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Reaction of Benzyltrimethylammonium Phenylenedioxy Tetrachlorophosphate with Phenylacetylene and Propargyl Chloride

Alfiya A. Shtyrlina^a; Vladimir F. Mironov^a; Elena N. Varaksina^a; Aleksander I. Konovalov^a

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

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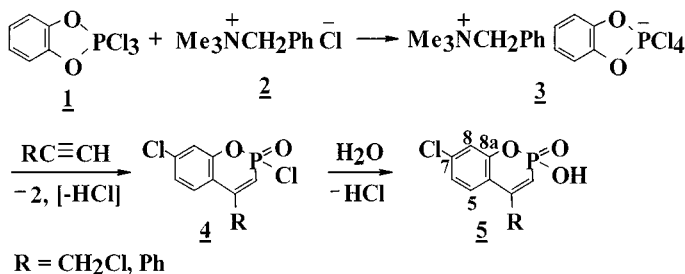
REACTION OF BENZYLTRIMETHYLAMMONIUM PHENYLENEDIOXY TETRACHLOROPHOSPHORATE WITH PHENYLACETYLENE AND PROPARGYL CHLORIDE

*Alfiya A. Shtyrlina, Vladimir F. Mironov, Elena N. Varaksina,
 and Aleksander I. Konovalov*

*A. E. Arbuzov Institute of Organic and Physical Chemistry,
 Russian Academy of Sciences, Russia*

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The interaction of phenylenedioxytrichlorophosphorane **1** with benzyltrimethylammonium chloride **2** gives the hexacoordinated derivative **3** (δ_P –97 ppm), which easily reacts (20°C , CH_2Cl_2) with phenylacetylene or propargylchloride and leads to the preferable formation (70–80%) of the substituted 2,7-dichloro-4-R-2-oxobenzo[e]-1,2-oxaphosphorines **4**. The selective chlorination of the benzo-substituent *meta* to endocyclic oxygen of the phosphorine heterocycle takes place. As it has been shown earlier,¹ the reaction of phosphorane **1** with $\text{PhC}\equiv\text{CH}$ without salt **2** yields 2,6-dichloro-2-oxo-4-phenylbenzo[e]-1,2-oxaphosphorine, and the reaction with propargyl chloride yields 2,8-dichloro-2-oxo-4-chloromethylbenzo-[e]-1,2-oxaphosphorine. The structure of 2-chloro- and 2-hydroxy-derivatives **4**, **5** was confirmed by ^1H , ^{13}C ,



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Address correspondence to Vladimir F. Mironov, A. E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Arbuzov Str, 8, Kazan, 420088 Russia. E-mail: mironov@iopc.kcn.ru

^{31}P NMR. The location of the chlorine atom in seventh position was established on the basis of multiplicity of the C^5 , C^8 , C^{8a} signals in ^{13}C NMR spectra.

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