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Synthesis of *O*-[2-Hydroxy-3-(vinyloxy)propyl]oximes and *O*-[(2-Methyl-1,3-dioxolan-4-yl)methyl]oximes

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Abstract—By oximes reaction with glycidyl vinyl ether *O*-[2-hydroxy-3-(vinyloxy)propyl]oximes of ketones and acetaldehyde were synthesized in 54–72% yield, and by acid catalysis the compounds were converted into *O*-[(2-methyl-1,3-dioxolan-4-yl)methyl]oximes in 61-88% yield.

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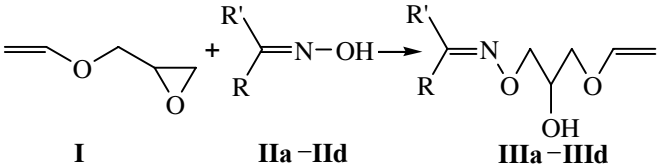
Scanty information exists on the synthesis of vinyl ethers of alcohols containing an oxime group. A synthesis was reported of *O*-(2-vinyloxyethyl)oximes by vinylation of appropriate alcohols [1] or by alkylation of oximes with 2-chloroethyl vinyl ether [2]. Some data were published on the preparation of *O*-[3-(ω-vinyloxyorganyloxy)-2-hydroxypropyl]ketoximes by reaction of ketoxime with vinyl glycidyl glycol ethers [3]. Inasmuch as such vinyl ethers attract interest as monomers and intermediate products in the fine organic synthesis we report here on investigation of reaction of ketoximes and acetaldoxime with the vinyl glycidyl ether and of acid-catalyzed cyclization of the *O*-[2-hydroxy-3-(vinyloxy)propyl]-oximes obtained into *O*-[(2-methyl-1,3-dioxolan-4-yl)methyl]-oximes.

The reaction of vinyl glycidyl ether (**I**) with oximes **IIa–IId** was carried out at 1.5-fold molar excess of epoxy compound **I** without solvent at heating to 95–100°C using triethylamine as catalyst (3 mol% to oxime amount). Under these conditions according to GLC data the reaction was completed within 3–3.5 h leading to the formation of *O*-[2-hydroxy-3-(vinyloxy)propyl]oximes **IIIb–IIId** in 54–72% yield.

When lesser amount of epoxy compound **I** was introduced into the reaction the unreacted oxime was partially recovered, and a larger excess of compound **I** decreased the target product yield due to its further oxyalkylation at the hydroxy group.

IR spectra of synthesized vinyl ethers **IIIa–IIId** contain absorption bands of vinyloxy group at 1600–1630 [ν(C=C), (C=N)], 3100–3105 [ν_{as}(=CH_2)], and of hydroxy group at 3395–3410 cm^{-1}.

In the ^{1}H NMR spectra the proton signals of the vinyloxy group of compounds **IIIa–IIId** appeared as three doublets of doublets, δ 3.98–4.00, 4.18–4.21, and 6.43–6.47 ppm ($^2J_{gem}$ 1.6–2.0, $^3J_{cis}$ 6.7–6.8 and $^3J_{trans}$ 14.2–14.4 Hz) belonging to protons *cis*-CH=C, *trans*-CH=C, and OCH=C respectively.



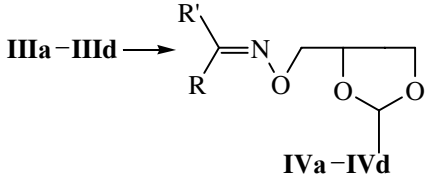
I **IIa–IId** **IIIa–IIId**

R = H, R' = Me (**a**); R = R' = Me (**b**); R = Me, R' = Ph (**c**); R + R' = $(CH_2)_5$ (**d**).

^{13}C NMR spectra contain signals from carbon atoms of vinyl and imino groups: 86.63–87.18 (=CH), 147.17–151.56 (OCH=), and 151.66–161.11 ppm (C=N).

Isolated *O*-[2-hydroxy-3-(vinyloxy)propyl]acetaldoxime (**IIIa**) according to ^{1}H NMR data was a mixture of two isomers in a molar ratio 1.4:1. Based on assumption of deshielding of the proton of CH=N–O group by oxygen it is likely that the prevailing isomer whose chemical shift of this proton is 7.41 ppm is *E*-isomer, and the *Z*-isomer (δ 6.75 ppm) is present in minor amount.

According to ^{1}H and ^{13}C NMR spectra synthesized *O*-[2-hydroxy-3-(vinyloxy)propyl]acetophenone oxime



IVa–IVd

(**IIc**) was obtained as a single isomer. The chemical shift of the methyl group protons (2.19 ppm) and published data on the ^{1}H NMR spectra of various derivatives of acetophenone oxime [4, 5] suggest that compound **IIc** is *E*-isomer.

Compounds **IIIa–IIId** obtained are colorless mobile liquids stable at long storage. However like all known vinyl ethers containing a hydroxy group in the β-position with respect to vinyloxy group compounds **IIIa–IIId** readily undergo cyclization into 2-methyl-1,3-dioxolanes [6].

Cyclization of vinyl ethers **IIIa–IIId** occurs with self-heating on adding thereto catalytic quantities of concn. hydrochloric acid. Yield of dioxolanes **IVa–IVd** was 61–88%.

In the IR spectra of dioxolanes **IVa–IVd** appeared absorption bands of imino group at 1600–1630 [ν (C=N)], and the bands of vinyloxy and hydroxy groups were lacking.

^{1}H and ^{13}C NMR spectra evidence that these dioxolanes exist as mixtures of two diastereomers. Therewith only dioxolane **IVb** is a virtually equimolar mixture of diastereomers. The diastereomers ratio in compounds **IVd** and **IVc** reached 1.5:1 and 1.7:1 respectively. Dioxolane (**IVa**) contains a mixture of two diastereomers which both contain *syn*- as well as *anti*-oxime groups. Therefore the ^{1}H NMR spectra was too complicated to estimate the content of individual forms. Signals of the methyl group attached to the position *2* of the dioxolane ring appeared in the ^{1}H NMR spectrum as a doublet at δ 1.32–1.36 ppm, and protons of OCHO group gave rise to a quartet at δ 4.99–5.10 ppm, with coupling constants for the protons of these groups equaling 4.5–4.8 Hz.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered at 26°C a spectrometer Bruker DPX-400 (at 400 and 100 MHz respectively) from solutions in $CDCl_3$ (internal reference HMDS). IR spectra were recorded on a spectrophotometer Specord 75IR from microfilms.

The purity of initial and obtained compounds was checked by GLC on a chromatograph LKhM-80, detector katharometer, carrier gas helium, steel column 3000×3 mm, stetionary phase 3% OV-17 on INERTON SUPER (0.160–0.200 mm), ramp from 60 to 200°C at a rate 4 deg/min. In syntheses were used commercial oximes and vinyl glycidyl ether of purity no less than 96% (GLC).

O-[2-Hydroxy-3-(vinyloxy)propyl]oximes IIIa–IIId. *General procedure.* A mixture of 0.1 mol of oxime **IIa–IId**, 0.15 mol of vinyl glycidyl ether (**I**), and 0.003 mol of triethylamine was heated at 95–100°C for 4 h. Oximes **IIIa–IIId** were isolated by distillation.

O-[2-Hydroxy-3-(vinyloxy)propyl]acetaldoxime (IIIa). Yield 54%, bp 80–83°C (3 mm Hg.), d_4^{20} 1.0564, n_D^{20} 1.4615. IR spectrum, ν, cm^{-1}: 800, 880, 935, 945, 990, 1020, 1100, 1190, 1300, 1380, 1420, 1445, 1600, 1630, 2880, 2920, 3100, 3395. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): prevailing isomer (58 mol%), 1.85 d (3H, Me, ^3J 5.7), 3.22 br.s (1H, OH), 3.56–3.91 m (4H, $NOCH_2$, OCH_2), 3.99 d.d (1H, *cis*-CH=C, $^2J_{gem}$ 2.0, $^3J_{cis}$ 6.8), 4.06 m (1H, OCH), 4.18 d.d (1H, *trans*-CH=C, $^2J_{gem}$ 2.0, $^3J_{trans}$ 14.3), 6.44 d.d (1H, OCH=C, $^3J_{cis}$ 6.8, $^3J_{trans}$ 14.3), 7.41 q (1H, CH, ^3J 5.8); minor isomer (42 mol%), 1.85 d (3H, Me, ^3J 5.7), 3.22 br.s (1H, OH), 3.56–3.91 m (4H, $NOCH_2$, OCH_2), 3.99 d.d (1H, *cis*-CH=C, $^2J_{gem}$ 2.0, $^3J_{cis}$ 6.8), 4.06 m (1H, OCH), 4.18 d.d (1H, *trans*-CH=C, $^2J_{gem}$ 2.0, $^3J_{trans}$ 14.3), 6.43 d.d (1H, OCH=C, $^3J_{cis}$ 6.8, $^3J_{trans}$ 14.3), 6.75 q (1H, CH, ^3J 5.8). ^{13}C NMR spectrum, δ, ppm: prevailing isomer, 15.26 (CH_3), 68.85 (OCH_2), 69.57 (HOCH), 74.17 ($NOCH_2$), 87.11 (=CH_2), 147.17 (OCH=), 151.66 (NC), minor isomer, 11.96 (CH_3), 69.11 (OCH_2), 69.30 (HOCH), 74.40 ($NOCH_2$), 87.18 (=CH_2), 147.25 (OCH=), 151.58 (NC). Found, %: C 52.97; H 8.43; N 8.69. $C_7H_{13}NO_3$. Calculated, %: C 52.82; H 8.23; N 8.80.

O-[2-Hydroxy-3-(vinyloxy)propyl]acetone oxime (IIIb). Yield 65%, bp 70–72°C (2.5 mm pt. Ct.), d_4^{20} 1.0401, n_D^{20} 1.4638. IR spectrum, ν, cm^{-1}: 810, 875, 905, 945, 955, 1000, 1025, 1200, 1260, 1305, 1365, 1400, 1440, 1455, 1600, 1625, 2860, 2915, 3105, 3395. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.85 s (6H, 2Me), 3.54 br.s (1H, OH), 3.73 m (2H, OCH_2), 4.00 d.d (1H, *cis*-CH=C, $^2J_{gem}$ 1.9, $^3J_{cis}$ 6.8), 4.10 m (3H, $NOCH_2$, OCH), 4.21 d.d (1H, *trans*-CH=C, $^2J_{gem}$ 1.9, $^3J_{trans}$ 14.4), 6.46 d.d (1H, OCH=C, $^3J_{cis}$ 6.8, $^3J_{trans}$ 14.3). ^{13}C NMR spectrum, δ, ppm: 15.37 (CH_3-*syn*), 21.76 (CH_3-*anti*), 68.86, 68.99 ($NOCH_2$), 69.49 (OCH_2), 73.69 (OCH), 86.76, 86.92 (=CH_2), 151.56 (OCH=), 155.38 (NC). Found, %: C 55.35; H 8.79; N 8.01. $C_8H_{15}NO_3$. Calculated, %: C 55.47; H 8.73; N 8.09.

O-[2-Hydroxy-3-(vinyloxy)propyl]acetophenone oxime (IIIc). Yield 72%, bp 145–147°C (3 mm Hg.), d_4^{20} 1.1052, n_D^{20} 1.5771. IR spectrum, ν, cm^{-1}: 550, 685, 750, 880, 915, 1030, 1100, 1140, 1190, 1300, 1360, 1400, 1440, 1495, 1565, 1600, 1625, 2865, 2920, 2975, 3050, 3075, 3100, 3410. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2,19 s (3H, Me), 3.48 br.s (1H, OH), 3.75 m (2H, OCH_2), 3.98 d.d (1H, *cis*-CH=C, $^2J_{gem}$ 1.6, $^3J_{cis}$ 6.7), 4,15–4.25 m (4H, *trans*-CH=C, OCH, $NOCH_2$), 6.45 d.d (1H, OCH=C, $^3J_{cis}$ 6.7, $^3J_{trans}$ 14.2), 7.29, 7.58 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 12.45 (CH_3), 63.44 (OCH_2), 68.81 ($NOCH_2$), 69.11 (OCH), 86.74 (=CH_2), 125.87 (C^2, C^6, Ph), 128.25 (C^3, C^5, Ph), 129.14 (C^4, Ph), 136.17 (C^1, Ph), 151.46 (OCH=), 155.39 (NC). Found, %: C

66.45; H 7.43; N 6.07. $C_{13}H_{17}NO_3$. Calculated, %: C 66.36; H 7.28; N 5.95.

O-[2-Hydroxy-3-(vinyloxy)propyl]cyclohexanone oxime (IIId). Yield 68%, bp 128–131°C (3 mm Hg.), d_4^{20} 1.0716, n_D^{20} 1.4922. IR spectrum, ν, cm^{-1}: 520, 695, 775, 815, 860, 930, 985,1035, 1100, 1195, 1245, 1305, 1400, 1440, 1600, 1625, 2850, 2915, 3105, 3400. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.63, 2.15, 2.45 m (10H, C_5H_{10}), 3.52 br.s (1H, OH), 3.73 m (2H, OCH_2), 4.00 d.d (1H, *cis*-CH=C, $^2J_{gem}$ 1.8, $^3J_{cis}$ 6.7), 4.20 d.d (1H, *trans*-CH=C, $^2J_{gem}$ 1.8, $^3J_{trans}$ 14.3), 4.10 m (3H, $NOCH_2$, OCH), 6.47 d.d (1H, OCH=C, $^3J_{cis}$ 6.7, $^3J_{trans}$ 14.3). ^{13}C NMR spectrum, δ, ppm: 25.04 (C^4), 25.54 (C^2 + C^6), 26.79, 31.96 (C^3, C^5), 68.81 ($NOCH_2$), 69.54 (OCH), 73.54 (OCH_2), 86.63(=CH_2), 151.54 (OCH=), 161.11 (NC). Found, %: C 62.01; H 8.91; N 6.62. $C_{11}H_{19}NO_3$. Calculated, %: C 61.95; H 8.98; N 6.57.

***O*-[(2-Methyl-1,3-dioxolan-4-yl)methyl]oximes IVa–IVd. General procedure.** To 0.05 mol of oxime **IIIa–IIId** was added at stirring 2 drops of concn. HCl. The reaction mixture self-heated to 45–55°C, then it was maintained for 2 h at 70°C, and oximes **IVa–IVd** were isolated by distillation in a vacuum.

***O*-[(2-Methyl-1,3-dioxolan-4-yl)methyl]acetaldoxime (IVa).** Yield 61%, bp 46–47°C (2.5 mm Hg.), d_4^{20} 1.0587, n_D^{20} 1.4419. IR spectrum, ν, cm^{-1}: 480, 650, 665, 720, 830, 905, 945, 1005, 1050, 1090, 1115, 1210, 1300, 1395, 1425, 1470, 1620, 2860, 2910, 2980. ^{1}H NMR spectrum, δ, ppm: 1.35 m (1.5H, Me), 1.38 m (1.5H, Me), 1.83 m (3H, MeCN), 3.42–4.38 m (5H, $NOCH_2CHCH_2O$), 5.02 m (0.5H, OCHO), 5.10 m (0.5H, OCHO), 6.75 m (0.5H, CH), 7.44 m (0.5H, CH). Found, %: C 52.71; H 8.19; N 8.67. $C_7H_{13}NO_3$. Calculated, %: C 52.82; H 8.23; N 8.80.

***O*-[(2-Methyl-1,3-dioxolan-4-yl)methyl]acetone oxime (IVb).** Yield 78%, bp 56–59°C (3 mm Hg.), d_4^{20} 1.0356, n_D^{20} 1.4449. IR spectrum, ν, cm^{-1}: 695, 815, 850, 925, 1035, 1065, 1100, 1145, 1205, 1270, 1360, 1400, 1445, 1625, 2875, 2920, 2980. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.32 m (3H, Me, ^3J 4.5), 1.88 m (6H, MeCMe), 3.61–4.30 m (5H, $NOCH_2CHCH_2O$), 4.97 q (0.5H, OCHO, ^3J 4.5), 5.08 q (0.5H, OCHO, ^3J 4.5). Found, %: C 55.31; H 8.68; N 8.11. $C_8H_{15}NO_3$. Calculated, %: C 55.47; H 8.73; N 8.09.

***O*-[(2-Methyl-1,3-dioxolan-4-yl)methyl]acetophenone oxime (IVc).** Yield 88%, bp 121–124°C (2 mm Hg.), d_4^{20} 1.1043, n_D^{20} 1.5278. IR spectrum, ν, cm^{-1}: 500, 545, 620, 675, 745, 860, 910, 1015, 1190, 1120, 1200, 1250, 1300, 1350, 1395, 1425, 1460, 1485, 1560, 1595, 1600, 1680, 2850, 2905, 2980, 3000, 3040, 3065. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): prevailing diastereomer (63 mol%), 1.36 m (3H, Me, ^3J 4.7), 2.18 s (3H, C$\underline{H}_3$CN), 3.65–4.40 m (5H, $NOCH_2CHCH_2O$), 4.99 q (1H, OCHO, ^3J 4.7), 7.28, 7.58 m (5H, Ph); minor diastereomer (37 mol%), 1.33 m (3H, Me, ^3J 4.7), 2.05 c (3H, C$\underline{H}_3$CN), 3.65–4.40 m (5H, $NOCH_2CHCH_2O$), 5.10 q (1H, OCHO, ^3J 4.7), 7.28, 7.58 m (5H, Ph). ^{13}C NMR spectrum, δ, ppm: 12.29, 12.34 ($\underline{C}H_3C$=N), 19.64, 19.72 (CH_3), 67.30, 67.41 ($NOCH_2$), 73.91, 74.32 (OCH_2), 74.10, 74.58 (OCH), 101.16, 101.74 (OCHO), 125.75 (C^2, C^6, Ph), 128.08 (C^3, C^5, Ph), 128.85 (C^4, Ph), 136.11 (C^1, Ph), 154.73, 154.81 (NC). Found, %: C 66.26; H 7.31; N 5.83. $C_{13}H_{17}NO_3$. Calculated, %: C 66.36; H 7.28; N 5.95.

***O*-[(2-Methyl-1,3-dioxolan-4-yl)methyl]cyclohexanone oxime (IVd).** Yield 73%, bp 127–130°C (6 mm Hg.), d_4^{20} 1.0596, n_D^{20} 1.4773. IR spectrum, ν, cm^{-1}: 665, 695, 780, 825, 860, 930, 990, 1100, 1040, 1145, 1210, 1255, 1315, 1345, 1400, 1450, 1630, 2850, 2920, 2985. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): prevailing diastereomer (60 mol%), 1.35 d (3H, Me, ^3J 4.8), 1.61, 2.15, 2.44 m (10H, C_5H_{10}), 3.80, 3.88 m (2H, OCH_2), 4.10 m (2H, $NOCH_2$), 4.28 m (1H, CHO), 5.01 q (1H, OCHO, ^3J 4.8); minor diastereomer (40 mol%), 1.33 d (3H, Me, ^3J 4.8), 1.61, 2.15, 2.44 m (10H, C_5H_{10}), 3.64, 3.80 m (2H, OCH_2), 3.98 m (2H, $NOCH_2$), 4.34 m (1H, CHO), 5.08 q (1H, OCHO, ^3J 4.8). ^{13}C NMR spectrum, δ, ppm: 20.68, 20.78 (CH_3), 26.07, 26.50, 26.59, 27.79, 32.84 (C^2, C^3, C^5, C^6); 68.30, 68.42 ($NOCH_2$), 74.27, 74.71 (OCH_2), 74.98, 75.40 (OCH), 102.16, 102.78 (OCHO), 161.31 (NC). Found, %: C 61.79; H 8.88; N 6.69. $C_{11}H_{19}NO_3$. Calculated, %: C 61.95; H 8.98; N 6.57.

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