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Synthesis of β-nitramino derivatives of *gem*-dinitroalkanes

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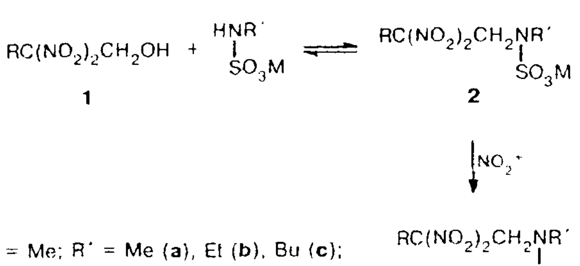
A method for the synthesis of β-nitramino derivatives of *gem*-dinitroalkanes by nitration of the products of condensation of sulfamic acid derivatives with the corresponding *gem*-dinitroalkanes was proposed.

Key words: *gem*-dinitroalkanes, formaldehyde, *N*-alkylsulfamates.

β-Nitramino derivatives of *gem*-dinitroalkanes can be synthesized in various ways. The main way includes reaction of *gem*-dinitroalkanes with amines and formaldehyde with subsequent nitration of the resulting Mannich bases.[1] The chief drawback to this scheme is the low stability of nonnitrated Mannich bases, which significantly reduces the yield of the final products.

Apparently, Mannich bases would be more stable when their amine component is replaced by the amide one. As the latter, we used derivatives of sulfamic acid because they are relatively easily available and their sulfamate group is readily transformed into a nitramino group.[2,3]

Dinitromethane, 1,1-*gem*-dinitroethane, and 1,1-*gem*-dinitropropane were selected as the initial dinitroalkanes. However, 1,1-*gem*-dinitroethane hardly reacted with potassium *N*-methylsulfamate and formaldehyde in aqueous alcoholic media. Much better results were obtained with *gem*-dinitroalkanols **1** as the starting compounds, which had been derived from *gem*-dinitroalkanes by hydroxymethylation.



$$\underset{\mathbf{1}}{RC(NO_2)_2CH_2OH} + \underset{SO_3M}{\overset{\displaystyle HNR'}{|}} \rightleftharpoons \underset{\mathbf{2}}{RC(NO_2)_2CH_2\underset{SO_3M}{NR'}} \xrightarrow{NO_2^+} \underset{\mathbf{3a-e}}{RC(NO_2)_2CH_2\underset{NO_2}{NR'}}$$

R = Me; R' = Me (**a**), Et (**b**), Bu (**c**);
R = Et; R' = Me (**d**), Et (**e**);
M = K, Na

As expected, condensation of compounds **1** with potassium or sodium *N*-methylsulfamate was a pH- and temperature-dependent reaction. The optimum pH value was found to be ~4.5—5.0. The condensation was terminated after forced removal of water to give products **2** in

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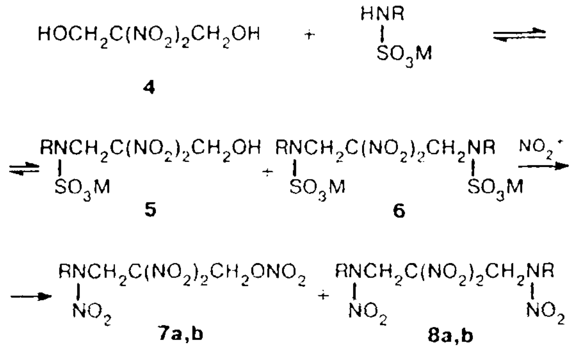
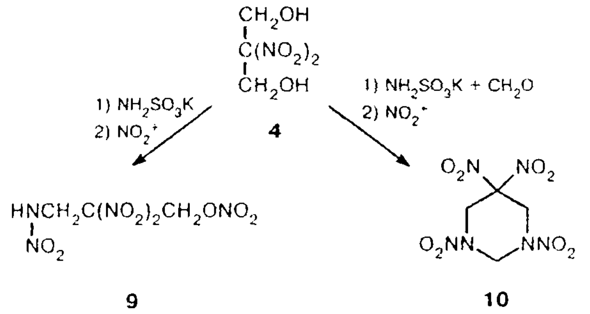
95—97% yields. Compounds **2** were nitrated with mixtures of nitric and sulfuric acids. The target nitro derivatives **3** were obtained in 80—85% yields (Table 1).

Condensation of 2,2-dinitropropane-1,3-diol (**4**) with *N*-alkylsulfamates was carried out under similar conditions, but resulted in the formation of both mono- (**5**) and disubstituted products (**6**).



We could not separate condensation products **5** and **6**, which is largery due to the reversibility of the reaction. Nitration of their mixture gave a mixture of products **7** and **8** in ~80 % overall yield (Table 1). The ratio of **7** to **8** in this mixture depends on that of the starting diol **4** to *N*-alkylsulfamate.

Condensation of diol **4** with potassium sulfamate gave a mixture of products in which the main component is unstable 3-nitramino-1-nitroxy-2,2-dinitropropane (**9**) (^{1}H NMR, δ: 4.96 s, 2 H; 5.60 s, 2 H). In some cases, 1,2,2-trinitroazetidine (~3—5%) was formed. Reaction of formaldehyde with a solution of dinitrodiol **4** and potassium sulfamate with subsequent nitration of the condensation product afforded 1,3,5,5-tetranitro-1,3-diazacyclohexane (**10**) in ~65% yield.



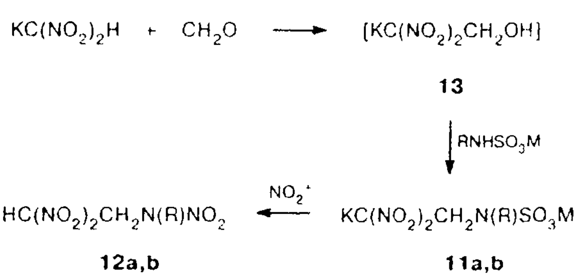
At the same time, attempts to perform condensation of derivatives of sulfamic acid with formaldehyde and dinitromethane followed by nitration resulted in the formation of a hard-to-separate mixture containing only traces of the target products **7a,b**, **8a,b**, and **10**. Better results were obtained with potassium dinitromethane as the starting compound. Its reaction with *N*-alkylsulfamate

Table 1. Characteristics of nitramino derivatives of *gem*-dinitroalkanes

Compound	Yield (%)	M.p./°C	Found/Calculated (%) C	H	N	Molecular formula	^{1}H NMR, δ
3a	84	67—68[1]					
3b	85	82—83[1]					
3c	82	22—23[1]					
3d	86	62—63	27.18 27.03	4.45 4.54		$C_5H_{10}N_4O_6$	1.03 (t, 3 H, C$\underline{H}_3$CH$_2$), 2.48 (q, 2 H, C$\underline{H}_2$C), 3.32 (s, 3 H, CH$_3$N), 4.81 (s, 2 H, CCH$_2$N)
3e	82	32	30.52 30.97	5.12 5.09		$C_6H_{12}N_4O_6$	1.0—1.2 (m, 6 H, 2 CH$_3$), 2.47 (q, 2 H, C$\underline{H}_2$C), 3.78 (q, 2 H, CH$_3$C$\underline{H}_2$N), 4.78 (s, 2 H, CCH$_2$N)
7a	78*	73	18.32 17.86	2.52 2.62	25.63 26.02	$C_4H_7N_5O_9$	3.5 (s, 3 H, CH$_3$), 5.09 (s, 2 H, CH$_2$N), 5.61 (s, 2 H, CH$_2$O)
7b	62*	54	21.44 21.21	3.40 3.21		$C_5H_9N_5O_9$	1.23 (t, 3 H, CH$_3$), 3.89 (q, 2 H, CH$_2$N), 5.06 (s, 2 H, CH$_2$N), 5.58 (s, 2 H, CH$_2$O)
8a	61**	138	21.69 21.28	3.40 3.57	46.01 45.36	$C_5H_{10}N_6O_8$	3.48 (s, 6 H, 2 CH$_3$), 5.12 (s, 4 H, 2 CH$_2$N)
8b	54**	114	27.09 27.16	4.52 4.73		$C_6H_{14}N_6O_8$	1.24 (t, 6 H, 2 CH$_3$), 3.90 (q, 4 H, 2 CH$_2$N), 5.08 (s, 4 H, 2 CH$_2$N)
10a	65	155[4]					
12a	80 71***	56[4]					3.48 (s, 3 H, CH$_3$), 4.80 (d, 2 H, CH$_2$N), 7.10 (t, H, CH)
12b	60 56***	Resin[4]					1.26 (t, 3 H, CH$_3$), 3.82 (q, 2 H, CH$_2$N), 4.68 (d, 2 H, CH$_2$N), 6.95 (t, H, CH)

* Compound **4** : sulfamate ratio of 1 : 0.5. ** Compound **4** : sulfamate ratio of 1 : 2.5. *** From potassium dinitromethane.

and formaldehyde yields products **11**, whose nitration gives compounds **12**.



Apparently, potassium dinitromethane first reacts with formaldehyde to give an intermediate (**13**), which is further condensed with *N*-alkylsulfamates. This mechanism was confirmed by direct reaction of *N*-alkylsulfamates with salt **13** (Table 1).

The results cited above suggest that the Mannich reaction of *gem*-dinitroalkanes with derivatives of sulfamic acid mainly proceeds *via* products of hydroxymethylation of *gem*-dinitroalkanes rather than sulfamates, as takes place in the classic case.

Experimental

^1H NMR spectra were recorded on a Bruker WM-250 spectrometer (250 MHz) in $(CD_3)_2CO$ with HMDS as the internal standard. IR spectra were recorded on a UR-20 instrument (KBr).

Condensation of potassium *N*-methylsulfamate with 2,2-dinitropropan-1-ol (4). Potassium *N*-methylsulfamate (1.49 g, 10 mmol) was added to a solution of 2,2-dinitropropan-1-ol (1.58 g, 10.5 mmol) in 5 mL of 40% ethanol, and pH was adjusted to ~4.7. The reaction mixture was concentrated on a rotary evaporator until a crystalline precipitate formed. The precipitate was washed with ether from the unreacted starting compound **4** to give potassium *N*-(2,2-dinitroprop-1-yl)-*N*-methylsulfamate **2a** (~2.77 g, 97%), m.p. 160—162 °C. IR (v/cm^{-1}): 1330 s, 1558 s, 584 s; ~1200—1210 s.

Nitration of condensation product 2a. Compound **2a** (2.77 g) was added with stirring to a mixture of 98% HNO_3 (6 mL) and 95% H_2SO_4 (4.6 mL) at −10 to −15 °C. The reaction mixture was stirred at −10 to −15 °C for an extra 30 min and poured into a mixture of water and ice (40 g). The crystalline product that formed was filtered off, washed with water, and dried in a desiccator over P_2O_5 *in vacuo* to give *N*-methyl-1-nitramino-2,2-dinitropropane (**3a**) (1.73 g, ~84%), m.p. 67—68 °C (*cf.* Ref. 1: m.p. 67—68 °C).

Compounds **3b**, **3c**, **3d**, **3e**, **7a**, **7b**, **8a**, **8b**, **10a**, **12a**, and **12b** were obtained in a similar way.

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Triterpenoids from *Abies* species

24.* Photochemical fragmentation of trinor-mariesiane hydroxy ketone

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Norrish (type II) photochemical fragmentation of 25,26,27-trinor-17,14-*frido*-9β-lanostane 23-ketone was performed to give the 17α-vinyl derivative, a promising intermediate for the synthesis of 4,4-dimethyl-9β-steroid derivatives.

Key words: triterpenoids, methyl ketones, Norrish photochemical fragmentation of ketones, two-dimensional NMR spectroscopy.

Acids **1** ((24*E*)- and (24*Z*-isomers) with the mariesiane[2] carbon skeleton are the main components of the natural pool of triterpenoid acids from the needles of the Siberian fir (*Abies sibirica* Ledb.). This fact was established by chromatography of the pool of their methyl esters[3] and from the GLC data for neutral methyl

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