

SYNTHESIS OF
1,3,5,5-TETRANITROHEXAHYDROPYRIMIDINE-2,2,4,4,6,6- d_6 (DNNC- d_6)
AND ITS ADIOL- d_4 PRECURSOR USING PARAFORMALDEHYDE- d_2 AND
UNLABELED REACTION INGREDIENTS

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SUMMARY

Using commercially available paraformaldehyde- d_2 , the subject compounds were synthesized with unlabeled reactants and ordinary solvents. The 2,2-dinitropropane-1,3-diol-1,1,3,3- d_4 (ADIOL- d_4) precursor was produced in greater than 99% isotopic purity with aqueous depolymerized paraformaldehyde- d_2 and CH_3NO_2 in alkaline solution followed by oxidative $AgNO_3/NaNO_2$ nitration; then, ADIOL- d_4 and depolymerized paraformaldehyde- d_2 with *t*-butylamine in methanol afforded cyclic 1,3-di-*t*-butyl-5,5-dinitrohexahydropyrimidine-2,2,4,4,6,6- d_6 (DBNP- d_6). The 97% isotopically pure DNNC- d_6 product resulted in 71% yield from an anhydrous HNO_3 nitration of DBNP- d_6 .

Key Words: Deuterioparaformaldehyde, Dinitropropanediol, ADIOL, Di-*t*-butyl-dinitrohexahydropyrimidine, Tetranitrohexahydropyrimidine, DNNC, TNDA

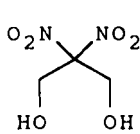
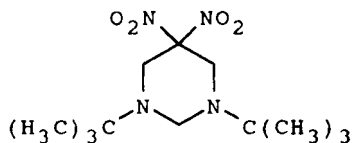
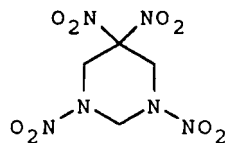
INTRODUCTION

The condensed phase kinetic deuterium isotope effect (KDIE) was first used with liquid 2,4,6-trinitrotoluene (TNT) and its α , α , α -trideuteriomethyl labeled TNT- α - d_3 analogue for identifying, *in-situ*, the rate-controlling covalent bond rupture which determines an energetic compound's energy release rate during its thermochemical decomposition process (1). Since then, a number of other high energy compounds have been investigated with this mechanistic approach. The thermochemical decomposition of solid 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and its amino-labeled TATB- d_6 analogue (2), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and HMX- d_8 , (3) hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and RDX- d_6 , (4,5) plus 3-nitro-1,2,4-triazol-5-one (NTO) and NTO- d_2 (6) subsequently were investigated with the KDIE approach using isothermal differential scanning calorimetry (1-3,5), isothermal thermogravimetric analysis (4) and direct concentration

depletion measurements on sequentially quenched isothermally decomposed samples (5,6). This mechanistic KDIE concept has also been extended into the rapid pyrolysis process with HMX/HMX- d_8 (3) and into the much higher pressure/ temperature/rate regimes involved with the combustion, (7, 8) thermal explosion, (2, 3) and detonation (4, 9) phenomena of TNT/TNT- d_3 (9), TATB/TATB- d_8 (2), HMX/HMX- d_8 (3, 4, 7) and RDX/RDX- d_6 (4, 8). Interestingly, these KDIE investigations reveal that the rate-controlling step which determines the energy release rate of an energetic compound's ambient pressure thermochemical decomposition process, can be the same as that which occurs during its high pressure combustion, thermal explosion, or possibly even its detonation phenomena (10). Because, the rate-controlling step in thermochemical decomposition appears to mirror the same rate-controlling mechanistic feature found in more drastic combustion and explosion phenomena, a condensed phase KDIE investigation of the 1,3,5,5-tetranitrohexahydropyrimidine (DNNC) **3** thermochemical decomposition process was conducted (11) after first synthesizing the perdeuterio-labeled DNNC- d_8 analogue and its deuterium labeled precursors. The syntheses of these isotopic compounds are described.

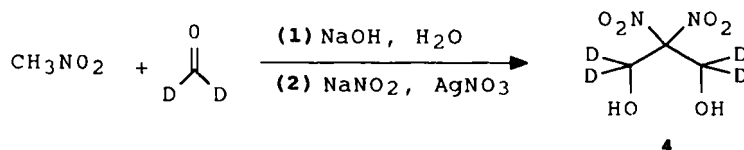
DISCUSSION

DNNC **3** (12), first reported in 1982 (13, 14), originally was viewed as a possible competitive high energy oxidizer with RDX. Its cyclic six-membered geminal 2,2-dinitroalkyl and nitramine hybrid chemical structure provides an initiation sensitivity much lower than the cyclic RDX and HMX nitramines and an energy output which rivals RDX. One synthesis procedure used 2,2-dinitropropane-1,3-diol (ADIOL) **1** as a starting material and produced 1,3-diisopropyl-5,5-dinitrohexahydropyrimidine as a reaction intermediate which was then nitrated to produce DNNC **3** (13). The other procedure nitrated the 1,3-di-*t*-butyl-5,5-dinitrohexahydropyrimidine (DBNP) **2** reaction intermediate (14) which was synthesized via the secondary 2,2-dinitroethyl-*t*-butylamine precursor (15). In

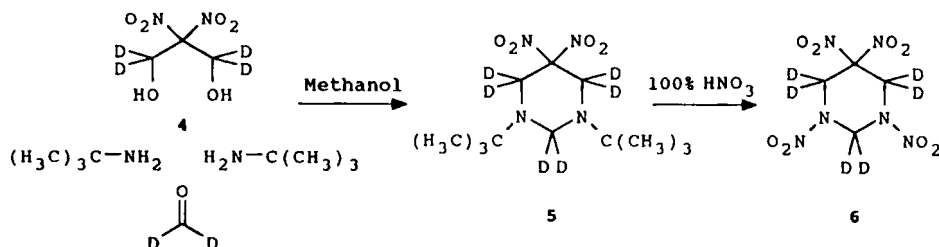
**1****2****3**

both cases, aqueous formaldehyde solution (formalin) was used to obtain the intermediate 1,3-dialkyl-5,5-dinitrohexahydropyrimidine. A more recent DNNC **3** synthesis employed precursor **1** and depolymerized solid paraformaldehyde in methanol solution to obtain the intermediate compound **2** which was then nitrated to DNNC **3** in 99% nitric acid (16).

Because it provided a potential means of using depolymerized paraformaldehyde-d₂ to obtain both the necessary ADIOL-d₄ **4** starting material and the DBNP-d₆ **5** intermediate, this most recent synthesis (16) was a key factor for obtaining DNNC-d₆ **6**. The synthesis of **4** represents a slight modification of a reported large-scale, one-pot procedure which produced **1** in a 77% yield. This former procedure used aqueous 36% formalin in an alkaline solution to effect the formalation of nitromethane (CH₃NO₂); nitration followed by adding NaNO₂ to the reaction suspension, which in turn, was added to an aqueous AgNO₃ solution (17). Precursor **4** was prepared from 4.61 g paraformaldehyde-d₂ which had been depolymerized in 15 mL deionized water with 20 mg anhydrous K₂CO₃ by heating at methanol reflux temperature for 30 hours. This aqueous depolymerization was a modification of the reported methanolic



paraformaldehyde depolymerization (16). The nitration step used NaNO₂ and the direct addition of solid AgNO₃ to the reaction suspension to obtain **4**. Compound **5** was obtained by reacting **4** and *t*-butylamine with depolymerized paraformaldehyde-d₂ in methanol. Finally, **6** resulted in a 71% yield by the nitration of **5** with unlabeled anhydrous nitric acid (18). As reported in the two-step nitration of octahydro-1,5-diacetyl-3,7-endomethylene-1,3,5,7-tetrazocine-d₈ to HMX-d₈ where unlabeled reaction ingredients also were used, no significant



hydrogen atom incorporation resulted (19). Attempts to selectively synthesize the partially labeled 1,3,5,5-tetranitrohexahydropyrimidine-4,4,6,6- d_4 compound by the Mannich condensation of 4 with normal depolymerized paraformaldehyde and *t*-butyl amine, followed by the nitration of DBNP- d_4 , was not possible because of a random rearrangement of the $-CH_2-$ methylene groups throughout the six-membered ring. The same problem occurred in the attempted synthesis of 1,3,5,5-tetranitrohexahydropyrimidine-2,2- d_2 starting with 1 and depolymerized paraformaldehyde- d_2 .

EXPERIMENTAL

The following chemicals used were either Aldrich, Baker, or EM Science reagents and were all reagent grade purity: silver nitrate, sodium nitrite, potassium nitrate, potassium carbonate, concentrated sulfuric acid and absolute methanol. The nitromethane was 96% pure (Aldrich Chemical Co. Cat. No. 10,817-0), and the *tert*-butylamine was Aldrich 99⁺% Gold Label grade. The distilled/deionized water was obtained from a Barnstead glass still/Barnstead NANO pure II deionizer combination apparatus and had an 18 megaohm-cm purity. The paraformaldehyde- d_2 was 99% D isotopically pure from Cambridge Isotope Laboratories and was purchased through Stohler/KOR Stable Isotopes. All reagents cited were used as received with no further purification. The 1H proton FTNMR spectra were obtained on a JOEL FXQ90 instrument using a TMS internal standard. Mass spectra were obtained using a direct insertion probe (DIP) analysis with a Hewlett-Packard 5985 spectrometer; Kubelka/Munk FTIR spectra were obtained under an N_2 gas atmosphere using approximately 1 mg solid sample per 80–100 mg anhydrous potassium bromide powder on a Bio-Rad FTS-7 spectrometer. All melting points were taken with a MEL-TEMP Laboratory Device in unsealed glass capillaries and are uncorrected. All reaction temperatures reflect those observed and are uncorrected for the 7000 foot elevation at the site of this laboratory. Fluorolube^R grease was used on all ground glass joints. Depolymerization of paraformaldehyde- d_2 was conducted in a custom glass blown 14/20 single-necked 25-mL round-bottom flask which was jacketed with a 100-mL single-necked round-bottom flask having an offset 14/20 neck. Methanol in the outer flask fitted with an H_2O cooled reflux condenser ensured the aqueous paraformaldehyde- d_2 depolymerization occurred at methanol reflux temperature.

Anhydrous Nitric Acid (100% HNO₃). To a 3-necked 1000-mL round-bottom flask equipped with a mechanical stirrer (center neck) plus a fitted thermometer and distillation head (side necks) connected to an H₂O-cooled condenser and receiving flask, was added 500 mL concentrated sulfuric acid. The receiving flask's adapter neck was connected to a vacuum trap submerged in an acetone/CO₂ bath; the trap in turn was connected to a glass 2-way valve which ran to an H₂O-driven aspirator. The sulfuric acid was cooled with stirring in an acetone/dry ice bath to 15°C, and then in several portions, 300 g potassium nitrate salt was added. Under an N₂ gas stream with a silicone oil bypass trap, the receiver flask was submerged in an acetone/dry ice bath. The N₂ gas stream was turned off as the H₂O-aspirator vacuum was activated. The reaction flask was gradually heated in an oil bath to 115°C. The reaction temperature inside the flask was kept between 115–127 °C under an 11 torr vacuum for 3 hours. The valve to the H₂O aspirator was closed; then the distillation apparatus was connected to the N₂ gas line, and the product in the reaction flask was put under a nitrogen atmosphere. The receiving flask with its solid nitric acid product was disconnected and immediately stoppered. After removing the frozen acetone clinging to the receiving flask's exterior, the receiver flask with its solid anhydrous nitric acid was placed into a dry box with N₂ atmosphere; where later, the thawed liquid nitric acid was transferred and sealed in a glass storage bottle with plastic acid-resistant screw cap. The 180 g (96.4% yield) colorless liquid product was stored until needed in a refrigerator freezer to prevent decomposition (18).

~~2,2-Dinitropropane-1,3-diol-1,1,3,3-d₄~~ (4). In the 25-mL jacketed reaction flask which contained a Teflon^R coated magnetic stir bar and absolute methanol in the outer 100-mL jacket flask, was placed 4.61 g (144.1 mmol) paraformaldehyde-d₂, 15 mL water and 20 mg anhydrous K₂CO₃. The 25-mL jacketed reaction flask and 100-mL outer jacket flask were each fitted with a water cooled reflux condenser and the stirred suspension was heated 30 hours at refluxing methanol temperature (64–65°C) using an oil bath. Next, a 100-mL three-necked round-bottom flask was fitted with an overhead mechanical stirrer (center neck) plus a thermometer assembly and glass stopper (side necks). To this 100-mL reaction flask was added 4.80 g (78.7 mmol) nitromethane; then, the colorless depolymerized paraformaldehyde-d₂ solution was added along with 5 mL water. The resulting suspension

was cooled with stirring in an acetone/dry ice bath to -1.4°C ; then, the cooling bath was replaced with an ice/ NaCl cooling bath. A solution containing 3.64 g (91.0 mmol) sodium hydroxide in 6 mL water was added dropwise to the suspension. The first few drops produced a reaction exotherm to 14.4°C ; then, over the next 1 hour, an addition rate was used where the reaction temperature remained at or below 6.4°C . The addition funnel was then rinsed with 1 mL water which was added to the reaction suspension. The suspension was stirred $2\frac{1}{4}$ hours at $2-3^{\circ}\text{C}$; then, 5.45 g (79.0 mmol) sodium nitrite was added to the stirred suspension followed immediately by the direct addition of 26.70 g (157.2 mmol) silver nitrate. Next, 5 mL water was used to wash all traces of sodium nitrite and silver nitrate sticking on the inner surface of the side neck into the reaction suspension. The suspension was stirred $1\frac{1}{4}$ hour at $1.8-3.0^{\circ}\text{C}$; then, 15 mL diethyl ether was added to the stirred reaction suspension. Within 5 minutes, the suspension was suction filtered using a porcelain Buchner funnel. The fine silver powder residue was washed with an additional 5 mL laboratory line deionized water. The aqueous filtrate was then extracted with (7 X 15 mL) diethyl ether. The combined ethereal extracts were dried overnight with anhydrous sodium sulfate; *in vacuo* removal of the diethyl ether gave 7.68 g yellow oil which soon began solidifying. The crude yellow solid was dissolved in 10 mL diethyl ether to which 10 mL carbon tetrachloride was added. The solution was concentrated to about 8 mL and was placed into a freezer for about 36 hours while a solid precipitate formed. Suction filtration followed; the solid product was washed with 10 mL freezer-cooled carbon tetrachloride. Drying under room temperature vacuum (0.6 torr) for $4\frac{3}{4}$ hours gave 6.04 g (50.5%) of a slightly off-white solid: mp $131.4-136.8^{\circ}\text{C}$; ^1H FTNMR (CDCl_3) δ 2.54 (br s) with no signal at δ 4.58 where 1 shows δ 4.58 (d, 4H, CH_2) and δ 2.55 (br t, 2H, OH). The FTIR and mass spectra of this isolated compound and a sublimed sample ($61-68^{\circ}\text{C}$ at 0.07–0.06 torr) showed little difference. For the sublimed sample: mp $144.8-145.2^{\circ}\text{C}$; FTIR (cm^{-1}) 3233 (OH), 2283 (C–D), 1568 and 1365 (NO_2); mass spectrum (70 eV) m/e (rel intensity), 172 (M+2, 0.5), 171 (M+1, 1.6), 154 (0.7), 153 (2.7), 139 (0.5), 38 (2.3), 122 (1.5), 121 (2.4), 120 (2.6), 108 (0.5), 106 (2.9), 105 (13.3), 92 (5.1), 78 (17.6), 77 (59.6), 76 (11.9), 75 (10.9), 73 (7.8), 60 (8.5), 58 (25.6), 49 (12.8), 46 (60.6), 45 (13.7), 44 (15.6), 33 (42.7), and 30 (base peak, 100.0). The unlabeled compound 1 synthesized in an identical manner using aqueous depolymerized paraformaldehyde gave a mp $130.2-132.6^{\circ}\text{C}$; sublimed 1 gave a mp $145.0-145.6^{\circ}\text{C}$ [lit $146-147^{\circ}\text{C}$ (17)].

1,3-Di-*tert*-butyl-5,5-dinitrohexahydropyrimidine-2,2,4,4,6,6-*d*₆ (5). Into the 25-mL jacketed round-bottom flask was placed 0.577 g (18.0 mmol) paraformaldehyde-*d*₂, 5 mL absolute methanol, and 2 mg anhydrous potassium carbonate. This suspension was stirred at reflux temperature 25 2/3 hours to effect depolymerization. A 50-mL 3-necked round bottom flask with a Teflon^R coated magnetic stir bar was fitted with a thermometer assembly and 15 mL pressure equalized addition funnel in the side necks; the center neck was stoppered. To the reaction flask was added 2.75 g (16.2 mmol) 4 and 3 mL absolute methanol; it was then cooled to 10°C using an ice bath. Into the addition funnel was placed 2.38 g (32.5 mmol) *tert*-butylamine in 3 mL absolute methanol. The methanolic *tert*-butylamine solution was added dropwise at a rate where the stirred reaction solution remained at or below 12°C, except for one momentary increase to 13°C. About 0.5 ml absolute methanol then was used to wash any residual *tert*-butylamine solution from the addition funnel into the reaction suspension. The suspension was stirred at 13–15°C for 30 minutes, except for a momentary period at 16°C; then, the colorless depolymerized paraformaldehyde-*d*₂ solution was pipetted into the addition funnel, and using an ice bath for temperature control, was added to the stirred suspension at a rate which kept the reaction temperature at 11–13°C. After addition, the ice bath was removed, and the reaction was stirred in an ambient temperature environment for 20 minutes; then, the reaction solution was refluxed 4½ hours. The reaction flask was placed into crushed ice, and the product solidified within 5 minutes. Suction filtration with a porcelain Buchner funnel gave a yellowish cream colored solid; some more product formed in the filtrate. After cooling the filtrate in the freezer about 15 minutes, it was refiltered under suction. The combined solids when dried at 0.07 torr at ambient temperature for 5 h and 10 min afforded 3.42 g (71.8%): mp 77.4–78.4°C. The product was stable from decomposition when stored in a freezer. The ¹H FTNMR (acetone-*d*₆) gave only a sharp peak at δ 1.14 (s, *t*-butyl). The unlabeled 2 analogue synthesized from 1 and normal depolymerized paraformaldehyde by this same procedure afforded a 75.3% yield: mp 74.8–75.6 [lit 80°C (16)]; ¹H FTNMR (acetone-*d*₆) δ 3.69 (s, 4H), δ 3.61 (s, 2H), and δ 1.14 (s, 18H). The missing peaks at δ 3.69 and δ 3.61 in 5 verify its perdeuterio-*d*₆ ring structure. Compound 5 also gave: FTIR (cm⁻¹) 2973, 2875 (C–H), 2094, 2064, 2013 (C–D), 1567, 1366 (NO₂); mass spectrum (70 eV) *m/e* (rel. intensity), 296 (M⁺+2, 0.4), 294 (M⁺, 2.4), 292 (17.9), 248 (4.0), 246 (8.7), 236 (3.6) 228 (5.6), 223 (22.6), 180 (6.4), 177 (7.2), 161 (3.6), 147

(32.1), 136 (3.8), 121 (11.0), 105 (5.0), 104 (5.2), 89 (27.2), 72 (25.1), 57 (base peak, 100.0), 46 (12.9), 41 (42.0), 30 (7.2), 29 (11.5).

1,3,5,5-Tetranitrohexahydropyrimidine-2,2,4,4,6,6-d₆ (6). A 3-necked 50-mL round bottom flask containing a Teflon^R coated magnetic stir bar was charged with 13.34 g (21.2 mmol) anhydrous nitric acid in a dry box under an N₂ atmosphere; the stoppered flask was then removed to a fume hood where one side neck was fitted with a thermometer and the other with a Drierite^R-containing drying tube. The center neck remained stoppered. The stirred nitric acid was cooled to 0.6°C using an ice/NaCl bath; then, the drying tube was removed and replaced with a powder funnel having a stem long enough to rest below the reaction flask's inner ground glass joint but above the stirred nitric acid. With a spatula, 1.57 g (5.4 mmol) **5** was added in small portions through the powder funnel at a rate where the reaction temperature remained at 2.2°C or below, until the last several portions when the temperature rose to 3.6°C despite the presence of the cooling bath. Occasionally, some of solid **5** had to be pushed through the funnel stem with a solid glass rod when **5** would stick and clog the stem. After addition of **5** was completed, the powder funnel was removed and replaced by a water cooled reflux condenser topped with a Drierite^R-containing drying tube. The cooling bath was removed. The reaction temperature gradually climbed toward 29°C when the cooling bath again was placed around the reaction flask. The reaction temperature peaked at 29.6°C. The cooling bath was removed within about 30 seconds, and the temperature climbed again to 28.6°C, but then began cooling toward ambient temperature. The reaction was stirred in an ambient temperature environment 1½ hours; then, the reaction flask contents were poured into 25 mL distilled/deionized water in a 125-mL Erlenmeyer flask. An additional 5 mL water was used to rinse the reaction flask, and this was poured into the 125-mL Erlenmeyer. The contents in the Erlenmeyer flask were stirred with a Teflon^R coated magnetic stir bar at ambient temperature for 15 minutes, and a fine white solid precipitated. Suction filtration in a porcalin Buchner funnel followed; the solid product was then washed with 10 mL water, followed by (3 X 3 mL) methylene chloride. Room temperature vacuum drying (0.07 torr) for 7 2/3 hours gave 1.03 g (71.0%) fine white solid mp 154.6–156.4°C. The unlabeled analogue **3** synthesized in the same manner with **2**, gave a 72.1% yield [lit. 15% (13), 86% (14) and 53% (16)]: mp 154.8–156.2°C [lit. 151–154°C (13),

152–154°C (14) and 150°C (16)]. The ¹H FTNMR of **6** (acetone-*d*₆) gave no peaks other than the TMS and acetone-*d*₆; the absence of the peaks seen at δ 6.30 (s, 2H) and δ 5.47 (s, 4H) with the unlabeled analogue **3** confirms the perdeuterio-*d*₆ structure of **6** and shows no appreciable exchange occurred during nitration with the unlabeled acid. Compound **6** also gave: FTIR (cm⁻¹) 2278 (C–D), 1574, 1548, 1320 (NO₂); mass spectrum (70eV) *m/e* (rel. intensity) 274 (M+2, 1.0), 180 (0.8), 176 (4.9), 166 (3.2), 150 (1.7), 148 (2.5), 130 (4.4), 118 (2.9), 116 (2.7), 114 (2.7), 100 (1.6), 86 (8.6), 84 (12.5), 72 (3.2), 60 (7.9), 58 (16.6), 46 (base peak, 100.0), 44 (14.0), 32 (5.1), 30 (74.0). A 3% presence of *m/e* 160 compared to the *m/e* 166 ion showed compound **6** to be 97% isotopically-*d*₆ pure.

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