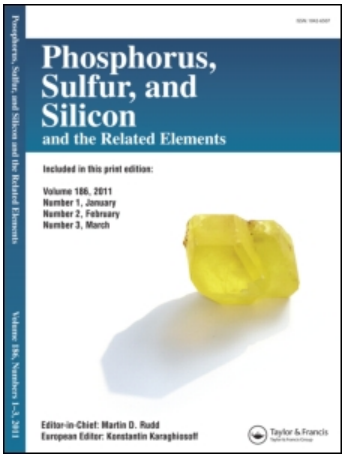

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[a] A. E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Russia

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Synthesis and Chemical Properties of Benzo[*e*]-1,2-Oxaphosphorinine Derivatives—Analogues of Coumarins

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The 4-aryl(alkyl)benzo[e]-1,2-oxaphosphorine derivatives (phosphacoumarins) were obtained by the reaction of 2,2,2-trihalogenobenzo[d]-1,3,2-dioxaphospholes with terminal acetylenes. The reactions of phosphacoumarins with halogens and Grignard reagents were investigated.

Keywords 2,2,2-trihalogenobenzo-1,3,2-dioxaphosphole; acetylene; alkenylphosphine oxide; Grignard reagent; phosphacoumarin; phosphorinine

INTRODUCTION

We have earlier shown that the interaction of 2,2,2-trihalogenobenzo[*d*]-1,3,2-dioxaphospholes with arylacetylenes unexpectedly gives the 4-aryl-2,6-dihalogenobenzo[*e*]-1,2-oxaphoshorinines,[1] which are the P-analogues of natural coumarins.[2] It was found that some highly selective transformations, such as P—C bond and phosphoryl group formation, unusually easy *ipso*-substitution of the phenylene oxygen, and at last, chlorination of the phosphole's benzene fragment takes place under mild conditions. In this connection, the mentioned above reaction is of considerable interest not only for the synthetic utilization in the phosphorus chemistry, but also as a versatile approach to the rare P-heterocyclic systems, which are P-analogues of the biologically active compounds (coumarins).

We have also shown that the 5-chloro- and 5-bromo-[3] 5,6-dibromo-,[4] and 5-methyl-2,2,2-trihalogenobenzo[*d*]-1,3,2-dioxaphospholes[5] easily

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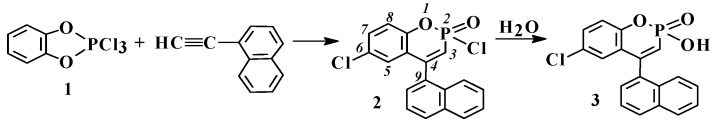
Address correspondence to E. N. Varaksina, A. E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Russia. E-mail: minorov@iopc.knc.ru

react with arylacetylenes with the formation of the substituted benzo[*e*]-1,2-oxaphoshorinine derivatives with a high regioseletivity of all the processes mentioned above.

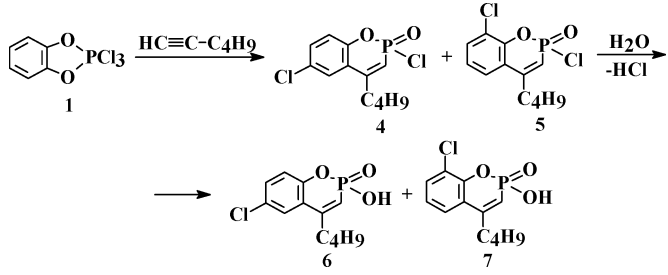
To determine the synthetic scope of the reaction the other types of acetylenes—sterically hindered naphthylacetylene, ordinary alkylacetylenes such as hex-1-yne were involved in the reaction with 2,2,2-trichlorophosphole **1**.

It was found, that the phosphole **1** easily reacts with naphthylacetylene in methylene chloride used as a solvent. According to ^{13}C NMR spectrum only two phosphorus containing compounds in the ratio 2:3 are formed, which are the diastereoisomers. This phenomena is caused by the fact that molecule of 2,6-dichloro-4-naphthylbenzo[*e*]-1,2-oxaphoshorinine **2** has asymmetric phosphorus atom and exhibits the athropoisomerism due to a hindered rotation around the C^4–C^9 bond. The diastereoisomerism disappears after hydrolysis of compound 2 (phosphorus atom in compound 3 is non-chiral) (Scheme 1).



SCHEME 1

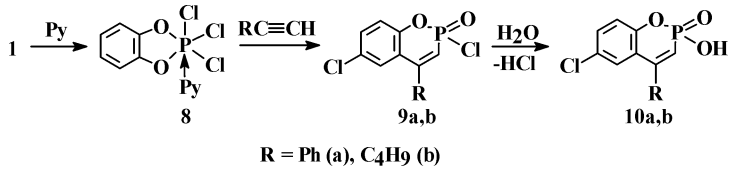
The reaction of hex-1-yne with 1 leads to the formation of two benzo[*e*]-1,2-oxaphosphorinines **4**, **5** in the 9 : 1 ratio (Scheme 2). The minor product contains a chlorine atom in *ortho*-position to endocyclic oxygen atom. Corresponding hydroxy-derivatives **6** and **7** were isolated by the fractional crystallization.



SCHEME 2

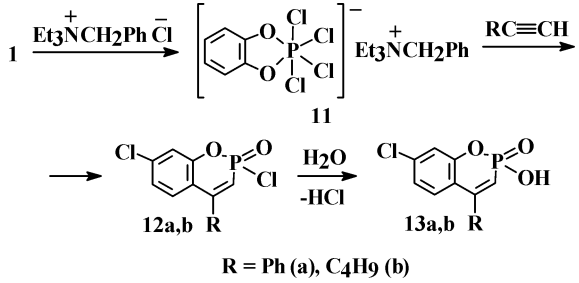
So, the reaction of the 2,2,2-trihalogenobenzo[*d*]-1,2,3-dioxaphospholes with various acetylenes is a selective and versatile approach to the rare benzo[*e*]-1,2-oxaphoshorinines with the alkyl, aryl, naphtyl substituents in the heterocyclic fragment.

The influence of the phosphorus nature of the phosphole on the course of the reaction was also investigated. The reaction of the hexacoordinated species **8** with phenylacetylene or hexyne mainly yields the *para*-chlorinated to endocyclic oxygen phosphorinines **9**, which were converted into the stable compounds **10** (Scheme 3).



SCHEME 3

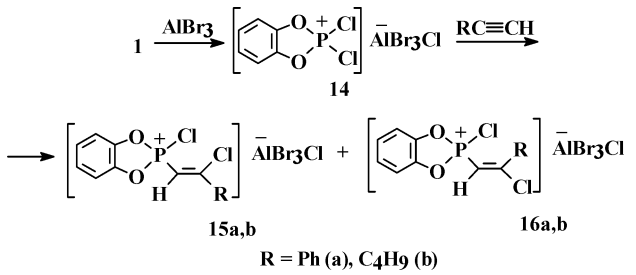
The anionic tetrachlorophenylendioxaphosphate **11**, which was also obtained from phosphole **1,** selectively forms with acetylenes isomers **12** *meta*-chlorinated to the endocyclic oxygen in the same conditions. The phosphonic acids **13** were isolated after hydrolysis of compounds **12** (Scheme 4).



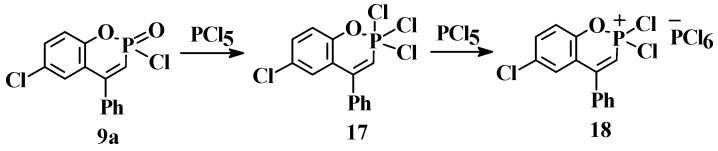
SCHEME 4

The reactions of phosphonium salts **14** unexpectedly leads only to the formation of *cis*- and *trans*- isomers **15** and **16**, which are obtained as the products of a classical electrophilic addition, both in the reaction with phenylacetylene and hex-1-yne (Scheme 5).

The chemical properties of phosphorinines were investigated for the first time. The reactions with halogenating agents—phosphorus pentachloride, chlorine, and bromine—were carried out. It turned out, that the reaction of phosphorinine **9a** with phosphorus pentachloride is of multistage character. At the initial stage, the chlorination of phosphoryl group with the formation of phosphorane **17** was observed by the ^{31}P NMR (Scheme 6). An excess of phosphorus pentachloride easily converts compound **17** into phosphonium derivative **18**.

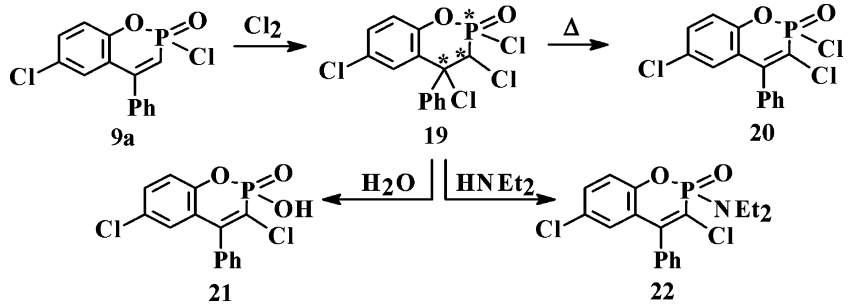


SCHEME 5



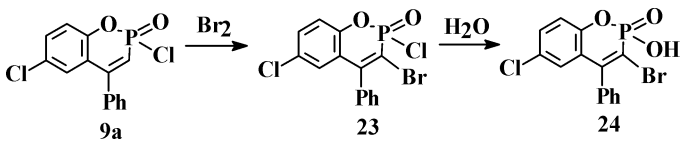
SCHEME 6

The reaction of compound **9a** with an excess of chlorine in of methylene chloride gives the addition product **19** as a mixture of two diastereoisomers (Scheme 7). The structure of the compound was unambiguously determined by ^{13}C, ^{13}C-^{1}H NMR. The hydrogen chloride can be eliminated by the prolonged heating, hydrolysis, and aminolysis. The resulting 3-chlorosubstituted phosphorinines **21** and **22** were obtained and characterized by the NMR.



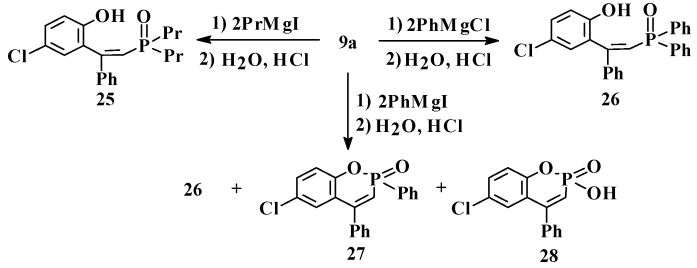
SCHEME 7

3-Bromosubstituted phosphorinine **23** was obtained by the reaction of phosphorinine **9a** with bromine. In this case, the intermediate addition product, like compound **19** was not detected by the ^{31}P NMR (Scheme 8).



SCHEME 8

The resulting benzo[*e*]-1,2-oxaphoshorinine can be selectively halogenated, that will allow to use them for the further modification in the palladium-catalyzed cross-coupling reactions.



SCHEME 9

It was recently found, that the reaction of chlorophosphorinine **9a** with equimolar amount of phenylmagnesium chloride leads to the mixture of phenyl-substituted phosphorinine **27** and acyclic derivative **26**. When an excess of the Grignar reagents is used the alkenylphosphineoxides can be obtained with the quantitative yield. The compounds like phosphineoxides **25** and **26** are very perspective as the complexing and extracting reagents (Scheme 9).

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