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by William M Sherrill, Eric C Johnson, and Joseph E Banning

ARL-RP-0515 **December 2014**

A reprint from Propellants, Explosives, Pyrotechnics. 2014;39:670–676.

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14. ABSTRACT

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A Method for the Synthesis of Tetranitroglycoluril from Imidazo-[4,5-*d*]-imidazoles with Loss of Dinitrogen Oxide

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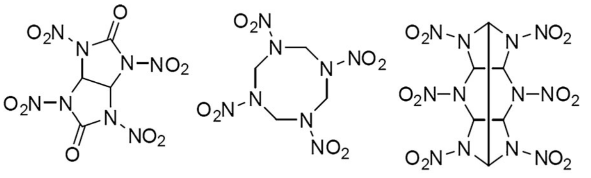
Abstract: A new method for the preparation of tetranitroglycoluril (TNGU, Sorguyl) is described, in which imidazo-[4,5-d]-imidazoles are nitrated with the elimination of N_2O to generate TNGU. This method of TNGU synthesis results in material that is less sensitive than material produced with alternative routes. Additionally, a new spherical morphology of TNGU is disclosed. This morphology exhibits an even higher resistance to external insult even than material synthesized with the new method.

Keywords: Tetranitroglycoluril · Sorguyl · TNGU

1 Introduction

Tetranitroglycoluril (TNGU, Sorguyl) (**1**) is a powerful high explosive first described in the 1970's by Boileau et al. [1]. This material, with a density of 2.01 $g\,cm^{-3}$ and heat of formation (ΔH_f) of 50 $kJ\,mol^{-1}$ has a predicted performance comparable to that of the standard military explosive octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (**2**), while approaching the performance of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) (**3**) [2]. (Figure 1)

Compound **1** has several characteristics that have prevented its adoption into military formulations to date. It is hydrolytically unstable even under normal atmospheric conditions [3], and is significantly more sensitive to external insult than HMX. If prepared using literature procedures [4], it exhibits a 50% initiation (H_{50}) value for impact sensitivity of 10.4 cm, whereas HMX is 24.4 cm on the same apparatus. Additionally, **1** has a friction measurement of 54 N, whereas HMX is typically 120 N. Taken together, these numbers place TNGU in a category of material that is usually deemed too sensitive for secondary explosive applications.



1 **TNGU** **2** **HMX** **3** **CL-20**

Figure 1. Structures of high explosives TNGU, RDX, and CL-20.

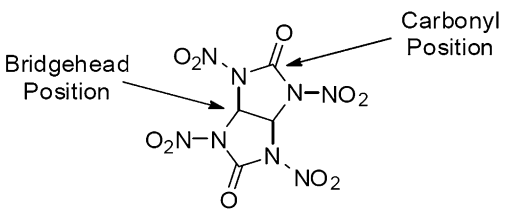


Figure 2. Structure of compound **1** showing location of bridgehead and carbonyl positions.

Recent attempts to rectify both the hydrolytic instability and the sensitivity of **1** through substitution of the bridgehead hydrogen atoms resulted in material that was energetically less powerful and still comparably sensitive and unstable [5]. This led to the idea of using substitution of the oxygen from the carbonyl position in the dinitrourea moiety as an additional means of potentially tuning both the sensitivity and the hydrolytic instability of the molecule. (Figure 2) To this end, several different imidazo imidazoles **5**–**7** were prepared using known literature procedures [6] and attempts were made to further nitrate them in an effort to produce a novel material **8** (Figure 3).

2 Results and Discussion

2.1 Computational Analysis

The target **8** is predicted by quantum mechanical models developed by Rice et al. [7] to have a density of

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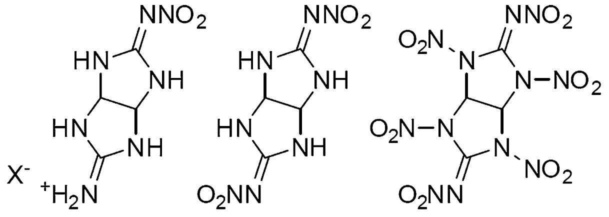


5 $X^- = Cl^-$ **7** **8**

6 $X^- = NO_3^-$

Figure 3. Structure of starting material imidazo imidazoles **5**–**7** and target **8**.

Table 1. Performance predictions from Cheetah 7.0 [2].

	8	TNGU[b]	HMX[b]	CL-20[b]
ρ	2.03[a]	2.01	1.90	2.044
ΔH_f [kJ mol^{-1}]	617.01[a]	50.0	75.02	386.0
H_{cj} [GPa]	42.51	41.77	37.19	47.09
D_v [km s^{-1}]	9.621	9.566	9.246	9.970
Δ_d [kJ mL^{-1}]	12.17	11.78	11.00	12.60
OB [%]	+11.70	+4.97	−21.61	−10.95

a) Predicted using the methods of Rice [7]. b) Heat of formation and density numbers obtained from Cheetah 7.0 database.

2.032 g cm^{-3} and a ΔH_f value of +617.01 kJ mol^{-1}. From these numbers, the predicted performance of this material exceeds HMX by almost 30% making it a highly desirable target (Table 1).

2.2 Synthesis

With the predicted performance numbers in hand, attempts were made to synthesize **8** from all three starting materials **5**, **6**, and **7**. None of the standard suite of acidic nitration conditions: 100% nitric acid (HNO_3), mixed sulfuric acid (H_2SO_4)/ <98% HNO_3, and acetic anhydride (Ac_2O)/ 100% HNO_3 were found to be strong enough to convert the lesser nitrated materials to the desired target. When subjecting materials **6** and **7** to >98% HNO_3, no reaction is observed; however, when using **5**, the material is recovered as the nitrate salt, **6**. All three materials exhibit decomposition in mixed H_2SO_4/HNO_3 conditions and no products from these reactions were successfully recovered. **5** and **6** are both converted into the dinitro compound **7** when subjected to Ac_2O/HNO_3 conditions, but were unable to be nitrated further even with extended reaction times and heating. It was discovered that all three starting materials can be further nitrated by employing a nitration mixture using trifluoroacetic anhydride (TFAA) in conjunction with nitric acid. In this case, when **5**–**7** were dissolved in <98% HNO_3 and TFAA was added slowly, a white powder slowly precipitated over time with the evolution of gas bubbles. After several hours, the powder was isolated and analyzed to find the material was not **8** as anticipated, but rather TNGU (**1**). This was further confirmed by obtaining a nuclear magnetic resonance (NMR) spectrum showing perfect overlap of signals from a mixture of **1** prepared via the nitration of **5**–**7** and of **1** prepared via the literature method [4]. All three starting materials **5**–**7** yield **1** as the product under the TFAA/HNO_3 conditions with reasonable yields although using **6** gives the best results with yields typically between 70 to 80%.

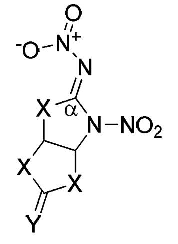
2.3 Mechanistic Discussions

Of the myriad of possible scenarios, it is postulated that two are the most likely. The first being the α-carbon of **8** is so electronincally withdrawn that the molecule is rapidly and completely hydrolyzed to **1** on exposure to moisture. This theory was quickly dismissed by repeating the experiments ensuring anhydrous conditions. Analysis of the material obtained showed it to be identical to material isolated in the original experiments indicating that hydrolysis of **8** is not responsible for the formation of **1** under the reaction conditions or under workup.

The second scenario employs intra- or intermolecular degradation with elimination of dinitrogen oxide (N_2O) as the driving force behind the formation of **1**. Once the material is subjected to the nitration conditions, it is plausible that each of the materials **5**–**7**, proceed through an intermediate resembling **9** (Figure 4) The α-carbon of this species is severely electron deficient making it highly susceptible to nucleophilic attack.

This type of reactivity with the elimination of N_2O has been documented previously by Wright and McKay [8] in their attempt to completely nitrate **10**, while only recovering **13**. (Figure 5) They proposed an intermediate **11**, which could easily rearrange under the nitration conditions with elimination of N_2O to form **12**. This was subsequently nitrated under their conditions to form **13**. Additionally, this type of reactivity has been used in the synthesis of 2,6-dioxo-1,3,4,5,7,8-hexanitrodecahydro-1H,5H-diimidazo[4,5-b:4′,5′-e]pyrazine (HHTDD) (**15**) starting from **14** [3].

The intramolecular decomposition mechanism is envisioned to employ the oxygen of the nitrimino moiety of **9**



$X = NH, NNO_2$ $Y = NH_2^+, NNO_2$

9

Figure 4. Postulated intermediate in the formation of **1**.

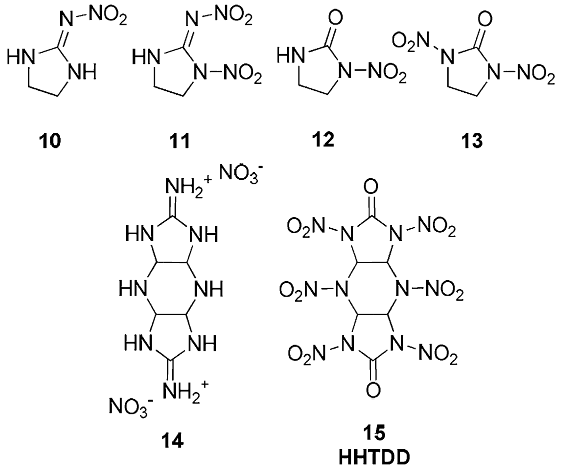
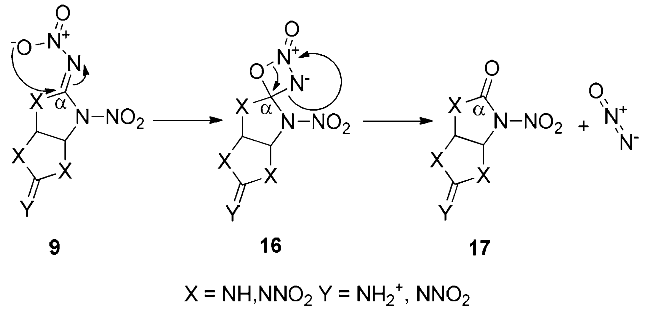


Figure 5. Literature examples of substrates believed to extrude N_2O.

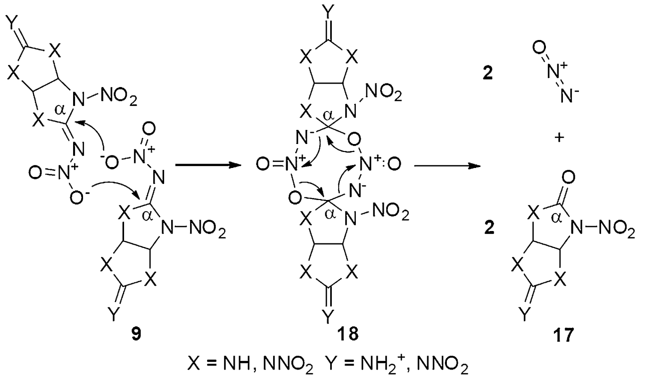


Scheme 1. Proposed mechanism for the intramolecular decomposition and extrusion of N_2O.

as the nucleophile and then proceed through a four-membered intermediate **16** (Scheme 1) The subsequent re-arrangement of the four-membered cycle results in the liberation of N_2O and a nitrourea type species **17**. This mechanism is plausible whether the starting intermediate is a dinitro- or trinitroimidazo imidazole.

Alternatively, the intermolecular mechanism starts from the same intermediate **9**. However, it uses an additional molecule of **9** as the nucleophilic oxygen source and proceeds through an intermediate resembling **18** before collapsing to release two molecules of **17** and two molecules of N_2O. (Scheme 2)

There are two possible ways to test the plausibility of the degradation theory. The first is utilizing ^{18}O labeled nitric acid to pinpoint the source of the oxygen nucleophile. The second is to monitor the headspace of the nitration mixture for the appearance of a higher than baseline concentration of N_2O. The latter of these methods was chosen as the preferable experimental method for this analysis. Dinitrogen oxide gas exhibits a very specific doublet in the infrared (IR) at ca. $2235\ cm^{-1}$. Using infrared spectroscopy it was possible to monitor the concentration of N_2O in the headspace of a nitration mixture with or without a substrate present.



Scheme 2. Proposed mechanism for the intermolecular decomposition and extrusion on N_2O.

Using a gas flow cell and injecting samples of the reaction headspace at 3 min intervals, the highest concentration of N_2O measured for the baseline nitration mixture never exceeded 0.05 absorbance units (AU). This value was used as the baseline for the subsequent nitration experiments. When glycoluril is nitrated under the baseline nitration conditions, the measured concentration of N_2O increases slightly; however the maximum concentration observed at <0.20 AU was still quite low. When **5**, **6**, or **7**, are subjected to the nitration conditions, the maximum amount of N_2O observed is more than five times higher than was observed from the nitration of glycoluril under the same conditions. (Figure 6) The fact that **1** is the only product recovered from the nitration of **5**–**7** together with the nitration of these compounds exhibiting a marked increase in the concentration of N_2O in the headspace of the reaction relative to both glycoluril and the baseline are strong indicators that a reaction mechanism similar to what is depicted in Scheme 1 and Scheme 2 is in operation.

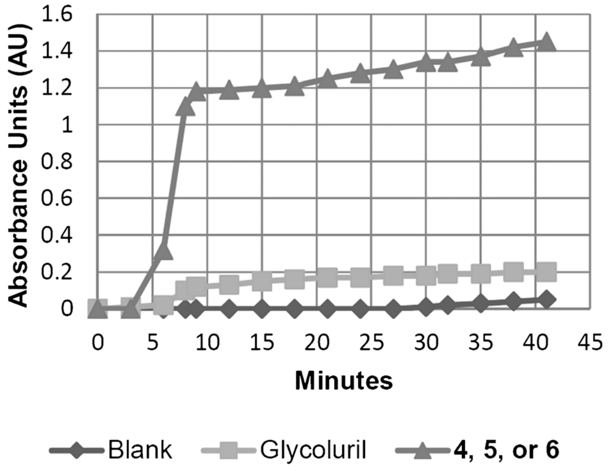


Figure 6. Concentration of N_2O in headspace of reactions over time.

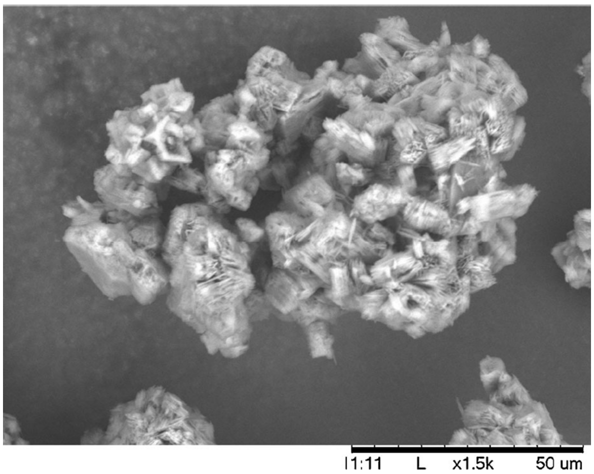


Figure 7. Compound **1** as isolated from literature method.

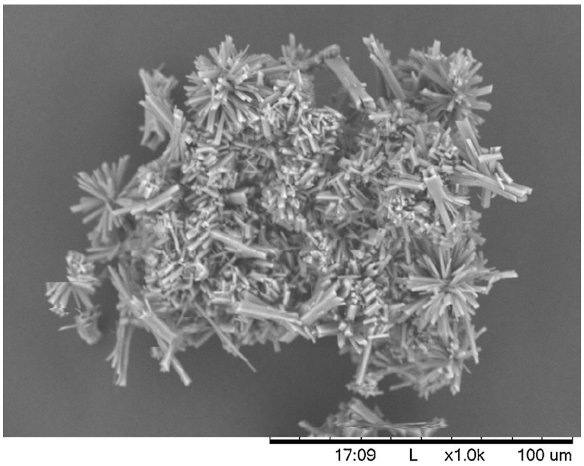


Figure 8. Compound **1** as isolated from imidazo imidazoles.

2.4 Morphological Discussions

TNGU as obtained from the nitration of glycoluril according to literature procedures [4] is recovered as small significantly porous clumps of fine needles (Figure 7).

When **1** is synthesized from **5**–**7** (Figure 8), a different morphology than that of the literature method is observed (Figure 7). While still composed of needles, the needles from **5**–**7** are significantly longer and thicker than what is observed from the literature material (Figure 8). This change in morphology is presumed to be partially responsible for the observed decrease in sensitivity of material obtained from **5**–**7**.

In efforts to obtain various other morphologies of **1** through recrystallization of the material a spherical morphology, which exhibits much improved sensitivity over even the material synthesized from the imidazo imidazoles, was discovered (Figure 9).

While many other morphologies of **1** have been described, this appears to be the first time a spherical morphology of the material has been documented. This morphology is easily obtained through solvent/anti-solvent interactions by first dissolving the material in 100% HNO_3 and precipitating it by introducing it below the surface of DCM. The size and quality of the spheres appears to be determined by the rate of addition of the TNGU solution as well as the ratio of HNO_3 to DCM.

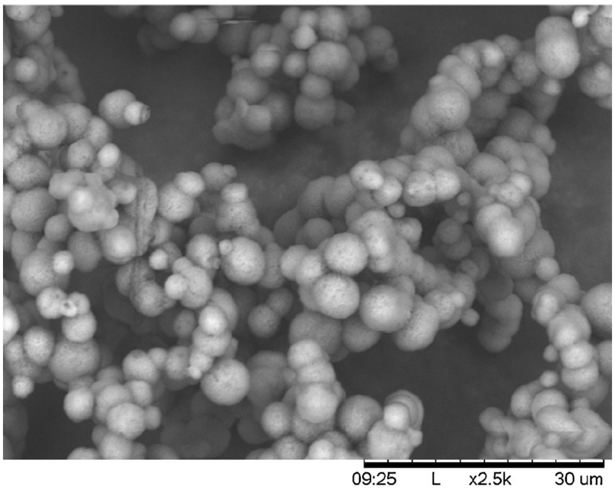


Figure 9. Compound **1** after sphericalization treatment.

2.5 Sensitivity

It is interesting to note that the sensitivity of **1** produced via the nitration of **5**–**7** with TFAA/HNO_3 is markedly improved over **1** produced using the literature Ac_2O/HNO_3 nitration of glycoluril [4]. TNGU produced via the literature method has a drop height of 10.4 cm on ARL's impact testing apparatus, while that produced via the TFAA method has a drop height of 28.1 cm. The friction and electrostatic discharge (ESD) measurement between both samples remain comparable.

Sphericalized TNGU obtained from treating TNGU prepared via the literature method and from TNGU prepared

Table 2. Sensitivity data.

Substance	Impact[a] [cm]	Friction[b] [N]	ESD[c] [J]
1[d]	28.1	70	3.25
1[e]	10.4	54	3.25
HMX	24.4	120	0.025
1[f]	33.2	72	3.25
1[g]	39.1	94	3.25

a) H_{50} impact height determined on an apparatus using a 2 kg weight by the Langlie one shot method [9]. b) Friction determined on a Julius Peter's BAM friction apparatus. c) ESD determined using an ABL Laboratories ESD Apparatus. d) **1** prepared from **5**–**7**. e) **1** prepared according to literature procedure [4]. f) Sphericalized **1**, which was synthesized according to literature procedure [4]. g) Sphericalized **1**, which was synthesized from the nitrate salt **6**.

from imidazo imidazoles was subjected to the standard suite of safety tests, impact, friction, and ESD. It was found the material prepared from the literature method had an H_{50} drop height value of 33.2 cm and material prepared from the imidazo imidazole had a drop height value of 39.1 cm (Table 2).

3 Experimental Section

Note: While these compounds were prepared without incident according the following procedures, these materials are energetic and should be prepared and handled cautiously by trained personnel.

3.1 General Considerations

Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker 600 MHz instrument. All NMR chemical shifts are reported in ppm relative to TMSCl. FTIR spectra were recorded with a Bruker Alpha-T fitted with a diamond attenuated total reflectance (DATR) attachment. Density was measured using gas pycnometry with a Micromeritics AccuPyc 1330 using nitrogen as the analysis gas. Elemental analysis was conducted with a PerkinElmer 2400 Series II CHNS/O combustion elemental analyzer using helium as the carrier gas. Differential scanning calorimetry (DSC) was performed with a TA instruments Q10 or Q20 calorimeter calibrated to the melting point of indium with a heating rate of 10 °C min^{-1} in an aluminum pan with a pin hole. All deuterated solvents were obtained from Cambridge Isotope Laboratories, Andover, MA, USA. All other materials used were obtained from Sigma Aldrich Corp. St. Louis, MO, USA and were used as received unless otherwise noted.

3.2 Synthetic Procedures

3.2.1 Synthesis of 5–7

The syntheses of these compounds were carried out according to the methods detailed by Kony [6]. His procedures were quickly and accurately reproduced to yield **5–7** and analysis of the resulting products matched the data given in his publication.

3.2.2 Alternate Preparation of 6

Compound **6** was originally prepared by the action of 100 % HNO_3 on the purified hydrochloride salt **5** [6]. It was discovered **6** is most easily prepared by taking the crude **5** obtained from the procedures described in the paper and dissolving it in 70 % HNO_3. Once all the material was dissolved, it could be crash precipitated by pouring over ice followed by purification from dilute HNO_3 as in literature [6].

3.2.3 Synthesis of 1 from 5–7

Representative Procedure from 5: Compound **5** (100 mg, 0.45 mmol) was dissolved in HNO_3 (2 mL, 100 %) at 0 °C in an inert nitrogen atmosphere. To this solution was added TFAA (2 mL) dropwise at such a rate as to keep the temperature of the solution below 10 °C. After the addition was completed, the reaction was allowed to warm to room temperature and stirred for 2 h at which point stirring was stopped and the precipitant was allowed to settle. The mother liquor was decanted, and the residual solid was washed with anhydrous DCM (5–7×5 mL). Afterwards, the solid **1** was dried under vacuum (1333.22 Pa) at ambient temperature for 2 h. The total amount of **1** recovered from this process was 70.1 mg (0.22 mmol, 49 %) Peak decomposition was observed to be 217–220 °C in the DSC. **^{1}H NMR** (600.182 MHz, [D$_6$]acetone): $\delta = 7.78$ (s, 2 H). **^{13}C NMR** (150.046 MHz, [D$_6$]acetone): $\delta = 141.8$, 65.3. **FT-IR** (DATR): $\tilde{\nu} = 2997$, 2894, 1798, 1652, 1617, 1594, 1255, 1144, 1090, 768, 730, 698 cm^{-1}. $C_4H_2N_4O_{10}$: calcd. C 14.92; H 0.63; N 34.79 %; found: C 14.89; H 0.63; N 34.72 %.

From 6: **1** was prepared from **6** according to the above representative procedure. The total amount of **1** recovered from 100 mg (0.40 mmol) of **5** was 104 mg (0.32 mmol, 80 %).

From 7: **1** was prepared from **7** according to the representative procedure. The total amount of **1** recovered from 100 mg (0.43 mmol) of **6** was 89.2 mg (0.28 mmol, 65 %).

3.2.4 Scale up to 2 g of 1 from 6

The nitrate salt **6** (2.027 g, 8.16 mmol) was dissolved into HNO_3 (40 mL, 100 %) at 0 °C in an nitrogen atmosphere. To this solution was added dropwise TFAA (40 mL) at a rate to keep the temperature under 10 °C. Upon completion of the addition, the material was allowed to warm to ambient temperature and stirring was continued for 2 h. After the time had elapsed, the suspension was cooled to 0 °C, stirring was stopped, and the suspended solid was allowed to settle. The mother liquor was decanted, and the remaining solid was washed with DCM (5×20 mL). The material was vacuum dried (1333.22 Pa, 20 °C) for 2 h. The total amount of **1** recovered from this process was 1.89 g (5.86 mmol, 72 %).

3.2.5 Procedure for Headspace Analysis

The Bruker Alpha-T was fitted with the transmission module and in it was placed a 5-cm long gas flow cell fitted with ZnSe windows. A sample injection port covered with a septum was fitted in the gas supply line on the gas supply side of the gas cell approximately 15 cm prior to the cell. The exhaust of the cell was vented into the fume hood. Nitrogen carrier gas at 12 mL min^{-1} was flowed through the cell at all times, while measuring the concentration of N_2O in the headspace. A background of pure nitrogen was used, and a sample of pure N_2O was injected into the cell to confirm the setup was functioning correctly. A 6 mL sample of the headspace gases from a 100 mg scale reaction was injected and analyzed at 3 min intervals. The amount of N_2O present in the sample was determined by measuring the absorbance unit values for the N_2O peak of the doublet at ca. 2235 cm^{-1}.

3.2.6 Sphericalization Procedure

A Typical Procedure at the 2 mmol Scale: TNGU (640 mg, 2 mmol) prepared via literature methods, was dissolved in HNO_3 (6.4 mL, $\geq 98\%$) at 20–25 °C. This homogeneous solution was introduced below the surface to a stirring beaker of DCM containing ca. 100 mL at a rate approx. 1 mL min^{-1}. Once addition is completed, stirring was stopped, and the TNGU settled to the bottom of the beaker. The supernatant was decanted and the TNGU was resuspended in ca. 25 mL of DCM then allowed to settle. This washing procedure was repeated 4–6 times until no HNO_3 remained. The TNGU was vacuum dried to remove the residual DCM and stored in a desiccator over Drierite®. The amount of spherical TNGU recovered from this process was 462 mg (1.43 mmol, 72 %). Scanning electron microscopy of the material from this process stirred at a rate of 250 RPM yielded spheres ca. 3 μM in diameter.

A Typical Procedure at the 7 mmol Scale: TNGU (2.27 g, 7 mmol) prepared via the literature methods was dissolved in HNO_3 822.7 mL, $\geq 98\%$) at 20–25 °C. This homogeneous solution was introduced below the surface to a stirring beaker of DCM containing ca. 200 mL at a rate of approx. 1 mL min^{-1}. Once addition was completed, stirring was stopped, and the TNGU settled to the bottom of the beaker. The supernatant was decanted, the TNGU was resuspended in ca. 50 mL of DCM, and then allowed to settle. This washing procedure was repeated 4–6 times until no HNO_3 remained. The TNGU was vacuum dried to remove the residual DCM and stored in a desiccator over Drierite®. The amount of spherical TNGU recovered from this process was 1.66 g (5.15 mmol, 73 %). Scanning electron microscopy of the material from this process stirred at a rate of 250 RPM yielded spheres ca. 3 μM in diameter.

4 Conclusions

During the attempted synthesis of target compound **8**, a new method for the synthesis of **1** from imidazo imidazoles was discovered. These imidazo imidazoles, **5–7**, are susceptible to the loss of N_2O under the nitration conditions, and **1** obtained with this new route is more than twice more stable to external insult than **1** produced according to traditional literature methods. TNGU isolated from the nitration of **5–7** still exhibits analytics matching that of **1** synthesized by literature methods. Furthermore, a new morphology of TNGU was discovered from solvent/anti-solvent interactions of HNO_3 and DCM. This new, spherical morphology shows remarkably improved sensitivity over other morphologies previously reported. Additionally, sphericalized **1** as well as TNGU isolated from the nitration of **5–7** appears to exhibit similar hydrolytic stability to TNGU prepared with alternative methods. Both of these materials were observed to decompose if left exposed to a moist atmosphere or upon dissolution in wet solvents.

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