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Diels–Alder Reactions of 3- and 5-Methyl-1-vinylpyrazoles with Cyclohexa-1,3-diene and Hydrogenation of the Reaction Products

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Abstract—The behavior of isomeric vinylpyrazoles in the Diels–Alder reactions with cyclohexa-1,3-diene was studied to show that the spatial location of the vinyl group on the N^2 atom does not affect the diene synthesis.

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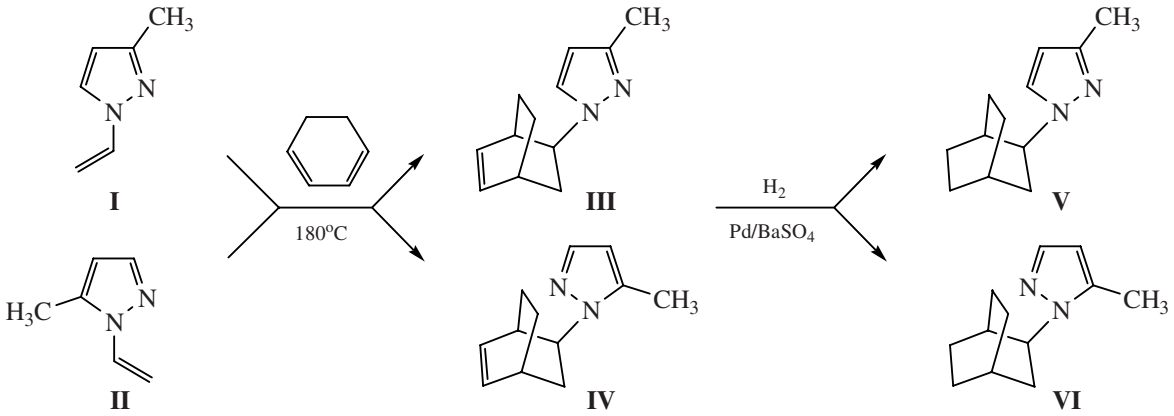
Synthesis, structure, and polymerization of 3- and 5-methyl-1-vinylpyrazoles (**I, II**) are fairly well documented [1–11]. At the same time, no data on their behavior as dienophiles in Diels–Alder reactions are available. This problem is still more important because, according to ^1H and ^{13}C NMR data [5], 5-methyl-1-vinylpyrazole (**II**) exists mainly as the *S-cis*-N^2 isomer, while 3-methyl-1-vinylpyrazole (**I**) is a roughly equimolar mixture of steric isomers. In this connection we have studied the behavior of compounds **I, II** in the Diels–Alder reaction with cyclohexa-1,3-diene.



The reactions of the cyclic diene with *cis*-**II** and *cis-trans*-**I** proceed only at 180°C. No characteristic differences in the behavior of these compounds in the diene synthesis were found. Both compounds difficultly add to cyclohexa-1,3-diene to form products **III, IV** in 20–25% yields. Surprisingly, the rates of the cyclohexa-1,3-diene mixtures to 1 : 9 and 9 : 1 mixtures of compounds **I** and **II** are the same, and the ratios are preserved in the reaction products.

As the reaction temperature is increased to 220°C, fast polymerization of the diene and dienophile is observed. Therefore, it was suggested that spatial location of the vinyl group in 1-vinylpyrazoles **I, II**

with respect to N^2 takes no part in the Diels-Alder reaction.

The structure of compounds **III, IV** was established by means of IR and ^{1}H NMR spectroscopy and elemental analysis. The ^{1}H NMR spectra of compounds **III, IV** show downfield ring protons (H^3, H^5) signals (7.11–7.19 ppm). The chemical shifts of the H^4 ring protons in the spectra of compounds **III, IV** are practically the same (5.8–5.82 ppm), and the methyl proton signals are shifted upfield (2.11–2.21 ppm). The signals of protons at the double bond in compounds **III, IV** form an AB system with δ 6.05–6.40 ppm (J_{AB} 5.91 Hz). The other proton signals are multiplets, and their integral intensities are completely consistent with the structures of [1-bicyclo[2.2.2]oct-5-en-2-yl]-3-methyl- and [1-bicyclo[2.2.2]-oct-5-en-2-yl]-5-methyl-1*H*-pyrazoles **III, IV**.

In the IR spectra of compounds **III, IV**, the absorption band of the pyrazole ring is observed at 1510–1520 cm^{-1}, and the absorption at 1650–1660 ppm relates to CH=CH stretching vibrations. The double bond in compounds **III, IV** is easily hydrogenated with hydrogen at room temperature in the presence of the $Pd/BaSO_4$ catalyst. The yields of [1-bicyclo[2.2.2]oct-2-yl]-3-methyl- and [1-bicyclo[2.2.2]oct-2-yl]-5-methyl-1*H*-pyrazoles **V, VI** reach 90–95%.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer in thin layer. The ^{1}H NMR spectra were taken on a Varian Mercury-300 instrument. GLC analysis was carried out on an LKHM-8MD chromatograph, column 1 m, packing 10% of Carbowax-20M on Inerton AW-HMDS; carrier gas helium, flow rate 40 ml min^{-1}; detector temperature 220°C.

[1-Bicyclo-[2,2,2]oct-5-en-2-yl]-3-methyl-1*H*-pyrazole (III). A mixture of 12.9 g of 3-methyl-1-vinylpyrazole (**I**) and 8.0 g of cyclohexa-1,3-diene was heated in an ampule for 24 h at 180°C. Adduct **III** was isolated by vacuum distillation of the reaction mixture. Yield 4.1 g (22%), bp 120°C (1 mm Hg), n_D^{20} 1.5335. IR spectrum, ν, cm^{-1}: 1510 (ring vibrations), 1650 (C=C). ^{1}H NMR spectrum (DMSO-d_6, 300 MHz), δ, ppm (*J*, Hz): 1.25–1.65 m (6H, cyclohexene), 2.11 s (3H, 3-CH_3), 2.2 m (2H, NCH–CH_2), 4.41 m (1H, NCH), 6.05 t (1H, CH=, *J* 5.9), 5.80 d (1H, 4-H_{pyr}, *J* 2.2), 7.19 d (1H, 5-H_{pyr}, *J* 2.2). Found, %: C 76.68; H 8.92; N 15.1. $C_{12}H_{16}N_2$. Calculated, %: C 76.59; H 8.51; N 14.89.

[1-Bicyclo[2,2,2]oct-5-en-2-yl]-5-methyl-1*H*-pyrazole (IV) was obtained analogously from 12.9 g of 5-methyl-1-vinylpyrazole (**II**) and 8.0 g of cyclohexa-1,3-diene. Yield 4.7 g (25%), bp 123°C (1 mm Hg), n_D^{20} 1.5375. IR spectrum, ν, cm^{-1}: 1520 (ring), 1660 (C=C). ^{1}H NMR spectrum (DMSO-d_6, 300 MHz), δ, ppm (*J*, Hz): 1.25–1.65 ppm (6H, cyclohexene), 2.2 m (2H, NCH–CH_2), 2.28 s (3H, 5-CH_3), 4.38 m (1H, NCH), 6.05 t (1H, CH=, *J* 5.9), 6.40 t (1H, CH=, *J* 5.9), 5.82 d (1H, 4H_{pyr}, *J* 1.9), 7.11 d (1H, 3H_{pyr}, *J* 1.9). Found, %: C 76.71, H 8.82, N 15.6. $C_{12}H_{16}N_2$. Calculated, %: C 76.59, H 8,51; N 14.89.

[1-Bicyclo-[2,2,2]oct-2-yl]-3-methyl-1*H*-pyrazole (V). Hydrogenation of compound **III** was carried out at room temperature and atmospheric pressure in the presence of reduced $Pd/BaSO_4$. The reaction was carried out in a shaking 100-ml long-necked flask loaded with 9.5 g of compound **III**, 20 ml of glacial acetic acid, and 0.5 g of catalyst (5% $Pd/BaSO_4$). The system was sealed, and hydrogen was fed from a gas meter until hydrogen no longer absorbed (slight exotherm). The reaction mixture was then poured in a flat-bottom flask and left overnight to precipitate the catalyst, after which the transparent solution was decanted and strongly diluted with water until phase separation. The organic layer was separated, and the water layer was twice extracted with ether. The combined organic phases were washed with water and sodium carbonate solution and dried over Na_2SO_4. The solvent was removed, and the residue was distilled in a vacuum. Yield 8.5 g (90%), bp 124°C (1 mm Hg), n_D^{20} 1.5240. ^{1}H NMR spectrum (DMSO-d_6, 300 MHz), δ, ppm, (*J*, Hz): 1.65 m (10H, cyclohexane), 2.12 s (3H, 3-CH_3), 2.2 m (2H, NCHCH_2), 4.28 m (1H, NCH), 5.8 d (1H, 4-H_{pyr}, *J* 2.2), 7.19 d (1H, 5-H_{pyr}, *J* 2.2). Found, %: C 75.95; H 9.01; N 14.23. $C_{12}H_{18}N_2$. Calculated, %: C 75.74; H 9.53; N 14.72.

[1-Bicyclo-[2.2.2]oct-2-yl]-5-methyl-1*H*-pyrazole (VI) was obtained analogously from 9.5 g of compound **IV**. Yield 8.9 g (95%), bp 127°C (1 mm Hg), n_D^{20} 1.5280. ^{1}H NMR spectrum (DMSO-d_6, 300 MHz), δ, ppm (*J*, Hz): 1.68 m (10H, cyclohexane), 2.22 m (2H, NCHCH_2), 2.28 s (3H, 5-CH_3), 4.25 m (1H, NCH), 5.82 d (1H, 4-H_{pyr}, *J* 1.9), 7.11 d (1H, 3-H_{pyr}, *J* 1.9). Found, %: C 75.98; H 9.12; N 14.04. $C_{12}H_{18}N_2$. Calculated, %: C 75.74; H 9.53; N 14.72.

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