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Reaction of Chlorophosphazenes with 1,2-Epoxides

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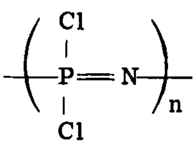
ABSTRACT

Studies on the reaction of chlorophosphazenes with 1,2-epoxides with a catalyst, in the presence or absence of solvent, are discussed. The physicochemical properties of the obtained chlorophosphazenes are described as well as the results of infrared spectroscopic measurements and examination of thermal properties.

Phosphazenes are included among phosphorus-containing compounds extensively used for many applications from biologically active agents to thermally stable plastics [1-7]. There is considerable interest in this group of compounds, as a consequence of the high reactivity of the chlorophosphazenes,



$n \geq 3$

which are parent substances for many syntheses [1, 2, 4], giving products with very valuable properties. The reaction of chlorophosphazenes with alcohols and phenols is of great importance in industry

[1, 7-14]. Alkoxy- and aryloxyphosphazenes obtained in this reaction, owing to the presence of the P–O–C group which is relatively resistant to hydrolysis, are used as flame retardants for plastics and man-made fibers, particularly viscose fibers [11, 15-17].

Chlorophosphazenes have special importance among the agents designed for viscose fibers. This is due to the synergism arising from the presence of chlorine atoms in the molecule containing phosphorus atoms [18, 19]. Up to now, some of these compounds have been obtained by prolonged reaction of phosphazenes with suitable halohydrines in the presence of a hydrogen chloride acceptor [11] [Eq. (1)].

$$(PNCl_2)_n + 2nHO{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}R \xrightarrow{2nC_5H_5N} [PN(OCH_2{-}\overset{\displaystyle Cl}{\overset{|}{CH}}{-}R)_2]_n + 2n\, C_5H_5N \cdot HCl \qquad (1)$$

Based on the literature on the reactions of 1,2-epoxides with orthophosphoric acid [20-22], phosphonyl chlorides [23, 24], phosphorus oxychloride [25, 26] and phosphorus trichloride or tribromide [27-29], one can conclude there is a possibility of reaction between chlorophosphazenes and 1,2-epoxides according to the scheme shown in Eq. (2).

$$(PNCl_2)_n + nx\,\underbrace{CH_2{-}CH}_{O}{-}R \xrightarrow{cat.} [PNCl_{2-x}(OCHClR)_x]_n \qquad (2)$$

where

$0 < x \leq 2$

$R = -H, -CH_3, -CH_2Cl, -C_6H_5$

In our Institute we have confirmed the possibility of this reaction [30-32] and have prepared a series of chloroalkoxyphosphazenes. References which appeared recently [33, 34] have supported our research results.

The present paper is concerned with the reactions of chlorophosphazenes with 1,2-epoxides by use of anhydrous aluminum chloride as catalyst in the presence or absence of solvent. The properties of the products obtained are also described.

EXPERIMENTAL

Chlorophosphazene oligomers obtained in the reaction of phosphorus pentachloride with ammonium chloride [35] were used for synthesis of chloroalkoxyphosphazenes. The properties of the starting materials are given in Tables 1 and 2.

Anhydrous aluminum chloride (BDH Chem. Ltd., England) was used as catalyst. Synthesis of chloroalkoxyphosphazenes was performed both in the presence of organic solvents, of which 1,1',2,2'-tetrachloroethane appeared to be most suitable, and without solvents. The reaction between chlorophosphazenes and 1,2-epoxides was carried out in a four-necked flask equipped with liquid-sealed stirrer, a dropper (or a bubbler for the introduction of ethylene oxide), a thermometer and a reflux condenser. Chlorophosphazenes, anhydrous aluminum chloride, and solvent, if used, were introduced into the reaction flask. The contents of the flask were mixed for 15 min and then a suitable 1,2-epoxide was introduced. The reaction was stopped after a specified time of heating, and the product was washed successively with dilute aqueous hydrochloric acid, sodium carbonate, and water to neutrality. Then the solution was dried with anhydrous sodium sulfate and the solvent was distilled off under a reduced pressure. The chloroalkoxyphosphazenes thus obtained were purified with activated carbon in carbon tetrachloride. The solvent was removed by distillation after the purification, and the residue constituting the reaction product was dried at 60-70°C under a pressure of 9.8×10^4 N/m^2.

The conditions of the reaction of chlorophosphazenes with 1,2-epoxides are given in Table 3.

The obtained phosphazene compounds were subjected to a quantitative microanalysis. The carbon and hydrogen content was determined by the Praegl method, phosphorus content by the Püschell method, and nitrogen content according to the Dumas method. The obtained products were also examined by infrared spectroscopy with the use of a Specord 71 IR instrument.

To determine the thermal behavior of the products, examinations were performed in the temperature range 20-500°C in air, at a heating rate of 10°C/min by use of a MOM instrument (Budapest, Hungary) based on the system of F. Paulik, I. Paulik, and L. Erdey.

TABLE 1. Properties of the Chlorophosphazenes

Property	Hexachlorocyclo-triphosphazene	Oligomers		
		Cyclic[a]	Liquid[b]	Mixture of phosphazenes[c]
Form	White crystals	White crystals	Liquid	Thick mass
Melting point (°C)	113-114	87-88	-	-
Frequency of the stretching vibrations of the PN group (cm^{-1})	1215, 875	1315, 1215, 875	1315-1270, 870	1315-1270, 1215, 870
^{31}P-NMR (ppm)	-19.0	-19.0; + 7, 1	-19.0; + 1, 1; + 2.0 + 7, 1; + 15.2; + 17, 0	-
Density (g/cm^3)	-	-	1.753	1.626

[a]Cyclic oligomers were obtained by recrystallization of the crystalline fraction. They contain mainly cyclic trimer and tetramer.

[b]Liquid oligomers containing mainly linear chlorophosphazenes were obtained as a filtrate from the chlorophosphazene mixture.

[c]40% of crystalline oligomers is found in the mixture of the chlorophosphazene oligomers.

TABLE 2. Properties of 1,2-Epoxides Used in Reaction with Chlorophosphazenes

Reagent	Chemical formula	Molecular weight	Boiling temperature (°C)	n_D^{20}	Source
Ethylene oxide	CH_2–CH_2–O	44.05	13	-	BDH Laboratory Chemicals Great Britain
Propylene oxide	CH_3–CH–CH_2O	58.08	33-36	1.3670	BDH Laboratory Chemicals Great Britain
Epichlorohydrin	$ClCH_2$CH–CH_2–O	92.53	116-117	1.4380	Dow Chem. Co.
Styrene oxide	C_6H_5–CH–CH_2–O	120.15	129/100 mm Hg	1.5355	Koch-Light Laboratories Great Britain

TABLE 3. Reaction Conditions of Chlorophosphazenes with 1,2-Epoxides

Type of reaction conditions	Amount of $AlCl_3$ (mole/mole $PNCl_2$)	Amount of 1,2-epoxide (moles/mole of $PNCl_2$)	Temperature t of the system during epoxide introduction (°C)	Temperature of the system after epoxide introduction (°C)	Time at temperature t during epoxide introduction (min)	Reaction time after epoxide introduction (min)	Concentration of chlorophosphazene (moles/liter solvent) $\times 10^2$
I	-	3.0	20	40	10	60	8.62
II	1.738	3.0	20	20	30	60	8.62
III	0.0869	4.0	20	40	10	60	8.62
IV	0.869	4.0	80	100	60	120	8.62
V	0.1738	4.0	80	100	120	120	17.24
VI	1.738	5.5	25	40	60	60	8.62
VII	1.738	3.0	20	35	120	60	8.62
VIII	0.0869	5.0	20	40	120	60	249.5
IX	0.869	3.6	80	100	120	60	43.1
X	0.1738	4.0	80	100	120	60	a
XI	0.1738	4.0	80	100	120	60	172.4
XII	0.0869	4.0	80	100	120	60	249.5
XIII	0.0869	3.6	80	100	60	60	86.2

[a]Without solvent.

TABLE 4. Effect of Anhydrous Aluminum Chloride Catalyst on the Properties of Reaction Product of Chlorophosphazene Cyclic Oligomers with Propylene Oxide (Synthesis Conditions Type I)

Amount of $AlCl_3$ (mole/mole of $PNCl_2$)	Product		
		Analysis	
	Melting point (°C)	C (%)	H (%)
0	87-88	-	-
0.4345	Thick liquid	7.6	1.1
1.738	Thick liquid	16.4	2.6

RESULTS AND DISCUSSION

The reaction of chlorophosphazenes with 1,2-epoxides and properties of the resulting products depend on a number of factors: the amount of catalyst used, time and temperature of the reaction, and the ratio of reacting substances. The catalyst, i.e., anhydrous aluminum chloride, exerts a great influence on the synthesis of chloroalkoxyphosphazenes. The effect of the amount of anhydrous aluminum chloride on the properties of the product obtained in the reaction of chlorocyclophosphazene oligomers with propylene oxide, is shown in Table 4. The results confirm that the extent of reaction of cyclic oligomers with propylene oxide is greatly affected by the amount of anhydrous aluminum chloride.

The amount of catalyst depends first of all on the type of chlorophosphazene oligomers. Linear oligomers, as is well known, are more reactive than the cyclic ones [36]. Therefore, a higher extent of reaction should be expected for liquid chlorophosphazene oligomers with 1,2-epoxide than for the cyclic oligomers. This assumption was confirmed experimentally, and the results are shown in Table 5. The results of elementary analysis confirm the higher reactivity of liquid chlorophosphazene oligomers, as products containing relatively large amounts of carbon were obtained with much lower content of the catalyst in the reaction medium. The other parameters of this process have less influence [32] on the reaction.

Several reaction products of chlorophosphazenes with 1,2-epoxides were obtained in the course of these experiments. Their properties are given in Table 6. Solubility of the reaction products in typical organic solvents was also ascertained.

A characteristic of the reaction of chlorophosphazenes with 1,2-epoxides, as is evident from the data given in Tables 3 and 6, is the relatively short duration of the reaction and the high yield of the product.

TABLE 5. Effect of the Amount of Anhydrous Aluminum Chloride as Catalyst on the Properties of the Reaction Product of Chlorophosphazenes with 1,2-Epoxide

Reaction conditions[a]	$PNCl_2$ oligomers	1,2-epoxide	$AlCl_3$ (mole/mole $PNCl_2$)	Form of product	Analysis of product: Found				Analysis of product: Calculated				Formula of the product	Reaction yield (%)
					C (%)	H (%)	P (%)	N (%)	C (%)	H (%)	P (%)	N (%)		
II	Hexachlorocyclotriphosphazene	Propylene oxide	1.738	Very thick liquid	15.3	2.6	19.8	9.0	15.5	2.6	20.0	9.1	$P_3N_3Cl_4(OC_3H_6Cl)_2$	90
III	Liquid	Propylene oxide	0.0869	Thick liquid	26.9	4.5	15.9	5.6	27.1	4.5	14.0	5.7	$P_6N_5Cl_4(OC_3H_6Cl)_{10}$	73
IV	Cyclic	Epichlorohydrin	0.869	Thick liquid	16.8	2.6	15.0	7.0	17.2	2.5	14.8	6.7	$P_3N_3Cl_3(OC_3H_5Cl_2)_3$	89
V	Liquid	Epichlorohydrin	0.1738	Thick liquid	20.8	3.2	10.5	4.2	20.4	2.9	10.9	4.4	$P_6N_5Cl_5(OC_3H_5Cl_2)_9$	71

[a]See Table 3.

TABLE 6. Properties of the Reaction Products of Chlorophosphazenes with 1,2-Epoxides

Reaction conditions[a]	$PNCl_2$ oligomers	1,2-Epoxide	Form of the product	Analysis of product: Found C (%)	Found H (%)	Found P (%)	Found N (%)	Calculated C (%)	Calculated H (%)	Calculated P (%)	Calculated N (%)	Formula of product	Reaction yield (%)
VI	Cyclic	Ethylene oxide	Thick, light, straw-colored paste	11.0	1.9	22.5	-	-	-	-	-	-	60
VII	Hexachlorocyclotriphosphazene	Propylene oxide	Thick, light, straw-colored liquid	27.8	4.7	14.6	6.6	28.2	4.8	14.6	6.6	$P_3N_3Cl(OC_3H_6Cl)_5$	79
VII	Cyclic	"	"	27.1	4.5	14.8	6.7	28.2	4.8	14.6	6.6	$P_3N_3Cl(OC_3H_6Cl)_5$	78
III	Liquid	"	Very thick, light straw-colored liquid	26.9	4.5	15.9	5.6	27.1	4.5	14.0	-	$P_6N_5Cl_4(OC_3H_6Cl)_{10}$	73
VIII	Mixture	"	Thick, light, straw-colored liquid	24.0	4.4	13.6	-	24.8	4.1	16.0	-	$P_3N_3Cl_2(OC_3H_6Cl)_4$	97

(continued)

TABLE 6 (continued)

Reaction conditions[a]	$PNCl_2$ oligomers	1,2-Epoxide	Form of the product	Found C (%)	Found H (%)	Found P (%)	Found N (%)	Calculated C (%)	Calculated H (%)	Calculated P (%)	Calculated N (%)	Formula of product	Reaction yield (%)
IX	Hexa-chloro-cyclotri-phospha-zene	Epichlo-rohydrin	Thick, dark straw-colored liquid	30.8	5.2	3.1	-	33.7	4.7	3.5	-	$P_3N_3Cl(O_5C_{15}H_{25}Cl_6)_5$[b]	91
X	Liquid	"	"	26.9	4.5	5.6	-	24.6	3.4	9.1	-	$P_6N_5(OC_3H_5Cl_2)_{14}$	78
XI	Liquid	"	"	23.6	3.7	8.6	-	24.6	3.4	9.1	-	$P_6N_5(OC_3H_5Cl_2)_{14}$	70
XII	Mixture	"	"	26.2	4.1	6.4	2.3	-	-	-	-	-	84
XIII	Liquid	Styrene oxide	Yellow-brown liquid	53.4	4.9	-	2.2	55.3	4.6	-	2.9	$P_6N_5(OC_8H_8Cl)_{14}$	-

[a]See Table 3.
[b]X-Product having several-mer substituents.

In this respect the reaction is superior to the synthesis of chloroalkoxyphosphazenes from chlorophosphazenes and halohydrins. An additional advantage is the lack of by-products. Based on the experiments, it can be also stated (Table 6) that the properties of the product obtained in the reaction of liquid chlorophosphazene oligomers with epichlorohydrin without solvent do not differ greatly from these of the product obtained in the presence of solvent. However, carrying out the synthesis in the presence of solvent shows several technological advantages: among them, the greater yield of reaction under the same operational conditions.

The general empirical formula of the obtained chloroalkoxyphosphazenes, when liquid oligomers were used, was calculated from the results of elementary analysis as $P_6N_5Cl_n(OR)_{14-n}$, where the R group depends on the 1,2-epoxide used, and n is a quantity dependent on the conditions of the process, $0 \leq n < 14$.

It must be pointed out that the above general empirical formula is an approximation of the real state, even more so as cyclic chlorophosphazenes appear together with the linear ones in the liquid oligomers. Thus, the obtained product contains cyclic products as well as linear chloroalkoxyphosphazenes.

A mixture of the chlorophosphazene oligomers was used as a starting material in the experiments. The separation of liquid chlorophosphazenes (mainly linear oligomers) and cyclic oligomers from this mixture requires additional technological operations and is justified only if the cyclic oligomers were to have different application from the liquid oligomers. It is advisable for economical reasons to use a mixture of oligomers, when the products of the reaction of chlorophosphazenes with 1,2-epoxides are used as flame retardants.

All the products obtained were investigated by infrared spectroscopy. An absorption band was observed at 1040-1020 cm^{-1} which is characteristic for the stretching vibrations of the aliphatic P–O–C bonds.

The products obtained in the reaction of 1,2-epoxides with chlorophosphazenes are usually straw-colored or yellow-brown, viscous liquids showing neutral or acid reaction for the compounds containing free chlorine atoms.

The obtained chlorophosphazenes were soluble in organic solvents such as carbon tetrachloride, chloroform, tetrachloroethane, benzene, tetrahydrofuran, and insoluble in methanol and partly in acetone.

Infrared Spectrophotometric Measurements

The frequencies of absorption bands, characteristic for the fundamental vibrations of the arrangements of atoms existing in the obtained derivatives were determined to define the chemical structure of the products obtained in the reaction of chlorophosphazenes with 1,2-epoxides. Table 7 shows results of these measurements. Daasch,

TABLE 7. Bands for the Obtained Chloroalkoxyphosphazenes[a]

Compounds	Type of chlorophosphazene oligomer	Frequency, cm^{-1}												
		C–H									–(P=N)–			P–O–C (aliphatic)
		$\nu_{arom.}$	ν_a $-CH_3$	ν_a $-CH_2-$	ν_s $-CH_2-$	σ_s $-CH_2$	σ_s $-CH_3$	ω $-CH_2$	ω $-CH_2Cl$	ρ $-CH_2$	C–Cl ν	ν_a	ν_s	ν
(2-Chloro ethoxy)phosphazenes	Cyclic	-	-	2920	2850	1450	-	1350	1305	760	680	1300, 1240-1210	870	1030
(2-Chloropropoxy)phosphazenes	Cyclic trimers	-	2960	2920	-	1460	1385	1345	-	745	705	1210-1200	870	1040-1035
"	Cyclic	-	2980	2920	2860	1455	1375	1340	-	755	703	1305, 1225-1200	875	1040-1030
"	Liquid	-	2960	2940	2920	1460	1385	1335	-	750	700	1300-1260 1240, 1205	870	1040-1020
"	Mixture	-	2980	2930	-	1450	1370	1330	-	750	700	1305, 1240-1210	875	1040-1020
(2,3-Dichloropropoxy)phosphazenes	Cyclic trimer	-	-	2930	2870	1420	-	1330	1280	740	690	1240, 1200	860	1030
"	Cyclic	-	-	2930	2880	1430	-	1320	1260	745	690	1305-1270, 1240, 1210	860	1040-1030

"	Liquid	-	-	2950	2900	1450	-	1350--1300	1300	755	700	1300-1210	875	1040-1030
"	Mixture	-	-	2950	2890	1435	-	1350	1350	750	700	1270-1215	875	1040-1030
(2-Chloro-2-phenyl-ethoxy)-phosphazenes	Liquid	3100 3060	-	2960	2920	1430	-	1420	-	x	x	1305-1250, 1220	860	1030
Literature values [40]		3100--3000	2962	2926	2853	1465	1375	1350--1150	1300--1150	720	850--550	1400-1200	950--700	1090-1000

[a] IR bands: ν_a = asymmetric stretching; ν_s = symmetric stretching; σ_s = bending deformation; ω = wagging deformation; ρ = rocking deformation; x = bands difficult to interpret.

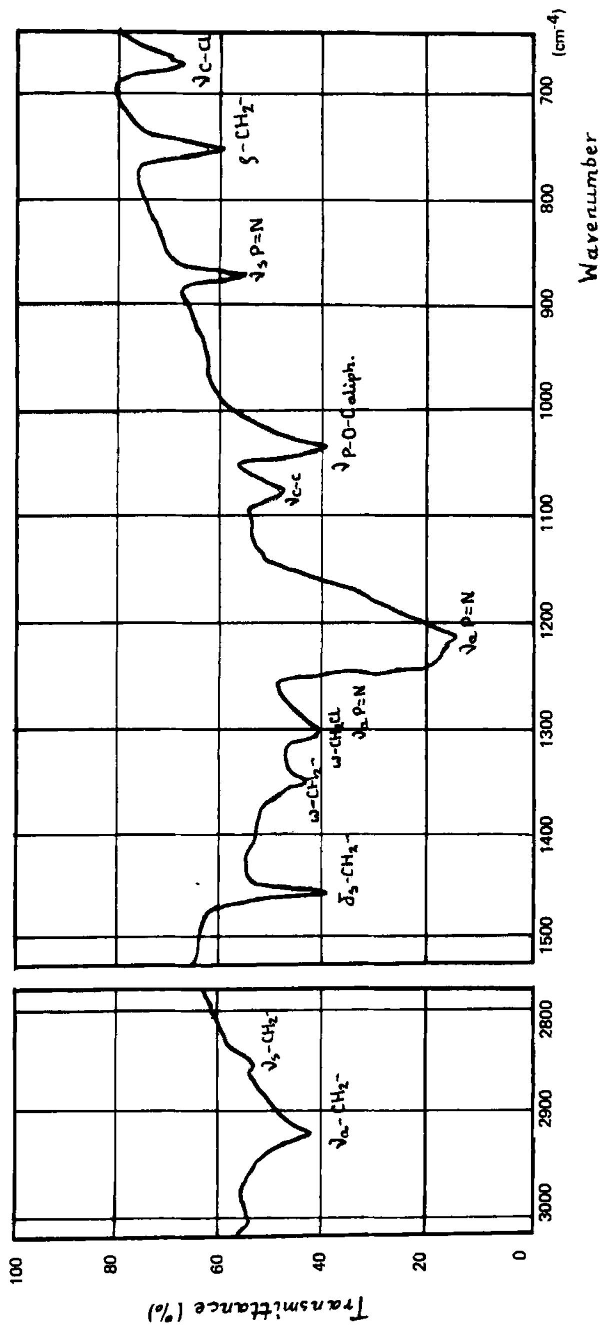


FIG. 1. IR spectrum of the product of reaction of cyclic chlorophosphazenes with ethylene oxide.

Smith and others [4, 37-41] have shown that the absorption band typical for the P–O–C aliphatic stretching vibrations occurs at the frequency 1088-950 cm^{-1}, while the absorption bands of most compounds occur at 1030 cm^{-1}. The absorption band typical for the stretching vibrations of the chloroalkoxyphosphazenes occurs at 1040-1030 cm^{-1} [4, 37]. In our case, the absorption band occurs at 1040-1020 cm^{-1}.

Cyclo- and polyphpsphazenes exhibit two typical absorption bands: one at 1100-1200 cm^{-1} corresponding to asymmetric P=N stretching, and another one at 950-700 cm^{-1} corresponding to symmetric stretching of P=N [4].

The absorption band corresponding to asymmetric stretching vibrations of P=N and arising from a cyclic trimer, is situated at 1240-1220 cm^{-1}. The bands are at 1305-1260, 870, and 840 cm^{-1} for higher oligomers, symmetric stretching vibrations for the cyclic trimer and for higher oligomers, respectively. The shift towards higher frequencies of the absorption band typical for P=N of the cyclic trimer as compared with hexachlorocyclotriphosphazene can be considered a confirmation of the course of reaction between chlorophosphazenes and 1,2-epoxides.

Figures 1-4 show infrared spectra for some of the obtained products. It can be concluded from the data given in Tables 6 and 7 and Figs. 1-4 that 2-chloroalkoxyphosphazenes were obtained.

Thermal Properties of Chloroalkoxyphosphazenes

Thermal examination of chloroalkoxyphosphazenes is necessary to show the effect of heat on the properties of these compounds, which can be vital for establishing their applicability as flame retardants. The results are given in Table 8. Figure 5 shows the curves of thermal changes occurring during the heating of these compounds. For (2-chloropropoxy)- and (2,3-dichloropropoxy)phosphazenes, a relatively small endothermic effect is observed prior to a clear exothermic effect which results from thermal decomposition of these compounds. The presence of the endotherm is probably related to isomerization of chlorophosphazenes [4, 42].

A distinct exotherm is observed in the case of the reaction product of chlorophosphazenes with styrene oxide, which is probably due to decomposition of the compounds under investigation. Because of possible use of the compounds in question as flame retardants, it is very important to know the weight loss corresponding to the evolution of volatile products during thermal decomposition. Such information was provided by TG analysis (Table 8). The maximum weight loss in the temperature range 250-400°C, i.e., in the temperature range for the cellulose decomposition, was shown by (2,3-dichloropropoxy)-phosphazenes.

Infrared spectra and the results of elementary quantitative analysis

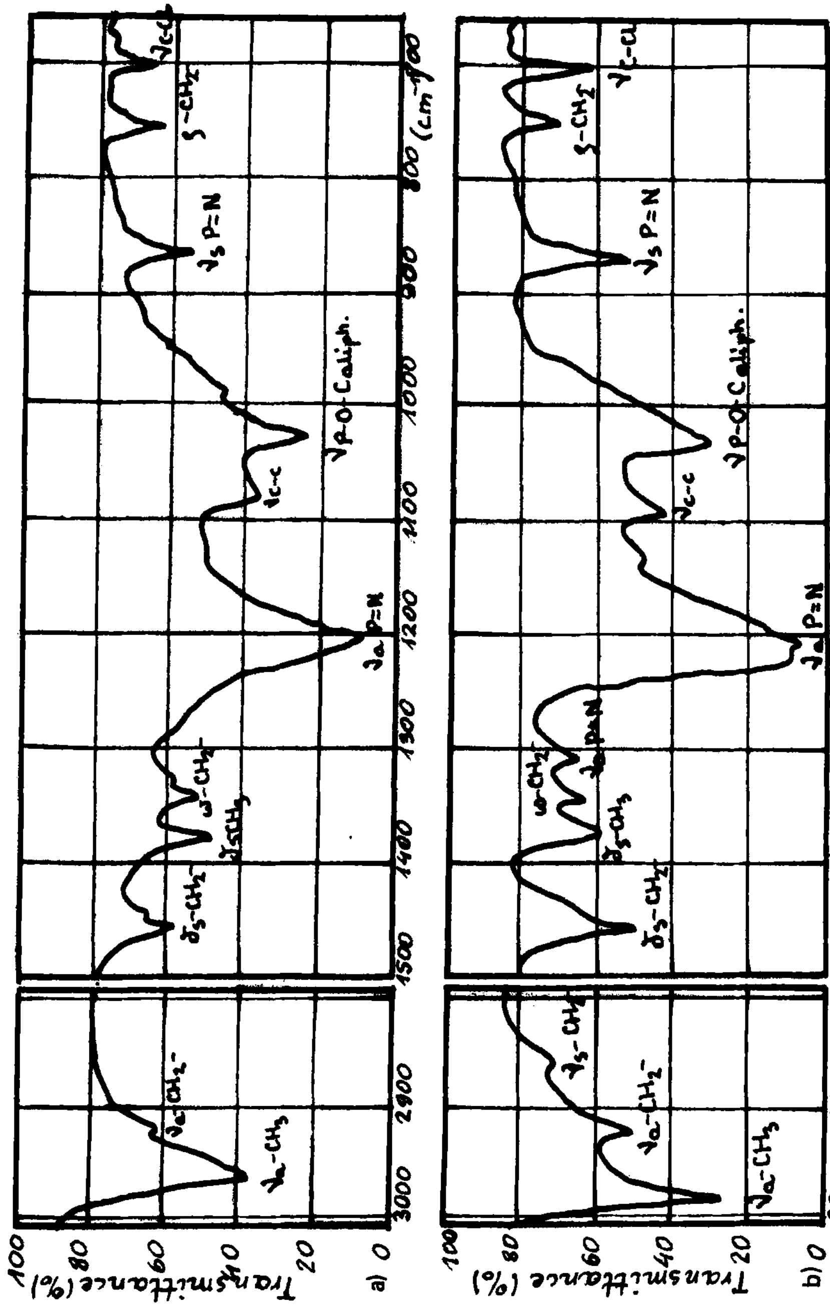
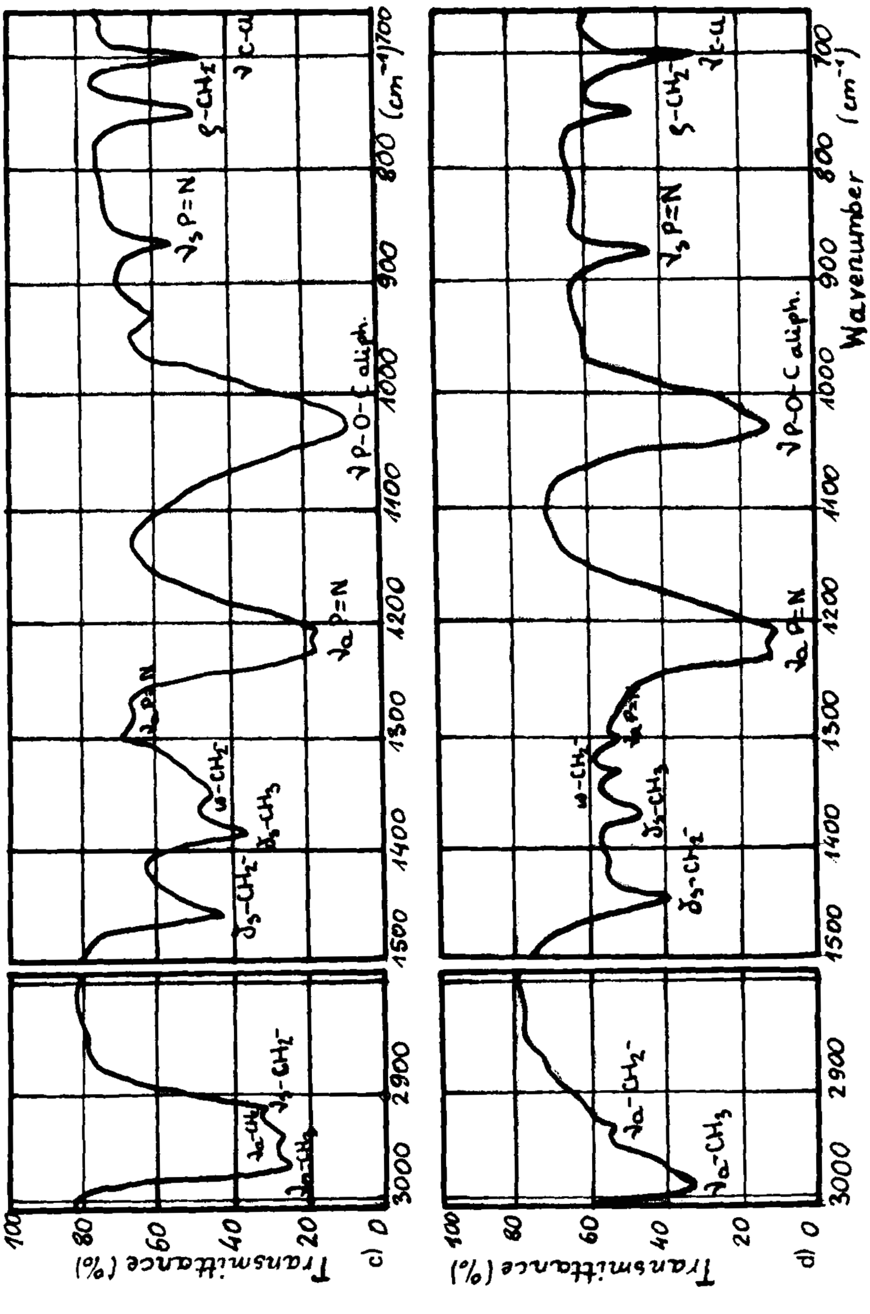


FIG. 2. IR spectra of the products of reaction of propylene oxide with (a) hexachlorocyclotriphosphazene; (b) chlorophosphazene cyclic oligomers; (c) chlorophosphazene liquid oligomers; (d) chlorophosphazenes mixture.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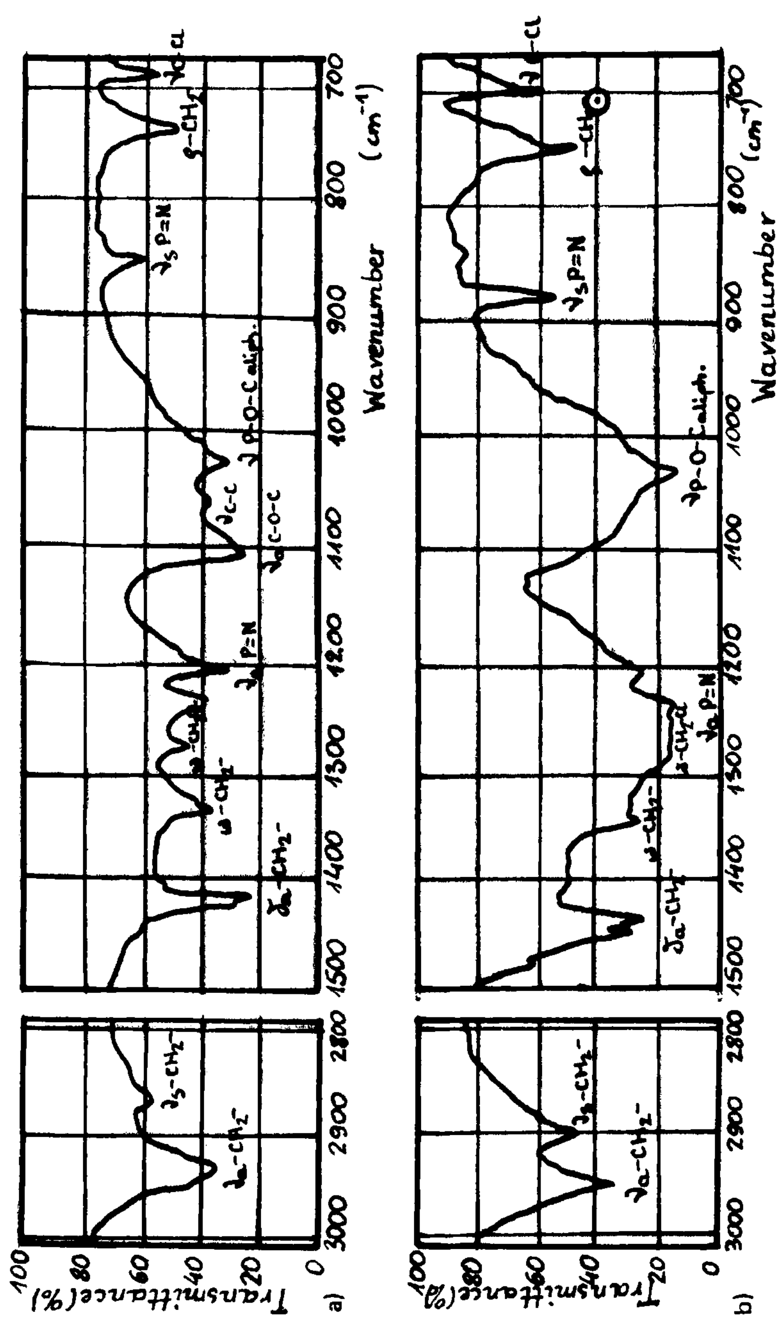

FIG. 3. IR spectra of the products of reaction epichlorhydrin with: (a) hexachlorocyclotriphosphazene; (b) chlorophosphazene liquid oligomers.

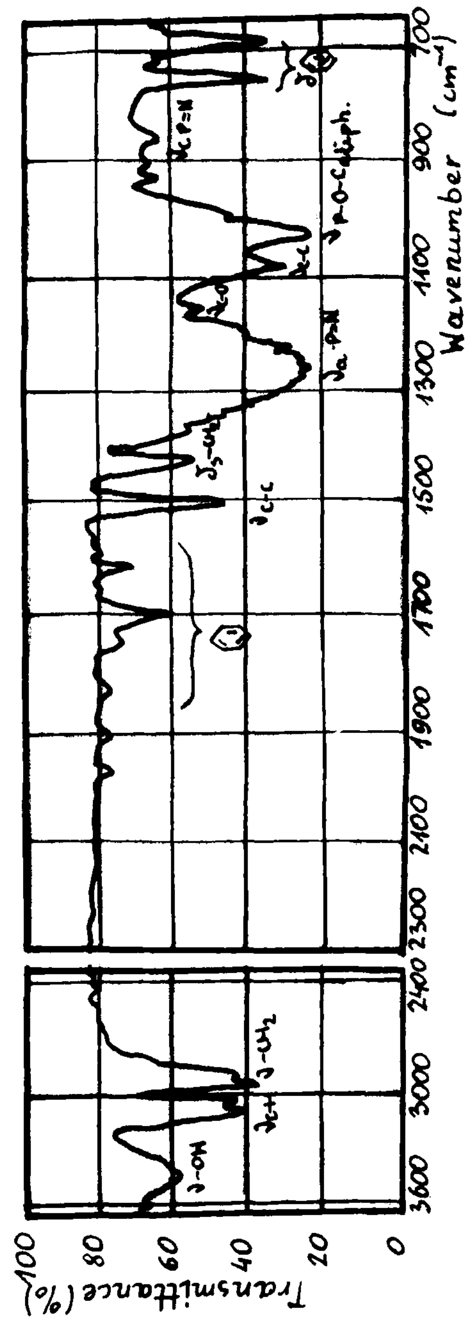

FIG. 4. IR spectrum of the product of reaction of chlorophosphazene liquid oligomers with styrene oxide.

TABLE 8. Thermal Properties of Chloroalkoxyphosphazenes

Compounds	$PNCl_2$ oligomers	Range of violent weight loss (°C)	Temperature of max. rate of weight loss (°C)	Temperature of endothermic effect (°C)			Temperature of exothermic effect (°C)			Mass decrement at various temperatures (%)				
				Begin	Maximum	End	Begin	Maximum	End	100 °C	200 °C	300 °C	400 °C	500 °C
(2-Chloropropoxy)phosphazenes	Mixture	145-250	230	225	230	239	239	248	380	1	20	51	52	54
(2,3-Dichloropropoxy)phosphazenes	Liquid	190-318	255	278	300	308	308	318	357	2	13	56	59	65
(2,3-Dichloropropoxy)phosphazenes	Mixture	225-325	253	203	220	228	228	315	380	3	12	63	69	72
(2-Chloro-2-chlorophenylethoxy)phosphazenes	Liquid	175-255	233	-	-	-	230	248	305	1	12	31	33	35

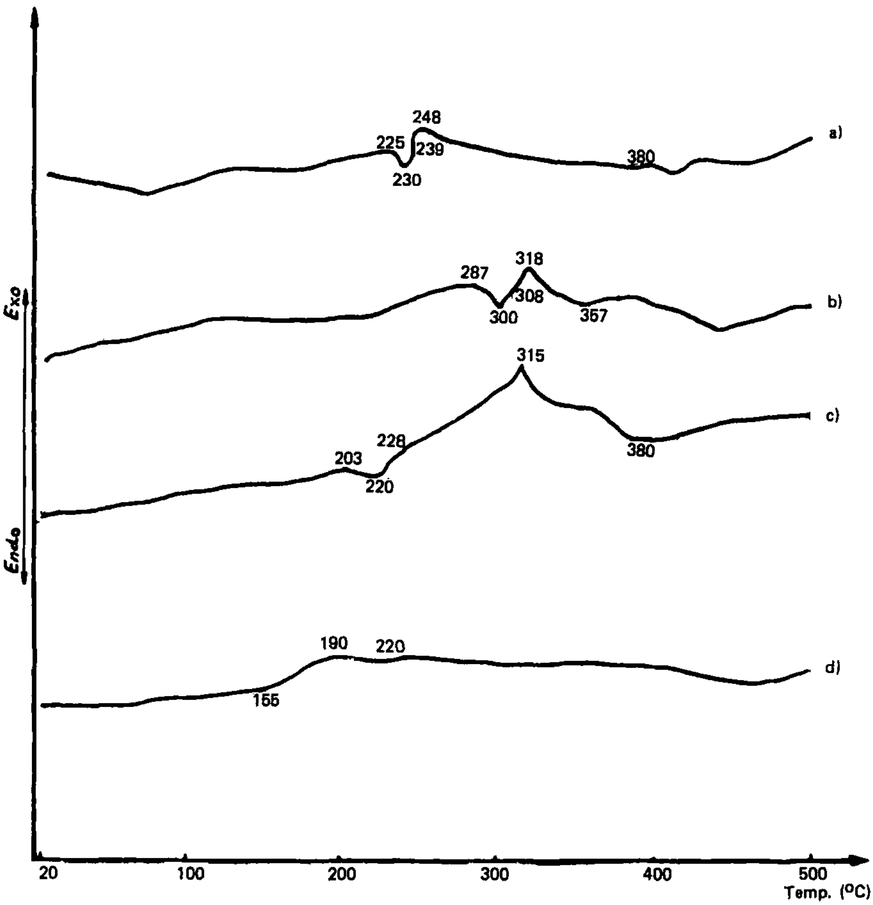

FIG. 5. Thermograms of the products of reaction: (a) chlorophosphazenes mixture with propylene oxide; (b) chlorophosphazene liquid oligomers with epichlorhydrin; (c) chlorophosphazenes mixture with epichlorhydrin; (d) chlorophosphazene liquid oligomers with styrene oxide.

lead to the conclusion that 2-chloroalkoxyphosphazenes are formed during the reaction of chlorophosphazenes with 1,2-epoxides. The amount of catalyst used in the reaction has great effect on the course of this reaction. The obtained products are usually straw-colored or yellow-brown viscous liquids which are water-, alkali-, and acid-resistant.

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