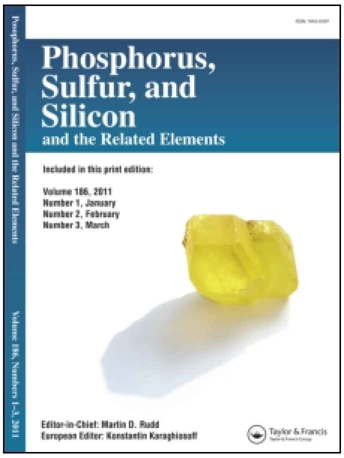

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An Unusual Reaction of Triphenylphosphine with Dichlorodinitrobenzofuroxan

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A novel phosphorylation reaction of dichlorodinitrobenzofuroxan by triphenylphosphine has been studied. An unusual course of the reaction with the participation of benzofuroxan nitro groups as reactive centers has been established. It is shown that as final product of the reaction, a stable diphenolate diphosphabetaine with strong participation of the mesomeric ketoylide structure is formed. The structure of the product has been confirmed by X-ray diffraction.

Keywords Dichlorodinitrobenzofuroxan; NO generation; phosphorylation; triphenylphosphine

INTRODUCTION

5,7-Dichloro-4,6-dinitrobenzofuroxan (**1**) is a highly reactive system containing the electrophilic benzofuroxan cycle, which is prone to nucleophilic substitution, owing to the presence of electron-acceptor substituents and easy leaving groups. In particular, the reactions of chlorine substitution by various amines have been frequently investigated.[1] It is essential that amination products as well as initial furoxane **1**

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Dedicated to Professor Marian Mikołajczyk from the CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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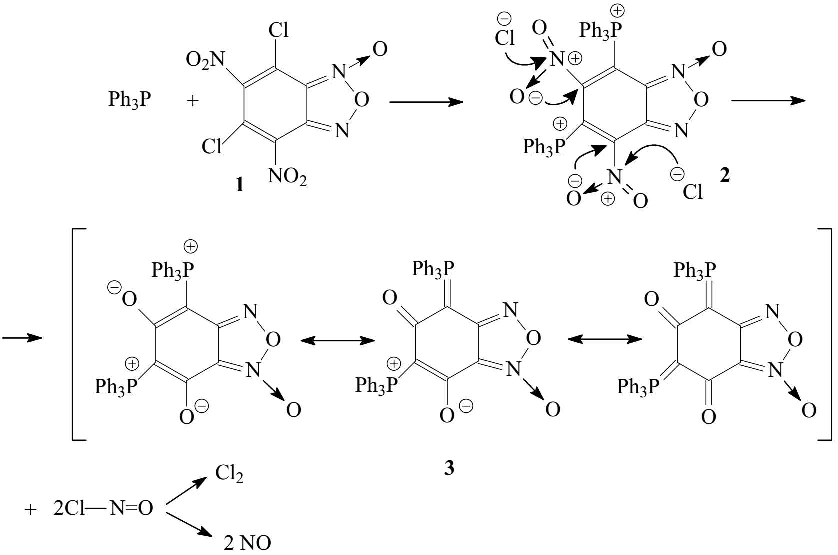
possess pronounced antibacterial and fungicidal activity.[2,3] Introduction of biogenic organophosphorus substituents to the benzofuroxan ring might even increase the activity of these compounds; however, no data on the phosphorylation of benzofuroxan is available in the literature until now.

RESULTS AND DISCUSSION

In this article, we report the interaction of benzofuroxan **1** with triphenylphosphine. The reaction proceeds readily at room temperature to give the bisphosphorylation product, the ratio of **1** to triphenylphosphine being 1:2.5. The reaction most probably is not a simple nucleophilic substitution, as it does not stop upon the formation of 5,7-(bis-triphenylphosphonio)-4,6-dinitrobenzofuroxanyldichloride (**2**), but rather continues with the elimination of two nitrogen oxide and chlorine molecules, as is shown in Scheme 1. The final product **3** can be described by a series of mesomeric structures.



SCHEME 1 Phosphorylation of benzofuroxan **1**.

The structure of **3** has been determined by X-ray single-crystal diffraction (Figure 1) and mass spectrometry.

The distribution of the bond lengths shows that the molecular structure of **3** in crystal is closer to the ylide mesomeric form. The average value for the ylide P=C bond (1.72 Å) derived from the Cambridge

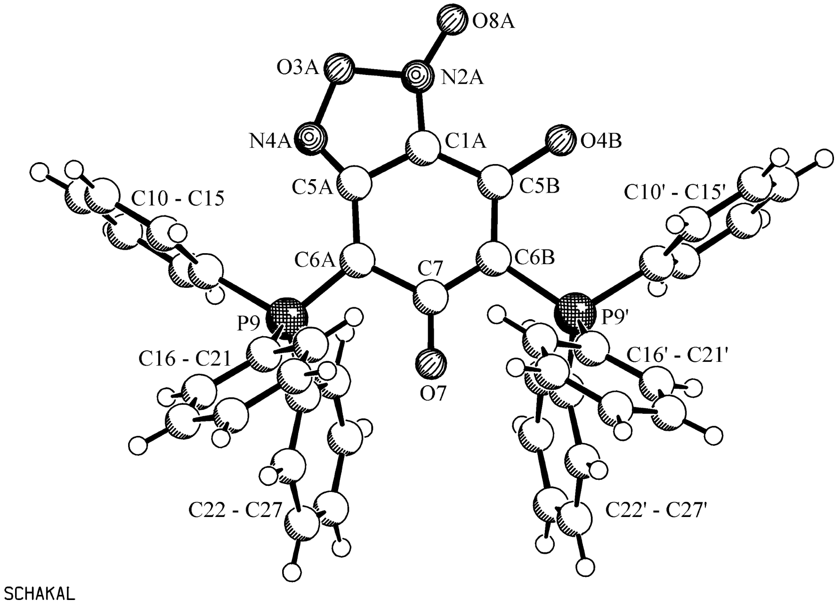


FIGURE 1 Molecular structure of **3** in the crystal. Selected bond lengths: C1A-C5A 1.47(1), C1A-C5B 1.447(8), C5A-C6A 1.431(6), C5B-C6B 1.432(6), C6A-C7 1.457(5), C6B-C7 1.441(6), C7=O7 1.259(4), P9-C6A 1.70(1), P-Ph(average) 1.809(3) Å.

Crystallographic Database[4] is the same within experimental errors as in compound **3**. The C=O bonds are slightly elongated, while the C-C bonds in the benzo-ring are shorter than typical C-C bonds. The molecule lies on a special position on a symmetry plane *m*, implying the symmetrical positions of the triphenylphosphine groups and the disorder of the furoxan cycle. The latter causes low accuracy of the geometrical parameters. The cavity between the triphenylphosphine substituents is filled with disordered water molecules which are bound to the C=O and N→O bonds of the neighboring molecules via hydrogen bonds.

In the mass spectrum (ESI-MS positive), the observed peak at *m*/*z* 689 corresponds to the protonated molecule $C_{42}H_{31}N_2O_4P_2$ [M + H$^+$].

EXPERIMENTAL

Compound 3

To a solution of Ph_3P (1.64 g, 6.25 mmol) in 10 mL of 1:1 (in volume) mixture of EtOH and Et_2O, a solution of 5,7-dichloro-4, 6-dinitrobenzofuroxan (0.73 g, 2.5 mmol) was added dropwise in 20 mL of the same solvent mixture. The reaction mixture was stirred under argon atmosphere for 2.5 h at r.t. After 2 months, the precipitate was collected by filtration, washed with the same solvent mixture (2 × 30 mL), and dried in vacuo, affording compound **3** as a white solid; 1.28 g (75%). DSC/TG: mp 235°C (dec.). ^{31}P NMR (DMSO-d_6): $\delta = 23.7$ (s). ESI-MS: Mass spectra were measured with a Quattro LCZ (Waters-Micromass, Manchester, UK) with nanospray inlet. ESI-MS positive: The observed peak at *m/z* 689 corresponds to the protonated molecule $C_{42}H_{31}N_2O_4P_2$ [M + H$^+$]. Anal. Calcd. for $C_{42}H_{30}N_2O_4P_2$: C, 73.26; H, 4.36; N, 4.07; P, 9.01. Found: C, 73.33; H, 4.27; N, 4.21; P, 9.36.

X-Ray Structure Determination

Data were collected with Nonius Kappa CCD diffractometer equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN,[5] absorption correction Denzo,[6] structure solution SHELXS-97,[7] structure refinement by full-matrix least-squares against F^2 using SHELXL-97,[8] and the absolute configuration was assessed by Flack's enantiopole parameter. CCDC 652720 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033, E-mail: deposit@ccdc.cam.ac.uk].

X-Ray Crystal Data for 3

Formula $C_{42}H_{30}N_2O_4P_2$ H_2O, M = 706.64, colorless crystal 0.35 × 0.30 × 0.06 mm, a = 20.5066(5), b = 9.9288(2), c = 9.1246(1) Å, V = 1857.82(6) Å^3, $\rho_{calc} = 1.263$ g cm^{-3}, $\mu = 0.164$ mm^{-1}, empirical absorption correction ($0.945 \leq T \leq 0.990$), Z = 2 (molecule in a special position on plane *m*), orthorhombic, space group Pmn2$_1$ (No. 31), $\lambda = 0.71073$ Å, T = 198 K, ω and φ scans, 24053 reflections collected (± h, ± k, ± l), [(sinθ)/λ] = 0.66 Å^{-1}, 4357 independent ($R_{int} = 0.073$) and 3316 observed reflections [$I \geq 2\sigma(I)$], 268 refined parameters, R = 0.055, wR2 = 0.134, max. residual electron density 0.75 (–0.31) e Å^3, hydrogen atoms calculated and refined as riding atoms.

REFERENCES

[1] W. R. Roger and W. P. Norris, *Aust. J. Chem.*, **38,** 435 (1985).

[2] G. P. Sharnin, R. I. Mukharlyamov, and V. V. Golovin, *Zh. Org. Chem.*, **19,** 2358 (1983).

[3] L. M. Yusupova, I. F. Falyakhov, L. V. Spatlova, and T. V. Garipova, Pat. 2255935 (Russia) (2005).

[4] Cambridge Structural Database System. Version 5.27. Cambridge Crystallographic Data Centre, Cambridge, UK (2006).

[5] Z. Otwinowski and W. Minor, *Methods Enzymol.*, **276,** 307 (1997).

[6] Z. Otwinowski, D. Borek, W. Majewski, and W. Minor, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, **A59,** 228 (2003).

[7] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, **A46,** 467 (1990).

[8] G. M. Sheldrick, Universität Göttingen, 1997.