Brief Communications

Preparation of *N,N'*-dialkyl methylenebisnitramines

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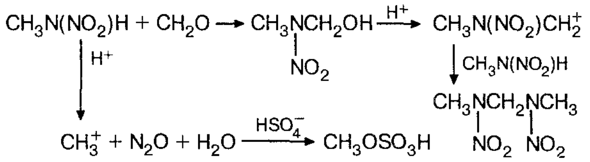
The possibility of obtaining *N,N'*-dialkyl methylenebisnitramines from primary nitramines and formaldehyde in dilute H_2SO_4 (65—85%) has been shown. The reaction starting from two different nitramines results in a mixture of one asymmetrically and two symmetrically substituted products.

Key words: *N,N'*-dialkyl methylenebisnitramines; primary nitramines.

N,N'-dialkyl methylenebisnitramines (**1**) were first obtained by the condensation of primary nitramines with formaldehyde in H_2SO_4.[1] *N*-Alkylnitracetamides[2] afford one more possible source of bisnitramines **1**. Recently, compounds **1** were studied as components of compositions for power production.[3] Convenient procedures for synthesizing primary nitramines are known.[4] Therefore, the elaboration of a procedure for obtaining bisnitramines **1** from primary nitramines is of practical interest.

The main feature of the procedures previosly reported for the synthesis of bisnitramines **1** from primary nitramines was the use of concentrated H_2SO_4 (90—95%) which required cooling (−5÷−10°C) due to the decomposition of primary nitramines. Furthermore, one had to use organic solvents, *viz.*, CH_2Cl_2, ethyl acetate, *etc.*, in order to obtain sufficiently high yields of compounds **1**. The yields of bisnitramines **1** reached 75%.[5]

We studied in detail the dependence of the yield of compounds **1** on various factors, primarily acid concentration, using the example of the reaction of *N*-methylnitramine with formaldehyde solution:



It turned out that this reaction can be performed in a wider range of H_2SO_4 concentrations than was assumed previously. The maximum yield of 2,4-dinitro-2,4-diazapentane (DNP) is achieved at 70—80% H_2SO_4. An increase in H_2SO_4 concentration to 93% results in a decrease in the product yield to 75%. If H_2SO_4 concentration is below 50%, only a methylol derivative of *N*-methylnitramine is formed.

The use of dilute H_2SO_4 makes it possible to perform the reaction at positive temperatures (0÷20°C). For example, the optimum temperature of the process in 75% H_2SO_4 is 0—10°C (the yield of DNP is 85%) or 10—20°C for 65% H_2SO_4 (yield 75%). At lower H_2SO_4 concentrations (60—75%), the formation of the methyl-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 1999—2001, November, 1993.

Table 1. Time dependence of the composition of products of the reaction of *N*-methylnitramine with formaldehyde solution (65% H_2SO_4, 18°C, molar ratio CH_3NHNO_2:CH_2O = 2:1)*

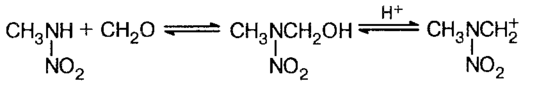
Run	Time (min)	CH_3OSO_3H	$CH_3NNO_2CH_2NNO_2CH_3$	$CH_3NNO_2CH_2OH$	CH_3NHNO_2
1	10	6	19	35	40
2	25	11	44	24.5	20.5
3	65	23	63	12.5	1.0
4	90	27.5	62.5	9.5	—
5**	65	21.5	72	4.0	1.5

* ^1H NMR of the reaction mixture (acetone-d_6), δ: CH_3NHNO_2, 3.10 (s, 3 H, Me); $CH_3NNO_2CH_2OH$, 3.40 (s, 3 H, Me), 5.12 (s, 2 H, NCH_2OH); CH_3OSO_3H, 3.90 (s, 3 H, Me); $CH_3NNO_2CH_2NNO_2CH_3$, 3.50 (s, 6 H, Me); 5.50 (s, 2 H, CH_2).

** At the ratio CH_3NHNO_2:CH_2O = 2:0.92.

ene carbocation of *N*-methylnitramine is likely to be the rate-determining step. In this range of H_2SO_4 concentrations ^1H NMR spectroscopy detected a methylol derivative of *N*-methylnitramine, along with the original compounds, CH_3NHNO_2 and CH_2O (Table 1). However, this methylol derivative is not formed at H_2SO_4 concentrations of 90% or more.

When the H_2SO_4 concentration is 65%, a significant amount of the original *N*-methylnitramine undergoes decomposition. The rest of the methylol derivative of *N*-methylnitramine does not participate in the formation of DNP but just contaminates the main reaction product. The rate of decomposition is higher in this case then the rate of formation of the methylene carbocation of *N*-methylnitramine. A similar situation is also observed in 75% H_2SO_4. Apparently, the only difference is that under these conditions, the methylol derivative of *N*-methylnitramine regenerates both the free nitramine and the methylene carbocation of *N*-methylnitramine more quickly:



$$\underset{NO_2}{CH_3\underset{|}{N}H} + CH_2O \rightleftharpoons \underset{NO_2}{CH_3\underset{|}{N}CH_2OH} \overset{H^+}{\rightleftharpoons} \underset{NO_2}{CH_3\underset{|}{N}CH_2^+}$$

To involve a greater fraction of *N*-methylnitramine in the formation of DNP, formaldehyde should be taken in some deficiency (5÷10%). To obtain the maximum yield of DNP, the lower the concentration of H_2SO_4, the greater the deficiency should be.

In a similar way, 3,5-dinitro-3,5-diazaheptane was obtained from *N*-ethylnitramine in 86% yield, and 5,7-dinitro-5,7-diazaundecane was obtained from *N*-*n*-butylnitramine in 84% yield.

The addition of *N*-methyl- and *N*-ethylnitramines to dilute H_2SO_4 resulted in a mixture containing 2,4-dinitro-2,4-diazapentane, 2,4-dinitro-2,4-diazahexane, and 3,5-dinitro-3,5-diazaheptane (a ternary CH_3/C_2H_5 mixture (**1a**)).

$$\begin{matrix} RNHNO_2 \\ R^1NHNO_2 \end{matrix} + CH_2O \longrightarrow \begin{matrix} RNNO_2CH_2NNO_2R \\ RNNO_2CH_2NNO_2R^1 \\ R^1NNO_2CH_2NNO_2R^1 \end{matrix}$$

1

1a: R = Me, R^1 = Et **1b**: R = Me, R^1 = Pr **1c**: R = Me, R^1 = Bu **1d**: R = Et, R^1 = Bu

The ternary CH_3/C_2H_5 mixture was analyzed by gas chromatography. The composition of the products depends on the ratio of the original components and is

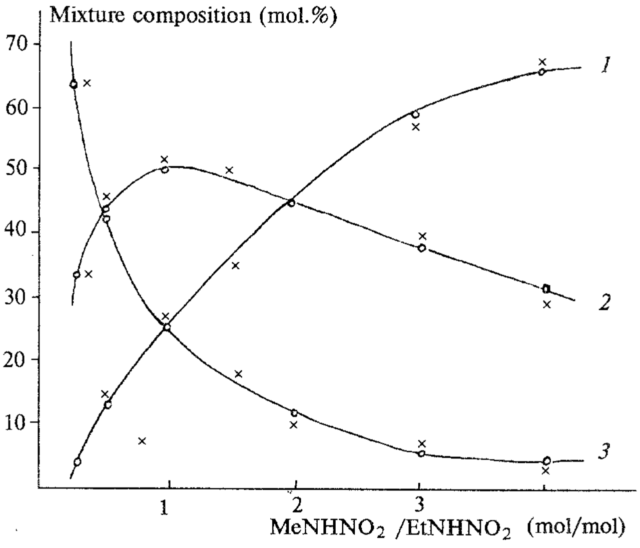


Fig. 1. Effect of the ratio of the original components on the composition of the ternary CH_3/C_2H_5 mixture. ×, experiment; o, calculated data.

1. $[MeN(NO_2)]_2CH_2$; *2.* $MeN(NO_2)CH_2N(NO_2)Et$; *3.* $[EtN(NO_2)]_2CH_2$

solely determined by statistical factors. Figure 1 presents the calculated and experimental compositions of the ternary CH_3/C_2H_5 mixture.

The maximum yield of the ternary CH_3/C_2H_5 mixture from *N*-methyl- and *N*-ethylnitramines in 75% H_2SO_4 reaches 86%, while an increase in H_2SO_4 concentration results in a decrease in the yield of the ternary CH_3/C_2H_5 mixture to 76% due to decomposition reactions. The reaction does not occur in dilute H_2SO_4 (<50%).

In a similar way, $CH_3/n\text{-}C_3H_7$ (yield 80%), $CH_3/n\text{-}C_4H_9$ (yield 86%), and $C_2H_5/n\text{-}C_3H_7$ (yield 84%) ternary mixtures were obtained.

Nonsymmetrically substituted *N,N'*-dialkyl methylenebisnitramines were isolated from the respective mixtures by thin-layer chromatography.

Experimental

^{1}H NMR spectra were recorded on a JEOL FX-90 spectrometer.

Synthesis of 2,4-dinitro-2,4-diazapentane. *N*-methylnitramine (3.04 g) and paraform (0.59 g) were added at 0—5°C to stirred 75% H_2SO_4 (10 mL). The mixture was stirred for 30 min at 0—5°C and poured into a water—ice mixture (50 mL). The resulting mixture was extracted with CH_2Cl_2 (3×10 mL). The extract was washed with water (10 mL), 5% sodium carbonate (10 mL), and water (10 mL), and then concentrated. The product yield was 2.78 g (85%), m.p. 54°C (*cf.* Ref. 1).

In a similar way, 3,5-dinitro-3,5-diazaheptane (yield 86%, m.p. 76°C) and 5,7-dinitro-5,7-diazaundecane (yield 84%, m.p. 92°C) were obtained (*cf.* Ref. 1).

Synthesis of a mixture of symmetric and asymmetric *N,N'*-dialkyl methylenebisnitramines. *N*-methylnitramine (1.52 g, 0.02 mol), *N*-ethylnitramine (1.80 g, 0.02 mol), and paraform (0.59 g) were added at 0—5°C to a stirred mixture of 75% H_2SO_4 (10 mL) and CH_2Cl_2 (5 mL). The mixture was stirred for 30 min at 0—5°C and poured into a water—ice mixture (50 mL). The resulting mixture was extracted with CH_2Cl_2 (3×10 mL). The extract was washed with water (10 mL), 5% sodium carbonate (10 mL), and water (10 mL), and then concentrated. The yield of the ternary CH_3/C_2H_5 mixture was 3.06 g (86%), m.p. 7—10°C, composition (mol. %): $MeNNO_2CH_2NNO_2Me$ (25), $MeNNO_2CH_2NNO_2Et$ (50), $EtNNO_2CH_2NNO_2Et$ (25). The product composition was determined by GLC using DMCS impregnated with 10% SE-30 as the support and helium as the carrier gas. The column temperature was 160°C.

In a similar way, the following ternary mixtures of *N,N'*-dialkyl methylenebisnitramines were obtained: $CH_3/n\text{-Pr}$, m.p. 14—18°C; $CH_3/n\text{-}C_4H_9$, m.p. 18—22°C; $C_2H_5/n\text{-}C_4H_9$, m.p. 25—30°C.

The following products were isolated from the ternary mixtures by TLC on Silufol ($CHCl_3$+ethanol as the eluent):

a. $MeNNO_2CH_2NNO_2Et$, m.p. 32°C. IR (KBr), ν/cm^{-1}: 1285, 1510—1540 (NNO_2). ^{1}H NMR (acetone-d$_6$), δ: 1.24 (t, 3 H, Et); 3.48 (s, 3 H, Me); 3.66 (quin, 2 H, NEt); 5.52 (s, 2 H, NCH_2N).

b. $MeNNO_2CH_2NNO_2Pr$, m.p. 36°C. ^{1}H NMR (acetone-d$_6$), δ: 1.04 (t, 3 H, Me); 1.36 (m, 2 H, Pr); 3.48 (s, 3 H, MeN); 3.71 (quin, 2 H, NCH_2C); 5.50 (s, 2 H, NCH_2N).

c. $MeNNO_2CH_2NNO_2Bu$, m.p. 36°C. ^{1}H NMR (acetone-d$_6$), δ: 0.85—1.40 (m, 7 H, Pr); 3.48 (s, 3 H, Me); 3.64 (t, 2 H, NCH_2C); 5.50 (s, 2 H, NCH_2N).

d. $EtNNO_2CH_2NNO_2Bu$, m.p. 50°C. ^{1}H NMR (acetone-d$_6$), δ: 0.80—1.40 (m, 3 H, Et; 7 H, $CH_3CH_2CH_2$); 3.64 (m, 2 H, CH_2N; 2 H, NCH_2); 5.50 (s, 2 H, NCH_2N).

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Received April 27, 1993