T. A. Mastryukova, M. V. Lazareva, and V. V. Perekalin

One of the extensively used methods for the synthesis of aliphatic amino derivatives is based on the reduction of the corresponding nitro compounds, which in recent years have become readily available compounds. In the chemistry of organophosphorus compounds this method of preparation has received little development, since organophosphorus nitro compounds are quite difficultly accessible.

The two most promising routes for the preparation of organophosphorus nitro compounds are: the addition of nitroalkanes to organophosphorus compounds that contain a multiple bond, or the addition of organophosphorus compounds to nitroolefins. Both of these methods make it possible to obtain organophosphorus nitro compounds with different substituents in the alkyl radicals. The first method was used by us to obtain 1-hydroxy-2-aminoisopropylphosphonates [1, 2] and γ -aminopropylphosphonic acid [3].

The addition of organophosphorus compounds, containing a labile hydrogen atom, to nitroolefins was first accomplished by Pudovik and Sitdikova [4]

 $(RO)_2PHO + C = CHNO_2 \rightarrow (RO)_2P(O)C - CH_2NO_2$

However, the obtained nitroalkylphosphonates were not subjected to reduction. We employed this method, with some modifications, and ran the reaction of dialkyl phosphites and thiophosphites not only with nitroisoamylene [4] and nitropropylene, but also with ω -nitrostyrene. In [4] the authors observed only the polymerization of the ω -nitrostyrene. We found that the reaction can be directed toward addition if a large excess of the dialkyl phosphite is used and the reaction is run in the presence of an equimolar amount of a mild base (triethylamine); polymerization to the polystyrene is observed here, but it does not exceed 50-60%. The obtained O,O-dialkyl 1-phenyl-2-nitroethylphosphonates are crystalline compounds [Table 1, compounds (I)-(III)].

In contrast to the data given in [4], the phosphonoacetic ester adds easily to nitroisoamylene and nitropropylene, provided

 $CH_{3}CH = CHNO_{2} + (C_{2}H_{5}O)_{2}P(O)CH_{2}COOC_{2}H_{5} \rightarrow (C_{2}H_{5}O)_{2}P(O)CHCOOC_{2}H_{5}$

CH₃CH−CH₂NO₂

the reaction is run in absolute alcohol medium, using an equimolar amount of sodium alcoholate, and the reaction mixture is heated for 30-40 min on the water bath.

The catalytic reduction of the obtained nitroalkylphosphonates with hydrogen on Raney nickel led to the corresponding aminoalkylphosphonates, which were also characterized as the picrates. The free 1-alkyl-2-aminoalkylphosphonic acids were obtained by the hydrolysis of the esters with hydrochloric acid. They give an intense color with 0.1% ninhydrin solution [5].

The constants, analyses and yields of the obtained compounds are given in Table 1. Their structure was corroborated by the data of the IR spectra. The spectra of compounds (I)-(VII) (see Table 1) contain absorption bands in the regions 1559-1565 and 1370-1384 cm⁻¹ (NO₂ group); 1248-1256 cm⁻¹ (P=O); 968-995 and 1015-1047 cm⁻¹ (P-O-C); P=S absorption is observed in the spectra of compounds (III) and (V) in the region 777-789 cm⁻¹. The IR spectra of the reduction products (VIII), (X), (XIII) and (XIV) contain absorption bands at 3390-3420 and 3315-3322 (NH₂); 1233-1237 (P=O); 1022-1045 and 948-1027 cm⁻¹

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. A. I. Gertsen Leningrad State Pedagogic Institute. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1164-1168, May, 1972. Original article submitted July 14, 1970.

© 1972 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.

Empirical for-	mula	$C_{10}H_{14}NO_5P$	C ₁₂ H ₁₈ NO ₅ P	C12H18NO1PS	C11H24NO5P	C9H20NO4PS	C ₁₃ H ₂₆ NO ₇ P	C11H22NO7P	$C_{12}H_{20}NO_{8}P$	C18H23O10PN4	C9H22NO3P	C15H25N4010P	C ₁₃ H ₂₀ NO ₃ PS	C ₁₁ H ₂₆ NO ₃ P	C ₉ H ₂₂ NO ₂ PS	C ₆ H ₁₂ NO ₃ P	C ₅ H ₁₄ NO ₃ P
	2° %			$\frac{10,24}{10,57}$	Ι.	$\frac{11,59}{11,89}$	l	1	1	1	I		$\frac{11,57}{11,76}$		$\frac{13,24}{13,38}$	1	l
To characterize the second	20 11	$\frac{11,93}{11,96}$	$\frac{10,80}{10,80}$	$\frac{10,15}{10,21}$	$\frac{11,10}{11,03}$	$\frac{11,59}{11,52}$	$\frac{8,90}{9,13}$	I		$\frac{6,11}{6,37}$	1	$6,81 \\ 6,85$	1	I		$\frac{15,43}{15,42}$	$\frac{18,57}{18,56}$
culated	-N, %	$\frac{5,48}{5,40}$	$\frac{4,85}{4,88}$	$\frac{4,69}{4,62}$	$\frac{5,09}{4,98}$	5,36 5,20	$\frac{4,05}{4,13}$	$\frac{4,44}{4,50}$	$\frac{5,49}{5,44}$	$\frac{11,73}{11,52}$	$\frac{6,30}{6,28}$	$\frac{13,07}{13,05}$	$\frac{5,03}{5,13}$	5,75 5,57	5,96 5,85	6,96 6,96	$\frac{8,34}{8,32}$
Found/cal	<u></u> д, %	$\frac{5,38}{5,40}$	6,53 6,29	$\frac{6,00}{5,98}$	$\frac{8,79}{8,54}$	$\frac{7,67}{7,43}$	$\frac{7,52}{7,72}$	l	1	$\frac{5,03}{4,80}$	I	5,66 $5,53$	1	1	1	6,03 5,97	$\frac{8,48}{8,32}$
	2° 5	$\frac{46}{46}, \frac{36}{44}$	50,14 50,17	$\frac{47,75}{47,53}$	$\frac{47,08}{47,00}$	$\frac{40,35}{40,27}$	$\frac{46,13}{46,01}$	1	1	$\frac{44,64}{44,45}$	1	39,87 39,82	1	1	I	$\frac{47,82}{47,76}$	$\frac{35,92}{35,94}$
	CLAR.		l	1	69, 27 69, 36	68,00 68,37	$\frac{80,62}{80,81}$	$\frac{72,27}{72,37}$	1	1	$\frac{57,99}{58,21}$	1	1	$\frac{67,31}{67,50}$	$\frac{65,89}{66,11}$	1	I
²⁰	ģ	ť	l	1	1,4450	1,4730	1,4488	1,4341	1,4868		1,4491	1	1,5405	1,4478	1,4767	l	1
d ²⁰	4	l	1	1	1,0787	1,1112	1,1213	1,1240	1,0949		1,0342	1	1,1226	0,9985	1,0261		1
Mp, °C or bp.°C (p,	mm of Hg)	103104	6566	3839	106-107 (0,1)	$113-114 \\ (0,1)$	$\begin{array}{c} 147-149 \\ (0,1) \end{array}$	9596 (0,1)	$103-104 \\ (0,1)$	163—164	88—89 (0,1)	112113	$\begin{array}{c} 107-108 \\ (0,1) \end{array}$	89_{-0}^{-90}	86-87 (0,1)	295—296 /decompn	270—272 (decompn.
Yield,	0/0	13	27	29	31	48	54	48	73	75	80	64	40	82	59	62	65
Compound		$NO_z-CH_2-CH-P(O)(OCH_3)_2$ $\int_{C_6H_5}^{I}$	NO2-CH2-CHP(0)(OC2H6)2 CcH6	$NO_2-CH_2-CH-P(S)(OC_2H_k)_2$ C_6H_5	NO2-CH2-CH-P(0)(i-OC3H,)2 CH(CH4,)2	NO _z CH ₂ CHP(S)(OC ₂ H ₈) ₂ ĊH(CH ₃) ₂	C00G2H5 N02-CH2-CH-CH-P(0)(0C2H3)2 CH(CH3)2	$\begin{array}{ccc} CH_2 - CH - CH - P(0)(OC_2H_6)_2 \\ & & \\ NO_a & CH_3 & COOC_2H_6 \end{array}$	$\begin{array}{c} H_{z}N-CH_{z}-CH-P(O)(OC_{z}H_{s})_{z}\\ C_{a}^{\dagger}H_{s} \end{array}$	Picrate	H ₂ N~CH ₂ -CH-P(O)(OC ₂ H ₆) ₂ CH(CH ₃) ₂	Picrat e	H2NCH2CHP(S)(OC2H6)2 CtH5	H2NCH2CHP(0)(i-OC3H-)2 CH(CH3)8	H ₂ N-CH ₂ -CH-P(S)(OC ₂ H ₆) ₂ CH(CH ₃) ₂	$H_2N-CH_2-CH-P(O)(OH)_2$ C_6H_5	$\begin{array}{c} H_2N-CH_2-CH-P(0)(OH)_2 \\ \downarrow \\ CH(CH_4,2) \end{array}$
No.		I	II	III	IV	>	IN	ΛII	VIII	IX	×	XI	ЛIX	шх	XIV	XV X	XVI

TABLE 1. Constants and Analyses of Nitro- and Aminoalkylphosphonates

(P-O-C). In the IR spectrum of acids (XV) and (XVI) are present a broad "ammonium" band at 3075 cm⁻¹ and a band at 1155-1160 cm⁻¹ [P(O) OH(O⁻)].

EXPERIMENTAL METHOD

Preparation of O, O-Dialkyl 1-Phenyl-2-nitroethylphosphonates. To a mixture of 0.01 M of β -nitrostyrene, dissolved in 100 ml of absolute benzene, and 0.25 M of the dialkyl phosphite [6] or thiophosphite [7], with stirring, was added 60 drops of freshly distilled absolute triethylamine. The mixture was kept at room temperature for 7-9 days. A copious precipitate of the polymer deposited, and the color of the solution changed to orange-red. The polymer was filtered, washed with absolute benzene, and the solvent and excess dialkyl phosphite were vacuum-distilled. The thick dark residue was transferred to a beaker, 50 ml of either hexane, heptane or petroleum ether was added, and the mixture was stirred vigorously. After some time the entire mass crystallized; it was purified by pressing on a porous plate and recrystallized from hexane containing several drops of CCl_4 . Colorless needle crystals were obtained [see Table 1, compounds (I)-(III)].

Preparation of O,O-Dialkyl 1-Isopropyl-2-nitroethylphosphonates. With stirring and cooling to $0-5^{\circ}$, to a mixture of 0.1 M of nitroisoamylene and 0.1 M of the dialkyl phosphite or thiophosphite was added in drops a solution of C_2H_5ONa , which was prepared from 0.05 g-atom of Na and 20 ml of absolute ethanol. The mixture was stirred for 1 h at room temperature, neutralized with acetic acid, and poured into 200 ml of a mixture of water and ice. The product was extracted with ether (5 × 50 ml) and then dried over MgSO₄. The ether was distilled off and the residue was vacuum-distilled [compounds (IV) and (V)].

Preparation of O, O-Diethyl 1-Carbethoxy-2-alkyl-3-nitropropylphosphonates. The addition of the phosphonoacetic ester of nitroisoamylene was run by the above given procedure, taking for reaction 0.1 M of C_2H_5ONa in 40 ml of absolute alcohol per 0.1 M of starting components. The mixture was heated on the water bath for 30 min. The further workup was the same as indicated above.

The addition of the phosphonoacetic ester to nitropropylene was run in absolute benzene medium, in the presence of triethylamine, using a 1:1:1 ratio of the components [compounds (VI) and (VII)].

The O,O-dialkyl 1-phenyl (or isopropyl)-2-aminoethylphosphonates and their picrates, and the 1-phenyl (or isopropyl)-2-aminoethylphosphonic acids, were prepared as described in [3].

CONCLUSIONS

Some new O, O-dialkyl nitroalkylphosphonates were synthesized by the addition of dialkyl phosphites and thiophosphites to nitroolefins. The corresponding aminophosphonates were obtained from them by reduction. The hydrolysis of the latter gave the corresponding aminoalkylphosphonic acids.

LITERATURE CITED

- 1. T. A. Mastryukova, G. M. Baranov, V. V. Perekalin, and M. I. Kabachnik, Dokl. Akad. Nauk SSSR, 171, 1341 (1966).
- 2. G. M. Baranov, T. A. Mastryukova, V. V. Perekalin, M. V. Ponomarenko, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 179 (1969).
- 3. T. A. Mastryukova, M. V. Lazareva, and V. V. Perekalin, Izv. Akad. Nauk SSSR, Ser. Khim., 1353 (1971).
- 4. A. N. Pudovik and F. N. Sitdikova, Dokl. Akad. Nauk SSSR, 125, 826 (1959).
- 5. S. G. Warren, J. Chem. Soc., 1349 (1966).
- 6. Preparative Organic Chemistry, Coll. Vol. 3 [in Russian], Khimiya (1952), p. 504.
- 7. Taro Jamasaki, Sci. Repts. Res. Inst. Tohoku Univ., A <u>11</u>, 73 (1959); C. A. <u>54</u>, 24339 (1960).