

Condensation of 1-Alkylamino-3-(2-vinyloxyethoxy)propan-2-ols with Carbonyl Compounds

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Abstract—Condensation of 1-alkylamino-3-(2-vinyloxyethoxy)propan-2-ols with carbonyl compounds furnished 5-(2-vinyloxyethoxy)methyl-1,3-oxazolidines in 56–93% yield.

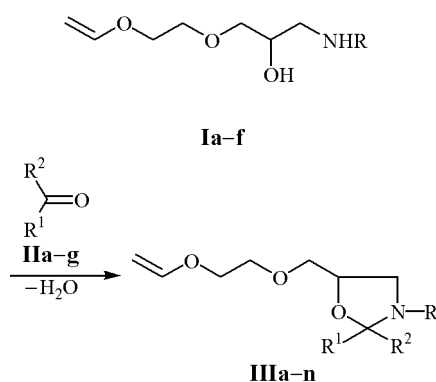
Aminoalcohol derivatives as vinyl ethers and cyclic O,N-acetals (1,3-oxazolidines) are widely used in organic synthesis, in manufacture of technically important products, and they possess a versatile physiological and biological activity [1]. A combination in a single molecule of a vinyloxy group and O,N-acetal moiety gives hope for extension both of synthetic prospects and biological activity range of these compounds. Only our short communication [2] was published up till now on the synthesis of several such substances.

We report now on the study of the effect of the carbonyl compound character and the nature of substituent attached to nitrogen in 1-alkylamino-3-(2-vinyloxyethoxy)propan-2-ols on the yield and structure of condensation products obtained therefrom.

The condensation of 1-alkylamino-3-(2-vinyloxyethoxy)propan-2-ols **Ia-f** with aldehydes and ketones **IIa-g** was carried out by heating at reflux of equimolar reagents mixtures in benzene with water removal by azeotropic distillation. Under these conditions in the most cases formed the expected oxazolidines **IIIa-l** in 56–93% yield. The lowest yields were obtained with cyclic ketones which alongside with condensation into oxazolidines partially underwent crotonic condensation as was proved by isolation of 2-cyclohexylidencyclohexanone from the reaction products of 3-(2-vinyloxyethoxy)-1-methylamino-2-propanol (**Ia**) with cyclohexanone.

With 1-*tert*-butyl-3-(2-vinyloxyethoxy)propan-2-ol (**Ic**) the desired oxazolidine was obtained only in condensation with formaldehyde. We failed to involve into reaction with aminoalcohol **Ic** isobutyraldehyde, salicylaldehyde or cyclohexanone even at the use of high-boiling solvents (toluene, *o*-xylene) and acid catalysts (*p*-toluenesulfonic acid, orthophosphoric

Scheme 1.



I, R = Me (**a**), Bu (**b**), *t*-Bu (**c**), CH₂CH₂OEt (**d**), CH₂CH₂OCH=CH₂ (**e**), CH₂CH₂CH₂OCH=CH₂ (**f**); **II**, R¹ = R² = H (**a**); R¹ = H, R² = *i*-Pr (**b**); R¹ = H, R² = Ph (**c**); R¹ = H, R² = *o*-HOC₅H₄ (**d**); R¹ + R² = (CH₂)₄ (**e**); R¹ + R² = (CH₂)₅ (**f**); R¹ + R² = (CH₂)₆ (**g**); **III**, R = Me, R¹ = R² = H (**a**); R = Bu, R¹ = R² = H (**b**); R = *t*-Bu, R¹ = R² = H (**c**); R = CH₂CH₂OEt, R¹ = R² = H (**d**); R = CH₂CH₂OCH=CH₂, R¹ = R² = H (**e**); R = CH₂CH₂CH₂OCH=CH₂, R¹ = R² = H (**f**); R = Me, R¹ = H, R² = *i*-Pr (**g**); R = Me, R¹ = H, R² = Ph (**h**); R = Me, R¹ = H, R² = *o*-HOC₆H₄ (**i**); R = Me, R¹ + R² = (CH₂)₄ (**j**); R = Me, R¹ + R² = (CH₂)₅ (**k**); R = Me, R¹ + R² = (CH₂)₆ (**l**).

acid). This behavior is apparently due to steric hindrances caused by the presence of the *tert*-butyl group attached to the nitrogen of the aminoalcohol.

We also revealed that the vinyloxyethoxy substituent present in the amino alcohol also caused significant steric hindrances. This fact underlies the high sensitivity of the reaction to the structure of carbonyl compound. For instance, we failed to carry out the condensation of 3-(2-vinyloxyethoxy)-1-methylamino-

Table 1. Yields, boiling points, density, molecular refractions, and elemental analyses of compounds synthesized **IIIa-1, VI**

Compd. no.	Yield, %	bp, °C (<i>p</i> , mm Hg)	d_4^{20}	n_D^{20}	Found, %			Formula	Calculated, %		
					C	H	N		C	H	N
IIIa	93	107–108 (4)	1.0400	1.4630	57.78	8.95	7.71	C ₉ H ₁₇ NO ₃	57.73	9.15	7.48
IIIb	81	152–155 (5)	0.9713	1.4605	62.17	10.21	6.03	C ₁₂ H ₂₃ NO ₃	62.85	10.11	6.11
IIIc	84	124.5–127 (2)	0.9843	1.4626	62.88	10.09	6.52	C ₁₂ H ₂₃ NO ₃	62.85	10.11	6.11
IIId	84	151–154 (3)	1.0356	1.4617	58.14	9.25	5.31	C ₁₂ H ₂₃ NO ₄	58.75	9.45	5.71
IIIe	91	156–158 (3)	1.0378	1.4780	59.76	8.87	5.69	C ₁₂ H ₂₁ NO ₄	59.23	8.70	5.75
IIIf	74	167–168 (4)	1.0277	1.4767	60.54	9.29	5.44	C ₁₃ H ₂₃ NO ₄	60.68	9.01	5.44
IIIg	88	178–180 (8)	1.0576	1.5135	67.54	8.25	5.10	C ₁₅ H ₂₁ NO ₃	68.42	8.04	5.32
IIIh	75	195–197 (3)	1.1379	1.5262	64.93	7.62	4.95	C ₁₅ H ₂₁ NO ₄	64.50	7.58	5.01
IIIi	70	112–114 (1)	0.9637	1.4553	62.32	9.96	6.09	C ₁₂ H ₂₃ NO ₃	62.85	10.11	6.11
IIIj	83	163–164 (3)	1.0206	1.4792	64.28	9.41	5.52	C ₁₃ H ₂₅ NO ₃	64.70	9.61	5.80
IIIk	85	154–156 (5)	1.0390	1.4820	65.68	9.74	5.46	C ₁₄ H ₂₅ NO ₃	65.85	9.87	5.49
IIIl	56	164–167 (3)	1.0089	1.4850	66.96	10.25	5.52	C ₁₅ H ₂₇ NO ₃	66.88	10.10	5.20
VI	99.99	–	1.1381	1.4975	55.76	8.45	8.15	C ₂₄ H ₄₅ N ₃ O ₉	55.47	8.73	8.09

2-propanol (**Ia**) with methyl isobutyl ketone and acetophenone even in the presence of the above-mentioned high-boiling solvents and acid catalysts, although these carbonyl compounds were known to readily react with *N*-methylaminoethanol in benzene without any catalyst [3].

In the course of condensation of 1-amino-3-(2-vinyloxyethoxy)propan-2-ol (**IV**) with formaldehyde the arising oxazolidine **V** readily underwent trimerization into triazine **VI** as was known to occur with the other oxazolidines prepared from formaldehyde and aminoalcohols possessing a primary amino group [4]. The attempt to isolate triazine **VI** by vacuum distillation led to its partial decomposition into oxazolidine **V** and to tarring. The product was distilled in a wide temperature range, 130–235°C (2 mm Hg), and just after distillation had n_D^{20} 1.4775 and d_4^{20} 1.0953. On storage the refractive index and density gradually increased and after standing for a month reached the following values: n_D^{20} 1.4940 and d_4^{20} 1.1202. If the

reaction mixture was not subjected to distillation, but the solvent was merely evaporated, the still residue had the following constants: n_D^{20} 1.4975 and d_4^{20} 1.1381 and contained according to ¹H NMR data virtually pure triazine **VI** in almost quantitative yield.

The yields of oxazolidines **IIIa-1**, triazine **VI**, and their physicochemical characteristics are compiled in Table 1. The structure of compounds synthesized is fully confirmed by the data of ¹H NMR and IR spectra presented respectively in tables 2 and 3.

The IR spectra of the compounds contain the absorption bands of the vinyloxy group at 1605–1640 [$\nu(\text{C}=\text{C})$], 3035–3110 [$\nu_{\text{as}}(\text{=CH}_2)$] and oxazolidine ring at 1030–1070, 1100–1110, 1180–1200 cm⁻¹. In the ¹H NMR spectra appear doublets of doublets with the chemical shifts 3.93–3.99, 4.05–4.27, and 6.45–6.47 ppm (coupling constants ³ J_{gem} 1.9–2.2, ³ J_{cis} 6.6–6.9, and ³ J_{trans} 14.0–14.3 Hz) belonging to the protons of the vinyloxy group, and also the signals

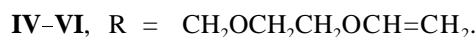
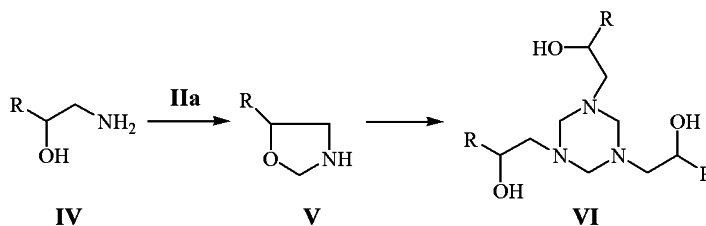
Scheme 2.

Table 2. ^1H NMR spectra of compounds synthesized **IIIa–I**, **VI**

Compd. no.	Chemical shifts, δ , ppm (J , Hz)
IIIa	2.38 s (3H, CH_3), 2.68–3.00 m (2H, NCH_2), 3.43–3.76 m (6H, $\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{O}$), 3.95 d.d (1H, <i>cis</i> - $\text{HC}=\text{CO}$, $^2J_{\text{gem}}$ 2.2, $^3J_{\text{cis}}$ 6.8), 4.05–4.24 m (4H, <i>trans</i> - $\text{HC}=\text{CO}$, CHOCH_2N), 6.46 d.d (1H, $\text{OCH}=\text{C}$, $^3J_{\text{cis}}$ 6.8, $^3J_{\text{trans}}$ 14.2)
IIIb	0.90 t (3H, CH_3), 1.39 m (4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.65–3.02 m (4H, $\text{CHCH}_2\text{NCH}_2\text{CH}_2$), 3.54–3.77 m (6H, $\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{O}$), 3.97–4.27 m (5H, $\text{OC}=\text{CH}_2$, CHOCH_2N), 6.45 d.d (1H, $\text{OCH}=\text{C}$, $^3J_{\text{cis}}$ 6.6, $^3J_{\text{trans}}$ 14.1)
IIIc	1.08 s (9H, 3CH_3), 2.67–3.06 m (2H, NCH_2), 3.54–3.77 m (6H, $\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{O}$), 3.96 d.d (1H, <i>cis</i> - $\text{HC}=\text{CO}$, $^2J_{\text{gem}}$ 2.0, $^3J_{\text{cis}}$ 6.7), 4.15 d.d (1H, <i>trans</i> - $\text{HC}=\text{CO}$, $^2J_{\text{gem}}$ 2.0, $^3J_{\text{trans}}$ 14.3), 4.17 m (1H, CHO), 4.37 d (1H, OCH_2N , $^2J_{\text{gem}}$ 3.3), 4.44 d (1H, OCH_2N , $^2J_{\text{gem}}$ 3.3), 6.46 d.d (1H, $\text{OCH}=\text{C}$, $^3J_{\text{cis}}$ 6.7, $^3J_{\text{trans}}$ 14.3)
IIId	1.18 t (3H, CH_3), 2.72–3.05 m (4H, $\text{CHCH}_2\text{NCH}_2\text{CH}_2$), 3.49–3.77 m (10H, $\text{NCH}_2\text{CH}_2\text{OCH}_2$, $\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{O}$), 3.96 d.d (1H, <i>cis</i> - $\text{HC}=\text{CO}$, $^2J_{\text{gem}}$ 2.1, $^3J_{\text{cis}}$ 6.8), 4.14 m (2H, <i>trans</i> - $\text{HC}=\text{CO}$, CHO), 4.33 s (2H, OCH_2N), 6.45 d.d (1H, $\text{OCH}=\text{C}$, $^3J_{\text{cis}}$ 6.8, $^3J_{\text{trans}}$ 14.2)
IIIe	2.62–3.01 m (4H, $\text{CHCH}_2\text{NCH}_2\text{CH}_2$), 3.54–3.83 m (8H, $\text{NCH}_2\text{CH}_2\text{O}$, $\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{O}$), 3.93–4.04 m (2H, <i>2cis</i> - $\text{HC}=\text{CO}$), 4.07–4.26 m (3H, <i>2trans</i> - $\text{HC}=\text{CO}$, CHO), 4.34 s (2H, OCH_2N), 6.46 m (2H, $2\text{OCH}=\text{C}$)
IIIf	1.80 m (2H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.59–3.09 m (4H, $\text{CHCH}_2\text{NCH}_2\text{CH}_2$), 3.53–3.80 m (8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{O}$, $\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{O}$), 3.96 m (2H, <i>2cis</i> - $\text{HC}=\text{CO}$), 4.07–4.25 m (3H, <i>2trans</i> - $\text{HC}=\text{CO}$, CHO), 4.28 s (2H, OCH_2N), 6.30–6.57 m (2H, $2\text{OCH}=\text{C}$)
IIIg	0.91 m [6H , $\text{CH}(\text{CH}_3)_2$], 1.66 m [1H, $\text{CH}(\text{CH}_3)_2$], 2.30 s (3H, NCH_3), 2.66–3.04 m (2H, NCH_2), 3.46–3.77 m (6H, $\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{O}$), 3.99–4.26 m (4H, $\text{H}_2\text{C}=\text{CO}$, CHOCHN), 6.47 d.d (1H, $\text{OCH}=\text{C}$, $^3J_{\text{cis}}$ 6.8, $^3J_{\text{trans}}$ 14.2)
IIIh	2.19 s (3H, CH_3), 2.65–2.99 m (2H, NCH_2), 3.60–3.79 m (6H, $\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{O}$), 3.98 d.d (1H, <i>cis</i> - $\text{HC}=\text{CO}$, $^2J_{\text{gem}}$ 2.2, $^3J_{\text{cis}}$ 6.9), 4.08–4.26 m (2H, <i>trans</i> - $\text{HC}=\text{CO}$, CHO), 4.59 s and 4.64 s (1H, OCHN), 6.47 d. d (1H, $\text{OCH}=\text{C}$, $^3J_{\text{cis}}$ 6.9, $^3J_{\text{trans}}$ 14.2), 7.35 m (5H, C_6H_5)
IIIi	2.34 s and 2.39 s (3H, CH_3), 2.60–2.91 m (2H, NCH_2), 3.33–3.78 m (6H, $\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{O}$), 3.99 m (1H, <i>cis</i> - $\text{HC}=\text{CO}$), 4.17 m (2H, <i>trans</i> - $\text{HC}=\text{CO}$, CHO), 4.75 s and 4.86 s (1H, OCHN), 4.98 s (1H, OH), 6.47 d.d (1H, $\text{OCH}=\text{C}$, $^3J_{\text{cis}}$ 6.8, $^3J_{\text{trans}}$ 14.2), 6.82–7.22 m (4H, C_6H_4)
IIIj	1.68 m (8H, C_4H_8), 2.33 s (3H, CH_3), 2.64–3.06 m (2H, NCH_2), 3.46–3.87 m (6H, $\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{O}$), 3.99 d.d (1H, <i>cis</i> - $\text{HC}=\text{CO}$, $^2J_{\text{gem}}$ 1.9, $^3J_{\text{cis}}$ 6.9), 4.07–4.26 m (2H, <i>trans</i> - $\text{HC}=\text{CO}$, CHO), 6.46 d.d (1H, $\text{OCH}=\text{C}$, $^3J_{\text{cis}}$ 6.9, $^3J_{\text{trans}}$ 14.1)
IIIk	1.53 m (10H, C_5H_{10}), 2.31 s (3H, CH_3), 2.74–3.04 m (2H, NCH_2), 3.52–3.77 m (6H, $\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{O}$), 3.96 d.d (1H, <i>cis</i> - $\text{HC}=\text{CO}$, $^2J_{\text{gem}}$ 2.2, $^3J_{\text{cis}}$ 6.6), 4.09–4.28 m (2H, <i>trans</i> - $\text{HC}=\text{CO}$, CHO), 6.47 d.d (1H, $\text{OCH}=\text{C}$, $^3J_{\text{cis}}$ 6.6, $^3J_{\text{trans}}$ 14.2)
IIIl	1.55–1.65 m (12H, C_6H_{12}), 2.31 s (3H, CH_3), 2.73–3.06 m (2H, NCH_2), 3.46–3.80 m (6H, $\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{O}$), 3.96 d.d (1H, <i>cis</i> - $\text{HC}=\text{CO}$, $^2J_{\text{gem}}$ 1.9, $^3J_{\text{cis}}$ 6.9), 4.07–4.25 m (2H, <i>trans</i> - $\text{HC}=\text{CO}$, CHO), 6.47 d.d (1H, $\text{OCH}=\text{C}$, $^3J_{\text{cis}}$ 6.9, $^3J_{\text{trans}}$ 14.0)
VI	2.69 m (2H, NCH_2CH), 3.52–3.76 m (6H, $\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{O}$), 3.95 d.d (1H, <i>cis</i> - $\text{HC}=\text{CO}$, $^2J_{\text{gem}}$ 2.1, $^3J_{\text{cis}}$ 6.8), 4.05–4.24 m (2H, <i>trans</i> - $\text{HC}=\text{CO}$, CHO), 4.29 s (2H, NCH_2N), 4.75 br. s (1H, OH), 6.46 d.d (1H, $\text{OCH}=\text{C}$, $^3J_{\text{cis}}$ 6.8, $^3J_{\text{trans}}$ 14.2)

from acetal protons of the oxazolidine ring at 4.18–4.86 ppm.

Compounds **IIIg–i** are mixtures of *cis*- and *trans*-isomers. According to the integral intensities of protons in NCH_3 and NHCO groups both isomers in compounds **IIIh**, **i** are present in equal amounts. We failed to unambiguously establish the isomers ratio in compound **IIIg** for the proton signal from the NCH_3 group was a singlet, the proton signals of NCHO and vinyloxy groups were overlapped, and the protons of methyls from the isopropyl group appeared as multiplet due to their diastereotopicity.

The primary screening of compounds synthesized revealed high algicidal activity of oxazolidines **IIIa**, **i**, **k**.

EXPERIMENTAL

IR spectra were recorded on spectrophotometer Specord 75IR from thin films. ^1H NMR spectra were registered on spectrometer Jeol FX 90Q (90 MHz) in CDCl_3 with HMDS as internal reference at 27°C.

5-(2-Vinyloxyethoxy)methyl-1,3-oxazolidines IIIa–l. A mixture of 0.1 mol of vinyloxyalkylamine

Table 3. Data of IR spectra of compounds synthesized **IIIa-I**

Compd. no.	IR spectrum, ν , cm^{-1}
IIIa	590, 655, 685, 700, 800, 875, 950, 995, 1030, 1060, 1110, 1185, 1225, 1270, 1300, 1345, 1360, 1400, 1440, 1605, 1615, 1640, 2845–2930, 3035, 3100
IIIb	680, 720, 800, 875, 950, 960, 1030, 1070, 1120, 1190, 1225, 1300, 1345, 1360, 1440, 1605, 1620, 1640, 2820, 2860, 2920, 2945, 3035, 3110
IIIc	600, 695, 730, 815, 820, 840, 885, 940, 960, 970, 1040, 1090, 1120, 1195, 1245, 1315, 1360, 1390, 1460, 1470, 1610, 1630, 2820, 2865, 2900, 2920, 2955, 3000, 3040, 3115
III d	810, 875, 940, 960, 1035, 1070, 1115, 1190, 1235, 1310, 1340, 1370, 1450, 1610, 1630, 1640, 2810, 2850, 2870, 2920, 2970, 3110
IIIe	595, 690, 815, 885, 960, 1015, 1070, 1090, 1120, 1195, 1255, 1290, 1320, 1355, 1450, 1615, 1630, 2820, 2865, 2910, 3035, 3110
III f	685, 810, 880, 960, 965, 1030, 1070, 1125, 1185, 1305, 1350, 1365, 1440, 1605, 1620, 1640, 2810, 2865, 2920, 2935, 3040, 3110
III g	525, 550, 600, 630, 675, 685, 725, 805, 865, 895, 925, 955, 975, 1045, 1075, 1125, 1175, 1195, 1250, 1290, 1310, 1355, 1380, 1410, 1450, 1460, 1605, 1630, 2860–2955, 3040, 3110
III h	510, 600, 620, 680, 740, 800, 830, 895, 910, 935, 960, 1000, 1040, 1070, 1120, 1155, 1190, 1220, 1275, 1300, 1360, 1405, 1440, 1480, 1605, 1620, 2835, 2860, 2910, 2930, 3020, 3055, 3075, 3105
III i	510, 525, 555, 615, 645, 695, 760, 815, 880, 970, 980, 1040, 1085, 1140, 1180, 1200, 1270, 1325, 1370, 1390, 1460, 1475, 1505, 1595, 1605, 1620, 1640, 2865, 2905, 2920, 2935, 3040, 3115
III j	600, 690, 810, 955, 960, 1030, 1080, 1120, 1190, 1240, 1310, 1440, 1460, 1610, 1625, 1640, 2865, 2910, 2950, 3040, 3110
III k	490, 540, 585, 600, 630, 690, 720, 765, 800, 840, 885, 900, 940, 970, 985, 1025, 1050, 1100, 1115, 1175, 1195, 1245, 1270, 1305, 1355, 1430, 1605, 1625, 2855, 2925, 3040, 3115
III l	810, 835, 945, 959, 965, 990, 1050, 1080, 1123, 1195, 1235, 1280, 1315, 1360, 1450, 1610, 1630, 2850, 2860, 2910–2940, 3115

Ia-f, 0.11 mol of an appropriate aldehyde (paraformaldehyde was used in place of formaldehyde) or ketone **IIa-g**, and 100 ml of benzene was heated at reflux with a Dean-Stark trap till the end of water liberation. Products **IIIa-l** were isolated by distillation.

N, N', N''-[3-(2-vinyloxy)ethoxy-2-hydroxypropyl]perhydro-1,3,5-triazine (VI). A mixture of 6.12 g (0.1 mol) of 1-amino-3-(2-vinyloxyethoxy)propan-2-ol (**IV**), 3.3 g (0.11 mol) of paraformaldehyde, and 100 ml of toluene was heated at reflux with a Dean-Stark trap till the end of water liberation. On evaporating the solvent from the reaction mixture at 80°C and 2 mm Hg triazine **VI** was obtained in 99.99% yield.

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