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DESILYLATION OF α-TRIMETHYLSILYL NITRAMINES: THE FIRST NITRAMINE α-ANION

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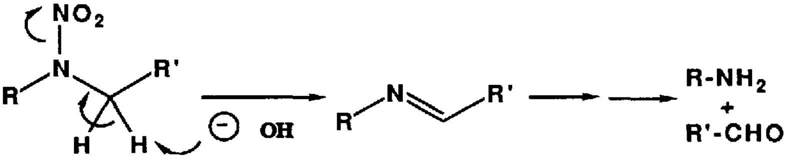
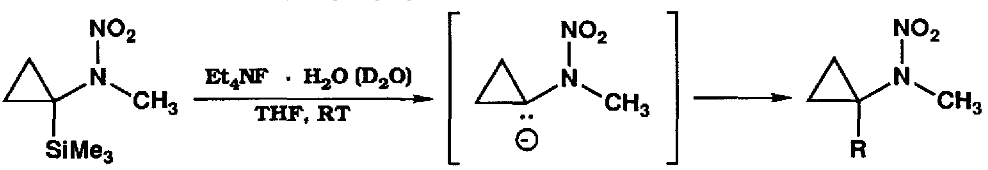
Summary: Fluoride-induced desilylation of a trimethylsilylcyclopropyl nitramine generated the first known nitramine α-anion, which was trapped *in situ* by electrophiles (H_2O, D_2O, and CH_3CHO). In contrast, a trimethylsilylmethyl nitramine gave a product resulting from elimination of the elements of trimethylsilyl nitrite under identical reaction conditions.

Secondary nitramines, **1**, have long been known to undergo decomposition in refluxing aqueous base to primary amines and aldehydes.[1] This process presumably occurs by elimination of the elements of nitrous acid, followed by hydrolysis of the resulting imine, **2**. Grignard reagents[2] and alkyllithiums[3] give products which suggest attack by the organometallic on the nitramine nitro group. No evidence to date has been observed for the formation of a stable nitramine α-anion, even upon reaction with hindered bases at low temperature. In these latter cases, the imines **2** are isolated.[3,4]



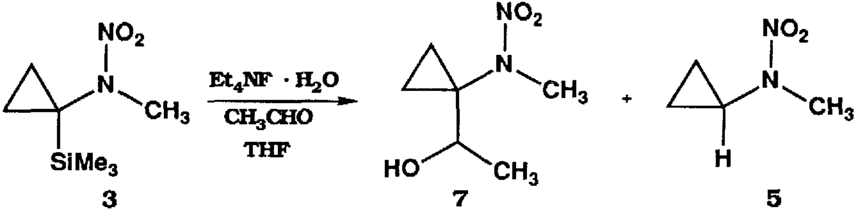
1 **2**

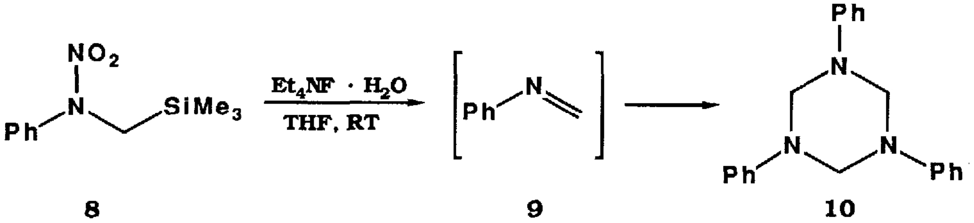
We have found that a nitramine α-anion can be generated and trapped by desilylation[5] of trimethylsilylcyclopropyl nitramine **3**[6] in the presence of electrophiles. Thus, treatment of **3** with 2 equivalents of tetraethylammonium fluoride (TEAF) hydrate in THF, furnished protiodesilylation product **5**[7] in 88% yield. Reaction of **3** with TEAF which had been subjected to several wetting/drying cycles with D_2O afforded a 4:1 mixture (by ^1H NMR) of deuterated product **6** and its protic analogue **5** in 74% yield. This implies that the residual water in the TEAF is responsible for trapping of the intermediate carbanion **4**.[8] Reaction of **3** with TEAF in the presence of 5 equivalents of acetaldehyde afforded nitramino alcohol **7**,[6] isolated in 47% yield after flash chromatography, as well as 24% of the product **5**.



3 **4** **5** R = H
6 R = D

The presence of the cyclopropyl group appears to be critical to the stability of the intermediate carbanion, as expulsion of nitrite by this species would produce a strained exocyclic imine. Indeed, treatment of trimethylsilyl nitramine **8**[6] with TEAF does not cause protiodesilylation, but instead leads to rapid decomposition, mainly to hexahydrotriazine **10**.[10] This product suggests the intermediacy of elimination product *N*-methyleneaniline **9**, since this latter compound is known to trimerize to **10**.[11]





The results with nitramine **3** constitute evidence for the first nitramine α-anion, and imply that nitramines in which similar geometric inhibitions of elimination operate (such as caged high-energy polynitramines) could be functionalized via a carbanionic intermediate.

References and Notes

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6. All new compounds exhibit satisfactory IR, ^{1}H NMR, and combustion or high resolution mass spectral analyses. Compound **3** was prepared from 1-(trimethylsilyl)cyclopropanecarboxylic acid as follows: (i) Et_3N, $ClCO_2Et$; NaN_3; Δ. (ii) $LiAlH_4$, Et_2O. (iii) $NaNO_2$, H_2O, HOAc. (iv) CF_3CO_3H, CH_2Cl_2. Compound **8** was prepared by reaction of potassium *N*-nitroanilide with chloromethyltrimethylsilane in DMF.
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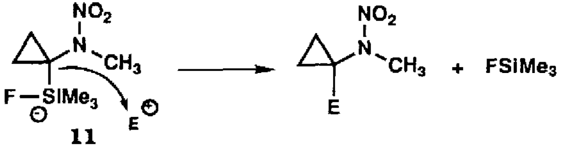
8. Stereochemical evidence on desilylation of α-trimethylsilylcyclopropylsulfides[9] implicates an α-thiacarbanion intermediate. The rate of formation of **7** from **3** is independent of acetaldehyde concentration, eliminating the mechanism involving rate determining reaction of acetaldehyde with the pentacovalent fluorosiliconate **11**:



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