Synthesis of 3,3-Dinitroazetidine from 1-*t*-Butyl-3,3-dinitroazetidine

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Received August 13, 1992

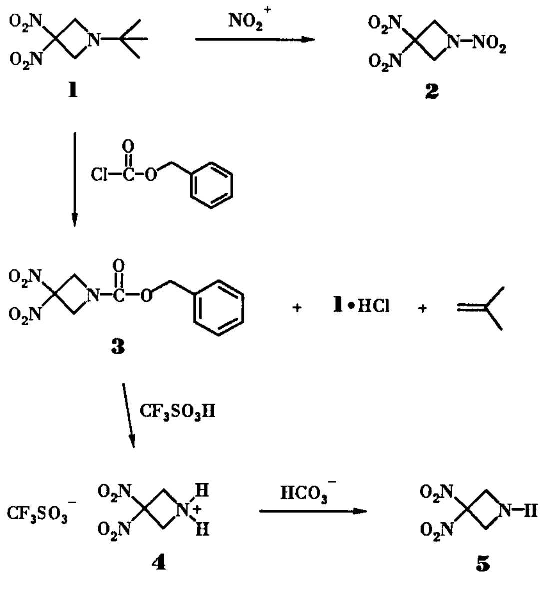
Treatment of 1-*t*-butyl-3,3-dinitroazetidine (**1**) with benzyl chloroformate resulted in a novel elimination of isobutylene to yield equimolar amounts of 1-(benzyloxycarbonyl)-3,3-dinitroazetidine (**3**) and 1-*t*-butyl-3,3-dinitroazetidine hydrochloride. The carbamate **3** was effectively cleaved by trifluoromethanesulfonic acid to yield 3,3-dinitroazetidinium trifluoromethanesulfonate (**4**). Free 3,3-dinitroazetidine (**5**) has also been isolated.

J. Heterocyclic Chem., **29**, 1855 (1992).

The salts of 3,3-dinitroazetidine (**5**), as well as the free base, have been of interest in recent years due to the synthesis of 1,3,3-trinitroazetidine (TNAZ) (**2**) as a melt castable high performance explosive [1], although none have been successfully prepared [2]. In an effort to prepare **5** and its salts, we thought it might be possible to cleave the *t*-butyl group from **1** using electrophiles in much the same way as nitronium ion cleaves **1** to produce TNAZ (**2**).

We have found that the treatment of 1-*t*-butyl-3,3-dinitroazetidine (**1**) with various chloroformates effectively eliminates the *t*-butyl group, with very little ring opening, to yield carbamates [3]. For example, benzyl chloroformate reacted with two equivalents of **1** to produce equimolar amounts of the carbamate **3** and the hydrochloride of **1** with elimination of isobutylene (Scheme 1). This reaction represents the first example, we believe, of the cleavage of a tertiary amine with elimination of an olefin. The carbamate moiety of **3** was easily removed by trifluoromethanesulfonic acid at room temperature with elimination of carbon dioxide to yield the trifluoromethanesulfonate **4** [4].

Scheme 1



The pK_a of **4** was determined to be 7.5 by aqueous titration. Neutralization of **4** gave the free base **5** as a colorless oil. We are currently investigating the polymerization of **5** and these results will be published elsewhere. We are also evaluating other salts of **5** as new energetic materials.

EXPERIMENTAL

All reagents were purchased from commercial sources except 1-*t*-butyl-3,3-dinitroazetidinium trifluoroacetate which was obtained from Fluorochem Inc., Azusa, CA. All nmr spectra were obtained on a JEOL GSX-270 spectrometer. Chemical shifts are relative to internal tetramethylsilane for ^{1}H and ^{13}C spectra. Microanalyses were performed at Los Alamos National Laboratory by W. F. King. All melting points were determined at 2°/minute with a Mettler FP1 apparatus and are corrected.

1-(Benzyloxycarbonyl)-3,3-dinitroazetidine (**3**).

To 1-*t*-butyl-3,3-dinitroazetidine (20.0 g, 0.099 mole) in 25 ml of chloroform is added benzyl chloroformate (9.24 g, 0.054 mole). The mixture is stirred under reflux for 24 hours during which time isobutylene is generated [5] and a white precipitate forms. The mixture is allowed to cool and filtered. The filter cake is washed with methylene chloride, air dried and weighed to yield 6.4 g (27%) of 1-*t*-butyl-3,3-dinitroazetidine hydrochloride. The filtrate is evaporated under vacuum to yield a yellow solid. The solid is taken up in warm toluene, the mixture is filtered hot, and the filtrate treated with hexanes to crystallize the product, which was collected by filtration and dried to yield 7.3 g (26%) of pure **3**, mp 77.5-78°; ^{1}H nmr (deuteriochloroform): δ 4.81 (s, 4H), 5.16 (s, 2H), 7.37 (s, 5H); ^{13}C nmr (deuteriochloroform): δ 58.1, 68.2, 128.3, 128.7, 135.2, 155.5.

Anal. Calcd. for $C_{11}H_{11}N_3O_6$: C, 46.98; H, 3.94; N, 14.94. Found: C, 46.86; H, 4.34; N, 15.40.

3,3-Dinitroazetidinium Trifluoromethanesulfonate (**4**).

To a solution of **3**, (4.0 g, 0.014 mole) in 40 ml of methylene chloride containing anisole (4.62 g, 0.04 mole) is added trifluoromethanesulfonic acid (10.0 g, 0.067 mole), slowly with vigorous stirring at room temperature. Carbon dioxide is evolved and the solution turns red in color. Stirring is continued for 30 minutes after the addition. Diethyl ether is added slowly to quench the reaction and precipitate **4**. The solid is filtered and washed with diethyl ether and air dried to yield 4.10 g (97%) of pure **4**, mp 176° dec; ^{1}H nmr (deuteriomethyl sulfoxide): δ 4.97 (s, 4H), 3.5 (bs, 2H); ^{13}C (deuteriomethyl sulfoxide): δ 53.4, 107.2, 113.6, 118.3, 123.1, 127.8.

Anal. Calcd. for $C_4H_6N_3O_7F_3S$: C, 16.17; H, 2.04; N, 14.14. Found: C, 16.58; H, 2.03; N, 13.85.

Caution: Compound **4** is highly flammable and may be ignited by a strong hammer blow.

3,3-Dinitroazetidine (**5**).

Compound **4** (2.0 g, 0.0067 mole) is dissolved in water (20 ml) and neutralized with sodium bicarbonate (0.62 g, 0.0074 mole). The free base is extracted into chloroform (3 x 5 ml) and dried over sodium sulfate. The chloroform is removed under vacuum to quantitatively yield **5** (0.98 g) as a light yellow oil; ^{1}H nmr (deuteriochloroform): δ 4.48 (s, 4H), 2.18 (s, 1H); ^{13}C nmr (deuteriochloroform): δ 55.10, 111.57.

Anal. Calcd. for $C_3H_5N_3O_4$: C, 24.50; H, 3.43; N, 28.57. Found: C, 24.59; H, 3.56; N, 26.80.

Acknowledgement.

The authors wish to thank D. G. Ott for many helpful discussions and suggestions. This work was performed under the auspices of the U. S. Department of Energy.

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