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Dedicated to Full Member of the Russian Academy of Sciences B.A. Trofimov on the 65th Anniversary of His Birth

First Representatives of *O*-(2-Vinyloxyethyl)oximes

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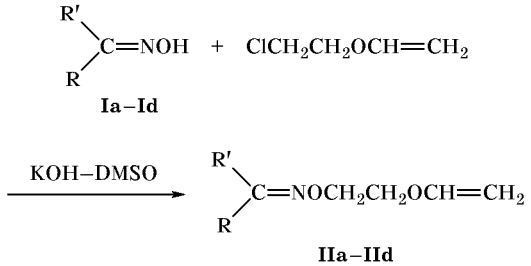
Abstract—Previously unknown ketone and acetaldehyde *O*-(2-vinyloxyethyl)oximes were synthesized in 22–88% by reaction of the corresponding oximes with 2-chloroethyl vinyl ether in the system KOH–DMSO.

Vinyl ethers having nitrogen-containing functional groups, such as amino, amido, cyano, isocyano, isothiocyanato, isocyanato, etc., attract interest as monomers and intermediate products for the synthesis of compounds possessing biological activity and various practically useful properties [1]. Ketone oxime *O*-vinyl ethers are well studied representatives of vinyl ethers [2, 3]. On the other hand, vinyl ethers derived from more complex ketone oxime derivatives, ketone *O*-(hydroxyalkyl)oximes, remain almost not studied. The only report is that by Nedolya *et al.* [4] on the synthesis of ketone *O*-[3-(ω-vinyloxyalkoxy)-2-hydroxypropyl]oximes from ketone oximes and vinylglycidyl glycol ethers.

The present work was aimed at synthesizing *O*-(2-vinyloxyethyl)oximes. Our attempts to obtain these compounds by vinylation of *O*-(2-hydroxyethyl)-oximes with acetylene under conditions of base catalysis resulted in formation of only decomposition products. Therefore, we tried to synthesize *O*-(2-vinyl-oxyethyl)oximes by alkylation of the corresponding oximes with 2-chloroethyl vinyl ether.

Trofimov and co-workers [5] previously reported on successful *O*-alkylation of ketone oximes with allyl chloride and 2-propynyl bromide in the system KOH–DMSO. We thought it reasonable to use the same system in the reaction under study. The reactions were carried out in DMSO at 35–45°C with 3 equiv of KOH and a small (5 mol %) excess of 2-chloroethyl vinyl ether. According to the GLC data, under these conditions the reaction was complete in 2–3 h, and ketone *O*-(2-vinyloxyethyl)oximes **IIb**–**IId** were thus obtained in 74–88% yield. 2-Vinyloxyethanol was also formed as by-product (GLC). When the amount of the base was reduced to 2 equiv, the yield of the O-alkylation products decreased by 12–19%. No increase in the yield of the target products was achieved with the use of a larger excess of the alkylating agent (up to 100 mol %), but the fraction of 2-vinyloxyethanol increased considerably.

In the reaction with acetaldehyde oxime (**Ia**) we succeeded in isolating the corresponding alkylation product **IIa** in only 22% yield. A considerable difference in the yields of the O-alkylation products from ketone oximes **Ib**–**Id** and acetaldehyde oxime (**Ia**) may be explained by the known ready base-catalyzed dehydration of aldehyde oximes to nitriles in DMSO [6]. This is confirmed by the presence of acetonitrile (GLC) in the reaction mixture.



I, **II**, R = H, R′ = Me (**a**); R = R′ = Me (**b**); R = Me, R′ = Ph (**c**); RR′ = $(CH_2)_5$ (**d**).

Compounds **IIa**–**IId** are colorless mobile liquids with a specific odor (typical of vinyl ethers), which can be stored for a long time. Their structure was confirmed by the IR and ^1H and ^{13}C NMR spectra. The

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IR spectra of vinyl ethers **IIa**–**IId** contain absorption bands belonging to the vinyloxy group at 1605–1608 [ν(C=C)] and 3020–3120 cm^{-1} [$\nu_{as}(=CH_2)$] and imino group at 1625–1630 cm^{-1} [ν(C=N)]. In the ^1H NMR spectra, protons of the vinyloxy group give rise to three doublets of doublets at δ 3.99–4.07, 4.10–4.23, and 6.35–6.53 ppm (^2J = 1.7–2.2, $^3J_{cis}$ = 6.8–6.9, $^3J_{trans}$ = 14.3–14.4 Hz) from the *cis*-CH=C, *trans*-CH=C, and OCH=C protons, respectively.

According to the ^1H and ^{13}C NMR spectral data, acetophenone *O*-(2-vinyloxyethyl)oxime (**IIc**) was obtained as a single isomer. Taking into account the chemical shift of the methyl protons (δ 2.24 ppm) and published data for various acetophenone oxime derivatives [3, 7], it was assigned *E* configuration. Acetaldehyde *O*-(2-vinyloxyethyl)oxime (**IIa**) was isolated as a mixture of two isomers at a ratio of 78:22 (^1H NMR data). We performed no detailed assignment of the isomers; however, on the basis of general considerations concerning deshielding of the CH=N–O proton by oxygen, the major isomer (δ 7.49 ppm) was assigned *E* configuration, and the minor one (δ 6.80 ppm), *Z* structure.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400 and 100 MHz, respectively, using $CDCl_3$ as solvent and HMDS as internal reference (26°C). The IR spectra were measured on a Specord 75IR spectrophotometer from samples prepared as thin films. The purity of the initial compounds and final products was checked by GLC on an LKhM-80 chromatograph equipped with a thermal-conductivity detector; carrier gas helium; steel column, 3000 × 3 mm, packed with 3% of OV-17 on Inerton Super, 0.160–0.200 μm; oven temperature programming from 60 to 200°C at a rate of 4 deg/min.

Commercial ketone and acetaldehyde oximes were used; 2-chloroethyl vinyl ether contained no less than 98% of the main substance (GLC); DMSO contained ~1% of water; and potassium hydroxide contained 12% of water.

***O*-(2-Vinyloxyethyl)oximes IIa–IId.** 2-Chloroethyl vinyl ether, 17.05 g (0.21 mol), was added dropwise over a period of 0.5 h to a mixture of 0.2 mol of oxime **Ia**–**Id** and 0.3 mol of powdered KOH in 200 ml of DMSO while stirring at 35–45°C. The mixture was stirred for 2 h at that temperature, diluted with 5 volumes of water, and extracted with ether (3 × 200 ml). The extracts were combined, washed with 50 ml of water, and dried over K_2CO_3. Removal of the solvent, followed by vacuum distillation, gave *O*-(2-vinyloxyethyl)oximes **IIa**–**IId**.

Acetaldehyde *O*-(2-vinyloxyethyl)oxime (IIa). Yield 22%. bp 64–65°C (28 mm), d_4^{20} = 0.9387, n_D^{20} = 1.4400; MR_D = 36.26, calcd. 35.65. IR spectrum, ν, cm^{-1}: 454, 492, 557, 608, 653, 698, 750, 808, 857, 875, 907, 940, 952, 974, 1056, 1135, 1188, 1212, 1270, 1286, 1312, 1352, 1394, 1435, 1448, 1607, 1628, 2872, 2915, 3044, 3075, 3115. ^1H NMR spectrum, δ, ppm: major isomer: 1.87 d (3H, Me, ^3J = 5.8 Hz), 3.93 t (2H, OCH_2, ^3J = 4.8 Hz), 4.04 d.d (1H, *cis*-CH=C, ^2J = 2.2, $^3J_{cis}$ = 6.9 Hz), 4.23 d.d (1H, *trans*-CH=C, ^2J = 2.2, $^3J_{trans}$ = 14.4 Hz), 4.26 t (2H, $NOCH_2$, ^3J = 4.8 Hz), 6.53 d.d (1H, OCH=C, $^3J_{cis}$ = 6.9, $^3J_{trans}$ = 14.4 Hz), 7.49 q (1H, CH, ^3J = 5.8 Hz); minor isomer: 1.88 d (3H, Me, ^3J = 5.5 Hz), 3.95 t (2H, OCH_2, ^3J = 4.9 Hz), 4.03 d.d (1H, *cis*-CH=C, ^2J = 2.2, $^3J_{cis}$ = 6.8 Hz), 4.24 d.d (1H, *trans*-CH=C, ^2J = 2.2, $^3J_{trans}$ = 14.4 Hz), 4.32 t (2H, $NOCH_2$, ^3J = 4.9 Hz), 6.51 d.d (1H, OCH=C, $^3J_{cis}$ = 6.8, $^3J_{trans}$ = 14.4 Hz), 6.80 q (1H, CH, ^3J = 5.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: major isomer: 15.06 (CH_3); 66.41 ($NOCH_2$); 71.51 (OCH_2); 86.59 ($=CH_2$); 147.35 (OCH=); 151.67 (NC); minor isomer: 11.84 (CH_3); 66.14 ($NOCH_2$); 71.89 (OCH_2); 86.59 ($=CH_2$); 147.35 (OCH=); 151.77 (NC). Found, %: C 55.42; H 8.71; N 10.41. $C_6H_{11}NO_2$. Calculated, %: C 55.80; H 8.58; N 10.84.

Acetone *O*-(2-vinyloxyethyl)oxime (IIb). Yield 74%. bp 92–93°C (68 mm), d_4^{20} = 0.9286, n_D^{20} = 1.4428; MR_D = 40.86, calcd. 40.07. IR spectrum, ν, cm^{-1}: 530, 575, 600, 690, 803, 875, 905, 930, 955, 968, 995, 1060, 1185, 1233, 1260, 1270, 1308, 1357, 1425, 1443, 1608, 1635, 2865, 2912, 2978, 3120. ^1H NMR spectrum, δ, ppm: 1.73 s (6H, 2Me), 3.77 t (2H, OCH_2, ^3J = 4.8 Hz), 3.86 d.d (1H, *cis*-CH=C, ^2J = 1.7, $^3J_{cis}$ = 6.8 Hz), 4.07 d.d (1H, *trans*-CH=C, ^2J = 1.7, $^3J_{trans}$ = 14.4 Hz), 4.10 t (2H, $NOCH_2$, ^3J = 4.8 Hz), 6.35 d.d (1H, OCH=C, $^3J_{cis}$ = 6.8, $^3J_{trans}$ = 14.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 15.99 (C_{syn}); 21.76 (C_{anti}); 66.49 ($NOCH_2$); 71.48 (OCH_2); 86.51 ($=CH_2$); 151.86 (OCH=); 155.38 (NC). Found, %: C 58.76; H 9.08; N 9.47. $C_7H_{13}NO_2$. Calculated, %: C 58.72; H 9.15; N 9.78.

Acetophenone *O*-(2-vinyloxyethyl)oxime (IIc). Yield 88%. bp 138–140°C (6 mm), d_4^{20} = 1.0441, n_D^{20} =1.5358; MR_D = 61.28, calcd. 60.76. IR spectrum, ν, cm^{-1}: 515, 528, 543, 600, 620, 677, 742, 804, 875, 900, 922, 945, 965, 978, 1045, 1075, 1184, 1215, 1225, 1255, 1270, 1308, 1345, 1356, 1433, 1440, 1485, 1560 1608, 1625, 2870, 2928, 3020, 3050,

3096, 3109. ^{1}H NMR spectrum, δ, ppm: 2.24 s (3H, Me), 3.78 t (2H, OCH_2, ^3J = 4.7 Hz), 4.01 d.d (1H, *cis*-CH=C, ^2J = 2.0, $^3J_{cis}$ = 6.8 Hz), 4.22 d.d (1H, *trans*-CH=C, ^2J = 2.0, $^3J_{trans}$ = 14.3 Hz), 4.40 t (2H, $NOCH_2$, ^3J = 4.7 Hz), 6.49 d.d (1H, OCH=C, $^3J_{cis}$ = 6.8, $^3J_{trans}$ = 14.3 Hz), 7.35 m and 7.62 m (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 12.97 (CH_3); 66.65 ($NOCH_2$); 72.45 (OCH_2); 86.80 (=CH_2); 126.17 (C^2, C^6, Ph); 128.47 (C^3, C^5, Ph); 129.20 (C^4, Ph); 136.66 (C^1, Ph); 151.97 (OCH=); 155.50 (NC). Found, %: C 70.62; H 7.11; N 6.93. $C_{12}H_{15}NO_2$. Calculated, %: C 70.22; H 7.37; N 6.82.

Cyclohexanone *O*-(2-vinyloxyethyl)oxime (IId). Yield 83%. bp 106–109°C (5 mm), d_4^{20} = 0.9901, n_D^{20} = 1.4800; MR_D = 52.61, calcd. 51.72. IR spectrum, ν, cm^{-1}: 550, 595, 645, 688, 765, 805, 840, 855, 900, 915, 930, 945, 965, 990, 1055, 1125, 1190, 1225, 1240, 1265, 1275, 1305, 1345, 1375, 1425, 1435, 1605, 1630, 2852, 2855, 2930, 3105. ^{1}H NMR spectrum, δ, ppm: 1.61 m, 2.18 m, and 2.46 m [10H, $(CH_2)_5$]; 3.90 t (2H, $NOCH_2$, ^3J = 4.8 Hz); 3.99 d.d (1H, *cis*-CH=C, ^2J = 1.9, $^3J_{cis}$ = 6.8 Hz); 4.19 d.d (1H, *trans*-CH=C, ^2J = 1.9, $^3J_{trans}$ = 14.3 Hz); 4.22 t (2H, $NOCH_2$, ^3J = 4.8 Hz); 6.48 d.d (1H, OCH=C, $^3J_{cis}$ = 6.8, $^3J_{trans}$ = 14.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 24.84 (C^4); 25.23, 25.33, 26.53, 31.66 (C^2, C^3, C^5, C^6); 66.02 ($NOCH_2$); 70.23 (OCH_2); 86.04 (=CH_2); 151.44 (OCH=); 160.24 (NC). Found, %: C 65.52; H 9.18; N 7.87. $C_{10}H_{17}NO_2$. Calculated, %: C 65.54; H 9.35; N 7.64.

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