

(2-Vinyloxyethyl)hydrazines

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Abstract—Reaction of hydrazine hydrate with 2-chloroethyl vinyl ether afforded (2-vinyloxyethyl)hydrazine and 1,1-bis(2-vinyloxyethyl)hydrazine in 20–38% yield.

Vinyl ethers derived from nitrogen-containing alcohols attract interest as monomers and intermediate products in the synthesis of biologically active substances and other compounds possessing practically useful properties [1]. Among these, aminoalkyl vinyl ethers have been studied most extensively. On the other hand, hydrazinoethyl vinyl ethers remain almost unknown. Presumably, this is explained by difficulties in the preparation of such compounds by the classical method, i.e., based-catalyzed vinylation of alcohols with acetylene, which arise from the low energy of dissociation of the nitrogen–nitrogen bond and hence its easy cleavage [2].

We previously reported on the synthesis of 1-(2-vinyloxyethyl)-1,1-dimethylhydrazinium chloride by quaternization of 1,1-dimethylhydrazine with 2-chloroethyl vinyl ether [3]. In the present work we examined the possibility for synthesizing hydrazinoethyl vinyl ethers by alkylation of hydrazine with 2-chloroethyl vinyl ether.

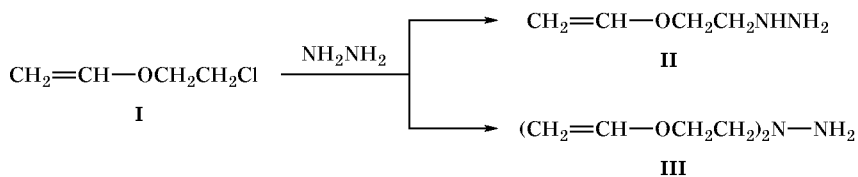
According to the GLC and ^1H NMR data, the reaction of hydrazine hydrate with 2-chloroethyl vinyl ether in the presence of sodium hydroxide leads to formation of a mixture of alkylation products **II** and **III** (Scheme 1). The monoalkylation product was obtained in a satisfactory yield only when the reaction was performed with 10 equiv of hydrazine hydrate; bisalkylation product **III** was isolated in the reaction

with 5 equiv of 2-chloroethyl vinyl ether. The structure of compounds **II** and **III** was confirmed by the IR and ^1H , ^{13}C , and ^{15}N NMR spectra.

The IR spectra of hydrazines **II** and **III** contain absorption bands typical of the vinyloxy group at 1610–1640 ($\nu\text{C}=\text{C}$) and 3040–3115 cm^{-1} ($\nu_{\text{as}}=\text{CH}_2$). A narrow band at 3345 cm^{-1} in the spectrum of **II** and a broad band in the region 3250–3340 cm^{-1} in the spectrum of **III** correspond to stretching vibrations of the N–H bonds.

In the ^1H NMR spectra of products **II** and **III** we observed a doublet of doublets at δ 6.40–6.44 ppm, which belongs to the vinyl proton at the ether oxygen atom. Also, doublets of doublets at 3.95–3.98 and 4.14–4.18 ppm were present, which belong, respectively, to the *cis* and *trans* protons of the $\text{H}_2\text{C}=\text{C}$ fragment. The coupling constants in the vinyl group are as follows: $^2J = 2.1$, $^3J_{\text{cis}} = 6.8$, and $^3J_{\text{trans}} = 14.3$ Hz. The structure of compounds **II** and **III** was also confirmed by the ^{15}N NMR spectrum recorded in the inverse heteronuclear correlation mode (NMVS) with a gradient pulse. In the reaction with excess 2-chloroethyl vinyl ether, $\text{CH}_2=\text{CHOCH}_2\text{CH}_2$ fragments can add to different nitrogen atoms of the hydrazine molecule. The ^{15}N NMR spectrum of **III** contains two signals at δ_{N} 71.87 and 87.78 ppm. In keeping with published data [4], these signals were assigned to $\text{N}(\text{CH}_2)_2$ and NH_2 groups, respectively.

Scheme 1.



EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer (400 MHz) in CDCl_3 using HMDS as internal reference. The ^{15}N NMR spectra were obtained on the same instrument in $\text{DMSO}-d_6$ using NH_3 as internal reference. The IR spectra were measured on a Specord 75IR spectrophotometer from samples pelleted with KBr.

(2-Vinyloxyethyl)hydrazine (II). 2-Chloroethyl vinyl ether, 5.33 g (0.05 mol), was added with stirring at 80–85°C to a mixture of 25.03 g (0.5 mol) of hydrazine hydrate and 2 g (0.05 mol) of NaOH. The mixture was stirred for 11 h at that temperature, cooled, filtered from NaOH, saturated with K_2CO_3 , and extracted with ether (3×10 ml). The extract was distilled to isolate 1.93 g (38%) of compound **II**, bp 77–78°C (13 mm), $d_4^{20} = 0.9848$, $n_D^{20} = 1.4574$. IR spectrum, ν , cm^{-1} : 525, 600, 610, 700, 810, 865, 955, 1025, 1070, 1100, 1180, 1250, 1280, 1310, 1350, 1375, 1455, 1610, 1620, 2865, 2925, 3040, 3115, 3180, 3190, 3250–3340. ^1H NMR spectrum, δ , ppm: 2.97 t (2H, NCH_2 , $^3J = 5.1$ Hz), 3.15 br.s (3H, NH, NH_2), 3.75 t (2H, OCH_2 , $^3J = 5.1$ Hz), 3.95 d.d (1H, *cis*- $\text{HC}=\text{CO}$, $^2J = 2.1$, $^3J_{\text{cis}} = 6.8$ Hz), 4.14 d.d (1H, *trans*- $\text{HC}=\text{CO}$, $^2J = 2.1$, $^3J_{\text{trans}} = 14.3$ Hz), 6.40 d.d (1H, $\text{OCH}=\text{C}$, $^3J_{\text{cis}} = 6.8$, $^3J_{\text{trans}} = 14.3$ Hz). ^{13}C NMR spectrum, δ_{C} , ppm: 54.16 (NCH_2); 65.88 (OCH_2); 87.03 ($=\text{CH}_2$); 151.65 ($\text{OCH}=\text{C}$). ^{15}N NMR spectrum, δ_{N} , ppm: 64.31 [NH , $1/2^2J(\text{NHCH}) = 0.8$ Hz, $^2J(\text{NCH}) = 0.8$ Hz], 74.23 [NH_2 , $1/2^3J(\text{NHNCH}) = 0.17$ Hz, $^3J(\text{NNCH}) = 3.0$ Hz]. Found, %: C 46.71; H 10.20; N 26.92. $\text{C}_4\text{H}_{10}\text{N}_2\text{O}$. Calculated, %: C 47.04; H 9.87; N 27.43.

1,1-Bis(2-vinyloxyethyl)hydrazine (III) was synthesized in a similar way from 2.5 g (0.05 mol) of

hydrazine hydrate, 10 g (0.25 mol) of NaOH, and 26.64 g (0.25 mol) of 2-chloroethyl vinyl ether. Yield 1.71 g (20%), bp 108–109°C (9 mm), $d_4^{20} = 0.9623$, $n_D^{20} = 1.4732$. IR spectrum, ν , cm^{-1} : 565, 615, 700, 820, 900, 965, 1000, 1075, 1140, 1195, 1260, 1290, 1320, 1360, 1380, 1415, 1465, 1615, 1640, 2820–2840, 2875, 2920–2955, 3040, 3115, 3345. ^1H NMR spectrum, δ , ppm: 2.85 t (2H, NCH_2 , $^3J = 5.5$ Hz), 3.03 br.s (2H, NH_2), 3.89 t (2H, OCH_2 , $^3J = 5.5$ Hz), 3.98 d.d (1H, *cis*- $\text{HC}=\text{CO}$, $^2J = 2.1$ Hz, $^3J_{\text{cis}} = 6.8$ Hz), 4.18 d.d (1H, *trans*- $\text{HC}=\text{CO}$, $^2J = 2.1$ Hz, $^3J_{\text{cis}} = 14.3$ Hz), 6.44 d.d (1H, $\text{OCH}=\text{C}$, $^3J_{\text{cis}} = 6.8$, $^3J_{\text{trans}} = 14.3$ Hz). ^{13}C NMR spectrum, δ_{C} , ppm: 60.15 (NCH_2); 66.10 (OCH_2); 86.81 ($=\text{CH}_2$); 151.69 ($\text{OCH}=\text{C}$). ^{15}N NMR spectrum, δ_{N} , ppm: 71.87 [NH , $1/2^3J(\text{NCH}) = 3.0$ Hz, $^3J(\text{NCCH}) = 3.0$ Hz], 87.78 [NH_2 , $^3J(\text{NNCH}) = 3.0$ Hz]. Found, %: C 55.10; H 9.67; N 15.82. $\text{C}_8\text{H}_{16}\text{N}_2\text{O}_2$. Calculated, %: C 55.79; H 9.36; N 16.27.

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