SELECTIVE HYDROGENATION OF THE VINYL GROUP OF 1-VINYLPYRROLES

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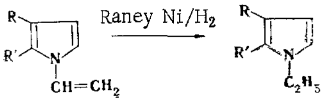
UDC 547.753:542.941.7

The hydrogenation of 1-vinylpyrroles over Raney nickel in ethanol at 50-90°C proceeds exclusively at the 1-vinyl group and leads to the formation of 1-ethylpyrroles in 80-90% yields. The IR and PMR spectra are presented.

The recently discovered base-catalyzed condensation of acetylene with ketoximes [1. 2] makes it possible to obtain ring-substituted 1-vinylpyrroles.

The results of selective hydrogenation of the vinyl group in 1-vinylpyrroles are presented in the present communication:



I–VI

Hydrogenation proceeds only at the vinyl group with retention of the pyrrole ring at atmospheric pressure (in a hydrogenation flask) and room temperature, as well as in an autoclave at 50-90°C and an initial hydrogen pressure of 40-60 atm (over Raney nickel, whereas the benzene ring is also hydrogenated in the case of 1-vinyl-2-phenylpyrrole. The second variant of hydrogenation under pressure shortens the time of the process by a factor of ~10. Thus the reaction can be successfully used for the preparation of 1-ethylpyrroles along with the previously proposed methods [3, 4].

The IR spectrum of 1-ethyl-2-phenylpyrrole does not contain the absorption band at 1642 cm^{-1} and other bands of the vinyl group. Two intense peaks at 1500 and 1600 cm^{-1}, which characterize the pyrrole ring [5], are retained. The PMR spectrum of 1-ethyl-2-phenylpyrrole contains a quartet (3.78 ppm) and triplet (1.16 ppm) of an ethyl group and signals at 6.05 (3-H and 4-H) and 6.52 ppm (5-H). Signals of protons of an N-vinyl group [6] are absent.

EXPERIMENTAL

The IR spectra of films of the compounds were obtained with a UR-20 spectrometer. The PMR spectra of CCl_4 solutions of the compounds were obtained with a BS-4878 spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. Chromatographic analysis was accomplished with a Khrom-4 chromatograph with a catharometer as the detector (the column was 2.5-m long and had a diameter of 3 mm, the solid phase was Chromatom N-AW-DMCS, the liquid phase was 15% DS550 silicone, the thermostat temperature was 170°, and the carrier gas was helium).

1-Ethyl-2-phenylpyrrole (I). A) A hydrogenation flask was charged with 1.35 g (0.007 mole) of 1-vinyl-2-phenylpyrrole, 15 ml of ethanol, and 0.5 g of Raney nickel, and the reaction was carried out at 20° with constant stirring of the mixture (~70 h) until the theoretical amount of hydrogen had been absorbed. At the end of the process, the catalyst was removed by filtration, and the ethanol was removed from the filtrate by distillation on a water bath. The residue was vacuum fractionated to give 1.43 g (93%) of pyrrole I (Table 1).

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsilicheskikh Soedinenii, No. 2, pp. 215-216, February, 1077. Original article submitted January 20, 1076; revision submitted June 25, 1976.

TABLE 1. Physicochemical Constants and Yields of 1-Ethylpyrroles

Compound	R	R′	bp, °C (mm)	n_D^{20}	d_4^{20}	Yield, %
I	H	C_6H_5	114 (4—5)	1,5795	1,0175	93
II	CH_3	C_6H_5	94 (1)	1,5730	1,0169	85
III	C_2H_5	C_6H_5	135—136 (2)	1,5595	0,9931	81
IV	n-C_3H_7	C_6H_5	126 (1)	1,5535	0,9846	80
V	i-C_3H_7	C_6H_5	136—137 (4)	1,5480	0,9760	85
VI	$(-CH_2-)_4$		66—67 (1)	1,5200	0,9783	90

B) A reaction mixture consisting of 6 g (0.035 mole) of 1-vinyl-1-phenylpyrrole, 1 g of Raney nickel, and 50 ml of ethanol was heated in a 1-liter steel rotating autoclave at 50° for 6 h (the initial hydrogen pressure was 60 atm). Standard workup yielded 5.1 g (82.5%) of pyrrole I. Pyrroles II-V were similarly synthesized (Table 1).

1-Ethyl-4,5,6,7-tetrahydroindole (VI). A reaction mixture consisting of 5.3 g (0.04 mole) of 1-vinyl-4,5,6,7-tetrahydroindole, 1 g of Raney nickel, and 50 ml of ethanol was heated in a hydrogen atmosphere in a steel rotating autoclave at 80-90° for 8 h. Standard workup yielded 5.5 g (90%) of pyrrole VI (Table 1).

According to the GLC data, products I and VI were 99.9% and 99.5% pure, respectively.

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