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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Oligomeric Hydroxy-Aryloxy Phosphazene Based on Cyclic Chlorophosphazenes

I. S. Sirotin[a], Yu. V. Bilichenko[a], K. A. Brigadnov[a], V. V. Kireev[a], O. V. Suraeva[a], and R. S. Borisov[b]

[a]*Mendeleev University of Chemical Technology of Russia, Moscow, Russia*
[b]*Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia*
e-mail: kireev@muctr.ru

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Abstract—Reaction of hexachlorocyclotriphosphazene and a mixture of cyclic chlorophosphazene $[NPCl_2]_{n=3-8}$ with an excess of diphenylolpropane under different conditions affords corresponding oligomeric hydroxy-aryloxy phosphazenes, which were characterized by gas chromatography-mass spectrometry, laser mass spectrometry, ^{31}P and ^{1}H NMR spectroscopy. Side reactions was found with participation of decomposition products of diphenylolpropane.

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Products of polycondensation of chlorocyclophosphazenes with diphenols are of ever-increasing practical interest since based on them polymeric materials for various purposes can be synthesized. For example, in [1] poly(hydroxy-aryloxy)phosphazenes (PHAP) with a molecular weight of up to 15 000 were synthesized and characterized by interaction of hexachlorocyclotriphosphazene (HCP) with a mixture of diphenylolpropane sodium mono- and diphenolates. Macromolecules of these polymers consist of phosphazene cycles linked by dioxyaromatic radicals, in which substantially all of the remaining chlorine atoms were substituted for the remaining hydroxyaryl groups. A reaction of the latter with methacryloyl or epichlorohydrin affords corresponding phosphazene-containing methacrylic or epoxy polymers [1].

It was found that methacrylic derivatives of PHAP were effective modifiers of dental filling materials [2, 3], and their epoxy derivatives, of glass and carbon composites [4].

However, the synthesis of PHAP using diphenylolpropane phenolates is uncomfortable due to the additional production stage and complicated by heterogeneity of the process.

In the study we attempted to synthesize these polymers by direct interaction of diphenylolpropane with hexachlorocyclotriphosphazene and mixture of chlorocyclophosphazenes.

EXPERIMENTAL

Chlorophosphazene was synthesized according to a technique of [5]. Hexachlorocyclotriphosphazene is white crystalline solid, mp 113°C, the ^{31}P NMR spectrum: singlet with δ_P = 19.9 ppm. Mixture of chlorocyclohosphazenes $[NPCl_2]_{3-8}$ is the gray powder containing according to ^{31}P NMR spectroscopy, mol %, 49 of the trimer, 24 of tetramer, 3 of cyclic pentamer $[NPCl_2]_5$, 6 of hexamer $[NPCl_2]_6$, and 12 of heptamer with octamer $[NPCl_2]_{7-8}$.

Diphenylolpropane was purified by repeated recrystallization from chlorobenzene till achieving T_m = 156.5°C.

Solvents were purified according to known techniques, their physical characteristics matched to the literature data [6].

Diphenylolpropane in an amount of 31.45 g (0.1379 mol, 8-fold excess per the link of $NPCl_2$) as a solution in 40 mL of chlorobenzene and 2 g (0.0057 mol)

of chlorocyclophosphazenes (hexachlorocyclotriphosphazene $N_3P_3Cl_6$ or mixtures of chlorocyclophosphazenes $[NPCl_2]_{n=3-8}$) dissolved in 10 mL of chlorobenzene were charged in a three-necked flask equipped with a mechanical stirrer, thermometer, reflux with continuous stirring. The mixture was heated to 110°C and maintained till complete dissolution of the solid reactants. Then 3.5 mL of pyridine (0.0431 mol) was added. The synthesis was conducted with stirring at 110°C for 12 h. After the reaction chlorobenzene was evaporated in vacuo. The resulting product was dissolved in acetone or alcohol and precipitated in acidified water. The aqueous layer was decanted, the precipitated product was washed with a solution of soda, then several times with distilled water, and dried in vacuo. The yield was 30.60 g (95%), the product contained 8.17 g of hydroxy-arylenoxy phosphazenes and 22.42 g of diphenylolpropane.

^{31}P and ^{1}H NMR spectroscopy was performed on a Bruker CXP-200 device at the operating frequency of 145 and 200 MHz, respectively.

Mass spectrometry analysis MALDI-TOF was carried out on an instrument Bruker Auto Flex II.

Chromatography–mass spectrometry analysis was performed on an instrument Varian 3800CP/4000MS. Compounds were identified by the mass spectra using the software NIST MS Search 2.0 and the mass spectra library NIST.

RESULTS AND DISCUSSIONS

Synthesis of hydroxy-aryloxy phosphazene was performed by Scheme 1 in the presence of HCl acceptors in the melt or in a solvent medium. An excess of di-phenylolpropane ($NPCl_2$: DPP = 1 : 8) was used for compensating polyfunctionality of chlorophosphazenes.

It should be noted that the reaction (Scheme 1) does not proceed during heating of the initial materials in the excess of DPP melt to 200°C or in solvents such as acetone, tetrahydrofuran, dioxane or chlorobenzene at boiling. In introducing potassium carbonate into the melt of the initial materials at 170°C the reaction is completed in 30–60 minutes.

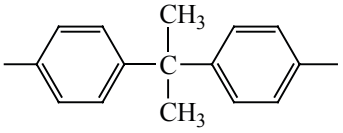
Reaction product containing the hydroxy-aryloxy phosphasene the target and excess diphenylolpropane was analyzed without separating by a chromatography-mass spectrometry, which determined only bisphenol fraction with a molecular weight up to 1000, and a laser mass spectrometry MALDI-TOF, detecting only phosphazene fraction with a molecular weight of more than 1000. The analysis by gas chromatography–mass spectrometry (Fig. 1), in which small molecules are identified, showed that the reaction mixture contains only DPP and its thermal decomposition products (Fig. 1, Table 1). It is known [7] that in the presence of acids, bases, and some salts at temperatures above 200°C DPP decomposed to phenol and *p*-isopropenylphenol by the Scheme 2.

Both of these compounds (Fig. 1, nos. 3, 4) are appeared on the mass spectra of the corresponding low molecular weight fractions (Fig. 1b, fractions 3 and 4). Figure 1 shows that the low molecular weight bisphenol fraction contains about 68% of DPP and its *o*-isomer and 20% of their decomposition products (phenol and *p*-isopropenylphenol). Amounts of these compounds in the mixture are distinguished: the *p*-isopropenylphenol amount is less because of his involvement in side reactions with the formation of compounds *5* and *6* (Fig. 1). The most probable side reaction involving *p*-isoprope-

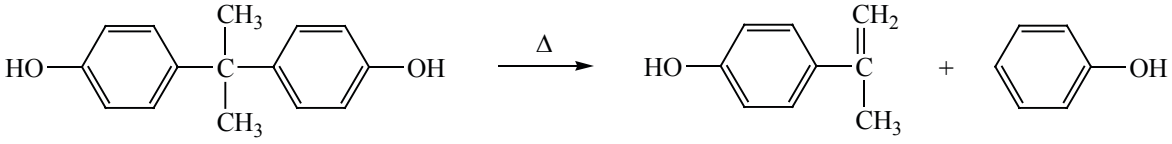
Scheme 1.

$$N_nP_nCl_{2n} + (\text{exc})\ HOArOH \rightarrow N_nP_n(OArO)_x(OArOH)_{2n-x},$$

where $n = 3$ or $n = 3$–8; $x = 0$–5; Ar =



Scheme 2.



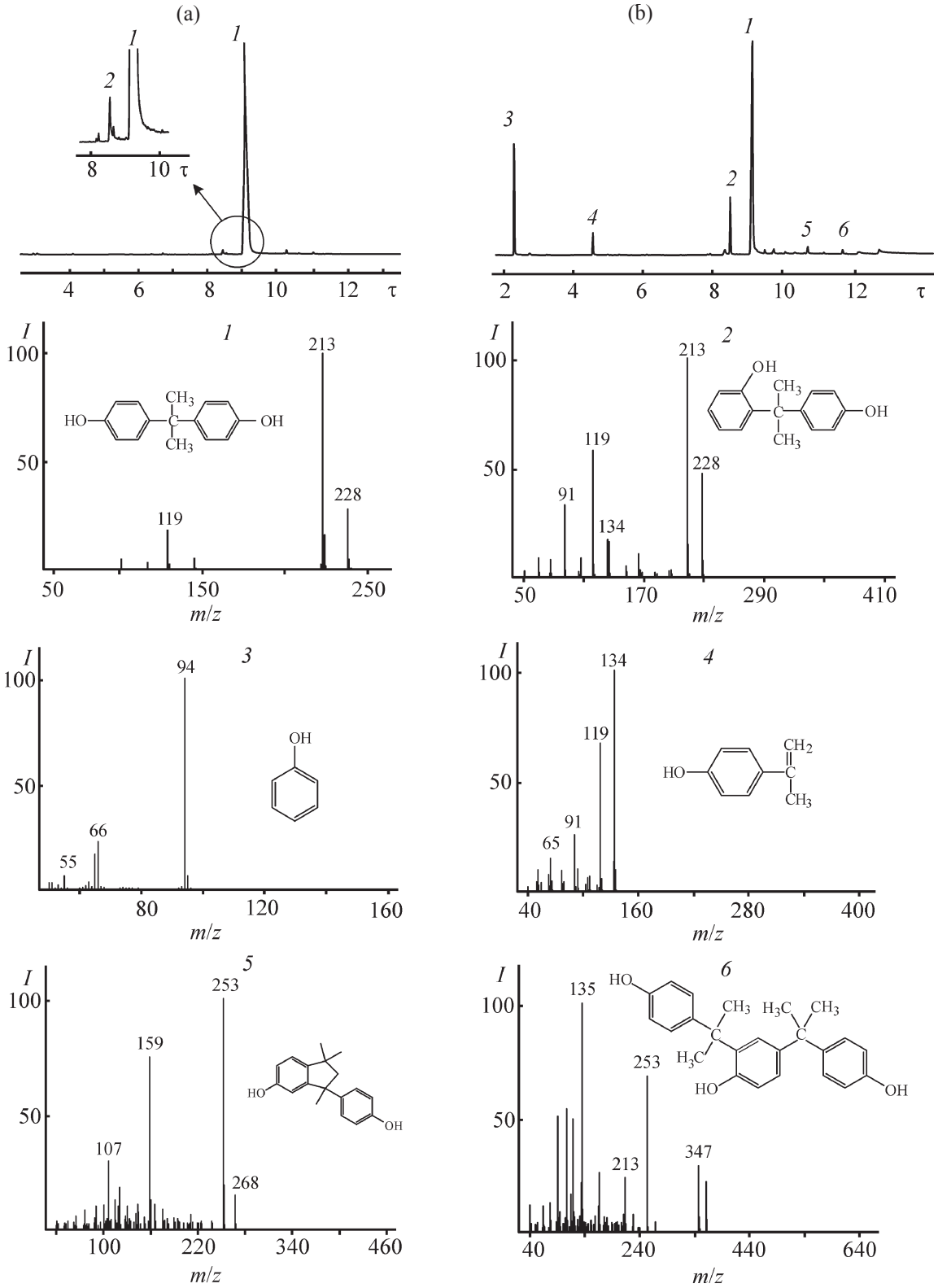


Fig. 1. Chromatograms of (a) pure DPP and (b) the low molecular weight fraction of the product of the reaction of DPP and HCP in the melt at 170°C in the presence of K_2CO_3. The reaction time 2 h. (*I*) intensity, (τ) Retention time (min). (*1–6*) Mass spectra of substances contained in the respective fractions.

Table 1. Composition of low molecular weight fraction of the products of the reaction of DPP and HCP in the melt at 170°C in the presence of K_2CO_3 (according to data of chromatography–mass spectrometry)

Fraction (Fig. 1)	Retention, min	Relative content, %	Compound
1	9.2	58	4,4'-Dihydroxydiphenyl-2,2-propane (DPP)
2	8.5	9	2,4'-Dihydroxydiphenyl-2,2- propane
3	2.3	15	Phenol
4	4.6	3	*p*-Isopropenylphenol
5	9.8	3	Bisphenol indan
6	12.6	12	2,4-Bis[2-(4'-hydroxyphenyl-)-2-propyl]phenol

nylphenol and other compounds of low molecular weight bisphenol fraction are shown in the Scheme 3.

Phosphazene-contaning portion of the reaction product in the melt, which is not detected by the gas chromatography–mass spectrometry, according to data of MALDI-TOF (Fig. 2a) contains two main fractions: the first fraction with molecular weight of compounds 1300–2000 corresponds to compounds having one phosp-

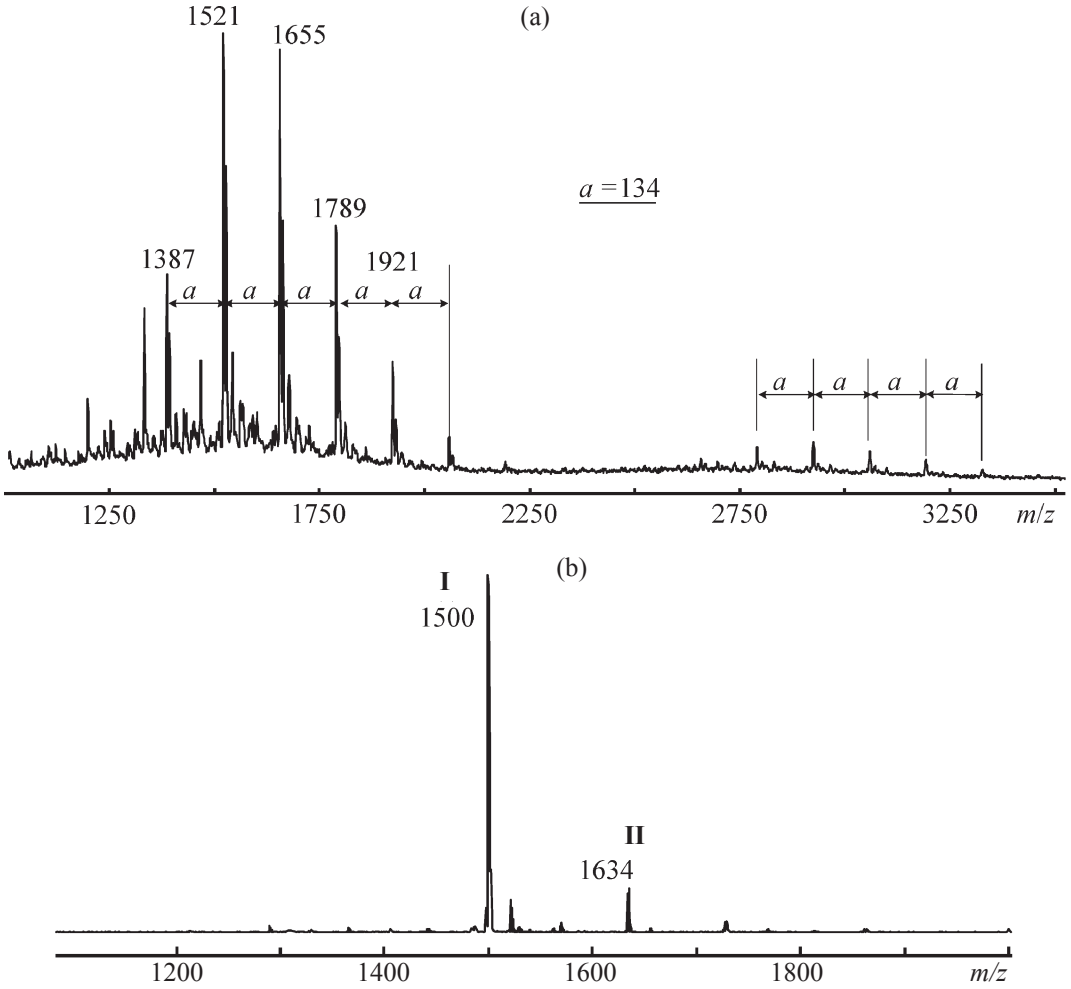
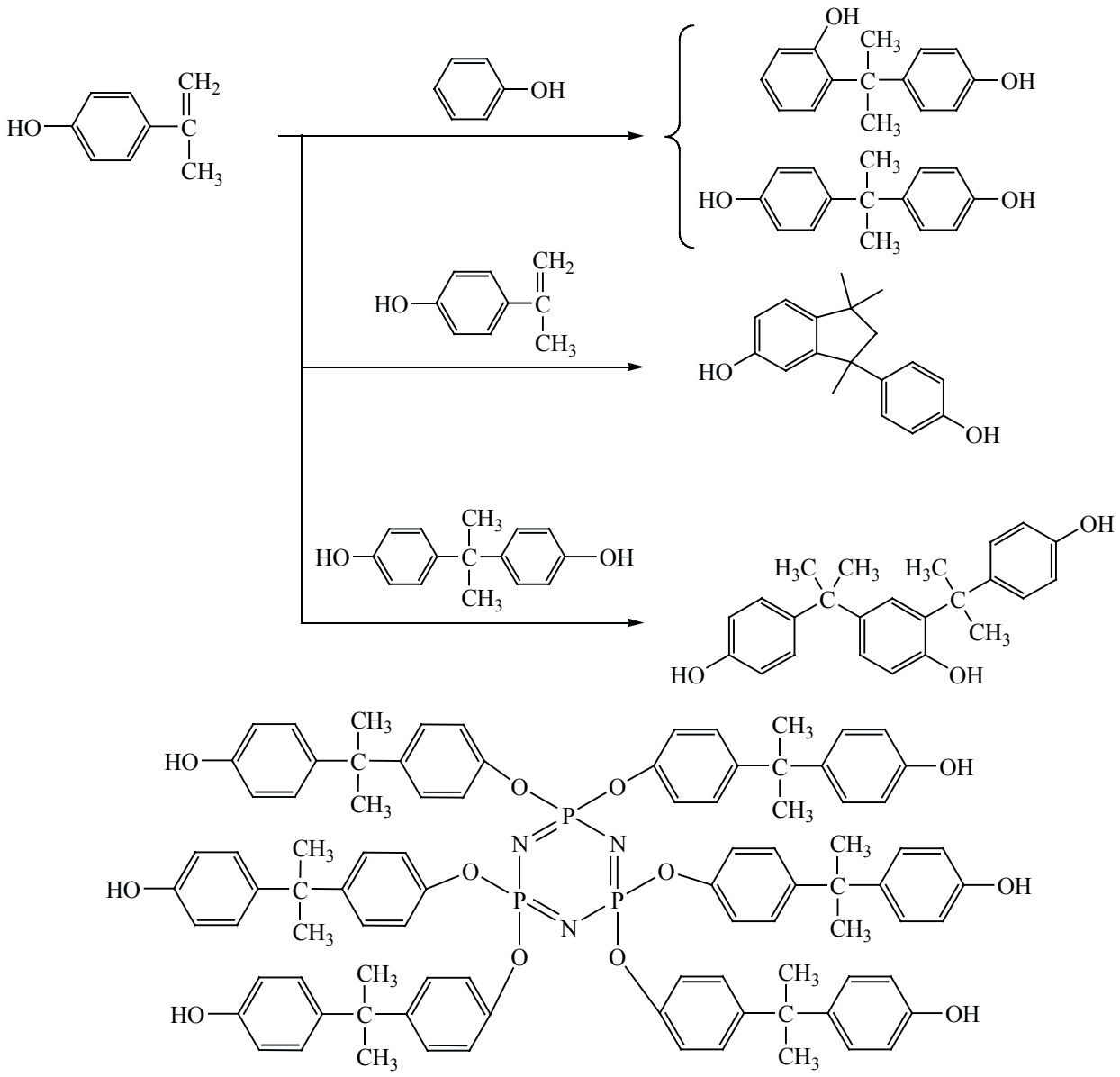


Fig. 2. Mass spectra MALDI-TOF of the product of the reaction of HCP with the excess DPP (a) in the melt at 170°C in the presence of K_2CO_3 and (b) in the chlorobenzene solution in the presence of pyridine at 110°C.

Scheme 3.



I

$m/z = 1500$

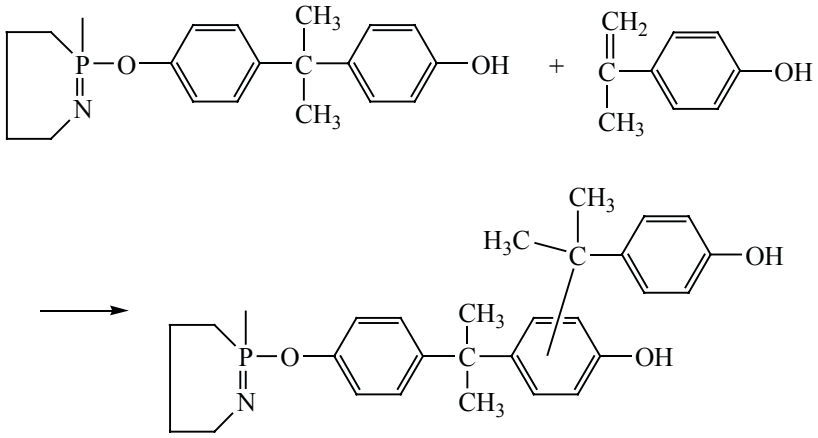
hazene cycle with six substituted chlorine atoms and also to main product **I** with $m/z = 1500$ (Scheme 3).

The second group with double values of m/z corresponds to compounds with two substituted phosphazene cycles linked by dioxyaryl radical.

It is noteworthy that the distances between the peaks in the MALDI spectrum in both fractions are equal and $a = 134$, which corresponds to the molecular weight of *p*-isopropenylphenol. Obviously, the latter alkylates aromatic radicals in phosphazene according to the Scheme 4.

Despite the simplicity of the substitution of chlorine atoms in chlorocyclophosphazenes in the DPP melt and its high speed, this process is complicated by side transformations of the DPP excess, since the reaction (Scheme 1) was carried out in inert solvents in the presence of a heterogeneous (K_2CO_3) and homogeneous (pyridine) acceptors of HCl. Chlorobenzene was selected as the solvent (Table 2). As follows from the ^{31}P NMR

Scheme 4.



spectra (Fig. 3a) of the reaction products with HCP with 24-fold molar excess of DPP in the acceptance by potassium carbonate the full replacement of the chlorine atoms can not be achieved even for 20 hours, in the reaction mixture prevails pentasubstituted derivative (Fig. 3a, the set of signals A_2B; δ_P, ppm: 6.5 d and 21.5 t). Pyridine was more effective acceptor, in the presence of which hexahydroxy-aryloxy cyclotriphosphazene (**I**) with δ_P = 9.0 ppm was formed in 10–12 h (Fig. 3b).

Due to the lower temperature the decomposition processes of DPP in a solvent is expressed slightly: no more than 5%. ^{1}H NMR spectrum of the reaction product of HCP with the excess DPP in the presence of pyridine (Fig. 4*B*) is similar to that of the original DPP (Fig. 4*A*). However, the MALDI-TOF spectrum (Fig. 2b) apart from the main hexasubstituted product **I** with *m/z* =

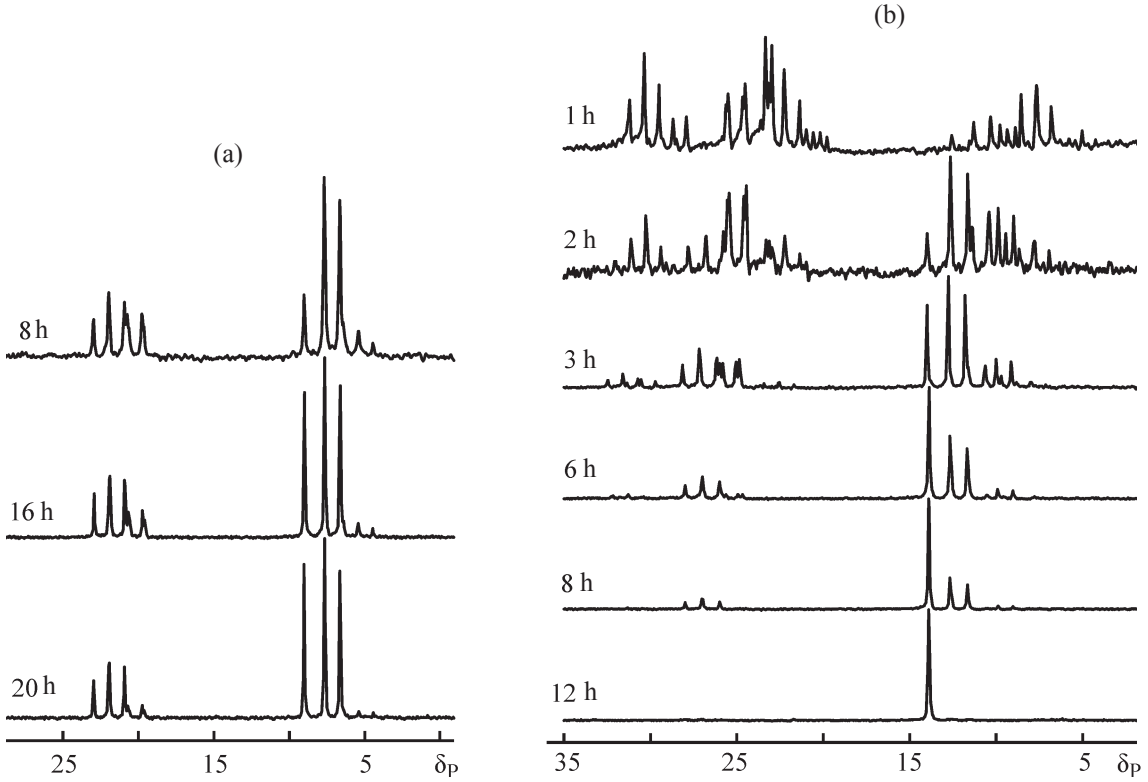
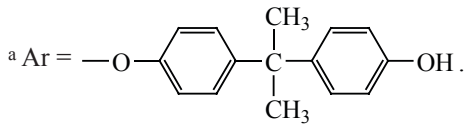


Fig. 3. ^{31}P NMR spectra of the the product of the reaction of HCP with the excess DPP in the presence of (a) excess K_2CO_3 and (b) pyridine. (δ_P) Chemical shift (ppm); The same is for Fig. 5.

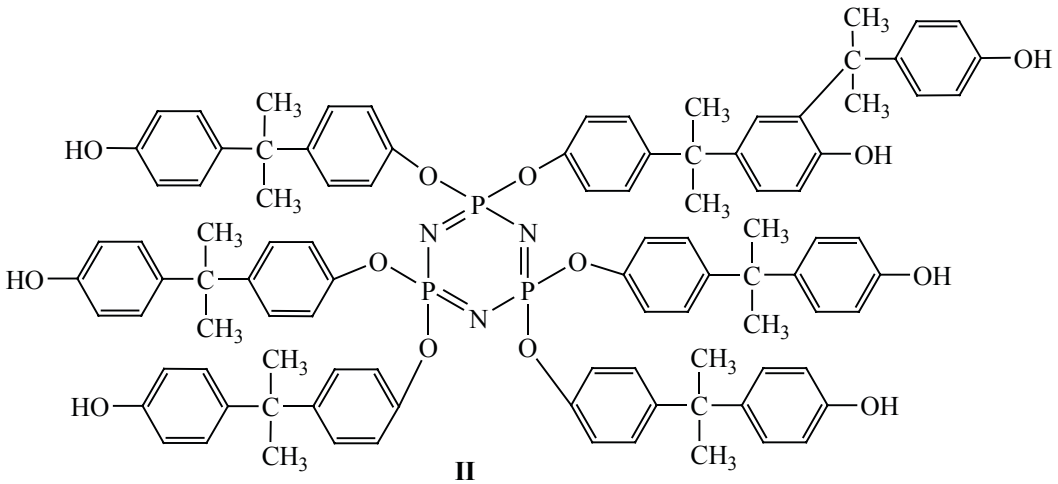
Table 2. Conditions of the reaction chlorophosphazenes with diphenylolpropane and content of the main compounds in the resulting products

Original chlorophosphazene	Solvent	Acceptor	T, °C	Reaction time, h	Relative amount of the products with various degree of chlorine substitution on chlorocyclophosphazene,[a] mol %	Decomposition degree of DPP,[b] mol %
$[NPCl_2]_3$	– (DPP melt)	–	170	8–24	No reaction occurs	2–5
	The same	K_2CO_3	170	1	100 $N_3P_3Ar_6$	50
	Chlorobenzene	–	131	8–24	No reaction occurs	<1
	"	K_2CO_3	131	24	30 $N_3P_3Ar_6$ 70 $N_3P_3Ar_5Cl$	5
	"	Pyridine	110	12	100 $N_3P_3Ar_6$	3
$[NPCl_2]_{3–8}$	– (DPP melt)	–	170	8–24	No reaction occurs	3–10
	The same	K_2CO_3	170	1	100 $N_nP_nAr_{2n}$, n = 3–8	52
	Chlorobenzene	–	131	24	No reaction occurs	<1
	"	K_2CO_3	131	24	18 $N_3P_3Ar_6$ 42 $N_3P_3Ar_5Cl$ 40 $N_nP_nAr_{2n}$, n = 4–8	6
$[NPCl_2]_3$	– (DPP melt)	–	170	8–24	No reaction occurs	2–5
	The same	K_2CO_3	170	1	100 $N_3P_3Ar_6$	50
	Chlorobenzene	–	131	8–24	No reaction occurs	<1
	"	K_2CO_3	131	24	30 $N_3P_3Ar_6$ 70 $N_3P_3Ar_5Cl$	5
	"	Pyridine	110	12	100 $N_3P_3Ar_6$	3
$[NPCl_2]_{3–8}$	– (DPP melt)	–	170	8–24	No reaction occurs	3–10
	The same	K_2CO_3	170	1	100 $N_nP_nAr_{2n}$, n = 3–8	52
	Chlorobenzene	–	131	24	No reaction occurs	<1
	"	K_2CO_3	131	24	18 $N_3P_3Ar_6$ 42 $N_3P_3Ar_5Cl$ 40 $N_nP_nAr_{2n}$, n = 4–8	6

[a] Ar =  .

[b] DPP decopmposition degree was found by data of chromatography-mass spectrometry.

Scheme 5.



II
$m/z = 1634$

1500 indicates the presence of impurities of the product of alkylation by the Scheme 4 of one of the bisphenyl substituents by *p*-isopropenylphenol with the formation of compound **II** with $m/z = 1634$ (Scheme 5).

The ratio of HCP : DPP is important, since it affects the molecular weight of the resulting poly(hydroxy-aryloxy)phophazenes: with its decreasing, respectively, to 1 : 9–1 : 4 the fraction of phosphazene cycles linked by dioxyaryl radicals increases, thereby increasing the molecular weight.

It was found that hexachlorocyclotriphosphazene in the reaction may be replaced by a mixture of chlorocyclophosphazene $[NPCl_2]_{n=3-8}$. The only peculiarity in this case is the increased reactivity of homologues with $n = 4–8$: other conditions being equal the substitution of chlorine at higher cycles $[NPCl_2]_{n = 4-8}$ is faster than in HCP. Thus, according to the ^{31}P NMR spectra cycles of $[NPCl_2]_n = 4–8$ have completely replaced for 4 h (Fig. 5e)

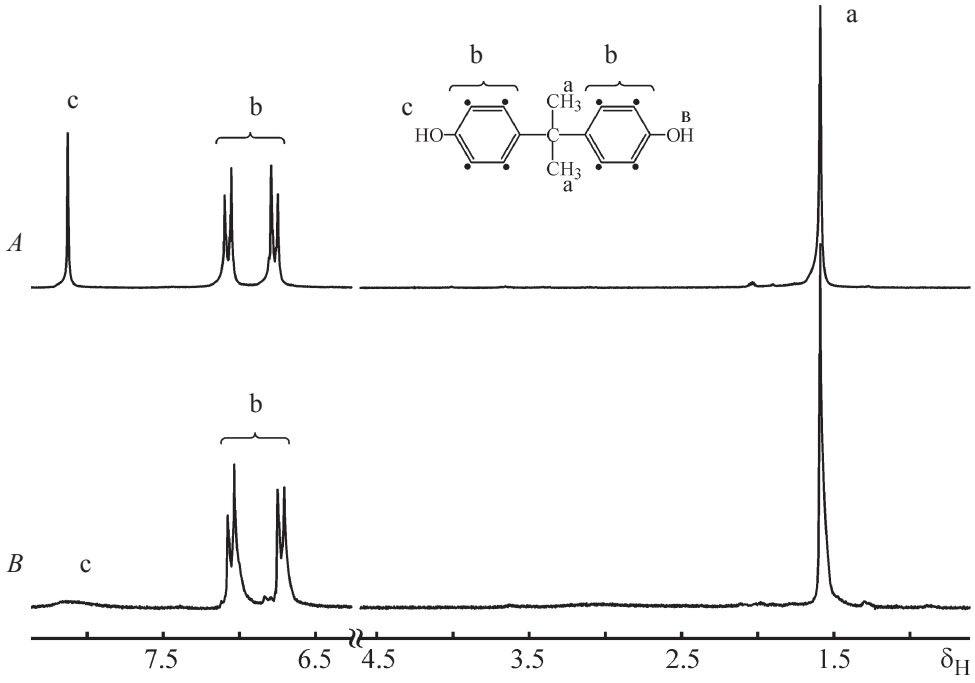


Fig. 4. ^1H NMR spectra of (*A*) original diphenylolpropane and (*B*) hydroxy-aryloxy phophazene basedon HCP or mixtures $[NPCl_2]_{n=3-8}$. (δ_H) Chemical shift (ppm).

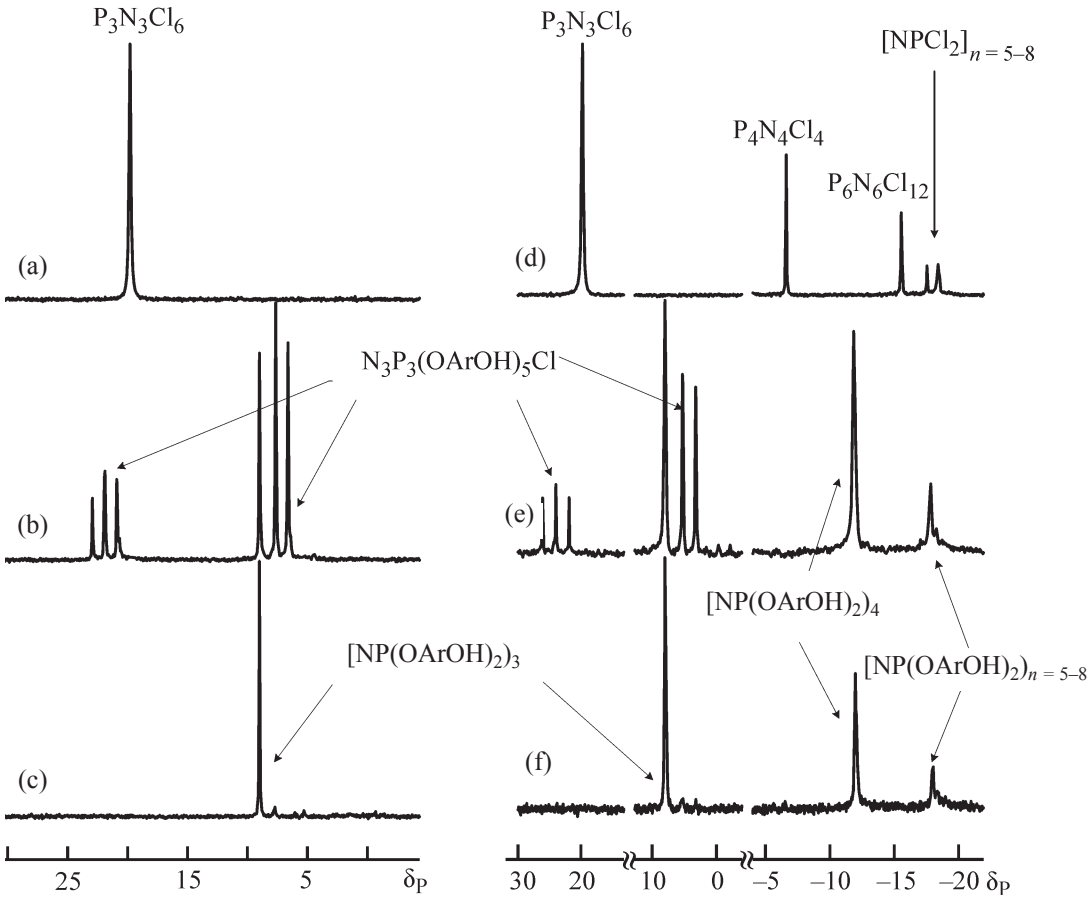


Fig. 5. ^{31}P NMR spectra of (a) original HCP and (d) mixtures of $[NPCl_2]_{n=3–8}$, hydroxy-aryloxy phophazenes based on (b, c) HCP and (e, f) mixtures of $[NPCl_2]_{n=3–8}$. Conditions of hydroxy-aryloxy phophazenes synthesis: chlorobenzene, $NPCl_2$: DPP = 1 : 8, (b) at 131°C in the presence of K_2CO_3 and the synthesis time 20 h, (c, e, f) in the presence of pyridine at 110°C and the synthesis time, h: (c) 10, (e) 4, (f) 12.

and those of HCP, only for 10–12 h (Fig. 5f). In addition, there is somewhat more intensive decomposition of the DPP.

The resulting mixtures of hydroxy-aryloxy phosphazenes and diphenylolpropane can be separated by fractional crystallization or by a sublimation of diphenylolpropane in high vacuum. However, it seems more appropriate to use these mixtures without separation. Thus, phosphazene-containing analogues of diphenylolpropane-formaldehyde oligomers with low flammability are obtained in the reaction of hydroxy-aryloxy phosphazenes with formaldehyde. Reaction of hydroxy-aryloxy phosphazenes with epichlorohydrin proceeds under standard conditions of synthesis of epoxy resin with the formation of a fire-resistant oligomers.

An important direction of practical use of hydroxy-aryloxy phosphazenes already implemented in pilot scale is the use of methacrylic derivatives for modifying the dental filling compositions resulting in a significant improvement in the mechanical and physico-chemical characteristics of the latter [8].

CONCLUSIONS

(1) By the reaction of hexachlorocyclotriphosphazene and mixture $[NPCl_2]_{n=3–8}$ with the diphenylolpropane excess the relevant hydroxy-aryloxy phosphazenes were synthesized in various conditions and characterized.

(2) It was found that cycles $[NPCl_2]_{n=4–8}$ in a nucleophilic substitution reaction of the chlorine atoms are more reactive than hexachlorocyclotriphosphazene. Thus, according to ^{31}P NMR spectroscopy chlorine in cycles $[NPCl_2]_{n=4–8}$ are completely replaced by diphenylolpropane already for 4 hours and by

hexachlorocyclotriphosphazene, only for 10–12 h.

(3) Using mass spectrometry the fact of partial decomposition of diphenylolpropane in the course of the reaction with chlorophosphazenes with the formation of phenol and *p*-isopropenylphenol was recorded. It was revealed that *p*-isopropenylphenol can partially alkylate hydroxy-aryloxy phosphazene and diphenylolpropane in both the melt at 170°C and the chlorobenzene solution at 110°C.

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