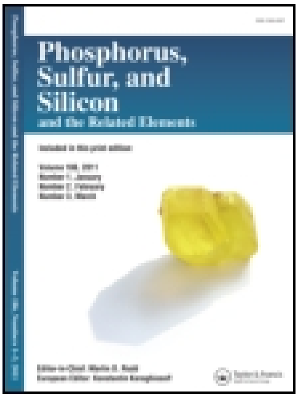

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New P-Containing Linear and Macrocyclic Polyphenols

Alexander R. Burilov [a] , Irina R. Knyazeva [a] , Elmira M. Kasymova [a] , Yulia M. Sadykova [a] , Michael A. Pudovik [a] , Wolf D. Habicher [b] & Oleg G. Sinyashin [a]

[a] A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of the Russian Academy of Sciences, Kazan, Russia

[b] Drezden University of Technology Institute of Organic Chemistry, Drezden, Germany

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NEW P-CONTAINING LINEAR AND MACROCYCLIC POLYPHENOLS

Alexander R. Burilov,[1] Irina R. Knyazeva,[1] Elmira M. Kasymova,[1] Yulia M. Sadykova,[1] Michael A. Pudovik,[1] Wolf D. Habicher,[2] and Oleg G. Sinyashin[1]
[1]*A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of the Russian Academy of Sciences, Kazan, Russia*
[2]*Drezden University of Technology Institute of Organic Chemistry, Drezden, Germany*

Abstract *We synthesized new phosphorus-containing linear and macrocyclic polyphenols using organic compounds containing phosphorus-carbon bonds and the phosphorus atom of various coordination, and also with reactive acetal, aldehyde, vinylethoxy, and methylene quinone fragments as starting materials. These achievements are briefly summarized.*

Keywords Calixarenes; condensation; intermolecular cyclization; phosphorylation; resorcinol and its derivatives

Recently macrocyclic and open chain compounds with phosphorus–carbon bonds, containing phenolic fragments in their structure, and also phosphorus-containing counterparts of natural compounds, have been intensively studied. Compounds with phosphorus–carbon bonds can be considered formal counterparts of phosphates with the difference that their biological action is substantially higher and more varied due to certain difficulties of enzyme-promoted cleavage of phosphorus–carbon bonds in comparison with phosphorus–oxygen bonds. In this article, we will show the most recent data on the synthesis of new linear and macrocyclic polyphenols with phosphorus–carbon bonds.[1,2]

The interaction of triamidophosphites, containing linear and cyclic amino groups at a phosphorus atom, with diethylacetal of bromoacetaldehyde leads to the formation of new triamidophosphonium acetals **1a–e**. The structure of compounds **1a** and **1c** was established on the basis of X-ray analysis data. Condensation of triamidophosphonium acetals **1a–d** with resorcinol and its derivatives in the presence of acids results in the formation of new compounds of diarylmethane type **2a–e**, **3a–e**, and **4a–d** (Scheme 1). The formation of linear structures instead of expected calix[4]resorcinols is probably determined by the

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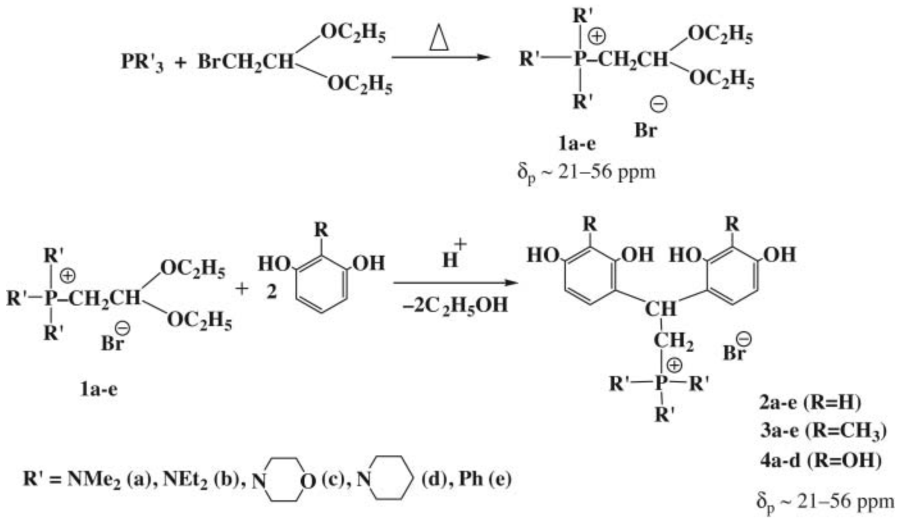
Address correspondence to Alexander R. Burilov, A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of the Russian Academy of Sciences, Arbuzov St. 8, Kazan 420088, Russia. E-mail: burilov@iopc.ru

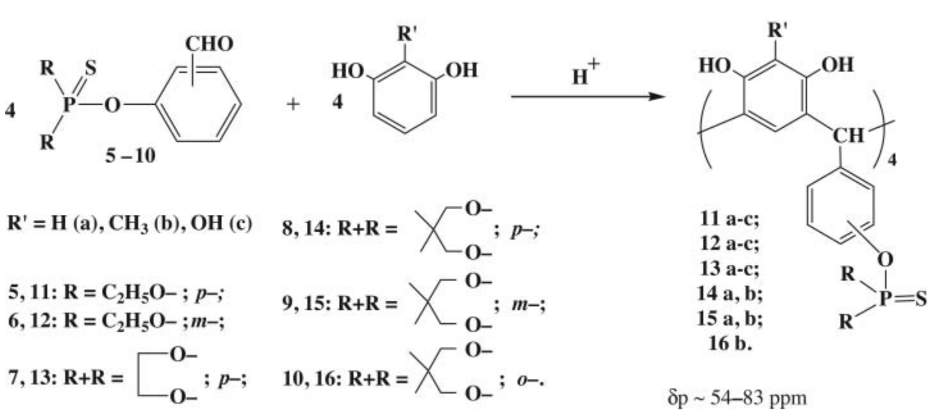


Scheme 1

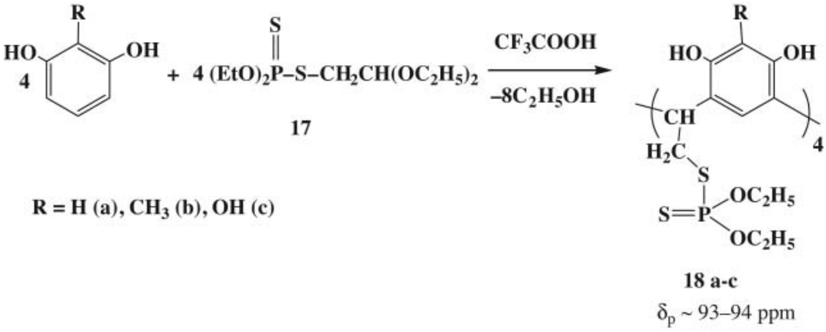
steric factors—the presence of large substituents at phosphorus atoms, which interfere in the further condensation of the product obtained in macrocyclic structure.

Varying the nature of phosphorus-containing acetals and aldehydes in condensation reactions of resorcinol and its derivatives, we have chosen the aldehydes from **5** to **10** as new subjects of research**,** which include phosphoric and aldehyde fragments separated by an aromatic spacer. For the synthesis of thiophosphorylated calixarenes **11**–**16**, bearing bulky phosphorus-containing fragments on the lower rim of the molecule, we carried out the condensation reactions of thiophosphatoaldehydes **5**–**10**, synthesized by a known procedure, with resorcinol, 2-methylresorcinol, and pyrogallol in acidic conditions (Scheme 2).

The formation of the phosphorus-containing calixarene matrix was realized in one step by the interaction of resorcinol, 2-methylresorcinol, or pyrogallol with dithiophosphate acetal **17** in trifluoroacetic acid, which was used both as the catalyst and solvent (Scheme 3).



Scheme 2

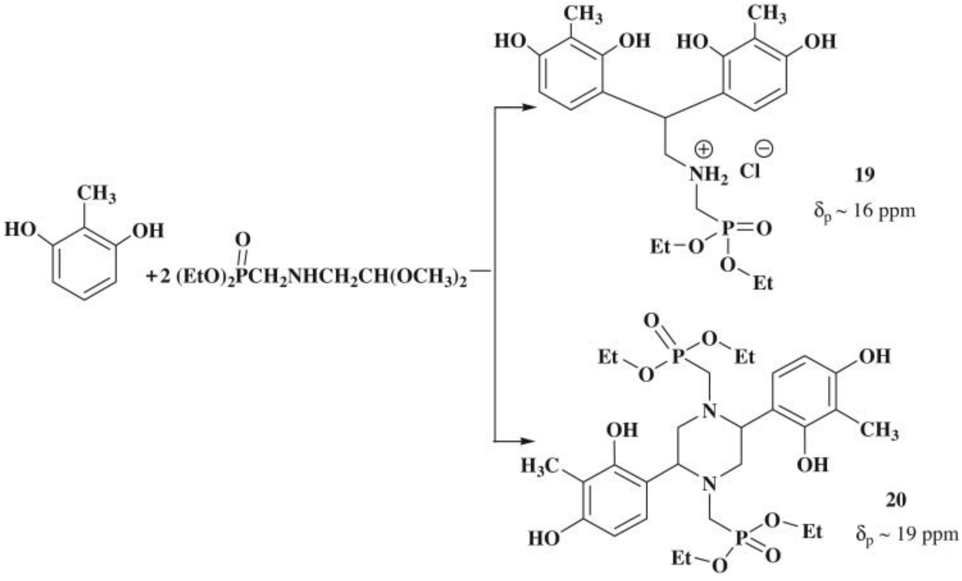


Scheme 3

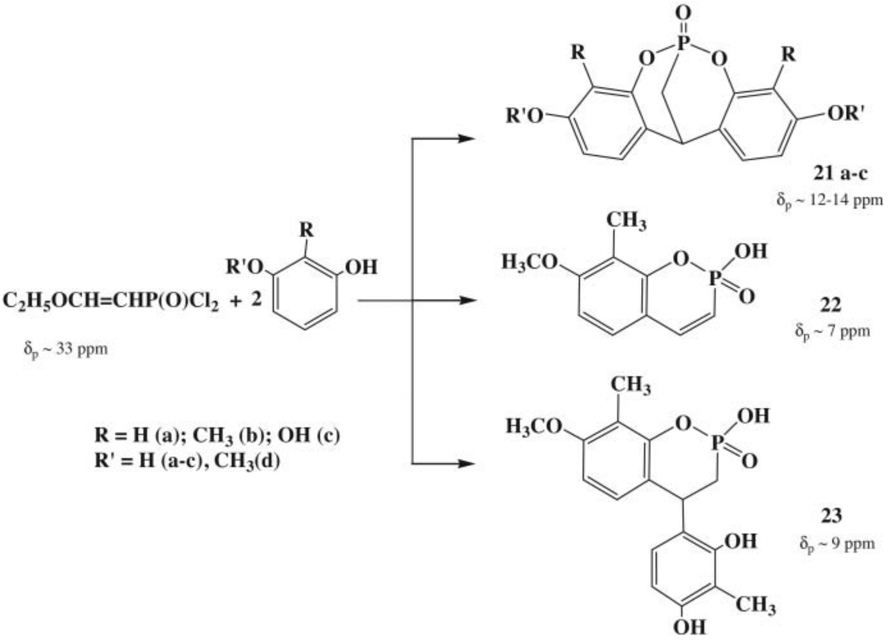
As a result, the first representatives of calix[4]resorcinols **18a–c** containing dithiophosphate methyl fragments on the lower rim of the molecule were obtained.^{3}

For the first time, we studied the condensation of aminophosphonate acetal with resorcinol and 2-methylresorcinol in acidic conditions. As a result, the main product, phosphorus-containing polyphenol of diarylmethane type **19**, was obtained. However, a detailed study of the reaction revealed that in the case of aminophosphonate acetal, along with condensation, the second direction of reaction is realized—intermolecular cyclization of aminophosphonate with the formation of piperazine derivative **20** (Scheme 4).

We have developed a convenient one-step method for the synthesis of new skeleton, phosphonates **21a–c**, by the condensation of available 2-ethoxyvinyldichlorophosphonate with resorcinol and its derivatives in dichloromethane in the presence of trifluoroacetic acid (Scheme 5). The compounds obtained contain several hydroxyl groups; that makes these cyclic phosphonates interesting as starting compounds for the synthesis of new



Scheme 4



Scheme 5

polymeric and macrocyclic structures. It is necessary to note that during condensation of 2-ethoxyvinyldichlorophosphonate with 3-methyl-2-ethoxyphenol, the products are bicyclic phosphonate and oxaphosphorine **22** in 1:1 ratio and also oxaphosphorine **23,** which was isolated in pure state with 5% yield. The structure of compound **22** was also established on the basis of X-ray analysis data.[4]

The structure and composition of the products obtained were confirmed by ^{1}H, ^{31}P, IR, and mass spectrometry data; X-ray analysis data; and elemental analysis.

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