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Abstract

Full Text

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ORGANOPHOSPHORUS DERIVATIVES OF AZETIDINE. AZETIDIDES OF PHOSPHORIC ACIDS

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Organophosphorus derivatives of azetidine have not, up to the present time, been subjected to systematic study. Only one communication has been published in the chemical literature (^1) on the preparation of diethoxyphosphonazetidide.

At the same time, organophosphorus derivatives of azetidine may be of considerable interest from the standpoint of studying their biological

Table 1

Azetidides of phosphoric acids

Compound formula	B.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR, found	MR, calcd.	N, %, found	N, %, calcd.	Yield, %
$(CH_3O)_2P(O)N-C_3H_6$	108–109/11	1.4447	1.1801	37.18	37.28	8.358.46	8.48	76.5
$(C_2H_5O)_2P(O)N-C_3H_6$	109–110/11	1.4410	1.0933	46.62	46.52	7.357.48	7.25	85.5
(iso-$C_3H_7O)_2P(O)N-C_3H_6$	123–124/11	1.4355	1.0310	55.98	55.75	6.246.21	6.33	80.5
(n-$C_3H_7O)_2P(O)N-C_3H_6$	133–134/10	1.4423	1.0469	55.90	55.75	6.536.63	6.33	88.5
(iso-$C_4H_9O)_2P(O)N-C_3H_6$	140–141/10	1.4401	1.0090	65.10	64.99	5.705.78	5.62	86.0
(n-$C_4H_9O)_2P(O)N-C_3H_6$	158–159/10	1.4446	1.0134	65.36	64.99	5.46	5.62	86.5
(iso-$C_5H_{11}O)_2P(O)N-C_3H_6$	164–165/10	1.4458	0.9956	74.07	74.23	5.015.20	5.05	85.0
$(C_6H_5O)_2P(O)N-C_3H_6$	203–204/6	1.5548	1.2186	76.10	76.26	4.644.90	4.84	83.6
$(C_2H_5O)P(O)(N-C_3H_6)_2$	82–83/1.2	1.4746	1.1209	51.20	51.14	13.8613.98	13.73	73.0
(n-$C_3H_7O)P(O)(N-C_3H_6)_2$	102–103/2.5	1.4735	1.0936	55.98	55.76	12.80	12.84	55.0
(n-$C_4H_9O)P(O)(N-C_3H_6)_2$	130–131/3	1.4723	1.0720	60.63	60.37	12.0112.22	12.07	72.0

Compound formula	B.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR, found	MR, calcd.	N, %, found	N, %, calcd.	Yield, %
$OP(NC_3H_6)_3$	144/2.5	crystalline substance, strongly hygroscopic	crystalline substance, strongly hygroscopic	crystalline substance, strongly hygroscopic	crystalline substance, strongly hygroscopic	19.60	19.80	19.56	74.0

activity. Interest in this field of application of azetidine derivatives has increased considerably, chiefly owing to the successes achieved in recent years in the study of organophosphorus derivatives of ethylenimine (the lower homolog of azetidine) and their practical significance.

By the action of azetidine on dialkylphosphoric acid chlorohydrides, the synthesis of a series of azetidides of dialkylphosphoric acids was carried out.

$$(RO)_2POCl + 2HNC_3H_6 \rightarrow (RO)_2P(O)NC_3H_6 + C_3H_6NH \cdot HCl$$

By an analogous reaction, diazetidides of alkylphosphoric acids and triazetidide of phosphoric acid were obtained.

The properties of the compounds obtained by us are given in Table 1.

Using the reactivity of the azetidine ring, we have begun a study of certain transformations of azetidides of dialkylphosphoric acids. Thus, by the action of chlorine on diethoxyphosphonazetidide, N-chloro-, N-γ-chloropropylamide of diethylphosphoric acid was obtained.

$$(C_2H_5O)_2P(O)N\begin{matrix} & CH_2 & \\ CH_2 & & CH_2 \end{matrix} + Cl_2 \rightarrow (C_2H_5O)_2P(O)N\begin{matrix} CH_2CH_2CH_2Cl \\ Cl \end{matrix}$$

Toward a number of chemical agents possessing labile hydrogen (amines, thiophenol, etc.), the azetidine ring in its organophosphorus derivatives proved to be considerably more stable than the aziridine ring.

Experimental Part

1. Preparation of azetidides of phosphorous acids. All azetidides of dialkylphosphorous, alkylphosphonous, and phosphoric acids were obtained under identical conditions. Example: preparation of ethylphosphonic acid diazetidide.

To a solution, cooled to (−) 5-0°, of 12.4 g of azetidine in 60 ml of benzene, a solution of 8.9 g of ethylphosphonous acid dichloroanhydride in 50 ml of benzene

is slowly added dropwise with vigorous stirring. The reaction mixture is then stirred for 2 hours at room temperature and for about 1 hour at reflux temperature. The precipitate is then filtered off, and the filtrate, after removal of the solvent, is distilled twice. The bath temperature must not exceed 200°, since above this temperature polymerization of the product occurs in the distillation flask. This gives 8.1 g of product with b.p. 82–83°/1.2 mm.

2. Addition of chlorine to diethylphosphoric acid azetidide (2). To a solution of 4.85 g of the amide in 40 ml of carbon tetrachloride, a solution of 1.8 g of chlorine in the same amount of solvent was added. The temperature was maintained at 0°. After the reagents had been combined, the whole was left overnight. The next day the solvent was removed under vacuum, and the residue was distilled twice. Obtained: 4.64 g (70% of theory) of a thick oily substance with b.p. 124–5°/2 mm, n_D^{20} 1.4565; d_4^{20} 1.2174; MR found 59.00; calculated 58.45.

$C_7H_{16}O_3PNCl_2$.	Found %: Cl 26.60; 26.46
	Calculated %: Cl 26.89

On standing for a long time it crystallizes in the form of needles.

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References Cited

[1] N. P. Grechkin, *Izv. AN SSSR, OKhN*, 1962, No. 8, 1495.
[2] N. P. Grechkin, *Izv. AN SSSR, OKhN*, 1957, No. 9, 1053.

Note: Figure translations are in progress. See original paper for figures.