Synthetic Use of Phosphites of Novolac Resins

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Abstract

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Synthetic Use of Phosphites of Novolac Resins

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In connection with the great attention that has recently been devoted to the chemistry of oligomers, we considered it of interest to investigate the pathways of chemical transformations of phosphites of novolac resins both into diverse oligomeric phosphates and phosphonates—analogs of known pesticides—and into high-molecular compounds of new types. The synthesis of phosphites of novolac resins was recently described by us (^{1}).

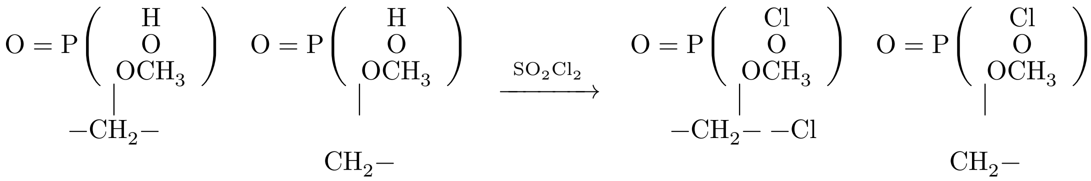
Acid phosphites of novolacs, containing as the principal unit fragments

$$\mathrm{Ar-O-P(=O)(H)(OCH_3)} \qquad \text{(I)}$$

on interaction with chlorine are converted into the corresponding trichloroethyl phosphonates.

The reaction described proceeds considerably more moderately than the interaction of the simplest acid phosphites with chlorine. Special experiments established that the synthesis of oligomeric trichloroethyl phosphonates is not accompanied by the side process of condensation of chlorine with the active hydrogens of the aromatic nucleus, and that no rearrangement of the trichloroethyl phosphonate into the corresponding dichlorovinyl phosphate occurs.

In our work the chlorination of I with sulfuryl chloride was studied, and it was shown that the reaction develops in two directions: Cl replaces H atoms bound both to P and to the aromatic nucleus:



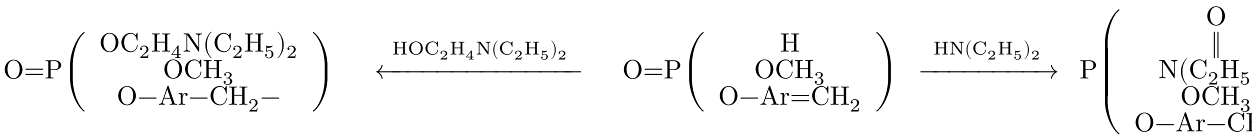
$$\mathrm{O=P}\begin{pmatrix}\mathrm{H}\\ \mathrm{O}\\ \mathrm{OCH_3}\end{pmatrix}\ \mathrm{O=P}\begin{pmatrix}\mathrm{H}\\ \mathrm{O}\\ \mathrm{OCH_3}\end{pmatrix} \ \ldots\ \mathrm{-CH_2-}\ \ldots\ \mathrm{CH_2-} \xrightarrow{\mathrm{SO_2Cl_2}} \mathrm{O=P}\begin{pmatrix}\mathrm{Cl}\\ \mathrm{O}\\ \mathrm{OCH_3}\end{pmatrix}\ \mathrm{O=P}\begin{pmatrix}\mathrm{Cl}\\ \mathrm{O}\\ \mathrm{OCH_3}\end{pmatrix} \ \ldots\ \mathrm{-CH_2-\ -Cl}\ \ldots\ \mathrm{CH_2-}$$

The formation of chlorophosphate fragments in the oligomers obtained was proved by the appearance in the IR spectrum of a strong absorption band at

500 cm^{-1}, and also by the chemical transformations described below. The entry of chlorine into the aromatic nucleus is evident from the results of hydrolysis of the products studied—chlorinated novolac resin containing no P was isolated.

Chlorophosphates of novolac resins were introduced into reaction with secondary amines and mercaptans, and the corresponding amido- and thiolophosphates were obtained. Similar thiolophosphates (but not containing chlorine in the aromatic nuclei) are conveniently obtained from phosphites I and sulfur chlorides [2].

Amidophosphates and neutral phosphates were also synthesized from phosphites I by Todt' s method ([3]):

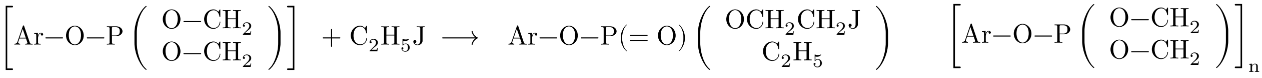


$$O{=}P\left(\begin{matrix}OC_2H_4N(C_2H_5)_2\\OCH_3\\O{-}Ar{-}CH_2{-}\end{matrix}\right) \xleftarrow{HOC_2H_4N(C_2H_5)_2} O{=}P\left(\begin{matrix}H\\OCH_3\\O{-}Ar{=}CH_2\end{matrix}\right) \xrightarrow{HN(C_2H_5)_2} P\left(\begin{matrix}O\\ \|\\ N(C_2H_5\\OCH_3\\O{-}Ar{-}C\end{matrix}\right.$$

The work demonstrates the possibility of obtaining thiophosphates based on amidophosphites of novolac resins. The first stage of the synthesis is the alcoholysis of the amidophosphite (4), for example with diethylaminoethanol, and the second is the addition of sulfur.

The oligomers synthesized in the present work contain fragments that determine the biological activity of modern phosphorus-containing pesticides (5). A study of the anticholinesterase activity of some of these compounds* showed that in this respect they correspond to known insecticides. It may be assumed that the oligomeric phosphates and phosphonates, in addition, will possess a number of valuable specific properties (for example, prolonged action), which low-molecular-weight insecticides lack.

The second direction in the synthetic use of phosphites of novolac resins is their conversion into high polymers. We have shown that alkylene phosphites of this type are converted into three-dimensional polymers when heated with a small amount of alkyl iodides. The process carried out is a stepwise alkylation of phosphites according to the Arbuzov reaction scheme and resembles the polymerization of alkylene phosphonites previously carried out by one of us together with other authors (6). However, whereas in the cited work (6) it was possible to obtain polyphosphonates with molecular weights up to 3100, in the present study true high polymers of network structure were obtained for the first time:



$$\left[Ar{-}O{-}P\left(\begin{matrix}O{-}CH_2\\O{-}CH_2\end{matrix}\right)\right] + C_2H_5J \longrightarrow Ar{-}O{-}P({=}O)\left(\begin{matrix}OCH_2CH_2J\\C_2H_5\end{matrix}\right) \quad \left[Ar{-}O{-}P\left(\begin{matrix}O{-}CH_2\\O{-}CH_2\end{matrix}\right)\right]_n$$

$$\mathrm{Ar{-}O{-}P(=O)}\left(\begin{matrix}\mathrm{O{-}}\\ \mathrm{C_2H_5}\end{matrix}\right) \longrightarrow \left[\ \mathrm{-CH_2CH_2{-}P(=O)(O{-}Ar{-}CH_2{-}){-}OCH_2CH_2{-}}\ \right]_m \mathrm{J}$$

Another route for the conversion of phosphites of novolac resins into high polymers is their copolymerization with unsaturated compounds, for example methyl methacrylate, in the presence of peroxides. There are indications in the literature that the simplest medium phosphites and phosphonites copolymerize with methyl methacrylate, forming a linear polymer containing phosphorus atoms in the main chain (7). Evidently, in our case an analogous reaction took place, but, because of the presence of several phosphite groups in the starting compound, the polymer obtained has a three-dimensional structure; it is insoluble in any solvent and decomposes on heating without melting (∼ 400°).

* Detailed data on testing the obtained polymers for anticholinesterase activity will be presented separately.

Experimental Part

Interaction of I with chloral. **A.** A solution of 1.84 g of I (1) in 7 ml of tripropyl phosphate and 1.5 g of chloral was heated* to 80° for 2 h. It was then cooled, 2 ml of chloroform was added, and the product was precipitated with petroleum ether. The precipitate was filtered off and washed 3 times with 10 ml portions of petroleum ether (by decantation). Yield 1.85 g, m.p. 125–130°, η_{ud} 0.048**.

Found, %: P 8.74; 8.91; Cl 15.36; 15.38

B. A solution of 1.84 g of I in 10 ml of tripropyl phosphate and 7 g of chloral was heated under analogous conditions for 1 h. Yield 1.91 g, m.p. 125–135°, η_{ud} 0.045.

Found, %: P 8.30; 8.15; Cl 20.37; 20.56

Chlorination of I. To a solution of 5.3 g of I in 20 ml of tripropyl phosphate at 30–40°, 19.3 g of sulfuryl chloride was added dropwise. The reaction mixture was kept for 30 min at 40°, and the gaseous products and excess sulfuryl chloride were distilled off in the vacuum of a water-jet pump. The residue was dissolved in 3 ml of chloroform and precipitated with petroleum ether. The precipitate was filtered off and washed with 30 ml of petroleum ether. Yield 4.95 g, m.p. 160–165°, η_{ud} 0.03.

Found, %: P 11.23; 11.30; Cl (total) 18.89; 18.84; Cl (ionic) 12.71; 12.80

Interaction of II with diethylamine. To a solution of 2.7 g of II in 10 ml of tripropyl phosphate at 30–40°, 4 ml of sulfuryl chloride was added dropwise. The mixture was kept at 40° for 30 min, excess sulfuryl chloride and gaseous products were distilled off, and 3.25 g of diethylamine was added; the mixture was stirred thoroughly at 20° for 3 h and poured into 25 ml of ethyl acetate. The precipitate was separated and washed (by decantation) with petroleum ether, and then with water. Yield 1.9 g, m.p. 190–195°, η_{ud} 0.052.

Found, %: P 4.3; 4.6; N 2.04; 2.08

Interaction of II with butyl mercaptan. To a solution of 1.6 g of freshly prepared II in 10 ml of tripropyl phosphate, 0.95 ml of triethylamine and 0.75 g of butyl mercaptan were added dropwise. The mixture was heated for 2 h at 90°, excess triethylamine and butyl mercaptan were distilled off, and 50 ml of ether was added. An oil separated, which was washed several times with moist ether, a small amount of water, and again with ether. Yield 1.05 g, η_{ud} 0.047.

Found, %: P 9.81; 10.02; N 7.50; 7.63

Interaction of I with diethylamine and carbon tetrachloride. To a solution of 2.38 g of I in 15 ml of dimethylformamide, 2.35 ml of CCl_4 and 5.25 ml of diethylamine were added. The mixture was stirred thoroughly and heated for 1 h at 80°. Then dimethylformamide and excess diethylamine were distilled off in vacuo (10 mm Hg). The residue was dissolved in 15 ml of alcohol. On addition of acidified water a precipitate formed. The precipitate was filtered off and washed with water and ether. Yield 1.5 g, m.p. 187–195°, η_{ud} 0.058.

Found, %: P 7.1; 6.8; N 2.54; 2.31

Interaction of I with diethylaminoethanol. To a solution of 1.5 g of I in 15 ml of dimethylformamide, 1 g of diethylaminoethanol, 3.4 ml of triethylamine, and 1.5 ml of CCl_4 were added. The mixture was heated for 1 h at 80°. The precipitate that formed was filtered off, and the solvent was distilled from the filtrate in vacuo. To the residue, 10 ml of water was added; a flocculent precipitate formed, which was filtered off and washed with water and ether. Yield 0.56 g, m.p. 170–175°, η_{ud} 0.048.

Found, %: P 8.5; 8.3; N 3.17; 3.25

* This and the following experiments were carried out in an atmosphere of inert gas.
** Here and below the viscosities are given for 0.1% solutions of the substances in dimethylformamide.

Reaction of I with ethylsulfenyl chloride. To 1.3 g of diethyl disulfide, 1.43 g of sulfuryl chloride was added dropwise at −30 to −20°. The mixture was kept for 5 min in vacuo (150 mm Hg) at 20°. Then, at −10°, a solution of 3.8 g of I in 30 ml of dimethylformamide was added dropwise, and the mixture was left for 1 day at 20°. The solvent was distilled off; the residue was dissolved in tripropyl phosphate and precipitated with a mixture of chloroform and petroleum ether (1:5). The flocculent precipitate that separated was filtered off and washed with petroleum ether. Yield 3.2 g, mp 127–135°, η_{red} 0.057.

Found, %: P 10.28; 10.07; S 10.43; 10.33

Reaction of I with β,β'-diethylthioethyl disulfide. Analogously to that described above, from 3.74 g of I and 2.42 g of β,β'-diethylthioethyl disulfide, 3.5 g of thiolophosphate was obtained. Mp 155-160°, η_{red} 0.095.

Found, %: P 10.69; 10.79; S 10.33; 10.32

Reaction of novolac tetraethyldiamidophosphite with diethanolamine and sulfur. A solution of 1.86 g of novolac amidophosphite (1) in 15 ml of dimethylformamide with 2.34 g of diethanolamine was heated in a distillation apparatus for 6 h at 110°. During heating, 0.4 ml of diethylamine distilled off. To the reaction mixture 0.64 g of sulfur was added, and the mixture was heated for 4 h at 130°. Dimethylformamide was distilled off in vacuo. The residue was dissolved in 15 ml of a 5% solution of caustic potash in methanol and filtered. The filtrate was acidified with hydrochloric acid (1:1). The precipitate that separated was filtered off and washed with water. Mp 127-134°, η_{red} 0.057.

Found, %: P 9.71; 9.90; N 7.50; 7.71; S 10.10; 10.23

Reaction of novolac ethylene phosphite with ethyl iodide. To a solution of 1 g of ethyl phosphite, prepared by method (1), in 10 ml of anisole, 0.05 ml of ethyl iodide was added. The mixture was heated in a closed vessel for 3 h at 70° and then for 12 h at 130°. A gelatinous precipitate gradually formed; it was washed repeatedly with ether. The substance does not melt, decomposes at $\sim 400°$, and is insoluble in water and organic solvents. The qualitative reaction for trivalent phosphorus is negative.

Found, %: P 13.6; 13.8

0.5 g of the resulting substance was heated for 10 h with a 30% solution of caustic potash on a water bath. The substance gradually went into solution; the solution was acidified, and a precipitate separated, which was filtered off and washed with water. Mp 120-130°. The qualitative reaction for phosphorus is negative. In chromatographic mobility on an alumina plate it corresponds to the starting novolac resin.

Reaction of novolac ethylene phosphite with methyl methacrylate. A solution of 2 g of phosphite in 5 g of methyl methacrylate and 0.05 g of benzoyl peroxide was heated for 12 h at 130°. A rubber-like white mass formed. The mass was washed repeatedly with ether and dissolved in dimethylformamide. The insoluble portion was filtered off and washed with ether. The substance does not melt; it chars above $\sim 400°$. It is insoluble in water and common organic solvents.

Found, %: P 5.0; 5.1

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named after M. V. Lomonosov

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Note: Figure translations are in progress. See original paper for figures.

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