

## A Convenient Preparation of Acetamidine

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Surprisingly, no satisfactory procedure for the preparation of crystalline acetamidine seems to exist in the literature.<sup>1,2</sup> Contrary to a previous report,<sup>3</sup> we have found that deprotonation of acetamidinium chloride<sup>4</sup> with sodium methoxide in methanol, followed by vacuum distillation and recrystallization, affords a satisfactory yield of acetamidine, stable at room temperature, but undergoing decomposition to ammonia and acetonitrile at 95 °C.

*Experimental.* A solution of acetamidine hydrochloride<sup>4</sup> (9.4 g) in methanol (35 ml) was added in one portion to a sodium methoxide solution, prepared from sodium (2.3 g) and methanol (25 ml). The suspension was stirred and cooled in ice water for 10 min, filtered through Celite, concentrated *in vacuo*, and distilled. Yield 4.1 g (70%), b.p. 82–85 °C/10 mmHg, m.p. 59–66 °C. The distillate did not crystallize spontaneously at room temperature (20 °C), but crystallization took place at 0 °C. Recrystallization from methylene chloride (10 ml) at 0 °C gave colourless needles. Yield 3.53 g (61%), m.p. 65–67 °C. Repeated recrystallization raised the m.p. 66–67 °C. Standard microanalysis gave erratic results due to the very hygroscopic character of the compound. Titration with nitric acid to pH 7 in water gave equivalent weight 58.5 ( $M = 58.0$ ). MS [IP 70 eV;  $m/z$  (% rel. int.)]: 58 (100, M), 43 (79), 42 (75) 41 (28). CI (isobutane) MS [ $m/z$ ]: 59. <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>):  $\delta$  1.97, 5.7 (s, variable  $\delta$ , H on N), 7.38 (CHCl<sub>3</sub>, due to exchange of deuterium with hydrogen). The sum of integrals at  $\delta$  5.7 and 7.38 is equal to the integral at  $\delta$  1.97). After 2 h at 20 °C a triplet appeared.  $\delta$  1.96,  $J(D,H)$  2 Hz. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 22.93 MHz, <sup>1</sup>H decoupled):  $\delta$  23.2, 165.4, 77.6 (CHCl<sub>3</sub> from deuterium exchange). The product has a mousy odor.

The stability was evaluated by keeping acetamidine (100 mg) in an evacuated ampoule (10 ml) at 95 °C for 12 h. The ampoule was cooled (0 °C) and carefully opened (pressure, ammonia) and shown (NMR, G.C.) to contain acetamidine (30%) and acetonitrile (70%).

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