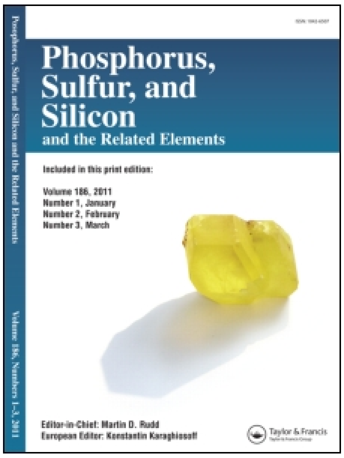

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Reaction of Phenylenedioxytrihalogenophosphoranes with Arylacetylenes. Synthesis and Spatial Structure of the Derivatives of 2-Oxo-4-Aryl-5,6-Benzo-1,2-Oxaphosphorin-2-Enes

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Reaction of Phenylenedioxytrihalogenophosphoranes with Arylacetylenes. Synthesis and Spatial Structure of the Derivatives of 2-Oxo-4-Aryl-5,6-Benzo-1,2-Oxaphosphorin-2-Enes

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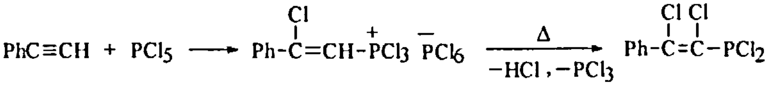
New method of synthesis of six-membered heterocycles – 2-R-2-oxo-4-aryl-2H-benzo[e][1,2]-oxaphosphorin-3-enes has been developed. It includes the interaction of arylenedioxy trihalogenophosphoranes with arylacetylenes. The formation of phosphoryl group and P-C bond, *ipso*-substitution of the aromatic oxygen and halogenation of the benzene ring take place in this unusual reaction. The influence of the phosphorane structure on synthetic result is discussed. If both *para* positions at benzene ring of the phosphorane are occupied by halogens, the evolving of halogen molecule occurs. The structures of 2-R-2-oxo-4-aryl-2*H*-benzo[e][1,2]-oxaphosphorin-3-enes are determined by X-ray analysis.

Keywords: phosphoranes; arylacetylenes; reactions; 2H-benzo-[e][1; 2]-oxaphosphorin-3-enes; *ipso*-substitution; halogenation; crystal structure

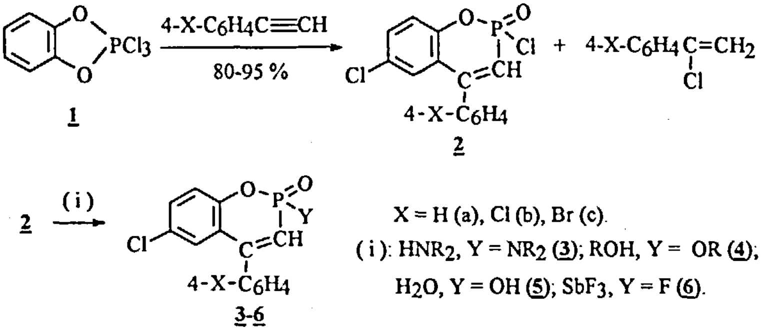
The first observations concerning the interaction of PCl_5 with phenylacetylene were made by Bergman and Bondi [1] in 1933. In 1954 the reaction was investigated by Anisimov [2]. Since that time the interaction of arylacetylenes with PCl_5 and some its derivatives has been considered as an important method of synthesis of unsaturated phosphonates. The synthetic applications of the reaction were summarized by Fridland [3]. The reaction is presumed to include the stage of the electrophilic addition to a triple carbon-carbon bond. Only PCl_5 has been used practically in all reactions considered [3].



$$PhC\equiv CH + PCl_5 \longrightarrow Ph\text{-}\overset{Cl}{C}=CH\text{-}\overset{+}{P}Cl_3\ \overset{-}{P}Cl_6 \xrightarrow[-HCl,\,-PCl_3]{\Delta} Ph\text{-}\overset{Cl}{C}=\overset{Cl}{C}\text{-}PCl_2$$

Meanwhile it is known that such fragment as the phenylenedioxyphospholane cycle increases the stability of phosphorus bipyramide. In this work we attempted to find out the synthetic consequences of an introduction of the catehol fragment in phosphorus halogenide molecule by the example of the reaction with arylacetylenes.

The interaction of simplest clorophosphorane (1) with arylacetylenes has really proved to lead to the unusual result. The six-membered phosphorus heterocycles - benzo-1,2-oxaphosphorines (2) were obtained with high yields. The reaction is accompanied by the formation of chlorostyrenes. Treatment of phosphorines (2) by alcohols, amines, water or SbF_3 gives the corresponding derivatives (4-6). All products were characterized by ^1H, ^{13}C, ^{19}F, ^{31}P NMR spectroscopy [4].



X = H (a), Cl (b), Br (c).
(i): HNR_2, Y = NR_2 (3); ROH, Y = OR (4);
H_2O, Y = OH (5); SbF_3, Y = F (6).

A cyclic structure of several phosphorines and location of chlorine atom have been established by X-ray studies. The structure of morpholine derivative (3) is presented on fig. 1. It is easy to see that the chlorine atom is arranged in *para* position about the *endo*-cyclic oxygen atom. The molecule (3) forms the stable solvate with dioxan. Conformation of the phosphorine heterocycle is a distorted boat. Torsion angle between the heterocycle and phenyl plains is about 40°.

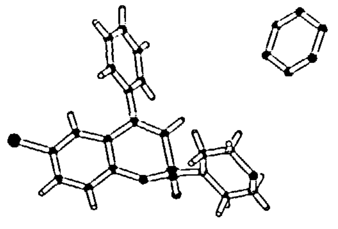
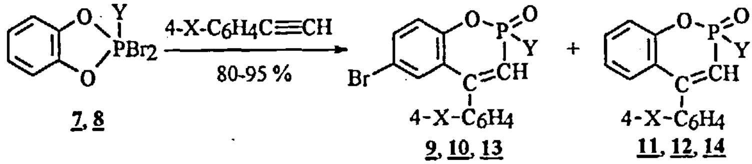


Fig. 1

The replacement of chlorine atoms with bromine ones does not change the direction of the reaction. So, the interaction of bromophosphoranes (7, 8) with arylacetylenes results in two phosphorines (9, 10). The corresponding phosphonic acids (13, 14, Y = OH) were obtained as a result of the hydrolysis of compounds (9-12). The brominated acid (13a) has been separated owing to the lower solubility in dioxan. The P-F bond is not active in these reactions. A direct relationship between the concentration of the fluorophosphorane (8) and the ratio of the products (10) and (12) indicates on the intermolecular character of bromination. The spatial structure of molecules (10, 14a) in crystal is presented on fig. 2, 3. The bromine atom occupies the *para* position to *endo*-cyclic oxygen (fig. 2).



X = H (a), Br (c); Y = Br (7, 9, 11), F (8, 10, 12)

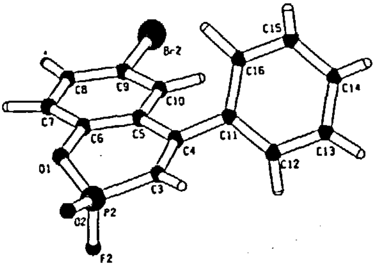


Fig. 2

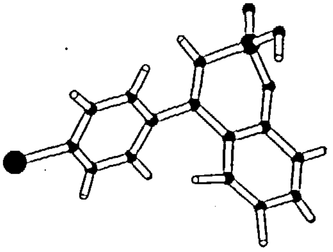
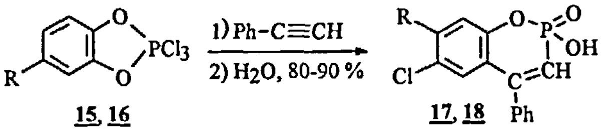


Fig. 3

To investigate the influence of the phosphorane structure on the synthetic result the phosphoranes containing the various substituents at benzene ring have been obtained. The presence of halogen at benzene ring of the molecules (15, 16) has no effect on the course of the reaction. The six-membered phosphorines (17, 18) have been also obtained. The incorporated chlorine atom has been found out by X-ray analysis to occupy the *para* position to oxygen and in *ortho* position to halogen (R). The solvate of molecule (18) with dioxan is shown on fig. 4.



R = Cl (15, 17),
Br (16, 18)

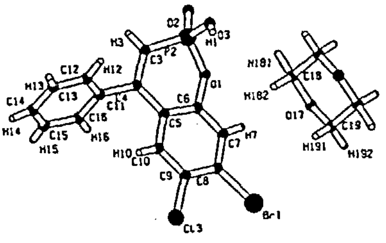
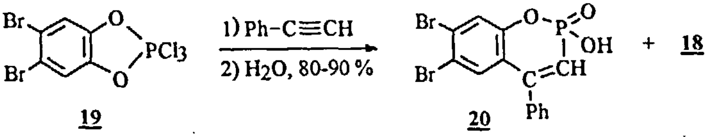
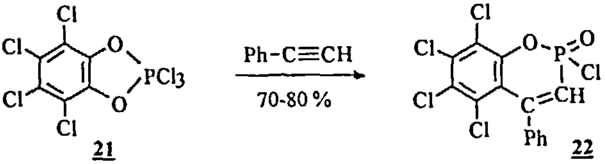


Fig. 4

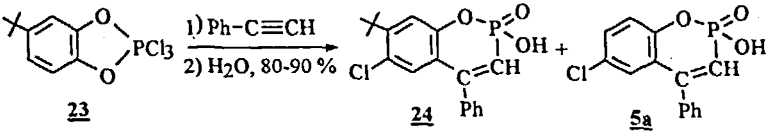
An including of two bromine atoms in benzene ring also has no influence on the result of the reaction of phosphorane (19) with phenylacetylene. Dibromophosphorine (20) is the main product after hydrolysis of the reaction mixture. The compound (18) has been obtained as by-product. Thus, we are concerned with a limiting case when an incorporating of the third halogen atom does not occur.



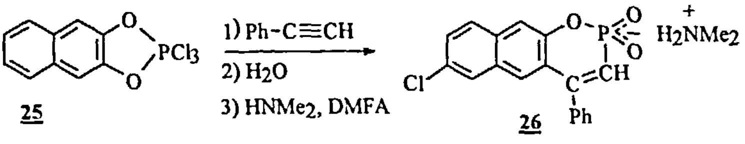
In spite of the presence of the *ortho* chlorine atoms in starting phosphorane (21), a formation of the cyclic product (22) takes place in the reaction between the hexachlorinated derivative (21) and phenylacetylene. The structure of halogenated phosphorines (20, 22) has been verified by X-ray analysis.



It is well known that a *tert*-butyl group is a frequently used substituent for steric shielding of the neighbouring positions at the benzene ring. Nevertheless the phosphorane (23) lightly reacts with phenylacetylene to give the phosphorine (24). In a small extent the product of *ipso*-replacement (5a) is obtained too. The relative arrangement of chlorine and *tert*-butyl group has been determined by comparison of the calculated carbon chemical shifts with the experimental ones. These latter are better consistent with the calculated chemical shifts for the structure in which chlorine atom is arranged in *para* position about oxygen.



It is interesting to note that the naphthalene derivative (25) reacts with phenylacetylene by the same way. The treatment of the intermediate chlorophosphorine by water and dimethylamine yields the salt (26).



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