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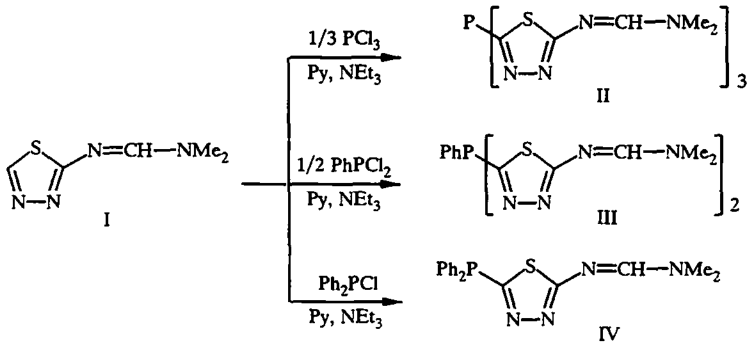
THIADIAZOLYLPHOSPHINES WITH NITROGEN CONTAINING SUBSTITUENTS

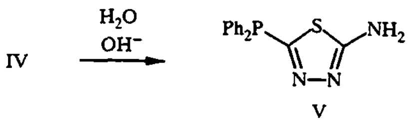
**G. V. Oshovskii, F. F. Tolmachev, A. S. Merkulov,
and A. M. Pinchuk**

We first prepared C-(P^{III})phosphorylated derivatives of 1,3,4-thiadiazole I by the reaction of N,N-dimethyl-N′-(2-thiadiazolyl)formamidine with PCl$_3$ or the less reactive PhPCl$_2$ and Ph$_2$PCl in basic media. The reaction to give the corresponding functionally substituted phosphines II-IV occurred readily. This is the first example of electrophilic C-phosphorylation in the 1,3,4-thiadiazole series.



N,N-Dimethyl-N′-(2-thiadiazolyl)formamidine is a considerably more active substrate than N,N-dimethyl-N′-(2-thiazolyl)formamidine [1] for electrophilic phosphorylation.

Removal of the formamidine group was carried out by alkaline hydrolysis without aminothiadiazolyl-triazolylthione rearrangement [2]:



Considering the previous report [1], it may be concluded that C-phosphorylation of N,N-dialkyl-N′-heteraryl-formamidines has considerable promise for the synthesis of C-phosphorylated aminoheterocycles.

Tris{5-[2-(3-methyl-1,3-diazabut-1-enyl)thiadiazolyl]}phosphine (II, $C_{15}H_{21}N_{12}PS_3$). Triethylamine (0.11 mol) was added dropwise to a solution of N,N-dimethyl-N′-(2-thiadiazolyl)formamidine I (0,03 mol) in pyridine (45 cm^3), followed by PCl$_3$ (0.01 mol) with cooling. The reaction mixture was kept for one day. The precipitate was filtered off, washed with acetonitrile, then with cold water to wash out salt, the residue was washed with ether, dried, and recrystallized from dry cyclohexane. Yield 72%. M.p. 191-193°C. ^{31}P NMR spectrum (pyridine): −46.8 ppm. ^{1}H NMR spectrum (CF_3CO_2D): 8.52 (3H, +CH), 3.55, 3.46 ppm (18H, s, s, Me$_2$N).

Bis{5-[2-(3-methyl-1,3-diazabut-1-enyl)thiadiazolyl]phenylphosphine (III, $C_{16}H_{19}N_8PS_2$). Triethylamine (0.05 mol) was added to a solution of N,N-dimethyl-N′-(thiadiazolyl)formamidine I (0.02 mol) in pyridine (30 cm^3), and PhPCl$_2$ (0.01 mol) was then added with cooling. After 2 days, the reaction mixture was evaporated to dryness, treated with dry benzene and

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Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kiev 252600. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1422-1424, October, 1997. Original article submitted May 29, 1997.

the residue filtered off. Phosphine III was purified by reprecipitation from the benzene mother liquid with dry hexane. The oil obtained solidified after drying in vacuum. Yield 67%. M.p. 45-47.5°C. ^{31}P NMR Spectrum (pyridine): −31.3 ppm. ^1H NMR spectrum ($CDCl_3$): 8.22 (2H, s, =CH), 7.61 [2H, m, *o*-H(PhP)], 7.41 [3H, m, H(*m*-,*p*-PhP)], 3.12, 3.08 ppm (12H, s. s, Me_2N).

5-[2-(3-Methyl-1,3-diazabut-1-enyl)thiadiazolyl]diphenylphosphine (IV, $C_{17}H_{17}N_4PS$). Triethylamine (0.02 mol) was added dropwise to a solution of N,N-dimethyl-N′-(2-thiadiazolyl)formamidine (0.01 mol) I in pyridine (15 cm^3), followed by Ph_2PCl (0.01 mol), with cooling. The reaction mixture was evaporated to dryness after three days, treated with dry benzene and filtered. The filtrate was evaporated to dryness and treated with propanol-2 (20 cm^3). The crystals were filtered off and recrystallized from propanol-2. Yield 91%. M.p. 122-122.5°C. ^{31}P NMR spectrum (pyridine): −17.0 ppm. ^1H NMR Spectrum ($CDCl_3$): 8.20 (1H, s, =CH), 7.42 (10H, m, Ph_2P), 3.12, 3.07 ppm (12H, s. s, Me_2N).

5-(2-Aminothiadiazolyl)diphenylphosphine (V, $C_{14}H_{12}N_3PS$). Propanol-2 (50 cm^3), KOH (9 mmol) and water (0.12 mol) were added to compound IV (0.01 mol), and the mixture was boiled for 3h. The reaction mixture was evaporated to dryness to give compound V, yield 92%, m.p. 203-204°C (propanol-2). ^{31}P NMR spectrum (propanol-2): −17.62 ppm. ^1H NMR spectrum ($CDCl_3$): 7.41 (10H, m, Ph_2P), 6.14 ppm (2H, br s, NH_2).

^{31}P NMR spectra were recorded with a Varian machine, with a working frequency of 121.212 MHz, ^1H NMR spectra of compounds III, IV, and V on a Bruker CXP-200 WB machine and compound II on a Bruker WP-200 SY spectrometer.

Results of elemental analyses corresponded with calculated values.

REFERENCES

1. A. A. Tolmachev, G. V. Oshovskii, A. S. Merkulov, and A. M. Pinchuk, Khim. Geterotsikl. Soedin., No. 9, 1288 (1996).
2. J. Sandstrom, Advances in Heterocyclic Chemistry, A. R. Katritzky and A. J. Boulton (eds.), Academic Press, New York and London (1968), p. 194.