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LETTERS TO THE EDITOR

3,5-BISPHOSPHORYLATED 4-ARYL-1,2,4-TRIAZOLES

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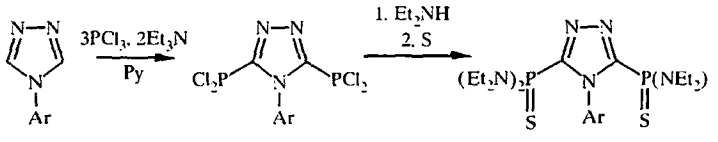
Phosphorylation of 1,3-azoles by trivalent phosphorus halides allows to prepare 2-azolyldichlorophosphines which are promising reagents unavailable by other methods [1]. It might be expected that the use of 1,2,4-triazoles (in particular 4-aryl-1,2,4-triazoles) in this reaction would lead to both mono- and bisdichlorophosphines depending on the ratio of reagents.

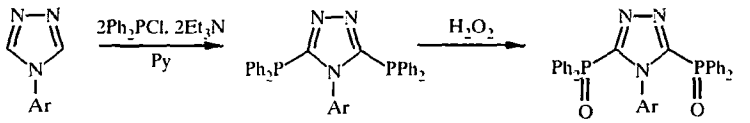


I II III

Ar = 4-$CH_3C_6H_4$–

We have shown that 4-aryl-1,2,4-triazoles (I) react with excess of PCl_3 to give the bischlorophosphine II. The latter is only stable in solution but can be successfully used as starting reagent, e.g. for the preparation of the bisthiophosphonate III. At the same time, for a 1:1 ratio of 4-aryl-1,2,4-triazole to PCl_3 the reaction proceeds non-regioselectively to give a difficult to separate mixture of mono- and bisphosphorylation products.

Monophosphorylation of triazoles does not take place regioselectively, even with the less active phosphorylating agent diphenylchlorophosphine since the bisphosphines IV are very readily formed.



Ia,b IVa,b Va,b

a Ar = Ph, b 4-$CH_3C_6H_4$–

3,5-Bisphosphorylated 1,2,4-triazoles have not been reported in the literature whereas 3-phosphorylated derivatives are obtained using the 3-lithium derivatives of triazoles [2] and also by cyclization of C-dialkoxyphosphoryl-N-arylcarbohydrazines [3].

The structure of the compounds obtained was confirmed by NMR data and also *via* chemical reactions.

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3,5-Bis(tetraethyldiamidothiophosphono)-4-phenyl-1,2,4-triazole (III, $C_{25}H_{47}N_7P_2S_2$). Triethylamine (0.02 mol) and phosphorus trichloride (0.03 mol) were added successively to a solution of compound I (0.01 mol) in pyridine (10 ml). After 1 h, the reaction mixture was cooled to 0°C, diethylamine (0.16 mol) was added and sulfur (0.03 mol) after 10 min. After 30 min the pyridine was evaporated *in vacuo*, benzene (30 ml) was added to the residue, and the precipitate was filtered, benzene evaporated off, the residue chromatographed on a column (Geduran SI 60 silica gel, hexane–ethyl acetate (3:1) eluent), and finally recrystallized from hexane. Yield 44%; mp 111-112°C. ^{31}P NMR spectrum ($CHCl_3$): 56.00 ppm. PMR spectrum ($CDCl_3$): 7.17 (4H, s, $C_6\underline{H}_4CH_3$); 3.15 (16H, m, $NC\underline{H}_2CH_3$); 2.41 (3H, s, $C_6H_4C\underline{H}_3$); 1.05 ppm (24H, t, J = 6.9 Hz, $NCH_2C\underline{H}_3$).

3,5-Bisdiphenylphosphino-4-phenyl-1,2,4-triazole (IVa, $C_{32}H_{25}N_3P_2$). Triethylamine (0.04 mol) and diphenylchlorophosphine (0.04 mol) were added to a solution of compound I (0.02 mol) in pyridine (25 ml). After 24 h the reaction mixture was evaporated, benzene (40 ml) was added, the solution was heated to reflux and filtered. The precipitate was washed with hot benzene (20 ml). The filtrate was evaporated in vacuo and the residue was recrystallized from benzene. Yield 58%; mp 153-155°C. ^{31}P NMR spectrum (CH_2Cl_2): -31.60 ppm. PMR spectrum ($CDCl_3$): 7.49 (8H, m, *o*-Ph_2P); 7.30 (13H, m, *m*- and *p*-PhP + *p*-PhN); 7.19 (2H, t, J = 7.8 Hz, *m*-PhN); 6.74 ppm (2H, d, J =7.7 Hz, *o*-PhN). ^{13}C NMR spectrum ($CDCl_3$): 156.77 ppm (dd, J_1 = 19.5, J_2 = 2.2 Hz, C_3 and C_5).

3,5-Bisdiphenylphosphino-4-*p*-tolyl-1,2,4-triazole (IVb, $C_{33}H_{27}N_3P_2$) was obtained similarly to compound IVa with recrystallization from ethyl acetate. Yield 57%; mp 133-134°C, ^{31}P NMR spectrum ($CHCl_3$): -31.54 ppm. PMR spectrum ($(CD_3)_2CO$): 7.46 (8H, m, *o*-Ph_2P); 7.37 (12H, m, *m*- and *p*-Ph_2P); 7.11 (2H, d, J = 8.4 Hz, *m*-PhN); 6.81 (2H, d, J = 8.4 Hz, *o*-PhN); 2.34 ppm (3H, s, CH_3).

3,5-Bisdiphenylphosphinoxido-4-*p*-tolyl-1,2,4-triazole (V, $C_{32}H_{25}N_3O_2P_2$). A solution of hydrogen peroxide (0.02 mol) in water (10 ml) was added to a solution of compound IVa (0.01 mol) in methylene chloride (20 ml), stirred for 20 min, and then washed twice with water (20 ml) and methylene chloride, evaporated in vacuo, and the residue recrystallized from toluene. Yield 81%; mp 218°C. ^{31}P NMR spectrum (CH_2Cl_2): 14.96 ppm. PMR spectrum ($CDCl_3$): 7.70 (8H, m, *o*-Ph_2PO); 7.50 (4H, m, *p*-Ph_2PO); 7.38 (8H, m, *m*-Ph_2PO); 7.19 (1H, t, J = 7.7 Hz, *p*-PhN); 7.01 (2H, t, J = 7.7 Hz, *m*-PhN); 6.87 ppm (2H, d, J = 7.7 Hz, *o*-PhN). ^{13}C NMR spectrum ($CDCl_3$): 153.60 ppm (dd, J_1 = 20.9, J_2 = 4.7 Hz, C_3 and C_5).

Elemental analytical data for the compounds obtained agreed with that calculated. ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on a Varian VXR-300 instrument (300, 121, and 75 MHz respectively).

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