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SHORT COMMUNICATIONS

Reaction of 5,7-Dinitrobenzofuroxane with Triphenylphosphine

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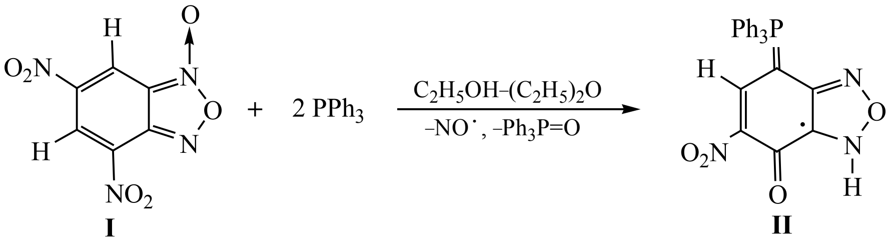
We showed previously that in reaction of triphenylphosphine with 5,7-dichloro-4,6-dinitrobenzofuroxane [1] a stable diphosphabetain was obtained. We describe here a similar reaction of 5,7-dinitrobenzofuroxane (**I**) lacking chlorine atoms and resulting in the same conditions in the formation of NH-radical **II** stable already for the last three years.

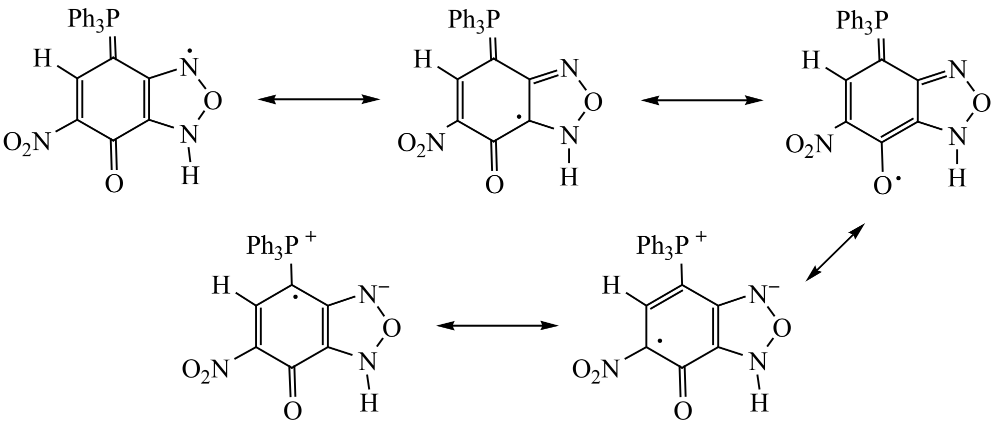
According to the data of ESR spectroscopy the reaction starts with the formation of NO-centered benzofuroxane radical whose ESR spectrum changes with time. The integral intensity of the ESR signal grows at the beginning of the reaction, and in 20 min decreases to zero. Within two weeks the reaction mixture has turned into plate-like dark-red crystals which according to XRD study have the structure of phosphorus(II) ylide. The data of ^{31}P NMR spectrum and of the elemental analysis confirm this conclusion.



IR spectrum from the mull in mineral oil contains a characteristic absorption band of the NH group in the region 3266 cm^{-1} and the absorption bands of C=N and C=C at 1740 and 1600 cm^{-1} respectively. According to TG/DSC compound **II** has mp 71.3°C, decomposition temperature 177.7°C, and these parameters have not changed within 3 years.

We believe that the most probable scheme of the reaction involves the formation of free radical intermediates whose structure now is not yet possible to establish, and their subsequent transformation results in the final product, stable NH-radical **II**. Its stability originates from the resonance of structures where the unpaired electron is localized on diverse atoms.

6-Nitro-7-oxo-4-(triphenylphosphoranylidene)-1,4,7-dihydro-2,1,3-benzoxadiazole-radical (II). To a solution of 0.1 g (0.442 mmol) of benzofuroxane **I** in 10 ml of the mixture ethanol–ether, 1:3, was added dropwise in an argon atmosphere 0.232 g (0.885 mmol) of triphenylphosphine in 10 ml of the same solvent. In the course of the reaction the color o the reaction mixture



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changed from light-yellow to dark red. In two weeks a druse of bright red crystals formed in the reaction mixture, it was separated and washed with ethanol and ether. Yield 0.235 g (71%), mp 71.3°C, t.decomp. 177.7°C. IR spectrum (mull in mineral oil), ν, cm^{-1}: 3266, 1740, 1629, 1600, 1430. ^{31}P NMR spectrum (DMSO-d_6), δ, ppm: 20.77. Found, %: C 65.54; H 4.03; N 9.77; P 7.37. $C_{24}H_{17}N_3O_4P$. Calculated, %: C 65.16; H 3.85; N 9.50; P 7.05. The structure is confirmed by XRD analysis; its results will be published elsewhere.

^{31}P NMR spectrum was registered on a spectrometer Avanse-400 Bruker at operating frequency on ^{31}P nuclei 161.68 MHz, external reference 85% H_3PO_4 (^{31}P). ESR spectra were taken on spectrometrs Varian E-12 and Bruker Elexys 680, SHF 9.7 GHz. In the study a mixture of anhydrous solvents–ethyl ether, 1:3, was used. IR spectra were recorded on an IR Fourier spectrophotometer Tensor 27 Bruker applying an IR microscope Hyperion 2000, Bruker (Germany). The XRD experiment was carried out on a diffractometer Bruker SMART 1000 CCD. TG-DSC measurements were performed on an instrument NETZSCH STA 449C TGA/S6TA85/E in the temperature range 20–400°C, heating rate 10 deg/ min in an argon.

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