NITROIMIDAZOLONES.
SYNTHESIS OF DEAZA ANALOGUES OF 3-NITRO-1,2,4-TRIAZOL-5-ONE

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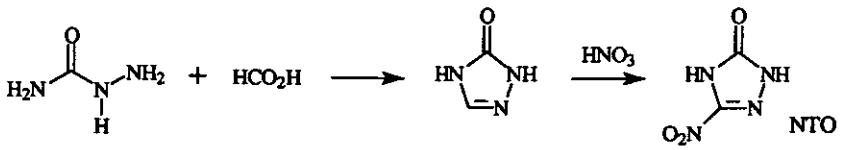
Abstract - Analogues of 3-nitro-1,2,4-triazol-5-one (NTO) have been synthesized. The strategy revolves around a new method for the synthesis of imidazolones, namely the addition-elimination reaction of the sodium salt of trimethylsilylethanol with a trimethylsilylethoxymethyl (SEM)-protected dinitroimidazole followed by the acid-catalyzed conversion to the desired nitroimidazole (**5**). The *N*-methyl derivatives of **5** were prepared in a similar manner starting from the *N*-methyldinitroimidazoles.

Introduction

The discovery of 3-nitro-1,2,4-triazol-5-one (NTO)[2] as a less sensitive explosive has generated much interest within the Air Force because of its potential use in general purpose munitions. Candidate explosives need to be powerful yet insensitive[3] in order to decrease the possibility of accidental or sympathetic detonation. Interestingly, the Los Alamos group found that NTO not only has a detonation pressure rivaling that of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), it also compares favorably in terms of impact sensitivity to such standard explosives as cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX) and the eight membered-ring analogue HMX.[2,4] Furthermore, NTO is relatively inexpensive and easy to synthesize on a large scale in high yield and purity (Scheme 1).

Scheme 1

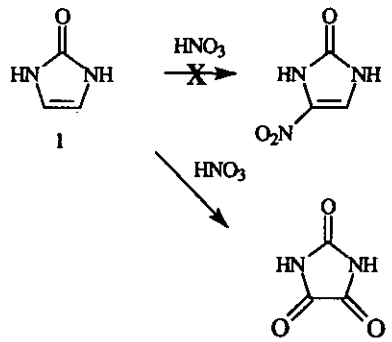


Our studies on NTO were prompted by an interest in the electron spin resonance (esr) spectroscopy of energetic materials in order to gain insight into the detailed nature of their thermal and photochemical decompositions.[5] Since the couplings of the four nitrogen atoms in NTO result in a complex esr spectrum, we sought to synthesize isoelectronic analogues which contained fewer atoms capable of coupling to any radicals generated. In addition, the systematic replacement of the ring nitrogen atoms may provide important structural information concerning these radicals. Finally, since our initial studies[5b] suggest that the hydrogen atoms bonded to the ring nitrogen atoms in NTO play a role in its decomposition, we also required the corresponding *N*-methyl derivatives. We now report the syntheses of 4-nitroimidazol-2-one (**5**) and its *N*-methyl derivatives (**6** and **7**).

Results

Our initial approach to the target compounds was the nitration of the parent heterocycle, as in the synthesis of NTO. Unfortunately, nitration of the known imidazolone (**1**)[6] with nitric acid or a variety of other nitrating agents resulted not in formation of a nitrated heterocycle, but in oxidation to parabanic acid (Scheme 2).

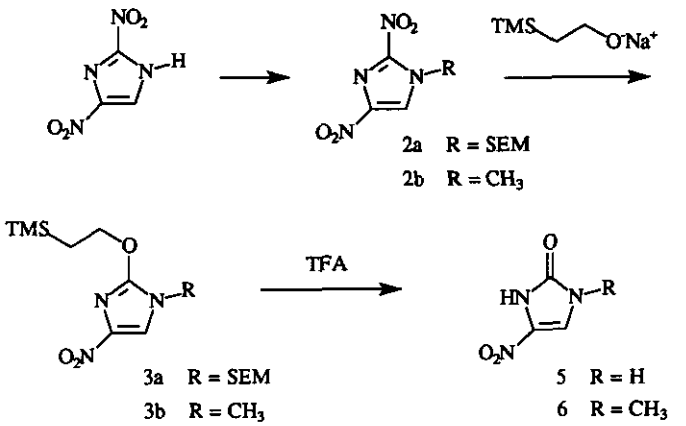
Scheme 2



We then examined the possibility of functional group manipulation of 4- and 5-nitroimidazole derivatives, specifically, the formation of a carbon-oxygen bond at the 2 position. As nucleophilic displacements of imidazoles are well documented,[7] we reasoned that the C-O bond could be formed by an addition-elimination

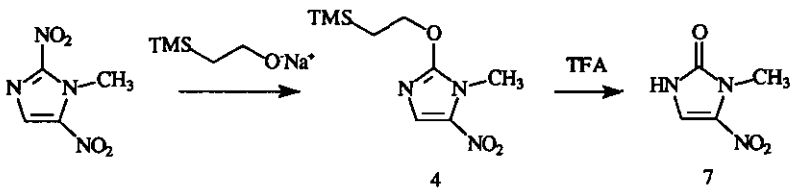
reaction of an alkoxide with an appropriately substituted imidazole. This was accomplished by the addition of sodium 2-(trimethylsilyl)ethoxide to the SEM-protected[8] dinitroimidazole (**2a**), itself prepared in 90% yield by treatment of the sodium salt of 2,4-dinitroimidazole[9] with SEM-Cl (Scheme 3). The alkoxide addition proceeds smoothly to yield trimethylsilylethoxyimidazole (**3a**) in 87% yield. Treatment of **3a** with trifluoroacetic acid then leads to the desired imidazolone (**5**) in 83% yield.

Scheme 3



The synthesis of the *N*-methylimidazolone (**6**) followed a similar protocol: sodium 2-(trimethylsilyl)ethoxide addition to dinitroimidazole (**2b**)[10] gave trimethylsilylethoxyimidazole (**3b**) in 82% yield. Treatment of **3b** with trifluoroacetic acid gave imidazolone (**6**) in 82% yield. Likewise, imidazolone (**7**) was synthesized from *N*-methyl-2,5-dinitroimidazole[11] in 89% overall yield (Scheme 4).

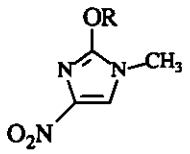
Scheme 4



4 7

The choice of the SEM-protecting group became necessary after attempts to make the t-butyldimethylsilyl,[12] trityl,[13] t-BOC,[14] or dimethylaminomethylnitroimidazoles[15] resulted in unacceptable yields or isolation of unchanged starting material. 2-(Trimethylsilyl)ethanol was chosen as the nucleophile due to the ease of hydrolysis of the resulting alkoxyimidazoles. Although sodium methoxide, isopropoxide and even t-butoxide underwent addition-elimination to form alkoxyimidazoles (**8a-c**) respectively, the alkoxyimidazoles were stable to hydrolysis conditions. Alkoxyimidazole (**8a**) was also stable to typical trimethylsilyl iodide[16] cleavage reaction

conditions. Finally, the direct method of synthesizing imidazolones from imidazoles recently reported by Lipshutz[17] returned only unchanged starting material from SEM-protected 4-nitroimidazole.



8a R = CH_3
8b R = i-C_3H_7
8c R = t-C_4H_9

The assignment of nitro group position in compounds (**6**) and (**7**) is based on ^{13}C nmr spectral data and is confirmed by the X-ray crystallographic analysis of compound (**3b**) (see supplementary materials). Spectroscopic studies of 4- and 5-nitroimidazoles have recently been reported.[18] The authors made position assignments by comparing changes in ^{1}H nmr chemical shifts in mixed solvent systems, differences in ^{13}C nmr chemical shifts of C(4) and C(5), and characteristic fragmentations in the mass spectra. Our ^{13}C nmr data are in agreement with the conclusions of this study. For example, for a 5-nitroimidazole, the reported ^{13}C chemical shift of C(5) is approximately 139 ppm.[18b] For a 4-nitroimidazole, the reported ^{13}C chemical shift of C(5) is approximately 122 ppm. The corresponding chemical shifts in our series are 135 ppm for the 5-nitro isomer (**4**) and 117 ppm for the 4-nitro isomer (**3b**). This information, coupled with the X-ray crystallographic analysis of compound (**3b**), unequivocally established the nitro group position.

In conclusion, we have developed a new method for the synthesis of nitrated imidazolones in high yields. The synthetic scheme relies on carbonyl formation via an addition-elimination and subsequent hydrolysis of the resulting alkoxyimidazole. Decomposition studies will be reported separately.

EXPERIMENTAL SECTION

Melting points (mp) were obtained on a Mel-Temp melting point apparatus and are uncorrected. Analytical tlc was performed on 0.25 mm silica plates (Merck) with QF-254 indicator. Visualization was accomplished by uv light or iodine. Solvents for extraction and chromatography were reagent grade and were used as received from commercial sources. All solvents used in reactions were freshly distilled from appropriate drying agents before use: THF (sodium benzophenone ketyl), hexane, dichloromethane, DMF, and chloroform all over CaH_2. ^{1}H Nmr spectra were recorded at 300 MHz with tetramethylsilane (0.00 ppm) or chloroform (7.26 ppm) as internal references in $CDCl_3$ or DMSO-d_6 solutions. ^{13}C Nmr spectra were recorded at 75.5 MHz with chloroform (77.0 ppm) or DMSO-d_6 (39.5 ppm) solutions. Chemical shifts are given in ppm (δ); multiplicities are indicated by

s (singlet) or t (triplet). Coupling constants, J, are reported in hertz. Diffuse reflectance[19] infrared spectra (ir) were obtained by on a Bio-Rad FTS-7 spectrophotometer. Peaks are reported in cm^{-1} with the following relative intensities: s (strong, 67-100%), m (medium, 34-66%), w (weak, 0-33%), sh (shoulder), and br (broadened). Mass spectra (EI) were obtained with an ionization voltage of 70 eV. Data are reported in the form m/z (intensity relative to base = 100). High resolution mass spectra (HRms) were performed by the Midwest Center for Mass Spectrometry at the University of Nebraska-Lincoln. X-Ray crystallographic data were obtained on a Seimans R3m/V X-ray diffractometer. Elemental combustion analyses were performed by Galbraith Laboratories. The following compounds were prepared by literature methods: 4-imidazol-2-one (**1**),[6] 2,4-dinitroimidazole,[9] *N*-methyl-2,4-dinitroimidazole (**2b**),[10] and *N*-methyl-2,5-dinitroimidazole.[11]

N-[2-(Trimethylsilyl)ethoxymethyl]-2,4-dinitro-1H-imidazole (2a). An oven-dried, 25-ml, 3-necked, round-bottomed flask equipped with a stirring bar, septum, N_2 inlet, and thermometer was charged with 100 mg (2.5 mmol) of NaH dispersion (60%). The NaH dispersion was rinsed with hexane (3X), suspended in 5 ml of DMF, and cooled to 5°C. A solution of 375 mg (2.4 mmol) of 2,4-dinitroimidazole[9] in 3 ml of DMF was added via syringe. After stirring for 30 min, 475 mg (2.8 mmol) of 2-(trimethylsilyl)ethoxymethyl chloride was added via syringe and the mixture was warmed to room temperature. After stirring for 20 min, the reaction mixture was quenched with water (10 ml) and extracted with ether (3 X 25 ml). The organic layers were washed with water (10 ml) and brine (10 ml), dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the crude product by radial chromatography (hexane/acetone, 4/1) afforded 614 mg (89.9%) of **2a**. Data for **2a**: mp 47-48.5°C; ^{1}H nmr (300 MHz, $CDCl_3$) 8.10 (s, 1H, HC(5)), 5.87 (s, 2H, CH_2N), 3.76 (t, J = 8.5, 2H, CH_2O), 1.03 (t, J = 8.5, 2H, CH_2Si), 0.02 (s, 9H, $(CH_3)_3Si$); ^{13}C nmr (75.5 MHz, $CDCl_3$) 143.7, 140.7, 121.3 (C(5)), 80.8 (CH_2N), 69.7 (CH_2O), 18.0 (CH_2Si), -1.5 ($(CH_3)_3Si$); ir (diffuse reflectance) 3153 w, 2954 w, 2897 w, 1560 m, 1555 m, 1512 m, 1492 m, 1464 w, 1364 m, 1329 s, 1311 m, 1251 m, 1200 w, 1126 m, 910 w, 861 m, 834 m; ms (70 eV) 215 (M^+-73, 66.8) 104 (13.7), 103 (18.6), 75 (10.3), 74 (10.0), 73 (100), 45 (17.9), 43 (10.8), 30 (22.2); tlc Rf 0.30 (hexane/acetone, 4/1); Anal. Calcd for $C_9H_{16}N_4O_5Si$: C, 37.49; H, 5.59; N, 19.43. Found: C, 37.73; H, 5.76; N, 19.37.

General Procedure for the Synthesis of 2-[2-(Trimethylsilyl)ethoxy]imidazoles. An oven-dried, 25-ml, 3-necked, round-bottomed flask equipped with a stirring bar, septum, N_2 inlet, and thermometer was charged with 280 mg (7.0 mmol) of NaH dispersion (60%). The NaH dispersion was rinsed with hexane (3X) and suspended in 5 ml of THF. The suspension was cooled to 5°C and 2-(trimethylsilyl)ethanol (3.75 ml, 26 mmol) was added via syringe. After the mixture was stirred for 30 min, a solution of 300 mg (1.75 mmol) of *N*-

methyl-2,5-dinitroimidazole[11] in 3 ml of THF was added via syringe. After stirring for 30 min, the reaction mixture was quenched with water (10 ml) and extracted with ether (3 X 25 ml). The organic layers were washed with brine (15 ml), dried over $MgSO_4$, filtered, and concentrated in vacuo. The excess 2-trimethylsilylethanol was removed and collected by Kugelrohr distillation (50°C, 0.1 mm Hg).

N-[2-(Trimethylsilyl)ethoxymethyl]-4-nitro-2-[(2-trimethylsilyl)ethoxy]-1H-imidazole (3a). Purification of the crude product by radial chromatography (hexane/acetone, 4/1) afforded 218 mg (87.4%) of **3a**. Data for **3a**: mp 76-77°C (petroleum ether); ^{1}H nmr (300 MHz, $CDCl_3$) 7.56 (s, 1H, HC(5)), 5.17 (s, 2H, CH_2N), 4.56 (t, J = 8.5, 2H, CH_2O), 3.56 (t, J = 8.5, 2H, CH_2O), 1.17 (t, J = 8.5, 2H, CH_2Si), 0.92 (t, J = 8.5, 2H, CH_2Si), 0.08 (s, 9H, $(CH_3)_3Si$), 0.00 (s, 9H, $(CH_3)_3Si$); ^{13}C nmr (75.5 MHz, $CDCl_3$) 150.6 (C(2)), 143.4 (C(4)), 115.9 (C(5)), 73.7 (CH_2N), 69.9 (CH_2O), 67.2 (CH_2O), 17.9 (CH_2Si), 17.7 (CH_2Si), -1.45 ($(CH_3)_3Si$); ir (KBr) 3147 m, 2956 m, 2928 m, 2898 m, 1718 w, 1685 w, 1654 w, 1578 s, 1538 s, 1497 s, 1474 s, 1460 s, 1442 s, 1406 s, 1359 s, 1334 s, 1290 m, 1271 s, 1250 s, 1216 m, 1181 m, 1224 m, 1092 s, 1065 s, 1034 m, 989 m, 957 s, 941 m, 923 m, 861 s, 836 s, 800 s, 766 m, 732 m; ms (70 eV) 273 (M^+-86, 14.1) 258 (30.2), 154 (24.1), 104 (10.5), 103 (24.4), 101 (17.2), 74 (11.5), 73 (100), 45 (10.0); tlc Rf 0.35 (hexane/acetone, 4/1); Anal. Calcd for $C_{14}H_{29}N_3O_4Si_2$: C, 46.76; H, 8.13; N, 11.69. Found: C, 46.74; H, 7.91; N, 11.61.

N-Methyl-4-nitro-2-[(2-trimethylsilyl)ethoxy]-1H-imidazole (3b). Purification of the crude product by radial chromatography (hexane/acetone, 4/1) afforded 290 mg (82.2%) of **3b**. Data for **3b**: mp 121-123°C (ethanol/petroleum ether); ^{1}H nmr (300 MHz, $CDCl_3$) 7.45 (s, 1H, HC(5)), 4.51 (t, J = 8.5, 2H, CH_2O), 3.50 (s, 3H, CH_3N), 1.16 (t, J = 8.5, 2H, CH_2Si), 0.06 (s, 9H, $(CH_3)_3Si$); ^{13}C nmr (75.5 MHz, $CDCl_3$) 150.8 (C(2)), 142.7 (C(4)), 117.4 (C(5)), 69.7 (CH_2O), 31.5 (CH_3N), 17.8 (CH_2Si), -1.4 ($(CH_3)_3Si$); ir (diffuse reflectance) 3153 w, 2962 m, 1598 w, 1573 s, 1550 m, 1537 s, 1501 m, 1478 m, 1461 s, 1409 m, 1397 m, 1365 m, 1313 s, 1294 s, 1247 m, 1224 m, 1178 w, 1053 m, 956 m, 943 m, 843 s, 800 m; ms (70 eV) 200 (M^+-43, 18.1), 73 (100), 45 (20.3), 43 (17.2), 42 (43.9), 30 (19.5); tlc Rf 0.31 (hexane/acetone, 4/1); Anal. Calcd for $C_9H_{17}N_3O_3Si$: C, 44.42; H, 7.04; N, 17.27. Found: C, 44.29; H, 6.98; N, 17.15.

N-Methyl-5-nitro-2-[(2-trimethylsilyl)ethoxy]-1H-imidazole (4). Purification of the crude product by radial chromatography (hexane/acetone, 4/1) afforded 403 mg (95%) of **4**. Data for **4**: mp 61-61.5°C (petroleum ether); ^{1}H nmr (300 MHz, $CDCl_3$) 7.75 (s, 1H, HC(4)), 4.57 (t, J = 8.5, 2H, CH_2O), 3.73 (s, 3H, CH_3N), 1.20 (t, J = 8.5, 2H, CH_2Si), 0.09 (s, 9H, $(CH_3)_3Si$); ^{13}C nmr (75.5 MHz, $CDCl_3$) 154.3 (C(2)), 135.2 (C(5)), 130.6 (C(4)), 69.5 (CH_2O), 31.0 (CH_3N), 18.0 (CH_2Si), -1.5 ($(CH_3)_3Si$); ir (KBr) 3128 w,

2959 m, 1553 s, 1528 s, 1507 s, 1472 s, 1411 m, 1376 s, 1358 s, 1262 s, 1250 s, 1199 s, 1179 s, 1162 s, 1067 s, 994 s, 938 m, 822 s, 721 s; ms (70 eV) 200 (M^+-43, 10.6), 170 (7.0), 96 (7.6), 74 (9.2), 73 (100); tlc Rf 0.48 (hexane/acetone, 4/1); Anal. Calcd for $C_9H_{17}N_3O_3Si$: C, 44.42; H, 7.04; N, 17.27. Found: C, 44.71; H, 7.04; N, 17.25.

General Procedure for the Synthesis of Imidazolones. An oven-dried, 25-ml, single-necked, round-bottomed flask equipped with a stirring bar was charged with 250 mg (0.695 mmol) of imidazole (**3a**) and 2 ml of chloroform. After the imidazole dissolved, 3 ml of trifluoroacetic acid was added dropwise. The reaction mixture was stirred for 2 h and the crude product was obtained by removal of the solvents.

1,3-Dihydro-4-nitro-2H-imidazol-2-one (5). Radial chromatography (hexane/acetone, 1/1) afforded 74.4 mg (82.9%) of **5**. Data for **5**: mp 170°C (slow decomp.); ^{1}H nmr (300 MHz, DMSO-d_6) 11.80 (br s, 1H, NH), 11.60 (br s, 1H, NH), 8.05 (s, 1H, HC(5)); ^{13}C nmr (75.5 MHz, DMSO-d_6) 151.3, 130.9, 118.2; ir (KBr) 3123 m, 2282 w, 1686 s (C=O), 1590 m, 1509 s, 1458 s, 1340 s, 1210 m, 1086 m, 985 m, 856 w, 755 m; ms (70 eV) 129 (M^+, 20.8), 55 (48.8), 54 (15.0), 53 (12.5), 44 (23.0), 30 (30.4), 28 (100), 27 (11.1); tlc Rf 0.23 (hexane/acetone, 1/1); HRms for $C_3H_3N_3O_3$: Calcd 129.0174. Found 129.0172.

N-Methyl-1,3-dihydro-4-nitro-2H-imidazol-2-one (6). Radial chromatography (hexane/acetone, 1/1) afforded 242.0 mg (82.3%) of **6**. Data for **6**: mp 194°C (decomp.) (methanol/dichloromethane); ^{1}H nmr (300 MHz, DMSO-d_6) 12.00 (br s, 1H, NH), 8.19 (s, 1H, HC(5)), 3.24 (s, 3H, CH_3N); ^{13}C nmr (75.5 MHz, DMSO-d_6) 150.6, 129.2, 121.4, 30.3 (CH_3N); ir (diffuse reflectance) 3010 m, (br), 1697 s (C=O), 1589 m, 1499 s, 1458 s, 1453 s, 1400 m, 1370 s, 1286 s, 1253 m, 1195 w, 1132 w, 1052 w, 979 m, 848 m; ms (70 eV) 143 (M^+, 40.3), 69 (80.8), 67 (17.7), 44 (10.9), 42 (100), 41 (19.5), 40 (19.1), 32 (12.3), 30 (21.7), 28 (62.6), 15 (30.3); tlc Rf 0.28 (hexane/acetone, 1/1); Anal. Calcd for $C_4H_5N_3O_3$: C, 33.57; H, 3.52; N, 29.36. Found: C, 33.61; H, 3.51; N, 29.16.

N-Methyl-1,3-dihydro-5-nitro-2H-imidazol-2-one (7). Radial chromatography (hexane/acetone, 1/1) afforded 148.8 mg (93.7%) of **7**. Data for **7**: mp 142-143°C (decomp.); ^{1}H nmr (300 MHz, DMSO-d_6) 11.90 (br s, 1H, NH), 8.17 (s, 1H, HC(4)), 3.41 (s, 3H, CH_3N); ^{13}C nmr (75.5 MHz, DMSO-d_6) 151.2, 131.7, 118.8, 29.1 (CH_3N); ir (KBr) 3122 s, 2854 m, 1697 s (C=O), 1579 s, 1496 s, 1461 s, 1403 s, 1364 s, 1304 s, 1261 s, 1153 s, 968 w, 832 m, 798 s, 752 m, 724 m, 687 s, 622 m; ms (70 eV) 143 (M^+, 38.0), 126 (14.4), 113 (10.2), 102 (12.8), 69 (11.1), 58 (35.9), 57 (10.8), 56 (24.3), 53 (16.3), 44 (29.2), 42 (83.9), 32 (11.6), 30 (75.3), 28 (100), 18 (24.2); tlc Rf 0.41 (hexane/acetone, 1/1); HRms for $C_4H_5N_3O_3$: Calcd 143.0330. Found 143.0333.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of the Air Force Office of Scientific Research/Directorate of Chemical and Atmospheric Sciences and Mr. J. Lloyd Pflug and Mr. Jack Greathouse for providing mass spectral data.

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Received, 6th March, 1992