

NEW METHOD OF SYNTHESIZING N-SUBSTITUTED 2,5-DIMETHYLPYRROLE  
AND 2,5-DIMETHYLPYRROLIDINE

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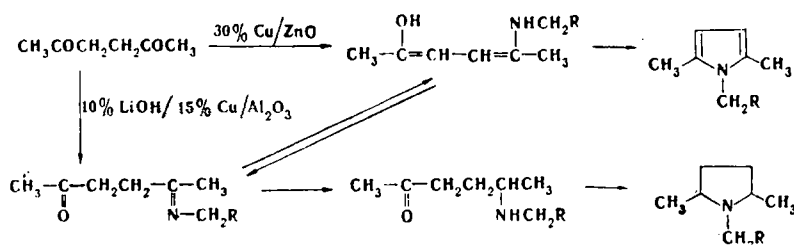
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The reductive amination of acetylacetone with amines has been investigated in a number of papers [1-3]. N-Substituted 2,5-dimethylpyrrole [1, 2] or a mixture of N-substituted 2,5-dimethylpyrrole and 2,5-dimethylpyrrolidine (2:1) [3] are the principal reaction products depending on the conditions.

The hydroamination of acetylacetone with nitriles has not at all been studied up to the present time. The employment of nitriles in the reaction considerably broadens the raw material base for the purposeful synthesis of the N derivatives of either 2,5-dimethylpyrrole or 2,5-dimethylpyrrolidine.

The investigations carried out showed that a mixture of N-substituted 2,5-dimethylpyrrole and 2,5-dimethylpyrrolidine is the principal reaction product. Depending on the reaction conditions the ratio between the pyrrole and pyrrolidine derivatives in the catalyzate varied over very wide ranges from 6:1 to 1:6. Thus the reaction can be directed toward the predominant formation of the pyrrole or pyrrolidine compounds. Although the ratio of the reaction products formed is affected by temperature and the hydrogen pressure, the nature of the catalyst (Table 1) nevertheless plays a deciding role.

Under the conditions studied no mutual conversion of the rings, hydrogenation of the pyrrole ring to pyrrolidine, or conversion of the latter to pyrrole, was detected. It probably can be assumed that intermediate complexes are formed on the surface of the catalyst depending on its chemical nature: the complexes can be converted to the N derivatives of pyrrole or pyrrolidine. Based on the experimental data obtained we feel that the formation of these compounds can be expressed by the following scheme:



Propio-, butyro-, and benzonitrile were used as the aminating agents. The preparative yields of the corresponding 2,5-dimethylpyrroles or 2,5-dimethylpyrrolidines are given in Table 1.

The individuality and structure of the compounds synthesized were demonstrated by PMR, IR, and mass spectroscopy. There are signals at  $\delta$  5.25 ppm (singlet) in the PMR spectra of the pyrrole derivatives for the protons at the double bond, at 2.01 ppm (singlet) for the protons of the methyl groups located in positions 2 and 5 of the pyrrole ring, and at 1.30-0.60 ppm (multiplet) for the protons of the methylene groups. There is no singlet at  $\delta$  5.25 ppm for the pyrrolidine derivatives. A characteristic band ( $\sim 1520$   $\text{cm}^{-1}$ ), which is attributable to the antisymmetric vibrations of the C=C bond in the ring, is observed in the IR spectra of the pyrrole derivatives. A band in the  $1310$   $\text{cm}^{-1}$  region, which is characteristic for the stretching vibrations of the exocyclic C-N bond, is present for all of the compounds synthesized. Peaks of the molecular ions  $M^+$  are present in the mass spectra of all of the

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TABLE 1. Results of the Hydroamination of Acetylacetone with Nitriles

Nitrile	Catalyst	Temperature, °C	Pressure, atm	Yield, %	
				N-alkyl-2,5-dimethylpyrrole	N-alkyl-2,5-dimethylpyrrolidine
Propionitrile	30% Cu/ZnO	220	7	21	19
		220	15	31	11
		240	7	22	14
	36% Cu/MgO	240	15	42	7
		220	7	23	8
		220	15	25	10
	15% Cu/Al <sub>2</sub> O <sub>3</sub>	240	7	23	8
		240	15	25	9
		220	7	10	6
		220	15	10	6
	10% LiOH/ 15% Cu/Al <sub>2</sub> O <sub>3</sub>	240	7	10	6
		240	15	13	7
		220	7	8	46
		220	15	15	24
		240	7	13	28
Butyronitrile	30% Cu/ZnO	240	15	20	23
		240	15	38	6
	10% LiOH/ 15% Cu/Al <sub>2</sub> O <sub>3</sub>	220	7	5	40
Benzonitrile	30% Cu/ZnO	240	15	38	6
	10% LiOH/ 15% Cu/Al <sub>2</sub> O <sub>3</sub>	220	7	7	40

compounds obtained. The physical constants and melting points of the hydrochlorides and picrates agree with those given in [2, 4, 5].

#### EXPERIMENTAL

Copper catalysts on supports of differing chemical nature, on oxides of a basic, acidic, and semiconducting type, and also copper catalysts on aluminum oxide promoted with an alkali to suppress the acidity of the support were used. The catalysts with 30% Cu/ZnO and 36% Cu/MgO were industrial samples, and those with 15% Cu/Al<sub>2</sub>O<sub>3</sub> and 10% LiOH/15% Cu/Al<sub>2</sub>O<sub>3</sub> were obtained by the impregnation method.

The reactions between acetylacetone and the nitriles were carried out in a flow-through apparatus in a hydrogen atmosphere. The acetylacetone-nitrile (1:2.1) mixture was passed through at a volume rate of 0.2 to 0.4 h<sup>-1</sup> at 220–240°C, and a hydrogen pressure of 7–15 atm. The catalyzate was treated differently depending on its composition. The catalyzate containing principally pyrrole derivatives was freed of water, dried with calcium chloride, and distilled at reduced pressure. The catalyzate which contained principally the pyrrolidine derivatives was saturated with alkali, separated from the water, dried with potassium hydroxide, and vacuum distilled. The mixtures of pyrroles with pyrrolidines were separated on a PAKhV-0.4 preparative chromatograph, 1.5 m × 2.6 mm column, packed with 15% Apiezon M on Chromosorb W with 10% alkali. The carrier gas was nitrogen.

The PMR spectra were run on a BS-487-C-80 spectrometer (80 MHz) as 10% solutions in CCl<sub>4</sub>, internal standard TMS. The IR spectra were run on a UR-20 spectrometer. The mass spectra were run on a Varian MAT-311 instrument; the energy of the ionizing electrons was 70 eV. The samples were evaporated at 150–200°C; the temperature of the ion source was 200°C.

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