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Studies on Phosphorus-Containing Polymers. VIII. On the Reaction of Triphosphonitrilic Chloride with Cyclohexanol or Allyl Alcohol

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Studies on Phosphorus-Containing Polymers. VIII. On the Reaction of Triphosphonitrilic Chloride with Cyclohexanol or Allyl Alcohol

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ABSTRACT

Triphosphonitrilic chloride $(PNCl_2)_3$ was prepared from phosphorus pentachloride with ammonium chloride. This paper is concerned with the reaction of triphosphonitrilic chloride and cyclohexanol or allyl alcohol, and with the properties of cyclohexyl or allyl triphosphonitrilic acid esters. We studied three methods: (1) reaction of triphosphonitrilic chloride with cyclohexanol or allyl alcohol by heating, (2) condensation of sodium cyclohexyl or allyl alcoholate with triphosphonitrilic chloride, (3) condensation of triphosphonitrilic chloride with cyclohexanol or allyl alcohol in the presence of pyridine as a catalyst. The result was that the synthesis of hexacyclohexyl or hexaallyl triphosphonitrilic acid esters can be accomplished by employing the second method, but the first and third methods do not work.

1. INTRODUCTION

Amorphous rubberlike polymers represented by the formula $(PNCl_2)_n$, derived from triphosphonitrilic chloride (TPNC), are the so-called "anorganic rubbers" [1] having elastic quality. Owing to their high heat resistance, the study of these has recently grown vigorous in the field of polymerization products. The purpose of our present study is to obtain basic knowledge of organic high molecular compounds containing phosphorus atom, prepared from TPNC by the substitution of the chlorine atom therein with an organic group. We previously investigated the reactions of TPNC with nucleophilic reagents such as aliphatic alcohols [2, 3] and reported on the condensation products and their properties. Similar reactions are expected to occur between TPNC and alicyclic alcohols and between TPNC and unsaturated alcohols, instead of saturated aliphatic alcohols, but no involved reaction product has been reported. The study is thus particularly aimed at making apparent the properties of the products resulting from the reactions of TPNC with cyclohexanol and allyl alcohol which were selected as typical alicyclic and unsaturated alcohols, respectively, and at throwing light on the mechanism of the reactions. Hereinafter will be described some experimental results obtained by the three reaction processes:

(1) Thermal condensation with the separation of hydrogen chloride
(2) Condensation with the separation of sodium chloride
(3) Condensation in the presence of pyridine as a catalyst, with the separation of hydrogen chloride

2. EXPERIMENT

2.1 Synthesis of TPNC and the Purification of Reagents

2.1.1 Synthesis of TPNC

TPNC was synthesized by a technique already reported [4, 5] from phosphorus pentachloride and ammonium chloride using tetrachloroethane as the solvent. The crude product was recrystallized from petroleum ether to produce white plate crystals, mp 112-113°C. (The value described in the literature [4, 5] is 114°C.)

Analysis: Calculated for $(PNCl_2)_3$: N, 12.08%; molecular weight, 348.

Found: N, 12.13%; molecular weight, 339.

2.1.2. Cyclohexanol

A commercial preparation of cyclohexanol was dried with quick lime and rectified. The distillate fraction of bp 160-161°C was used for experiments.

2.1.3. Allyl Alcohol

To a commercial preparation of allyl alcohol was added benzene at about 20% by the volume of the former, and the mixture was subjected to azeotropic distillation to remove water. Then the distillate fraction of bp 96-97°C was collected for experiments.

2.1.4. Pyridine

A commercial preparation of pyridine was refluxed with barium oxide for 24 h and filtered. The distillate fraction of bp 114.5-116°C was used for experiments.

2.2. Reaction of TPNC with Cyclohexanol

2.2.1. Thermal Condensation with the Separation of Hydrogen Chloride

For the reaction, the alcohol and $P_3N_3Cl_6$ were used in molar ratios of 3, 4, 5, and 7. They were placed in a three-necked flask fitted with a thermometer, a stirrer, and a reflux condenser, and refluxed for a fixed time. During the reaction, crystals came out. After completion of the reaction, the crystals were separated from the liquid material by filtration and recrystallized from water. The liquid material was distilled under reduced pressure to separate low boiling point substances. The distillate of low boiling point was rectified with a small Hempel's fractioning column while the residue of high boiling point was subjected to determination of molecular weight.

2.2.2. Condensation with the Separation of Sodium Chloride

The same reaction apparatus was used as in Section 2.2.1. In a three-necked flask were placed 6.9 g of metallic sodium and an equivalent excess of the alcohol. After the completion of reaction, surplus alcohol was distilled off. To the resultant was added 100 cc of xylene as a solvent, followed by 17.5 g of TPNC. Then the mixture was refluxed at 130-140°C for 15 h. As the reaction proceeded, the reaction mixture turned yellow and got red-brown when the reaction was completed. The solution, well cooled, was filtered from crystallized sodium chloride. The filtrate was transferred to a separatory funnel and washed with dilute (1:10) hydrochloric acid, followed by water until the Cl^- test was thoroughly negative. Then it was dehydrated with anhydrous sodium carbonate, distilled to be freed of xylene, and finally distilled at 140°C under reduced pressure of 10 mmHg to complete the removal of unchanged alcohol and TPNC. The residue was subjected to analysis.

2.2.3. Condensation in the Presence of Pyridine Used as a Basic Catalyst, with the Separation of Hydrogen Chloride

The reaction is regarded as represented by

$$P_3N_3Cl_6 + \chi R{\cdot}OH + \chi C_5H_5N \longrightarrow P_3N_3Cl_{6-x}(OR)_x + \chi C_5H_5N{\cdot}HCl$$

where R = C_6H_{11} and χ is an integer of from 1 to 6.

The reaction equation suggests that the addition of an adequate pyridine fully converts the by-product HCl into the salt of pyridine, and the assumed ester $P_3N_3Cl_{6-x}(OR)_x$ escapes from the secondary hydrolysis, resulting in a greater yield of the ester. The reaction was carried out with the same apparatus as in Section 2.2.1. After the completion of the reaction, the hygroscopic crystals of $C_5H_5N{\cdot}HCl$ were filtered off. The crystals were dissolved in xylene and thoroughly washed with water until the Cl^- test was negative. The solvent phase was adjusted to be neutral and was dried. The solvent was distilled off. Finally, distillation at 140°C under a reduced pressure of 10 mmHg was carried out to recover unchanged TPNC and alcohol. The residue was subjected to further study.

2.3. Reaction of TPNC with Allyl Alcohol

2.3.1. Thermal Condensation with the Separation of Hydrogen Chloride

Molar ratios of amount of alcohol to TPNC in experiments were 1, 2, 3, 4, and 5. Herein the description will be made by using Experiment 6 at a molar ratio of 4.

The TPNC and alcohol were placed in a three-necked flask fitted with a thermometer, a stirrer, and a reflux condenser, and refluxed for a fixed time. During the reaction, crystals separated. The crystals were filtered from liquid material, recrystallized from water, and analyzed. The liquid matter was distilled under ordinary pressure to expel surplus alcohol and in vacuo thoroughly freed of low boiling point substances. The low boiling point substances were rectified with a small Hempel's fractionating column while the residue was subjected to determination of molecular weight.

2.3.2. Condensation with the Separation of Sodium Chloride

In the same three-necked flask as in Section 2.3.1, 20 g of allyl alcohol and 4.14 g of metallic sodium in 40 cc of benzene were allowed to react to prepare the alcoholate. Surplus alcohol was distilled off. To the alcoholate, a solution of 10.5 g (0.03 mol) of TPNC in 50 cc of benzene was added drop by drop from a separatory funnel. The mixture was then refluxed for 5 h. The solution, well cooled, was filtered from a by-product of sodium chloride. The filtrate was transferred to another separatory funnel and washed with water until the Cl^- test was thoroughly negative, dehydrated with anhydrous sodium carbonate and finally distilled to expel benzene. The viscous residue was subjected to further study.

2.3.3. Condensation in the Presence of Pyridine Used as a Catalyst, with the Separation of Hydrogen Chloride

In the same three-necked flask as in Section 2.3.1, 0.18 mol (10.5 g) of alcohol, 0.03 mol (10.5 g) of TPNC, 0.18 mol (14.23 g) of pyridine and 100 cc of benzene used as a solvent were refluxed. The reaction mixture was transferred to a separatory funnel, washed with water, dehydrated, and distilled to expel benzene. No reaction product was obtained.

3. RESULTS AND DISCUSSION

3.1. Reaction of TPNC with Cyclohexanol

3.1.1. Thermal Condensation with the Separation of Hydrogen Chloride

Experiments were carried out according to the procedure mentioned in Section 2.2.1. After the first 30 to 60 min of reaction, hydrogen chloride evolved. The results obtained, together with the conditions for reaction, are given in Table 1.

With regard to the reaction products in Experiments 1 to 6 in Table 1, they are outlined as follows.

(a) Crystals Separated during Reaction. In the crystalline solid, Cl^-, PO_4^{3-} and NH_4^+ were qualitatively detected, and their contents were determined in the ordinary way. The results suggest that the crystalline solid mainly consists of ammonium chloride and a small amount of ammonium phosphate.

(b) Low Boiling Point Distillates. Rectification was made with a small Hempel's fractionating column. Figure 1 shows the distillation curve. By measuring their physical properties, the distillate fractions corresponding to Plateaus I, II, and III in the curve were identified as the azeotrope of cyclohexanol and water, cyclohexyl chloride, and cyclohexanol, respectively. Table 2 indicates the results in comparison to their literature values.

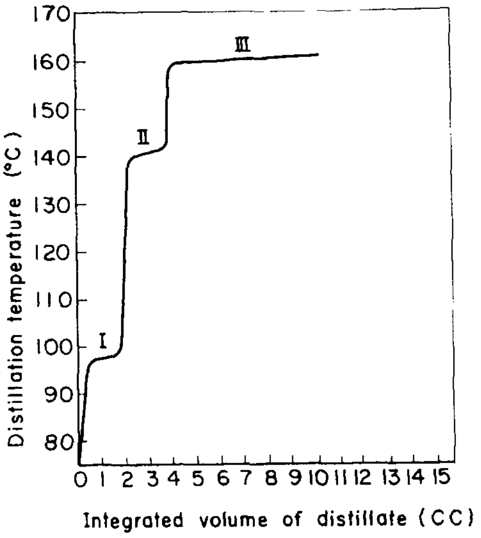
(c) Residue. After low boiling point substances were distilled off under reduced pressure, resinous high boiling point matter was left, whose analytical results are given by the examples in Table 3. No assumed compound as represented by the formula $P_3N_3Cl_{6-x}(OR)_x$, where x = 1 to 6, was found in the experiments.

These results show that the reaction products substantially consist of the crystals of ammonium chloride, and the substances of low boiling point of cyclohexyl chloride and water.

Table I. Conditions for and results of the reaction

a	b	c	d	e	f	g	h	i	j	k	l
1	17.5	0.05	90.0	0.9	3	120~130	3	6.0	34.4	25.5	*1
2	17.5	0.05	90.0	0.9	3	120~130	1	0.9	36.7	56.3	*2
3	10.5	0.03	90.0	0.9	5	120~130	5	5.1	38.1	14.5	*3
4	10.5	0.03	126.0	1.26	7	120~130	5	4.2	77.7	16.5	*4
5	34.8	0.10	240.0	2.4	4	120~130	3	13.5	142.0	60.3	*5
6	17.5	0.05	150.0	1.5	5	120~130	3	7.7	119.0	17.8	*6

a: Experiment No.
b: and c: Amounts of TPNC in gram and mol, respectively
d: and e: Amounts of Cyclohexanol in gram and mol, respectively
f: Molar ratio of Cyclohexanol to TPNC (6ROH/TPNC)
g: Reaction temperature (°C)
h: Reaction time (hour)
i: Yield of the crystalline product in gram
j: Yield of the low boiling point product in gram
k: Yield of the residual product in gram
l: Properties of the residual product
*1: Light orange, solid at ordinary temperature, resinous
*2: Whitish, resinous
*3: Reddish brown, resinous
*4: Reddish brown, resinous
*5: Dark reddish brown, somewhat fluid
*6: Reddish brown, resinous



I : Azeotrope of cyclohexanol and water
II : Cyclohexyl chloride
III : Cyclohexanol

FIG. 1. Distillation curve by the rectification of the primary distillate of the low boiling point (Exp. No. 3, molar ratio 5).

Table 2. Measurements of the low boiling point fractions obtained by the rectification

Fraction (identified name)	a	b	c	d
Fraction I : Azeotrope of cyclohexanol and water*	–	–	–	–
Fraction II : Cyclohexyl chloride	1.000	0.9609	1.4626	1.4626
Fraction III : Cyclohexanol	0.9624	0.9476	1.4650	1.4654

a and b : Described in the literature and found specific gravities (d^{20}_{4}), respectively

c and d Described in the literature and found refractive indexes (n^{20}_{D}), respectively

Notes : 1) Each specific gravity was of measurement with a specific gravity bottle.

2) Each refractive index was of measurement with an Abbe's refractometer.

3) The values described in the literature are from the book "Dictionary of organic compound" by Sir Ian Heilbron and H.M. Bunbury. (New York, Oxford University Press, 1953)

* The azeotrope was distilled at 97°C (The value described in the literature is 97.8 °C) with the separation of water.

Table 3. Elementary analysis of the residue

Exp. No.	Molar ratio of alcohol to TPNC	Cl(%)	N(%)	P(%)
5	4	0.54	3.08	16.59
6	5	0.46	0.56	15.65

This leads us to infer the following reaction mechanism: At the first stage of the mechanism a condensation occurs with the separation of hydrogen chloride:

$$P_3N_3Cl_6 + xC_6H_{11}OH \longrightarrow P_3N_3(OC_6H_{11})_x{\cdot}Cl_{6-x} + xHCl \qquad (1)$$

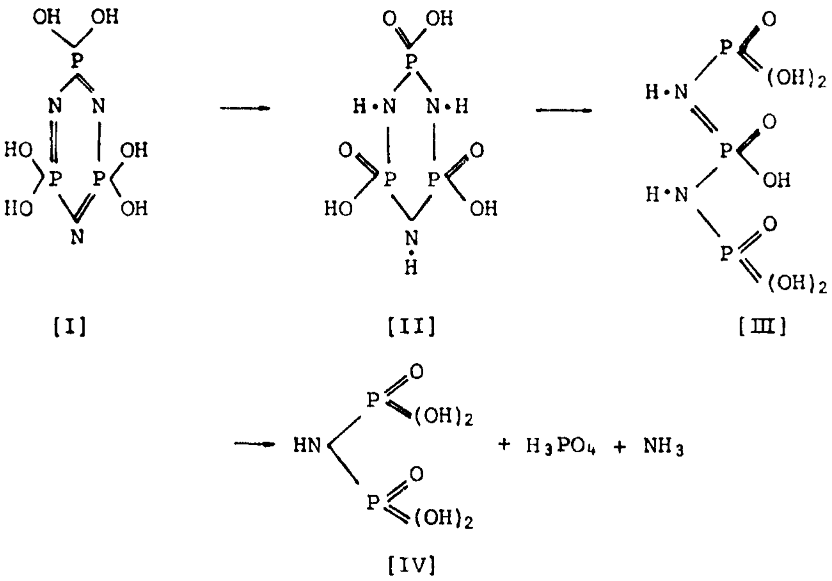
where x is an integer from 1 to 6.

Subsequently, the by-product hydrogen chloride reacts with surplus $C_6H_{11}OH$ and is converted into cyclohexyl chloride and water:

$$HCl + C_6H_{11}OH \longrightarrow C_6H_{11}Cl + H_2O \qquad (2)$$

Hydrogen chloride and water formed in accordance with Eqs. (1) and (2), respectively, react with a part of the cyclohexyl triphosphonitrilic ester, resulting in hydrolysis with the production of triphosphonitrilic acid $P_3N_3(OH)_6$ (I).

According to Stokes [6-8], referring to the reaction system illustrated later, Compound (I) is unstable and convertible by an intramolecular rearrangement into imidotriphosphonitrilic acid (II), which in turn decomposes with the opening of the ring in acid condition, through diimidotriphosphoric acid (III), to form, as end products, imidodiphosphoric acid (IV),



phosphoric acid, and ammonia. It is probable that in these experiments the same process was accomplished and the end products reacted with the by-product hydrogen chloride to form ammonium chloride and ammonium phosphate which crystallized during the reaction.

3.1.2. Condensation with the Separation of Sodium Chloride

The results of and the conditions for experiments by the procedure mentioned in Section 2.2.2 are listed in Table 4, and the properties of the reaction products are presented in Table 5. The data suggest that the resinous product is a compound represented by the formula $P_3N_3(OC_6H_{11})_6$. The reaction is expressed by

$$P_3N_3Cl_6 + 6C_6H_{11}ONa \longrightarrow P_3N_3(OC_6H_{11})_6 + 6NaCl$$

It is a hexa-substituted cyclohexylphosphonitrilic ester.

Table 4. Conditions for and results of the reaction

Amount of alcohol	$P_3N_3Cl_6$		$6NaOR/P_3N_3Cl_6$	Na		Solvent		Reaction		Yield of ester	
(g)[a)]	(g)	(mol)	(mol/mol)	(g)	(atom)	name	amount (cc)	temperature (°C)	time (hrs)	(g)	(%)[b)]
50.0	17.5	0.05	1	6.9	0.3	Xylene	100	130~140	15	21.7	59.0

Note: a) An excess of alcohol was used to be converted into alcoholate. The unchanged alcohol was distilled off.
b) Rate in relation to the calculated yield.

Table 5. Properties and analysis of the product

Produced ester	Property	Molecular formula[a)]	Molecular weight[b)]		Analysis					
					P (%)		N (%)		Cl (%)	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Cyclohexyl	Yellowish orange Resinous	$P_3N_3(OC_6H_{11})_6$	729	680	12.75	13.38	5.74	6.27	—	Trace

Note: a) By inference
b) Determined by cryoscopy, using benzene as a solvent.

Table 6. Conditions for and results of the reaction

a	b	c	d	e	f	g	h	i	j	k	l	m	n
1	30	0.3	17.5	0.05	24.0	0.3	1	xylene	100	110~120	4	—	10.0
2	18	0.18	10.5	0.03	18.0	0.2	1	toluene	100	100~110	4	9.5	10.8
3	18	0.18	10.5	0.03	18.0	0.2	1	toluene	100	100~110	10	38.5	10.5

a: Experimental number
b and c: Amounts of Cyclohexanol in gram and mol, respectively
d and e: Amounts of $P_3N_3Cl_6$ in gram and mol, respectively
f and g: Amounts of C_5H_5N in gram and mol, respectively
h: $6ROH/P_3N_3Cl_6$ (molar ratio)
i and j: Name of solvent and its amount used (cc)
k and l: Temperature (°C) and time (hour) of reaction, respectively
m and n: Amounts in gram of the crystalline and ester products, respectively

3.1.3. Condensation with the Separation of Hydrogen Chloride in the Presence of Pyridine as a Basic Catalyst

Table 6 lists the conditions for and the results of experiments by the procedure mentioned in Section 2.2.3, and Table 7 presents the properties of the reaction products.

Table 7. Properties and analysis of the product

Exp. No.	Produced ester	Property	Molecular formula[a]	Molecular weight[b]		Analysis			
						P (%)		N (%)	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
1	Cyclohexyl	Yellowish orange, Resinous	$P_3N_3Cl_4(OC_6H_{11})_2$	475	510	19.56	19.81	8,85	8.18
2	The same as above.		〃	–	–	19.56	19.89	8.85	8.23
3	The same as above.		〃	–	–	19.56	20.58	8,85	9.84

Notes : a) By inference
b) Determined by cryoscopy, using benzene as a solvent.

Compared with the ester produced by condensation with the separation of sodium chloride using the alcoholate as a reactant, the resultant ester in the catalytic experiment has a similar appearance but a different formula, $P_3N_3Cl_4(OC_6H_{11})_2$, inferred from the analytical data including the molecular weight. It is an incomplete substitution product of TPNC in which two of the six chlorine atoms are replaced. Therefore, a further study of such a technique, under particular reaction conditions, would permit the preparation of the hexa-substituted ester.

Measurement of the melting point showed that the crystals separated during the reaction were pyridine hydrochloride.

3.2. Reaction of TPNC with Allyl Alcohol

3.2.1. Thermal Condensation with the Separation of Hydrogen Chloride

Experiments were carried out according to the procedure mentioned in Section 2.3.1. Table 8 lists the results obtained as well as the reaction conditions.

Experiments 3 to 6 in Table 8 outline the products as follows.

(a) Crystals Separated during Reaction. The crystals gave positive tests for Cl^-, PO_4^{3+}, and NH_4^+, respectively, and their contents were determined. The results are indicated in Table 9.

Taking into consideration the calculated contents (N and Cl in ammonium chloride are 26.2 and 66.3%, respectively), the crystals may be mainly composed of ammonium chloride and a small amount of phosphoric acid and ammonium phosphate. The results in Table 9 show that the percentage of N to Cl is nearer to the composition of ammonium chloride with an increasing molar ratio of alcohol to TPNC.

(b) Low Boiling Point Distillates. For the purpose of making clear their constituents, the distillates of Experiment 6 were rectified with a small Hempel's fractionating column. The results

Table 8. Conditions for and results of the reaction

a	b	c	d	e	f	g	h	i	j	k	l
1	20.9	0.06	20.9	0.36	1	74~94	2	–	–	41~94°C 28.5	–
2	20.9	0.06	41.8	0.72	2	77~94	2	–	–	–	–
3	20.9	0.06	62.6	1.08	3	72~94	2	2.0	55.6	41~94°C 28.5	20.2
4	13.9	0.04	55.7	0.96	4	73~94	3	1.5	52.5	42~96°C 27.2	16.9
5	20.9	0.06	104.4	1.80	5	75~94	2	1.4	116.0	40~94°C 56.2	26.0
6	34.8	0.10	139.2	2.40	4	74~95	3	4.0	150.0	42~96°C 93.0	40.0

a : Experiment No.
b and c : Amounts of TPNC in gram and mol, respectively
d and e : Amounts of Allyl alcohol in gram and mol, respectively
f : Molar ratio of Allyl alcohol to TPNC (6ROH/TPNC)
g : Reaction temperature (°C)
h : Reaction time (hour)
i : Yield of the crystalline product in gram
j : Total yield of the liquid product in gram
k : Yield of the low boiling point in gram
l : Yield of the residual product in gram

Table 9. Elementary analysis of the crystalline product

Experiment No.	Molar ratio of Allyl alcohol to TPNC (6ROH/TPNC)	Analysis		
		P (%)	N (%)	Cl (%)
3	3	–	–	28.23
4	4	4.60	23.20	46.80
5	5	2.27	24.12	63.96
6	4	–	25.63	58.78

are plotted in Fig. 2. By measuring their physical properties, the distillate fractions corresponding to Plateaus I, II, and III in the curve were identified as allyl chloride, the azeotrope of allyl alcohol and water, and allyl alcohol, respectively. Table 10 gives the results in comparison with their literature values.

(c) Residue. The resinous matter obtained in Experiments 3 to 6 was extracted with water, and the extracts gave positive tests for PO_4^{3+}, Cl^-, and NH_4^+. Therefore, each contained a small amount of water-soluble ammonium chloride and ammonium phosphate, as described later. Table 11 lists each ion in the residue, the total and water-soluble contents as a percentage determined as well as the combined contents as a percentage produced by the subtraction of the soluble contents from the total contents.

The data in Table 11 infer that the residue is a compound having the formula $P_3N_3(OC_3H_5)_6$ because they agree substantially with the

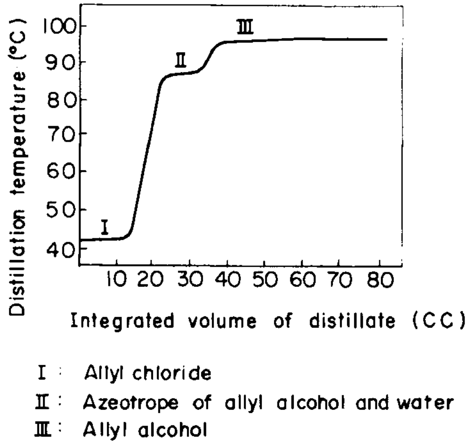


FIG. 2. Distillation curve by the rectification of the primary distillate of low boiling point.

Table 10. Measurements of the low boiling point fractions obtained by the rectification

Fraction (identified name)	a	b	c	d
Fraction I : Allyl chroride	0.9374	0.9357	1.4151	1.4157
Fraction II : Azeotrope of allyl alcohol and water	0.8573	0.8403	1.4135	1.4128
Fraction III : Allyl alcohol	0.8534	0.8871	1.4134	1.4134

a and b : Described in the literature and found specific gravities (d_4^{20}), respectively

c and d : Described in the literature and found refractive indexes (n_D^{20}), respectively

Notes : 1) Each specific gravity was of measurement with a specific gravity bottle.

2) Each refractive index was of measurement with an Abbe's refractometer.

3) The values described in the literature are from the book "Dictionary of organic compounds" Vols. I and II by Sir Ian Heilbron and H.M. Bunbury.

(New York, Oxford University Press, 1953)

Table 11. Elementary analysis of the residue

Exp. No.	Molar ratio of Allyl alcohol to TPNC (6ROH/TPNC)	Cl(%)			N(%)	P (%)		
		Total	Free	Combined		Total	Free	Combined
3	3	3.85	0.08	3.77	10.06	22.23	–	–
4	4	2.96	0.53	2.43	8.26	20.76	1.82	18.96
5	5	2.27	0.60	1.67	8.83	20.81	1.36	19.45
6	4	2.29	0.62	1.67	8.12	22.18	1.63	20.55

Table 12. Analysis of the product obtained as residue by the condensation with the separation of sodium chloride

	P (%)	N (%)	Cl (%)	Molecular weight
Found	18.63	9.15	trace	501
Calcd. as $P_3N_3(OC_3H_5)_6$	19.06	8.80	–	483

chemical composition of a six-membered ring allyl phosphonitrilic ester recognized as being produced by the condensation of TPNC with allyl alcohol and represented by the same formula. The calculated contents for the ester are N 8.80% and P 19.04%.

As described above, the crystals are recognized as a mixture of ammonium chloride and a very small amount of ammonium phosphate, the low boiling point distillates as allyl alcohol and water, and the resinous residue as $P_3N_3(OC_3H_5)_6$. Thus the following reaction mechanism is suggested.

In the first stage of the mechanism a condensation occurs with the separation of hydrogen chloride:

$$P_3N_3Cl_6 + \chi C_3H_5OH \longrightarrow P_3N_3(OC_3H_5)_x{\cdot}Cl_{6-x} + \chi HCl \qquad (3)$$

Where χ is an integer from 1 to 6.

The by-product hydrogen chloride subsequently reacts with surplus C_3H_5OH and is converted into allyl chloride and water:

$$HCl + C_3H_5OH \longrightarrow C_3H_5{\cdot}Cl + H_2O \qquad (4)$$

The hydrogen chloride and water resulting from Eqs. (3) and (4) react with part of the allyl triphosphonitrilic ester, which is subjected to hydrolysis with the production of triphosphonitrilic acid

$P_3N_3(OH)_6$, (I). The subsequential process of the reaction is the same as described in Section 3.1. Ammonia, one final product in the process, can react with hydrogen chloride. In this way the chloride and phosphate of ammonia would have been separated during the reaction.

3.2.2. Condensation with the Separation of Sodium Chloride

The residue in the experiments according to the procedure mentioned in Section 2.3.2 was analyzed and the results are given in Table 12.

Comparison between the values found and calculated in Table 12 establishes that the residue is a compound expressed by the formula $P_3N_3(OC_3H_5)_6$. The reaction may occur according to

$$P_3N_3Cl_6 + 6C_3H_5ONa \longrightarrow P_3N_3(OC_3H_5)_6 + 6NaCl$$

Thus the procedure has been shown to be usable for preparing hexa-substituted allyl triphosphonitrilic ester.

3.2.3. Condensation with the Separation of Hydrogen Chloride in the Presence of Pyridine as a Basic Catalyst

In the experiments according to the procedure mentioned in Section 2.3.3, both attempts failed to yield the desired ester from the benzene phase and to isolate pyridine hydrochloride as crystals, although a large amount of Cl^- and small amounts of NH_4^+ and PO_4^{3+} were detected in the washed benzene phase. In comparison with the two cases mentioned under the preceding method, it cannot be recognized clearly whether the unexpected result by this procedure is due to hydrolysis or to a different conversion due to the action of pyridine. Additional study of this question is intended later.

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