

N,N'-Bis(vinyloxyalkyl) Dicarboxamides

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Abstract—*N,N'*-Bis(vinyloxyalkyl)oxamides and *N,N'*-bis(vinyloxyalkyl)phthalamides were synthesized in 60–95% yield by reactions of vinyloxyalkylamines with diethyl oxalate and phthalimide, respectively.

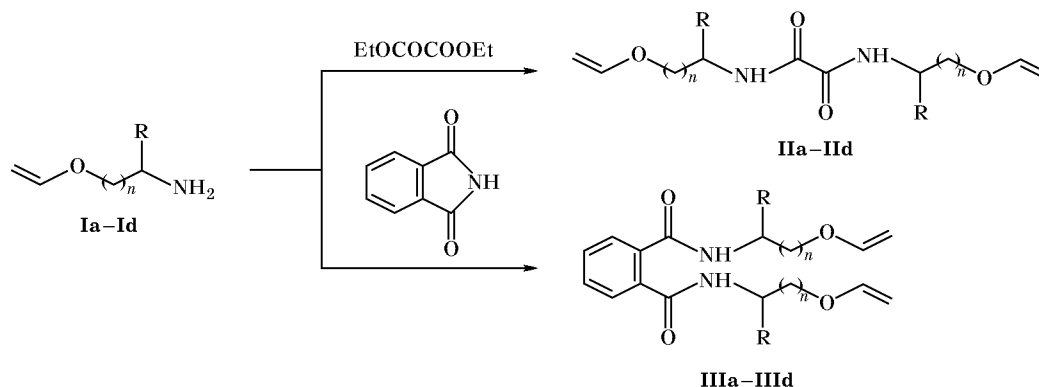
Vinyloxyalkylamides attract interest as intermediate products and monomers for the synthesis of compounds possessing biological activity and various other practically important properties [1, 2]. However, *N,N'*-bis(vinyloxyalkyl)amides derived from dicarboxylic acids remain poorly studied, although they are promising cross-linking agents and intermediate products in fine organic synthesis.

We previously reported on the synthesis of *N,N'*-bis(2-vinyloxyethyl)ureas and -thioureas from the corresponding urea derivatives and 2-vinyloxyethylamine [3]. Nedolya *et al.* [4] studied the reaction of 2-vinyloxyethyl isocyanate with C₃–C₁₀ dicarboxylic acids and found by ¹H NMR spectroscopy that this process is accompanied by formation of 5–8% of the corresponding *N,N'*-bis(2-vinyloxyethyl)amides. The goal of the present work was to obtain *N,N'*-bis(2-vinyloxyalkyl)oxamides and *N,N'*-bis(2-vinyloxyalkyl)phthalamides.

It is known that 2-vinyloxyethylamides readily undergo cyclization to 3-acyl-2-methyloxazolines on heating [5] or by the action of protic acids [6]. Therefore, it seemed reasonable to carry out the reaction under mild temperature conditions in a basic medium or with the use of weakly acidic reagents.

A well known procedure for preparation of carboxamides is based on the reaction of amines with esters. In such a way, 2-vinyloxyethylamides of monocarboxylic acids were obtained in 30–75% yield [1]. We thought it promising to synthesize *N,N'*-bis(vinyloxyalkyl)oxamides by reaction of diethyl oxalate with vinyloxyalkylamines. In fact, vinyloxyalkylamines **Ia–Id** very readily reacted with diethyl oxalate on mixing the reactants. The reactions were carried out with stoichiometric amounts of the reactants without a solvent at 25–30°C. The process was accompanied by heat evolution, and the yields of oxamides **IIa–IIId** were as high as 90–95% (Scheme 1).

Scheme 1.



I–III, $n = 1$, $R = \text{H}$ (**a**); $n = 2$, $R = \text{H}$ (**b**); $n = 3$, $R = \text{H}$ (**c**); $n = 1$, $R = \text{Et}$ (**d**).

Table 1. Yields, melting points, and elemental analyses of vinyloxyalkylamides **IIa–IIId** and **IIIa–IIId**

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
IIa	95.1	139–140	53.01	7.33	12.46	C ₁₀ H ₁₆ N ₂ O ₄	52.62	7.07	12.27
IIb	92.4	124–125	56.44	8.01	10.76	C ₁₂ H ₂₀ N ₂ O ₄	56.23	7.87	10.93
IIc	93.5	126–127	59.34	8.48	9.98	C ₁₄ H ₂₄ N ₂ O ₄	59.13	8.51	9.85
IIId	90.2	123–124	59.46	8.10	10.08	C ₁₄ H ₂₄ N ₂ O ₄	59.13	8.51	9.85
IIIa	69.2	78–79	63.21	6.36	9.90	C ₁₆ H ₂₀ N ₂ O ₄	63.14	6.62	9.20
IIIb	65.8	109–110	65.65	7.45	8.02	C ₁₈ H ₂₄ N ₂ O ₄	65.04	7.28	8.43
IIIc	68.6	124–125	66.78	7.51	7.62	C ₂₀ H ₂₈ N ₂ O ₄	66.64	7.83	7.77
IIId	60.3	127–128	66.53	7.81	7.26	C ₂₀ H ₂₈ N ₂ O ₄	66.64	7.83	7.77

Table 2. IR spectra of vinyloxyalkylamides **IIa–IIId** and **IIIa–IIId**

Comp. no.	Frequency ν , cm ⁻¹
IIa	545, 600, 745, 760, 805, 830, 950, 975, 1015, 1060, 1110, 1200, 1245, 1275, 1315, 1350, 1370, 1425, 1450, 1535, 1605, 1650, 2875, 2940, 2975, 3075, 3110, 3290
IIb	540, 660, 740, 790, 830, 940, 980, 995, 1040, 1120, 1140, 1205, 1295, 1330, 1405, 1480, 1495, 1550, 1620, 1680, 2910, 2950, 2980, 3080, 3270
IIc	540, 595, 730, 760, 790, 830, 860, 920, 940, 970, 1020, 1070, 1080, 1120, 1195, 1200, 1220, 1270, 1295, 1310, 1345, 1370, 1430, 1460, 1530, 1600, 1635, 2860, 2900, 2930, 3050, 3100, 3270
IIId	540, 600, 740, 770, 795, 870, 900, 940, 980, 1030, 1080, 1130, 1185, 1220, 1270, 1300, 1370, 1395, 1420, 1450, 1510, 1600, 1635, 2860, 2915, 2950, 3050, 3100, 3260
IIIa	540, 595, 730, 760, 790, 830, 860, 920, 940, 970, 1020, 1070, 1080, 1120, 1195, 1200, 1220, 1270, 1295, 1310, 1345, 1370, 1430, 1460, 1530, 1600, 1635, 2860, 2900, 2930, 3050, 3100, 3270
IIIb	550, 610, 675, 720, 750, 800, 870, 900, 950, 995, 1030, 1050, 1070, 1100, 1140, 1185, 1250, 1300, 1390, 1430, 1450, 1530, 1600, 1650, 2865, 2920, 3070, 3150, 3250
IIIc	545, 620, 675, 720, 740, 780, 815, 855, 875, 970, 1055, 1095, 1130, 1190, 1210, 1270, 1310, 1340, 1380, 1415, 1445, 1470, 1495, 1550, 1600, 1640, 2880, 2935, 2960, 3070, 3290
IIId	550, 640, 715, 750, 770, 800, 820, 855, 875, 970, 995, 1055, 1085, 1150, 1205, 1280, 1315, 1335, 1400, 1470, 1550, 1605, 1620, 1670, 2880, 2945, 2980, 3080, 3270

N,N'-Bis(vinyloxyalkyl)phthalamides **IIIa–IIId** were synthesized by reaction of amines **Ia–Id** with phthalimide in benzene at room temperature, the amine being taken in excess (25 mol %). Under these conditions, the reaction was slow (~6 days), and amides **IIIa–IIId** were obtained in 60–69% yield.

Compounds **IIa–IIId** and **IIIa–IIId** are colorless crystalline substances which can be stored for a long time. Their ¹H NMR spectra lack signals from OCHN proton and methyl group, which are typical of cyclization products (oxazolidines) whose formation could be expected on the basis of published data [5, 6].

The yields, melting points, and analytical data of products **IIa–IIId** and **IIIa–IIId** are given in Table 1. Their structure was confirmed by the IR and ¹H NMR spectra (Tables 2, 3). In the IR spectra of **IIa–IIId** and **IIIa–IIId** we observed absorption bands at 1510–1550 (δ NH), 1600–1620 (C=C), 1635–1680 (C=O), 3050–3110 (=CH₂, asym.), and 3250–3290 cm⁻¹ (NH). Protons of the vinyloxy group give rise to three doublets of doublets in the ¹H NMR spectra, δ , ppm: 3.95–4.05 (*cis*-H), 4.08–4.20 (*trans*-H), 6.39–6.46 (OCH) (²*J* = 1.8–2.3, ³*J*_{*cis*} = 6.6–6.8, ³*J*_{*trans*} = 13.8–14.4 Hz).

Table 3. ^1H NMR spectra of vinyloxyalkylamides **IIa–IIId** and **IIIa–IIIId**

Comp. no.	Chemical shifts δ , ppm (J , Hz)
IIa	3.62 d.t (4H, NCH_2 , $^3J = 5.2$, $^3J_{\text{CH}_2\text{NH}} = 5.6$), 3.77 t (4H, OCH_2 , $^3J = 5.2$), 4.05 d.d (2H, <i>cis</i> -H, $^2J = 2.3$, $^3J_{\text{cis}} = 6.8$), 4.15 d.d (2H, <i>trans</i> -H, $^2J = 2.3$, $^3J_{\text{trans}} = 14.3$), 6.44 d.d (2H, OCH, $^3J_{\text{cis}} = 6.8$, $^3J_{\text{trans}} = 14.3$), 7.81 br.s (2H, NH)
IIb	1.92 m (4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.44 d.t (4H, NCH_2 , $^3J = 5.7$, $^3J_{\text{CH}_2\text{NH}} = 6.4$), 3.74 t (4H, OCH_2 , $^3J = 5.7$), (2H, <i>cis</i> -H, $^2J = 1.8$, $^3J_{\text{cis}} = 6.8$), 4.17 d.d (2H, <i>trans</i> -H, $^2J = 1.8$, $^3J_{\text{trans}} = 14.4$), 6.44 d.d (2H, OCH, $^3J_{\text{cis}} = 6.8$, $^3J_{\text{trans}} = 14.4$), 7.71 br.s (2H, NH)
IIc	1.67 m (8H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 3.33 d.t (4H, NCH_2 , $^3J = 5.5$, $^3J_{\text{CH}_2\text{NH}} = 6.4$), 3.67 t (4H, OCH_2 , $^3J = 5.5$), 3.96 d.d (2H, <i>cis</i> -H, $^2J = 2.0$, $^3J_{\text{cis}} = 6.7$), 4.08 d.d (2H, <i>trans</i> -H, $^2J = 2.0$, $^3J_{\text{trans}} = 14.1$), 6.43 d.d (2H, OCH, $^3J_{\text{cis}} = 6.7$, $^3J_{\text{trans}} = 14.1$), 7.58 br.s (2H, NH)
IIId	0.93 t (6H, CH_3), 1.63 m (4H, $\text{NCHCH}_2\text{CH}_3$), 3.72–3.98 m (6H, NCH, OCH_2), 3.99 d.d (2H, <i>cis</i> -H, $^2J = 1.9$, $^3J_{\text{cis}} = 6.6$), 4.15 d.d (2H, <i>trans</i> -H, $^2J = 1.9$, $^3J_{\text{trans}} = 14.2$), 6.44 d.d (2H, OCH, $^3J_{\text{cis}} = 6.6$, $^3J_{\text{trans}} = 14.2$), 7.55 br.s (2H, NH)
IIIa	3.65–3.80 m (8H, $\text{NCH}_2\text{CH}_2\text{O}$), 4.03 d.d (2H, <i>cis</i> -H, $^2J = 2.2$, $^3J_{\text{cis}} = 6.8$), 4.20 d.d (2H, <i>trans</i> -H, $^2J = 2.2$, $^3J_{\text{trans}} = 14.3$), 6.46 d.d (2H, OCH, $^3J_{\text{cis}} = 6.8$, $^3J_{\text{trans}} = 14.3$), 6.95 br.s (2H, NH), 7.49 m (4H, C_6H_4)
IIIb	2.02 m (4H, $2\text{CH}_2\text{CH}_2\text{CH}_2$), 3.65–3.85 m (8H, NCH_2 , OCH_2), 3.95 d.d (2H, <i>cis</i> -H, $^2J = 2.0$, $^3J_{\text{cis}} = 6.7$), 4.17 d.d (2H, <i>trans</i> -H, $^2J = 2.0$, $^3J_{\text{trans}} = 14.0$), 6.39 d.d (2H, OCH, $^3J_{\text{cis}} = 6.7$, $^3J_{\text{trans}} = 14.0$), 7.10 br.s (2H, NH), 7.75 m (4H, C_6H_4)
IIIc	1.71 m (8H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 3.55–3.80 m (8H, NCH_2 , OCH_2), 3.96 d.d (2H, <i>cis</i> -H, $^2J = 1.8$, $^3J_{\text{cis}} = 6.6$), 4.14 d.d (2H, <i>trans</i> -H, $^2J = 1.8$, $^3J_{\text{trans}} = 13.8$), 6.41 d.d (2H, OCH, $^3J_{\text{cis}} = 6.6$, $^3J_{\text{trans}} = 13.8$), 7.04 br.s (2H, NH), 7.76 m (4H, C_6H_4)
IIIId	0.98 t (6H, CH_3), 1.64 m (4H, CHCH_2CH_3), 3.77–4.05 m (8H, OCH_2 , NCH, <i>cis</i> -H), 4.19 d.d (2H, <i>trans</i> -H, $^2J = 1.9$, $^3J_{\text{trans}} = 14.1$), 6.44 d.d (2H, OCH, $^3J_{\text{cis}} = 6.7$, $^3J_{\text{trans}} = 14.1$), 7.06 br.s (2H, NH), 7.59 m (4H, C_6H_4)

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer from samples pelleted with KBr. The ^1H NMR spectra were obtained on a Jeol FX 90Q instrument (90 MHz) in CDCl_3 at 27°C using HMDS as internal reference. Commercial diethyl oxalate and phthalimide were used. Vinyloxyalkylamines **Ia–Id** were prepared by vinylation of the corresponding amino alcohols with acetylene, following a procedure analogous to that reported in [7].

N,N'-Bis(vinyloxyalkyl)oxamides **IIa–IIId** (typical procedure). Vinyloxyalkylamine **Ia–Id**, 0.2 mol, was added with stirring to 0.1 mol of diethyl oxalate at such a rate that the temperature did not exceed 30°C. After cooling to room temperature, the mixture solidified and was recrystallized from ethanol.

N,N'-Bis(vinyloxyalkyl)phthalamides **IIIa–IIIId** (typical procedure). A mixture of 0.01 mol of phthalimide, 0.025 mol of vinyloxyalkylamine **Ia–Id**, and 40 ml of benzene was stirred at room temperature until it became homogeneous (~6 days). The solvent was evaporated, and the precipitate was purified by recrystallization from ethanol.

REFERENCES

- Kukharev, B.F., Stankevich, V.K., and Klimenko, G.R., *Usp. Khim.*, 1995, vol. 64, no. 6, p. 562.
- Amosova, S.V., Antsiferova, L.I., Shaulina, L.P., Golentovskaya, N.P., Toryashinova, D.-S.D., and Kustova, S.A., *Zh. Prikl. Khim.*, 2001, vol. 74, no. 1, p. 39.
- Lavrov, V.I., Parshina, L.N., Nedolya, N.A., Papsheva, N.P., Stankevich, V.K., and Kukharev, B.F., *Zh. Org. Khim.*, 1990, vol. 26, no. 2, p. 259.
- Nedolya, N.A., Tolmachev, S.V., and Zinov'eva, V.P., *Russ. J. Org. Chem.*, 2001, vol. 37, no. 8, p. 1074.
- Nedolya, N.A., Gerasimova, V.V., and Trofimov, B.A., *Sulfur Lett.*, 1991, vol. 13, no. 5, p. 203; Nedolya, N.A., Gerasimova, V.V., and Trofimov, B.A., *Zh. Org. Khim.*, 1992, vol. 28, no. 1, p. 8.
- Tarasova, O.A., Trofimov, B.A., Al'pert, M.L., Ivanova, N.I., Amosova, S.V., and Voronkov, M.G., *Zh. Org. Khim.*, 1981, vol. 17, no. 12, p. 2628; Nedolya, N.A., Dymchenko, V.I., and Sinitsina, L.E., *Zh. Org. Khim.*, 1994, vol. 30, no. 4, p. 503.
- US Patent no. 2969395, 1961; *Ref. Zh., Khim.*, 1962, no. 8L64.