New amidoesters of thiophosphoric acid

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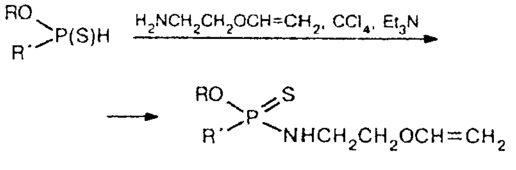
The Todd—Atherton reaction of dialkyl thiophosphonates or *O*-alkyl piperididothiophosphonates with monoethanolamine vinyl ether afforded the corresponding amidoesters of thiophosphoric acid.

Key words: Todd—Atherton reaction, dialkyl thiophosphonates, monoethanolamine vinyl ether; amidoesters of thiophosphoric acid, synthesis.

Esters and amides of thiophosphoric acid are widely used as physiologically active compounds, namely, pesticides, plant growth regulators, and drugs, as well as lubricating oil additives, plasticizers, and other practically useful compounds.

As part of our continuing studies devoted to the synthesis of phosphorylated derivatives of vinyl ethers,[1] in this work we prepared new amidoesters and diamidoesters of thiophosphoric acid by the Todd—Atherton reaction.[2] These studies have been carried out for the first time.

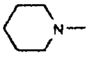
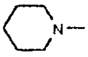
We have established that the Todd—Atherton reaction of dialkyl thiophosphonates and *O*-alkyl piperididothiophosphonates with monoethanolamine vinyl ether afforded the corresponding *O,O'*-dialkyl or *O*-alkyl piperididoaminothiophosphates (**1**—**7**), which are derivatives of monoethanolamine (Table 1).



1—7

The structures of the resulting compounds were confirmed by the data of ^{31}P NMR and IR spectroscopy (see Table 1). The IR spectra of compounds **1**—**7** have absorption bands assigned to the P=S (ν 630—650 cm^{-1}), P—N (ν 890—920 cm^{-1}), P—O—C (ν 1135—1180 cm^{-1}), C=C (ν 1605—1625 cm^{-1}), and N—H (ν 3260—3280 cm^{-1}) fragments.

Table 1. Physicochemical characteristics of the derivatives of thiophosphoric acid **1**—**7**

Compound	R	R'	Yield (%)	n_D^{20}	d_4^{20}	$^{31}P-\{^1H\}$ NMR, δ	$\frac{\text{Found}}{\text{Calculated}}$ (%) C	H	N	P	S	Molecular formula
1	Me	MeO	76	1.4762	1.0578	76.43 (s)	33.96 34.12	6.29 6.63	6.31 6.63	14.43 14.69	15.03 15.18	$C_6H_{14}NO_3PS$
2	Et	EtO	74	1.4870	1.0483	73.18 (s)	40.09 40.16	7.37 7.58	5.78 5.85	12.83 12.94	13.34 13.40	$C_8H_{18}NO_3PS$
3	Pr^n	Pr^{n}O	53	1.4774	0.9962	72.40 (s)	44.76 44.93	7.98 8.29	4.89 5.24	11.43 11.59	11.79 11.99	$C_{10}H_{22}NO_3PS$
4	Pr^i	Pr^{i}O	55	1.4965	0.9674	72.84 (s)	44.47 44.94	7.76 8.24	5.09 5.24	11.43 11.61	11.67 11.98	$C_{10}H_{22}NO_3PS$
5	Bu^n	Bu^{n}O	57	1.5005	0.9678	72.90 (s)	48.69 48.80	8.47 8.87	4.67 4.74	10.17 10.49	10.61 10.85	$C_{12}H_{26}NO_3PS$
6	Pr^i		79	1.4976	0.9659	74.10 (s)	49.17 49.30	8.27 8.62	9.16 9.58	10.49 10.59	10.69 10.97	$C_{12}H_{25}N_2O_2PS$
7	Bu^n		78	1.4780	0.9768	73.90 (s)	50.77 50.96	8.71 8.88	9.03 9.14	10.02 10.11	10.27 10.46	$C_{13}H_{27}N_2O_2PS$

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Experimental

The IR spectra were recorded on an UR-20 spectrophotometer. The ^{31}P NMR spectra were recorded on a Bruker WP-200 SY instrument (81.01 MHz, a 85% H_3PO_4 solution as the standard).

***O,O'*-Diethyl [*N*-2-(vinyloxy)ethylamido]thiophosphate (2).** *O,O'*-Diethyl thiophosphonate[3,4] (3.82 g, 0.025 mol) was added with stirring to a benzene solution of monoethanolamine vinyl ether (2.17 g, 0.025 mol), triethylamine (2.5 g, 0.025 mol), and CCl_4 (3.84 g, 0.025 mol) at 18 °C. The reaction mixture was heated at 48—50 °C for 35—40 min. Triethylamine hydrochloride was precipitated as the reaction mixture was cooled. The precipitate was filtered off. The filtrate was concentrated *in vacuo*, and the residue was chromatographed on a column with silica gel with the use of a 3 : 1 hexane—acetone mixture as the eluent.

O,O'-Dimethyl, *O,O'*-dipropyl, *O,O'*-diisopropyl, and *O,O'*-dibutyl [*N*-2-(vinyloxy)ethylamido]thiophosphates (**1** and **3—5**), *O*-isopropyl piperidido[*N*-2-(vinyloxy)ethylamido]thiophosphate (**6**), and *O*-butyl piperidido[*N*-2-(vinyloxy)ethylamido]thiophosphate (**7**) were prepared as described above. The physicochemical and analytical characteristics of the resulting compounds are given in Table 1.

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