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SHORT COMMUNICATIONS

Synthesis of 4-Substituted N-Nitrooxazolidines

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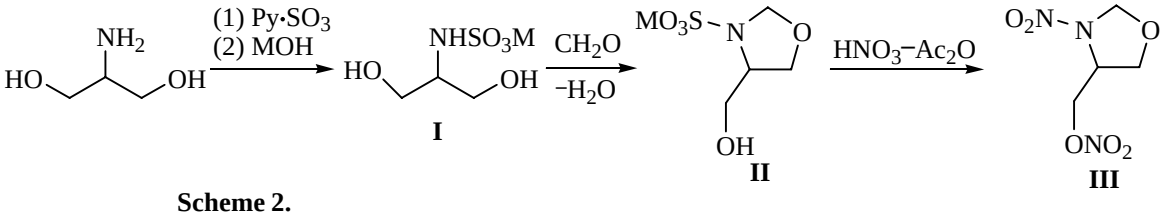
This study was performed in extension of systematic investigations on the synthesis and properties of *N*-nitrooxazolidines substituted in various positions [1, 2]. We showed formerly [1] that the condensation of β-hydroxyalkyl sulfamates with formaldehyde resulted in N-sulfo derivatives of oxazolidine, and the governing factor of this reaction was the pH of the environment. A subsequent nitration of N-sulfo derivatives of oxazolidine gave the corresponding 5-nitro-1,3-oxazolidine. Some compounds of this series are of interest as plasticizers of power-producing materials [3].

Inasmuch as the plasticizing ability of substances depended on their structure it was practical to synthesize other derivatives of 3-nitro-1,3-oxazolidine with substituents in various positions of the heterocycle, for instance, previously unknown 4-substituted *N*-nitrooxazolidines. We presumed that these compounds might be prepared based on the serinol sulfamate (**I**) we had synthesized. It was established that the optimum conditions for the condensation of serinol sulfamate (**I**) with formaldehyde leading to the formation of the oxazolidine ring was the pH of the medium 7.7–8.2 and temperature 110–115°C. Compound **II** thus obtained was not analyzed because of its hydrolytic instability, but was at once transformed into the corresponding 4-substituted *N*-nitrooxazolidine **III** by treating with a mixture HNO_3–Ac_2O (1:3 v/v) at –35...–30°C; the yield of nitronitrate **III** was 65% (Scheme 1).

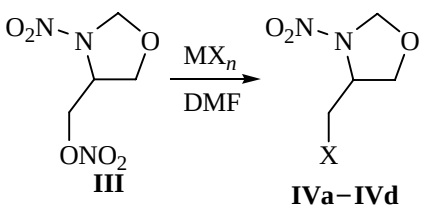
Compound **III** was further modified by a nucleophilic substitution of the nitroxy group by other substituents (Scheme 2). Yields of compounds **IVa–IVd** was ~60–90%.

The nitroxy group is significantly faster substituted by halogen at treating with calcium salts than with sodium halides presumably due to the stabilization with calcium of the transition state of the reaction.

Scheme 1.



Scheme 2.



X = SCN (**a**) M = NH_4^+; *n* = 1, N_3 (**b**) M = Na; *n* = 1, Cl (**c**) M = Ca, Na; *n* = 2,1, Br (**d**) M = Ca, Na; *n* = 2,1.

Potassium *N*-(1,3-dihydroxyisopropyl)sulfamate (I). To a solution of 6.60 g (73.33 mmol) of serinol in 10 ml of water was added 8.43 g (53.02 mmol) of $Py·SO_3$ at vigorous stirring and a temperature not exceeding 30°C, the mixture was thus maintained for 40 min, then also at cooling was added a solution of 4.20 g (75 mmol) of KOH in 7 ml of water, and the mixture was maintained for another 10 min. Then 33 ml of methanol was added,

the precipitated K_2SO_4 was filtered off, and the filtrate was evaporated. Yield 4.31 g. ^{1}H NMR spectrum (D_2O), δ, ppm: 3.53 m (1H, $CH_2C\underline{H}CH_2$), 3.87 m (4H, $C\underline{H}_2CHC\underline{H}_2$). Found %: C 16.91; H 3.84; N 6.69. $C_3H_8KNO_5S$. Calculated %: C 17.22; H 3.85; N 6.69.

3-Nitro-4-nitroxymethyl-1,3-oxazolidine(III). To a solution of 1.4 g (6.69 mmol) of salt **I** in 20 ml of water was added 0.87 g (12 mmol) of 32% aqueous formaldehyde. The pH of solution was adjusted at 8.1–8.3 (using water solutions of KOH or HCl respectively), and the solution was evaporated in a vacuum at 120–130°C. We obtained 1.38 g of 4-hydroxymethyl-3-sulfo-1,3-oxazolidine potassium salt (**II**).

To a mixture of 3 ml of 98% HNO_3 and 10 ml of acetic anhydride at –35...–30°C was added 1.00 g (4.5 mmol) of the sulfamate **II** obtained, the mixture was stirred for 30 min, then poured on 40 ml of ice and extracted with ethyl acetate (3×15 ml). The extract was washed with water (2×15 ml), with sodium carbonate (5×15 ml) till pH >11, and again with water (2×15 ml) till pH ~7, then the solution was evaporated in a vacuum at the temperature not exceeding 55°C. Yield 0.56 g (2.9 mmol) (64%), light yellow fluid. ^{1}H NMR spectrum (DMSO-d_6+CCl_4), δ, ppm (*J*, Hz): 3.96 d.d (1H, OCH_2N, *J* 13.85, 5.77), 4.26 d.d (1H, $OC\underline{H}_2CHN$, *J* 11.54, 10.39), 4.60 d.d (1H, CH_2ONO_2, *J* 12.69, 8.08), 4.81 m (2H, $OC\underline{H}_2CHN$; CH_2ONO_2), 5.15 d (1H, OCH_2N, *J* 11.54), 5,30 d (1H, OCH_2N, *J* 10.39). Found, %: C 25.47; H 3.74; N 21.20. $C_4H_7N_3O_6$. Calculated, %: C 24.88; H 3.65; N 21.76.

3-Nitro-4-thiocyanatomethyl-1,3-oxazolidine (IVa). To a solution of 1.85 g (9.6 mmol) of reagent **III** in 8 ml of DMF was added 1.37 g (18 mmol) of ammonium thiocyanate. The mixture was stirred for 40 h at 95–98°C, then poured into 25 ml of water, the precipitate was filtered off, washed with water on the filter, dried, and recrystallized from 30 ml of ethanol. Yield 0.78 g (43%), mp 94–95°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.36 d.d.d (2H, OCH_2CHN, *J* 14.86, 7.82), 4.06 d.d (1H, CH_2SCN, *J* 9.38, 5.47), 4.39 d.d (1H, CH_2SCN, *J* 11.34, 8.60), 4.78 m (1H, OCH_2CHN), 5.06 d (1H, OCH_2N, *J* 7.82), 5.54 d (1H, OCH_2N, *J* 7.82). Found, %: C 31.92; H 3.61; N 21.83. $C_5H_7N_3O_3S$. Calculated, %: C 31.74; H 3.73; N 22.21.

4-Azidomethyl-3-nitro-1,3-oxazolidine (IVb). To a solution of 1.00 g (5.2 mmol) of reagent **III** in 7 ml of DMF was added 0.67 g (10.3 mmol) of sodium azide and 1 g of $CaCl_2$. The mixture was stirred for 10 h at 95–98°C, then poured into 20 ml of water, extracted with benzene (3×13 ml), the extract was washed with water (7×8 ml) and evaporated in a vacuum at the temperature not exceeding 55°C. Yield 0.61 g (67%), yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.64 d.d.d (2H, OCH_2CHN, *J* 15.16, 4.55), 3.94 d.d (1H, CH_2N_3, *J* 8.34, 6.82), 4.24 d.d (1H, CH_2N_3, *J* 8.34, 6.82), 4.54 m (1H, OCH_2CHN), 4.94 d (1H, OCH_2N, *J* 7.58), 5.51 d (1H, OCH_2N, *J* 7.58). Found, %: C 27.56; H 3.87; N 40.99. $C_4H_7N_5O_3$. Calculated, %: C 27.75; H 4.08; N 40.45.

3-Nitro-4-chloromethyl-1,3-oxazolidine (IVc). To a solution of 0.34 g (1.76 mmol) of reagent **III** in 7 ml of DMF was added 1.17 g (10.54 mmol) of $CaCl_2$, the mixture was stirred for 10 h at 95–98°C, then poured into 20 ml of water, extracted with benzene (3×10 ml), the extract was washed with water (7×7 ml) and evaporated in a vacuum. Yield 0.27 g (92%), yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.70 d.d (1H, OCH_2CHN, *J* 10.28, 9.34), 3.83 d.d (1H, OCH_2CHN, *J* 10.97, 5.21), 4.07 d.d (1H, CH_2Cl, *J* 11.60, 8.90), 4.30 d.d (1H, CH_2Cl, *J* 12.05, 9.11), 4.63 m (1H, OCH_2CHN), 4.93 d (1H, OCH_2N, *J* 7.15), 5.50 d (1H, OCH_2N, *J* 7.15). Found, %: C 29.0; H 4.33; N 17.07. $C_4H_7ClN_2O_3$. Calculated, %: C 28.84; H 4.24; N 16.82.

4-Bromomethyl-3-nitro-1,3-oxazolidine (IVd) was similarly prepared. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 3.52 d.d (1H, OCH_2CHN, *J* 10.44, 8.42), 3.69 d.d (1H, OCH_2CHN, *J* 10.46, 3.55), 4.00 d.d (1H, CH_2Br, *J* 9.44, 6.01), 4.34 d.d (1H, CH_2Br, *J* 9.41, 6.88), 4.63 m (1H, OCH_2CHN), 4.97 d (1H, OCH_2N, *J* 6.38), 5.53 d (1H, OCH_2N, *J* 6.38). Found, %: C 23.26; H 3.45; N 14.0. $C_4H_7BrN_2O_3$. Calculated, %: C 22.77; H 3.34; N 13.28.

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