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A Simple Synthesis of Pure 2-Aminotroponimine, the Nitrogen Analogue of Tropolone

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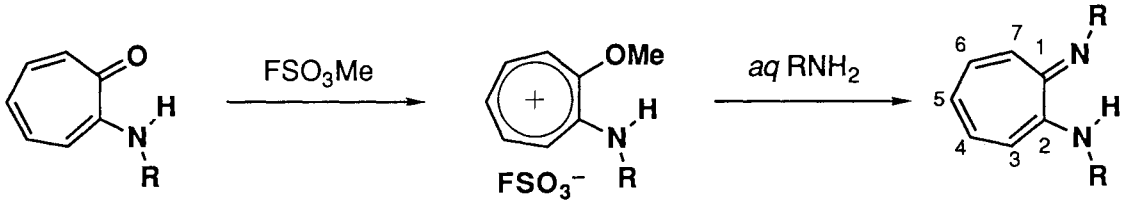
2-Aminotroponimine (**1**) is conveniently synthesized in high yield and is isolated in pure form, starting from 2-aminotropone via 2-methoxytroponiminium fluorosulfonate. *N,N'*-Dimethyl derivative of **1** is prepared similarly.

Although 2-aminotroponimine (**1**), the nitrogen analogue of tropolone (**2**), is one of the most fundamental novel aromatic compounds, the isolation of pure **1** has been unsuccessful. The atomic mutation in exocyclic heteroatom of [7]annulene system brings about the change in chemical and physical properties. This effect has been the object of theoretical and experimental interest.[1] Forbes et al. reported the synthesis and characterization of dithiotropolone,[2] the sulfur analogue of **2**. Though Brasen et al. reported the synthetic approach to **1**, they did not isolate the compound in pure form, but obtained the hemihydrate of **1**.[3] We report herein the synthesis, isolation, and characterization of the substituent-free compound **1**.

2-Aminotropone[4] (**4**) reacted with methyl fluorosulfonate in anhydrous ether at −5 °C to form 2-methoxytroponiminium fluorosulfonate (**5**),[5] a syrupy white solid, in quantitative yield. The salt **5** was dissolved in anhydrous methanol, and 28% aqueous ammonia was added dropwise into the solution at 0 °C with stirring for 1 h. Solvent removal in vacuo followed by addition of 30% aqueous NaOH solution caused precipitation of a yellow crystalline solid. After filtration and washing with water, the crystals were dried in vacuo at 100 °C and recrystallized from ether to afford the desired compound **1** as yellow plates in 76% yield. The compound is thermally stable and has a relatively high melting point of 109–110 °C. Elemental analysis[6] and ^{1}H NMR show that the desired compound, not the hemi- or monohydrate, was successfully isolated.



4: R = H **5**: R = H **1**: R = H

6: R = Me **7**: R = Me **3**: R = Me

The ^{13}C NMR spectrum[7] of **1** (100.6 MHz, $CDCl_3$) exhibits three doublet signals at δ 119.19 (2C, C-3,7), 120.71 (1C, C-5), and 132.26 (2C, C-4,6) accompanied by a singlet one at δ 158.08 (C-1,2). The 400-MHz ^{1}H NMR spectrum of **1** ($CDCl_3$) shows complex signals of the ring protons at δ 6.21 (1H, t, *J*=9.26 Hz, H-5), 6.52 (2H, d, *J*=10.36 Hz, H-3,7), and 6.61 (2H, dd, *J*=9.26 and 10.36 Hz, H-4,6) accompanied by a broad singlet one at δ 5.55 (3H, br s, NH). The data imply that **1** has a symmetrical structure and the two

nitrogen atoms are equivalent on a time average. EI-MS fragmentation[8] (75 eV) of **1** appears to be simple and characteristically different from that of **2**.[9] The UV-vis spectrum of **1** in methanol solution shows absorptions at 248 (log ε 4.50), 270 (3.96), 345 (4.05), 366 (4.01), and 394 nm (4.05). The IR spectrum (KBr) of **1** shows strong stretching vibrations of the N-H (3380 and 3260 cm^{-1}), C=C (1620), and C=N (1600) bonds.

In a similar way, we conveniently prepared an *N,N'*-dimethyl derivative[10] **3** starting with 2-methylaminotropone (**6**).[11] The reaction of **6** with methyl fluorosulfonate similarly gave an iminium salt **7**,[12] pale yellowish creamy white solid, in quantitative yield. The salt **7** reacted with methylamine in anhydrous methanol at −40 °C with stirring for 40 min. Alkaline treatment gave yellow precipitates, which were recrystallized from ether–methanol to form yellow plates of **3**, mp 66–67 °C (lit,[10] mp 66.5–67 °C) in 93% yield.

Thus, we have succeeded in the first preparation, isolation and characterization of the titled compound **1**.

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References

1) T. Machiguchi, H. Otani, Y. Ishii, and T. Hasegawa, *Tetrahedron Lett.*, **28**, 203 (1987); T. Machiguchi, T. Hasegawa, H. Otani, Y. Ishii, *J. Chem. Soc., Chem. Commun.*, **1987**, 1375; T. Machiguchi, H. Mizuno, T. Hasegawa, Y. Ishii, H. Otani, *Chem. Lett.*, **1987**, 1893; T. Machiguchi, T. Hasegawa, M. Ohno, Y. Kitahara, M. Funamizu, and T. Nozoe, *J. Chem. Soc., Chem. Commun.*, **1988**, 838; T. Machiguchi, T. Hasegawa, S. Itoh, and H. Mizuno, *J. Am. Chem. Soc.*, **111**, 1920 (1989); T. Machiguchi, Y. Kano, and T. Hasegawa, *Chem. Lett.*, **1990**, 563; T. Machiguchi and S. Yamabe, *Tetrahedron Lett.*, **31**, 4169 (1990); T. Machiguchi and S. Yamabe, *Chem. Lett.*, **1990**, 1511.

2) C. E. Forbes and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 6884 (1968); **92**, 2297 (1970).

3) W. R. Brasen, H. E. Holmquist, and R. E. Benson, *J. Am. Chem. Soc.*, **82**, 995 (1960).

4) 2-Aminotropone (**4**) can be prepared conveniently from tropone [T. Machiguchi, *Synth. Commun.*, **12**, 1021 (1982)] and hydrazine hydrate (G. L. Buchanan and D. R. Lockhart, *J. Chem. Soc.*, **1959**, 3586).

5) **5**: IR ν_{max} (KBr) 1635 (m), 1590 (m), 1495 (s), 1280 (vs), 1230 (s), 748 (s) cm^{-1}; ^1H NMR (90 MHz, Me_2SO-d_6) δ 4.18 (3H, s, OMe), 7.44–8.13 (5H, complex m, ring H), 9.43 (1H, br s, N^+H), 10.15 (1H, br s, N^+H); ^{13}C NMR (22.5 MHz, Me_2SO-d_6) δ 57.86 (q), 121.68 (d), 127.36 (d), 133.16 (d), 138.09 (d), 143.89 (d), 158.14 (s), 160.95 (s).

6) Anal. Calcd for $C_7H_8N_2$: C, 69.97; H, 6.71; N, 23.32. Found: C, 69.75; H, 6.75; N, 23.25. Cf. Calcd for $C_7H_8N_2 \cdot 1/2\ H_2O$ (hemihydrate): C, 65.09; H, 7.02; N, 21.69.

7) The assignments of NMR (^{13}C and ^1H) are confirmed by selective decoupling.

8) *m/z* 121 (M^++1, 21%), 120 (M^+, 88), 93 (M^+–CNH, base), 77 (C_6H_6, 66), 66 (36), 65 (22), 51 (7).

9) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, London (1967), pp. 540–541 .

10) W. R. Brasen, H. E. Holmquist, and R. E. Benson, *J. Am. Chem. Soc.*, **83**, 3125 (1961).

11) K. Kikuchi, *Bull. Chem. Soc. Jpn.*, **40**, 385 (1967).

12) **7**: ^1H NMR (90 MHz, Me_2SO-d_6) δ 3.17 (3H, d, *J*=5.6 Hz, NMe), 4.13 (3H, s, OMe), 7.17–8.16 (5H, complex m, ring H), 9.74 (1H, br s, NH).

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