

SHORT
COMMUNICATIONS

N-(1-Nitroalkylmethyl)-2(3)-vinyloxyalkylamines

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Vinyl ethers of aminoalcohols [1] and nitro compounds [2] are widely employed in industry and exhibit versatile biological action. Evidently N-(1-nitroalkylmethyl)-2(3)-vinyloxyalkylamines combining the main functions of the mentioned compounds are interesting as semiproducts of the fine organic synthesis, monomers, and new objects for the study of biological activity.

Primarily the synthesis of [2-(vinyloxy)ethyl]-2-methyl-2-nitropropan-1-amine (**IIIa**) was carried out by the procedure [3] maintaining the equimolar mixture of 2-vinyloxyethylamine (**IIa**), 2-nitropropane, and water solution of formaldehyde at pH 9.5 for 2 h at 20–25°C. The yield of compound **IIIa** was 7% in agreement with the results obtained in [3].

The significantly higher yields of nitroalkylamines are known to be obtained in the reaction of nitroalcohols with amines [4]. However it was found that at the use of the procedure [4] consisting in maintaining the equimolar mixture of 2-methyl-2-nitropropan-1-ol (**Ia**) and 2-(vinyloxy)ethylamine (**IIa**) at room temperature for 3 days compound **IIIa** was obtained in 9% yield.

Therefore we further carried out the reaction by boiling the reagents mixture in benzene and removing water into the Dean-Stark trap till the end of water evolution. As

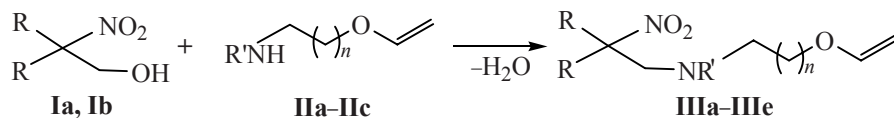
shown by GLC, the initial reagents remaining in the reaction mixture did not exceed 1–3%.

This procedure successfully afforded 2(3)-vinyloxyalkyl(1-nitroalkyl)amines **IIIa–IIIe** in 35–44% yields.

Relatively low yield of compounds **IIIa–IIIe** compared to the yield of products, obtained with the use of aliphatic amines (48–90%) [4] is presumably due to the polymerization of both initial and final vinyl ethers. This is confirmed by considerable tarring during the process.

2(3)-Vinyloxyalkyl(1-nitroalkyl)oxymethylamines IIIa–IIIe. General procedure. A mixture of 0.025 mol of 2-nitroalcohol **Ia** or **Ib**, 0.0275 mol of 2-vinyl-oxyalkylamine **IIa–IIc**, and 50 ml of benzene was refluxed with the Dean-Stark trap till the end of water evolution. The solvent was distilled off, and the residue was subjected to a fractional vacuum distillation.

[2-(Vinyloxy)ethyl]-2-methyl-2-nitropropan-1-amine (IIIa). Yield 39%, bp 105–108°C (3 mm Hg), d_4^{20} 1.0455, n_D^{20} 1.4596. IR spectrum, ν , cm^{-1} : 3347, 3113, 2980, 2927, 2867, 1620, 1607, 1527, 1453, 1389, 1359, 1333, 1307, 1184, 1121, 1060, 1027, 1000, 984, 952, 847, 807, 688, 543. ^1H NMR spectrum, δ , ppm: 1.56 s (6H, CMe_2), 2.63 br.s (1H, NH), 2.87 t (2H, $\text{OCH}_2\text{CH}_2\text{N}$,



I, R = Me (**a**), R,R = $(\text{CH}_2)_5$ (**b**); **II**, R' = H, $n = 1$ (**a**), 2 (**b**); R' = Me, $n = 1$ (**c**); **III**, R = Me, R' = H, $n = 1$ (**a**), 2 (**b**); R,R = $(\text{CH}_2)_5$, R' = H, $n = 1$ (**c**), 2 (**d**); R = R' = Me, $n = 1$ (**e**).

3J 5.2 Hz), 3.02 s (2H, NCH₂CNO₂), 3.72 t (2H, OCH₂CH₂N, 3J 5.2 Hz), 3.99 d.d (1H, *cis*-CH=CO, $^2J_{gem}$ 2.1, $^3J_{cis}$ 6.8 Hz), 4.17 d.d (1H, *trans*-CH=CO, $^2J_{gem}$ 2.1, $^3J_{trans}$ 14.3 Hz), 6.44 d.d (1H, C=CHO, $^3J_{cis}$ 6.8, $^3J_{trans}$ 14.3 Hz). ¹³C NMR spectrum, δ , ppm: 23.80 (CMe₂), 48.82 (OCH₂CH₂N), 57.34 (NCH₂CNO₂), 67.05 (OCH₂CH₂N), 86.53 (=CH₂), 88.29 (CMe₂), 151.31 (=CHO). Found, %: C 51.14; H 8.69; N 14.62. C₈H₁₆N₂O₃. Calculated, %: C 51.05; H 8.57; N 14.88.

[3-(Vinylxy)propyl]-2-methyl-2-nitropropane-1-amine (IIIb). Yield 35%, bp 118–120°C (3 mm Hg), d_4^{20} 1.0293, n_D^{20} 1.4610. IR spectrum, ν , cm⁻¹: 3347, 3107, 3033, 2933, 2867, 1620, 1602, 1523, 1459, 1389, 1357, 1335, 1307, 1187, 1120, 1059, 953, 876, 844, 800, 749, 693, 627, 548. ¹H NMR spectrum, δ , ppm: 1.75 s (6H, CMe₂), 1.95 m (2H, OCH₂CH₂CH₂N), 2.70 br.s (1H, NH), 2.91 t (2H, OCH₂CH₂CH₂N, 3J 6.2 Hz), 3.16 s (2H, NCH₂CNO₂), 3.91 t (2H, OCH₂CH₂CH₂N, 3J 6.2 Hz), 4.15 d.d (1H, *cis*-CH=CO, $^2J_{gem}$ 1.9, $^3J_{cis}$ 6.7 Hz), 4.35 d.d (1H, *trans*-CH=CO, $^2J_{gem}$ 1.9, $^3J_{trans}$ 14.2 Hz), 6.61 d.d (1H, C=CHO, $^3J_{cis}$ 6.7, $^3J_{trans}$ 14.2 Hz). ¹³C NMR spectrum, δ , ppm: 24.20 (CMe₂), 29.45 (OCH₂CH₂CH₂N), 47.21 (OCH₂CH₂CH₂N), 57.81 (NCH₂CNO₂), 66.11 (OCH₂CH₂CH₂N), 86.52 (CH₂=), 88.29 (CMe₂), 151.80 (=CHO). Found, %: C 53.21; H 9.08; N 13.63. C₉H₁₈N₂O₃. Calculated, %: C 53.45; H 8.97; N 13.85.

2-(Vinylxy)(1-nitrocyclohexylmethyl)ethan-amine (IIIc). Yield 38%, bp 136–139°C (2 mm Hg), n_D^{20} 1.4915. IR spectrum, ν , cm⁻¹: 3346, 3107, 3033, 2923, 2853, 1615, 1602, 1513, 1433, 1331, 1307, 1180, 1113, 1053, 979, 944, 893, 800, 683, 640, 587, 525. ¹H NMR spectrum, δ , ppm: 1.58–2.36 m [10H, (CH₂)₅], 2.78 t (2H, OCH₂CH₂N, 3J 5.4 Hz), 3.00 s (2H, NCH₂CNO₂), 3.50 br.s (1H, NH), 3.78 t (2H, OCH₂CH₂N, 3J 5.4 Hz), 3.99 d.d (1H, *cis*-CH=CO, $^2J_{gem}$ 1.5, $^3J_{cis}$ 6.9 Hz), 4.16 d.d (1H, *trans*-CH=CO, $^2J_{gem}$ 1.5, $^3J_{trans}$ 14.3 Hz), 6.45 d.d (1H, C=CHO, $^3J_{cis}$ 6.9, $^3J_{trans}$ 14.3 Hz). ¹³C NMR spectrum, δ , ppm: 22.17 (C³, C⁵ cyclohexyl), 24.89 (C⁴ cyclohexyl), 32.30 (C², C⁶ cyclohexyl), 49.05 (OCH₂CH₂N), 57.28 (NCH₂CNO₂), 66.43 (OCH₂CH₂N), 86.54 (CH₂=), 91.87 (C¹ cyclohexyl), 151.62 (=CHO). Found, %: C 57.91; H 8.94; N 12.08. C₁₁H₂₀N₂O₃. Calculated, %: C 57.87; H 8.83; N 12.27.

3-(Vinylxy)(1-nitrocyclohexylmethyl)propan-1-amine (IIIId). Yield 40%, bp 138–140°C (1 mm Hg), n_D^{20} 1.4922. IR spectrum, ν , cm⁻¹: 3347, 3113, 2933, 2853, 1620, 1605, 1532, 1427, 1363, 1327, 1307, 1264, 1185, 1133, 1119, 1063, 993, 953, 913, 884, 859, 831, 800, 729,

687, 525, 495. ¹H NMR spectrum, δ , ppm: 1.45–2.35 m [12H, (CH₂)₅, OCH₂CH₂CH₂N], 2.70 t (3H, OCH₂CH₂CH₂N, 3J 6.7 Hz), 2.95 s (2H, NCH₂CNO₂), 3.33 br.s (1H, NH), 3.72 t (2H, OCH₂CH₂CH₂N, 3J 6.7 Hz), 3.97 d.d (1H, *cis*-CH=CO, $^2J_{gem}$ 1.9, $^3J_{cis}$ 6.8 Hz), 4.17 d.d (1H, *trans*-CH=CO, $^2J_{gem}$ 1.9, $^3J_{trans}$ 14.3 Hz), 6.44 d.d (1H, C=CHO, $^3J_{cis}$ 6.8, $^3J_{trans}$ 14.3 Hz). ¹³C NMR spectrum, δ , ppm: 22.26 (C³, C⁵ cyclohexyl), 25.22 (C⁴ cyclohexyl), 31.16 (C², C⁶ cyclohexyl), 49.38 (OCH₂CH₂CH₂N), 57.53 (NCH₂CNO₂), 67.68 (OCH₂CH₂CH₂N), 86.62 (CH₂=), 92.39 (C¹ cyclohexyl), 152.01 (=CHO). Found, %: C 59.64; H 9.08; N 11.23. C₁₂H₂₂N₂O₃. Calculated, %: C 59.48; H 9.15; N 11.56.

N-[2-(Vinylxy)ethyl]-N,2-dimethyl-2-nitropropan-1-amine (IIIe). Yield 44%, bp 90–92°C (1 mm Hg), d_4^{20} 1.0219, n_D^{20} 1.4580. IR spectrum, ν , cm⁻¹: 3400, 3120, 2989, 2947, 2877, 2800, 1625, 1612, 1526, 1455, 1396, 1367, 1340, 1315, 1193, 1115, 1053, 1013, 989, 980, 960, 900, 848, 833, 800, 653. ¹H NMR spectrum, δ , ppm: 1.54 s (6H, CMe₂), 2.34 s (3H, NMe), 2.75 t (2H, OCH₂CH₂N, 3J 5.1 Hz), 2.94 s (2H, CH₂NCH₂CH₂O), 3.70 t (2H, OCH₂, 3J 5.1 Hz), 3.98 d.d (1H, *cis*-CH=CO, $^2J_{gem}$ 1.9, $^3J_{cis}$ 6.8 Hz), 4.16 d.d (1H, *trans*-CH=CO, $^2J_{gem}$ 1.9, $^3J_{trans}$ 14.3 Hz), 6.46 d.d (1H, CHO, $^3J_{cis}$ 6.3, $^3J_{trans}$ 14.3 Hz). Found, %: C 53.02; H 8.51; N 13.29. C₉H₁₈N₂O₃. Calculated, %: C 53.45; H 8.97; N 13.85.

¹H and ¹³C NMR spectra were registered on a spectrometer Bruker DPX-400 (400 and 100 MHz) in CDCl₃ at 26°C, internal reference HMDS. IR spectra were recorded on a spectrophotometer Specord 75IR from thin films.

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