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N-DENITRATION OF OCTAHYDRO-1,3,5,7-TETRANITRO-1,3,5,7-TETRAZOCINE (HMX) BY HYDRAZINE CATALYZED BY PALLADIUM

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Abstract: In palladium-catalyzed reactions between HMX (1) and hydrazine, the nitramine was denitrated. The ultimate products depended on particular reaction conditions. The initial intermediate in the presence of excess hydrazine in organic solvents or water is the reactive species formaldazine (4). Under oxidizing conditions with catalyst, this reacts further to form 4-amino-4*H*-1,2,4-triazole (5) as a final product. In neat hydrazine as solvent, hexamethylenetetramine (2) and reactive intermediates such as 1,2,4-triazolidine (6) are formed *in situ* following N-denitration.

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INTRODUCTION

The chemical degradation of nitramines has been of technical interest for years. Nitro has been used as a protecting group for amines, for example, as nitroarginine in polypeptide syntheses.[2] Various industrial-scale applications of nitramine degradation have included: the disposal of residual product and by-products from the production of nitramine materials; treatment of waste streams from the production processes; and recently for the demilitarization of nitramine-based ordnance by "denitration" of this energetic component. The interest and opportunity thus existed for the demonstration and development of an efficient and environmentally benign process for denitration of nitramine materials. We recently reported the efficient N-denitration of nitramines by dihydronicotinamides.[3]

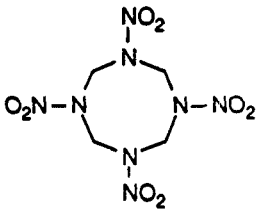
An alternative N-denitration reagent was also explored. In the chemical reduction process commonly known as "catalytic transfer hydrogenation,"[4] a reagent (e.g., cyclohexene or formate ion) capable of supplying hydrogen upon its conversion to a more oxidized form (usually catalyzed by precious metals or their compounds) may act as a "hydrogen transfer reagent" in effecting reduction of other compounds. Thus, the reduction of *C*-nitro groups to amino groups has been demonstrated using catalytic transfer hydrogenation in several reports over the years: aliphatic and aromatic nitro compounds reduced by cyclohexene-palladium;[5,6] nitroaromatics reduced by palladium-catalyzed formic, hypophosphorous, and phosphorous acids or salts;[7] and

palladium-catalyzed reductions of nitroaliphatics by ammonium formate.[8] A hydrogenolysis mechanism appeared to have prospects as a practical technical approach to nitramine denitration based on one relevant chemical system: Sivanandaiah et al. reported the deprotection of *N*-nitroarginine in protected polypeptides using palladium-catalyzed transfer hydrogenolysis by cyclohexene[9] and by hydrazine.[10] For example, the tetrapeptide BOC-Phe-Arg(NO_2)-Trp-Gly was deprotected to BOC-Phe-Arg-Trp-Gly·HOAc in 88% yield by reaction with cyclohexene and palladium black in acetic acid for 6 hours. Similarly, dipeptides containing Arg(NO_2) were denitrated in 90-95% yields in 0.5-1.0 h with ethanolic hydrazine catalyzed by palladium black.

RESULTS AND DISCUSSION

If N-denitration of HMX (1) by hydrazine were to proceed cleanly via transfer hydrogenolysis, as in the reported deprotection of *N*-nitroarginine, HMX would convert to the corresponding free amine, octahydro-1,3,5,7-tetrazocine. This unstable ring system may then depolymerize to "methyleneimine," $H_2C{=}NH$, a transient monomer that is a structural component of the most stable formaldehyde-ammonia adduct, hexamethylenetetramine (2). However, a complicating feature present in the proposed denitrating system is the hydrazine, a primary amine potentially reactive with "methyleneimine" as a possible formaldehyde synthon. The known product of condensation between excess hydrazine and formaldehyde is octahydro[1,2,4,5]tetrazino[1,2-*a*][1,2,4,5]-tetrazine (tetraformaltrisazine, TFTA, 3),[11] which was expected

potentially to form competitively with 2 in the presence of excess hydrazine.



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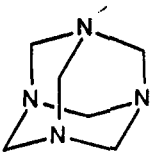

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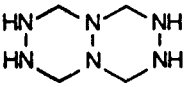

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HMX Denitration by Hydrazine in Organic Solvents

In the first test of this approach for denitration of HMX, conditions simulated those used by Sivanandaiah et al.[10] but with anhydrous hydrazine and with DMF as a superior solvent for HMX. The reaction was run with an HMX/hydrazine ratio ranging from 1:21 to 1:42, and with 10 wt% palladium black (based on HMX) at 50-55 °C. Although HMX clearly was converted to another product under these conditions (evidenced by clean disappearance of its NMR absorption), the concomitant appearance of a new pattern of NMR absorptions indicated greater complexity in this process than expected from a concerted denitration with concomitant dissociation and condensation to 2 or 3.

Upon observation of relatively rapid diminution of HMX content in the 50 °C reaction, the same system was repeated at ambient temperature, and ~98% destruction of HMX was observed by 66 h. As above, the initial product of catalytic transfer hydrogenolysis under these conditions was not 2. Rather, a product with a distinctive ^1H NMR absorption pattern appeared concomitantly

with disappearance of HMX. In the spectrum of the mixture at 66 h, a minor singlet seen at δ 6.35 was HMX that was almost gone; this shift matches that given in one report for HMX in DMSO-d_6.[12] A major AB quartet pattern was present with apparent doublets at δ 6.71 and δ 6.00 ($^2J_{HH}$ = 12.8 Hz). Formic-*d* hydrazide was also observed as an identifiable independent by-product from nucleophilic displacement by hydrazine of the dimethylamino moiety in DMF-d_7, a transformation exhibited by amides in general.[13] That the ^{1}H NMR spectrum from the reaction in DMF-d_7 showed the same multiplet, and the ^{13}C in this product was not distinctively coupled to a deuteron, proved that it did not result from a reaction involving DMF as a reactant. This reaction was then also conducted—and the same product observed—using acetonitrile solvent, but in this solvent the reaction was significantly slower, requiring 5.8 days at room temperature followed by 3.8 days at 55 °C.

A structure that appeared consistent with chemical transformations that could be occurring in this system and with the spectroscopic data was the monomeric condensation product of hydrazine and formaldehyde, formaldazine (4), a known compound formed by thermal depolymerization[14] of the insoluble amorphous condensation polymer[15] between hydrazine and formaldehyde or by their condensation below 0 °C.[16] Transient free "methyleneimine" may undergo nucleophilic substitution by the excess hydrazine to form 4 (Figure 1).

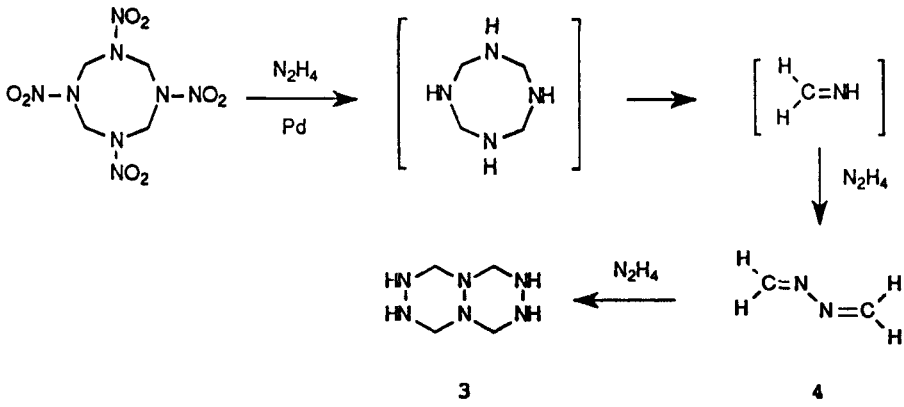


FIGURE 1.

Observed palladium-catalyzed denitration of HMX by hydrazine

This logical structural assignment was initially doubted based on some literature on this known compound. The following quotes suggested that the stability of 4 was unlikely under the conditions under which the HMX denitration product was formed and observed (48 h at 55 °C, 66 h at room temperature):

"On warming to room temperature (either neat or in solution) the material polymerized spontaneously, first to a viscous liquid and eventually to a white solid..."[14]

• "The scarcity of studies might be ascribed to the high polymerizability of formaldazine and the resulting difficulty of storage at room temperature."[17]

The direct condensation of aqueous solutions of formaldehyde and hydrazine is reported to produce the amorphous polymer.[15] Kamachi and Murahashi reported ^{1}H NMR spectra of 4 in THF solution, which showed an AB quartet at -30 °C and at 50 °C.[18]

The identity of the HMX denitration's initial product was confirmed as **4** when a sample of the reaction solution in DMF, separated from palladium catalyst and stored in an airtight bottle, precipitated **3** after several weeks. The identity of the product was confirmed by comparison of its spectral properties with those of an authentic sample of **3** prepared and purified according to literature methods.[11,15] After observing this expected product of reaction between formaldazine and excess hydrazine, the possible stability of **4** and particularly its observability by NMR were confirmed by an independent preparation. Simply mixing aqueous solutions of hydrazine and formaldehyde immediately produced a distinctive AB quartet of **4** in water: δ 6.38, 6.91 ($^2J_{HH}$ = 11.3 Hz). Under the arbitrary conditions used, no precipitate was immediately formed.

Before the identity of the initial product was confirmed as **4** by its eventual precipitation of **3** after removal of an aliquot, the sample in DMF-d_7 left under original reaction conditions took a different course. After 8 days at ~55 °C in DMF-d_7 (hydrazine/HMX ≈ 7:1), the intermediate (**4**) was replaced by a single predominant species (in addition to formic hydrazide) with a ^{13}C NMR chemical shift of δ 144.6. Proton NMR analysis of the product showed a broad absorption at δ 6.47-6.51 and a singlet at δ 8.51-8.56 in various spectra of the sample.

The identity of this later product was revealed by an analysis of its ^{13}C NMR spectrum *without* decoupling of protons. The ^1H-coupled resonance appeared as a doublet of doublets, centered at δ 144.84, with a one-bond coupling constant of 212 Hz and a long-range coupling constant of 4.2 Hz. C-H coupling

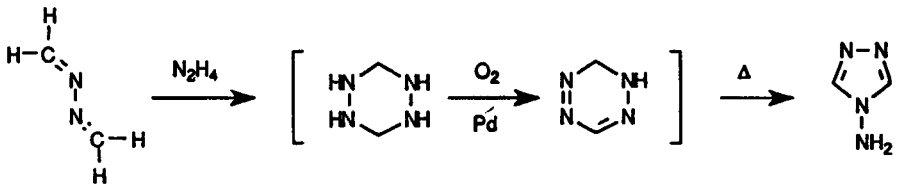
constants as large as 212 Hz are rare,[19] and among the classes of compounds that could come about in this reaction, this spectral characteristic clearly indicated the compound to be a 1,2,4-triazole. The ^1H spectrum—particularly the narrow and broad peaks with integrals in a ratio of 1:1—in conjunction with the expected chemistry in this system also pointed to 4-amino-4*H*-1,2,4-triazole (**5**) as the likely candidate. The observed ^{13}C NMR spectrum of the product agrees almost exactly with that reported in the literature for **5**:[20] δ 144.8, $^1J_{CH}$ = 212.5 Hz, $^3J_{CH}$ = 4.3 Hz. The ^1H NMR spectrum obtained for the reaction product was also close to the literature spectrum of **5**,[21] taking into account the expected solvent dependence of amine protons. Finally, an authentic commercial sample of **5** added to the solution of the reaction product produced no additional peaks in the ^{13}C NMR spectrum, demonstrating identical chemical shifts within ~3 Hz (0.04 ppm) and—in conjunction with the unusual coupling constants—essentially confirming the product as **5**.

The discovery of **5** as a final product of denitration of HMX by hydrazine indicates further interesting chemistry in this system. 4-Amino-4*H*-1,2,4-triazole (**5**) is reported to be formed simply by thermal rearrangement of 1,4-dihydrotetrazine upon melting at 125 °C.[22] Tetrazine derivatives may be recognized as reasonable products of condensation of aldehydes and hydrazine. Of course, TFTA (**3**), octahydro[1,2,4,5]tetrazino[1,2-*a*][1,2,4,5]-tetrazine, is an example that is bicyclic. As related precedent chemistry, Skorianetz and Kováts reported the condensation of various aldehydes and hydrazines to form, initially, hexahydrotetrazines, which oxidized via platinum(IV) oxide catalysis to

dihydrotetrazines.[23] For example, 1,6-dihydro-3,6-dimethyltetrazine is formed from condensation of hydrazine and acetaldehyde followed by PtO_2-catalyzed oxidation by oxygen of the intermediate hexahydrotetrazine. 1,6-Dihydro-3,6-dimethyltetrazine also reportedly decomposes upon melting at 114 °C, but the decomposition product was not characterized. 4-Amino-3,5-dimethyl-4*H*-1,2,4-triazole formed by thermal rearrangement of 1,4-dihydro-3,6-dimethyltetrazine upon melting,[23c] analogous to the behavior of 3,6-unsubstituted 1,4-dihydrotetrazine,[22] which was not mentioned in the later reports.[23]

It may be surmised, therefore, that the 4-amino-4*H*-1,2,4-triazole (5) observed in HMX denitration by hydrazine results from a similar mechanism (Figure 2), although intermediate tetrazines are not observed. This may mean either that they are transient because the subsequent thermal rearrangement of 3,6-*unsubstituted* dihydrotetrazine is faster than its formation or that the cyclization of *formaldazine* (4) under oxidizing conditions (oxygen in the presence of palladium) takes a somewhat different path directly to triazole 5.

The requirement for oxygen explains discrepant behavior that had been seen in two examples of this reaction. In the initial observation of this product, it had formed in 8 days at ~55 °C in DMF-d_7; no special precautions had been taken toward excluding air in the preparation of this sample. However, when the reaction was scaled up in order to produce an isolated sample of it, the reaction was conducted with a static atmosphere of nitrogen, and it was exposed to air only in the course of taking aliquots for



4 5

FIGURE 2.

Formation of 4-amino-4*H*-1,2,4-triazole (5)

observed in HMX denitration by N_2H_4

analysis. In the latter run, prolonged reaction on the order of 60 days at 55 °C was required for complete conversion of 4 → 5. In hindsight, it is recognized that oxygen is required for the oxidation of intermediate hexahydrotetrazine.

After removal of DMF under reduced pressure at room temperature, addition of dichloromethane produced an off-white precipitate. Proton NMR analysis of the dichloromethane-soluble portion showed none of the desired product. Purification of a sample by preparative TLC produced three fractions; analysis by ^1H NMR confirmed one of the isolated fractions as 5 and the others as formic hydrazide and *N,N'*-diformylhydrazine formed in this long-term reaction in DMF.

HMX Denitration by Hydrazine in Water

A test of possible N-denitration of HMX by hydrazine in *aqueous* solution was carried out at 50 °C for 8 days. Analysis of the residue (concentrated by evaporation) by ^1H NMR spectroscopy confirmed the complete disappearance of HMX in this reaction and

its conversion to the same intermediate (4) previously seen in the reactions in DMF and in acetonitrile, evidenced by a distinctive pair of doublets centered at δ 5.95 and δ 6.62. The AB quartet was a trace but distinct spectral component in the presence of a much larger, very broad absorption centered at δ 5.4 (indicative of the amorphous condensation polymer from spontaneous polymerization of 4).

In another test of reaction conditions in water as solvent (with dodecyltrimethylammonium bromide surfactant), a reaction between HMX and hydrazine held at 50 °C for only 5 days left some unreacted HMX, which reprecipitated upon cooling of the solution. However, when a similar reaction mixture without surfactant was held at *reflux* for only 21 h, the HMX totally dissolved and did not reprecipitate upon cooling.

HMX Denitration by Hydrazine in Neat Hydrazine Solvent

Neat hydrazine was attempted as both reagent and solvent in order to avoid complications of isolation from less-volatile and reactive DMF. HMX was added gradually to anhydrous hydrazine in the presence of palladium black at 5 °C. After 94 hours at 40-42 °C, HMX was totally consumed (according to ^{1}H NMR), and fractional distillation at reduced pressure removed excess hydrazine. According to ^{1}H NMR data, the product of the HMX-hydrazine-palladium reaction under these conditions was different from that previously observed in DMF solvent.

A single peak at δ 4.92 appeared predominant; small peaks were also present at δ 3.63 and δ 4.77 but were initially presumed to be minor by-products. In addition, ^{13}C NMR showed two major

peaks at δ 72.2 and δ 75.0 (vs. external sodium trimethylsilylpropionate-d_4 as δ 1.7)[19] in a ratio of 1:1.58, respectively. A heteronuclear correlation 2D-NMR analysis of this sample containing D_2O clearly showed that the carbon peaks were actually associated with the *minor peaks* seen in the ^1H NMR spectrum at δ 3.63 and δ 4.77, indicating that the major peak was residual hydrazine (exchanged with D_2O). The combination of a ^1H absorption at δ 4.77 and ^{13}C absorption at δ 72.2 is close to that reported in the literature[24] for hexamethylenetetramine (**2**): δ 4.75 and δ 74.5. (Note, however, that a figure in that reference showing the ^{13}C spectrum of **2** seems clearly to show that shift as closer to δ 72 rather than a tabulated value of δ 74.5. In comparison to the published figure, the current NMR data are an excellent match for **2**.) Although the ^1H chemical shift of δ 3.6 is close to that reported for **3**,[25] the lack of the distinctive AB quartet required for it rule it out as the identity of this by-product. Also, an authentic sample of **3** was prepared and purified according to literature procedures.[11,15] The AB quartet pattern is clearly apparent, centered at δ 3.59 (two doublets, $^2J_{HH}$ = 12 Hz, at δ 3.44, δ 3.73). Its ^{13}C chemical shift is δ 70.9 in D_2O (vs. sodium trimethylsilylpropionate-d_4 as δ 1.7). Therefore, neither reaction product's ^{13}C chemical shift corresponds exactly to that of **3**.

Another NMR analysis that was hoped to provide further insight into the identity of these components was the ^{14}N NMR. The ^{14}N NMR spectrum of this aqueous hydrazine solution showed the following relevant features. The predominant (~94%) constituency

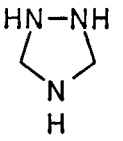
of nitrogen species was comprised of amine-type structures, occurring in the δ -320 to δ -340 region. This would include hydrazines (N_2H_4 as well as heterocyclic organics) and amines such as heterocyclic methyleneimines. Another interesting feature was an absorption at δ 230. Although it was relatively small (<2%), this chemical shift is characteristic for nitrite ion, perhaps confirmatory evidence that the mechanism obtaining in these conversions involves direct denitration of the nitramine group, as previously reported for the palladium-catalyzed deprotection by hydrazine of nitroarginine,[10] the observation upon which the current approach was based.

After the volatile solvent components (aqueous hydrazine based on the ^1H NMR spectrum) were removed under high vacuum, redissolution of the solid residue in D_2O showed a significantly different ^{13}C NMR spectrum from that exhibited by the crude product solution without reaction solvent completely removed! There was only *one* predominant peak, at δ 71.2. Furthermore, after standing at room temperature for 3 days, a new analysis showed still different ^{13}C peaks at δ 66.8 and δ 72.0 (ratio ~2:1), with a δ 70.9 peak now minor. The collective evidence of these analyses strongly suggests that the crude products from this reaction—as previously analyzed by NMR in its aqueous hydrazine solution—consisted of intermediates that were not ultimately stable in isolation, and that the following behavior was occurring in the course of this product analysis.

GC-MS analysis of the initial hydrazine solution of this product mixture was conducted for identification of the unknown component besides **2**. The analysis showed three volatile

components, with retention times of 2.3-2.7 min, 3.7-4.4 min, and 4.7-5.1 min. The first fraction had a base peak and apparent molecular ion peak at *m/z* 73; a second major peak is at *m/z* 44. The second fraction had a base peak at *m/z* 93 and an apparent molecular ion peak at *m/z* 94 (82%) or 95 (21%), which are both present. The third volatile fraction had a predominant base peak at *m/z* 32, which corresponds expectedly to hydrazine.

The 2D-NMR analysis showed hexamethylenetetramine, which is relatively involatile (subl. 263 °C) and may not readily be detected by GC under the conditions used here. Next, there are relatively few empirical formulas that correspond to a molecular mass of 73, as seen by mass spectrometry of the first GC fraction. Based on the expected chemistry occurring in this system, the likely assignment is 1,2,4-triazolidine (6). The significant *m/z* 44 peak is consistent with $H\dot{N}-NH^{+}=CH_2$.



6

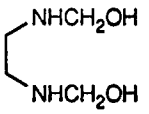
In the second GC fraction, the identities of the mass 93-95 peaks are not as clearly apparent. The simple 2D-NMR spectrum, showing 2 and, tentatively, 6 as the major components, suggests that the second GC fraction involves a thermal rearrangement of reactive 6.

1,2,4-Triazolidine (6) is interesting in not having been

reported in prior literature as a discrete compound. It is not surprising that it has not been and cannot be isolated, as it may be expected to rearrange to the most stable forms of the corresponding aldehyde-amine condensation products, **2** and **3** (or the amorphous condensation polymer). Nevertheless, this structure is also consistent with the observed 2D-NMR data, having a ^{1}H chemical shift (δ 3.63) similar to that of **3**, but occurring as a singlet (not being a constrained binuclear ring system) rather than an AB quartet, and a ^{13}C chemical shift in the typical range for methyleneimine carbons, δ 70-75. Although ^{13}C NMR data are scarce for 2-unsubstituted generic α,γ-diazacyclopentanes (**6** being an example), a relevant report is the chemical shift of 1,3-bis[(2-hydroxyphenyl)methyl]imidazolidine as δ 74.5,[26] compared to δ 75.0 observed from the second component (**6**) in the 2D-NMR spectrum. Upon removal of the solvent that allows its existence *in situ*, the components rearrange into more-stable forms; the unstable **6** may also volatilize during this process.

The complex chemical behavior suggested here is very similar to that described for a different amine-aldehyde condensation system. Zheng et al. reported their re-investigation of the ethylenediamine-formaldehyde condensation system as follows:[27] "The condensation product of 1,2-ethylenediamine with formaldehyde was thought to be compound [7] while it was present in condensation solution, but to be compound [8] or [9] after it was separated out as a solid by evaporating the reaction solution immediately after the condensation had completed. It seems to us that the key point of knowing the reaction mechanism is to understand whether [7] is the correct condensation product or not. In

order to do this the condensation liquor was examined by following techniques: (a) Gas Chromatography... (b) Mass Spectroscopy... (c) N.M.R. Spectroscopy... It may be inferred from these data that the correct condensation product is compound [10], 1,3-diazacyclopentane, not compound [7]."



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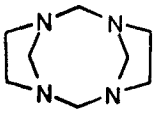

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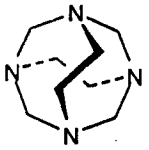

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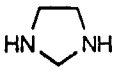

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Thus, it was seen that imidazolidine (10) is another small saturated heterocycle, similar to **6**, that is unstable in an isolated state but can exist in a solution of its condensation reactants.

RDX-Hydrazine-Palladium System

The reactivity of hexahydro-1,3,5-trinitro-1,3-triazine (RDX), the six-membered-ring congener of HMX, in the same conversion scheme was also tested by a reaction with hydrazine in DMF solvent at 55 °C. In 18 h, the RDX was all consumed, and the same characteristic intermediate (4) was observed. This result is evidence that this pathway does *not* depend on the instability of tetrazocine intermediates or on nitrosamine intermediates. The

nitrosamine analogue of RDX, hexahydro-1,3,5-trinitroso-1,3,5-triazine (R-salt), is a well-known, stable compound; it was not formed in this process. Mixed nitro-nitroso triazine derivatives are also known and characterized, and there was no evidence for such species either.

CONCLUSIONS

Reported here have been new examples of the N-denitration of aliphatic nitramines—specifically, cyclic methylenenitrimines HMX and RDX—under mild conditions, using hydrazine catalyzed by palladium. The denitration proceeds in water and in organic solvents. Under the conditions reported herein, formaldazine (4) is a surprisingly stable intermediate, in contrast to previous reports of its high reactivity. In neat hydrazine as solvent, the denitration of HMX yields 2 and also 1,2,4-triazolidine (6)—according to NMR and mass spectral evidence—as an unstable *in-situ* intermediate, a rare example of a simple saturated nitrogen heterocycle stable only in the presence of its condensation reactants under particular conditions.

Included in any further development of nitramine denitration by hydrazine should be an investigation of alternative, more economical catalysts for the catalytic transfer hydrogenation. In particular, our speculation about such feasibility is based on precedence for the efficacy of Raney nickel—in addition to precious metals such as palladium or platinum—in many of the catalytic transfer hydrogenations effected by hydrazine.[28]

EXPERIMENTAL SECTION

General. HMX and RDX were purified production-grade materials obtained from Pacific Scientific—Energy Dynamics Division (Goodyear, AZ and Chandler, AZ). *WARNING:* The nitramines used as models in this study are potentially dangerous high explosives! Many nitramines should be treated as such and should be handled by appropriately qualified personnel. The NMR spectrometer used for all analyses was a Bruker AC-300 (IBM NR-300) multinuclear spectrometer. GC-MS data were acquired at Los Alamos National Laboratory on a Hewlett-Packard 5890-A GC interfaced with a Hewlett-Packard 5971 Mass Selective Detector. The column was a Quadrex Corp. MPS 5 (SE-54 equivalent) capillary column, 0.25 mm × 25 m with 0.1 μm film thickness. All chemicals were reagent grade or better, unless specified by source.

HMX Denitration by Hydrazine (Dimethylformamide)—Formation of Formaldazine (4). A mixture of HMX (0.3484 g, 1.18 mmoles) and palladium black (0.0340 g) in DMF (7.7098 g) was warmed with an oil bath to 50-55 °C in a septum-capped flask with a stirring bar. Mesitylene (0.1789 g, 1.49 mmoles) was added as an internal NMR standard, and anhydrous hydrazine (0.8050 g, 25.12 mmoles) was added via syringe. After 24 h at 50-55 °C, more hydrazine (0.8033 g, 25.06 mmoles), palladium black (0.1040 g), and DMF (5.0 mL) were added to the reaction mixture. Analysis by NMR of the reaction solution after 39 h confirmed the complete disappearance of HMX (δ 6.35) and the formation of the characteristic AB quartet of formaldazine (4): δ 6.00, 6.71.

In a modification of this reaction, HMX (0.3473 g, 1.17 mmoles), palladium black (0.0816 g), hexamethyldisiloxane (0.1907 g, 1.17 mmoles) internal standard, DMF (10.2067 g), and hydrazine (1.8206 g, 56.79 mmoles) were mixed. The reaction was stirred at room temperature for 66 h, at which time an NMR spectrum indicated >98% consumption of HMX, with concomitant formation of **4**.

HMX Denitration by Hydrazine (Dimethylformamide)—Formation of 4-Amino-4*H*-1,2,4-triazole (5). A mixture of HMX (0.0938 g, 0.317 mmole) and palladium black (9.0 mg) in DMF-d_7 (0.7453 g) was warmed with an oil bath to 55 °C in a glass vial equipped with a rubber septum cap. Hexamethyldisiloxane (0.0573 g, 0.353 mmole) was added as an internal NMR standard, and anhydrous hydrazine (0.0749 g, 2.33 mmoles) was added via syringe. After 48 h at 55 °C, ^{1}H and ^{13}C NMR analysis showed intermediate **4** as the major component. At this time, more hydrazine (0.2061 g, 6.43 mmoles) was added to the reaction mixture, which was heated at 55 °C for another 6 days (8 days total). Proton and ^{13}C NMR analysis (see Results and Discussion) showed product **5** as the predominant component at this time.

In a separate reaction for isolation of **5**, a solution of HMX (5.03 g, 17.0 mmoles) in DMF (70 mL) was warmed with an oil bath to 55 °C in a septum-capped flask with a stirring bar. Palladium black (0.5205 g) was added, and the system was purged with nitrogen for 30 min at 55 °C. Hydrazine (3.2272 g, 0.1007 mole) was added via syringe, and the reaction flask was fitted with a nitrogen bubbler providing static N_2 pressure. After 40 h at 55 °C, HMX and intermediate **4** were still present. After 86 h at 55 °C, more hydrazine (1.7508 g, 54.63 mmoles) was added. After

175 h at 55 °C, half of the reaction solution was removed for characterization of the intermediate (**4**). Additional portions of hydrazine were added to the remainder of the continuing reaction at the following times until complete conversion of **4** to product **5** was observed: 20 days (1.96 g, 61.1 mmoles); 35 days (2.61 g, 81.4 mmoles); 45 days (3.18 g, 99.1 mmoles); 55 days (2.75 g, 85.7 mmoles). The reaction was terminated after 60 days at 55 °C. DMF solvent was removed under high vacuum. The addition of dichloromethane formed a solid precipitate, removed by filtration. Preparative thin-layer chromatography (500-μm silica gel/acetonitrile) produced three bands: R_f 0-0.15, 0.15-0.30, and 0.30-0.35. All of the fractions were extracted from the silica gel with methanol. The last of these fractions was confirmed as product **5** by NMR: ^{1}H NMR (DMF-d_7): δ 6.47-6.51 (b), 8.51-8.56 (s); ^{13}C NMR (DMF-d_7): δ 144.6.

HMX Denitration by Hydrazine (Dimethylformamide)—Formation of Tetraformalstrisazine (3). At the 175-h point of the reaction in the preceding paragraph, half of the supernatant reaction solution was carefully removed from settled palladium catalyst and transferred to an airtight bottle under nitrogen. After storage at room temperature for 93 days, the sample had precipitated white crystals in the solution. The DMF was decanted from the solution, and residual DMF was pumped off under high vacuum. The crystals had low solubility in CD_3CN but were soluble in D_2O. ^{1}H NMR (D_2O vs. TSP-d_4): δ 3.43, 3.71 (AB quartet, $^2J_{HH}$ = 11.8 Hz), identical to independently prepared **3**[15] and literature.[25]

HMX Denitration by Hydrazine (Acetonitrile). A mixture of HMX (0.3272 g, 1.10 mmole), hydrazine (1.1817 g, 36.87 mmoles),

and palladium black (48.0 mg) in acetonitrile (25 mL) was stirred at room temperature for 5.8 days. At this time, NMR analysis showed that conversion to **4** was progressing slower than in DMF; the reaction was then warmed with an oil bath to 55 °C for another 3.8 days. At this time, NMR analysis showed **4** as the major component, though **5** was already apparent. Compound **4**: ^{1}H NMR (CD_3CN): δ 6.05, 6.68 (AB quartet). Compound **5**: ^{1}H NMR (CD_3CN): δ 5.75 (b, NH_2), 8.28 (s, CH). After 8 months at room temperature in acetonitrile, **5** was the only appreciable product.

HMX Denitration by Hydrazine (Water). HMX (0.0747 g, 0.25 mmole) and dodecyltrimethylammonium bromide (0.5521 g, 1.79 mmoles, Aldrich) were added to water (100 mL) in a septum-capped flask with a stirring bar. Palladium black (8.5 mg) was added; the mixture was purged with nitrogen; and hydrazine (0.2950 g, 9.20 mmoles) was added via syringe. The reaction was warmed to 50 °C. After 8 days, evaporation of the water yielded 0.8424 g of a white solid, which was vacuum-dried for 16 h at room temperature. Proton NMR analysis of the residue (DMSO-d_6) confirmed the disappearance of HMX.

In a variation of these conditions, HMX (0.5031 g, 1.70 mmoles) and palladium black (0.0654 g) were added to HPLC-grade water (500 mL) in a septum-capped flask with a stirring bar and a reflux condenser. Hydrazine (2.5123 g, 78.39 mmoles) was added via syringe. The reaction was heated to reflux. After 21 h, the reaction mixture was clear and homogeneous. Proton NMR analysis (D_2O) of an aliquot from 35 mL of the solution concentrated to 15 mL confirmed the absence of HMX.

HMX Denitration by Hydrazine (Neat Hydrazine). A mixture of hydrazine (13 mL) and palladium black (0.0595 g) was purged with nitrogen and cooled to 5 °C in a flask equipped with a stirring bar, a condenser, and a powder addition funnel containing HMX (0.4965 g, 1.68 mmoles). The HMX solid was added slowly to the hydrazine over the course of 85 min at 5 °C. (*Warning:* Hydrazine added to solid HMX in a septum-capped flask caused the HMX to combust.) The mixture was then gradually warmed to 40–42 °C over the course of 3 h and then maintained for 94 h. The supernatant solution was transferred away from the palladium. Distillation of the solution at 3.0 torr removed most of the hydrazine at 22 °C. The pot residue was analyzed as described in the Results and Discussion. The GC temperature program started at 40 °C, ramping at 20 °C/min to a final temperature of 240 °C. GC fraction 1 MS: *m/z* 73 (100, M^+ for $C_2H_7N_3$), 72 (7.4), 44 (68), 33 (58), 32 (55), 29 (49), 28 (45). GC fraction 2 MS: *m/z* 95 (21), 94 (82), 93 (100), 66 (58), 54 (36), 28 (37). GC fraction 3 MS: *m/z* 32 (100, M^+ for N_2H_4).

RDX Denitration by Hydrazine (Dimethylformamide)—Formation of Formaldazine (4). A mixture of RDX (0.7037 g, 3.17 mmoles) and palladium black (0.0810 g) in DMF (10 mL) was purged with nitrogen, and then anhydrous hydrazine (2.8123 g, 87.75 mmoles) was added via syringe. The mixture was warmed with an oil bath to 55 °C for 18 h. Analysis by NMR of the reaction solution confirmed the complete disappearance of RDX (δ 6.22) and the formation of **4**.

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