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REACTION OF β-NITRO- AND β-HALO-β-NITROETHENYL-PHOSPHONATES WITH FURAN

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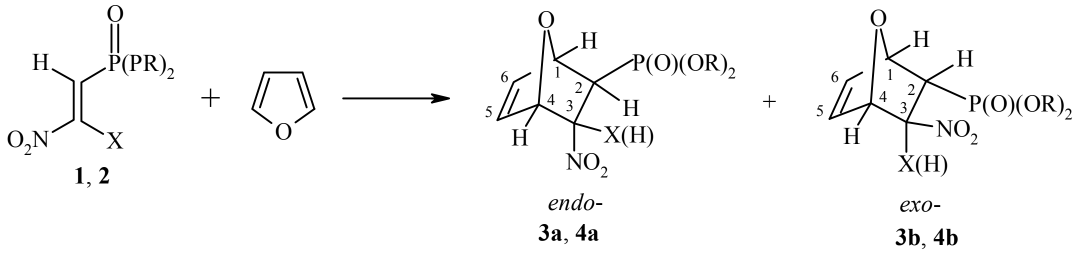
Conjugated nitroalkenes are active dienophiles in the Diels–Alder reaction and are widely used to construct fragments of natural compounds and biologically active substances [1-3].

There is increased interest in the behavior in these reactions of β-nitroethenylphosphonates, the molecules of which simultaneously have two strong vicinal electron acceptors (the nitro and the phosphoryl functional groups), because of their high reactivity [4, 5] and the possibility of using them to synthesize novel functionalized carbobicyclic and heterobicyclic structures, including oxygen-containing structures.

We have studied for the first time the reaction of bis(2-chloroethyl)-β-nitroethenylphosphonates **1, 2** with furan. We found that the reaction occurs under very mild conditions (~20°C, in benzene) for a 1:2 ratio of nitroalkene:furan, and ends in formation of phosphorylated nitro oxabicycloheptenes **3, 4**. Compounds **3, 4** were isolated using column chromatography (silica gel Chemapol 100/200, eluents chloroform, ether) as oils which were a mixture of the *endo* and *exo* stereoisomers **3a,b, 4a,b** in the ratio **3a:3b** = 3:2 and **4a:4b** = 3:1.



1-4 R = CH_2CH_2Cl; **1**, **3a**,**b** X = H, **2**, **4a**,**b** X = Br

The composition of compounds **3, 4** was confirmed by elemental analysis; the structure was established by IR and ^1H, ^{31}P NMR spectroscopy: the configurations and the *endo*/*exo* isomer ratio were determined based on comparing the spin–spin coupling constants (J_{PH}, J_{HH}) and the integrated intensities, and also by drawing on the similar 3-nitro-4-phenylsulfonyl-5-oxabicyclo[2.2.1]-5-heptenes with known configurations as the model structures [6].

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The IR spectra were obtained on an InfraLYUM FT-02 spectrometer (in $CHCl_3$, *c* 0.1-0.001 mol). The ^1H and ^{31}P NMR spectra (in $CDCl_3$) were recorded on a Bruker AC-200 (200 MHz); for the ^{31}P spectra, we used 85% phosphoric acid as the external standard. The R_f values were determined on Silufol UV-254 plates in a 3:2 hexane–acetone solvent mixture; the chromatograms were visualized in UV light.

The starting 2-nitro- and 2-bromo-2-nitroethenylphosphonates **1, 2** were synthesized by the familiar procedures in [7, 8].

Bis(2-chloroethyl)-3-nitro-7-oxabicyclo[2.2.1]-5-hepten-2-ylphosphonate (3). Yield 60% (oily substance), R_f 0.1. IR spectrum, ν, cm^{-1}: 1620 (C=C), 1561, 1367 (NO_2), 1253 (P=O), 1085, 1030 (P–O–C). Isomer **3a**, *endo*-NO_2. ^1H NMR spectrum, δ, ppm (*J*, Hz): 5.38 (1H, dd, $^3J_{HP}$ = 15, $J_{1,6}$ = 1.8, $H_{(1)}$); 5.34 (1H, ddd, $^3J_{HP}$ = 5.8, $J_{2,3}$ = 4.0, $J_{3,4}$ = 5.2, $H_{(3)}$); 5.40 (1H, dd, $J_{3,4}$ = 5.2, $J_{4,5}$ = 1.5, $H_{(4)}$); 6.50 (1H, dd, $J_{5,6}$ = 5.2, $J_{5,4}$ = 1.5, $H_{(5)}$); 6.32 (1H, dd, $J_{5,6}$ = 5.2, $J_{1,6}$ = 1.8, $H_{(6)}$); 4.38 (5H, m, 2 OCH_2 and $H_{(2)}$); 3.73 (4H, m, 2 CH_2Cl). ^{31}P NMR spectrum, δ, ppm: 23.5. *exo*-Isomer **3b**. ^1H NMR spectrum, δ, ppm (*J*, Hz): 5.35 (1H, ddd, $^3J_{HP}$ = 15, $J_{1,2}$ = 3.5, $J_{1,6}$ = 1.7, $H_{(1)}$); 4.75 (1H, ddd, $^2J_{HP}$ = 10.5, $J_{2,3}$ = 3.6, $J_{1,2}$ = 3.5, $H_{(2)}$); 4.70 (1H, ddd, $^3J_{HP}$ = 4.0, $J_{2,3}$ = 3.6, $J_{3,4}$ = 2.5, $H_{(3)}$); 5.54 (1H, dd, $J_{3,4}$ = 2.5, $J_{4,5}$ = 1.5, $H_{(4)}$); 6.75 (1H, dd, $J_{5,6}$ = 5.8, $J_{5,4}$ = 1.5, $H_{(5)}$); 6.68 (1H, dd, $J_{5,6}$ = 5.8, $J_{6,1}$ = 1.7, $H_{(6)}$); 4.38 (4H, m, 2 OCH_2); 3.73 (4H, m, 2 CH_2Cl). ^{31}P NMR spectrum, ppm: 25.5. Found, %: C 34.52, 34.50; H 4.09, 4.10; N 4.14, 4.15; P 8.94, 8.94. $C_{10}H_{14}Cl_2NO_5P$. Calculated, %: C 34.68; H 4.05; N 4.05; P 8.96.

Bis(2-chloroethyl)-3-bromo-3-nitro-7-oxabicyclo[2.2.1]-5-hepten-2-ylphosphonate (4). Yield 80%, R_f 0.23. IR spectrum, ν, cm^{-1}: 1616 (C=C), 1568, 1367 (NO_2), 1260 (P=O), 1084, 1030 (P–O–C). Isomer **4a**, *endo*-NO_2. ^1H NMR spectrum, δ, ppm (*J*, Hz): 5.85 (1H, ddd, $^3J_{PH}$ = 16.8, $J_{1,2}$ = 2.5, $J_{1,6}$ = 2.5, $H_{(1)}$); 4.68 (4H, dd, $^2J_{HP}$ = 13.0, $J_{1,2}$ = 2.5, $H_{(2)}$); 6.45 (1H, d, $J_{4,5}$ = 2.5, $H_{(4)}$); 7.14 (1H, dd, $J_{5,6}$ = 5.7, $J_{5,4}$ = 2.5, $H_{(5)}$); 7.03 (1H, dd, $J_{5,6}$ = 5.7, $J_{6,1}$ = 2.5, $H_{(6)}$); 4.45 (4H, m, 2 OCH_2); 3.72 (4H, m, 2 CH_2Cl). ^{31}P NMR spectrum, δ, ppm: 16.5. *exo*-Isomer **4b**. ^1H NMR spectrum, δ, ppm: 5.93 (1H, ddd, $^3J_{HP}$ = 18.0, $J_{1,2}$ = 2.0, $J_{1,6}$ = 2.5, $H_{(1)}$); 5.30 (1H, d, $^2J_{HP}$ = 15.0, $J_{1,2}$ = 2.0, $H_{(2)}$); 6.50 (1H, d, $J_{4,5}$ = 2.5, $H_{(4)}$); 7.14 (1H, dd, $J_{5,6}$ = 5.7, $J_{5,4}$ = 2.5, $H_{(5)}$); 7.03 (1H, dd, $J_{5,6}$ = 5.7, $J_{1,6}$ = 2.5, $H_{(6)}$); 4.45 (4H, m, 2 OCH_2); 3.72 (4H, m, 2 CH_2Cl). ^{31}P NMR spectrum, δ, ppm: 18.5. Found, %: C 28.18, 28.20; H 3.15, 3.20; N 3.28, 3.29; P 7.32, 7.30. $C_{10}H_{13}BrCl_2NO_6P$. Calculated, %: C 28.30; H 3.07; N 3.30; P 7.31.

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