REACTIONS OF THE TRIMER OF PHOSPHONITRILE CHLORIDE

V. Reaction of the Trimer of Phosphonitrile Chloride with Piperidine*

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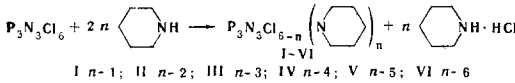
Replacement of the chlorine atoms of the trimer of phosphonitrile chloride by piperidine has yielded derivatives with a degree of replacement ranging from one to six chlorine atoms. In the case of the replacement of two and four chlorine atoms, isomeric di- and tetrapiperidino derivatives of the trimer of phosphonitrile chloride have been isolated.

Reaction of the trimer of phosphonitrile trichloride (TPNC) with piperidine has repeatedly attracted attention [1–5], but for a long time no one was able to obtain any piperidino derivatives of TPNC other than the completely substituted one. In recent years, communications have appeared on the replacement of the chlorine atoms of TPNC by piperidine and on the kinetics of this reaction [7, 8].

In view of the work carried out on the aminolysis of TPNC, we began the investigation of the reaction of TPNC with piperidine with a study of the successive replacement of the chlorine atoms in TPNC by piperidine in accordance with the scheme [6]:



I n-1; II n-2; III n-3; IV n-4; V n-5; VI n-6

The reaction of TPNC with piperidine was carried out in an inert organic solvent (ether or benzene). Piperidine was used as the acceptor of the hydrogen chloride liberated. With an increase in n, the temperature conditions and time of the reaction were changed. During the purification of the reaction products it was established that in all cases the reaction took place ambiguously. The reaction mixture always contained, in addition to the compound with the given number n of replaced chlorine atoms, derivatives with a larger (n + 1) or a smaller (n – 1) degree of replacement of the chlorine atoms by the piperidino group. The isolation of individual substances from the reaction mixtures was performed by means of chromatography or fractional crystallization.

All the piperidine derivatives of TPNC consist of colorless crystalline substances with sharp melting points which are soluble in the usual organic solvents.

EXPERIMENTAL

Chromatography was carried out on type KSK silica gel with a particle size of 0.25 mm dried at 150° C. Dry solvents were used for performing the reactions and for chromatography.

Pentachloropiperidinotriphosphonitrile (I). With stirring, 1 g (12 mM) of piperidine in 10 ml of ether was added to a solution of 2 g (5 mM) of TPNC in 50 ml of ether at 8–10° C. After the end of the addition, the reaction mixture was stirred for another 4 hr and was left to the following day. Then 0.69 g (97%) of piperidine hydrochloride was filtered off and the ether was driven off from the filtrate. The colorless crystalline residue (2.31 g) was dissolved in the minimum amount of hexane and transferred to a column of silica gel (15 g) in hexane. When hexane was passed through the column, 0.23 g of the initial TPNC was first eluted and then 1.62 g of a substance with mp 67.5–69° C. After crystallization from hexane, mp 68–69° C. Benzene eluted 0.3 g of tetrachlorodipiperidinotriphosphonitrile (II), mp 104–105° C (from petroleum ether).

*For part IV, see [6].

Table 1

Conditions for Obtaining the Products of the Reaction of the Trimer of Phosphonitrile Chloride with Piperidine

Amounts of reactants, g (mole)		Amount of ether, ml	Temperature, °C	Time of the reaction, hr	Yield of reaction product, %*								Notes
TPNC	$C_5H_{11}N$				I	II	IIa	III	IV	IVa	V	VI	
2 (0.005)	1 (0.012)	60	8–10	4	70[a]	10[b]	—	—	—	—	—	—	10% of the initial TPNC
15 (0.037)	15 (0.18)	200	from −3 to −5	5	—	54	9.3	—	—	—	—	—	
2 (0.005)	2.94 (0.035)	70	8–10	3	—	22[c]	—	34[c]	—	—	—	—	0.75 g of a substance of undetermined structure
5.2 (0.012)	16.5 (0.195)	120	20	4	—	—	—	—	56.2[b]	7.4[b]	8[d]	—	
3.47 (0.0085)	13 (0.15)	75	80	24	—	—	—	—	—	—	89.7	—	

*Compounds II, IIa, and VI were isolated by crystallization and the others by chromatography. The letters a–d denote the solvents used for isolation: a–hexane; b–benzene; c–petroleum ether; d–ether.

Table 2

$P_3N_3Cl_{6-n}(N\bigcirc)_n$

Compound	n	Mp, °C	Solvent for crystallization	Empirical formula	Found, %				Calculated, %			
					C	H	Cl	N	C	H	Cl	N
I	1	68—69	Hexane	$C_5H_{10}Cl_5N_4P_3$	15.51	2.55	44.26	14.07	15.15	2.54	44.72	14.13
II	2	104—105	Petroleum ether	$C_{10}H_{20}Cl_4N_5P_3$	26.71	4.59	31.76	—	26.98	4.53	31.86	—
IIa	2	127—129	Petroleum ether	$C_{10}H_{20}Cl_4N_5P_3$	27.16	4.72	—	15.66	26.98	4.53	—	15.73
III	3	113.5—114.5	Petroleum ether	$C_{15}H_{30}Cl_3N_6P_3$	36.42	6.03	21.87	17.70	36.49	6.13	21.54	17.02
IV	4	111—112	Hexane	$C_{20}H_{40}Cl_2N_7P_3$	44.52	7.35	13.25	18.03	44.28	7.43	13.08	18.08
IVa	4	113—115	Hexane–ether	$C_{20}H_{40}Cl_2N_7P_3$	44.53	7.49	13.54	18.05	44.28	7.43	13.08	18.08
V	5	121—123.5	Petroleum ether	$C_{25}H_{50}ClN_8P_3$	50.48	8.55	6.00	18.89	50.79	8.53	6.00	18.96
VI	6	258—262	Benzene	$C_{30}H_{60}N_9P_3$*	56.77	9.55	—	19.72	56.65	9.39	—	19.72

*Found, %: P 14.16. Calculated, %: P 14.54.

Tetrachlorodipiperidinotriphosphonitrile (II–IIa). With stirring, 15 g (0.18 mole) of piperidine in ether was added to a solution of 15 g (0.037 mole) of TPNC in 150 ml of ether at a temperature of from −3 to −5° C. After the end of the addition, the reaction mixture was stirred at −3° C for another 5 hr. On the following day the piperidine hydrochloride was filtered off and the solvent was driven off from the filtrate. Fractional crystallization of the residue (19.73 g) yielded substance A with mp 102–104° C, substance B with MP 89–90° C and a noncrystallizing oil.

Substance A, after recrystallization from petroleum ether, yielded **II**, mp 104–105° C. The fractional crystallization of substance B yielded 3.02 g of **II**, mp 104–105° C, and 1.8 g (9.3%) of an isomeric tetrachlorodipiperidinotriphosphonitrile **(IIa)**, mp 127–129° C.

The conditions for obtaining and isolating the piperidino derivatives are given in Table 1. The constants and elementary analyses of the compounds obtained are given in Table 2.

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