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LETTERS TO THE EDITOR

Reaction of 4-Chloro-5-Nitrobenzofurazane with Triphenylphosphine

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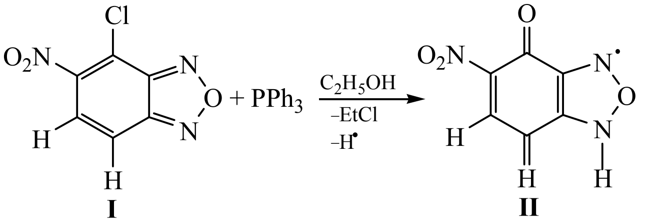
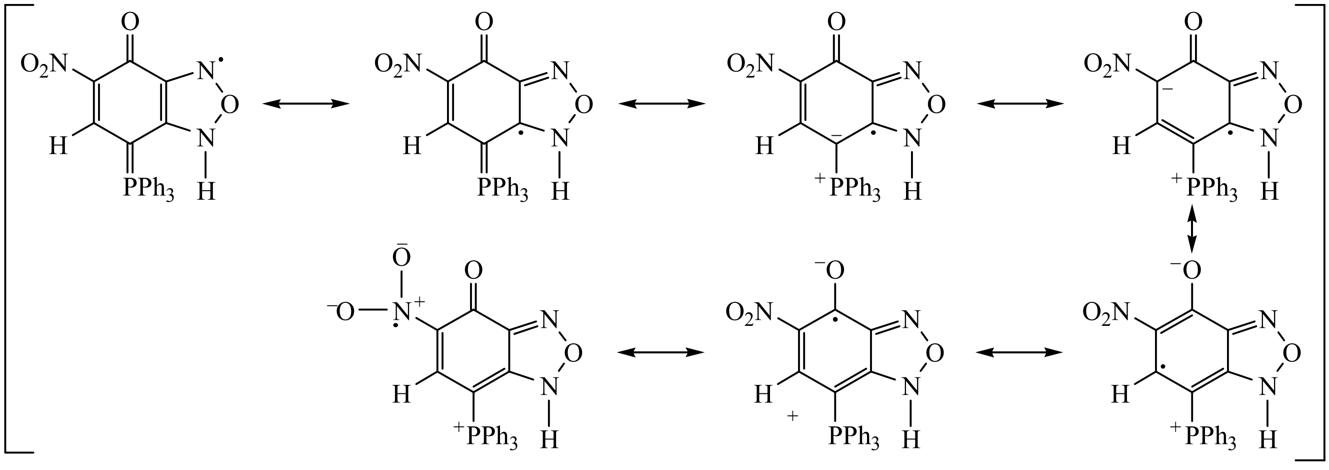
The reaction of triphenylphosphine with 5,7-dichloro-4,6-dinitrobenzofuroxane has been shown earlier [1] to yield a stable diphenolate diphosphobetaine. This work presents some results on the study of the phosphorylation reaction of 4-chloro-5-nitrobenzofurazane **I** under the same conditions. According to the XRD, ^{31}P NMR, IR, and ESR spectroscopy data, this reaction gives rise to a stable NH-radical **II**.



The ESR study of the reaction occurring at room temperature in an ether–alcohol medium indicates the intermediate formation of a free radical at the moment of the reagents mixing. After 30 min, the reaction was complete, which was accompanied by the disappearance of the ESR signal. The stable NH-radical **II** precipitates as green plate crystals from the reaction mixture within 24 h. Its formation is characterized by a clear ESR signal. The structure of **II** was confirmed by the ^{31}P NMR spectroscopy and elemental analysis data.

The IR spectrum of compound **II** contains a characteristic band at 3270 cm^{-1} (N–H). According to the TG/DSC data, its melting point is 142.3°C, and the thermal stability is not changed in 3 years.

Perhaps the formation and subsequent transformation of the free radical intermediates occur to give the stable NH-radical **II**, where the delocalization of unpaired electron over the system of conjugated bonds determines its stability. The most probable mesomeric structures of the product **II** are given below.



5-Nitro-4-oxo-7-(triphenylphosphoranylidene)-4,7-dihydro-2,1,3-benzoxadiazol-1-yl (II). To a solution of 0.1 g (0.501 mmol) of compound **I** in 10 ml of an alcohol–ether mixture was added while stirring a solution of 0.13 g (0.501 mmol) of triphenylphosphine in 5 ml of ether. Within 30 min the color of the reaction mixture changes from yellow to dark green. After 24 h, the green plate crystals formed were washed with alcohol and ether. Yield 0.15 g (75%), mp 142.3°C, decomposition point 291.2°C. IR spectrum, ν, cm^{-1}: 1430, 1600, 3270. ^{31}P NMR spectrum (DMSO-d_6): δ_P 30.27 ppm. Found, %: C 65.05; H 3.47; N 9.19. $C_{24}H_{17}N_3O_4P$. Calculated, %: C 65.16; H 3.85; N 9.50.

The structure of compound **II** was also confirmed by the X-ray analysis, which will be reported elsewhere.

The ^{31}P NMR spectrum was registered on a Bruker Avance-400 spectrometer relative to external 85% phosphoric acid. The ESR studies were performed on a Varian E-12 and Bruker Elexys 680 instruments operating at 9.7 GHz. The IR spectrum was recorded on a Tensor 27 Bruker FTIR spectrometer using a Bruker Hyperion 2000 infrared microscope. The TG/DSC analysis was performed on a NETZSCH STA 449C TGA/S6TA85/E instrument in the temperature range of 20–400°C under argon atmosphere with a heating rate of 10°C min^{-1}.

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