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Improved preparation of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1] nonane (DPT) from urea

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Abstract

An improved and facile preparation of 3,7-dinitro-1,3,5,7-tetraazabicyclo [3,3,1] nonane (DPT) has been developed starting from urea. In the procedure DPT was synthesized via N,N'-dinitrourea (DNU) as intermediate and various operating parameters such as temperature, pH and molar ratio of reagents have been optimized to give maximum yield of the desired product. The low cost method is concise, operationally simple and offers high purity and satisfactory yield of DPT.

Keywords: 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT); Urea; Nitration; N,N'-dinitrourea (DNU).

1. Introduction

3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT) is a key precursor to octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) [1,2], the most powerful explosive manufactured in bulk at present. Reported manufacturing process for HMX involved the modified Bachmann process [3-5], in which the nitrolysis of hexamine with ammonium nitrate-nitric acid solution and acetic anhydride occurred and DPT was identified as a key intermediate. The modified Bachmann process has been brought about industrialization but it costs lot and involves complex series and parallel reactions. In view of the vital importance of DPT in the synthesis of HMX, a low cost method for producing this intermediate would provide a significant contribution toward reducing cost of manufacturing HMX.

G.F. Wright and coworkers [6] found that DPT could be prepared by admixture of a solution of nitramide (NH_2NO_2) in aqueous formaldehyde with a solution of formaldehyde and ammonia, but nitramide cannot be used as a large-scale starting material for its hydrolytic instability. R. A. Strecker et al. [7] invented a process for producing DPT by utilizing nitrourea as starting material in place of nitramide. The nitrourea can be obtained from urea nitrate [8], which in turn can be produced from low cost urea [9], but this process was loaded down with trivial details and the yield of DPT was low.

Recently much attention has been paid to N,N'-dinitrourea (DNU) and its derivatives due to their relatively high densities [10-14]. DNU was also found to be a good precursor to nitramide.

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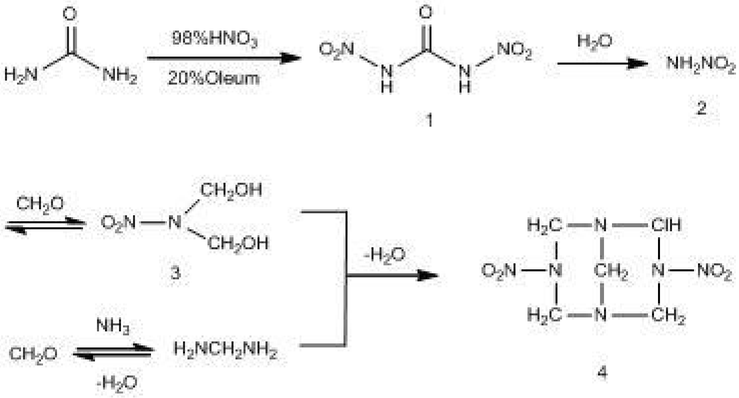
S.G. Il’yasov et al. [15] disclosed the application of DNU as intermediate for synthesis of DPT, but no systematic synthetic or mechanistic studies were reported.

Herein we report an improved and facile preparation of DPT, starting from low cost urea. In the procedure DNU (1) was prepared in situ without isolation of the compound, and the hydrolysis of DNU to give nitramide (2) in the presence of formaldehyde occurred through formation of N-dimethylol nitramide (3) since the subsequent neutralization with ammonia obtained DPT (4) (Scheme 1). We prepared the three intermediates to confirm the procedure and investigated various reaction conditions to get optimal conditions.



Scheme 1 Synthesis of DPT from urea.

2. Experimental

2.1. Materials and Methods

Melting points were determined on a Thomas Hoover capillary apparatus and were uncorrected. The IR spectra were recorded with a Bomem Michelson model 102 FTIR. ^{1}H NMR spectra were recorded on a Bruker DRX (500 MHz) spectrometer. Elemental analyses were performed on a Yanagimoto MT3CHN recorder. Mass spectra were recorded on a VG ZAB-HS mass spectrometer using fast atom bombardment (FAB) ionization mode. All starting chemicals (AR grade) were purchased from commercial suppliers and used without further purification.

2.2. Experimental procedures

To handle these energetic materials, best safety practices (leather gloves, face shield) are strongly encouraged.

2.3. Synthesis of DPT (4)

Urea, 6 g (0.1 mol), was added in portions to a mixture of 22.5 g of 98% nitric acid and 22.5g of oleum (20 % SO_3) at -5 to 0 °C under continuous stirring. After the addition the mixture was stirred for 1h at 0 to 5 °C and poured into 30 g of an ice-water mixture, and 50 mL of a 37 % ormaldehyde solution was added at a temperature not exceeding 20 °C. The mixture was heated to 35 °C, stirred for 30 min, cooled, and neutralized to pH 6 with 25 % aqueous ammonia at 20-25 °C. It was then stirred for 45 min at 20 °C, and the precipitate was filtered off, washed with water, and dried at room temperature until constant weight. Yield 14.7 g (67.4 %, calculated on urea), m.p. 209-210 °C; published data: 205-206 °C [16]. IR (cm^{-1}): 3032, 2937 (CH_2); 1529, 1288 (NNO_2). ^{1}H NMR (DMSO-*d6*): δ 5.49 (d, 4H), 4.93 (d, 4H), 4.11 (s, 2H). MS (FAB): 219 ([M+1]+). Anal. Calcd. for $C_5H_{10}N_6O_4$: C, 27.53; H, 4.62; N, 38.52; Found: C, 27.51; H, 4.59; N, 38.40 %.

2.4. Preparation of DNU(1)

Urea, 6 g (0.1 mol), was added in portions to a mixture of 21 g of 98 % nitric acid and 21 g of oleum (20 % SO_3) at -5 to 0 °C under continuous stirring. After the addition the mixture was stirred for 1h at 0 to 5 °C, during this time a white precipitate formed. The precipitate was quickly filtered off through a glass funnel, washed with trifluoroacetic acid (3×10 mL), and squeezed. The product was dried over vacuum at room temperature. Yield 10.34g (68.9%, calculated on urea). IR (cm^{-1}): 3217, 3194 (NH); 1744 (C=O); 1605, 1454, 1319 (NNO_2). ^1H NMR (DMSO-*d6*): δ 13.71 (s, 2H). Anal. Calcd. for $CH_2N_4O_5$: C, 8.00; H, 1.34; N, 37.34; Found: C, 7.96; H, 1.39; N, 37.65 %.

2.5. Preparation of nitramide (2)

The nitration of urea was carried out as described above. After keeping stirring for 1h at 0 to 5 °C, the mixture was poured into 30g of an ice-water mixture, maintaining the temperature below 10 °C. The mixture was extracted with ethyl acetate (4×30 mL), and the extract was washed with water (3×20 mL), kept for 2h at 20 °C, and evaporated to dryness under reduced pressure. The product was dissolved in 20 mL of ether, and the solution was poured into 250 mL of hexane, and the precipitate was filtered off. Additional recrystallization from dichloroethane and 2-propanol (9:1) gave nitramide. Yield 7.56 g (61.0 %, calculated on urea), m.p. 80-81 °C. IR (cm^{-1}): 3366, 3259 (NH); 1535, 1402, 1321 (NO_2). ^1H NMR (DMSO-*d6*): δ 11.18 (s, 2H). Anal. Calcd. for $H_2N_2O_2$: H, 3.25; N, 45.16; Found: H, 3.17; N, 45.12 %.

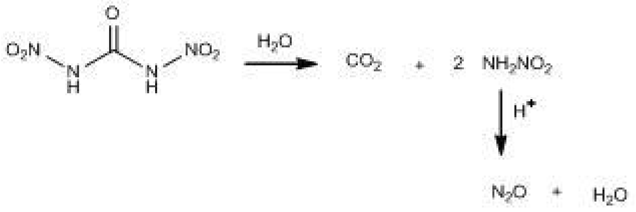
2.6. Preparation of N-dimethylol nitramide (3)

The nitration of urea was carried out as described above. After keeping stirring for 1h at 0 to 5 °C, the mixture was poured into 30 g of an ice-water mixture, and 50ml of a 37% formaldehyde solution was added at a temperature not exceeding 20°C. The mixture was heated to 35 °C, stirred for 30min, cooled, and extracted with ether (5×50ml). The extract was dried over $MgSO_4$, and the solvent was distilled off under reduced pressure to obtain a yellowish oily substance. Yield 11.3g (46.3%, calculated on urea). IR (cm^{-1}): 3500~3300 br (OH); 2974, 2918 (CH_2); 1541, 1296 (NNO_2). Anal. Calcd. for $C_2H_6N_2O_4$: C, 19.68; H, 4.95; N, 22.95; Found: C, 19.75; H, 4.97; N, 22.86 %.

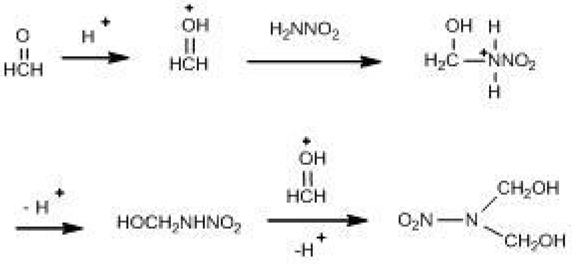
3. Results and discussion

In the procedure of DPT synthesis, DNU was an important intermediate. DNU was obtained via a direct nitration of urea with a mixture of equal parts of 98% HNO_3 and 20 % oleum at low temperature. DNU was initially reported to undergo decomposition at room temperature which could lead to spontaneous ignition [11]. This behavior was due to trace amounts of acids in crude DNU product. The drawback was overcome by washing with trifluoroacetic acid to remove all acidic impurities and the pure DNU was stable for several weeks in a desiccator over silica gel at room temperature [10, 13].

In our preliminary study, DNU was separated and added under stirring to a 37 % formaldehyde solution, and with subsequent addition of ammonia after hydrolysis of DNU the yield of DPT did not exceed 40 %. We optimized reaction conditions and developed a facile synthesis of DPT. In the modified process, DNU underwent hydrolysis to give nitramide without isolation of pure DNU. Due to instability of nitramide in acid medium (Scheme 2) [17], the presence of formaldehyde was requisite for the hydrolysis of DNU to form relatively stable N-dimethylol nitramide (Scheme 3).

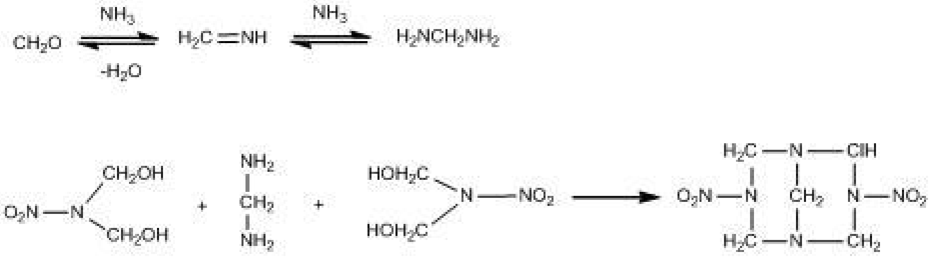


Scheme 2 The hydrolysis of DNU and the decomposition of nitramide in acid medium.



Scheme 3 The relatively stable N-dimethylol nitramide formed in the presence of formaldehyde.

The subsequent addition of ammonia in the presence of formaldehyde formed methylenediamine, which reacted with N-dimethylol nitramide to give the precipitation of DPT (Scheme 4) [6]. The precipitation of DPT was filtered off, water-washed and dried at room temperature. The yield of DPT was up to 67.4% (urea basis) with m.p. 209-210 °C (published data: 205-206 °C) [16].



Scheme 4 DPT formed with the addition of ammonia in the presence of formaldehyde.

3.1. Optimization of reaction conditions

To get a good yield of DPT, we investigated various reaction conditions and get optimal conditions as described in experimental section. Using the optimal conditions thus established, we altered some conditions to discuss their effect. The nitrolysis of urea was carried out with a mixture of 98 % HNO_3 and 20 % oleum at 0 to 5°C for DNU may undergo decomposition at higher nitration temperature. Oleum was requisite for the procedure and the usage of 98 % H_2SO_4 would obtain neither DNU nor DPT in the process. Our efforts here were directed toward the reduction of HNO_3 and oleum consumed. The results were summarized in Table 1.

Table 1
Nitrolysis of urea with a mixture of 98% HNO_3 and 20 % oleum [a].

entry	HNO_3 (mol)	98 % HNO_3 (g)	20 % Oleum (g)	Yield of DPT (%)
1	0.20	12.8	22.5	42.2
2	0.25	16.0	22.5	52.5
3	0.30	19.2	22.5	53.2
4	0.35	22.5	11.2	41.1
5	0.35	22.5	16.8	53.3
6	0.35	22.5	22.5	67.4
7	0.35	22.5	28.0	63.6
8	0.35	22.5	34.0	58.7
9	0.40	26.0	22.5	55.7

[a] urea, 0.1mol; 37% formaldehyde solution, 50 mL.

We noted that a molar ratio of HNO_3/urea 3.5:1 (mol:mol) led to a higher yield of DPT. We fixed the molar number of urea and HNO_3, and changed the amount of oleum to find the relationship among them. As the results shown in entries 4-8, there was a significant effect on the yield when changing the amount of oleum. The optimal amount of oleum was equal to 98% HNO_3, and the higher amount of oleum did not improve the result to a greater extent.

When the reaction was finished, DNU was prepared in situ without isolation of the compound. The hydrolysis of DNU in the presence of formaldehyde occurred under the optimized reaction conditions as described in experiment section. The yield of DPT altered with the amount of formaldehyde and the results were presented in Fig. 1. It can easily be seen that a molar ratio of formaldehyde/urea 5:1 (mol: mol) led to a higher yield of DPT. 1 mol of formaldehyde corresponds to 100 mL of a 37 % formaldehyde solution. In the presence of excess formaldehyde, the yield of DPT was decreased. The reason may be that nitramide reacts with excess formaldehyde to give a little polycondensate or cyclic product [17, 18].

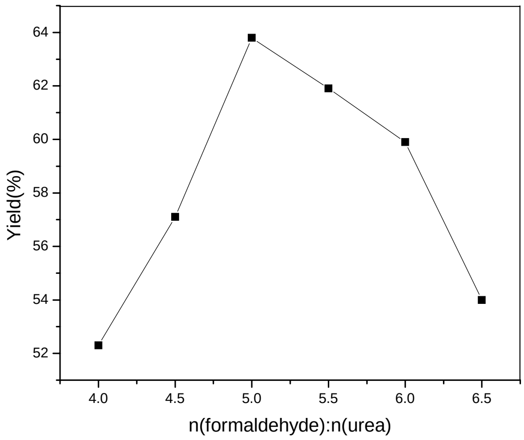


Fig. 1. Effect of n(formaldehyde) : n(urea) on the reaction.

In the procedure of the hydrolysis of DNU, the effect of temperature on the yield of DPT was studied. Experiments were carried out as shown in Fig. 2. Here one can observe that the appropriate temperature of the hydrolysis reaction was 30-40 °C.

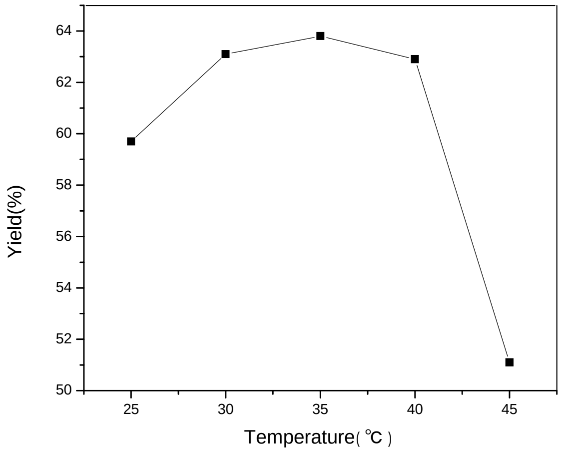


Fig. 2. Effect of temperature in the procedure of hydrolysis of DNU on the reaction.

After the hydrolysis of DNU in the presence of formaldehyde, the subsequent experiment of neutralization with ammonia was carried out as shown in Fig 3. A range of pH 6.0-7.0 was commendatory in the experiment, and the higher amount of ammonia did not improve the result to a greater extent.

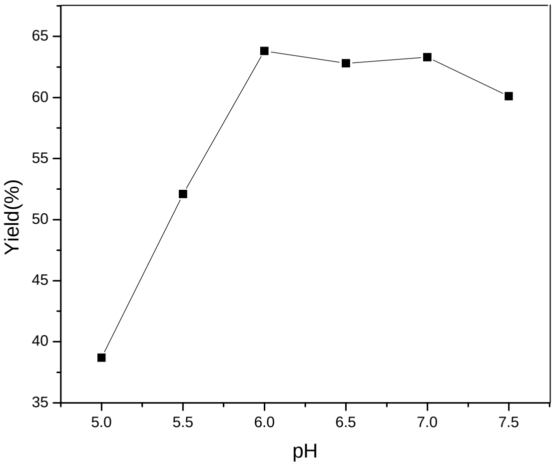


Fig. 3. Effect of pH on the reaction.

4. Conclusion

An improved and facile process to synthesize DPT from urea has been developed and various operating parameters such as temperature, pH and molar ratio of reagents have been optimized to give maximum yield of the desired product. The low cost method is concise, operationally simple and offers high purity and satisfactory yield of DPT. Further investigations of nitration of DPT to obtain stable energetic materials are currently underway.

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