An Improved Synthesis of 2-Methylpyrrole

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The elegant new synthesis of 2-formylpyrrole described by Silverstein, *et al.*[1] makes possible a convenient method for the ready preparation of pure 2-methylpyrrole. Early syntheses of 2-methylpyrrole[2-5] are cumbersome and indirect, and in some cases lead to mixtures of isomers which are not easily separated. More recently, the catalytic vapor phase conversion of alkylfurans to the corresponding pyrroles has proved fruitful, although highly specialized equipment is required, and even in the best process[6] conversion of only 28% of 2-methylfuran to 2-methylpyrrole is realized.

Our synthesis, which involves simply the pyrolysis of a mixture of 2-formylpyrrole semicarbazone with potassium hydroxide in a stream of dry nitrogen, is based on a somewhat analogous reaction of Shepard[7] in the thiophene series. It is simple and direct and leads to the production of pure 2-methylpyrrole in 67% yield starting with pyrrole.

EXPERIMENTAL

2-Formylpyrrole semicarbazone. A solution of 60.0 g. of 2-formylpyrrole, prepared by the method of Silverstein,[1] in 500 ml. of 50% aqueous ethanol was added to a 1-l., 3-necked, round-bottomed flask fitted with a mechanical stirrer, a dropping-funnel equipped with a nitrogen inlet, and a reflux condenser. A solution of 90 g. of sodium acetate in 200 ml. of water was added rapidly with stirring under a nitrogen atmosphere. Then a solution of 60.0 g. of semicarbazide hydrochloride in 200 ml. of water was added dropwise. The mixture was heated on a steam-bath with stirring for five minutes whereupon precipitation of the semicarbazone began. Filtration of the ice-chilled mixture afforded a quantitative yield (96.0 g.) of 2-formylpyrrole semicarbazone, m.p. 181–183° with decomposition.

2-Methylpyrrole. A finely ground, intimate mixture of 96.0 g. of 2-formylpyrrole semicarbazone and 100 g. of potassium hydroxide was placed in a 1-l. modified Claisen flask provided with a gas inlet tube for purified nitrogen, an efficient condenser, and an ice-cooled receiver. Then 20 ml. of water was added and the entire mass was stirred to effect thorough mixing. The flask then was heated cautiously with a free flame until no more liquid distilled. The distillate was transferred to a separatory-funnel, the oil layer was removed, the water layer was extracted with four 50-ml. portions of ether, and the combined extracts were dried over Drierite. After removal of the ether, the residue was distilled to give 38.2 g., 74.7%, of pure 2-methylpyrrole, b.p. 147–148° at 740 mm.

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[1] Silverstein, Ryskiewecz, and Chaiken, *J. Am. Chem. Soc.*, **76**, 4485 (1954).

[2] Pictet, *Ber.*, **37**, 2792 (1904).

[3] Harries, *Ber.*, **31**, 44 (1898).

[4] Benary, *Ber.*, **44**, 493 (1911).

[5] Andrews and McElvain, *J. Am. Chem. Soc.*, **51**, 888 (1929).

[6] Bordner, U. S. Patent 2,600,289 (1952).

[7] Shepard, *J. Am. Chem. Soc.*, **54**, 2951 (1932).

A New Primary Resin Acid from *Pinus Caribaea*

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It was observed in this laboratory that, in the course of precipitating the resin acids from the naturally occurring oleoresin by means of their cyclohexylamine salts,[1] higher yields of the amine salts were obtained from the oleoresin of longleaf than from the oleoresin of slash pine.

By evaporating the mother liquor from the amine salt precipitation to a small volume *in vacuo*, dissolving in ether, and extracting with 1% sodium hydroxide an acidic fraction was obtained which contained a residual amount of known resin acids which were removed by dissolving this acidic fraction in acetone and precipitating them as their insoluble butanolamine salts. The acidic material recovered from the mother liquor was further purified by dissolving in a large volume of pentane, shaking with fullers earth, filtering, and recovering. This fraction is amorphous and when obtained from fresh slash gum has a neutralization equivalent of 318 indicating the presence of one atom of oxygen. The carbon and hydrogen analysis also is correct for a molecular weight of 318, $C_{20}H_{30}O_3$. By observing the infrared spectra and running the usual chemical tests, we have not been able to confirm the presence of an oxygen atom, leading us to suspect it could be present as an ether linkage if present at all. The ultraviolet absorption curve showed a single maximum at 233 mμ. The specific absorption coefficient was 50.

Preliminary partition chromatography using an amine as the mobile phase indicated the fraction to be impure. This could be expected since it could neither be crystallized nor distilled. The principal fraction from the chromatographic column could not be crystallized.[2]

All the known resin acids from *P. palustris* and *P. caribaea* have identical infrared absorptions at 5.92 μ and 7.85 μ due to the carboxylic acid group.

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[1] G. E. Harris and T. F. Sanderson, *J. Am. Chem. Soc.*, **70**, 334 (1948).

[2] Further study of this material, including the use of partition chromatography, will emanate from the U. S. Department of Agriculture Laboratory at Olustee, Florida.