

## A New Synthesis of 2,5-Dimethyl-1-pyrroline

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A study was recently completed in our laboratory of new synthetic routes for the preparation of cyclic amines. During the course of this work a new synthesis of 2,5-dimethyl-1-pyrroline (I) was developed. This compound is of interest because of the presence of the pyrroline nucleus in compounds of biological importance (1,2). Compound I can also be easily hydrogenated (3) to *cis*-2,5-dimethylpyrrolidine (II), a valuable intermediate for the preparation of an active herbicide (4,5). Compound II is representative of a class of cyclic amines themselves components of biologically active materials (6,7,8).

Synthesis of the pyrroline nucleus has been accomplished in a variety of ways. The ring closure method of Cloke (9) modified by Craig and Hixon (10) uses a  $\gamma$ -chloroalkyl nitrile. A similar method (11) starts with a  $\gamma$ -bromovaleryl chloride which is converted to 5-bromohexanone-2 followed by ring closure in alcoholic ammonia. A third method (9,12) proceeds through a  $\gamma$ -aminocarbonyl compound. These routes all generate the desired  $\Delta$ -1-pyrrolines, but are effected in yields below 30% because of the steps involved in the synthesis of needed intermediates.

An alternate synthesis would reduce the pyrrole to the corresponding pyrroline. However, the reduction yields predominantly the  $\Delta$ -3-pyrroline which must be isomerized to the  $\Delta$ -1 isomer by heating in the presence of Raney Nickel (3).

We have found that catalyzed vapor phase condensation of allylacetone with ammonia gives good yields of I. The reaction probably proceeds through the intermediate 5-amino-1-hexene. This imine can cyclize or react intermolecularly to form polymeric byproducts. Because of this, the ammonia ratio is critical to obtaining good yields.

We have also found that the nature of the alumina catalyst is critical. Commercially available  $\gamma$ -alumina gave low yields of I in our system and was modified by sintering at temperatures of 1100°-1300°. This yielded a high porosity  $\alpha$ -alumina with pore volume and surface area characteristics necessary to give the yields reported.

## EXPERIMENTAL

The product mixtures were quantitatively analyzed by vapor phase chromatography using a Fisher Victoreen Chromatograph

equipped with a 3/16" x 6' ss column packed with 5% Amine 220 on High Performance Chromosorb G and operating at 100°. Mass spectra were obtained in a Varian MAT CH7 spectrometer.

The catalyst used was 5-8 mesh granular  $\alpha$ -alumina, pore volume 0.60 ml. per g., density 0.64 g. per ml., and surface area 10 m<sup>2</sup> per g.

A glass tubular reactor (20" x 0.75" ID) equipped with a preheater (10" x 0.75" ID) was packed with 200 g. of catalyst. The preheater temperature was 300° and the reactor was maintained at 460°. Ammonia and allylacetone (97%) are introduced into the top of the reactor in a mole ratio of 33:1 and at a rate of 10 g. of allylacetone per hour. A Dry Ice cooled condenser is used to collect the products. Following evaporation of ammonia quantitative vapor phase chromatographic analysis showed that 99.3% of the allylacetone was converted with a 73.4% yield of I. Although most of the by-product was nonvolatile oil, traces of acetone, methyl ethyl ketone, methyl isobutyl ketone, acetonitrile, propionitrile and  $\alpha$ -picoline were identified by mass spectral analysis. Drying over magnesium sulfate, and atmospheric distillation gave 99% pure I, b.p. 112-113°, which was identical with an authentic sample in ir, nmr, and mass spectra.

The effect of varying the ammonia ratio can be seen in the following table. The reactor and catalyst used were the same as described above.

NH <sub>3</sub> :ALA (a) (mole ratio)	Temperature (°C)	Conversion (%)	Yield (%)
58:1	460	98.5	62.0
45:1	440	99.0	62.7
25:1	435	92.0	56.9
12:1	445	96.1	47.4
8:1	450	98.7	44.8
7:1	420	81.7	32.4

(a) ALA = allylacetone (available from Aldrich Chemical Co.).

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