UTILIZATION OF PARAMAGNETIC ADDITIVES IN STRUCTURAL INVESTIGATIONS OF VINYL ETHERS OF PYRIDYLCARBINOLS

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The PMR spectra of vinyl ethers of pyridylcarbinols are discussed. The unusual paramagnetic shifts in the spectra of these ethers induced by tris(dipivaloylmethanato)europium are analyzed.

In the present paper we report the results of a study of the structure of vinyl ethers of 2-, 3-, and 4-pyridylcarbinols (I-III). Our analysis of the PMR spectra, the parameters of which are given in Table 1, showed that, despite the qualitative agreement, they do have certain distinctive peculiarities.

1. The resonance line of the protons of the CH_2 group in the spectrum of ether I is shifted to weak field by 0.14 ppm with respect to its position in the spectrum of ether II. This shift may be the result of a different contribution to the effect of the magnetic anisotropy of the nitrogen atom [1]. However, first, this shift is less than one should have expected, and, second, the shifts of the signals of the protons of this group in the spectra of II and III are actually identical. The difference in the position of the signal of the protons of the CH_2 group of ethers I, II and III is apparently due not only to the effect of the magnetic anisotropy of the nitrogen atom.

2. On passing from ether I to ether III the resonance lines of the H_A and H_B protons change their positions somewhat in the PMR spectra, and the signal of the H_A proton is shifted to a greater degree than the signal of the H_B proton. It is assumed [2] that the position of the signals of β-olefinic protons in the spectra of vinyl ethers is determined specifically by conjugation of the oxygen atom with the double bond and is characterized by the internal chemical shift $\delta'' = \delta_B - \delta_A$. The decrease in δ'' observed in our case on passing from I to III may therefore be a consequence of redistribution of the electron density in the molecules. This is also indicated by the difference in the J values of the protons of the pyridine ring (Table 1). In contrast to ethers II and III, the carbon atom of the CH_2 group in ether I is similar to the meta carbon atom of the pyridine ring with respect to its position in the spectrum. This, together with the closeness of the heteroatoms in the vinyl ether of 2-pyridylcarbinol, is apparently reflected in the electronic structure of the molecules, including the character of the conjugation of the oxygen atom with the double bond. The latter depends on the orientation of the unshared pair of the oxygen atom and the π system of the vinyl group [3, 4].

In order to study the structures of the vinyl derivatives of pyridylcarbinols we used the method of paramagnetic additives, which is based on the peculiarities of the NMR spectra of paramagnetic systems. We used tris(dipivaloylmethanato)europium [$Eu(DPM)_3$] as the additive [5, 6]. It is assumed [6] that the ether oxygen atom coordinates substantially more weakly with $Eu(DPM)_3$ than the pyridine nitrogen atom. We therefore assumed that ethers I-III should coordinate through the nitrogen atom. The PMR spectra of vinyl ethers of 2-, 3-, and 4-pyridylcarbinols with and without the $Eu(DPM)_3$ additive are presented in Fig. 1.

The transformation of the spectra of the vinyl ethers because of the appearance of a hyperfine interaction seems unexpected to us. In fact, the greatest shift in the spectrum of I recorded with the $Eu(DPM)_3$ additive (spectrum b) is observed for the signals of the CH_2 group and the α-olefinic proton. The δ'_B and

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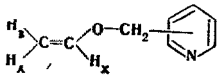
TABLE 1. Parameters of the PMR Spectra of Vinyl Ethers



Compound	Chemical shifts, δ, ppm									Spin–spin coupling constants, J, Hz
	δ_A	δ_B	δ_X	δ_2	δ_3	δ_4	δ_5	δ_6	δ CH₂	
I	3,96	4,21	6,45		7,30	7,55	7,03	8,40	4,80	$J_{56}=5{,}0$; $J_{43}=7{,}6$; $J_{54}=7{,}3$; $J_{46}=1{,}8$
II	3,98	4,16	6,43	8,41		7,51	7,11	8,38	4,66	$J_{42}=J_{46}=1{,}3$; $J_{45}=7{,}8$; $J_{56}==4{,}8$; $J_{52}=0{,}5$
III	4,01	4,14	6,44	8,44	7,10		7,10	8,44	4,68	

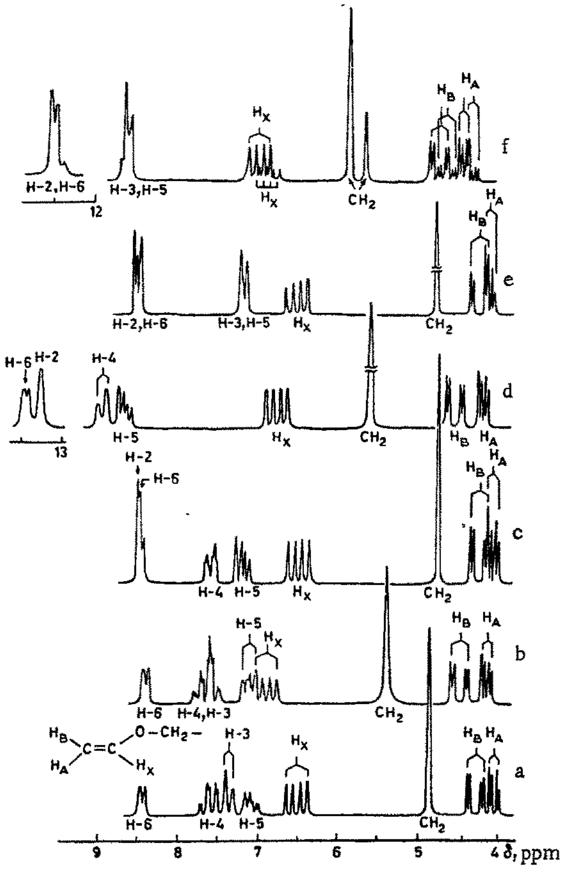


Fig. 1. PMR spectra of vinyl ethers of 2-, 3-, and 4-pyridylcarbinols without (a, c, e) and with (b, d, f) the Eu(DPM)$_3$ additive.

δ'_3 values are approximately equal and larger than the δ'_A value by a factor of two. The H-2, H-4, and H-5 signals are shifted slightly, and, in contrast to the δ' values of the remaining signals, the δ'_2 values turn out to be negative (the paramagnetic shift to weak field was assumed to be positive). The paramagnetic shifts observed in the spectrum of I correspond to coordination of it with Eu(DPM)$_3$ through the ether oxygen atom. In contrast to ether I, the H-2 and H-6 signal undergoes the greatest shift in the spectrum of II (Fig. 1, spectrum d). Moreover, δ'_2 and $\delta'_6 > \delta'_5 > \delta'_4$, and δ'_{CH_2} is lower than δ'_5 by a factor of ~1.5. The δ'_X and δ'_B values practically coincide and are less than 0.1 of the δ'_2 and δ'_6 values. The lowest δ' value was observed for the H_A signal. It is characteristic that the δ' values turn out to be different for H-2 and H-6. The signals of these protons are easily assigned, inasmuch as one of them is a singlet (H-2), whereas the other is a doublet (H-6). As in the preceding case, the greatest δ' value in the spectrum of ether III is observed for H-2 and H-6 (Fig. 1, spectrum f). However, one should note the peculiarity of this spectrum – the protons of the $-CH_2-$ and vinyl groups each give two signals.

An analysis of the three-dimensional structure of the vinyl ethers showed that in I, because of steric hindrance, for a certain conformation relative to the $C-CH_2$ bond, the pyridine ring cannot be situated in a plane that insures conjugation of the π system of the double bond and the p_z electrons of the oxygen atom. A different orientation of the heteroring and the vinyl group is possible in ethers II and III. In the final analysis, this is reflected in the character of the conjugation in the molecule and also in the coordination with $Eu(DPM)_3$. Insofar as vinyl ether of 4-pyridylcarbinol is concerned, two conformations with different orientations of the pyridine ring and the vinyl group are apparently energetically advantageous in it. Moreover, the signals of the protons of both conformations have identical chemical shifts. However, when the vinyl ether is incorporated in the coordination sphere of the paramagnetic complex, a different orientation of R in the ligand molecule shows up, inasmuch as the δ' value is determined specifically by the distance to the coordinating ion and the orientation of the resonating nucleus [7]. This confirms the nonidentical relationships between the δ' value of the signals of different protons and the temperature of the investigated sample, during which the ratio of the integral intensities of the signals of the conformers does not remain constant as the temperature changes. In fact, the effect of $Eu(DPM)_3$ reduces to an increase in the chemical nonequivalence of the resonating nuclei to such an extent that their signals are not superimposed in the spectrum at a given rate of the conformational transitions.

The vinyl ethers were obtained by reaction of the appropriate pyridylcarbinols with acetylene under pressure at 160-200° in the presence of a catalyst [8]. Their structures were proved by their IR and PMR spectra. Thus the IR spectra of the vinyl ethers of the pyridylcarbinols contain bands at 3120-3125, 1640, 1195-1200, 1150-1156, and 959-960 cm^{-1} due to vibrations of the vinyloxy group.

EXPERIMENTAL METHOD

The IR spectra of thin layers of the compounds were recored with a UR-20 spectrometer. The PMR spectra of CCl_4 solutions of the compounds were obtained with a BS 487B spectrometer (80 MHz) with tetramethylsilane as the internal standard.

2-(Vinyloxymethyl)pyridine (I). A rotating autoclave was charged with 10 g of 2-pyridylcarbinol, 4.88 g of $Cd(CH_3COO)_2 \cdot 2H_2O$, and 70 ml of dioxane. The initial acetylene pressure was 15 atm. The mixture was heated at 160-170° for 1 h, after which it was dried with potassium carbonate. The dioxane was then removed by vacuum distillation to give 8.5 g (69%) of ether I with bp 74° (7 mm), n_D^{20} 1.5130, and d_4^{20} 1.0264. Found: C 70.9; H 6.8; N 10.4%. C_8H_9NO. Calculated: C 71.1; H 6.7; N 10.4%.

3-(Vinyloxymethyl)pyridine (II). A total of 19.7 g (80%) of ether II, with bp 100° (17 mm), n_D^{20} 1.5210, and d_4^{20} 1.0368, was obtained from 20 g of 3-pyridylcarbinol, 3.08 g of KOH, and 110 ml of dioxane by heating with acetylene in an autoclave at 200° for 1 h. Found: C 70.7; H 7.0; N 10.4%. C_8H_9NO. Calculated: C 71.7; H 6.7; N 10.4%.

4-(Vinyloxymethyl)pyridine (III). This compound was obtained by heating 10 g of 4-pyridylcarbinol with acetylene in the presence of 1.54 g of KOH. The reaction was also carried out in dioxane at 180-190° for 1 h. Workup gave 4.6 g (37%) of ether III with bp 85° (7 mm), n_D^{20} 1.5160, and d_4^{20} 1.0321. Found: C 71.1; H 7.1, N 10.5%. C_8H_9NO. Calculated: C 71.1; H 6.7; N 10.4%.

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