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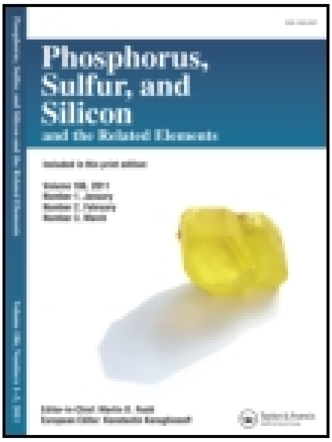

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3,3-Bis(diethylphosphono)-1(3H)-isobenzofuranone and Its Properties

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3,3-BIS(DIETHYLPHOSPHONO)-1(3*H*)-ISOBENZOFURANONE AND ITS PROPERTIES

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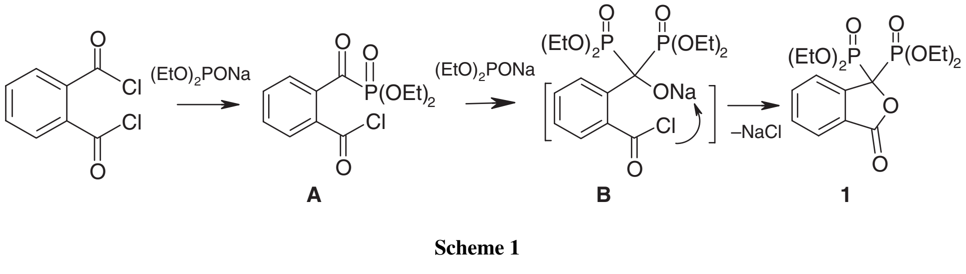
Abstract *The reaction of o-phthaloyl chloride with sodium diethylphosphite led to the formation of new 3,3-bis(diethylphosphono)-1-(3H)-isobenzofurane **1**. The reaction of bis-phosphonate with alkylamine occurs with replacement of an ester oxygen by an imine group to afford the crystalline isoindolyl-bis-phosphonate—a representative of this new type of organophosphorus heterocycles.*

Keywords Bisphosphonates; bisphosphonic acid; isobenzofurane derivatives; *o*-phthalyl chloride

The reaction of *o*-phthalyl chloride with sodium diethylphosphite occurs with the formation of cyclic bisphosphonate, 3,3-bis(diethylphosphono)-1-(3*H*)-isobenzofuranone **1**. In the first step of the reaction, the nucleophilic attack of sodium diethylphosphite on the C=O group of phthalic chloride gives the ketophosphonate **A**, which in the second step reacts with the second molecule of sodium diethylphosphite being converted into intermediate **B**, which via the intramolecular cyclization yields isobenzofuranone **1** (Scheme 1).



Scheme 1

The structure of bisphosphonate **1** was confirmed by NMR, mass spectra, IR spectra, X-ray analysis (Figure 1),[1] elemental analysis, and chemical reactions.

The signal δ_P of cyclic compounds **1** is shifted to a weak field in comparison with acyclic compounds and is revealed at 10 ppm. In the ^{13}C-NMR spectrum of bisphosphonate

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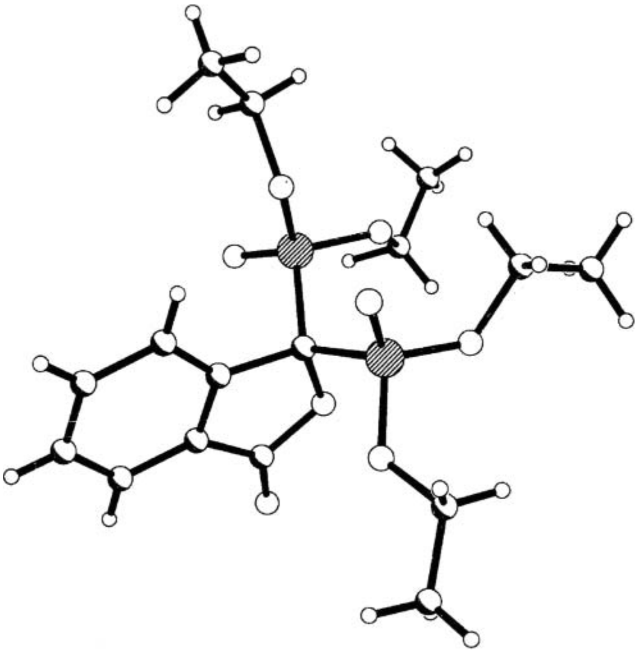
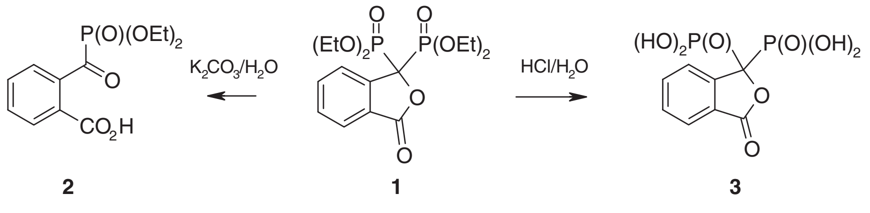


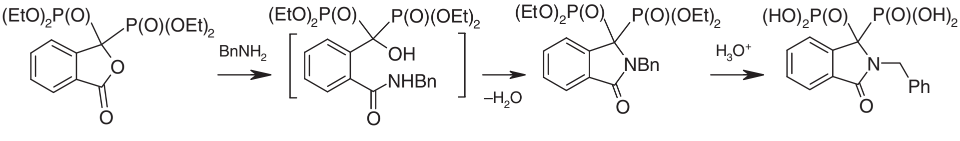
Figure 1 X-ray structure of **1**.

1 the signal of the α-carbon atom between two phosphorus is observed as a triplet at 83.26 ppm, $^1J_{PC} = 155.9$ Hz, which confirms the presence of a 1,1-bisphosphonate fragment.[2] The ethoxy groups at phosphorus are nonequivalent, which is indicated by their various disposition relative (over and out) to the benzene ring. The chemical properties of bisphosphonate **1** confirm its structure. A reflux with aqueous potash resulted in the elimination of one diethylphosphonate group and led to the formation of acyclic 1-ketophosphonate **2** in a good yield. The hydrolysis of bisphosphonate **1** with hydrochloric acid led to the formation of bisphosphonic acid **3** in good yield (Scheme 2).[3]



Scheme 2

The reaction of bisphosphonate **1** with benzylamine in the presence of triethylamine resulted in the formation of new organophosphorus heterocycle, phthalimide **4**.[3] The reaction proceeds via nucleophilic substitution at the C=O group and the formation of α-hydroxybisphosphonate intermediate (**D**), which was registered by ^{31}P-NMR spectra (signal δ_P +18.09 ppm). Then this intermediate (**D**) undergoes intramolecular cyclization with the formation of phthalimide **4**. The spectroscopic data of compound **4** are similar to



1 D 4 5

Scheme 3

that of compound **1**; in particular, the chemical shift δ_P is also shifted into a lower field (6 ppm). The ^{1}H-NMR spectrum shows the presence of conformers of compound **4** because of the effect of the NBn group. The ^{13}C-NMR spectrum shows the signals of the CH_3 and CH_2O groups, the singlet of the CH_2Ph group at 43.16 ppm, the double doublet of P-C group with a coupling constant J = 150 Hz, the singlet of C=O group, δ_C 170.55 ppm, and signals of aromatic carbons.[3] The bisphosphonate **4** is readily hydrolyzed by conc. hydrochloric acid with the formation of bisphosphonic acid **5** (Scheme 3).

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