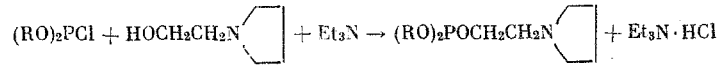
SYNTHESIS OF SOME β-PYRROLIDINOETHYL PHOSPHITES

N. P. Grechkin and L. N. Grishina

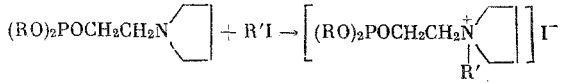
UDC 542.91:547.1'118

The organophosphorus compounds that we had synthesized previously, which contained the pyrrolidine ring in the molecule, exhibited interesting physiological properties in a number of cases [1, 2]. As an expansion of these studies we prepared a number of phosphorus acid esters that contained the pyrrolidine ring in the ester (ethyl) radical.

The dialkyl β-pyrrolidinoethyl phosphites were obtained by the reaction of β-pyrrolidinoethanol with the acid chlorides of dialkylphosphorous acids in the presence of Et_3N.



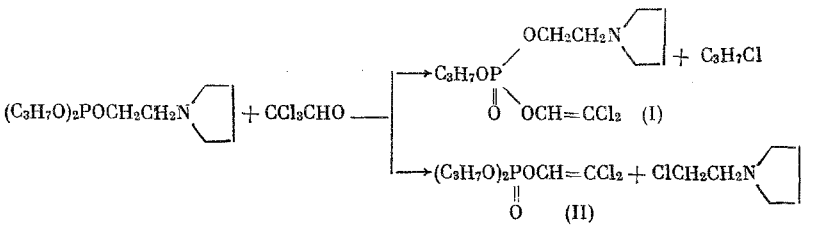
Tri(β-pyrrolidinoethyl) phosphite and the alkyl di(β-pyrrolidinoethyl) phosphites were obtained in a similar manner from the acid chlorides of phosphorous and alkylphosphorous acids. The yields, physical constants, and analyses of the obtained compounds are given in Table 1. The dialkyl β-pyrrolidinoethyl phosphites react with alkyl halides to give, after heating in a sealed tube at 60-70° for 4 h, compounds that, based on the elemental analysis and the NMR and IR spectral data, were assigned the structure of the salts of quaternary ammonium bases.



R = C_2H_5, C_4H_9; R′ = C_2H_5, C_4H_9

The ^{31}P NMR spectra have one signal with ρ = −136 ppm (R—C_2H_5) and ρ = −140 ppm (R—C_4H_9), which is characteristic for the phosphite grouping [3]. The absorption band of the P=O group (1170-1310 cm^{-1}) is absent in the IR spectra.

In order to obtain the β-pyrrolidinoethyl esters of pentavalent phosphorus acids we studied the reaction of dipropyl β-pyrrolidinoethyl phosphite with chloral. In this case the starting phosphite undergoes Perkov rearrangement, but instead of the expected product (I) we isolated dipropyl 2, 2-dichlorovinyl phosphate (II).



The structure of (II) is confirmed by its elemental analysis and IR spectrum, which has the absorption bands of the groups (cm^{-1}): P—O—C (1025-1050), CCl_2 820, C=C 1650 and P=O 1270. The alkyl di(β-pyrrolidinoethyl) phosphites also react vigorously with chloral, but the product decomposes when its isolation by distillation is attempted.

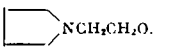
EXPERIMENTAL METHOD

Diethyl β-Pyrrolidinoethyl Phosphite. With stirring, to a benzene solution of 11 g of β-pyrrolidinoethanol and 10.5 g of Et_3N at −2° was added 15 g of diethylphosphorous chloride in drops. After removal

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1202-1203, May, 1975. Original article submitted October 1, 1974.

TABLE 1. β-Pyrrolidinoethyl Phosphites

Compound	Yield, %	Bp, °C (p, mm of Hg)	d_4^{20}	n_D^{20}	Found/calculated		
					MR	P, %	N, %
$(C_2H_5O)_2PR$	72	65(0,04)	1,0104	1,4548	62,81 / 63,19	13,01 / 13,33	5,79 / 5,96
$(C_3H_7O)_2PR$	66	77—78(0,03)	0,9843	1,4560	72,64 / 72,47	11,55 / 11,78	5,29 / 5,34
$(C_4H_9O)_2PR$	65	95—96(0,03)	0,9719	1,4562	81,39 / 81,71	10,54 / 10,65	4,75 / 4,81
$C_2H_5OPR_2$	61	104—105(0,03)	1,0324	1,4798	83,66 / 83,45	10,32 / 10,19	9,44 / 9,21
$C_4H_9OPR_2$	54	138(0,03)	1,0116	1,4779	92,83 / 92,69	9,57 / 9,33	8,29 / 8,43
PR_3	57	155—156(0,03)	1,0497	1,4950	104,5 / 103,67	8,37 / 8,26	11,19 / 11,26

Note. R =  .

of the $Et_2N \cdot HCl$ and solvent the residue was vacuum-distilled twice to give 14.9 g (72%) of product. The other compounds, listed in Table 1, were obtained in a similar manner from the corresponding phosphorous and alkylphosphorous chlorides in the presence of Et_3N.

Reaction of Diethyl β-Pyrrolidinoethyl Phosphite with EtI. A mixture of 1 g of the phosphite and 0.65 g of EtI was heated in a sealed tube at 60-65° for 4 h. We obtained 1.5 g (93%) of product, which after washing with ether had mp 56-58°. Found: C 36.90; H 7.11; I 31.73; N 3.56; P 7.62%. $C_{12}H_{27}INO_3P$. Calculated: C 36.85; H 6.91; I 32.48; N 3.57; P 6.91%.

From 2 g of dibutyl β-pyrrolidinoethyl phosphite and 1.5 g of BuI under the same conditions we obtained 2.25 g (70%) of product, which after washing with ether had mp 83-84°. Found: C 45.55; H 8.05; I 26.28; N 3.19; P 6.32%. $C_{18}H_{39}INO_3P$. Calculated: C 45.47; H 8.21; I 26.73; N 2.95; P 6.52%.

Reaction of Dipropyl β-Pyrrolidinoethyl Phosphite with Chloral. With stirring, to a benzene solution of 6 g of the phosphite at 50-70° was added 3.36 g of chloral in drops. After removal of the solvent and vacuum-distillation of the residue we obtained 3.9 g (61%) of dipropyl 2,2-dichlorovinyl phosphate with bp 82° (0.06 mm), d_4^{20} 1.2221, n_D^{20} 1.4493 [4].

CONCLUSIONS

The β-pyrrolidinoethyl esters of trivalent phosphorus acids were obtained for the first time and some of their properties were studied.

LITERATURE CITED

1. N. P. Grechkin and L. N. Grishina, Izv. Akad. Nauk SSSR, Ser. Khim., 1898 (1974).
2. N. P. Grechkin and L. N. Grishina, Izv. Akad. Nauk SSSR, Ser. Khim., 1670 (1973).
3. Topics in Phosphorus Chemistry, Vol. 5, Interscience, New York—London—Sydney (1967), p. 261.
4. W. F. Bartal, B. H. Alexander, F. A. Griang, and S. A. Hall, J. Am. Chem. Soc., 77, 2424 (1955).