



## Contribution to the Synthesis of 4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0<sup>5,9</sup>0<sup>3,11</sup>]dodecane (TEX)

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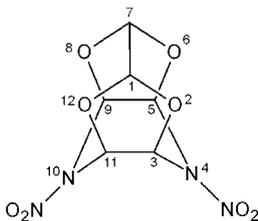
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**Abstract:** The influence of the reaction conditions on 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0<sup>5,9</sup>0<sup>3,11</sup>]dodecane (TEX) yield was studied. TEX was prepared by the reaction of 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine with glyoxal in nitric acid. The influence of the acidity of reaction mixture and ratios of starting materials on the yield of TEX was examined and synthesis was optimised. The highest yield (37%) was obtained at 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine/nitric acid molar ratio 67 and sulfuric acid/nitric acid molar ratio around 0.15. Starting material 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine was prepared from formamide and glyoxal using triethylamine or other tertiary amines to adjust suitable basicity. The best yield (84%) of 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine was reached at molar ratio triethylamine/formamide equal to 0.1.

**Keywords:** 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0<sup>5,9</sup>0<sup>3,11</sup>]dodecane, TEX, 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine, tertiary amines, insensitive explosives

## Introduction

4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0<sup>5,9</sup>0<sup>3,11</sup>]dodecane (also 4,10-dinitro-2,4,6-tetraoxa-4,10-diazaisowurtzitane, TEX, Figure 1) is well known insensitive high explosive [1], suggested by number of authors as an ingredient of various insensitive compositions [2-7].



**Figure 1.** 4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0.0]<sup>5,9,0<sup>3,11</sup></sup> dodecane with numbering of atoms.

The synthesis of TEX was first described by Ramakrishnan and co-workers in 1990 [8]. Afterwards, several improvements of original Ramakrishnan procedure have been reported [9-14]. The maximum yield of TEX is mostly reported not to exceed 25%, except of Talwar [13] and Ramakrishnan original procedure [8]. That is why we searched for possibilities for increasing the yield above 25%. The starting material for the synthesis is 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine (DFTHP), prepared by the reaction of formamide and glyoxal in the presence of inorganic base [15-17]. Sodium hydroxide [15, 17] or sodium hydrogen carbonate [16] were published for adjusting of pH to about 9. Maximum yield of DFTHP was reported to be 66% [17]. In this case, we also tried to increase the yield of the intermediate. We used organic bases (tertiary amines) instead of published inorganic ones to adjust the basicity.

## Experimental

The infrared spectra were obtained using Protégé 460 apparatus. OMNIC software (Thermo Electron Corporation) was used for both data acquisition and evaluation. ATR procedure was used for measuring of all samples. The thermal analysis of TEX and DFTHP was studied using differential thermal analyzer DTA 550Ex (OZM Research). The 50 mg samples were tested in open glass micro-test tubes (in contact with air) and the heating rate was 5 °C min<sup>-1</sup>. The melting points were measured on a Kofler bench and are uncorrected.

**CAUTION:** TEX is an explosive and should be handled with care. The synthesis and handling of TEX may be dangerous operations that require standard safety precaution for handling of explosives!

**1,4-Diformyl-2,3,5,6-tetrahydroxypiperazine (DFTHP)**

Triethylamine (2.02 g, 0.02 mol) was added to a mixture of formamide (4.5 g, 0.10 mol) and 40% water solution of glyoxal (14.5 g, 0.10 mol). The exothermic reaction started and the temperature was kept at 40–45 °C by external cooling. After several minutes, a solid precipitated. The reaction mixture was stirred for additional two hours, then the solid formed was filtered and washed with hot water, methanol and finally with acetone to give 8.2 g (80%) of white solid. Melting point >200 °C (decomposition); lit. 225 °C (decomposition) [15]. Decomposition of 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine, determined by DTA, starts at 185 °C. Anal. Calc. for C<sub>6</sub>H<sub>10</sub>N<sub>2</sub>O<sub>6</sub>: C, 34.96; H, 4.89; N, 13.59. Found: C, 34.78; H, 4.91; N, 13.45. IR (ATR, cm<sup>-1</sup>): 3316, 3217, 1666 (strong), 1468, 1433, 1402, 1351, 1322, 1292, 1262, 1192, 1071, 1049 (strong), 1008, 936 (strong), 795, 686.

Various ratios trimethylamine/formamide and triethylamine/formamide were examined for optimizing of 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine yield; the results are summarised in Table 1.

**4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0<sup>5,9</sup>.0<sup>3,11</sup>]dodecane (TEX)**

1,4-Diformyl-2,3,5,6-tetrahydroxypiperazine (11.5 g, 0.056 mol) and glyoxal trimer hydrate (80% of glyoxal, 4.5 g, 0.062 mol) were simultaneously added to a mixture of nitric acid (98%, 80 ml, 1.879 mol), sulfuric acid (16 ml, 0.287 mol) and urea (0.5 g, 0.008 mol) during 15 minutes at 4–6 °C. The cooling was removed; the solid dissolved during one hour and the mixture was stirred at room temperature for additional three hours. Then the reaction mixture was heated up to 65 °C, after several minutes the exothermic reaction took place, which was accompanied with intensive evolving of nitrogen oxides. The temperature was kept under 70 °C by external cooling. A solid started to precipitate, after one hour the mixture was cooled to 10 °C, filtered and washed with water to neutral reaction to give 5.1 g (35%) of white crystalline solid. Melting point 303–304 °C, by DTA decomposition starts at 250 °C. (lit. [8] >250 °C). Anal. Calc. for C<sub>6</sub>H<sub>6</sub>N<sub>4</sub>O<sub>8</sub>: C, 27.49; H, 2.31; N, 21.37. Found: C, 27.59; H, 2.39; N, 21.16. IR (ATR, cm<sup>-1</sup>): 3081, 3048, 3033, 1706, 1583, 1571, 1386, 1317, 1285 (strong), 1250, 1172, 1132, 1114, 1054, 1022, 995, 962, 897, 872 (strong), 847, 824, 768, 754 (strong), 708. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 5.96 s (2H, H-1, H-7), 6.98 s (4H, H-3, H-5, H-9, H-11); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ 82.7 (C-3, C-5, C-9, C-11); 102.7 (C-1, C-7).

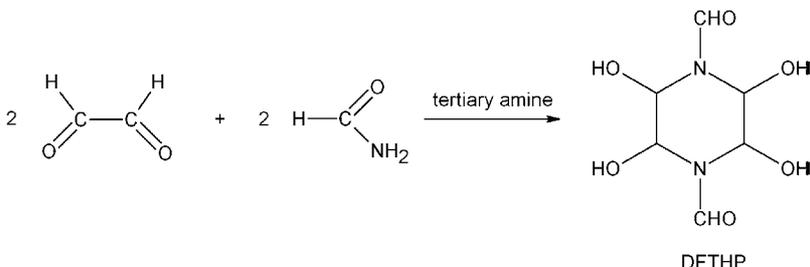
Series of other experiments with various ratios of sulfuric acid/nitric acid (see Figure 4) and nitric acid/DFTHP (see Table 2) were performed with the

aim to increase the TEX yield. The results are further discussed in Results and Discussion.

## Results and Discussion

### The optimization of 1,4-diformyl-2,3,5,6-tetrahydropiperazine (DFTHP) synthesis

The reaction of formamide and glyoxal to produce DFTHP is known. The inorganic bases (sodium hydroxide, sodium carbonate or bicarbonate) are described to adjust the basicity. The yields are reported from 34-81%; the reaction time is in range from several hours to several days [15-17]. We did not find the use of tertiary amines for adjusting of basicity in this reaction in literature. But, triethylamine was used for similar reaction of methansulfonamide with glyoxal to produce 1,4-bis(dimethylsulfonyl)-2,3,5,6-tetrahydropiperazine [16].



**Figure 2.** Scheme of DFTHP synthesis from formamide and glyoxal in the presence of tertiary amine.

Therefore, we applied tertiary amines to the reaction of formamide and glyoxal in aqueous media (Figure 2). The highest yields were obtained for triethylamine (84%) and trimethylamine (80%). In the case of other tertiary amines, the yields of DFTHP were considerably lower: dimethylcyclohexylamine (39%), dimethylbenzylamine (29%), *N,N*-dimethylisopropylamine (40%), *N,N*-dimethylaniline (0%) and *N,N*-diethylaniline (0%).

Influence of molar ratio of trialkylamine/formamide on the yield of DFTHP was investigated in detail in the case of trimethylamine and triethylamine (Table 1). Molar ratio trialkylamine/formamide was in the range from 0.01 to 0.5. The highest yield was obtained at molar ratio of trialkylamine/formamide

0.2 for trimethylamine and 0.1 for triethylamine. The increase in molar ratio over the optimal value causes slight decrease in DFTHP yield.

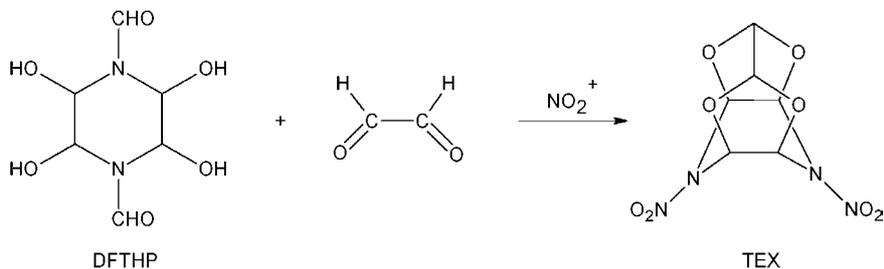
**Table 1.** Dependence of DFTHP yield on molar ratio trialkylamine/formamide

Molar ratio trialkylamine/formamide	DFTHP yield (%)	
	Trimethylamine	Triethylamine
0.01	0	0
0.02	0	0
0.05	19.8	67.1
0.1	59.7	84.0
0.2	78.8	80.3
0.5	74.7	78.6

### The optimization of 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0<sup>3,11</sup>]dodecane (TEX) synthesis

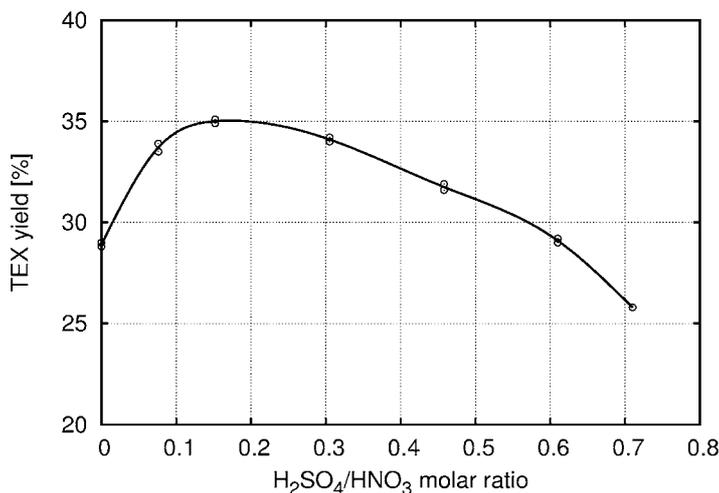
In the original procedure for preparation of TEX from DFTHP and glyoxal in nitric acid/sulfuric acid [8] (Figure 3), the yield of the product was published to be 92%. We were not able to reproduce published result according to this procedure; the product we obtained by quenching the reaction mixture in ice (as described in the original procedure [8]) was not pure TEX (results of our elemental analysis). Also, we obtained similar result by reproducing Talwar's procedure [8] in laboratory scale. Our further experiments showed that pure product is obtained only if TEX is isolated directly by cooling and filtering from reaction mixture (not poured into ice/water).

In our previous work we reached the maximum yield 26% [12] for nitric acid alone as a nitrating agent. This result is very similar to statements in patents [9, 11, 14] for mixtures of nitric acid/sulfuric acid. Urea, as a scavenger of nitrogen oxides, was also used as it was described previously [14]. Without urea, we did not obtain the yield of TEX above 20%.



**Figure 3.** Scheme of TEX synthesis from DFTHP and glyoxal.

In order to increase the yield of TEX, we used both higher and lower acidity of the nitration media. To increase the acidity of reaction medium (with respect to 98% nitric acid), various amounts of concentrated sulfuric acid in fume nitric acid were used. The yield of TEX highly increases with enhanced content of sulfuric acid in reaction mixture to 35% at the sulfuric/nitric acid molar ratio is 0.15. Further enhancing of sulfuric acid content in reaction mixture leads to slow decrease of TEX yield (Figure 4).



**Figure 4.** Dependence of the yield of TEX on the molar ratio sulfuric acid/nitric acid (for DFTHP/HNO<sub>3</sub> constant ratio 33.6).

Further optimization of TEX synthesis was performed by the change in the ratio of substrate to nitrating acid mixture. Constant molar ratio sulfuric/nitric acid was used 0.15 (see Figure 4). The results of experiments are presented in Table 2. The maximum yield 37.0% was obtained for the molar ratio of nitric acid/DFTHP = 67. The higher excess of acids reduces the yield of TEX.

**Table 2.** Yield of TEX at various molar ratio nitric acid/DFTHP for constant molar ratio sulfuric/nitric acid 0.15

Molar ratio nitric acid/DFTHP	Yield of TEX (%)
27.7	30.7
46.1	35.0
66.6	37.0
83.2	29.4

To examine lower acidity, the mixture nitric acid/acetic acid was used, but the yields of TEX were lower than 15%. The use of nitric acid/acetic acid anhydride and nitric acid/trifluoroacetic acid anhydride yielded 1,4-diformyl-2,3,5,6-tetraacetoxypiperazine and 1,4-diformyl-2,3,5,7-tetranitroxypiperazine, respectively, as described earlier [18, 19].

## Conclusion

1,4-Diformyl-2,3,5,6-tetrahydroxypiperazine can be easily prepared from glyoxal and formamide using tertiary amines to adjust the suitable basicity. The best results were obtained with triethylamine, the maximal yield was 84%. The advantage of the procedure is short reaction time that is less than three hours. The molar ratio amine/formamide is an important parameter; the optimal value for trimethylamine is 0.2 and 0.1 for triethylamine.

TEX is mostly prepared by the reaction of nitric acid, 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine and glyoxal. In nitric acid alone, the maximum yield of TEX was 26%. The acidity of reaction mixture and molar ratio of nitric acid/DFTHP are important factors. The yield of TEX increased up to 35% by using mixture sulfuric/nitric acids (for molar ratio 0.15) instead alone nitric acid. Other increase of TEX yield was obtained by the optimization of ratio 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine/nitric acid. The highest yield 37% was obtained for this molar ratio of 67. The mixtures of nitric acid/acetic acid or nitric acid/acetic acid anhydride did not lead to pure TEX formation.

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