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Synthesis of *N*-trinitroethyl derivatives of linear and heterocyclic nitrogen-containing compounds*

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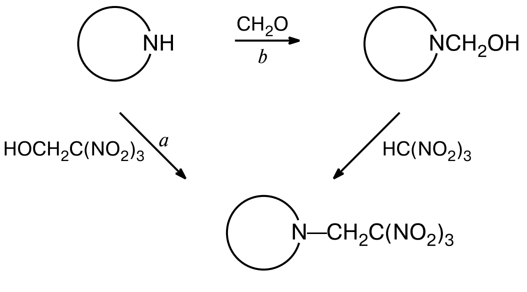
Earlier unknown *N*-trinitroethyl derivatives of acetylhydrazine, 4-amino-1,2,4-triazole, and 2,4,6-triamino-1,3,5-triazine, which are potential components for gas-generating formulations, were synthesized.

Key words: *N*-trinitroethyl derivatives, heterocyclic and linear amino derivatives, trinitroethanol, trinitromethane.

Compounds containing linear or heterocyclic *N*-trinitroethyl fragments (*N*-TNE) are of interest as components for gas-generating formulations.[1] Some of them have sufficiently long been known; however, relevant data were published mainly in the patent literature, often without reporting synthetic procedures or specifying the physicochemical (except for some explosive) characteristics of the compounds obtained. The goal of the present work was to study the possibility of preparing *N*-TNE derivatives of heterocyclic and linear nitrogen-containing compounds with a primary or secondary amino group.

Two known[2] basic approaches to the synthesis of *N*-TNE derivatives are condensation of the starting amino derivative with trinitroethanol (pathway *a*) and condensation of a hydroxymethyl intermediate (prepared by a reaction with formaldehyde) with trinitromethane (pathway *b*) (Scheme 1).

Scheme 1



The efficiency of either approach, as well as the fundamental possibility of obtaining *N*-TNE derivatives, depends on the basicity of the starting amino derivative. In particular, urea or its *N*-mono- and *N*,*N*′-bis(hydroxymethyl) derivatives easily form the corresponding mono-[3] or bis(*N*-TNE) derivatives,[4] depending on the ratio of the reagents. Nitroguanidine undergoes no condensation with trinitroethanol; its *N*-TNE derivative is obtained only through a monohydroxymethyl intermediate (pathway *b*).[5] Unfortunately, a number of amino derivatives of linear and heterocyclic nitrogen-containing compounds have not been studied as possible precursors for the synthesis of *N*-TNE derivatives. In the present work, we investigated the following precursors: oxamide **1**, biuret **2**, cyanuric acid **3**, 1,2,4-triazol-5-one (**4**), 3-nitro-1,2,4-triazol-5-one (**5**), 4-amino-1,2,4-triazole (**6**), 2,4,6-triamino-1,3,5-triazine (melamine, **7**), and acetylhydrazine **8**.

Taking into account a positive experience of the synthesis of *N*-TNE derivatives of urea, we used compounds structurally close to urea as starting material: oxamide **1**, biuret **2**, and cyanuric acid **3**. However, the reactions of these compounds in both pathways *a* and *b* gave no target *N*-TNE derivatives, although their hydroxymethyl derivatives were documented.[6—8] Nor were attempts at obtaining *N*-TNE derivatives successful when 1,2,4-triazol-5-one **4** and 3-nitro-1,2,4-triazol-5-one **5** were used, the syntheses of their *N*-hydroxymethyl derivatives being also reported[9,10] (Scheme 2).

Apparently, the low basicities of the starting reagents ($pK_a = 13.2$,[11] 6.5,[11] and 9.1 [12] for compounds **2**, **3**, and **4**, respectively) prevent a very important step of the process from occurring under the conditions studied. The step involves the Mannich reaction,[13] *i.e.*, the formation of immonium ion **9**, which then reacts with trinitromethane (Scheme 3).

In the only available publication[14] devoted to 2,4,6-tris(2,2,2-trinitroethylamino)-1,3,5-triazine (**10**),

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[*] Dedicated to Academician N. K. Kochetkov on the occasion of his 90th birthday.

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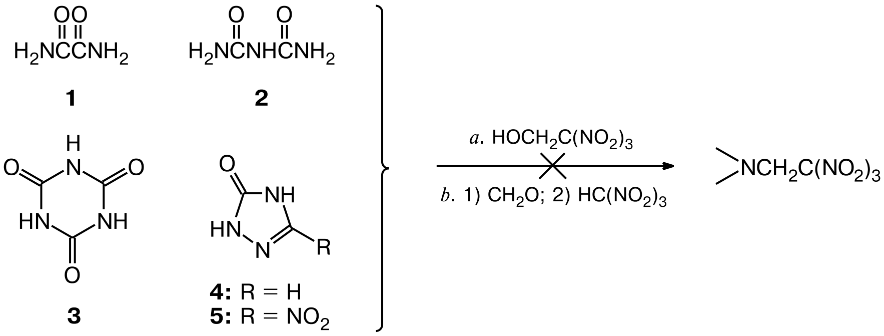
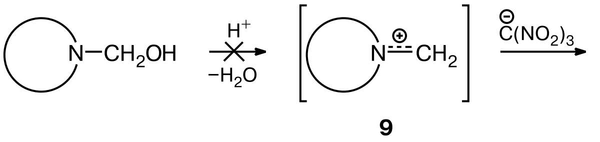
Scheme 2



Scheme 3



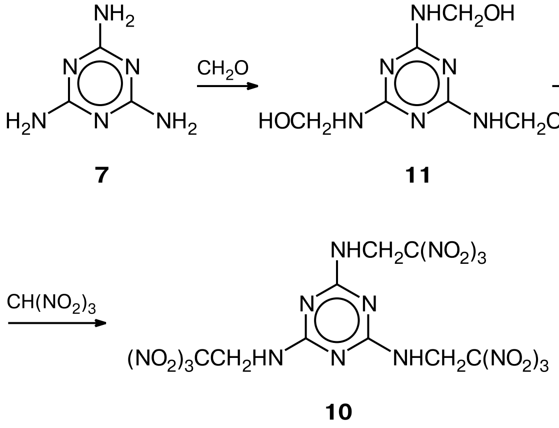
this compound was obtained by condensation of melamine **7** with trinitroethanol (pathway *a*). However, the detailed synthetic route to compound **10** was unavailable and its selected explosive characteristics were reported only. Our attempted condensation of melamine **7** ($\mathrm{p}K_\mathrm{a}$ = 5.1 [11]) with trinitroethanol (pathway *a*) in water at different temperatures failed. Pathway *b* proved to be more effective. Preparation of 2,4,6-tris(hydroxymethylamino)-1,3,5-triazine (**11**) followed by its condensation with trinitromethane gave the target product **10** in 81% yield. Hydroxymethyl intermediate **11** was not isolated; its aqueous solution was used *in situ* in the reaction with trinitromethane (Scheme 4).

4-(2,2,2-Trinitroethylamino)-1,2,4-triazole (**12**) was successfully synthesized from aminotriazole **6** ($\mathrm{p}K_\mathrm{a}$ = 0.6 [15]) in both pathways *a* and *b*. The yield of product **12** was 93%. Our attempts to introduce two trinitroethyl fragments into the amino group of the starting aminotriazole **6** failed; the sufficiently high basicity of compound **12** made it possible to obtain its nitrate **13** (Scheme 5).

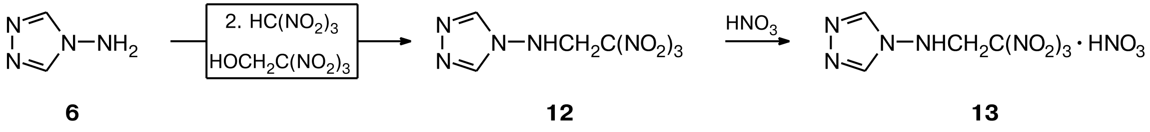
1-Acetyl-2-(2,2,2-trinitroethyl)hydrazine (**14**) was synthesized only in pathway *a* by condensation of acetylhydrazine **8** ($\mathrm{p}K_\mathrm{a}$ = −0.5 [16]) with trinitroethanol (Scheme 6). The yield of product **14** was 56%.

The structures of compounds **10** and **12**—**14** were determined from elemental analysis and spectroscopic data. It should be noted that their ^{1}H NMR spectra in solution suggest an equilibrium between the final products (Mannich bases) and the starting reagents (amino derivatives and trinitroethanol), which is always substantially shifted to the former (> 95%). However, in the solid state all the compounds obtained are authentic *N*-TNE derivatives with elemental analysis data matching the structures proposed. The yields, physicochemical parameters, and spectroscopic characteristics of all the new compounds are given in Tables 1 and 2.

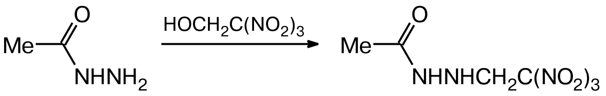
Scheme 4



Scheme 5



Scheme 6



8 **14**

Experimental

IR spectra were recorded on a UR-20 spectrometer (pellets with KBr). ^{1}H NMR spectra were recorded on a Bruker WM-250 spectrometer (250 MHz). ^{13}C and ^{14}N NMR spectra were recorded on a Bruker AM-300 spectrometer (75.5 and 21.5 MHz, respectively). Chemical shifts are given on the δ scale relative to Me_4Si (^{1}H and ^{13}C) and $MeNO_2$ (^{14}N). Melting points were determined on a Boetius RNMK 05 instrument.

2,4,6-Tris(2,2,2-trinitroethylamino)-1,3,5-triazine (10). A mixture of 2,4,6-triamino-1,3,5-triazine **7** (0.82 g, 6.5 mmol) and 30% aqueous formalin (2.0 g, 20 mmol) in water (2 mL) was heated in a water bath to 70 °C and stirred until compound **7** was completely dissolved. The stirred resulting solution of tris(hydroxymethyl) derivative **11** was diluted with water (11 mL) and cooled to 20 °C. Trinitromethane (3.02 g, 20 mmol) was added and the mixture was kept at 15 to 20 °C. The yellow oil that formed after ~0.5 h completely solidified after ~3 days. The precipitate was carefully triturated under a layer of the mother liquor, filtered off, thoroughly washed with water, and dried in a vacuum desiccator over KOH and P_2O_5 to give compound **10** (3.23 g, 81%).

4-(2,2,2-Trinitroethylamino)-1,2,4-triazole (12). A mixture of 4-amino-1,2,4-triazole **6** (1.36 g, 16.2 mmol) and a 86% aqueous solution of trinitroethanol (3.41 g, 16.2 mmol) in water (10 mL) was stirred at room temperature for 2 h. The precipitate was filtered off, washed with water (2×5 mL), and dried in a vacuum desiccator over P_2O_5 to give product **12** (3.73 g, 93.3%).

4-(2,2,2-Trinitroethylamino)-1,2,4-triazole, nitrate (13). Compound **12** (3.73 g, 15.1 mmol) was added to stirred HNO_3 (d = 1.358 g cm^{-3}) (6.6 mL). The reaction mixture was heated to 55 °C to complete homogenization. The resulting solution was slowly cooled and the precipitate of the salt was filtered off, thoroughly squashed on the filter for 1 h, and dried in a vacuum desiccator over P_2O_5 and KOH to give product **13** (3.76 g, 80.4%).

Table 1. Yields and physicochemical characteristics of the compounds obtained

Compound	Yield (%)	M.p. /°C	$\frac{\text{Found}}{\text{Calculated}}$ (%) C	H	N	Molecular formula
10	81	55—57	17.59 17.56	1.58 1.46	33.89 34.15	$C_9H_9N_{15}O_{18}$
12	93.3	120—123 (decomp.)	19.58 19.44	2.18 2.04	39.26 39.67	$C_4H_5N_7O_6$
13	80.4	101 (expl. without melting)	15.68 15.48	1.96 1.94	35.79 36.13	$C_4H_6N_8O_9$
14	56	95—98, 103 (expl.)	20.58 20.25	2.97 2.95	28.42 29.54	$C_4H_7N_5O_7$

Table 2. IR and NMR spectra of the compounds obtained

Compound	IR, ν/cm^{-1}	NMR (acetone-d$_6$), δ ^{1}H	^{14}N
10	3440, 3004, 2952, 2888, 1588, 1504, 1440, 1328, 1304, 1184, 1088, 1020, 876, 856, 808, 784	5.10 (d, 6 H, CH_2); 5.83 (s, 3 H, NH)**	−30.4 (NO_2)*
12	3240, 3156, 3128, 3100, 3044, 2988, 2940, 2892, 1616, 1604, 1588, 1504, 1420, 1352, 1304, 1200, 1128, 1072, 960, 940, 908, 880, 848, 804, 772, 716, 684, 624	5.36 (d, 2 H, CH_2, J = 6 Hz); 7.80 (t, 1 H, NH); 8.70 (s, 2 H, CH in the ring)	−30.8 (NO_2)
13	3244, 3128, 3000, 1608, 1588, 1432, 1400, 1340, 1300, 1212, 1172, 1120, 1080, 1048, 1024, 916, 884, 856, 820, 804, 780, 724, 700, 664, 628	5.25 (s, 2 H, CH_2); 9.47 (s, 2 H, CH in the ring)	−9.6*** (NO_3^-); −30.8*** (NO_2)
14	3322, 3288, 3000, 2976, 2960, 2920, 2884, 1660, 1604, 1584, 1528, 1408, 1372, 1336, 1312, 1164, 1136, 1112, 1008, 876, 856, 792, 764	1.90 (s, 3 H, Me); 5.00 (s, 2 H, CH_2); 8.75, 9.05 (both br.s, 1 H each, NH)	−30.2 (NO_2)

* ^{13}C NMR (acetone-d$_6$), δ: 45.4 (CH_2); 126.3 ($C(NO_2)_3$); 167.2 (ring C).

** ^{1}H NMR (DMSO-d$_6$), δ: 5.25 (s, 6 H, CH_2); 8.05 (s, 3 H, NH). ^{1}H NMR ($CDCl_3$), δ: 5.40 (s, 6 H, CH_2); 7.40 (s, 3 H, NH).

*** In CD_3OD.

1-Acetyl-2-(2,2,2-trinitroethyl)hydrazine (14). A mixture of acetylhydrazine **8** (1.0 g, 13.5 mmol) and a 86% aqueous solution of trinitroethanol (2.84 g, 13.5 mmol) in water (9 mL) was stirred at 20 °C for 1 h. The precipitate that formed was filtered off, washed with water (2×5 mL), and dried in a vacuum desiccator over P_2O_5 to give product **16** (1.78 g, 56%).

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