PYRROLES FROM KETOXIMES AND ACETYLENE.

45.* A NEW ROUTE TO 2,2-DIPYRROLES

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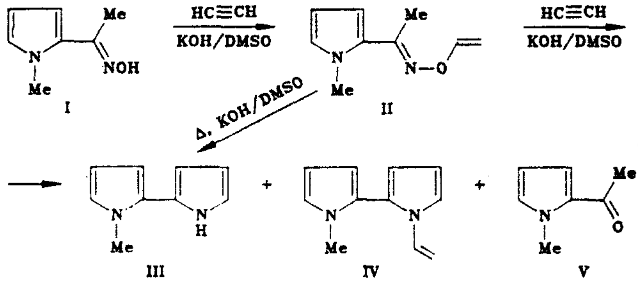
UDC 547.741'314.2:541.128

The reaction of 1-methyl-2-acetylpyrrole oxime with acetylene at atmospheric and increased pressure can be catalyzed by KOH—DMSO superbase to give 1-methyl-2-(2-pyrrolyl)pyrrole, N-vinyl-2-[1-methyl(2-pyrrolyl)]pyrrole, and the reaction intermediate methyl-2-(1-methylpyrrolyl)-O-vinyloxime.

Compounds with two or more pyrrole rings in a molecule attract the attention of investigators as precursors of the biologically important porphyrins, corrins, and prodigiosins [2-5]. The latter are the basis for synthesizing compounds which transfer oxygen in living organisms [6]. Among the dipyrroles the most important are the 2,2-dipyrroles since they can be used to prepare polypyrroles which have valuable practical properties [7-9]. Of more than twenty methods of synthesizing 2,2-dipyrroles known at this time, several [10-13] are high-yielding. However, N-vinyl 2,2-dipyrroles are currently unknown although they show considerable interest as valuable monomers and units for inserting the dipyrrole system into other molecules.

With the aim of developing synthetic methods for the inaccessible 1-methyl-2-(2-pyrrolyl)pyrrole (III), prepared by dehydrogenation of 1-methyl-2-(4,5-dihydropyrrol-2-yl)pyrrole in the presence of palladium catalyst [14], as well as the previously unrecorded N-vinyl-2-[1-methyl(2-pyrrolyl)]pyrrole (IV) we have now investigated the behavior of a pyrrole oxime (the oxime of 1-methyl-2-acetylpyrrole) in the Trofimov reaction. How the composition and yield of the final products depends on the reaction conditions can be seen from the data in Table 1.



Hence, oxime I can be condensed with acetylene under pressure at 70°C (experiment 1) to form the pyrrole III (35% yield), its N-vinyl derivative IV (7%), regenerated ketone (1-methyl-2-acetylpyrrole, V, 32%), and polymeric products. Under the same conditions, but with the temperature raised by 20°C (experiment 2), the pyrrole III is almost

TABLE 1. Effect of Reaction Conditions of Oxime I and Acetylene on the Composition and Yields of Final Products

Experiment	Reaction Conditions				Yield, %		
	oxime: KOH, mole.	T, °C	t, h	$P_{C_2H_2}$, at	O-vinyl-oxime II	pyrrole III	N-vinyl-pyrrole IV
1	1:1	70	3	10	Traces	35	7
2	1:1	90	3	10	Traces	2	35
3	1:1	90	3	12	3	Traces	40
4	1:2,5	80	7	—	41	11	—
5	1:1	96	6	—	Traces	31	12

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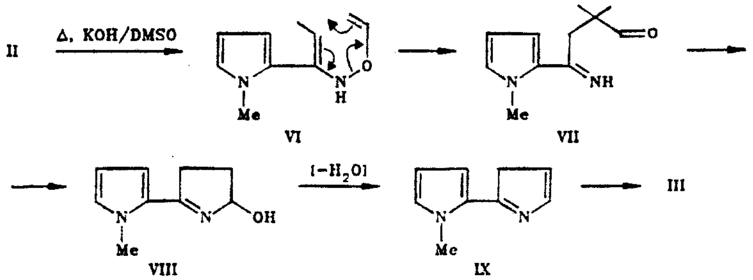
*See [1] for Communication 44.

Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 460-463, April, 1991. Original article submitted September 8, 1989.

fully vinylated by excess acetylene to the N-vinylpyrrole IV but much tar formation is observed due to polymerization of the intermediate and final materials [15]. The degree of reproducibility of the results can be judged by the data in experiments 2 and 3 under the same conditions. Although the yield of N-vinylpyrrole IV varies from 35-40% in the reaction mixture (GLC data), the pyrrole III content is 0-2% and its precursor the O-vinyloxime II 0-3%. Vacuum fractionation of this mixture caused the O-vinyloxime II to convert almost totally to the pyrrole III (GLC). This points to the rate of heterocyclization under these conditions being somewhat lower than the rate of vinylation of the latter. At atmospheric pressure the rate of vinylation is slowed both for the oxime I (and, therefore, the rate of formation of pyrrole III) and also of pyrrole III to N-vinylpyrrole IV. Compounds III and IV were obtained in 31 and 12% yields, respectively (experiment 5). The reaction can be stopped at the stage of formation of intermediate II if it is carried out at atmospheric pressure, a temperature of 80°C, and with an increased amount of potassium hydroxide in the reaction mixture (experiment 4). In this case the yield of pyrrole III is only about 11% and the N-vinylpyrrole IV is practically absent. As in other experiments, this is accompanied by tarring and by partial deoximation. Isolation of the O-vinyloxime II and its transition to pyrrole III upon heating is in agreement with a process of pyrrolization via a [3,3]-sigmatropic shift in the O,N-divinylhydroxylamine (VI) [16-19].



IR and PMR spectral data confirmed the structures of II-IV. The intermediates VI-IX could not be isolated because of their high reactivity at the temperature of the reaction in the presence of the superbase system KOH—DMSO.

We have therefore shown for the first time that condensation of the oxime of 1-methyl-2-acetylpyrrole with acetylene under Trofimov conditions can be used to synthesize 2,2-dipyrroles and their N-vinyl derivatives. We have also shown the possibility of direct vinylation of pyrrole oximes with acetylene at atmospheric pressure and mild temperatures.

EXPERIMENTAL

Analysis of the reaction mixtures and synthesized compounds was carried out by TLC (Silufol UV-254 plates, hexane—ether eluent, 2-5:1) and GLC [Tsvet-100 chromatograph, DIP, 0.8 m × 4 mm column, stationary phase Chromaton N-AW, liquid phase 5% XE-60 silicone, helium carrier, flow 36 ml/min, thermostat temperature 90-150°C (5°/min), injector 125°C].

The reactions used potassium hydroxide (pure for analysis grade) with a water content of about 15% and DMSO (chemically pure grade) with water content of about 0.4%. Conversion to the anhydrous materials was not carried out.

^1H NMR spectra were obtained on a Tesla BS-487A spectrometer (100 Mhz) and IR spectra on a Specord 75 IR instrument as thin films.

Methyl-2-(1-methyl)-pyrrolyl-O-vinyloxime (II, $C_9H_{12}N_2O$), 1-Methyl-2-(2-pyrrolyl)pyrrole (III, $C_9H_{10}N$). A mixture of oxime I (6.1 g, 40 mmole), KOH (2.8 g, 50 mmole), and DMSO (90 ml) was heated to 80°C and acetylene passed through for 5 h with intensive stirring. A further 2.8 g (50 mmole) of KOH was added without stopping the flow of acetylene or the stirring. After heating for a further 2 h at the same temperature, the product was cooled to room temperature, poured into cold water, extracted with ether, and the ether extracts washed with water and dried over potash. The ether was removed to give a residue (6 g) which was chromatographed on an alumina column (hexane-ether, 2:1) to give the O-vinyloxime II (3 g, 41%) as a yellow liquid (purity 99%) with d_4^{20} 0.9800 and n_D^{20} 1.5724. PMR spectrum ($CDCl_3$): 2.27 (3H, s, $-\underset{\|}{C}-CH_3$); 3.90 (3H, s, $N-CH_3$); 4.17 (1H, q, β-H_{cis}); 4.65 (1H, q, β-H_{trans}); 6.96 (1H, q, α-H); 6.13 (1H, q, 3-H); 6.52 (1H, q, 4-H); 6.70 ppm (1H, q, 5-H). IR spectrum: 1610 (C=C in $OCH=CH_2$); 3060 ($as=CH_2$); 3100 (C—H pyrrole); 930, 965 (N—O); 1240 (as=C—O); 1080 (s=C—O); 1515, 1580 (C=C pyrrole); 2840, 2930, 2970 cm^{-1} ($H-C_{sp}3$). Also crystallizing from the liquid was the pyrrole III (0.7 g, ≃11%) with mp 20-22°C. PMR spectrum ($CDCl_3$): 3.62 (3H, s, $N-CH_3$); 6.60 (1H, t, 5-H); 6.12 (2H, d, 3-H, 4-H); 8.23 (1H, br, NH); 6.72 (1H, q, 5'-H); 6.20 ppm (2H, m, 3'-H, 4'-H). IR spectrum: 3330 (NH), 3100 (C—H pyrrole); 735 (C—H pyrrole); 2910, 2945 cm^{-1} ($H-C_{sp}3$).

Thermolysis of Methyl-2-(1-methyl)-pyrrolyl-O-vinyloxime (III). A mixture of the O-vinyloxime (0.6 g, 3.3 mmole), KOH (0.19 g, 3.33 mmole) and DMSO (10 ml) were heated for 1.5 h at 100°C. Treatment as above gave an oily residue which was analyzed by TLC and GLC together with a known sample of the pyrrole III.

N-Vinyl-2-[2-(1-methyl)pyrrolyl]pyrrole (IV, $C_{11}H_{12}N_2$). A rotating steel autoclave of capacity 1 liter was charged with oxime I (5 g, 36 mmole), KOH (2.02 g, 36 mmole), and DMSO (72 ml), saturated with acetylene (initial pressure 12 atm), and heated at 90°C for 3 h. After treatment as above the residue in a small amount of ether was poured into a 100-fold excess (by volume) of hexane. The organic layer was carefully decanted from the oil, concentrated to minimum volume, and distilled in vacuo collecting the fraction with bp 40-62°C (5 mm Hg pressure). Chromatography on an alumina column (hexane-ether, 5:1) gave the vinylpyrrole IV (2.5 g, 40%) with purity 99%, d_4^{20} 1.0513 and n_D^{20} 1.5934. PMR spectrum ($CDCl_3$): 6.16 (2H, d, 3-H, 4-H); 6.69 (1H, t, 5-H), 6.27 (2H, m, 3'-H, 4'-H); 7.10 (1H, q, 5'-H); 5.02 (1H, q, β-H_{trans}); 4.56 (1H, q, β-H_{cis}); 6.67 ppm (1H, α-H). IR spectrum: 1625 (C=C in $NCH{=}CH_2$); 3090 (as$=CH_2$); 2990 (s$=CH_2$); 1500, 1590 (C—H pyrrole); 700, 705 (δC—H pyrrole); 2850, 2900, 2920 cm^{-1} (H—C_{sp^3}). Also separated were the O-vinyloxime II (0.14 g, ≈3%) and an unstable pyrrole (0.01 g) of unknown structure.

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