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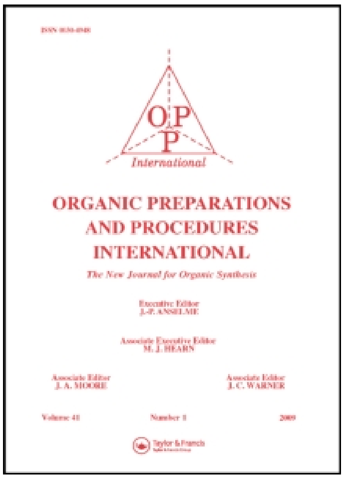

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3-METHYLSUCCINIMIDE AND 3-METHYLPYRROLIDINE

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3-METHYLSUCCINIMIDE AND 3-METHYLPYRROLIDINE

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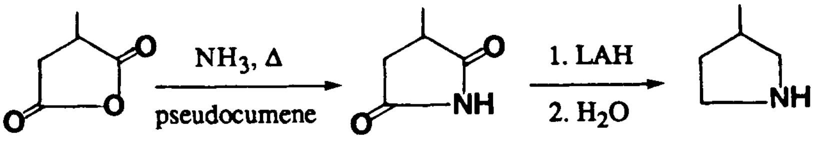
3-Methylpyrrolidine (**3**) which serves as a model coal liquid constituent is not commercially available and a substantial sized sample of pure material was needed for the study of its thermochemical and thermophysical properties.[1] We have developed procedures for the preparation of **2** and **3** from methylsuccinic anhydride (**1**). The preparation of **3** has been reported but the experimental details were meager.[2,3]



1 **2** **3**

The use of anhydrous ammonia in refluxing hydrocarbon is superior to ammonium hydroxide[4] in converting **1** to **2** in that tarry residue and decomposition products are avoided and a higher yield (95% vs. 85% reported for succinimide) is obtained. The reaction of ammonia with **1** was exothermic and caused the reaction temperature to rise from an initial 60° to about 115°. This latter temperature is inadequate to cause conversion to **2** and hence refluxing pseudocumene was used as a reaction medium.

We believe the yield of **3** from **2** (59% initial yield; 47% after purifying to 99.9+%) to be reasonable and it is low not because of an inefficient reaction but because **3** is volatile and its water solubility complicates the isolation and purification. The water solubility of **3** and its tendency to form stable hydrates has been observed previously.[2] Continuous extraction from water was time consuming, gave a low yield (12%) with lesser purity than the selected procedure which involved filtration of the reaction mixture and Soxhlet extraction of the remaining salts obtained from decomposing the LAH reduction with water.

EXPERIMENTAL SECTION

3-Methylsuccinimide (2). - To a 12-L flask equipped with a mechanical stirrer and condenser was added 6 L of pseudocumene and 912 g (8 mol) of methylsuccinic anhydride. The mixture was warmed to 60° and dry ammonia was bubbled through the solution with vigorous stirring. An exothermic reaction gradually raised the temperature to 115°. Completion of the reaction with ammonia was evident when no further increase in temperature was observed. The mixture was then heated to reflux at 160-165° to effect cyclization to **2**. The water formed from this reaction was removed as an azeotropic mixture with pseudocumene. The resulting solution was cooled overnight and 3-methylsuccinimide separated as a white solid. Pseudocumene was decanted and the residue was washed with n-hexane and distilled (Kugelrohr apparatus, 150°, 0.1 mm) to give 855 g (95%) of crystalline 2, mp, 65-66°, lit.[3] 65-66°.

^{1}H NMR (CDCl$_3$): δ 9.5 (s, 1H, NH), 2.9 (d, 2H), 2.4 (m, 1H), 1.38 (d, 3H).

^{13}C-NMR (CDCl$_3$): ppm 181.8, 177.6, 37.5, 36.1, 16.3.

3-Methylpyrrolidine (3). - To a mechanically stirred mixture of 100 g (2.63 mol) of lithium aluminum hydride and 3 L anhydrous ether under nitrogen in 12-L flask, was added 198 g (1.75 mol) of 3-methylsuccinimide as a slurry[5] in 2 L anhydrous ether. An exothermic reaction occurred and the rate of addition was controlled to maintain a steady reflux of ether throughout the addition. After addition, the reaction mixture was heated at reflux for an additional hour and then cooled to 15-20°. The reaction flask was cooled in an ice-water bath and deionized water (220 mL) was added dropwise with stirring until hydrogen evolution ceased. The resulting suspension was filtered and the inorganic residue was continuously extracted with ether under an argon atmosphere in a Soxhlet apparatus[6] for 6 hrs. This extract was combined with the ether filtrate, dried (Na_2CO_3) filtered and concentrated under an argon atmosphere using a fractionating column to give 82 g (59%). Further fractionation under argon gave 65 g (47% yield) of **3**, bp 104°, lit.[3] 92-94°. The product darkens within moments on exposure to air and must be handled in inert atmosphere.

^{1}H-NMR ($CDCl_3$): δ 8.4 (s, 1H, NH), 4.04 (t, 2H), 3.28 (m, 2H), 2.4 (m, 2H), 1.85 (m, 1H), 1.45 (d, 3H); ^{13}C-NMR ($CDCl_3$): ppm 78.4, 54.6, 46.6, 34.0, 19.0

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