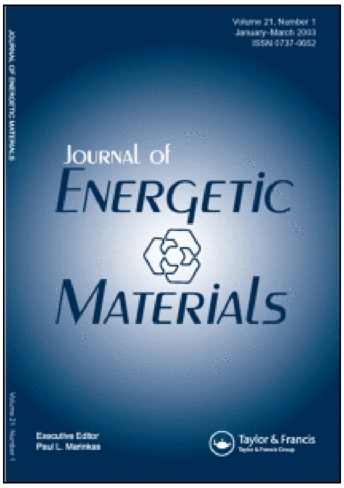

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A PARAMETRIC STUDY OF THE SYNTHESIS OF 2,3,4,6-TETRANITROANILINE

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ABSTRACT

As part of the synthesis scale-up of the explosive 7-amino-4,6-dinitrobenzofuroxan (ADNBF), the mixed-acid preparation of 2,3,4,6-tetranitroaniline (TNA) from *m*-nitroaniline has been reinvestigated. Yields of 80-97% were obtained under extremely mild reaction conditions. During the course of our study we had an incident which resulted in sudden and rapid ejection of reaction material onto laboratory personnel. The reaction conditions which underlie this potential hazard have been identified and safe reaction conditions are discussed. The improved procedure is now regarded as very safe with an easily controlled exotherm.

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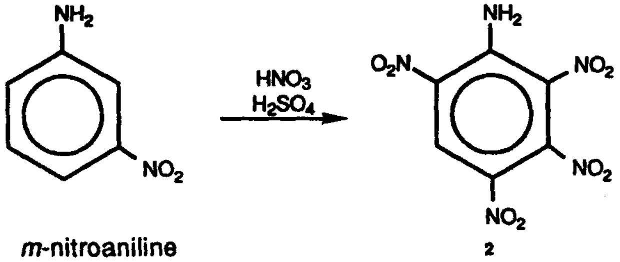
INTRODUCTION

An area of continuing interest and activity is the development of new explosives with increased stability and insensitivity without decreased energy. A promising candidate--7-amino-4,6-dinitrobenzofuroxan (ADNBF), 1,--is under study in our synthesis scale-up program. The synthesis of ADNBF, first reported by Hobin,[1] was improved by Norris,[2] whose straightforward, high yield preparation is shown in eqs. 1 & 2:



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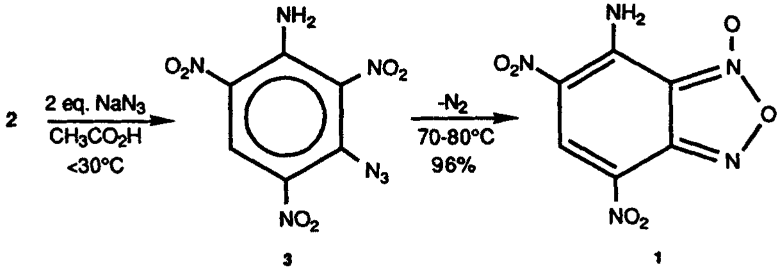

(2)

The above sequence differs only slightly from that of Hobin. The procedures are similar in that 2,3,4,6-tetranitroaniline

(TNA) is a precursor,[3] which is subsequently reacted with NaN_3 to give 3-azido-2,4,6-trinitroaniline, **3**; thermal degradation of **3** then generates the furoxan ring with accompanying loss of N_2. Norris changed the solvent in the second step to acetic acid and effected the thermal degradation of **3** without isolation. This simplified procedure resulted in a substantial improvement in yield as well as a significant increase in particle size. In several of our experiments, we have obtained pure, nearly cubic, 80 micron particle size ADNBF, directly from the last step (eq. 2).[4]

TNA was first prepared by Fluerscheim in 1910[5,6] and has considerable history as both an explosive and an intermediate in the synthesis of other explosives.[5,7,8] The early TNA literature contains considerable controversy concerning its synthesis,[9,10,11] stability,[9,10,12] and even melting point.[5,12] A summary of the TNA literature by Fluerscheim[9] briefly outlines or references[13] a considerable array of synthetic procedures, with specific mention given to the preparation of TNA on a substantial scale. In spite of this abundance of early literature, significantly detailed experimental procedures are not found until the more recent reports of Kaplan[14] and Shipp.[7]

At the start of our ADNBF synthesis scale-up work, we followed the procedure of Norris,[2] who prepared TNA in 63% yield.[15] This yield is consistent with those reported in all the earlier literature.

RESULTS AND DISCUSSION

We obtained TNA in the reported yield following Norris' procedure exactly (Procedure A; see experimental section). However, our yields diminished to 45-55% when scaled by 3-5 times and our first significant scale TNA preparation in a 50-liter kettle (Procedure A x 22) gave only an 8% yield. In addition to continuing the trend to lower yields at greater scale, the latter demonstrated the impracticality of the "drowning"[14] work-up. We modified the work-up to that suggested by Fluerscheim[9] (Procedure B). The second reaction in the 50-liter kettle with this more convenient work-up gave only a modest improvement in yield (23%). These disappointing results prompted us to initiate our own parametric study[16] of the TNA preparation. We subsequently carried out 70 TNA experiments in which the reaction conditions were modified or a modified procedure was scaled-up. No attempt is made to list the results of all 70 reactions, but rather an indication is given as to the direction of the modifications and the rationale for them. Table 1 lists the results of our initial modifications of Procedure A.

TABLE 1[a,b,c]

Reaction	Procedure modification	Yield (%)
1	reaction held at 75°C overnight	24
2	slow addition of mixed acids without any external cooling (6 h); T_{rxn} 75°C	42
3	*m*-nitroaniline dissolved in 100% H_2SO_4	65
4	repeat of #3	57
5	1.8 molar scale repeat of #3 & #4	51
6	less oleum in mixed acids composition	60

[a]All reactions carried out at 0.615 molar scale unless otherwise stated; [b]Procedure A; [c]Temperatures ±5°C; yields ±1%

Entries 1 & 2 in Table 1 showed the largest deviation from our earlier experiments and clearly showed that longer contact between TNA and the nitration medium at elevated temperatures significantly reduced the yield. Results from our subsequent work are shown in Tables 2, 3, and 4.

Although the procedure for the set of experiments in each table is slightly different, the general trend shown from Table 2 to 4 is the lowering of the reaction temperature. The positive effect of yields that approach 80% (Tables 2 & 3) was offset to some extent in that the TNA obtained was less pure (melting points from 202-212°C). Entry 4 in Table 3 was an exception to this and was pivotal to our later experiments (Table 4). As indicated, this reaction was allowed to stand at

TABLE 2[a,b,c]

Reaction	Procedure modification	Yield (%)
1	T_{rxn} 75°C, cooled to room temperature overnight	73
2	repeat of #1	70
3	T_{rxn} held at 55-57°C for 1 h then allowed to rise to 80°C	73
4	less oleum in mixed acid composition	71
5	T_{rxn} 56°C	73
6	1.8 molar repeat of #1	62
7	3.6 molar repeat of #1	64
8	less HNO_3 in mixed acid composition	61

[a]All reactions carried out at 0.615 molar scale unless otherwise stated; [b]Procedure B; [c]Temperatures ±5°C, yields ±1 %

room temperature for 3 days before work-up. From this reaction we obtained pure TNA (m.p. 216.3°C) as well as the highest yield to that point in our studies. We rationalize the results of this experiment according to the discussion in Kaplan's paper. TNA occurs by C-nitration together with N-nitration, followed by rearrangement of the N-nitramine derivative to the C-nitro derivative in the strongly acidic reaction media.[12] The kinetics of this rearrangement must be quite fast at the higher temperatures (75°C). However, when the reaction is carried out at lower temperatures, the kinetics of this rearrangment are sufficiently slow that the conversion is incomplete within 24 hours. Thus, the depressed melting points of earlier reactions reflect a mixture of TNA and

N-nitramine precursor. This hypothesis was confirmed, to some extent, by converting the TNA of depressed melting point to pure TNA by warming (60°C) in concentrated sulfuric acid.

TABLE 3[a,b,c]

Reaction	Procedure modification	Yield (%)
1	T_{rxn} 40°C followed by cooling to ambient temperature overnight	76
2	T_{rxn} 40°C and held at 40°C overnight	76
3	*m*-nitroaniline dissolved in approximately 100% H_2SO_4	74
4	T_{rxn} 40°C, left at room temperature for 3 days; 0.5 molar scale	83
5	1.8 molar scale repeat of #1	75

[a]All reactions carried out at 0.615 molar scale unless otherwise stated; [b]Procedure C; [c]Temperatures ±5°C, yields ±1%

The best results of our work are presented in Table 4. Good to excellent yields of TNA were obtained when the nitration was carried out at room temperature (20-25°C) followed by a "digestion" period of 3-5 days for the completion of the nitramine-to-TNA rearrangement. The purity of the TNA was high-melting points at or within 2-3 degrees of the literature value. Effecting the synthesis of TNA at room temperature or below is not novel; it was one of 11 methods mentioned in Fluerscheim's patent[5] which, however, lacked adequate detail of yield and purity of product.

TABLE 4[a,b,c]

Reaction	Procedure modification	Yield (%)
1	T_{rxn} 25°C	82
2	repeat of #1	87
3	T_{rxn} 15-17°C	83
4	1.8 molar scale of #1	80
5	5.5 molar scale of #1, mixed acid addition time 4 h	95
6	repeat of #5	97
7	repeat of #6	83

[a]All reactions carried out at 0.615 molar scale unless otherwise stated; [b]Procedure D; [c]Temperatures ±5°C, yields ± 1%

The yields obtained from procedure D, although consistently at or above 80%, fluctuated somewhat as indicated in reactions 4-7 of Table 4. The near quantitative yields of reactions 5 and 6 are not regarded as anomalous. Rather, we feel they reflect a subtle, and as yet not fully characterized, reaction temperature profile during the digestion period and that yields of greater than 90% may be routinely achieved. The temperature <u>during the digestion period</u> is a critical parameter. In one of our experiments, the temperature was maintained below 25°C throughout. The melting point of the product was very low (202-207°C). When this was repeated, and the temperature during the digestion period was maintained at 28-30°C, the TNA was quite pure (m.p. 214-215°C).

Our results indicate a distinct advantage in the synthesis of TNA by this procedure with regard to (a) yield, (b) safety of carrying out nitrations at lower temperatures, and (c) ease of control of reaction exotherm. Comparison of Procedure D with those of Kaplan[14] illustrates what appears to be an inherent compromise in the synthesis of TNA: Kaplan's nitration procedures are rapid and yield large quantities of product (albeit less pure) per unit time. The slow nitration procedure reported here has the advantage of significantly higher yields and excellent product purity offset by the lengthy "digestion" period, a not insignificant inconvenience for scale-up efforts.

The issue of safety in the TNA synthesis bears comment here as it has in the past.[9,14] During the course of this investigation, we had an incident which resulted in personnel injury. The synthesis of TNA is marked by the precipitation of the product from the nitrating solution and a significant amount of outgassing.[17] In all of our experiments in which the reaction temperature was maintained between 30-50°C for any significant period of time, the initial precipitate, TNA and/or N-nitramine precursor, agglomerated to the stirring shaft, paddle, and thermometer tip. Stirring became difficult and on two occasions the "sticky mass" broke the ,thermometer. After some time the "sticky mass" would harden and in an hour or two the reaction would consist of a freely stirring medium of acid with insoluble material suspended throughout. Initially, thinking that this phase of the reaction was merely a nuisance, we now feel that it may give rise to a hazardous situation. During one of our reactions, material was rapidly, and without warning, ejected from the flask, spraying acids onto the laboratory personnel. We surmise this incident may be due to the following sequence of events. As the "sticky" material accumulates around the stirring shaft and paddle, the heat flow and outgassing from within the mass are restricted. This could lead to local pressure buildup followed by rapid uncontrolled release. Any reaction in which initial precipitation leads to accumulation of material around the stirring device should be discontinued, cooled to room temperature, and carefully discarded.

Reactions carried out with the addition of the mixed acids at 50°C or higher are not complicated by agglomeration of the initial precipitate. Much to our surprise, the reactions carried out at room temperature or below are likewise uncomplicated. Thus, we recommend that TNA syntheses not be carried out between 30-50°C. It is our contention that procedure D is a safe synthetic method for the preparation of TNA. The other concern with this reaction is control of the exotherm. An ice-water bath is more than adequate for the reactions above 50°C and simple immersion of the reaction flask in a flowing tap-water bath (17°C) is sufficient for the room temperature procedure.

EXPERIMENTAL

2,3,4,6-tetranitroaniline, 2

Procedure A[2]: To an efficiently stirred, warm (60°C) solution of 85 g (0.615 mole) of *m*-nitroaniline dissolved in 750 mL conc. sulfuric acid was added a solution of 150 mL 90% HNO_3 (3.20 moles)/250 mL 27-33% oleum at such a rate, with additional cooling from an ice-water bath, to maintain a temperature of 75 ±5°C. Upon completion of the addition, the reaction was allowed to cool to 60°C, then poured, with vigorous stirring, onto ice. The insoluble product was collected, washed with additional cold water, and dried.

Procedure B: To an efficiently stirred solution of 85 g (0.615 mole) of *m*-nitroaniline dissolved in 750 mL conc. sulfuric acid was added, with cooling, a solution of 150 mL 90% HNO_3 (3.20 moles)/250 mL 27-33% oleum maintaining the solution at 20 ±2°C. After the addition of all the mixed acids, the reaction was heated to 40°C. The heating mantle or hot-water bath was removed and the temperature maintained at 40-50°C with an ice-water bath. Precipitation of the product generally was dependent on the temperature chosen (the higher the temperature, the faster the product precipitated). After the reaction's exotherm had abated (1-2 h), the reaction was allowed to cool to room temperature with continued stirring overnight. The product was collected by suction filtration[9] through a coarse fritted disc funnel, washed first with cold 50% aqueous sulfuric acid then with cold water, and finally dried.

Procedure C: Essentially the same as Procedure B except that the reaction was not heated to 40°C. The reaction's own exotherm was allowed to raise the reaction to a designated temperature (**CAUTIONARY NOTE!** the temperature rise profile, with all the mixed acids in the reaction, is exponential). Once the desired temperature was reached, the temperature was maintained with an ice-water bath, as needed. Work-up was as described in Procedure B.

Procedure D: Addition of reagents was as described in B with a temperature of 18-20°C during the addition [1-4 h depending on the scale]. The reaction was maintained at 20-25°C with tap-water (15-17°C) [The bulk of the flask immersed in a bath adapted in a fashion similar to a condenser so that the water is constantly being recharged.]. Within 1-2 h insoluble material was observed and the reaction exotherm abated shortly thereafter. The reaction was stirred at 28-30°C for an additional 3-5 days. Work-up was as described in Procedure B.

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REFERENCES

1. T.P. Hobin, Tetrahedron, 24, 6145 (1968).
2. W.P. Norris, NWC TP No. 6724, Naval Weapons Center, China Lake, California (1986), publication UNCLASSIFIED.
3. Hobin converted 3-bromo-2,4,6-trinitroaniline to ADNBF in the same manner as TNA.
4. M.P. Kramer, NWC TP No. 6943, Naval Weapons Center, China Lake, California (1988), publication UNCLASSIFIED.
5. B.J. Fluersheim, E.P. 3224 and 3907 (1910).
6. Beilstein lists a preparation of TNA. O.N. Witt & E. Witte, Chem. Ber., 41, 3095 (1908). Careful reading of this paper indicates TNA is not mentioned.
7. K. Shipp & M. Hill, NAVORD/WOL TR No. 6016, Naval Surface Warfare Center, Silver Spring, Maryland (1958), publication UNCLASSIFIED.

8. C.F. van Duin & B.C.R. van Lennep, Recl. Trav. Chim. Pays-Bas, 39, 145 (1920).

9. B.J. Fluerscheim, J. Chem. Soc. Ind., 40, 97 (1921).

10. C.F. van Duin & B.C.R. van Lennep, Recl. Trav. Chim. Pays-Bas, 37, 114 (1917).

11. A. Stettbacher, Z. ges. Shiess-. u. Sprengstoffw., 11, 112 (1916).

12. T. Urbanski, "Chemistry and Technology of Explosives," Vol. 1, Pergamon Press, London, U.K., Chap. 17, 556 (1964) and all references cited therein.

13. B.J. Fluerscheim, U.S. Pat. 1,045,011 (1912).

14. L.A. Kaplan, NAVORD/WOL TR No. 6223, Naval Surface Warfare Center, Silver Spring, Maryland (1958), publication UNCLASSIFIED.

15. This procedure was adapted from one of several in Kaplan's paper.

16. No significant effort was devoted to alteration of the HNO_3/*m*-nitroaniline molar ratio. The amount of oleum was modified on several occasions but the effect on the yield was consistently very minor.

17. The exact composition of the gases released from this reaction was not determined. The presence of CO_2 was established ($BaCO_3$ precipitation), indicating decomposition of the aromatic ring. The quantity of gas generated from procedure D was significantly less.