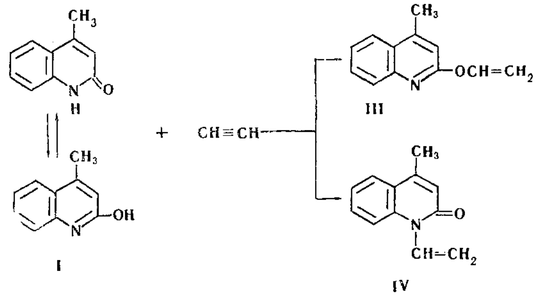
SYNTHESIS AND PMR SPECTRA OF VINYL DERIVATIVES OF 2-HYDROXYLEPIDINE

G. G. Skvortsova, S. M. Tyrina,
and V. K. Voronov

UDC 547.831.7.07:541.67

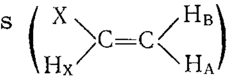
The reaction of 2-hydroxylepidine with acetylene under pressure in various catalytic systems was investigated. 2-(Vinyloxy)lepidine and N-vinyl-2-lepidone were obtained, and their IR and PMR spectra were studied.

The synthesis of α,β-unsaturated derivatives of 2-hydroxylepidine (I) has not yet been reported. In analogy with the vinylation of 2-hydroxypyridine (II) [1,2] it might be expected that the reaction of I with acetylene under pressure would also lead to the formation of O- and N-vinyl derivatives.



In fact, depending on the nature of the catalyst, the reaction of acetylene with I is directed primarily to the oxygen or nitrogen atom. In contrast to the products of the vinylation of II, in this case, one or the other form of vinyl derivative always predominates: III is formed in 78% yield under the influence of cadmium acetate at 210-220°C; IV is obtained in 30% yield in the presence of potassium hydroxide. The presence of 2-(vinyloxy)lepidine (III) and N-vinyllepidone (IV) together is detected by means of thin-layer chromatography. More severe temperature conditions are required for the vinylation of I than for the vinylation of II.

Bands characteristic for the vibrations of the vinyl double bond (960, 1640, 3100 cm^{-1}) are present in the IR spectra of III and IV. Compound IV has a broad band at 1640-1680 cm^{-1} due to the superimposition of the vibrations of the vinyl and carbonyl groups.

The signals of the olefinic protons  $\left(\begin{smallmatrix}X & & H_B\\ & C{=}C & \\ H_X & & H_A\end{smallmatrix}\right)$ in the PMR spectrum of III (Fig. 1) have the following chemical shifts (δ) and spin–spin interaction constants (J): δ_A 4.42, δ_B 4.83, δ_X 7.83 ppm; J_{AX} 6.0, J_{BX} 14.0, J_{AB} 1.5 Hz. The $H_{(3)}$ protons and the methyl groups give singlets at 6.37 and 2.24 ppm, respectively. The remaining signals belong to the protons of the benzene ring: $H_{(6)}$, triplet, and $H_{(8)}$, doublet (δ_6 7.02, δ_8 7.61 ppm; $J_{56} = J_{67} = 8.0$, J_{78} 7.0, J_{86} 1.5 Hz). The unsymmetrical triplet at 7.19-7.45 ppm is due to the superimposition of the $H_{(5)}$ (doublet) and $H_{(7)}$ (triplet) signals.

Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 798-800, June, 1971. Original article submitted November 4, 1970.

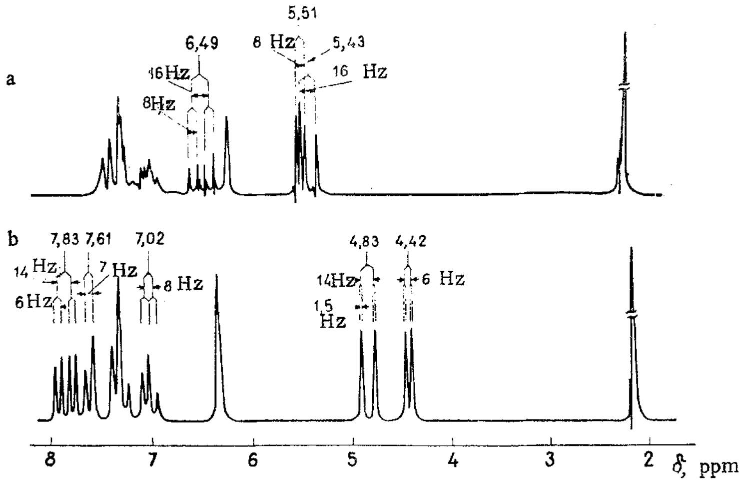


Fig. 1. PMR spectra in CCl_4: a) N-vinyl-2-lepidone; b) 2-(vinyloxy)lepidine.

The spectrum of IV (Fig. 1), in which the strong-field singlet belongs to the methyl protons (2.31 ppm) while the weak field singlet belongs to the $H_{(3)}$ proton (6.24 ppm), was similarly interpreted. The H_A and H signals are doublets, while the H_X signal is a quartet (δ_A 5.51, δ_B 5.43, δ_X 6.49 ppm; J_{AX} 8.0, J_{BX} 16.0 Hz). The signals at 6.88-7.55 ppm belong to the protons of the benzene ring.

The difference in the spectra of III and IV is interesting. Thus the spin-spin relationship of the H_A and H_B protons is not displayed in the spectrum of IV (if it is there, then $J_{AB} < 1$ Hz). In addition, $\delta_A^{IV} > \delta_B^{IV}$, although $\delta_A^{III} < \delta_B^{III}$, i.e., the cis-β-olefin proton (with respect to the heteroatomic proton) in the spectrum of IV resonates at stronger field than the trans-β-proton. This phenomenon may be due to the mutual orientation of the anisotropic C=C and C=O groups and the quinoline ring. Owing to the available conjugation, it is more likely that they are situated in the same plane, but one cannot exclude the possibility that the C=C bond may be deflected from the plane of the ring because of steric hindrance.

EXPERIMENTAL

2-(Vinyloxy)lepidine (III). A 0.5 liter rotary autoclave was charged with 10 g (0.06 mole) of I, 5 g (0.02 mole) of $Cd(CH_3COO)_2 \cdot 2H_2O$, and 80 ml of dioxane, and the mixture was heated at 210-220° for 1 h. The dark-brown liquid was filtered away from the precipitate, the dioxane was removed from the filtrate by distillation, and the residue was vacuum distilled to give 9.1 g (78%) of III. After repeated vacuum distillation, III had the following constants: bp 104-105° (2 mm), d_4^{20} 1.0985, and n_D^{20} 1.6070. Found %: C 77.9; H 6.0; N 7.4; MR_D 58.22. $C_{12}H_{11}NO$. Calculated %: C 77.8; H 6.0; N 7.6; MR_D 57.86.

N-Vinyl-2-lepidone (IV). The reaction of 10 g (0.06 mole) of I, 1.76 g (0.03 mole) of KOH, 6 ml of water, and 80 ml of dioxane under similar conditions gave 4 g (34%) of IV with mp 65°. Found %: C 77.7; H 6.1; N 7.6. $C_{12}H_{11}NO$. Calculated %: C 77.8; H 6.0; N 7.6.

The PMR spectra were recorded at room temperature with a JNM-4H-100 spectrometer. The solvent was CCl_4, and the internal standard was hexamethyldisiloxane (δ scale).

LITERATURE CITED

1. M. F. Shostakovskii, G. G. Skvortsova, S. M. Tyrina, Yu. L. Frolov, N. M. Deriglazov, V. K Voronov, and N. A. Ivanova, Dokl. Akad. Nauk SSSR, 186, 620 (1969).
2. G. G. Skvortsova and S. M. Tyrina, Khim. Geterotsikl. Soedin., 1132 (1968).