^{1}H AND ^{13}C NMR SPECTRA OF N-VINYLPYRROLES

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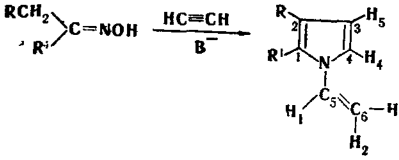
UDC 547.751:541.67

The position of the substituents in 2,3-dialkyl-1-vinylpyrroles and 7-methyl-1 vinyl-4,5,6,7-tetrahydroindole was established on the basis of the ^{1}H and ^{13}C NMR spectra. It was found that the S-trans conformation of the N-vinyl group is preferred. It is shown that the condensation of ketoximes with acetylene proceeds through the formation of free pyrroles and that vinyl oximes are not intermediates in the condensation.

We have recently obtained a number of N-vinylpyrroles by reaction of aliphatic ketoximes with acetylene under base-catalysis conditions:



I-VI

I R=H, R^1=C_2H_5; II R=R^1=CH_3; III R=CH_3, R^1=C_2H_5; IV R=C_3H_7, R^1=C_4H_9;
V R—R^1=$(CH_2)_4$; VI R—R^1=$(CH_2)_3CH(CH_3)$

In the present paper the ^{1}H and ^{13}C NMR spectra of N-vinylpyrroles I-IV and N-vinyltetrahydroindoles V and VI, which were synthesized via the scheme presented above, are analyzed. The yields and fundamental physicochemical constants of the investigated heterocycles are given in Table 1, and the parameters of the NMR spectra are given in Tables 2 and 3.

The chemical shifts (CS) and spin-spin coupling constants (SSCC) of the protons are in good agreement with the corresponding values for vinylamines and pyrroles (for example, see [2, 3]).

The assignment of the ^{13}C signals of the alkyl substituents attached to C_1 and C_2 of the pyrrole ring independently confirms the calculation of their chemical shifts on the basis of the method of additive increments proposed for aliphatic hydrocarbons by Clerc and co-workers [3]. Thus the ^{13}C chemical shifts calculated by this method for R and R^1 in IV are, respectively, (ppm): 33.4 (1),* 22.8 (2), 14.2 (3), and 24.0 (1), 29.8 (2), 22.8 (3), and 14.1 (4). These values are in excellent agreement with the experimentally found values (Table 3). In VI the location of the CH_3 substituent attached to the carbon atom closest to the nitrogen atom is confirmed by the direction and magnitude of the changes in the $^{13}C_1$ and $^{13}C_2$ chemical shifts in the spectrum of VI as compared with that of V (β- and γ-substituent effects [4]) and is in agreement with the calculation of the ^{13}C chemical shift of the saturated portion of the molecule by the above-indicated method [3].

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*Here and in Tables 2 and 3, the orders of the numbers of the hydrocarbon atoms of the groups commencing from the heteroring are given in parentheses.

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 360-363, March, 1975. Original article submitted February 20, 1974.

TABLE 1. Physicochemical Constants of N-Vinylpyrroles*

No.	Compound	bp, °C (mm)	n_D^{20}	d_4^{20}	Empirical formula	Found, %			Calc., %			Yield,† %
						C	H	N	C	H	N	
III	3-Methyl-2-ethyl-1-vinylpyrrole	59—60 (6)	1,5175	0,9158	$C_9H_{13}N$	—	—	10,2	—	—	10,4	47
IV	3-Propyl-2-butyl-1-vinylpyrrole	86—87 (2)	1,5025	0,8925	$C_{13}H_{21}N$	81,6	10,9	7,2	81,6	11,1	7,3	85
V	1-Vinyl-4,5,6,7-tetrahydroindole	91—92 (4)	1,5560	1,0010	$C_{10}H_{13}N$	81,5	9,0	9,3	81,6	8,9	9,5	66
VI	7-Methyl-1-vinyl-4,5,6,7-tetrahydroindole	68—69 (2)	1,5465	0,9801	$C_{11}H_{15}N$	81,8	9,2	—	82,0	9,4	—	53

*Compounds I and II were obtained as mixtures (≈1:1) with the corresponding pyrroles (see the text) in 38% yield with bp 70-71° (20 mm), n_D^{20} 1.5270 and d_4^{20} 0.9297.

†Not under optimum condtions.

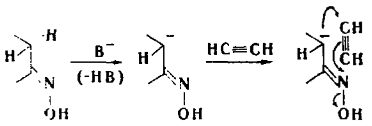
It follows from the PMR spectra that a mixture of I and II in almost equal amounts is formed in the case of methyl ethyl ketoxime. In addition, the corresponding 2,3-dimethyl- and 2-ethylpyrroles are apparently present in the mixture, inasmuch as the spectrum contains additional signals of CH_3 groups (1.92 ppm), two broad lines of NH protons (≈7.00 and 7.20 ppm), and overlapped multiplets of CH protons (5.80-6.30 ppm).

Insofar as the conformational isomers relative to the C_5-N bond are concerned, the S-cis conformer* is apparently sufficiently populated, inasmuch as the $^{13}C_6$ chemical shift decreases by 0.8 ppm in the series of compounds III-VI as the $^{13}C_5$ chemical shift increases by only 0.2 ppm. This decrease in the $^{13}C_6$ chemical shift scarcely reflects the different electronic effect of alkyl substituents but is more likely due to the development of steric compression between C_6 and the closest carbon atom of the radical, an increase in which, as is well known [5], leads to a shift in the signals of the interacting carbon atoms in the ^{13}C NMR spectrum to the region of stronger shielding. The preferableness of the S-trans conformation is evident from a comparison of the $^1H_1$ chemical shifts in II and V (6.55 ppm), III and VI (6.66 ppm), and IV (6.75 ppm), inasmuch as the decrease in the shielding of H_1 due to dispersion interaction [6] with the substituent attached to C_1 is possible only in the S-trans conformation of the molecules under consideration. The $^1H_1$ chemical shifts for I-VI are an additional confirmation of the correctness of the above conclusion regarding the position of the substituents in the pyrrole ring.

Thus the ^1H and ^{13}C NMR spectra make it possible in this case not only to unambiguously prove the formation of substituted N-vinylpyrroles as a result of the reaction of ketoximes with acetylene but also to establish the position of substituents R and R^1 (if they are different) and also make it possible to expose the preferred conformations of the N-vinyl fragment.

It is significant that vinyl oximes are not detected in the reaction mixture.

Shortening of the reaction time and reduction of the reaction temperature only decrease the conversion of the ketoxime up to the point of its complete recovery but do not lead to the development of oxygen-containing products (although the reaction may be stopped at the step involving the formation of the N-unsubstituted pyrrole). It was established by special experiments that the ketoximes do not add to acetylene under the conditions of the formation of an O-vinyl oxime from acetophenone oxime and dimethyl acetylenedicarboxylate [7]. Thus there is no basis for the assumption that O-vinyl oximes are intermediates in the condensation under consideration. At this stage of the investigations all of the available data are in good agreement with the following scheme for the condensation:



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*The conformer with the shortest distance between the C_6 atoms and the closest carbon atom of the radical was thus arbitrarily called the S-cis conformer.

TABLE 2. Chemical Shifts of the Protons (δ, ppm, ±0.01) of N-Vinylpyrroles I-VI*

Compound	H_1	H_2	H_3	H_4	H_5	R(R–R')	R'
I	6,61	4,40	4,84	6,77	5,89	5,80	2,36 (1), 1,06 (2)
II	6,56	4,35	4,79	6,71	5,92	1,89	1,95
III	6.66	4,35	4,81	6.69	5.91	1,95	2,42 (1), 0.96 (2)
IV	6,75	4,40	4,85	6,75	5,96	2,37 (1) 1,58 (2) 0,94 (3)	2,50 (1), ≈1,40 (2,3) 0,94 (4)
V	6,55	4,33	4,78	6,66	5,88	2,26 (1) ≈1,60 (2,3) 2,38 (4)	
VI	6.66	4,36	4,81	6,70	5.89	2,44 (1) 2,72 (4)	≈1,65 (2,3) 1,07 (CH_3)

*The spin-spin coupling constants in the investigated series of compounds change only slightly and are as follows (Hz, ±0.1): $^3J_{12}$ 8.8, $^3J_{13}$ 15.5, $^2J_{23}$ 0.8, $^3J_{45}$ 3.1, $^4J_{4R'}$ 1.7, and $^3J_{5R}$ 3.9.

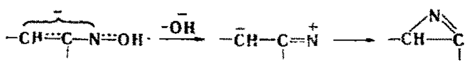
TABLE 3. Chemical Shifts in the ^{13}C NMR Spectra (δ, ppm, ±0.01) of N-Vinylpyrroles III-VI*

Compound	C_1	C_2	C_3	C_4	C_5	C_6	$C_{R(R-R')}$	$C_{R'}$
III	130.73	115,26	111,72	114.45	130,22	95,50	14,89	17,12 (1) 11,44 (2)
IV	128.50	121,34	110,37	114,69	130,86	95,39	33,25 (1) 22.65 (2) 14.16 (3)	24,60 (1) 28,52 (2) 23,75 (3) 14,03 (4)
V	127,21	118,86	109,65	114,46	130,41	94,75	23,42 23,79 23,49 21,92†	
VI	131,60	117,96	109,33	114,94	130,40	94.71	23,48 21,20 25,90 31.31† 19,31 (CH_3)	

*The ^{13}C chemical shifts of I and II, which were analyzed in a mixture with 2,3-dimethyl- and 2-ethylpyrroles, are not presented, inasmuch as the sensitivity of the apparatus used was inadequate for their determination.

†The chemical shift of the carbon atom is close to that of the nitrogen atom.

1,3-Dehydration of the ketoxime,* which commences with detachment of a "allylic" proton by the base, evidently precedes the key step. It might be expected that the intermediate carbanion would split out an OH group to give a peculiar 1,3-dipole capable of stabilization by closing to the corresponding azirine (similar to the first step in the Neber rearrangement [8]):



The possibility of the formation of azirines from ketoximes by the action of bases was proved in [9]. The splitting out of the OH group most likely occurs simultaneously with the addition of an anion to the acetylene.

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*Aldoximes, for which 1,2-dehydration is possible, do not form pyrroles under similar conditions but are converted to nitriles. For example, acetonitrile was obtained in 65% yield from acetaldehyde oxime.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded with a Varian XL-100/12 spectrometer without an accumulator and a Fourier transformer. The spectra of pure liquids were recorded at 25° with tetramethylsilane as the internal standard. The ^{13}C NMR spectra were recorded under both conditions of complete noise decoupling with the protons and by the "off-resonance" method (see [7]), which makes it possible to determine the number of protons directly bonded to the ^{13}C nucleus of interest from the character of the multiplicity of the signals. Double heteronuclear resonance made it possible not only to unambiguously assign the ^{13}C signals and the signals of the ^1H atoms directly bonded to them but also to find the chemical shifts of the signals of the protons that form strongly overlapped multiplets in the PMR spectrum from the optimum decoupling conditions.

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