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Synthesis of 1,3,3-Trinitroazetidine

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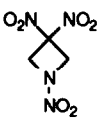
Abstract: The t-butyldimethylsilyl ether of 3-(p-toluenesulfonamido)propane-2-ol-1-(p-toluenesulfonate) on treatment with LiH undergoes ring closure to the corresponding azetidine which is readily converted to N-tosyl-3-azetidinone oxime. By oxidative nitrolysis the latter affords 1,3,3-trinitroazetidine.

Introduction

The synthesis of 1,3,3-trinitroazetidine **1**, the simplest member of the class of cyclic nitramines containing gem dinitro groups, has recently been described.[1] This compound has attracted considerable



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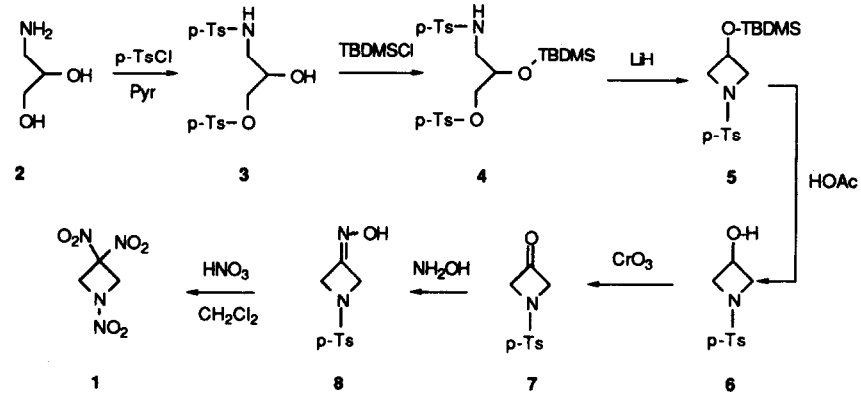
attention as an important new energetic material because of its favorable properties[2] which include a low melting point (mp 101 °C), good thermal stability (>240 °C), moderate density (1.84 g cm^{-3}) and low sensitivity. The energetics of its initial dissociation processes,[3] thermolysis[4] as well as infrared dynamic motion studies[5] have been reported. Despite the intense interest in this material, there exists only one preparative method starting from t-butyl amine and epichlorohydrin to form 1-t-butyl-3-azetidinol and subsequent functionalization of this alcohol. The overall yield in this synthesis is poor, being principally limited by the steps involving the formation of the intermediate 1-t-butyl-3-mesyloxyazetidine and the S_N2 nitrite ion displacement of mesylate ion in the latter to introduce the first C-nitro group. We describe herein a new synthesis of 1,3,3-trinitroazetidine via a route in which key roles are played by protection of a secondary hydroxyl group to effect azetidine ring closure and by oxidative nitrolysis methods for the simultaneous introduction of the N-NO_2 and C(NO_2)$_2$ groups.

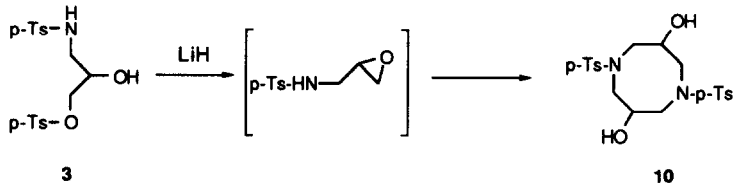
Results and Discussion

The synthesis of 1,3,3-trinitroazetidine was achieved by the sequence of steps outlined in Scheme 1. Conversion of 3-amino-1,2-propanediol **2** to the ditosyl derivative **3** by reaction with p-toluenesulfonyl

Scheme 1

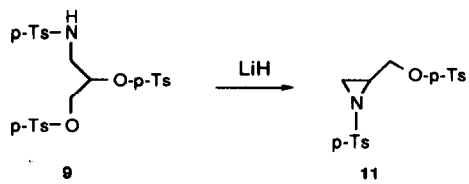


chloride in pyridine was accompanied by the formation of the tritosylated 3-amino-1,2-propanediol **9**. Compounds **3** and **9** were obtained in 66% and 26% yields respectively, after separation by silica gel chromatography. Treatment of **3** with LiH/THF failed to give the desired azetidinol, rather the cyclodimerization products, cis and trans 1,5-bis-(p-toluenesulfonyl)-3,7-dihydroxyoctahydro-1,5-diazocines



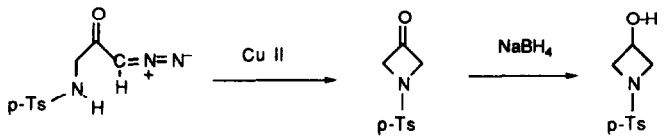
(1)

10 were obtained (see eq 1). By analogy with related systems, it is likely that these materials arise from an intermediate epoxide as has been previously observed[6] and confirmed in our laboratories. Similarly, reaction of tritosylate **9** with LiH led, not unexpectedly,[7] to the exclusive formation of aziridine **11** in 80% yield (see eq 2).



(2)

In contrast to the many known Gaertner-type ring closures involving the reaction of p-toluenesulfonamide anions and 1,3-disubstituted propane derivatives to give azetidines,[8] there do not appear to be any reports of 3-azetidinols being formed when the central C-2 carbon of the propane unit bears a hydroxyl group, although gem dimethyl substitution apparently leads to successful cyclization.[10] Treatment of **3** with t-butyldimethylsilyl chloride and imidazole in dimethylformamide afforded the silyl protected ether **4** in 88% yield. When the latter was subjected to treatment with LiH/THF, smooth cyclization to the azetidine **5** in 91% yield resulted. Deprotection of **5** by heating in acetic acid readily afforded N-tosyl-3-azetidinol **6** in 83% yield. Confirmation of the structure of **6** was obtained by the $NaBH_4$ reduction of N-tosyl-3-azetidinone **7** independently prepared from diazoketone **12** by the Cu II promoted intramolecular N-H insertion reaction[9] (see eq 3).



12 **7** **6** (3)

Transformation of N-tosyl-3-azetidinol **6** to ketone **7** in 95% yield was effected by oxidation with CrO_3/HOAc and the latter on treatment with hydroxylamine was quantitatively converted to N-tosyl-3-azetidinone oxime **8** using the conditions developed by Corey et al. [11] In the final step this oxime was treated with 99% HNO_3 in refluxing methylene chloride to simultaneously nitrolyze the p-tosyl group and oxidize the oxime function to produce the desired 1,3,3-trinitroazetidine **1** in 40-50% yield.

In conclusion, a new synthesis of the potentially important energetic compound, 1,3,3-trinitroazetidine, has been developed. Significantly, in this preparative method the three nitro groups are introduced simultaneously in the final step of the reaction sequence. All new compounds prepared in the course of this work have been fully characterized by ^1H and ^{13}C NMR and MS. These data will be reported in a more complete account of this and related studies currently under investigation.

CAUTION. Reactions with 99% HNO_3 should be carried out behind a protective barrier as should the handling of nitro azetidines which are potentially heat and shock sensitive.

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