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Synthesis of 1,4-Butanediamine-1,1,4,4-d_4, 1,4-Butanediamine-2,2,3,3-d_4 and Their Respective BIS (Ammonium Nitrate) Salts

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Synthesis of the title compounds from diethyl succinate and from dimethyl acetylenedicarboxylate in 16 percent overall yield, respectively, and their bis(ammonium nitrate) salts in 62 and 60 percent yields, respectively, are described. Physical properties and nuclear magnetic resonance, infrared and mass spectral data are presented.

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PREFACE

This report describes the work performed by personnel at the Department of Chemistry, North Texas State University, NT Station, Box 5068, Denton TX 76203-5068 under contracts F08635-86-K-0078 and F08635-87-K-0101 during the period January 1986-September 1987 and by personnel at the Energetic Materials Branch (MNE), Munitions Division (MN), Air Force Armament Laboratory (AFATL), Armament Division (AD), Eglin AFB FL 32542-5434, under project 2502, "Conventional Ordnance Technology", Task 10, "Advanced Explosives", Work Unit 12, "Explosive Response to Thermal and Shock Stimuli" during the time period of October 1985 to Octobert 1987. The contract program manager was Dr Alan P. Marchand and the AFATL in-house program manager was Dr Robert L. McKenney Jr.

This report is one of several planned reports that will describe the synthesis and complete thermal characterization of specific organodi- and polyammonium nitrate salts. Other reports will follow at appropriate times during the progress of this effort.

TABLE OF CONTENTS

LIST OF FIGURES

SECTION I

INTRODUCTION

There is considerable current interest in the study of kinetic isotope effects in thermal decompositions of explosives.[1-3] As part of a study of deuterium isotope effects on the decomposition of 1,4-butanediammonium dinitrate (BDD), it was necessary to synthesize 1,4-butanediamine-1,1,4,4-d_4 (putrescine-1,1,4,4-d_4 **1a**), the corresponding 2,2,3,3-d_4 isomer (putrescine-2,2,3,3-d_4, **1b**) and the bis(ammonium nitrate) salts of **1a** and **1b** (i.e., **1c** and **1d**, respectively). The synthesis of the bis(ammonium acetate) salt of **1a** via lithium aluminum deuteride reduction of succinonitrile has been reported by Mayerl and Hesse;[4] however, their reported yield was only ca. 1.4%. Our own experience with this reaction similarly produced **1a** in disappointingly low yield. In contrast to this result, deuterogenation of succinonitrile over platinum oxide catalyst in aqueous ethanolic (C_2H_5OD) hydrochloric acid (DCl) solution has been reported to afford 1,4-butanediamine-1,1,4,4-d_4 dihydrochloride in 40% yield.[5]

It is most advantageous to prepare BDD directly via reaction of putrescine with nitric acid. It *is not convenient* to liberate the free amine from one of its free bases directly.

SECTION II

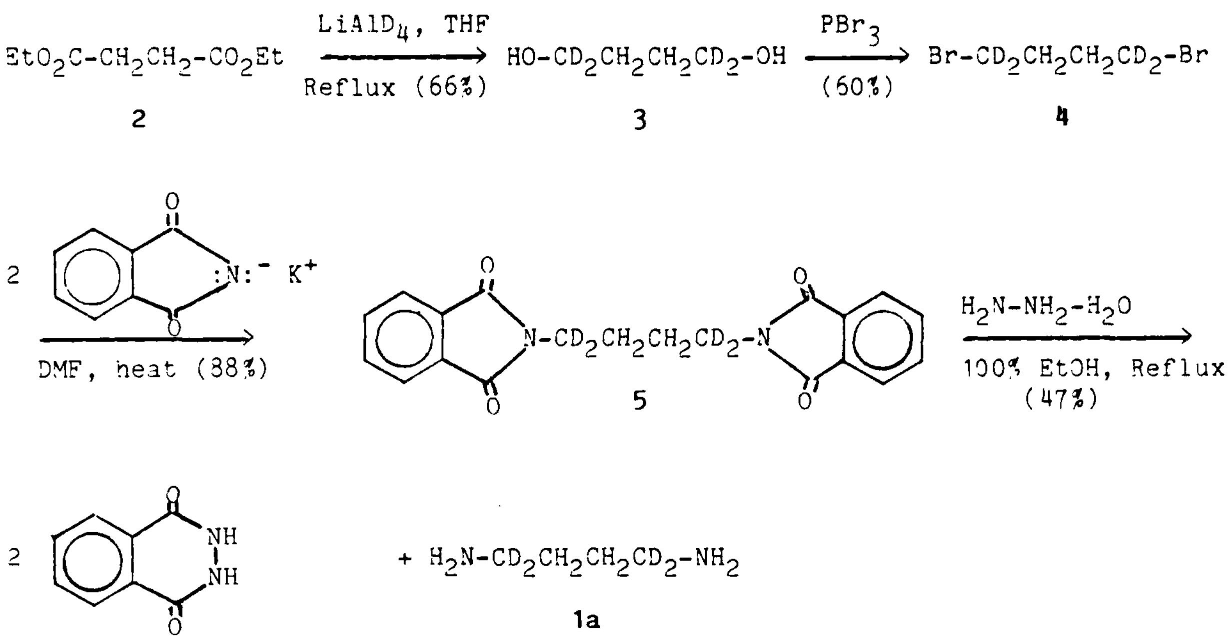
DISCUSSION

To synthesize **1a**, we employed a Gabriel synthesis[6] as outlined in Scheme I of Figure 1. Lithium aluminum deuteride reduction of diethyl succinate (**2**) afforded 1,4-butanediol-1,1,4,4-d_4 (**3**) in 66% yield. Reaction of **3** with phosphorus tribromide afforded the corresponding dibromide (**4**, 60%). Subsequent reaction of **4** with two equivalents of potassium phthalimide afforded the corresponding diphthalimido derivative (**5**, 88%). Finally, pure **1a** was produced in 47% yield (16% overall from diethyl succinate) by refluxing a solution of **5** in absolute ethanol with excess hydrazine hydrate.

Our corresponding synthesis of **1b** is summarized in Scheme II of Figure 1. Dimethyl acetylenedicarboxylate (**6**) was deuterogenated with deuterium gas over 5% palladized charcoal catalyst in methanol, thereby affording dimethyl succinate-2,2,3,3-d_4 (**7**, 35%). Lithium aluminum hydride reduction of **7** afforded 1,4-butanediol-2,2,3,3-d_4 (**8**, 85%). Thereafter, conversion of **8** to **1b** followed the steps outlined in Scheme I (Figure 1) for the conversion of **3** to **1a**. Application of this reaction sequence afforded **1b** in 18% overall yield.

The conversion of **1a** and **1b** to their respective bis(ammonium nitrate) salts (**1c** and **1d**, respectively) was effected in 62% and 60% yield, respectively, via reaction of each diamine with concentrated nitric acid.[7] The Mass spectra of **1c** and **1d** were obtained by using the direct inlet solids probe technique at a temperature slightly above their melting points. Anaylsis of the fragmentation patterns thereby obtained suggests that in each case the salt undergoes initial decomposition into the free diamine and nitric acid.

Scheme I



Scheme II

$$\underset{\mathbf{6}}{MeO_2C\text{-}C{\equiv}C\text{-}CO_2Me} \xrightarrow[\text{MeOH, 16 h (85\%)}]{D_2,\ 5\%\ Pd/C} \underset{\mathbf{7}}{MeO_2C\text{-}CD_2CD_2\text{-}CO_2Me} \xrightarrow[\text{Reflux (85\%)}]{LiAlH_4,\ THF}$$

$$\underset{\mathbf{8}}{HO\text{-}CH_2CD_2CD_2CH_2\text{-}OH} \xrightarrow{\text{(as in Scheme I, above)}} \xrightarrow{\hspace{3em}} \underset{\mathbf{1b}}{H_2N\text{-}CH_2CD_2CD_2CH_2\text{-}NH_2}$$

Figure 1. Summary of Reaction Schemes (I and II) for the Preparation of 1,4-Butanediamine-1,1,4,4-d_4 (1a) and 1,4-Butanediamine-2,2,3,3-d_4 (1b).

SECTION III

EXPERIMENTAL

Melting points and boiling points are uncorrected. Proton NMR spectra of **1a** and **1b** were obtained on a Hitachi-Perkin Elmer Model R-243 NMR spectrometer (60 MHz) and by using a JEOL FX-90Q FT-NMR spectrometer (90 MHz). Proton NMR spectra of **1c** and **1d** were obtained on a Varian EM-390 spectrometer (90 MHz). Signals are reported in ppm (δ) downfield from internal tetramethylsilane for **1a** and **1b** and downfield from internal sodium 3-(trimethylsilyl)propionate-2,2,3,3-d_4 for **1c** and **1d**. Infrared spectra of **1a** and **1b** were obtained on a Perkin-Elmer Model 1330 IR spectrophotometer. Infrared spectra of **1c** and **1d** were obtained on a Mattson Cygnus 25 FTIR spectrometer. Mass spectra of **1a** and **1b** were obtained by using a Hewlett-Packard Model 5970A GC/MS system operating at 70eV. Mass spectra of **1c** and **1d** were obtained on a Finnigan MAT Model 5100 GC/MS system operating at 70 eV.

1,4-Butanediol-1,1,4,4-d_4 (3). A solution of **2** (13.92 g, 80 mmol) in dry tetrahydrofuran (THF, 100 ml) was added dropwise to a stirred slurry of lithium aluminum deuteride (10.08 g, 240 mmol) in dry THF (100 ml). The reaction mixture was refluxed for 4 h, at which time the reaction mixture was cooled and then quenched via successive addition of water (10 ml), 10% aqueous sodium hydroxide solution (10 ml), and water (30 ml). The resulting mixture was then filtered to remove precipitated aluminum salts. The filtrate was dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford crude **3** (5.1 g). The crude product was purified via column chromatography (silica gel absorbent, ethyl acetate eluent). The material thereby obtained was distilled in vacuo to afford pure **3** (5.0 g, 66%): bp 80 °C (0.5 mm). Upon cooling, the distillate solidified to afford colorless needles: mp 15 °C, (lit[8] bp 127 °C (20 mm), mp 16 °C). IR (neat) 3300 (vs), 2095 (s), 2005 (s), 950 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.65 (br s, 4H), 3.68 (br s, 2H); mass spectrum (70 eV), m/e (relative intensity) (no molecular ion), 76 (1.7), 75 (15.4), 58 (14.1), 46 (15.8), 45 (73.0), 44 (100.0), 43 (35.7), 42 (13.6), 33 (98.3), 32 (23.7), 31 (13.6).

1,4-dibromobutane-1,1,4,4-d_4 (4). Phosphorous tribromide (14.14 g, 52 mmol) was added dropwise to cooled **3** (4.9 g, 52 mmol); the reaction mixture was cooled via application of an external ice bath. After the addition of PBr_3 had been completed, the ice bath was removed, and the reaction mixture was stirred at ambient temperature for 18 h. The reaction mixture was then poured into water and extracted with chloroform. The organic layer was washed successively with water, aqueous sodium bicarbonate solution, and brine. The organic layer was then dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo. The residue was distilled in vacuo to afford **4** as a colorless oil (7.0 g, 60%): bp 115 ^{o}C (290 mm), [lit.^{9} bp 197 ^{o}C (1 atm)]; IR (neat) 2155 (s), 660 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 2.04 (s); mass spectrum (70 eV), m/e (relative intensity) 220 (molecular ion, 0.6), 141 (64.7), 139 (67.5), 109 (14.1), 81 (18.4), 79 (16.7), 59 (100.0), 43 (25.6), 41 (27.1), 40 (27.1), 32 (26.2), 31 (29.6).

1,4-Diphthalimidobutane-1,1,4,4-d_4 (5). A mixture of **4** (4.95 g, 20 mmol), potassium phthalimide (13.35 g, 72 mmol) and dimethylformamide (DMF, 60 ml) was heated on a steam bath for 4 h. The reaction mixture was then concentrated in vacuo, and the residue was poured over crushed ice. The crude product was collected via suction filtration; the residue was washed with water and then air-dried. The crude product was extracted with boiling carbon disulfide to remove N-(4-bromobutyl)phthalimide. Pure 5 (6.9 g, 38%) was thereby obtained as a colorless microcrystalline solid: mp 226 ^{o}C, (lit^{5} mp 230 ^{o}C); IR (KBr) 3065 (m), 3025 (m), 2175 (m), 2125 (m), 1700 (br, vs), 1600 (s), 900 (s), 800 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.70 (s, 4H), 7.61-7.86 (m, 8H); mass spectrum (70 eV), m/e (relative intensity) 352 (molecular ion, 6.8), 205 (14.1), 204 (18.3), 190 (25.7), 163 (13.3), 162 (100.0), 134 (15.7), 130 (15.7), 106 (14.7), 104 (14.1), 78 (18.3), 76 (17.8).

1,4-Butanediamine-1,1,4,4-d_4 (1a). A mixture of **5** (6.5 g, 18.5 mmol), hydrazine hydrate (2.22 g, 44.4 mmol), and absolute ethanol (120 ml) was refluxed for 4 h under nitrogen. The reaction mixture was cooled and then filtered to remove phthalhydrazide. The filtrate was dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo. The residue was distilled in vacuo to afford **1a** (0.8 g, 47%) as a colorless oil: bp 85 ^{o}C (290 mm); IR (neat) 3300 (br, s), 2195 (s), 2095 (s), 1570 cm^{-1} (br, s); ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 4H), 1.52 (s, 4H); mass spectrum (70 eV), m/e (relative intensity) 92 (molecular ion, 0.1), 75 (0.4), 58 (0.6), 44 (17.0), 32 (100).

Dimethyl Succinate-2,2,3,3-d_4 (7). A stirred mixture of acetylenedicarboxylate (**6**, 10.0 g, 70.4 mmol) and 5% palladized charcoal (1.0 g) in methanol (400 ml) was purged with nitrogen gas. A balloon containing excess deuterium gas was connected to the reaction flask, and the reaction mixture was deuterogenated with stirring for 16 h at room temperature. The resulting mixture was filtered to remove catalyst, and the filtrate was concentrated in vacuo. The residue was distilled under reduced pressure, thereby affording pure **7** (9.0 g, 85%): bp 95 °C (1 mm); IR (neat) 2245 (w), 2155 (w), 2135 (w), 2095 (w), 1735 (vs), 1445 (s), 1045 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 3.66 (s); mass spectrum (70 eV), m/e (relative intensity) (no molecular ion), 119 (100.0), 118 (42.2), 117 (24.0), 91 (18.8), 59 (72.9), 58 (54.5), 57 (19.3), 32 (32.2), 21 (17.1).

1,4-Butanediammonium-1,1,4,4-d_4 Dinitrate (1c). A solution of **1a** (426 mg, 4.63 mmol) in 95 % aqueous ethanol (4 ml) was cooled at 0°C by application of an external ice bath. To this cold solution was added concentrated nitric acid (0.6 ml, 9.5 mmol) dropwise with vigorous stirring. The temperature of the reaction mixture was not permitted to exceed 0°C during the period of addition of nitric acid. After all of the nitric acid had been added, the ice bath was removed and the reaction mixture was permitted to warm to ambient temperature. After stirring for 10 minutes at room temperature, the reaction mixture was then filtered. The residue was washed with cold 95% ethanol and suction dried. The resulting material was recrystallized from ethanol-water mixed solvent, thereby affording pure **1c** (0.625 g, 62%) as a colorless microcrystalline solid: mp 140 °C, (lit[7] mp 139 °C for non-deuterium labelled **1c**); IR (KBr pellet) 3048 (br, vs), 2400 (m), 1995 (m), 1759 (w), 1628 (m), 1520 (vw), 1354 (br, vs), 1073 (d, w), 1026 (m), 825 (m), 710 (m); ^1H NMR (DMSO-d_6) δ 1.6 (s, 4H), 5.2 (s, 6H); mass spectrum (70 eV), m/e (relative intensity) (no molecular ion), 74 (2.4), 73 (3.3), 62 (3.0), 61 (4.5), 57 (2.3), 46 (41), 44 (18), 32 (100), 30 (18).

1,4-Butanediammonium-2,2,3,3-d_4 Dinitrate (1d). The procedure described above for the preparation of **1c** was employed for the synthesis of **1d**. Pure **1d** was thereby obtained in 60% yield as an off-white microcrystalline solid: mp 139°C; IR (melt) 2350 (br, m), 1616 (w), 1517 (w), 1311 (br, vs), 1161 (vw), 1040 (vw), 826 (w), 722 (vw); ^1H NMR (DMSO-d_6) δ 2.3 (s, 4H), 7.9 (s, 6H); mass spectrum (70 eV), m/e (relative intensity) (no molecular ion), 75 (3.0), 74 (2.6), 73 (2.8), 63 (6.5), 62 (3.9), 47 (7.8), 46 (66.7), 45 (28.8), 44 (17.3), 43 (9.0), 31 (15.0), 30 (100.0).

SECTION IV

CONCLUSIONS

It has been demonstrated that the free bases 1a and 1b can be prepared in high purity by the non-aqueous methods described herein in relatively low, but reasonable yields. The free bases were reacted with concentrated nitric acid to provide their respective bis(ammonium nitrate) salts, 1c and 1d, in moderate yields. The NMR and mass spectra of the free bases and salts are consistent with the proposed structure and site-specific deuteration.

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