Reactions of diethyl 3-methylbuta-1,2-dienylphosphonate with 2-aminobenzothiazole*

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A reaction of diethyl 3-methylbuta-1,2-dienylphosphonate with 2-aminobenzothiazole afforded 1-diethoxyphosphoryl-2-(2-imino-2,3-dihydrobenzothiazol-3-yl)-3-methylbut-2-ene.

Key words: buta-1,2-dienylphosphonate, 2-aminobenzothiazole, β-amino alkenylphosphonates.

In recent years, aminoalkyl(alkenyl)phosphonates have attracted much attention not only as compounds with a broad spectrum of biological activities but also as complexones, emulsifiers, and membrane carriers.[1—4] Reactions of primary and secondary aliphatic amines with unsaturated derivatives of four-coordinate phosphorus acids are thoroughly studied and used to obtain β-aminoalkyl(alkenyl)phosphonates in good yields.[2,5,6] However, only a few studies have been devoted to the synthesis of phosphonates functionalized in the β-position with nitrogen-containing heterocyclic fragments.[2,7,8]

We investigated a reaction of diethyl 3-methylbuta-1,2-dienylphosphonate **1** with 2-aminobenzothiazole **2**. For this reaction, two pathways are possible: the central C atom of the allene system could be attacked by the ring N atom (adduct **3**) or the N atom of the exocyclic amino group (adduct **4**, Scheme 1).

Heating of an equimolar mixture of the reagents gave a crystalline product. Its ^{31}P NMR spectrum in solution shows a single signal at δ_P 26.2. The ^1H NMR spectrum contains doublets for the protons of two methyl groups at the sp^2-hybridized C atom at δ 1.53 ($^5J_{P,H}$ = 5.8 Hz) and 1.94 ($^5J_{P,H}$ = 4.4 Hz). The spectrum shows a signal at δ 3.03 ($^2J_{P,H}$ = 20 Hz) for the protons of the α-methylene group relative to the phosphoryl fragment. The signals for

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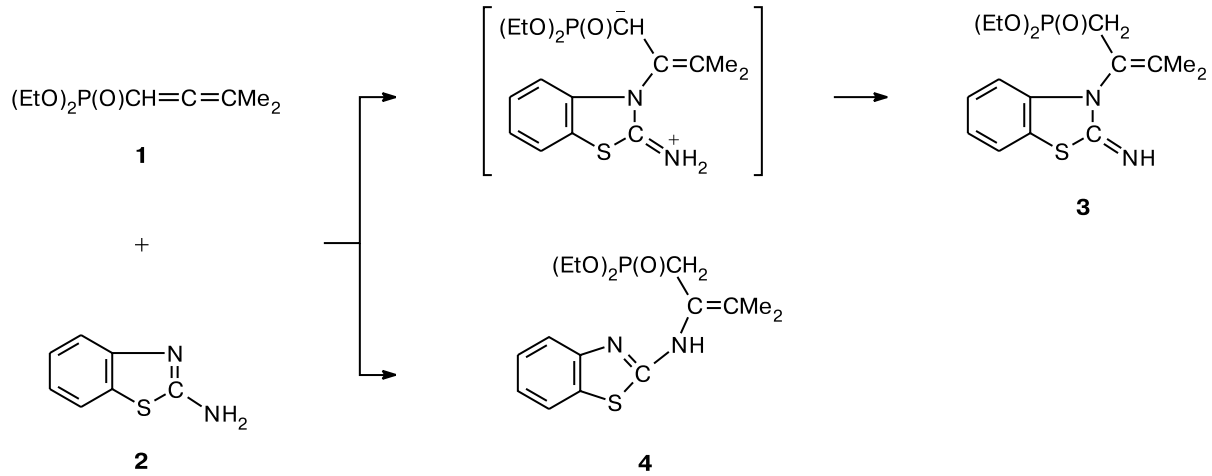
Scheme 1



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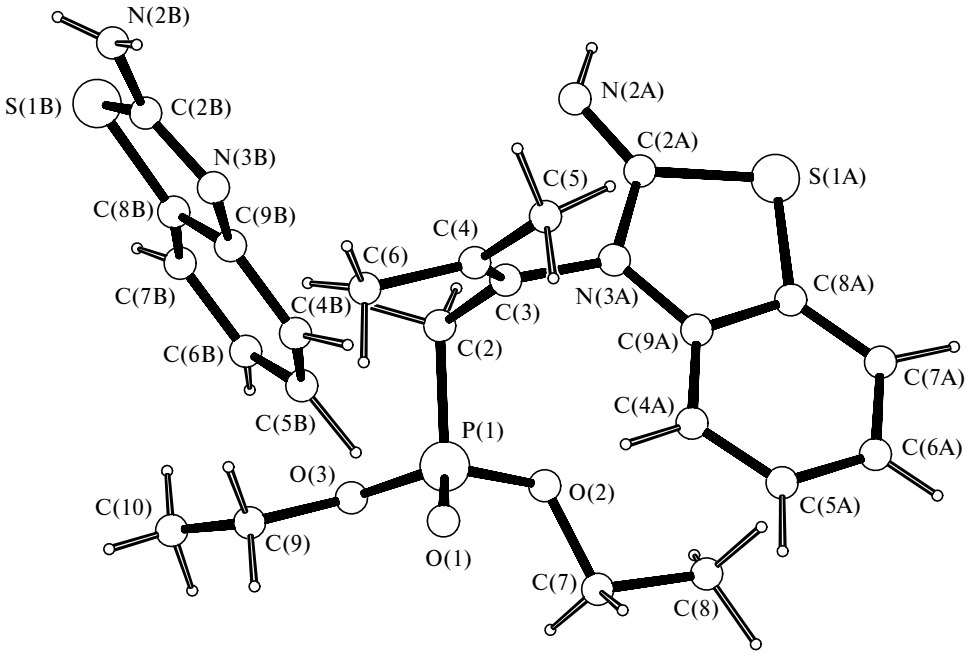

Fig. 1. Geometry of complex **3**·**2** in the crystal.

the protons of the benzothiazole ring appear as a multiplet at δ 7.3 and the signals for the protons of the ethoxy groups at the P atom appear in their characteristic range. The proton of the NH group manifests itself as a broadened singlet at δ 5.95. The high-resolution mass spectrum of the product contains a peak for the molecular ion $C_{16}H_{23}N_2O_3PS$ (found: *m*/*z* 354.1161 $[M]^+$; calculated: $M = 354.1167$).

The molecular and crystal structures of adduct **3** were determined by X-ray diffraction analysis (Fig. 1). Thus, the reaction of butadienylphosphonate **1** with thiazole **2** involves the endocyclic N atom of compound **2** and the 1,2-double bond of phosphonate **1**. The resulting adduct **3** cocrystallizes with the starting aminobenzothiazole **2**. The geometries of both benzothiazole fragments are planar (the largest deviation of the atoms from the benzothiazole plane in fragment A is 0.025(1) Å and from that in fragment B is 0.026(3) Å; the endocyclic N(2A) and N(2B) atoms deviate from the plane by 0.008(3) and 0.045(3) Å, respectively). The bond lengths agree with the models represented in the scheme. Selected bond lengths are given in Table 1.

The formation of a stable molecular complex in the crystal can be explained by intermolecular hydrogen bonding: molecules of adduct **3** are united into infinite chains along the axis 0*b*, which are cross-linked in pairs by a benzothiazole dimer (Fig. 2). The parameters of the hydrogen bonds are specified in Table 2.

Table 1. Selected bond lengths in structure **3**·**2**

Bond	*d*/Å	Bond	*d*/Å
S(1A)—C(2A)	1.776(3)	S(1B)—C(2B)	1.760(4)
S(1A)—C(8A)	1.744(4)	S(1B)—C(8B)	1.736(3)
N(2A)—C(2A)	1.262(4)	N(2B)—C(2B)	1.342(4)
N(3A)—C(2A)	1.387(4)	N(3B)—C(2B)	1.296(4)
N(3A)—C(9A)	1.389(4)	N(3B)—C(9B)	1.399(4)

Experimental

IR spectra were recorded on a UR-20 spectrometer (Nujol). ^1H and ^{31}P NMR spectra were recorded on a Varian—Unity-300 spectrometer (300 and 121.42 MHz, respectively) in $CDCl_3$ with the residual signals for a deuterated solvent (δ_H 7.24) as the internal standard (^1H) and 85% H_3PO_4 as the external standard (^{31}P). The mass spectrum was recorded on a MAT-212 mass spectrometer (ionizing voltage 60 eV, emission current 0.1 mA, direct inlet probe, gradual rise in the evaporator tem-

Table 2. Parameters of the hydrogen bonds in structure **3**·**2**

Fragment	Symmetry operation	*d*/Å	φ(N—H...O)/deg
N(2A)—H(2A)...O(1′)	*x*, −1 + *y*, *z*	0.86 (N—H), 2.01 (H...O), 2.860(4) (N...O)	170
N(2B)—H(21B)...N(3B″)	−*x*, *y*, 1/2 − *z*	1.02 (N—H), 2.09 (H...N), 3.103(4) (N...N)	172
N(2B)—H(22B)...N(2A″)	−*x*, *y*, 1/2 − *z*	0.79 (N—H), 2.11 (H...N), 2.894(4) (N...N)	176

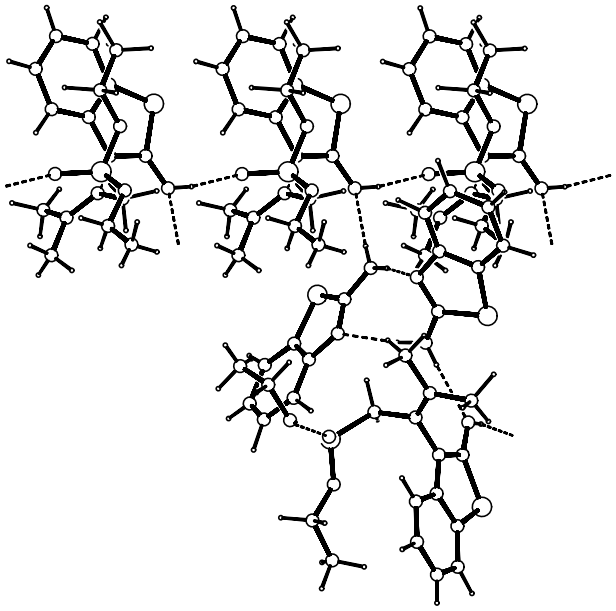

Fig. 2. Hydrogen bonds in structure **3·2**.

perature). The exact ion masses were determined by the peak coincidence method at a resolution of 10 000.

Complex of 1-diethoxyphosphoryl-2-(2-imino-2,3-dihydrobenzothiazol-3-yl)-3-methylbut-2-ene (3) with 2-aminobenzothiazole (2). Benzothiazole **2** (2.47 g, 0.016 mol) was added to phosphonate **1** (3.36 g, 0.016 mol). The reaction mixture was heated at 80—95 °C for 6 h and then kept at room temperature for two days. The resulting white crystals were separated by decantation, washed with ether, and recrystallized from benzene to give complex **3·2** (2.14 g, 51.5%), m.p. 105—106 °C. Found (%): C, 54.33; H, 5.17; P, 5.84. $C_{23}H_{29}N_4O_3PS_2$. Calculated (%): C, 54.75; H, 5.79; P, 6.14. IR, ν/cm^{-1}:1250 (P=O); 1150 (P—O—C); 1600 (C=N); 1650 (C=C); 3210 (NH). MS, m/z (I_{rel} (%)): 354 $[M]^+$, 150 $[M]^+$.

X-ray diffraction analysis. Crystals of complex **3·2** are monoclinic, $C_{23}H_{29}N_4O_3PS_2$; at 20 °C, a = 27.19(2) Å, b = 8.504(7) Å, c = 22.32(2) Å, β = 96.49(7)°, V = 5133 Å^3, d_{calc} = 1.37 g cm^{-3}, Z = 8, space group $C2/c$. The unit cell parameters and the intensities of 5350 independent reflections (3279 with $I \geq 3\sigma$) were measured on an Enraf—Nonius CAD4 diffractometer (ω-scan mode, θ ≤ 74.40°, λ(Cu-$K\alpha$), graphite monochromator). An absorption correction was applied empirically (μCu 27.03 cm^{-1}). The structure was solved by the direct method with the SIR program[9] and refined by the full-matrix least-squares method with the MolEN program package.[10] Non-hydrogen atoms were refined in the anisotropic approximation. Hydrogen atoms were located from electron-density difference maps and included in the final refinements with fixed coordinates and isotropic thermal parameters. Final reliability factors are R = 0.055 and R_w = 0.068 for 1044 independent reflections with $F^2 \geq 3\sigma^2$. All calculations were performed with an Alpha Station 200 computer. The molecular pictures were drawn with the PLATON program.[11]

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