR spectrum (CH_2Cl_2): -25.00 ppm. ^1H NMR spectrum ($CDCl_3$): 8.00 (2H, d, J = 6.6 Hz, o-Ph); 7.59 (4H, m , *o*-Ph_2P); 7.45 ppm (9H, m, *m*-, *p*-Ph + *m*-, *p*-Ph_2P).

All reactions were carried out in anhydrous solvents in atmosphere of argon.

The elemental analyses of the compounds prepared agreed with calculated values. ^1H, ^{31}P, and ^{13}C NMR spectra were recorded with Varian VXR-300 spectrometer (300, 121, and 75 MHz respectively).

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