

Table 1. Yields, melting or boiling points, and elemental analyses of oxazolidines **Ia–Ie**, **IIb**, **IIIb–IIIe**, and **IV**

Comp. no.	Yield, %	mp, °C, or bp, °C (<i>p</i> , mm)	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
Ia	90	140–143 (1.0–1.2)	44.77	7.16	–	C ₈ H ₁₅ N ₃ O ₄	44.23	6.96	–
Ib	85	165–166 (0.9–1.1)	37.67	6.80	21.98	C ₆ H ₁₃ N ₃ O ₄	37.69	6.85	21.98
Ic	90	52 153–155 (0.8–1.0)	41.18	7.47	20.69	C ₇ H ₁₅ N ₃ O ₄	40.97	7.37	20.48
Id	90	109–111 (0.9–1.1)	47.85	8.46	20.35	C ₈ H ₁₈ N ₃ O ₃	47.28	8.43	20.67
Ie	72 ^a	93–94 (0.8–1.0)	–	–	20.84	C ₅ H ₁₁ N ₃ O ₃ ^b	–	–	21.26
IIb	87	30–31 108–109 (0.7–0.9)	19.34	2.90	10.97	C ₄ H ₇ IN ₂ O ₃	18.62	2.73	10.86
IIIb	77	58.5–59.5	26.09	4.00	25.73	C ₆ H ₁₁ N ₅ O ₈	25.63	3.94	24.91
IIIc	91	95.5–96.5	28.50	4.47	24.00	C ₇ H ₁₃ N ₅ O ₈	28.48	4.44	23.72
IIId	70	Oily substance	–	–	22.77	C ₈ H ₁₇ N ₄ O ₅	–	–	22.57
IIIe	30 67 ^a	110–111 162–163 (0.8–1.0) ^c	29.82	5.02	27.18	C ₅ H ₁₀ N ₄ O ₅	29.13	4.89	27.18
IV	71	Oily substance	–	–	21.76	C ₄ H ₇ N ₃ O ₆	–	–	21.76

^a From **IIb**.

^b The data of elemental analysis are given for the corresponding hydrochloride, mp 128–130°C.

^c Decomposes during distillation.

iodide **IIb** gave 67% of compound **IIIe** which was identical to the product obtained by nitration of **Ie**. It should be emphasized that methyl-*N*-nitroamine anion adds mainly through its nitrogen atom. Treatment of compound **IIb** with silver nitrate led to formation of 3-nitro-5-nitroxymethyloxazolidine (**IV**) in 71% yield (Scheme 4).

Thus we have developed a general procedure for synthesizing functionally substituted 5-(alkylamino-methyl)-3-nitrooxazolidines **I** and 5-(alkyl-*N*-nitroaminomethyl)-3-nitrooxazolidines **III** based thereon, starting from 5-halomethyl-3-nitrooxazolidines **II**.

EXPERIMENTAL

The ¹H NMR spectra were recorded on Bruker WM-250 (250.13 MHz) and Bruker AM-300 instruments (300.13 MHz, compound **IIb**) in (CD₃)₂CO using HMDS as internal reference (Table 2).

5-(2-Hydroxyethylaminomethyl)-3-nitrooxazolidine (Ib). A solution of 3.4 g (20 mmol) of 5-chloromethyl-3-nitrooxazolidine (**IIa**) in 3.6 g (60 mmol) of 2-aminoethanol was heated for 5 h at 120–125°C, and the mixture was then evaporated under reduced pressure. The residue was dissolved in 50% ethanol, and the solution was adjusted to pH 12.1–12.3 (with

KOH) and evaporated under reduced pressure. The residue was treated with ethyl acetate (3 × 10 ml), the combined extracts were evaporated under reduced pressure, and the residue was subjected to fractional distillation. Yield 3.23 g.

Compounds **Ia**, **Ic**, and **Id** were synthesized in a similar way.

5-Methylaminomethyl-3-nitrooxazolidine (Ie). Compound **IIb**, 5.06 g (19.6 mmol), was added to a solution of 3 g (100 mmol) of methylamine in 52.5 ml of acetonitrile. The mixture was heated for 38 h at 50–55°C in an ampule and was evaporated under reduced pressure. The residue was dissolved in 50% ethanol, and the solution was adjusted to pH 12.1–12.3 (KOH) and evaporated under reduced pressure. The residue was extracted with benzene (3 × 15 ml), the combined extracts were evaporated under reduced pressure, and the residue was subjected to fractional distillation. Yield 2.25 g.

5-Iodomethyl-3-nitrooxazolidine (IIb). A solution of 3.35 g (20.1 mmol) of compound **IIa** in 40 ml of DMF was heated to 85–90°C, 23 g (124 mmol) of NaI · 2H₂O was added, and the mixture was stirred for 15 h. It was then poured into 120 ml of water and extracted with benzene (4 × 25 ml), the combined extracts were washed with water (7 × 30 ml) and

Table 2. ^1H NMR spectra of compounds **Ia–Ie**, **Iib**, **IIIb–IIIe**, and **IV**

Comp. no.	Chemical shifts δ , ppm (J , Hz)
Ia	2.64 m (6H, CHCH_2N , CH_2NCH_2), 3.55 d.d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{CH}$, $J = -10.6$, 8.0], 3.72 m (4H, CH_2OCH_2 , $J = 4.3$, 4.3), 4.14 d.d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{CH}$, $J = -12.2$, 6.9], 4.56 m (1H, CHO), 5.14 d (1H, NCH_2O , $J = -6.4$), 5.46 d (1H, NCH_2O , $J = -6.4$)
Ib	2.80 m (2H, $\text{NCH}_2\text{CH}_2\text{OH}$), 3.00 m (2H, $\text{CHCH}_2\text{NCH}_2\text{CH}_2\text{OH}$), 3.60 d.d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{CH}$, $J = -11.0$, 6.0], 3.80 t (2H, $\text{NCH}_2\text{CH}_2\text{OH}$, $J = 5.5$), 4.10 d.d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{CH}$, $J = -11.0$, 5.5], 4.42 m (1H, CHO), 5.10 d (1H, NCH_2O , $J = -6.6$), 5.46 d (1H, NCH_2O , $J = -6.6$)
Ic	1.06 d (3H, CHCH_3 , $J = 4.1$), 2.55 m (2H, $\text{NCH}_2\text{CHCH}_3$), 2.85 m (2H, $\text{CH}_2\text{NCH}_2\text{CHCH}_3$), 3.72 m (2H, CHCH_3 , OCH_2NCH_2), 4.05 d.d (1H, OCH_2NCH_2 , $J = -7.7$, 4.6), 5.07 d (1H, NCH_2O , $J = -5.1$), 5.40 d (1H, NCH_2O , $J = -5.1$)
Id	0.87 t (3H, CH_2CH_3 , $J = 6.0$), 1.38 m (4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.62 t (2H, $\text{NCH}_2\text{CH}_2\text{CH}_2$, $J = 6.0$), 2.84 d (2H, $\text{CH}_2\text{NCH}_2\text{CH}_2$, $J = 3.0$), 3.76 d.d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{CH}$, $J = -9.5$, 6.0], 4.04 d.d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{CH}$, $J = -9.5$, 6.0], 4.40 m (1H, CHO), 5.07 d (1H, NCH_2O , $J = -5.4$), 5.41 d (1H, NCH_2O , $J = -5.4$)
Ie	2.41 s (3H, NCH_3), 2.82 d (2H, CH_2NCH_3 , $J = 5.1$), 3.75 d.d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{CH}$, $J = -10.2$, 8.5], 4.08 d.d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{CH}$, $J = -10.2$, 8.5], 4.43 m (1H, CHO), 5.12 d (1H, NCH_2O , $J = -6.8$), 5.45 d (1H, NCH_2O , $J = -6.8$)
Iib	3.50 m (2H, CH_2I), 3.72 d.d (1H, NCH_2CH , $J = -12.0$, 8.2), 4.23 d.d (1H, NCH_2CH , $J = -12.0$, 7.6), 4.43 m (1H, NCH_2CH), 5.21 d (1H, NCH_2O , $J = -7.1$), 5.50 d (1H, NCH_2O , $J = -7.1$)
IIIb	3.77 d.d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{CH}$, $J = -11.8$, 7.1], 4.30 m [5H, $\text{N}(\text{NO}_2)\text{CH}_2\text{CH}$, $\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{CH}_2$], 4.75 m (1H, CHO), 4.92 t (2H, CH_2ONO_2 , $J = 3.5$), 5.20 d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{O}$, $J = -7.1$], 5.50 d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{O}$, $J = -7.1$]
IIIc	1.42 d (3H, CH_3 , $J = 6.4$), 3.77 d.d [1H, $\text{OCH}_2\text{N}(\text{NO}_2)\text{CH}_2$, $J = -10.5$, 6.4], 4.22 m [5H, $\text{OCH}_2\text{N}(\text{NO}_2)\text{CH}_2$, $\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2\text{CHCH}_3$], 4.75 m (1H, CHO), 5.17 d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{O}$, $J = -5.1$], 5.45 d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{O}$, $J = -5.1$], 5.62 m (1H, CHONO_2)
IIIId	0.92 t (3H, CH_3 , $J = 7.0$), 1.20–1.70 m [4H, $\text{N}(\text{NO}_2)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$], 3.40–4.25 m [6H, $\text{OCH}_2\text{N}(\text{NO}_2)\text{CH}_2$, $\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2$], 4.75 m (1H, CHO), 5.17 d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{O}$, $J = -7.0$], 5.45 d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{O}$, $J = -7.0$]
IIIe	3.45 s (3H, CH_3), 3.78 d.d [1H, $\text{OCH}_2\text{N}(\text{NO}_2)\text{CH}_2$, $J = -12.1$, 7.3], 4.22 m [3H, $\text{OCH}_2\text{N}(\text{NO}_2)\text{CH}_2$, $\text{CH}_2\text{N}(\text{NO}_2)\text{CH}_2$], 4.75 m (1H, CHO), 5.20 d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{O}$, $J = -6.5$], 5.50 d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{O}$, $J = -6.5$]
IV	3.90 d.d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{CHO}$, $J = -12.6$, 8.1], 4.22 d.d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{CHO}$, $J = -12.6$, 8.1], 4.40 m (1H, CHO), 4.77 m (2H, CH_2ONO_2), 5.20 d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{O}$, $J = -6.8$], 5.45 d [1H, $\text{N}(\text{NO}_2)\text{CH}_2\text{O}$, $J = -6.8$]

evaporated under reduced pressure, and the residue was recrystallized from ether. Yield 4.53 g.

3-Nitro-5-(*N*-nitro-2-nitroxyethylaminomethyl)-oxazolidine (IIIb). 5-(2-Hydroxyethylaminomethyl)-3-nitrooxazolidine (**Ib**), 1.26 g (6.63 mmol), was added at 0°C to a mixture of 3.5 ml of 97% HNO_3 , 11.5 ml of Ac_2O , 3 ml of 2-nitropropane, and 0.12 g (1.78 mmol) of $\text{MeNH}_2 \cdot \text{HCl}$. The mixture was stirred for 40 min, poured into 50 ml of an ice–water mixture, and extracted with ethyl acetate (3 × 15 ml). The extract was washed with water and a solution of

sodium carbonate and evaporated under reduced pressure. The residue was recrystallized from ethanol. Yield 1.44 g.

Compounds **IIIc** and **IIIId** were synthesized in a similar way. Product **IIIId** was purified by vacuum sublimation at 120°C (1 mm).

5-(Methyl-*N*-nitroaminomethyl)-3-nitrooxazolidine (IIIe). Methyl-*N*-nitroamine, 0.5 g (6.58 mmol), was added to a solution of 1.29 g (5 mmol) of compound **Iib** and 0.70 g (6.58 mmol) of Na_2CO_3 in 15 ml of DMF, heated to 85–90°C. The mixture was

stirred for 8 h, poured into 40 ml of water, and treated with benzene (4×10 ml). The extract was washed with water (7×10 ml) and evaporated under reduced pressure, and the residue was recrystallized from ethanol. Yield 0.69 g.

3-Nitro-5-(nitroxymethyl)oxazolidine (IV).

Silver nitrate, 1.40 g (8.24 mmol), was added to a solution of 1 g (3.88 mmol) of compound **Ib** in 10 ml of DMF, heated to 75–80°C, and the mixture was stirred for 1 h. It was then filtered from the precipitate

of AgI, and the filtrate was poured into 30 ml of water and extracted with benzene (5×10 ml). The extract was washed with water (7×15 ml) and evaporated under reduced pressure. Yield 0.53 g.

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