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N-Denitration of Nitramines by Dihydronicotinamides

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Abstract: N-NO₂ bond scission in organic nitramines occurs in high yields by reaction with 1,4dihydronicotinamides. HMX (3) and tetryl (4) were used as model aliphatic and aromatic nitramines in reactions with 1-benzyl-1,4-dihydronicotinamide (BNAH, 1), resulting in hexamethylenetetramine and *N*-methylpicramide (5), respectively, as the predominant products. Radical initiation of the electrontransfer denitrohydrogenation mechanism is achieved either by photolysis or chemically by dithionite ion. A polymer-supported analogue of BNAH effects similar, though slower, N-denitration. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The chemical degradation of nitramines has been of technical interest for years, since the nitro group has been used for protecting amines—for example, as nitroarginine in polypeptide syntheses.² Industrial applications of nitramine degradation have included the disposal of residual product and by-products from nitramine production, treatment of waste streams from the production processes, and, recently, the demilitarization of nitramine degradation processes that have been used on a small scale or considered for development has included incineration,³ acid degradation,⁴ alkaline degradation,⁵ biodegradation,⁶ and miscellaneous approaches, such as adsorption-oxidation and photochemical processes.⁷ However, none is amenable to bulk-material treatment on a large scale without deleterious effects on the environment or significant (perhaps prohibitive) handling problems. The interest and opportunity thus existed for the demonstration and development of a new, efficient, and environmentally benign process for denitration of nitramine materials.

Our approach to an efficient N–NO₂ bond cleavage reagent is based on a general transformation originally described in 1980 by Ono *et al.*⁸ A chemical model, 1-benzyl-1,4-dihydronicotinamide (BNAH), for a naturally occurring biochemical, reduced nicotinamide-adenine dinucleotide (NADH), was reported to effect the replacement by hydrogen of nitro groups in certain nitroaliphatic compounds. This replacement using BNAH was demonstrated to involve an electron-transfer chain reaction mechanism. The subject of C-denitration of nitroorganics has been reviewed by Ono.⁹ Another free-radical reaction system was later described by Tanner *et al.*¹⁰ and by Ono *et al.*¹¹ in which tributyltin hydride effected replacement of nitro groups in nitroaliphatic compounds by hydrogen. The mechanism was shown by Kamimura and Ono to proceed via (tributylstannyloxy)nitroxyl radical intermediates.¹²

Finally, one of the present authors has previously reported that BNAH was a suitable reagent for effecting $N-NO_2$ bond scission in a specific nitramine under very mild conditions.¹³ In that example, commercially available BNAH (1) reacted with a model nitramine, bis(2-aminoethyl)nitramine dihydrochloride (2), in aqueous

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dimethylformamide at ambient temperature. (Compound 2 is known from prior literature.¹⁴) Photolytic radicalinitiation by irradiation with a 275-W tungsten sunlamp overnight gave 74% conversion of 2 to the corresponding unnitrated product, diethylenetriamine dihydrochloride, with the expected BNAH oxidation product, a 1benzyl-3-carboxamidopyridinium salt, as the only nicotinamide derivative present (Scheme 1).



Scheme 1. N-Denitration of a model aliphatic nitramine by 1-benzyl-1,4-dihydronicotinamide (1)

A two-step process through nitrosamine intermediates has been reported for the reduction of aliphatic nitramines using the radical-initiated tributyltin hydride system.¹⁵ That system exhibits distinct disadvantages, however, in that the nitrosamine intermediates and all tributyltin derivatives are toxic materials, and the optimized yields (\leq 55%) were lower than that obtained in the single BNAH reaction described above.

The reactions with dihydronicotinamide were expected to proceed under mild conditions, as reported in the literature for other replacements of nitro groups by hydrogen.⁸ The reactions had also been shown to proceed in a great variety of different solvents, including benzene, acetonitrile, dimethyl sulfoxide, hexamethyl-phosphoramide, and dimethylformamide. In addition, reductions of less-polar organics by BNAH have been carried out in *aqueous* solutions by the use of appropriate surfactants. For example, the photoreduction of (1,2-dibromoethyl)benzene by BNAH was achieved in aqueous borate buffer (containing 4% acetonitrile) in the presence of sodium dodecylsulfate or dodecyltrimethylammonium chloride surfactant.¹⁶ That report suggested the prospect of conducting denitrations in predominantly aqueous systems. Although photochemical activation is convenient in homogeneous, optically transparent systems, alternative *chemical* initiation schemes may ultimately be preferable for some applications. The denitration mechanism described here is also ideal in being amenable to other, chemical initiations. Thus, Ono *et al.* also demonstrated that the BNAH reduction of nitro-aliphatics could be carried out in high yield *in the dark* by the use of sodium dithionite (Na₂S₂O₄) as a one-electron-transfer reagent to initiate the BNAH reaction.⁸ (They also report that the nitro compounds are *not* reduced by dithionite in the absence of BNAH.)

RESULTS AND DISCUSSION

1. Denitration of HMX by BNAH

Our initial effort was devoted to the demonstration of the denitration of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX, 3) using BNAH (1) as a net hydride transfer agent. In the proposed sequence (Scheme 2), HMX would be denitrated to the corresponding free amine (octahydro-1,3,5,7-tetrazocine), an unstable intermediate which would dissociate to reform the most stable formaldehyde-ammonia adduct,¹⁷ hexamethylenetetramine (HMTA).



Scheme 2. Proposed N-denitration of HMX by BNAH

Without speculating about the detailed mechanism of the reorganization of octahydro-1,3,5,7-tetrazocine, a transient intermediate, the process can be seen to have the following stoichiometry:

 $3(CH_2)_4(NH)_4 \rightarrow 2(CH_2)_6N_4 + 4NH_3$

An implied by-product of BNAH oxidation in Scheme 2 would be 1-benzyl-3-carboxamidopyridinium nitrite.

In the first experiment, the reaction of HMX with BNAH in dimethylformamide (DMF) at ambient temperature, irradiated by a 200-W tungsten light bulb in a photochemical reactor cabinet, resulted in complete disappearance of the HMX in 24 h, according to ¹H NMR analysis. A control reaction under the same conditions without BNAH showed no reaction in 5 days. Other conditions used in the HMX-BNAH system are summarized in Table 1. Isolation of product from one successful denitration yielded a water-soluble solute with a single ¹H NMR (D₂O) absorption at δ 4.67 distinct from residual HOD, being therefore consistent with hexamethylenetetramine.¹⁸ A ¹³C NMR absorption at δ 74.38 was also indicative of hexamethylenetetramine.¹⁷ The sample upon being spiked with authentic hexamethylenetetramine showed no additional peaks in the ¹³C NMR spectrum, only an increase in intensity of the δ 74.38 peak.

An alternative initiator of the electron-transfer denitrohydrogenation was sodium dithionite, which may allow denitrations to be conducted in the dark. In an experiment otherwise similar to the light-initiated reactions, the HMX-BNAH reaction in DMF with $Na_2S_2O_4$, at room temperature in the dark, showed complete conversion of HMX after 4 days.

Attempts to explore the feasibility of aqueous denitration of nitramines (HMX in particular) were made, employing conditions that resembled those reported in literature for other aqueous hydrogenations by BNAH,¹⁶ which confirmed that the denitration transformation is feasible. HMX (2.6 mM) and BNAH (41 mM) dissolved in pH 9 aqueous borate buffer (5.3% acetonitrile) containing 16 mM dodecyltrimethylammonium bromide as a surfactant. Denitration occurred to extents shown in Table 1. ¹H NMR analyses of the dry product mixtures (after removal of water under vacuum) showed absorptions attributable to the BNAH oxidation product and the surfactant. The product mixture from the sunlight photolysis included an absorption near δ 4.5 in DMSO-d₆, consistent with hexamethylenetetramine.¹⁸

2. Denitration of Tetryl by BNAH

By an N-denitration transformation similar to that observed in other nitramines, N-methyl-2,4,6,N-tetranitroaniline (tetryl, 4) would be denitrated to N-methyl-2,4,6-trinitroaniline (N-methylpicramide, 5). DMF and benzene were expected to be good solvents for this reaction (Scheme 3).

Nitramine	Equivalents of BNAH per N–NO ₂	Initiator	Conditions ^a (solvent, temp)	Reaction time	Extent of N-denitration
нмх	2.9	W lamp ^b	DMF, ambient	24 h	100%
HMX	0	W lamp ^b	DMF, ambient	5 days	0%
НМХ	2.9	W lamp ^b	DMF, 5 °C	24 h	80%
				5 days	93%
				8 days	100%
НМХ	2.9	sunlight	DMF, 18 to 32 °C	3 days	93%
				8 days	100%
НМХ	3.0	$Na_2S_2O_4$	DMF, ambient	65 h	~100% (trace HMX)
				4 days	100%
HMX	3.9	W lamp ^b	H ₂ O, ^c ambient	45 h	100%
HMX	3.9	none	$H_2^{-}O,^c$ reflux	6 days	0%
HMX	3.9	sunlight	$H_2^{-}O,^{c}-7$ to 13 °C	18 days	100%
tetryl	1.0	none	acetone, ambient	1 day	100%

Table 1. Denitration of Nitramines by 1-Benzyl-1,4-dihydronicotinamide.

^a All reactions were conducted under nitrogen atmosphere. ^b 200-W tungsten lamp used in a photochemical reactor cabinet.

^c pH 9 aqueous borate buffer, 5.3% CH₂CN, 16 mM dodecyltrimethylammonium bromide.



Scheme 3. N-Denitration of tetryl (4) by BNAH

We had initially hoped that the progress of the denitrations could be monitored by a comparison of ¹H NMR data, which have been reported in the literature for tetryl¹⁹ and for $5.^{20}$ Several BNAH-tetryl mixtures were prepared: a tetryl/BNAH ratio of 1:3 in benzene solvent, with the homolytic reaction catalyzed by a 200-W tungsten light bulb; the same reactants in benzene- d_6 , also catalyzed by a 200-W tungsten bulb; the same reactants and solvent, catalyzed by sodium dithionite in the dark as a radical initiator. In all of these cases, the original tetryl disappeared according to ¹H NMR analysis, but the reaction product could not be definitively assigned as 5. One reason for uncertainty in the assignments of products became apparent upon comparison of the ¹H NMR spectrum of pure tetryl in benzene- d_6 to that reported in the literature with dimethyl sulfoxide- d_6 as solvent.¹⁹ In the latter solvent, the two types of protons

absorb at δ 9.30 (aromatic) and 3.65 (CH₃). In contrast, the absorptions in benzene- d_6 occurred in our analysis at δ 7.77 (aromatic) and 2.93 (CH₃). This great difference suggested an extrinsic phenomenon other than expected minor solvent effects. The phenomenon responsible for this large effect appears to be formation of a *charge-transfer complex* (electron donor-acceptor adduct), which has been reported to occur between tetryl and benzene or toluene^{21,22} as well as between tetryl and other aromatic hydrocarbons.²³ In none of these reports was an NMR characterization of the effect described.

Because of this complication, the solvent of choice was changed to DMF- d_7 solely for purposes of diagnosis of the course of the reaction. In this variation, a run with a 1:1 ratio of tetryl/BNAH proved more enlightening. In particular, the initial spectrum of this mixture at room temperature prior to photolysis showed that an immediate reaction occurred between these two reactants. In another variation—which allowed higher solubility of the reagents and products—simple mixing of *acetone* solutions of tetryl and of BNAH in stoichiometric proportion produced immediate darkening of the reaction solution and gradual significant precipitation of a brownish solid. ¹H and ¹³C NMR analysis of the solution showed formation of a picryl-related intermediate within the first minutes of the reaction that is distinct from starting material 4 and product 5. After reaction at room temperature for one day, the supernatant soluble portion was purified by preparative TLC, giving a predominant fraction that was confirmed by ¹H and ¹³C NMR and by elemental analysis to be *N*-methylpicramide (5). A minor fraction isolated by TLC appeared by NMR to be picric acid, presumably from adventitious hydrolysis. Analysis by ¹H and ¹³C NMR of the precipitate from this reaction, which was only very sparingly soluble in acetone but soluble in DMF- d_7 , proved it to contain the 1-benzyl-3-carboxamidopyridinium ion (6)—the expected oxidation product of BNAH in this conversion—as the only organic constituent, with no trace of picryl-related or other organic species. The salt is presumably the nitrite expected from the N-denitration.

Ohno *et al.* described a reaction of 1-propyl-1,4-dihydronicotinamide with 1,3,5-trinitrobenzene.²⁴ The aromatic ring was reduced to a 1,4-cyclohexadienylnitronate anion species (with a ¹H NMR absorption at δ 3.85 for the geminal dihydro protons) which readily re-oxidized, upon workup, to 1,3,5-trinitrobenzene. There is no evidence of such NMR absorptions (or such a product) in our reaction with tetryl, in which competition by N-denitration is available.

3. Denitrations With Polymer-Supported Dihydronicotinamides

Reports of immobilized NADH models with *polymer-bound* dihydronicotinamides suggested the possible utility of these physicochemical variants which might be more easily recovered from nitramine conversion procedures. Thus, Eling *et al.* have reported the synthesis and properties of dihydronicotinamide bound to a polystyrene resin (7).²⁵ Later, Bourguignon and co-workers optimized the preparation of this resin, based on alkylation of nicotinamide with commercial Merrifield resin (chloromethylated polystyrene) followed by reduction of the nicotinamide to the dihydronicotinamide with dithionite.²⁶ Following this approach, chloromethylated polystyrene with a degree of functionalization of 61% was used by us for alkylation of nicotinamide.

Tetryl was subjected to an N-denitration reaction with polymer-supported dihydronicotinamide. The reaction was conducted in tetrahydrofuran as a superior swelling solvent for polystyrene polymers. The electron-transfer radical reaction was also initiated in this run by photolysis, as expected to be required for typical nitro compounds. Reaction for four days gave $\sim 30\%$ conversion of tetryl to a mixture of three constituents: *N*-methylpicramide (5), a related picryl-based intermediate seen at short reaction times in earlier "free" BNAH reactions, and a minor amount of picric acid, presumably from adventitious hydrolysis. Continued reaction for a total of 11 days resulted in complete denitration of the tetryl to a mixture of 5 (predominant) and a minor amount (<10%) of picric acid.



The polymer-supported dihydronicotinamide was also used in a reaction with HMX in water solvent for development of an economical, practical denitration process using this approach. After 11 days of reaction at ambient temperature (catalyzed by a 200-W light bulb), filtration of an aliquot followed by evaporation of water to the air produced a light-yellow oily solid that was insoluble in acetonitrile- d_3 but soluble in D₂O. The remainder of reaction continued for a total reaction time of 14 days. At that time, the polymer residue was extracted three times with boiling acetone, and the acetone extract showed no sign of HMX according to ¹H NMR. Our assessment is that the polymer-supported dihydronicotinamide denitration of HMX under aqueous conditions is also feasible, although this reagent is less reactive than the "monomeric" equivalent, BNAH. The prospect of regenerating the recoverable, polymer-supported reagent 7 conveniently and inexpensively makes this denitration option attractive.

Related to the success of N-denitration by dihydronicotinamides, a recent report of similar chemistry involving tetryl is worthy of note. Shah and Spain described N-denitration of tetryl using a biochemical system involving ferredoxin-NADP oxidoreductase, an oxygen-sensitive nitroreductase, in the presence of NADPH.²⁷ The usual biochemical role of ferredoxin-NADP oxidoreductase is to transfer electrons from reduced ferredoxin (an electron source) to oxidized NADP to form NADPH *in situ*:

 $2Fd_{red}^{2+} + 2H^+ + NADP^+ \rightarrow 2Fd_{ox}^{3+} + NADPH + H^+$

As NADPH, a phosphate ester of NADH, was provided as a reagent in the system used there,²⁷ the participation of oxidoreductase to effect electron transfer should be unnecessary if an electron-transfer initiator were used. Our current study has shown the same feasibility with industrially practical variations of dihydronicotinamides, and inexpensive sodium dithionite is the initial electron source.

CONCLUSIONS

N-Denitration of aliphatic and aromatic nitramines has been demonstrated under various conditions. The large-scale practicality of dihydronicotinamides as electron-transfer denitrohydrogenation reagents would depend on the technical feasibility of regenerating them economically, as they are otherwise relatively expensive specialty chemicals. Fortunately, methodology has been developed and published for such regeneration. BNAH (1) is prepared by reduction of 1-benzyl-3-carboxamidopyridinium salts,²⁸ identified here as the oxidation product of denitration reactions. The preparation of a polymer-bound variation (7) of BNAH from its oxidized form offers the prospect for easy use and recovery of the reagent from reaction solutions.²⁶ The success of homogeneous aqueous systems for denitration of HMX suggests the prospect of nitramine degradation under conditions in which the material may not be amenable to conventional means of removal, reclamation, or destruction—e.g., material entrapped in components permeable to homogeneous aqueous solutions under mild

conditions but not otherwise conveniently accessible.

N-Denitration of nitramines by tributyltin hydride yields nitrosamine intermediates via (tributylstannyloxy)nitroxyl radicals (β -scission of the N-NO bond).¹² In contrast, radical anions of nitramines, formed in an electron-transfer mechanism in reactions with dihydronicotinamides, undergo cleavage of the N-N bond, avoiding formation of nitrosamines. Thus, denitrated free amines were the only ultimate products detected here.

EXPERIMENTAL SECTION

General. HMX (3) and tetryl (4) were production-grade materials obtained from Pacific Scientific----Energy Dynamics Division (Goodyear, AZ and Chandler, AZ). WARNING: The nitramines used as models in this study (HMX and tetryl) are potentially dangerous high explosives! Many nitramines should be treated as such and should be handled by appropriately qualified personnel. NMR analyses were performed with a 300-MHz spectrometer. All chemicals were reagent grade or better, unless specified by source.

HMX denitration by BNAH (DMF). The following example is representative of the reagent scale. BNAH 1 (1.4936 g, 6.97 mmol, TCI America) was added to a dried 3-neck round-bottom flask equipped with a Teflon stirring bar and rubber septum cap. The flask was evacuated and then refilled with nitrogen. DMF (3.50 mL) and mesitylene (71.5 mg, 0.59 mmol) were added via syringe; the latter compound was used as an internal standard for NMR, with a ¹H absorption in a noninterfering region. This solution was transferred via cannula (nitrogen pressure) to a single-neck round-bottom flask, equipped with a Teflon stirring bar and rubber septum cap, containing HMX (0.1779 g, 0.60 mmol) in 1.0 mL DMF. The mixture produced a clear orange solution. This reaction was placed in a photochemical reactor cabinet and purged with nitrogen for 1 h. The electrontransfer hydrogenation reaction was initiated by a 200-W tungsten light bulb. (In the closed cabinet, the light bulb elevated the ambient temperature of the solution.) After 4 h of light exposure, the reaction turned red in color; after 20 h, it had turned very dark. After 24 h, the reaction was terminated. ¹H NMR analysis of an aliquot in acetone- d_6 confirmed the disappearance of the HMX absorption peak.

In variations of this procedure, the reaction flask was held in a water cooling bath at 5 °C, and photolysis was conducted as above in the photochemical reactor cabinet. A solution of BNAH 1 (2.3100 g, 10.81 mmol) in 15 mL DMF was transferred via cannula (nitrogen pressure) into a round-bottom flask, equipped with a Teflon stirring bar and reflux condenser, containing a solution of HMX (0.5336 g, 1.80 mmol) in 15 mL DMF. Photolysis of the reaction was conducted with a 200-W tungsten light bulb. After 1 h of exposure, the solution turned red in color; after 16 h, it turned very dark. Some of the solution (4 mL) was concentrated under reduced pressure to remove DMF, yielding a red-brown viscous oil. Water (10 mL) was added and the solution was filtered. The aqueous filtrate was again concentrated by rotary evaporation, yielding a solute with a single ¹H NMR absorption at δ 4.67 (D₂O) and a single ¹³C NMR absorption at δ 74.38 (D₂O). Spiking the sample with authentic hexamethylenetetramine yielded no additional peaks in the ¹³C NMR spectrum, only an increase in intensity of the δ 74.38 peak.

Alternatively, in a mixture prepared similarly, the reaction proceeded outdoors via photolysis by direct sunlight, with results as described in the text.

In a variation initiated by dithionite, HMX (0.1728 g, 0.58 mmol), BNAH 1 (1.5021 g, 7.01 mmol), mesitylene internal standard (88.7 mg, 0.74 mmol), and sodium dithionite (1.2245 g, 5.98 mmol, Aldrich 85% sodium hydrosulfite) were mixed in 4.43 mL DMF. The reaction flask was equipped with a Teflon stirring bar, condenser, and nitrogen bubbler. The reaction was covered with aluminum foil, purged with nitrogen, and stirred at ambient temperature in the dark. After 18 h, water (0.50 mL) was added to the yellow slurry. Aliquots were analyzed by ¹H NMR in acetone- d_6 . After 4 days, consumption of HMX was complete.

HMX denitration by BNAH (water). HMX (0.1463 g, 0.493 mmol) was dissolved in acetonitrile (10.0 mL). BNAH 1 (0.8310 g, 3.88 mmol) and dodecyltrimethylammonium bromide (0.9484 g, 3.08 mmol, Aldrich) were dissolved in 180 mL of pH 9 borate buffer solution. Both solutions were transferred into a round-bottom flask equipped with a Teflon stirring bar and rubber septum. A portion (25 mL) of this solution was subjected to photolysis, under nitrogen atmosphere, by a 200-W tungsten light bulb in a photochemical cabinet. After 45 h, an aliquot was removed; analysis by ¹H NMR (DMSO- d_6) confirmed the disappearance of HMX.

In a modification, 15 mL of the HMX–BNAH solution in a septum-capped round-bottom flask was placed outside for sunlight photolysis (temperatures ranged from -7 to +13 °C). The complete consumption of HMX was achieved in 18 days, according to NMR analysis.

Tetryl denitration by BNAH (acetone). A solution of tetryl (1.5064 g, 5.25 mmol) in 3 mL of acetone was added to a solution of BNAH (1.1161 g, 5.21 mmol) in 9 mL of acetone in a round-bottom flask equipped with a Teflon stirring bar. The solution immediately turned very dark, and gradual significant precipitation of a brownish solid occurred. The reaction mixture was stirred for 3 h. After 1 day at room temperature, the supernatant soluble portion was purified by preparative TLC (silica gel/ethyl acetate), which produced a major fraction that was confirmed by ¹H and ¹³C NMR and by elemental analysis to be *N*-methylpicramide (5): ¹H NMR (DMF- d_7) δ 2.99 (s, 3 H, CH₃), 9.02 (s, 2 H, CH); ¹³C NMR (DMF- d_7) δ 32.96, 127.29, 133.43, 136.73, 144.19. Elemental analysis (mean of two): C, 34.55%; H, 2.41; N, 22.30. Calcd. for C₇H₆N₄O₆: C, 34.72; H, 2.50; N, 23.14. A minor fraction isolated by TLC appeared by NMR to be picric acid: ¹H NMR (DMF- d_7) δ 8.71 (s, CH); ¹³C NMR (DMF- d_7) δ 126.18, 156.0. The insoluble precipitate from the reaction appeared by NMR to be predominantly 1-benzyl-3-carboxamidopyridinium salt (6), the oxidized form (BNA⁺) of BNAH: ¹H NMR (DMF- d_7) δ 6.16 (s, 2 H), 7.46 (m, 3 H), 7.74 (m, 2 H), 8.18 (b, 2 H), 8.40 (t, 1 H), 9.23 (d, 1 H), 9.60 (d, 1 H), 10.08 (s, 1 H); ¹³C NMR (DMF- d_7) δ 64.74, 129.14, 129.92, 130.02, 130.18, 134.85, 135.40, 145.25, 145.82, 147.42, 163.11.

Polystyrene-supported dihydronicotinamide (7).²⁶ Chloromethylated polystyrene (25.19 g, 0.1146 mol Cl) with a degree of functionalization of 61% (Fluka, 16.09% Cl) was stirred in acetonitrile (200 mL) for 20 min in a 1-L round-bottom flask before adding a slurry of nicotinamide (32.85 g, 0.2690 mol) in acetonitrile (100 mL). After reaction for 7 days at reflux, the polymer was filtered and washed with acetonitrile (300 mL) and warm water (300 mL), yielding 157 g of wet, golden-colored polymer. FTIR analysis (diffuse reflectance with KBr) confirmed the disappearance of CH₂Cl (1268 cm⁻¹) in the polymer. To the wet resin in 300 mL water in a round-bottom flask was added sodium carbonate (38.00 g, 0.358 mol) in 100 mL H₂O and, slowly, solid sodium dithionite (175.50 g, 0.857 mol, Aldrich 85%). More H₂O (450 mL) was added, and the flask was fitted with a rubber septum cap and a syringe needle vent. The mixture was stirred at ambient temperature; after 5 min, the reaction turned red-orange and eventually yellow. After 24 h, the polymer was filtered (glass frit) and washed with H₂O (300 mL) and acetonitrile (100 mL). The yellow polymer was dried under vacuum at 40 °C for 48 h, yielding 41.22 g of yellow powder that was stored under argon in a refrigerator. Elemental analysis: C, 61.00%; H, 5.61; N, 6.94; S, 5.98; Cl, <0.05; residue, 12.65; (Na + O), 20.47 by difference. Calcd. for 66.75 wt% 7 + 11.87 wt% sulfinate intermediate + 21.38 wt% Na₂SO₃: C, 61.07%; H, 5.34; N, 7.05; S 6.00; Na + O, 20.53.

To a suspension of impure polymer 7 (27.98 g) in 200 mL H_2O were added solutions of Na_2CO_3 (10.25 g, 96 mmol) in 100 mL H_2O and then $Na_2S_2O_4$ (44.15 g, 216 mmol, Aldrich 85%) in 200 mL H_2O , all solutions being purged with nitrogen. This aqueous mixture was stirred under nitrogen for 56 h at room temperature. The yellow polymer was filtered off and then washed with deionized H_2O (1 L), CH_3CN (800 mL), warm H_2O (500 mL), HPLC-grade H_2O (200 mL), and then CH_3CN . The solid was suction-dried for 10 min and then dried under vacuum (0.35 torr) for 12 h at room temperature and then for 48 h at 40–50 °C (0.35

torr). The product (27.93 g) was stored under nitrogen in a refrigerator.

Tetryl denitration by polystyrene-supported dihydronicotinamide (tetrahydrofuran). Repurified polystyrene-supported dihydronicotinamide 7 (2.11 g) was stirred in 100 mL of nitrogen-purged THF for 16 h prior to use. A solution of tetryl (0.260 g, 0.906 mmol) in nitrogen-purged THF (5 mL) was added via syringe. The reaction flask was fitted with a reflux condenser, and a nitrogen atmosphere was maintained. The reaction, while stirring, was photolyzed by a 200-W tungsten light bulb in a photochemical reaction cabinet. The reaction mixture, initially yellow in color, turned orange within 4 days. At that time, analysis by ¹H NMR (acetone- d_6) of a sample of the solution—from which THF had been removed under reduced pressure—confirmed the conversion of 30% of the tetryl (δ 9.37 for aromatic CH) to a mixture of *N*-methylpicramide (the major product, δ 9.02 for aromatic CH), a presumed intermediate (δ 8.88) which appeared early in the course of the reaction but diminished in later stages as 5 built up, and a minor amount of picric acid (δ 8.71). After 11 days, the reaction was terminated. The mixture was filtered and concentrated to dryness under reduced pressure. Analysis by ¹H and ¹³C NMR confirmed 100% denitration of tetryl to a mixture of 5 and a minor amount of picric acid. Compound 5: ¹³C NMR (acetone- d_6) δ 33.15, 127.56, 133.38, 136.52, 144.49. Picric acid: ¹³C NMR (acetone- d_6) δ 126.09, 153.60.

HMX denitration by polystyrene-supported dihydronicotinamide (water). Polymer 7 (1.9652 g) was stirred in 200 mL H₂O under a nitrogen atmosphere for 2 days prior to use. HMX (0.4253 g, 1.44 mmol) was added to the polymer suspension. The mixture was purged with nitrogen before initiation of photolysis by a 200-W tungsten light bulb in a photochemical cabinet, which maintained a slightly elevated ambient temperature. After 11 days, the polymer was filtered off of an aliquot of the reaction mixture. Evaporation of water at ambient pressure and temperature left a light-yellow oily solid, which was insoluble in CD₃CN but soluble in D₂O. ¹H NMR analysis (predominant δ 4.78, minor peaks at δ 4.05, 4.42) was consistent with hexamethylenetetramine as the major soluble product. After 14 days total, the polymer residue was extracted three times with hot acetone, yielding only 10 mg of a yellow oil; ¹H NMR analysis confirmed the absence of HMX.

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