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LETTERS TO THE EDITOR

PHOSPHORYLATION OF N,N-DIMETHYL-N'-(2-THIAZOLYL)FORMAMIDINE — A SIMPLE ROUTE TO 5-PHOSPHORYLATED 2-AMINOTHIAZOLE

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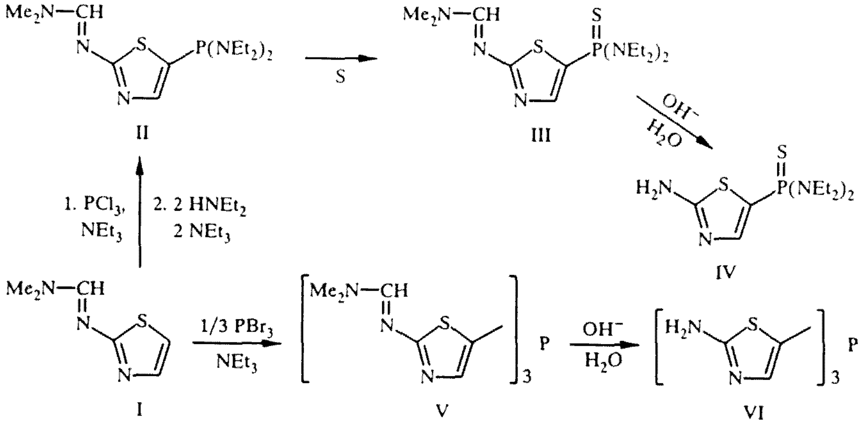
5-Phosphorylated thiazoles have been studied very little: only a few derivatives of pentavalent phosphorus are known, prepared by cyclization [1] or by phosphorylation of 5-Li derivatives of thiazole [2].

We have obtained 5-phosphorylated thiazole derivatives containing P(III) for the first time by the reaction of N,N-dimethyl-N'-(2-thiazolyl)formamidine (I) with either PBr_3 or PCl_3 in basic media, which gives 1 or 3 heterocyclic groups bonded to the phosphorus atom.

The formamidine group in the phosphine (V) or phosphorus (V) derivatives of type may be easily removed by normal methods to give the corresponding 5-phosphorylated 2-aminothiazoles (IV, VI) in high yield.



Tetraethyldiamide of 5-(2-(3-Methyl-1,3-diazabut-1-enyl)thiazolyl)phosphinic Acid (II, $C_{14}H_{28}N_5PS$). Triethylamine (0.02 moles) and PCl_3 (0.02 moles) were added slowly over 4 d to a solution of thiazole I (0.01 moles) in a 1:1 mixture of pyridine and CH_2Cl_2 (25 cm^3). The mixture was evaporated to dryness, the residue was dissolved in benzene (35 cm^3) and a solution of Et_2NH (0.03 moles) and Et_3N (0.03 moles) in benzene (10 cm^3) was added dropwise with stirring and cooling. After 1.5 h the mixture was evaporated to dryness and the product was extracted with pentane to give an oil in 81% yield. ^{31}P NMR spectrum (pyridine): +82.4. ^1H NMR spectrum ($CDCl_3$ 8.22 (1H, s, =CH−), 7.15 (1H, s, 3-H), 3.08 and 3.06 (6H, s, s, $(CH_3)_2N$), 3.14 (8H, m, $-CH_2-$), 1.08 (12H, t, J = 7 Hz, $CH_3-(CH_2)$).

Tetraethyldiamide of 5-(2-(3-Methyl-1,3-diazabut-1-enyl)thiazolyl)thiophosphonic Acid (III, $C_{14}H_{28}N_5PS_2$). Amide (0.01 moles) was dissolved in benzene (20 cm^3) and finely divided sulfur (0.01 moles) was added. The mixture was kept for 2 h (at room temperature) and then refluxed for 2 h. The solution was evaporated to dryness and the product was crystallized from hexane. Yield 93%, mp 63-65°C (hexane). ^{31}P NMR spectrum (benzene): +65.3. ^1H NMR spectrum ($CDCl_3$): 8.40 (1H,

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s, =CH−), 7.69 (1H, d, J_{3P} = 5.4 Hz, 3-H), 3.22 and 3.10 (6H, s, s, $(CH_3)_2N$), 3.16 (8H, m, $-CH_2-$), 1.08 (12H, t, J = 7 Hz, $CH_3-(CH_2)$).

Tetraethyldiamide of 5-(2-Aminothiazolyl)thiophosphonic Acid (IV, $C_{11}H_{23}N_4PS_2$). Yield 94%, mp 136-137°C (cyclohexane). ^{31}P NMR spectrum (MeOH): +65.7. ^1H NMR spectrum ($CDCl_3$): 7.47 (1H, d, J_{3P} = 5.4 Hz, 3-H), 5.53 (2H, br s, NH_2), 3.14 (8H, m, $-CH_2-$), 1.09 (12H, t, J = 7 Hz, $CH_3-(CH_2)$).

Tris(5-(2-(3-methyl-1,3-diazabut-1-enyl)thiazolyl)phosphine (V, $C_{18}H_{24}N_9PS_3$). Triethylamine (0.02 moles) and PBr_3 (0.0033 moles) were added to a solution of thiazole I (0.01 moles) in pyridine (20 cm^3) and the mixture was kept for 4 d. The precipitate was filtered off, dissolved in CH_2Cl_2 (150 cm^3), washed with water and evaporated to dryness. The product was crystallized from MeCN. Yield 69%, mp 211-213°C. ^{31}P NMR spectrum (pyridine): −62.2. ^1H NMR spectrum ($CDCl_3$): 8.18 (3H, s, =CH−), 7.49 (3H, d, J_{3P} = 4.8 Hz, 3-H), 3.10 and 3.07 (6H, s, s, $(CH_3)_2N$)).

Tris(5-(2-aminothiazolyl)phosphine (VI, $C_9H_9N_6PS_3$). Yield 91%, mp 222-224°C (water). ^{31}P NMR spectrum (MeOH): −61.1. ^1H NMR spectrum (DMSO-D_6): 7.08 (1H, d, J_{3P} = 5.4 Hz), 7.30 (2H, s, NH_2).

Elemental analyses agreed with calculated values.

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