[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

THE THERMAL CONVERSION OF ETHYL (1-PYRRYL)-ACETATE TO PYRIDINE

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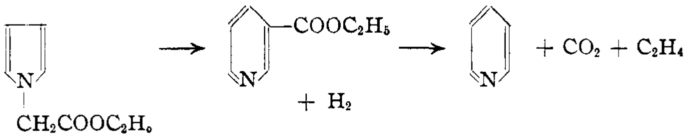
The conversion of 1-substituted pyrroles into 2-pyrrole derivatives is a well-known rearrangement brought about by heat. Ciamician[1] has rearranged the 1-acetyl, 1-alkyl and 1-phenylpyrroles into the 2-pyrrole derivatives by heating them in a sealed tube at 250–300°. Pictet[2] passed the vapors of 1-α-pyridylpyrrole through a tube heated to 700° and obtained the 2-pyrrole derivative. Wibaut[3] rearranged α,α-nicotyrine to 2-(α-pyridyl)-5-methylpyrrole. By passing the vapors of 1-methyl- and 1-benzylpyrrole[4] through a tube heated to dull redness, pyridine and 3-phenylpyridine were obtained in addition to the 2-pyrrole derivatives. No data are given as to the exact temperature, length of tube or rate of flow of vapors for the rearrangement of these simple pyrroles.

In the present investigation attempts were made to convert ethyl (1-pyrryl)-acetate to ethyl (2-pyrryl)-acetate which would be a useful intermediate in the synthesis of homohygric acid. Both of the above methods of rearrangement were tried but in no case was any ethyl (2-pyrryl)-acetate obtained. Instead, the compound underwent a pyrogenic decomposition to yield pyridine, carbon dioxide, ethylene and hydrogen.

Since 1-benzylpyrrole yielded 3-phenylpyridine[4] it seemed reasonable to suppose that the first step in the above decomposition consisted in the rearrangement of the 1-pyrrylacetic ester to pyridine-3-carboxylic ester. The latter then decomposed to yield pyridine, ethylene and carbon dioxide, as shown by the equations



However, no trace of ethyl nicotinate could be found in the reaction products, indicating that it was decomposed as rapidly as it was formed. In order to test the above theory, ethyl nicotinate was subjected to thermal decomposition under exactly the same conditions as used in the experi-

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[1] Ciamician and Magnaghi, *Ber.*, **18**, 1828 (1885); Ciamician and Silber, *ibid.*, **20**, 698 (1887); Ciamician and Zanetti, *ibid.*, **22**, 659, 2518 (1889); Wibaut, *Verslag. Akad. Wet. Amsterdam*, **35**, 552 (1927).

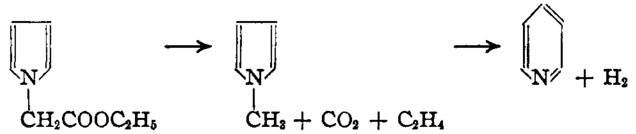
[2] Pictet and Crépieux, *Ber.*, **28**, 1904 (1895); *ibid.*, **31**, 2018 (1898); Pictet and Rotschy, *ibid.*, **37**, 1225 (1904).

[3] Wibaut, *Rec. trav. chim.*, **45**, 671 (1926).

[4] Pictet, *Ber.*, **38**, 1946 (1905); *ibid.*, **37**, 2797 (1904); Ciamician, *ibid.*, **37**, 4200 (1904).

ments on ethyl (1-pyrryl)-acetate. It was found that ethyl nicotinate was completely converted to pyridine, carbon dioxide and ethylene at 550–600°.

A second possible mechanism for the decomposition of ethyl (1-pyrryl)-acetate would involve a preliminary decomposition of the ester grouping to yield 1-methylpyrrole, carbon dioxide and ethylene. The 1-methylpyrrole could then rearrange to give pyridine as shown by the equations



However, if this represented the course of the reaction, some 2-methylpyrrole should have been found in the reaction products in addition to the pyridine. It has been shown[4] that under the above conditions only 10% of 1-methylpyrrole is converted to pyridine and the remainder to 2-methylpyrrole. None of the latter compound could be isolated in the present experiments. Hence the first mechanism appears more probable.

Experimental Part

Preparation of Ethyl (1-Pyrryl)-acetate.—A slight modification of the method described by Clemo and Ramage[5] was used. Potassium shavings (19.5 g.) were added to 33.5 g. of pyrrole dissolved in 100 cc. of dry toluene. The mixture was warmed gently until the reaction started and finally heated in an oil-bath to 110° for eighteen hours. Then 61.25 g. of chloroacetic ester was dropped slowly into the potassium pyrrole with vigorous stirring. The mixture was stirred for twelve hours and then 200 cc. of water added. The toluene layer was separated, washed with water, dried with anhydrous magnesium sulfate and fractionally distilled *in vacuo*. The ethyl (1-pyrryl)-acetate boiled at 90–96° (6 mm.); yield, 25.7 g. or 33.6%; d^{20}_{20} 1.066; n^{20}_{D} 1.4862. When ether was used as the medium for the reaction, the yield dropped to 17–20%. By the action of concentrated ammonia on the ester the amide was obtained as colorless crystals. After recrystallization from alcohol they melted at 168°, which checked the value given by Clemo and Ramage.[5] That this ester was actually the nitrogen substituted product was shown by the fact that the Schotten–Baumann reaction did not yield a benzoate, and alkali fusion did not give 2-pyrrole-carboxylic acid.

Attempts to Rearrange Ethyl (1-Pyrryl)-acetate

I. (1) A sealed tube containing 6.3 g. was heated at 300° for three hours in an electrically heated furnace. The tube was cooled, opened and the contents fractionally distilled. Ninety per cent. of the original material was recovered unchanged.

(2) A second sealed tube experiment was tried in which the temperature was 250° and the time twenty hours. Only 20% of the original weight was recovered by distillation. The remainder consisted of carbon and tarry materials which could not be distilled in a vacuum and which could not be identified.

II. The vapors of ethyl (1-pyrryl)-acetate were passed through glass tubes heated by means of an electric furnace. The experimental conditions which were varied were: (a) length of tube, (b) temperature, (c) rate of flow of vapor and (d) filling tube with porous clay plate. The results of a large number of experiments may be summarized

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[5] Clemo and Ramage, *J. Chem. Soc.*, 49 (1931).

as follows: (1) Short tubes (50 cm.) and empty tubes (50 cm. and 100 cm.) gave very slight decomposition at the lower temperatures, 350–400°. A slight charring took place but the condensate corresponded to 80–90% of the original weight of material. Fractional distillation of this condensate yielded only ethyl (1-pyrryl)-acetate. In order to be certain that this distillate was the original, it was converted to the amide by means of concentrated ammonia and the amide subjected to fractional crystallization. The amide melted at 168° and proved to be homogeneous. No trace of the amide of nicotinic acid (m. p. 125°) could be found.

(2) The use of temperatures ranging from 400 to 650° with short empty tubes gave a very small amount of low-boiling material on fractionation. This was identified as pyridine by odor and conversion to the picrate, m. p. 164–165°. The remainder of the material (50–80% of original weight) was unchanged ethyl (1-pyrryl)-acetate.

(3) The use of temperatures of 550–600° in 1-meter tubes filled with porous clay plate yielded from 20 to 50% pyridine and the remainder unchanged ester. When the vapors were passed through the heated tube rapidly (10 g. in ten minutes), only a very small amount of pyridine was obtained but when the vapors were swept through slowly (10 g. in three hours) by means of a stream of hydrogen or nitrogen, considerable decomposition occurred and the condensate yielded over 50% of pyridine. After the vapors issuing from the furnace tube had been run through a long condenser and receiver packed in ice, the non-condensable gases were examined. The gases contained carbon dioxide as shown by the precipitation of barium carbonate from barium hydroxide. The gases also decolorized bromine water, forming ethylene dibromide, and reduced permanganate, indicating the presence of unsaturated hydrocarbons, chiefly ethylene.

Decomposition of Ethyl Nicotinate.—The vapors of 17 g. of ethyl nicotinate were swept through a 1-meter tube by means of a stream of pure nitrogen. The tube was filled with porous clay plate and kept between 550–600°; time of decomposition, three hours. The liquid condensate obtained was composed entirely of pyridine, as shown by conversion to the picrate (m. p. 164–165°). The non-condensable gases were bubbled through barium hydroxide solution, which yielded barium carbonate. The gases were next passed through a tube containing bromine covered with water. A heavy oil separated which was purified and distilled. This oil was found to be ethylene dibromide by comparison of its boiling point, 129°, and refractive index, n^{25}_{D} 1.5390 obs. (n^{15}_{D} 1.5407, Dionneau).[6]

The vapors issuing from the hot tube gave no test for pyrrole when allowed to come in contact with a pine splinter moistened with hydrochloric acid.

Summary

Attempts to rearrange ethyl (1-pyrryl)-acetate by the action of heat gave only a pyrogenic conversion to pyridine, carbon dioxide, ethylene and hydrogen. This decomposition is analogous to the conversion of 1-benzylpyrrole to 3-phenylpyridine, since the probable intermediate, ethyl nicotinate, yields pyridine, carbon dioxide and ethylene under the same conditions.

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[6] Dionneau, *Ann. chim.*, [9] **3**, 255 (1915).