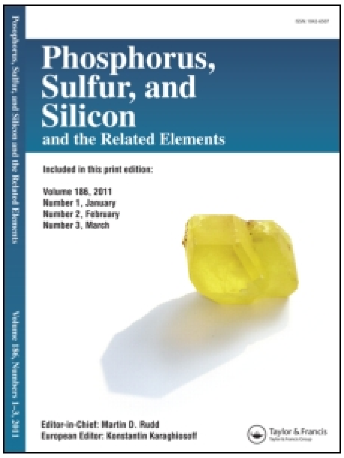


Phosphorus, Sulfur, and Silicon and the Related Elements

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

The Reaction of 1,2-Naphthoquinones with Some P(III) Derivatives—A Versatile Synthetic Approach to Potentially Useful Naphthoquinones and Dihydroxynaphthalenes Containing Phosphorus-Carbon Bond

A. V. Bogdanov[a]; V. F. Mironov[a]; N. R. Khasiyatullina[a]; D. B. Krivolapov[a]; I. A. Litvinov[a]; A. I. Konovalov[a]
[a] A. E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Russia

To cite this Article Bogdanov, A. V. , Mironov, V. F. , Khasiyatullina, N. R. , Krivolapov, D. B. , Litvinov, I. A. and Konovalov, A. I.(2008) 'The Reaction of 1,2-Naphthoquinones with Some P(III) Derivatives—A Versatile Synthetic Approach to Potentially Useful Naphthoquinones and Dihydroxynaphthalenes Containing Phosphorus-Carbon Bond', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 2, 571 — 575

To link to this Article: DOI: 10.1080/10426500701764965

URL: http://dx.doi.org/10.1080/10426500701764965

Phosphorus, Sulfur, and Silicon, 183:571–575, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701764965

Taylor & Francis
Taylor & Francis Group

The Reaction of 1,2-Naphthoquinones with Some P(III) Derivatives—A Versatile Synthetic Approach to Potentially Useful Naphthoquinones and Dihydroxynaphthalenes Containing Phosphorus–Carbon Bond

A. V. Bogdanov, V. F. Mironov, N. R. Khasiyatullina, D. B. Krivolapov, I. A. Litvinov, and A. I. Konovalov
A.E.Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, Russia

The reactions of 1,2-naphthoquinones with hexaethyltriaminophosphine or tri(n-butyl)-phosphine followed by bromine or hydrogen bromide treatment has been shown to lead to the quantitative formation of the new 1,2-naphthoquinones and 1,2-dihydroxynaphthalenes containing phosphorus-carbon bond. Its structure established by NMR and single crystal X-ray diffraction.

Keywords 1,2-naphthoquinones; tri(*n*-butyl)phosphine; hexaethyltriamino-phosphire; 1,2-dihydroxynaphthalenes; 1,2-naphthoquinone; one-electron transfer; betaines; phosphonium salts; crystal structure

INTRODUCTION

Ortho-quinones and their derivatives are of great interest due to their significance in nature. They play an important role in electron transport and possess various kinds of biological activity. They are also used in the synthesis of the metal complexes, nitrogen-, or oxygen-containing heterocycles and in enantioselective synthesis.[1–6]

Trivalent phosphorus compounds are widely used in *ortho*-quinone chemistry as a rule for the preparation of the pentacoordinated phosphorus derivatives—phosphoranes, or tetracoordinated ones—quasiphosphonium salts having betaine structure with P^+—OC bond,

---

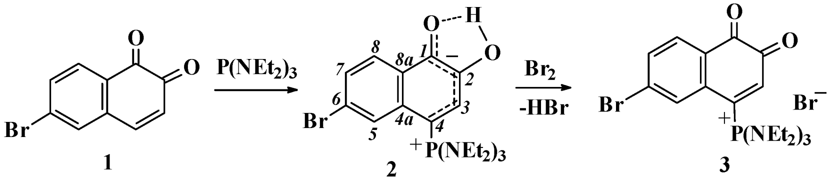
Financial support from RFBR (grant 07-03-00180a) and President of Russian Federation grant (MK-2444.2007.3) is gratefully acknowledged.

Thanks are also expressed to the Mayor of the Kazan City Ilsur R. Metshin and Committee of Youth Affairs of Kazan City Administration for financial support to attend the 17th International Conference on Phosphorus Chemistry (Xiamen, China, 2007).

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

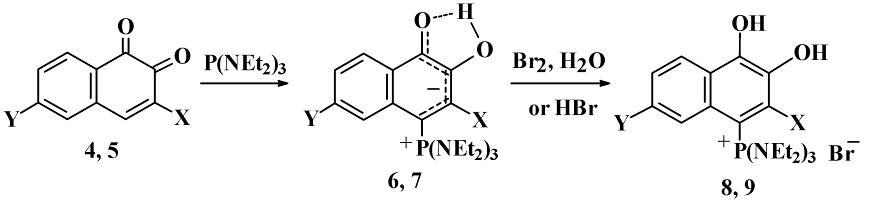
which are used in organic synthesis.[7,8] 1,2-Naphthoquinones is the least investigated in reactions with P(III) derivatives. It was shown only that they react with phosphites to form phosphoranes.[7] At the same time, a great number of 1,2-naphthoquinones, especially 4-substituted 1,2-naphthoquinones, exhibit various physiological properties. They can be used as models of the polycyclic carcinogenic hydrocarbons binding by aminoacids.[9]

Recently, we have shown that the reaction of 6-bromo-1,2-naphthoquinone **1** with hexaethyltriaminophosphine in mild conditions leads to the almost quantitative formation of 6-bromo-2-hydroxy-4-(hexaethyltriaminophosphonium)naphthol-1-ate **2** which easily turns into the 4-(hexaethyltriaminophosphoniumbromide)-1,2-naphthoquinone **3** after bromine treatment[10] (Scheme 1).



SCHEME 1

Furthermore, we also have found[11] that 3-substituted 1,2-naphthoquinones **4**,**5** react with hexaethyltriaminophosphine by the similar way to give betaines **6**,**7**, the same as betaine **2**, with a high yield. It should be noted that the corresponding 1,2-dihydroxynaphthylphosphonium salts **8**,**9**, was obtained instead of quinones after both the bromination of betaines **6**,**7** and after the hydrogen bromide treatment or after an isolation of the reaction products from moist acetone (Scheme 2).

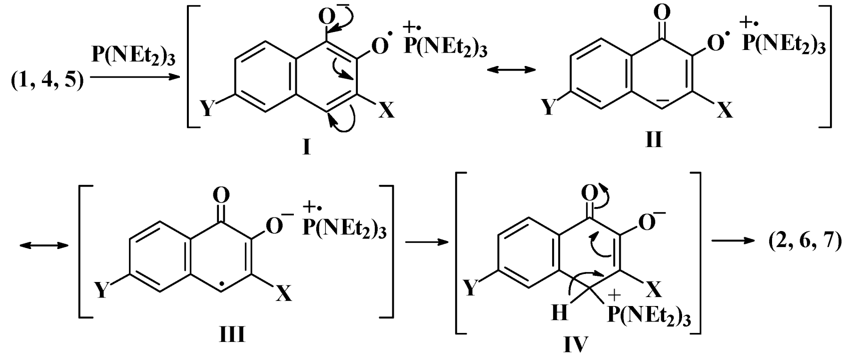


X = Br, Y = H (4, 6, 8), X = Cl, Y = Br (5, 7, 9)

SCHEME 2

The possible mechanism of the process is shown in Scheme 3.

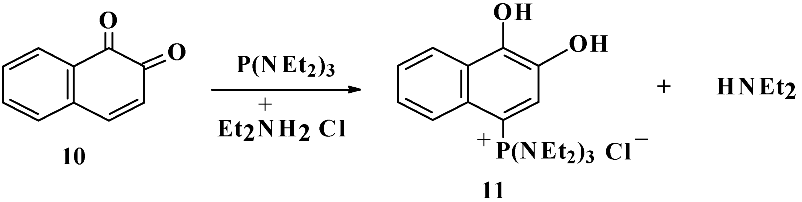
The first stage of the reaction probably includes the one-electron transfer from phosphorus atom to *ortho*-quinone molecule to form the



SCHEME 3

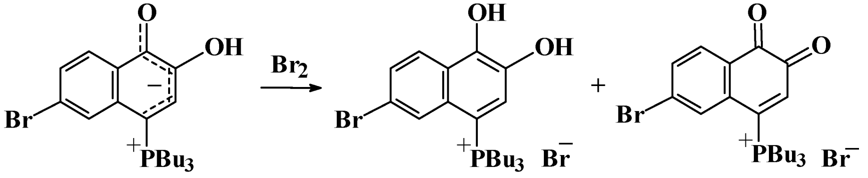
ion-radical pair (**I**). The structures (**II**) and (**III**) with different localization of negative charge and a lone electron in naphthalene moiety can be proposed as the resonance structures of the intermediate. The localization of a lone electron in the fourth position of naphthalene nucleus probably decreases the energy because of the conjugation with benzene ring. Then the recombination of electrons takes place in ion-radical (**III**) to form P-C bond (structure **IV**). The following proton transfer with redistribution of an electron density gives the final reaction products – phosphonium betaines **2**, **6**, **7**. The analogous processes of the one-electron transfer were investigated earlier by ESR on the example of the reaction of the substituted 1,2-benzoquinone derivatives with triaminophosphines and lead to the formation of λ^5-1,3,2-dioxaphospholanes.[12,13] The suggested mechanism is in accordance with an intensive color change that takes place during the reactions.

We have also found that the similar synthetic result can be obtained by the one-pot three-component reaction of 1,2-naphthoquinone **10** with hexaethyltriaminophosphine in the presence of diethylammonium chloride that leads to the formation of 1,2-dihydroxynaphthylphosphonium chloride **11** (Scheme 4).



SCHEME 4

Further, one of the trialkylphosphines, namely, tributylphosphine was also used in these reactions.[14] An interesting result was obtained in the reaction of betaine **12**, prepared from the quinone **1** and tributylphosphine, with bromine, which leads to the formation of the two compounds—quinone **13** and diol **14**. Probably, the oxidation of the betaine **12** with formation of quinone **13** and an evolving of the hydrogen bromide are likely to proceed in the first stage of the reaction. Initial betaine is then protonated by the hydrogen bromide to form naphthalenediol **14**. The formation of compounds **13**, **14** with the equal yields confirms the proposed reaction mechanism (Scheme 5).



12 **13** **14**

SCHEME 5

Thus, the reaction of 1,2-naphthoquinones with hexaethyltriaminophosphine followed by a treatment of the phosphonium betaines with bromine (or hydrogen halogenide) is a versatile approach to the synthesis of the 1,2-naphthoquinones and 1,2-dihydroxynaphthalenes containing phosphorus in fourth position.

REFERENCES

[1] L. N. Mander and C.M. Williams, *Tetrahedron*, **59,** 1105 (2003).

[2] M. Oh, G. B. Carpenter, and D.A. Sweigart, *Acc. Chem. Res.*, **37,** 1 (2004).

[3] H. Amouri and J. Le Bras, *Acc. Chem. Res.*, **35,** 501 (2002).

[4] R.W. Van De Water and T.R.R. Pettus, *Tetrahedron*, **58,** 5367 (2002).

[5] C. C. Liao and R. K. Peddinti, *Acc. Chem. Res.*, **35,** 856 (2002).

[6] D. Magdziak, S. J. Meek, and T. R. R. Pettus, *Chem. Rev.*, **104,** 1383 (2004).

[7] (a) H. Fauduet and R. Burgada, *Synthesis*, **8,** 642 (1980); (b) F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, *J. Am. Chem. Soc.*, **89,** 6267 (1967).

[8] F. H. Osman and F. A. El-Samahy, *Chem. Rev.*, **102,** 629 (2002).

[9] (a) F. J. Bullock, J. F. Tweedie, D. D. McRitchie, and M. A. Tucker, *J. Med. Chem.*, **13,** 97 (1970); (b) J. H. Ahn, S. Y. Cho, S. Y. Chu, S. H. Jung, Y. S. Jung, J. Y. Baek, I. K. Choi, E. Y. Shin, S. K. Kang, S. S. Kim, H. G. Cheon, S.-D. Yang, and J.-K. Choi, *Bioorg. and Med. Chem. Lett.*, **12,** 1941 (2002).

[10] A. V. Bogdanov, N. R. Khasiyatullina, V. F. Mironov, A. I. Konovalov, A. A. Balandina, and Sh. K. Latypov, *Zh. Org. Khim. (Rus. J. Org. Chem.)*, **41,** 1879 (2005).

[11] A. V. Bogdanov, V. F. Mironov, N. R. Khasiyatullina, D. B. Krivolapov, I. A. Litvinov, and A. I. Konovalov, *Mendeleev Comm.*, **17**(3), 183 (2007).

[12] A. N. Pudovik, E. S. Batyeva, A. V. Il'yasov, V. Z. Kondranina, V. D. Nesterenko, and V. I. Morozov, *Zh. Obshch. Khim. (Rus. J. Gener. Chem.)*, **46,** 1964 (1976).

[13] A. N. Pudovik, E. S. Batyeva, A. V. Il'yasov, V. D. Nesterenko, A. Sh. Mukhtarov, and N. P. Anoshina, *Zh. Obshch. Khim. (Rus. J. Gener. Chem.)*, **43,** 1451 (1973).

[14] A. V. Bogdanov, V. F.Mironov, N. R. Khasiyatullina, and A. I. Konovalov, *Russ. Chem. Bull.,* **56**(3), 555 (2007).