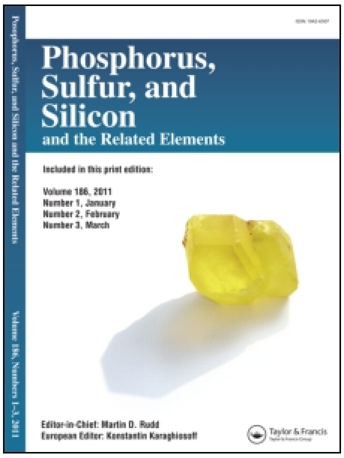

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The New Data for the Reaction of Arylenedioxy Trihalogenophosphoranes with Alkyl- and Arylacetylenes

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THE NEW DATA FOR THE REACTION OF ARYLENEDIOXY TRIHALOGENOPHOSPHORANES WITH ALKYL- AND ARYLACETYLENES

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*The new data concerning the reaction between substituted arylenedioxy trihalogenophosphoranes and monoalkyl- or arylacetylenes are summarized. The reaction leads to formation of six-membered heterocycles–2-oxo-4-R-benzo[*e*]-1,2-oxaphosphorin-3-enes. The substituent effects in the phosphorane and acetylene molecules on the* ipso*-substitution and halogenation regiochemistry are discussed. The* ipso*-substitution of* tert*-butyl group on chlorine and the exchange of bromine on chlorine and iodine on hydrogen have been observed, along with formation of benzophosphorines. The interaction of tetrachloro-*ortho*-benzoquinone with phosphorus trichloride and arylacetylenes is proposed as a new modification of the reaction leading to the formation of benzo[*e*]-1,2-oxaphosphorines. The structures of some benzo[*e*]-1,2-oxaphosphorines are determined by the single crystal X-ray diffraction.*

Keywords: Acetylenes; halogenation; *ipso*-substitution; phosphoranes; phosphorus trichloride; reactions; tetrachloro-*ortho*-benzoquinone

Earlier[1] we have shown that the interaction of the trichlorophosphorane **1** with arylacetylenes gives an unusual synthetic result. The six-membered phosphorus heterocycle–benzoxaphosphorine **2** was obtained with a high yield. An easy formation of phosphoryl group and P—C bond, *ipso*-substitution of oxygen, and selective chlorination in the *para*-position to endocyclic oxygen took place under the soft conditions in this reaction.

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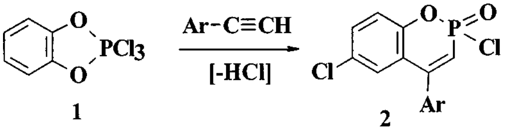
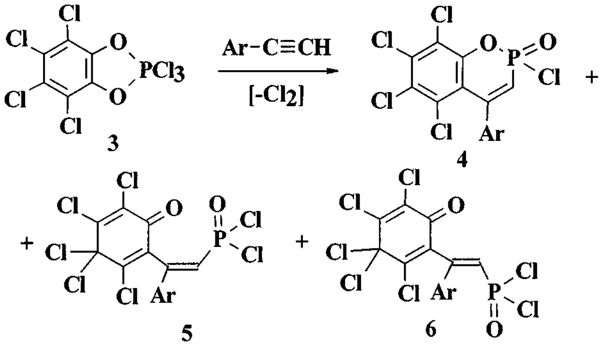
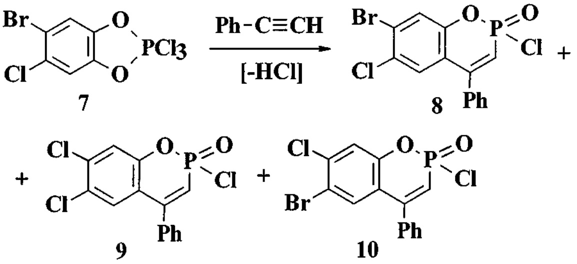


The further investigation of the reaction between cathehol trihalogenophosphoranes and monosubstituted acetylenes has been considered in this report. To study the influence of the phosphorane structure on the synthetic result, we introduced both donor and acceptor substituents to the benzene ring.

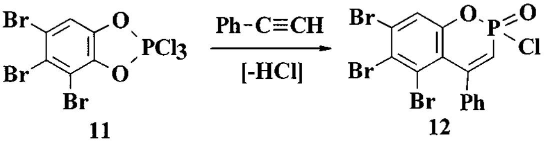
The presence of the *ortho*-chlorine atoms at the benzene ring of phosphorane **3** leads to appearance of some peculiarities in the reaction with arylacetylene. The reaction mixture contains two isomeric vinylphosphonates **5** and **6** of the quinoid type along with the heterocyclic product **4**. The isomeric phosphonates were identified according to their three bonds phosphorus-carbon and proton-carbon couplings. Obviously, two *ortho*-chlorine atoms essentially hinders cyclization.



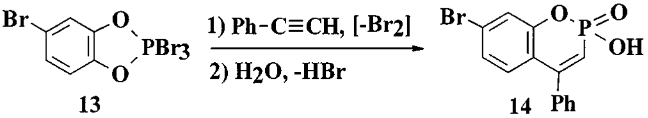
The most interesting situation arises when the phosphorane molecule contains two different kinds of halogen, such as chlorine and bromine. The compound **7** reacts with phenylacetylene to give three types of phosphorines: **8**, **9** and **10**. The identification of the compounds has been made by the proton and carbon NMR as well as the comparison with the spectra of the pure substances **8** and **9** described earlier.[2]



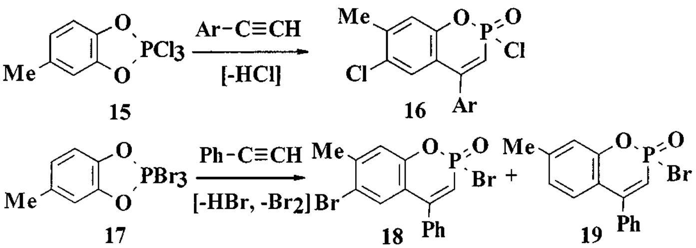
The high regioselectivity of the oxygen *ipso*-substitution has been observed in the reaction of the unsymmetrical tribromophosphorane **11** with phenylacetylene. Exclusively, the *ipso*-substitution of the oxygen connected with the brominated *ortho*-carbon occures. The major product of the reaction is phosphorine **12**.



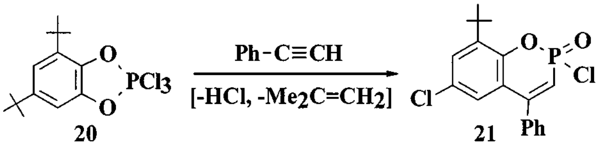
The reaction of the phosphorane **13** containing bromine in a benzene ring with phenylacetylene unexpectedly leads to the preferable formation of the monosubstituted compound **14** containing the bromine atom *meta* to oxygen with a high yield. This result is in accordance with the lower ability of bromine in comparison with chlorine to migrate to the benzene ring.



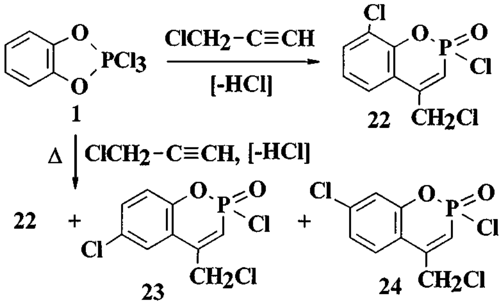
Phosphorane **15** containing a donor methyl group easily reacts with arylacetylenes, giving the compound **16** with a high regioselectivity. The location of a chlorine atom was determined by the NMR and single crystal X-ray diffraction. The similar reaction of bromophosphorane **17** with phenylacetylene turned out to yield two phosphorines, **18** and **19**. The main product **18** contains a bromine *para* to the endocyclic oxygen.



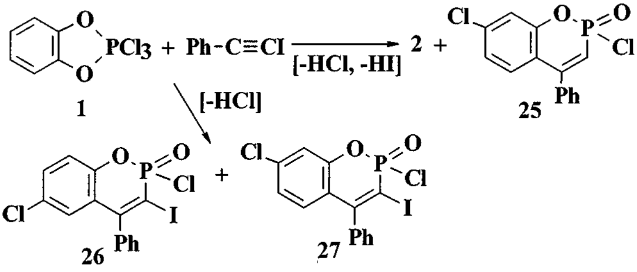
The *ipso*-substitution of the *tert*-butyl group situated *para* to oxygen by the chlorine proceeds in the reaction of the phosphorane **20** with phenylacetylene. The structure of **21** was determined by the single crystal X-ray diffraction.



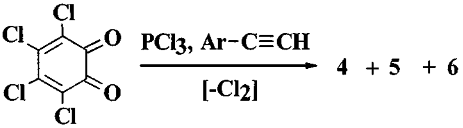
Alkylacetylenes like propargyl chloride can also react with phosphorane **1** to give phosphorine **22** under soft conditions. An unusual peculiarity of the reaction is an incorporation of chlorine in the *ortho*-position to the endocyclic oxygen. The interaction of phosphorane **1** with propargyl chloride has lost the regioselectivity of the chlorination under heating—that is, three isomers **22–24** are formed. However the *para*-isomer **23** predominates.



Disubstituted iodophenylacetylene can also react with phosphorane **1** and unexpectedly gives four compounds **2**, **25–27**. Phosphorines **2**, **27** contain hydrogen instead of iodine. Compounds **2**, **26** are predominant. The structure of phosphorines was established by carbon NMR spectroscopy.



In some cases, it is enough to use the mixture of quinone and phosphorus trihalogenide instead of phosphorane. So, the interaction of the tetrachlorobenzoquinone with arylacetylene and PCl_3 gives the heterocycles **4** with the moderate yield. The open-chain structures **5**, **6** were also obtained.



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[2] V. F. Mironov, I. A. Litvinov, A. A. Shtyrlina, A. T. Gubaidullin, R. R. Petrov, A. I. Konovalov et al., *Zh. Obshch. Khim.*, **70,** 1117 (2000).