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NEW METHOD FOR THE GENERATION AND TRAPPING OF 1-AZABICYCLO[1.1.0]BUTANE. APPLICATION TO THE SYNTHESIS OF 1,3-DINITROAZETIDINE

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Abstract. 1-Azabicyclo[1.1.0]butane (**1**) has been prepared via a two-step, one-pot procedure that involves (i) reaction of a heptane solution of allylamine with *N*-chlorosuccinimide at 0 °C followed by (ii) codistillation of the product from basic solution along with heptane-octane. Compound **1** thereby obtained was extracted from the distillate by using cold aqueous $NaNO_2$. Subsequent treatment of the aqueous extract with cold concentrated aqueous HCl afforded *N*-nitroso-3-nitroazetidine (**4**) in 5.5% yield. Oxidation of **4** with 100% HNO_3 produced *N*,3-dinitroazetidine (**5**, 90%). This reaction sequence constitutes a formal synthesis of 1,3,3-trinitroazetidine (TNAZ), an important energetic material.

Introduction. 1-Azabicyclo[1.1.0]butane (**1**) was first synthesized in the late 1960s.[1,2] Despite its unusual and highly strained bicyclic structures, surprisingly little initial interest was shown in exploring the chemistry of this novel heterocyclic compound. However, the current decade has witnessed a renaissance of interest in 1-azabicyclo[1.1.0]butane chemistry.[3] Thus, reactions of carbenes[4] and a variety of other electrophiles[5,6] with substituted 1-azabicyclo[1.1.0]butanes have been

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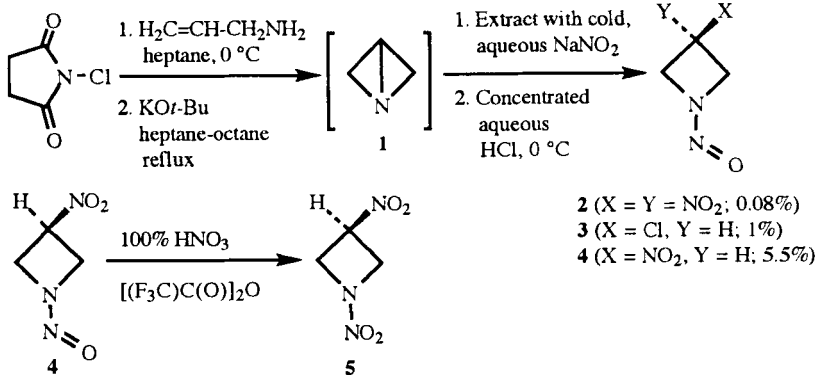
reported. In addition, the use of compounds of this type as intermediates in the synthesis of energetic materials, particularly 1,3,3-trinitroazetidine ("TNAZ"), has been reported.[7] As part of a continuing study of the synthesis and chemistry of 1-azabicyclo[1.1.0butanes,[3] we now report a novel method for generating **1** from allylamine and *N*-chlorosuccinimide (NCS), both of which are inexpensive and readily available starting materials.

Results and Discussion. The procedure that was used to generate and subsequently to trap **1** is shown in Scheme 1. The first two synthetic steps are performed as a one-pot reaction wherein **1** is removed from the reaction mixture by distillation as it is formed. Subequently, the distillate is reacted with HCl-$NaNO_2$. Two "trapping products" are thereby obtained, i.e., *N*-nitroso-3-chloroazetidine (**3**) and *N*-nitroso-3-nitroazetidine (**4**) in low yield (i.e., 1% and 5.5%, respectively) along with a trace amount of *N*-nitroso-3,3-dinitroazetidine (**2**). Although the yield of **4** is relatively low, this route is competitive with another previously published route by which this compound has been synthesized.[8]

Subsequent oxidation of **4** with 100% HNO_3[9] afforded *N*,3-dinitroazetidine (**5**)[8] in 90% yield. Since **5** previously has been converted into TNAZ, the methodology reported herein constitutes a novel formal synthesis of this important energetic material.

Scheme 1



Experimental Section

Melting points are uncorrected. Elemental microanalytical data was obtained by personnel at M-H-W Laboratories, Inc., Phoenix, AZ. High-resolution mass

spectral data for **3** were obtained at the Mass Spectrometry Facility at the Department of Chemistry and Biochemistry, University of Texas at Austin by using a ZAB-E double sector high-resolution mass spectrometer (Micromass, Manchester, England) that was operated in the chemical ionization mode.

Base Promoted Reaction of Allylamine with *N*-Chlorosuccinimide. A suspension of *N*-chlorosuccinimide (NCS, 14.0 g, 0.105 mmol) in heptane (80 mL) was cooled to 0 °C via application of an external ice-water bath. To the this cooled suspension was added allylamine (7.7 mL, 0.10 mmol), dropwise with stirring during 15 minutes. After all of the allylamine had been added, the reaction mixture was stirred at 0 °C for an additional 15 minutes. The reaction mixture then was filtered, and the residue was washed with heptane (20 mL). The com-bined filtrates were added dropwise with stirring during 1.5 h to a refluxing suspension of KO*t*-Bu (22.4 g, 0.20 mmol) in a mixture of heptane (60 mL) and octane (90 mL) in a 3 neck 1 L round-bottom flask that had been fitted with a distillation condenser. During this time, the reaction mixture was maintained at reflux via application of an external oil bath (bath temperature = 118 °C). Throughout the reaction period, 1-azabicyclo[1.1.0]butane (**1**) codistilled from the reaction vessel along with a mixture of heptane and octane. After the addition of the combined filtrates had been completed, distillate was collected during an additional 5 minues. The total volume of distillate thereby obtained was *ca.* 140 mL. The distillate was extracted three times with cold (0 °C) 25% aqueous $NaNO_2$ (35 mL, 30 mL, and 15 mL) and then with water (30 mL). The combined aqueous extracts were cooled to 0 °C via application of an external ice-water bath. To this cooled solution was added dropwise with stirring cold concentrated aqueous HCl (30 mL) during 0.5 h. After all of the aqueous HCl had been added, the resulting mixture was stirred at 0 °C for an additional 0.5 h. The resulting aqueous solution was extracted with EtOAc (3 x 60 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (2 x 50 mL). The combined aqueous extracts subsequently were extracted with EtOAc (2 x 30 mL). All EtOAc extracts subsequently were combined, dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The yellow residue (*ca.* 1.4 g) was purified via column chromatography on silica gel by using a 10-30% EtOAc-hexane gradient elution scheme.

The first chromatography fraction was collected and subsequently was concentrated *in vacuo*. Pure **2** (15 mg, 0.08%) was thereby obtained as a pale yellow

microcrystalline solid: mp 100-101 °C; IR (KBr) 2976 (w), 1566 (vs), 1417 (m), 1333 (vs), 848 (m), 648 cm^{-1} (m); ^1H NMR (DMSO-d_6) δ 5.10 (s, 2 H), 5.91 (s, 2 H); ^{13}C NMR (DMSO) δ 62.2 (t), 63.6 (t), 106.5 (s). Anal. Calcd for $C_3H_4N_4O_5$: C, 20.46 ; H, 2.29 ; Found: C, 20.60 ; H, 2.06.

Continued elution of the chromatography column afforded a second fraction that contained 3-chloro-1-nitrosoazetidine (**3**, 114 mg, 1.0%), as a yellow oil; IR (film) 2962 (m), 1649 (m), 1404 (vs), 1323 (vs), 1167 (s), 985 (m), 887 (s), 792 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 4.07–4.20 (m, 1 H), 4.50–4.73 (m, 2 H), 4.78–4.88 (m, 1 H), 5.23-5.34 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 44.2 (d), 62.6 (t), 64.8 (t); Exact Mass (CI-HRMS) Calcd for $C_{14}H_{20}N_2O_6$: $[M_r + H]^+$ 121.016866. Found: $[M_r + H]^+$ 121.016741.

The third chromatography fraction, when concentrated *in vacuo*, afforded pure 3-nitro-1-nitrosoazetidine[8] (**4**, 719 mg, 5.5%), as a pale yellow microcrystaline solid: mp 80-81 °C (lit.[8] mp 77-78 °C). The IR, ^1H NMR, and ^{13}C NMR of the material thereby obtained are essentially identical to the corresponding spectra that have been published previously for authentic **4**.[8]

1,3-Dinitroazetidine (5). A solution of trifluoroacetic anhydride (TFAA, 8.0 mL, 57 mmol), and freshly prepared[9] 100% HNO_3 (8 mL, excess) was cooled to 0 °C via application of an external ice-water bath. To this vigorously stirred solution under argon was added solid **4** (830 mg, 6.33 mmol) in one portion, and the resulting mixture was stirred at 0 °C for 0.5 h. The reaction mixture then was poured over crushed ice (60 g), and resulting aqueous suspension was extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (2 x 60 mL). Then, the combined aqueous $NaHCO_3$ extracts were extracted with EtOAc (2 x 40 mL). All EtOAc extracts were combined, dried ($MgSO_4$), and filtered, and the filtrate was concentrated *in vacuo*. The pale yellow residue thereby obtained was purified via column chromatography on silica gel by eluting with 20% EtOAc-hexane. The eluate was concentrated *in vacuo*, and the residue was recrysallized from EtOAc-hexane. Pure **5** (846 mg, 90%) was thereby obtained as a colorless microcrystalline solid: mp 64-65 °C (lit.[8] 62-63 °C); The IR, ^1H NMR, and ^{13}C NMR spectra of the material thereby obtained are essentially identical to the corresponding spectra that have been published previously for authentic **5**.[8]

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