

SHORT
COMMUNICATIONSReaction of 2-Vinyloxymethyl-
and 2-(2-Vinyloxyethoxymethyl)oxirane with Hydrazine

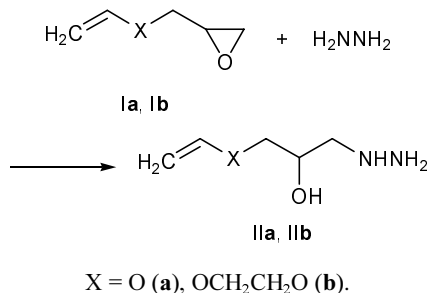
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Reactions of 2-vinyloxymethyl- and 2-(2-vinyloxyethoxymethyl)oxiranes **Ia** and **Ib** with ammonia and amines were reported in [1–5]. In the present communication we describe the reaction of compounds **Ia** and **Ib** with hydrazine. The reaction occurs under mild conditions, and the products (compounds **IIa** and **IIb**) attract interest as monomers and intermediate products in the synthesis of biologically active substances. To obtain compounds **IIa** and **IIb** in a satisfactory yield, the molar ratio hydrazine–epoxy ether **I** should be no less than 10:1. With a lesser amount of hydrazine, the yield of isolated compounds **IIa** and **IIb** strongly decreases, presumably due to formation of thermally unstable products via addition of two epoxide molecules to hydrazine or hydroxy group in **IIa** and **IIb** and their decomposition during vacuum distillation.



1-Hydrazino-3-(vinyloxy)propan-2-ol (IIa). Compound **Ia**, 10.02 g (0.1 mol), was added dropwise under stirring to 40 g (1 mol) of hydrazine hydrate, maintaining the temperature below 30–35°C, and the mixture was kept for 24 h at room temperature. The mixture was then dried over K₂CO₃ and subjected to vacuum distillation to isolate compound **IIa**. Yield 10.9 g (82.5%), bp 145–147°C (4 mm), $d_4^{20} = 1.0863$,

$n_D^{20} = 1.4963$. IR spectrum, ν , cm⁻¹: 615, 660, 695, 805, 930, 945, 980, 1060, 1100, 1180, 1310, 1445, 1605, 1625, 2855, 2905, 3250–3295. ¹H NMR spectrum, δ , ppm (J , Hz): 2.88 d.d (1H, H_A in NCH_AH_BCH_X, ² $J_{AB} = 12.6$, ³ $J_{AX} = 8.0$, ³ $J_{BX} = 3.3$), 2.96 d.d (1H, H_B in NCH_AH_BCH_X, ² $J_{AB} = 12.6$, ³ $J_{BX} = 8.0$, ³ $J_{AX} = 3.3$), 3.34 br.s (4H, OH, NHNH₂), 3.72 d.d (1H, H_A in OCH_AH_BCH_C, ² $J_{AB} = 10.2$, ³ $J_{AC} = 5.9$, ³ $J_{BC} = 4.8$), 3.77 d.d (1H, H_B in OCH_AH_BCH_C, ² $J_{AB} = 10.2$, ³ $J_{BC} = 5.9$, ³ $J_{AC} = 4.8$), 4.06 d.d (1H, *cis*-CH₂=, ² $J = 2.2$, ³ $J_{cis} = 6.7$), 4.12 m (1H, CHOH), 4.24 d.d (1H, *trans*-CH₂=, ² $J = 2.2$, ³ $J_{trans} = 14.3$), 6.52 d.d (1H, =CH, ³ $J_{cis} = 6.7$, ³ $J_{trans} = 14.3$). ¹³C NMR spectrum, δ_C , ppm: 56.49 (NCH₂), 68.51 (OCH₂), 70.19 (CHOH), 87.06 (=CH₂), 151.66 (OCH=). Found, %: C 45.29; H 9.15; N 21.42. C₅H₁₂N₂O₂. Calculated, %: C 45.44; H 9.15; N 21.20.

1-Hydrazino-3-[2-(vinyloxy)ethoxy]propan-2-ol (IIb). Compound **Ib**, 14.42 g (0.1 mol), was added dropwise under stirring to 40 g (1 mol) of hydrazine hydrate, maintaining the temperature below 30°C, and the mixture was kept for 24 h at room temperature. The mixture was then dried over K₂CO₃ and subjected to vacuum distillation to isolate compound **IIb**. Yield 13.4 g (76%), bp 129–131°C (2 mm), $d_4^{20} = 1.0691$, $n_D^{20} = 1.4758$. IR spectrum, ν , cm⁻¹: 585, 685, 750, 815, 875, 960, 985, 1060, 1100, 1175, 1225, 1275, 1310, 1345, 1440, 1605, 1620, 2855, 2900, 2910, 3250–3360. ¹H NMR spectrum, δ , ppm (J , Hz): 2.22 br.s (3H, NHNH₂), 2.70 d.d (1H, H_A in NCH_AH_BCH_X, ² $J_{AB} = 12.9$, ³ $J_{AX} = 7.1$, ³ $J_{BX} = 4.1$), 2.81 d.d (1H, H_B in NCH_AH_BCH_X, ² $J_{AB} = 12.9$, ³ $J_{BX} = 7.1$, ³ $J_{AX} = 4.1$), 3.46 d.d (1H, H_A in OCH_AH_BCH_C, ² $J_{AB} = 9.8$, ³ $J_{AC} = 6.7$, ³ $J_{BC} = 3.9$), 3.54 d.d (1H, H_B in OCH_AH_BCH_C, ² $J_{AB} = 9.8$, ³ $J_{BC} = 6.7$, ³ $J_{AC} = 3.9$), 3.70 br.s (1H, OH),

3.71–3.85 m (5H, OCH₂CH₂O, CHOH), 4.02 d.d (1H, *cis*-CH₂=, ²J = 1.7, ³J_{cis} = 6.7), 4.19 d.d (1H, *trans*-CH₂=, ²J = 1.7, ³J_{trans} = 14.3), 6.47 d.d (1H, =CH, ³J_{cis} = 6.7, ³J_{trans} = 14.3). ¹³C NMR spectrum, δ_C, ppm: 44.15 (NCH₂), 67.26 (CHOH), 69.80 (=CHOCH₂), 70.98 (=CHOCH₂CH₂O), 73.67 (OCH₂CH), 86.85 (=CH₂), 151.63 (OCH=). Found, %: C 47.87; H 9.56; N 15.73. C₇H₁₆N₂O₃. Calculated, %: C 47.71; H 9.15; N 15.90.

The ¹H and ¹³C NMR spectra were recorded at 26°C on a Bruker DPX-400 spectrometer at 400 and 100 MHz, respectively, using CDCl₃ as solvent and HMDS as internal reference. The IR spectra were obtained on a Specord 75IR spectrophotometer from samples prepared as thin films (neat).

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