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LETTERS TO THE EDITOR

Synthesis of Phosphorylated Nitrocyclohexenes and Nitronorbornenes

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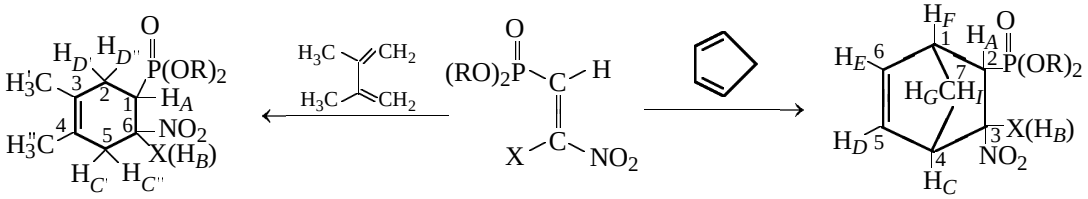
Due to the presence of an activated multiple bond, conjugated nitroalkenes are widely used as dienophiles in the Diels–Alder reaction and hold promise as synthetic blocks for designing natural and biologically active compounds [1–3].

Highly reactive nitro- and *gem*-halonitroethenylphosphonates [4–7] present undoubted interest for the diene synthesis of functionalized cyclic systems with a preset arrangement of substituents. Only one diene synthesis involving the former compounds has been reported [8].

We showed that nitroethenylphosphonates **II** and **III** react with 2,3-dimethyl-1,3-butadiene and cyclopentene under rather mild conditions (refluxing in benzene for 1–2 h). The reagent ratio was 1:3 for nitroalkene and 2,3-dimethyl-1,3-butadiene and 1:2 for nitroalkene and cyclopentadiene. The reactions gave phosphorylated nitrocyclohexenes **III** and **IV** and nitronorbornenes **V** and **VI**.



III, IV **I, II** **Va, Vb, VI**

R = CH_2CH_2Cl (**I**–**VI**); X = H (**I, III, Va, Vb**), Br (**II, IV, VI**).

Compounds **IV**–**VI** were isolated by column chromatography on SiO_2 as viscous yellowish oils. Nitronorbornene **VI** crystallized on handling. Decreasing the reflux time from 8 [8] to 1 h in the case of compound **V** improved the total yield from 40 [8] to 80%; therewith, the product was isolated as a mixture of the *endo* and *exo* isomers (6:1). The composition of compounds **III**–**VI** was confirmed by elemental analysis, and their structure was established by means of ^1H and ^{31}P NMR spectroscopy. The *endo*:*exo* ratio was determined on the basis of the Alder rule [2] and the integral intensities of signals in the ^1H NMR spectra.

2-Nitro- and 2-bromo-2-nitroethenylphosphonates **I** and **II** were synthesized as described in [9, 10].

Bis(2-chloroethyl) (3,4-dimethyl-6-nitro-3-cyclohexene-1-yl)phosphonate (III). Yield 90%, mp 86–87°C (from hexane–benzene, 5:1), beige crystals. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.96 m (1H, H_A, $^2J_{PA}$ –17.6 Hz, $^3J_{AB}$ 8.8 Hz, $^3J_{AD'}$ 8.8 Hz, $^3J_{AD''}$ 6.8 Hz), 4.85 m (1H, H_B, $^3J_{PB}$ 7.3 Hz, $^3J_{AB}$ 8.8 Hz, $^3J_{BC'}$ 7.3 Hz, $^3J_{BC''}$ 5.8 Hz), 2.14 m (2H, $H_{D'}$, $H_{D''}$), 2.66 m (2H, $H_{C'}$, $H_{C''}$), 1.65 s (6H, CH'_3, CH''_3), 4.30 m (4H, OCH_2), 3.70 t (4H, CH_2Cl). ^{31}P NMR spectrum ($CDCl_3$), δ_P 27.50 ppm. Found, %: C 39.81, 39.85; H 5.73, 5.75; N 3.94, 3.95; P 8.33, 8.33. $C_{12}H_{20}Cl_2 \cdot NO_5P$. Calculated, %: C 40.00; H 5.55; N 3.89; P 8.61.

Bis(2-chloroethyl) (6-bromo-3,4-dimethyl-6-nitro-3-cyclohexen-1-yl)phosphonate (IV). Yield

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68%, oil, R_f 0.46. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.41 m (1H, H_A, $^2J_{PA}$ –19.5 Hz, $^3J_{AD'}$ 8.5 Hz, $^3J_{AD''}$ 7.1 Hz), 2.40 m, 2.54 m (2H, $H_{D'}$, $H_{D''}$), 2.90 d, 3.20 d (2H, $H_{C'}$, $H_{C''}$), 1.48 s, 1.60 s (6H, CH'_3, CH''_3), 4.26 m (4H, OCH_2), 3.67 t (4H, CH_2Cl). ^{31}P NMR spectrum ($CDCl_3$): δ_P 23.40 ppm. Found,%: C 32.76, 32.75; H 4.38, 4.39; N 3.19, 3.20; P 7.21, 7.16. $C_{12}H_{19}BrCl_2NO_5P$. Calculated,%: C 32.80; H 4.33; N 3.78; P 7.06.

Bis(2-chloroethyl) (3-nitro-5-norbornen-2-yl)-phosphonate (Va, Vb). Yield 80%, R_f 0.36. Isomer **Va** (*endo*-NO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.48 m (1H, H_F, $^3J_{PF}$ 18.0 Hz, $^3J_{FE}$ 18.0 Hz, $^3J_{FE}$ 5.0 Hz), 3.65 m (1H, H_A, $^3J_{AB}$ 4.5 Hz, $^3J_{AF}$ 2.5 Hz, $^2J_{PA}$ 5.0 Hz), 5.22 m (1H, H_B, $^3J_{BC}$ 3.0 Hz), 3.24 m (1H, H_C, $^3J_{CB}$ 3.0 Hz, $^3J_{CD}$ 2.5 Hz), 6.44 d.d (1H, H_D, $^3J_{DE}$ 5.0 Hz, $^3J_{DC}$ 2.5 Hz), 5.96 m (1H, H_E, $^3J_{ED}$ 5.0 Hz, $^3J_{EF}$ 5.0 Hz, $^4J_{PE}$ 4.5 Hz), 1.52 m (1H, H_G, $^2J_{GI}$ 9.5 Hz), 1.92 m (1H, H_I, $^2J_{IG}$ 9.5 Hz), 4.29 m (4H, OCH_2), 3.65 m (4H, CH_2Cl). ^{31}P ($CDCl_3$): δ_P 28.50 ppm. Isomer **Vb** (*exo*-NO_2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.10 m (1H, H_F), 3.65 m (1H, H_A), 4.50 m (1H, H_B), 3.47 m (1H, H_C), 6.35 d.d (1H, H_D), 6.10 m (1H, H_E), 1.62 m (1H, H_G), 1.90 m (1H, H_I), 4.29 m (4H, OCH_2), 3.65 (4H, CH_2Cl). ^{31}P NMR spectrum ($CDCl_3$): δ_P 27.80 ppm. Found, % C 38.48, 38.44; H 4.74, 4.77; N 4.20, 4.19; P 9.03, 9.11. $C_{11}H_{17}Cl_2NO_5P$. Calculated, %: C 38.37; H 4.65; N 4.06; P 9.01.

Bis(2-chloroethyl) (3-bromo-3-nitro-5-norbornen-2-yl)phosphonate (VI). Yield 85%, mp 86°C (from hexane–benzene), beige crystals. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.18 d.d (1H, H_F, $^3J_{PF}$ 23.7 Hz, $^3J_{FE}$ 5.5 Hz), 3.75 (1H, H_A, $^3J_{AE}$ 3.0 Hz), 3.37 m (1H, H_C $^3J_{CD}$ 2.5 Hz), 6.55 d.d (1H, H_D, $^3J_{DE}$ 5.0 Hz, $^4J_{PE}$ 4.6 Hz), 1.90 d (1H, H_G, $^2J_{GI}$ 9.2 Hz), 2.50 d (1H, H_I, $^2J_{IG}$ 9.2 Hz), 4.45 (4H, CH_2O), 3.75 (4H, CH_2Cl). ^{31}P NMR spectrum: δ_P 22.50 ppm. Found, %: C 31.31, 31.33; H 3.56, 3.57; N 3.40, 3.40; P 7.37, 7.40. $C_{11}H_{16}C_{12}BrNO_5$. Calculated, %: C 31.21; H 3.55; N 3.31; P 7.33.

The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker AC-200 spectrometer (200 MHz). The ^{31}P NMR spectra were measured against 85% phosphoric acid. The R_f values were obtained on Silufol plates, eluent hexane–acetone, 3:2.

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