Synthesis of β-nitroxyalkylnitramines

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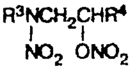
β-Nitroxyalkylnitramines were obtained by nitration of β-hydroxyalkyl sulfamates, products of the condensation of derivatives of sulfamic acid with alkene oxides, by a mixture of HNO_3 and H_2SO_4.

Key words: *N*-alkyl sulfamates; β-hydroxyalkyl sulfamates; β-nitroxyalkylnitramines.

Earlier,[1,2] β-hydroxyalkyl sulfamates (**1**) were obtained by the reaction of derivatives of sulfamic acid with alkene oxides (Scheme 1). In the present work, β-nitroxyalkylnitramines (**2**) were synthesized by nitration of β-hydroxyalkyl sulfamates **1**.

Only a few examples of the synthesis of nitramines from derivatives of sulfamic acid are known so far.[3–6] But this method has not been used to synthesize β-nitroxyalkylnitramines. The main method for the synthesis of these compounds is based on nitration of

Table 1. Characteristics of β-nitroxyalkylnitramines **2**



$\underset{NO_2}{R^3N}CH_2\underset{ONO_2}{CH}R^4$

Compound	R^3	R^4	Yield (%)	$\frac{\text{Found}}{\text{Calculated}}$ (%)			M.p./°C	^1H NMR, δ
				C	H	N		
2a	Me	H	91	—	—	—	40—41[7]	—
2b	Me	Me	94	—	—	—	22—23[7]	—
2c	Et	H	90	—	—	—	22—23[7]	—
2d	Et	Me	95	—	—	—	4—5[7]	—
2e	$CH_2CH_2ONO_2$	Me	55	$\frac{23.69}{23.62}$	$\frac{4.09}{3.96}$	—	Resin	1.41 (d, 3 H, Me); 4.28 (m, 4 H, 2 CH_2N); 4.82 (t, 2 H, CH_2O); 5.50 (m, 1 H, CHO)
2f	$(CH_2)_3ONO_2$	Me	60	$\frac{27.06}{26.86}$	$\frac{4.39}{4.53}$	—	Resin	1.39 (d, 3 H, Me); 2.15 (m, 2 H, CH_2); 4.00 (m, 4 H, 2 CH_2N); 4.60 (t, 2 H, CH_2O); 5.50 (m, 1 H, CHO)
2g	Me	CH_2ONO_2	92	$\frac{19.81}{20.05}$	$\frac{3.54}{3.35}$	—	35—36	3.52 (s, 3 H, Me); 4.20—4.80 (m, 2 H, NCH_2, 2 H, CH_2O); 5.66 (m, 1 H, CHO)
2h	Me	CH_2Cl	81	$\frac{22.78}{22.49}$	$\frac{3.66}{3.74}$	—	85—86	3.50 (s, 3 H, Me); 3.85 (m, 2 H, CH_2Cl); 4.30 (m, 2 H, NCH_2); 5.65 (m, 1 H, CHO)
2i	Et	CH_2Cl	80	$\frac{26.71}{26.38}$	$\frac{4.91}{4.43}$	—	60—62	1.30 (t, 3 H, Me); 3.80—4.20 (m, 6 H, 2 CH_2N, CH_2Cl); 5.65 (m, 1 H, CHO)
2j	Bu^n	Me	75	—	—	$\frac{18.64}{18.99}$	Resin	0.95 (t, 3 H, $C\underline{H}_3CH_2CH_2CH_2$); 1.30—1.80 (m, 7 H, Me, $CH_3C\underline{H}_2C\underline{H}_2CH_2$); 3.70—4.30 (m, 4 H, CH_2N);
2k	$CH_2CH_2ONO_2$	H	60	—	—	—	56[8]	5.60 (m, 1 H, CHO)

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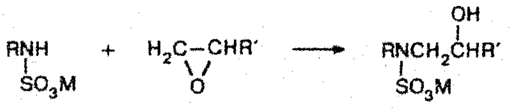
Scheme 1



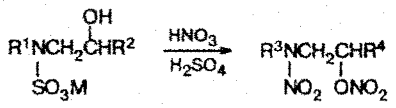
1

R = H, Alk, $(CH_2)_nOH$; R′ = H, Alk, CH_2OH, CH_2Cl;
M = K, Na, NH_4

β-hydroxyalkylamines by HNO_3—$(MeCO)_2O$ mixture in the presence of chloride ions.[7,8]

β-Hydroxyalkyl sulfamates **1** obtained according to the known procedures[1,2] were *O,N*-nitrated with HNO_3—H_2SO_4 mixtures at −5 to −15 °C for 30—60 min (Scheme 2). Products **2** were isolated in 55—95% yields (Table 1).

Scheme 2



1a—k **2a—k**

1: R^1, R^2 = Me, H (**a**); Me, Me (**b**); Et, H (**c**); Et, Me (**d**); $HOCH_2CH_2$, Me (**e**); $HOCH_2CH_2CH_2$, Me (**f**); Me, CH_2OH (**g**); Me, CH_2Cl (**h**); Et, CH_2Cl (**i**); Bu^n, Me (**j**); $HOCH_2CH_2$, H (**k**); M = K, Na

2: R^3, R^4 = Me, H (**a**); Me, Me (**b**); Et, H (**c**); Et, Me (**d**); $O_2NOCH_2CH_2$, Me (**e**); $ONO_2CH_2CH_2CH_2$, Me (**f**); Me, CH_2ONO_2 (**g**); Me, CH_2Cl (**h**); Et, CH_2Cl (**i**); Bu^n, Me (**j**); $O_2NOCH_2CH_2$, H (**k**)

Experimental

^1H NMR spectra were recorded on a Bruker WM-250 instrument (250 MHz) in acetone-d_6 with HMDS as the internal standard.

***N*-Methyl-*N*-β-nitroxyethylnitramine (2a).** Potassium *N*-β-hydroxyethyl-*N*-methylsulfamate (3.67 g) was added to a mixture of 7 mL of HNO_3 (d = 1.51 g cm^{-3}) and 5 mL of H_2SO_4 (d = 1.83 g cm^{-3}) at −10 to −15 °C. The reaction mixture was stirred for 40 min, poured out into a mixture of 30 mL of water and ice, and extracted with ethyl acetate (3×10 mL). The extract was washed successively with water (1×10 mL), a solution of sodium carbonate (2×10 mL), and water (1×10 mL) and then concentrated. *N*-Methyl-*N*-β-nitroxyethylnitramine (1.52 g, 91%) was obtained, m.p. 40—41 °C (*cf.* Ref. 7).

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