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Failure to Isolate the First *N*-Nitrosiminium Cation

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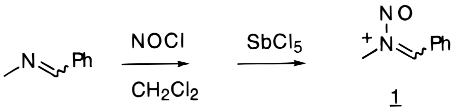
Introduction

The synthesis of the $SbCl_6$ salt of the first N-nitrosiminium ion, **1**, was reported, along with limited physical characterization.[1] The purported isolation of this cation was claimed as evidence of the pervasive intermediacy of *N*-nitrosiminium ions in the decomposition of carcinogenic α-acetoxy-*N*-nitrosamines.[1,2] We had need of the ion, **1**, as a precusor to various α-substituted nitrosamines in which we have an ongoing interest. We report here that the method briefly described[1] in fact gives the $SbCl_6$ salt of the simple iminium ion **2**, and that the limited physical data originally reported indicate that the salt of **2** was also the product in the initial[1] report.



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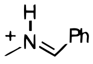
(1)



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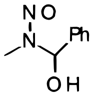

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Experimental Section

The solvent CH_2Cl_2 was dried by distillation from CaH_2. NOCl was generated according to the procedure of Schenk.[3] The $SbCl_5$ and $NOBF_4$ were used as obtained from Aldrich Chemical Co. (Milwaukee, WI).

Slow addition to NOCl (0.56 g, 8.4 mmol), eq 1, in 20 mL of CH_2Cl_2 at −30 °C of 1 equivalent of imine (1 g, 8.4 mmol, in 10 mL of CH_2Cl_2) followed by addition of $SbCl_5$ (2.54 g, 8.4 mmol, in 5 mL of CH_2Cl_2) gave a faintly yellowed whitish precipitate, as reported.[1] This was filtered and washed with additional CH_2Cl_2 and dried under vacuum. ^{1}H-NMR (CD_3CN) δ 3.59 (3H, d); 7.67 (2H, m); 7.90 (3H, m); 8.78 (1H, d); 10.4−11.25 (1H, t (br)). ^{13}C-NMR (CD_3CN) δ 39.70, 127.47, 131.05, 132.46, 138.73, 173.50. C, H, N analysis found: C, 21.09; H, 2.22; N, 3.04. Calcd for $SbCl_6$ salt of **1**: C, 19.87; H, 1.88; N, 5.79. Calcd for $SbCl_6$ salt of **2**: C, 21.13; H, 2.22; N, 3.08.

Results and Discussion

We had hoped to generate the α-hydroxy compound **3**, in order to study its decomposition chemistry, by directly injecting polar aprotic solutions of **1** into aqueous solutions. We have recently reported that the cation **1** is hydrated in predominantly aqueous media with rate constants on the order of 10^6 s^{-1}.[4] So we expected that, depending on the stability of **3**, the proposed experiments using conventional spectrophotometry would give initial UV spectra consistent either with **3** ($\lambda_{max} \sim 230$ for the N−NO group) or, the ultimate product benzaldehyde ($\lambda_{max} = 253$).

Our suspicion about the identity of the product of our synthesis initially arose from the following observations. The solid material when dissolved in acetonitrile exhibited a $\lambda_{max} = 271$, quite similar to that reported previously[1] ($\lambda_{max} = 272$ nm, solvent unreported). An aliquot of a more concentrated solution of the salt in acetonitrile, when diluted 100-fold into buffered water (0.05 M cacodylic acid buffer, 50% anion), exhibited a $\lambda_{max} = 268$ nm. This absorbance decayed over the course of 1 min ($t_{1/2} \sim 7$ s), with an isosbestic point at 258 nm, to a product with a $\lambda_{max} = 253$, identical with the λ_{max} of benzaldehyde under identical conditions.

The ^{1}H-NMR analysis of the products of the decay of the salt in D_2O containing 20% CD_3CN indicated benzaldehyde and methylammonium ion only. No methanol was detected, in contrast to what was expected from previous analyses of products of reactions that involve the intermediacy of **1** in aqueous solutions.[5]

The ^{13}C-NMR (CD_3CN) of the product of our synthesis contains a signal at δ 173.5, nearly identical with that (δ 172.1, solvent not reported) originally ascribed[1] to the iminium carbon of **1**, but all the spectral lines correlate quite well with the spectrum reported for **2** in HSO_3F/SO_2ClF.[6] The ^{1}H-NMR is inconsistent with the structure **1** in that it contains a broad triplet at δ 10.4−11.25 consistent with coupling of the NH in **2** to the nitrogen quadrapole, and the signal from the methyl group is split into a doublet by coupling with the NH.[7] The ^{1}H-NMR spectrum is nearly identical with that reported for **2** in $HSO_3F-SbF_5-SO_2$.[8] Finally, the C and N elemental analyses are inconsistent with that expected for the $SbCl_6$ salt of **1** but in good agreement with that calculated for the $SbCl_6$ salt of **2**.

It is concluded that the first *N*-nitrosiminium ion salt is yet to be isolated. We have not investigated the mechanism by which the product **2** is formed from the given reagents, but **2** (presumably the BF_4 salt) is formed upon addition of $NOBF_4$ to the starting imine (eq 1) in $CDCl_3$ that had been stored over molecular seives.

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(7) This NH to methyl coupling is variable, with the signal from the methyl group appearing as a broadened singlet in some samples that otherwise give identical spectra.

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