

SHORT
COMMUNICATIONS***N*-(2-Vinyloxyethyl)-4,5-dihydro-1*H*-pyrazoles**

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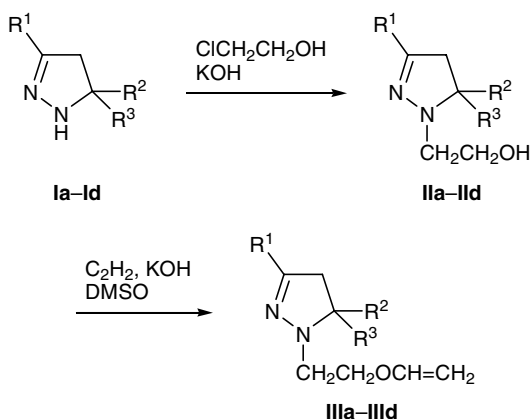
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Although a large number of vinyl ethers derived from acyclic and heterocyclic nitrogen-containing alcohols have been reported [1], vinyl ethers having a dihydropyrazole ring remain so far unknown. Taking into account the presence in their molecules of a vinyloxy group and dihydropyrazole ring, such compounds may be promising as biologically active substances and monomers for the synthesis of anion exchangers.

4,5-Dihydropyrazoles **Ia–Id** were brought into reaction with 2-chloroethanol and potassium hydroxide to obtain 1-(2-hydroxyethyl)-4,5-dihydropyrazoles **IIa–IIId**. The latter were isolated, purified, and subjected to vinylation with acetylene in dimethyl sulfoxide in the presence of KOH. As a result, 1-(2-vinyloxyethyl)-4,5-dihydro-1*H*-pyrazoles **IIIa–IIIId** were isolated in 55–79% yield.



$\text{R}^1 = \text{R}^2 = \text{H}, \text{R}^3 = \text{Me}$ (a); $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Me}$ (b); $\text{R}^1 = \text{R}^2 = \text{Et}, \text{R}^3 = \text{Me}$ (c); $\text{R}^1 = \text{R}^2 = \text{H}, \text{R}^3 = \text{Ph}$ (d).

1-(2-Hydroxyethyl)-4,5-dihydropyrazoles IIa–IIId (general procedure). 2-Chloroethanol, 0.75 mol, was added under stirring to a mixture of 0.5 mol of

compound **Ia–Id** and 0.75 mol of KOH in 100 ml of water at such a rate that the temperature did not exceed 30°C. When the reaction was complete, the organic phase was separated, the aqueous phase was extracted with benzene (3×50 ml), and the extracts were combined with the organic phase and dried over K_2CO_3 . Compounds **IIa–IIId** were isolated by distillation under reduced pressure.

2-(5-Methyl-4,5-dihydro-1*H*-pyrazol-1-yl)-ethanol (IIa). Yield 67%, bp 103–107°C (18 mm), $d_4^{20} = 1.0403$, $n_D^{20} = 1.4817$. ^1H NMR spectrum, δ , ppm (J , Hz): 1.28 d (3H, Me, $^3J = 6.2$), 2.27 d.d.d (1H, 4-H, $^2J = 16.6$, $^3J = 13.3$, 1.5), 2.72–2.84 m (2H, 4-H, NCH_2), 3.09–3.13 m (2H, NCH_2 , 5-H), 3.68 br.s (1H, OH), 3.92 m (2H, OCH_2), 6.78 m (1H, 3-H). Found, %: C 56.11; H 9.36; N 21.75. $\text{C}_6\text{H}_{12}\text{N}_2\text{O}$. Calculated, %: C 56.22; H 9.44; N 21.86.

2-(3,5,5-Trimethyl-4,5-dihydro-1*H*-pyrazol-1-yl)-ethanol (IIb). Yield 72%, bp 98–103°C (7 mm), $d_4^{20} = 0.9917$, $n_D^{20} = 1.4762$. ^1H NMR spectrum, δ , ppm (J , Hz): 1.14 s (6H, 5-Me), 1.92 s (3H, 3-Me), 2.42 s (2H, CH_2), 2.85 t (2H, NCH_2 , $^3J = 5.5$), 3.65 br.s (1H, OH), 3.85 t (3H, OCH_2 , $^3J = 5.5$). Found, %: C 61.66; H 10.57; N 17.33. $\text{C}_8\text{H}_{16}\text{N}_2\text{O}$. Calculated, %: C 61.50; H 10.32; N 17.93.

2-(3,5-Diethyl-5-methyl-4,5-dihydro-1*H*-pyrazol-1-yl)ethanol (IIc). Yield 69%, bp 98–102°C (2 mm), $d_4^{20} = 0.9760$, $n_D^{20} = 1.4781$. ^1H NMR spectrum, δ , ppm (J , Hz): 0.88 t (3H, 5- CH_2CH_3 , $^3J = 7.5$), 1.02 s (3H, Me), 1.09 t (3H, 3- CH_2CH_3 , $^3J = 7.5$), 1.55 m (2H, 5- CH_2), 1.85 d (1H, 4-H, $^2J = 17.1$), 2.24 m (2H, 3- CH_2), 2.52 d (1H, 4-H, $^2J = 17.1$), 2.80 m (1H, 1- CH_2), 2.91 m (1H, 1- CH_2), 3.86 m (2H, OCH_2), 3.99 br.s (1H, OH). Found, %: C 65.57; H 10.86; N 15.99. $\text{C}_{10}\text{H}_{20}\text{N}_2\text{O}$. Calculated, %: C 65.18; H 10.94; N 15.20.

2-(5-Phenyl-4,5-dihydro-1H-pyrazol-1-yl)ethanol (IIId). Yield 61%, bp 135–139°C (3 mm), $d_4^{20} = 1.1005$, $n_D^{20} = 1.5721$. ^1H NMR spectrum, δ , ppm: 2.66 m (1H, 4-H), 2.85–3.05 m (3H, NCH_2 , OH), 3.52 m (1H, 4-H), 3.87 m (2H, OCH_2), 4.02 m (2H, 5-H), 6.79 m (1H, 3-H), 7.35 m (5H, Ph). Found, %: C 69.79; H 7.60; N 14.48. $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}$. Calculated, %: C 69.45; H 7.42; N 14.73.

1-(2-Vinyloxyethyl)-4,5-dihydro-1H-pyrazoles IIIa–IIIId (general procedure). A mixture of 0.2 mol of compound **IIa–IIId**, 100 ml of DMSO, and 10 wt % (relative to **II**) of KOH in a 0.5-l steel rotating high-pressure reactor was saturated with acetylene to a pressure of 16 atm. The mixture was heated for 6 h at 120°C, cooled, and diluted with 300 ml of water. The organic phase was separated, the aqueous phase was extracted with diethyl ether (3×50 ml), and the extracts were combined with the organic phase and dried over K_2CO_3 . Compounds **IIIa–IIIId** were isolated by vacuum distillation.

5-Methyl-1-(2-vinyloxyethyl)-4,5-dihydro-1H-pyrazole (IIIa). Yield 63%, bp 88–95°C (13 mm), $d_4^{20} = 0.9715$, $n_D^{20} = 1.4750$. IR spectrum, ν , cm^{-1} : 490, 540, 585, 615, 690, 725, 760, 810, 875, 900, 955, 990, 1020, 1065, 1080, 1100, 1115, 1160, 1185, 1245, 1265, 1300, 1310, 1340, 1360, 1370, 1425, 1445, 1565, 1605, 1630, 2825, 2875, 2925, 2960, 3050, 3115. ^1H NMR spectrum, δ , ppm (J , Hz): 1.29 d (3H, Me, $^3J = 6.0$), 2.31 m (1H, 4-H), 2.76 d.d.d (1H, 4-H, $^2J = 16.4$, $^3J = 13.8$, 1.0), 3.05 m (1H, NCH_2), 3.14 m (1H, 5-H), 3.21 m (1H, NCH_2), 3.96–4.06 m (4H, OCH_2 , OH, *cis*- $\text{CH}_2=$), 4.21 d.d (1H, *trans*- $\text{CH}_2=$, $^2J = 1.5$, $^3J_{\text{trans}} = 14.4$), 6.49 d.d (1H, $\text{CH}=$, $^3J_{\text{cis}} = 6.9$, $^3J_{\text{trans}} = 14.4$), 6.76 m (1H, 3-H). Found, %: C 62.18; H 9.05; N 18.61. $\text{C}_8\text{H}_{14}\text{N}_2\text{O}$. Calculated, %: C 62.31; H 9.15; N 18.17.

3,5,5-Trimethyl-1-(2-vinyloxyethyl)-4,5-dihydro-1H-pyrazole (IIIb). Yield 79%, bp 107–109°C (18 mm), $d_4^{20} = 0.9549$, $n_D^{20} = 1.4697$. IR spectrum, ν , cm^{-1} : 425, 480, 520, 550, 585, 620, 645, 680, 720, 740, 795, 815, 895, 940, 955, 1020, 1060, 1090, 1100, 1115, 1130, 1160, 1185, 1210, 1235, 1255, 1275, 1300, 1305, 1315, 1355, 1375, 1415, 1425, 1450, 1465, 1610, 1625, 2700, 2740, 2865, 2880, 2905, 2935, 2960, 3035, 3065, 3110. ^1H NMR spectrum, δ , ppm (J , Hz): 1.14 s (6H, 5-Me), 1.92 s (3H, 3-Me), 2.43 s (2H, 4-H), 2.99 t (2H, NCH_2 , $^3J = 6.4$), 3.98 m (3H, OCH_2 , *cis*- $\text{CH}_2=$), 4.21 d.d (1H, *trans*- $\text{CH}_2=$, $^2J = 2.1$, $^3J_{\text{trans}} = 14.3$),

6.49 d.d (1H, $\text{OCH}=$, $^3J_{\text{cis}} = 6.7$, $^3J_{\text{trans}} = 14.3$). Found, %: C 66.01; H 10.02; N 15.69. $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}$. Calculated, %: C 65.90; H 9.95; N 15.37.

3,5-Diethyl-5-methyl-1-(2-vinyloxyethyl)-4,5-dihydro-1H-pyrazole (IIIc). Yield 77%, bp 89–92°C (1 mm), $d_4^{20} = 0.9431$, $n_D^{20} = 1.4740$. IR spectrum, ν , cm^{-1} : 450, 540, 600, 655, 700, 725, 755, 815, 870, 905, 945, 960, 975, 1000, 1075, 1115, 1130, 1180, 1200, 1265, 1295, 1315, 1370, 1385, 1415, 1435, 1465, 1615, 1630, 2880, 2935, 2965, 3045, 3070, 3115. ^1H NMR spectrum, δ , ppm (J , Hz): 0.89 t (3H, 5- CH_2CH_3 , $^3J = 7.6$), 1.01 s (3H, Me), 1.09 t (3H, 3- CH_2CH_3 , $^3J = 7.6$), 1.56 m (2H, 5- CH_2CH_3), 1.88 d (1H, 4-H, $^2J = 16.3$), 2.26 m (2H, 3- CH_2CH_3), 2.56 d (1H, 4-H, $^2J = 16.3$), 3.01 m (2H, NCH_2), 3.96–4.01 m (3H, OCH_2 , *cis*- $\text{CH}_2=$), 4.22 d.d (1H, *trans*- $\text{CH}_2=$, $^2J = 2.0$, $^3J_{\text{trans}} = 14.2$), 6.48 d.d (1H, $\text{OCH}=$, $^3J_{\text{cis}} = 6.7$, $^3J_{\text{trans}} = 14.2$). Found, %: C 68.83; H 10.43; N 13.11. $\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}$. Calculated, %: C 68.53; H 10.54; N 13.32.

5-Phenyl-1-(2-vinyloxyethyl)-4,5-dihydro-1H-pyrazole (IIId). Yield 55%, bp 133–138°C (2 mm), $d_4^{20} = 1.0463$, $n_D^{20} = 1.5720$. IR spectrum, ν , cm^{-1} : 510, 585, 610, 635, 655, 720, 825, 875, 930, 960, 975, 1010, 1040, 1105, 1120, 1165, 1180, 1240, 1260, 1290, 1325, 1415, 1465, 1530, 1560, 1570, 1610, 1650, 1730, 1795, 1865, 1935, 2830, 2920, 2950, 3015, 3045, 3090. ^1H NMR spectrum, δ , ppm (J , Hz): 2.65 m (1H, 4-H), 3.03–3.21 m (3H, 4-H, NCH_2), 3.90–3.93 m (3H, OCH_2 , *cis*- $\text{CH}_2=$), 4.08–4.12 m (2H, 5-H, *trans*- $\text{CH}_2=$), 6.41 d.d (1H, $\text{OCH}=$, $^3J_{\text{cis}} = 6.8$, $^3J_{\text{trans}} = 14.4$), 6.79 m (1H, 3-H), 7.35 m (5H, Ph). Found, %: C 72.01; H 7.11; N 13.01. $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}$. Calculated, %: C 72.19; H 7.46; N 12.95.

The ^1H NMR spectra were recorded at 30°C on a Bruker DPX-400 spectrometer (400 MHz) from solutions in CDCl_3 using HMDS as internal reference. The IR spectra were measured on a Specord 75IR instruments from thin films.

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