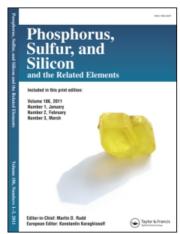
This article was downloaded by:

On: 28 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713618290

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

Vladimir F. Mironov^a; Alfiya A. Shtyrlina^a; Ravil R. Petrov^a; Tamara A. Baronova^a; Fedor F. Alekseev^a; Elena N. Varaksina^a; Aleksander I. Konovalov^a

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

Online publication date: 27 October 2010

To cite this Article Mironov, Vladimir F. , Shtyrlina, Alfiya A. , Petrov, Ravil R. , Baronova, Tamara A. , Alekseev, Fedor F. , Varaksina, Elena N. and Konovalov, Aleksander I.(2002) 'The New Data for the Reaction of Arylenedioxy Trihalogenophosphoranes with Alkyl- and Arylacetylenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 177:6,1381-1385

To link to this Article: DOI: 10.1080/10426500212243 URL: http://dx.doi.org/10.1080/10426500212243

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:1381–1385 Copyright © 2002 Taylor & Francis 1042-6507/02 \$12.00 + .00

DOI: 10.1080/10426500290093766



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

Vladimir F. Mironov, Alfiya A. Shtyrlina, Ravil R. Petrov, Tamara A. Baronova, Fedor F. Alekseev, Elena N. Varaksina, and Aleksander I. Konovalov

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

(Received July 29, 2001; accepted December 25, 2001)

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

Earlier¹ 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.

Address correspondence to V. 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.ken.ru

$$\begin{array}{c|c}
O \\
PCl_3 \\
\hline
 & |-HCl| \\
\hline
 & |-H$$

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**.

$$\begin{array}{c|c}
Br & O \\
Br & O
\end{array}
PCl_3 & Ph-C \equiv CH & Br & O P C \\
\hline
[-HCl] & Br & Ph
\end{array}$$

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.

Br
$$O$$
 PBr3 $\frac{1) \text{ Ph-C} \equiv \text{CH, [-Br2]}}{2) \text{ H2O, -HBr}}$ Br O P O OH

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.

$$Me = O PCl_{3} \xrightarrow{Ar-C \equiv CH} Me O PCl_{3} \xrightarrow{I-HCl_{3}} I_{6} Ar$$

$$15 \qquad 16 Ar$$

$$16 Ar$$

$$16 Ar$$

$$16 Ar$$

$$16 Ar$$

$$17 PBr_{3} \xrightarrow{Ph-C \equiv CH} Me O P^{O}_{3} O Me O P^{O}_{3} O Me$$

$$17 Ph$$

$$18 Ph$$

$$19 Ph$$

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.

$$\begin{array}{c|c}
 & Ph-C \equiv CH \\
\hline
 & O. PCl_3 \\
\hline
 & [-HCl, -Me_2C = CH_2]
\end{array}$$

$$\begin{array}{c|c}
 & Cl \\
\hline
 & 21 \\
\hline
 & Ph
\end{array}$$

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.

PCI3
$$CICH_2-C\equiv CH$$
 CI $O \cdot p = 0$ $O \cdot p = 0$

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 PCl₃ gives the heterocycles **4** with the moderate yield. The open-chain structures **5**, **6** were also obtained.

ACKNOWLEDGMENTS

The work is supported by the Russian Foundation for Basic Research (grant 00-03-32835).

REFERENCES

- V. F. Mironov, A. I. Konovalov, I. A. Litvinov, A. T. Gubaidullin, R. R. Petrov, A. A. Shtyrlina et al., Zh. Obshch. Khim., 68, 1482 (1998).
- [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).