Rotational Isomerism in a Vinylogous Amide

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WE have prepared the substance (I), which is the neutral conjugate base of 4-pyridylacetaldehyde methiodide, and observed its unusual n.m.r. behaviour attributable to restricted internal rotation. The current interest in such phenomena[1–4] prompts us to report our results.

Compound (I) is obtained in 33% yield by the base-catalyzed condensation of 4-picoline methiodide and ethyl formate. It crystallizes as yellow prisms from diethyl ether, m.p. 54–55°, decomposing after several days at room temperature, and having the following spectral characteristics: i.r. (KBr) 2·90, 6·00, 6·35, 7·31, 8·40, 11·89μ; u.v. (95% ethanol) λ_{max} 385 mμ (38,500); mass spectra m/e 135 (M^+), 134 ($M - 1$) are the principal peaks.

The substance (I) is a vinylogous amide and as such would be in resonance with either one or the other of the isomeric dipolar forms, (Ia) and (Ib). The contribution of (Ia) or (Ib) to the properties of (I) should be substantial as they each contain an aromatic pyridinium ring.

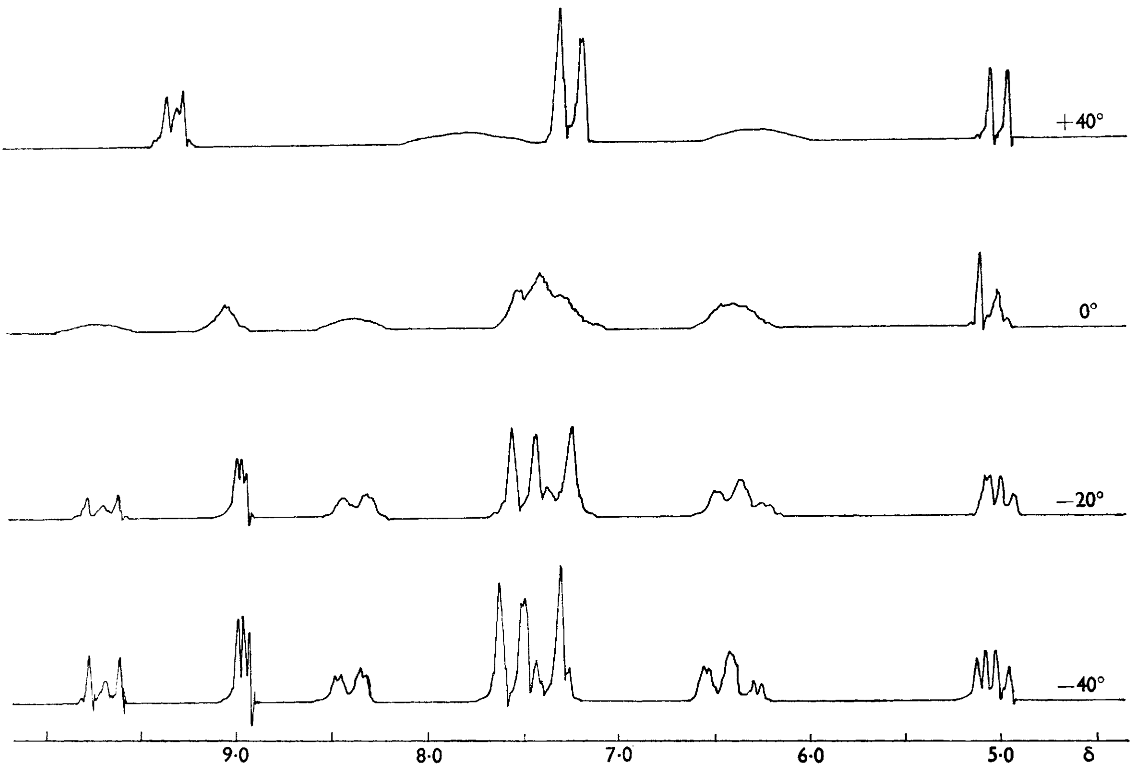
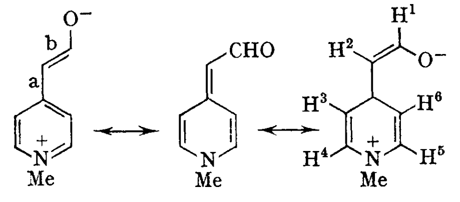


FIGURE. *Effect of temperature on the n.m.r. spectrum of* (I). *The* N-*methyl protons and water absorbances are not shown; further cooling to* −60° *produced no significant changes in the spectrum.*

The Figure indicates the changes which occur in the n.m.r. spectrum† of (I) between +40 to −40°. At +40°, the spectrum contains the following absorbances:‡ a singlet (3H) at 3·61δ, N-methyl protons; a doublet (1H) centred at 5·14 δ, J = 5·5 c./sec., H_2; a very broad signal (1H) *ca.* 6·34 δ, H-3; a doublet (2H) centred at 7·26 δ, J = 8·0 c./sec., H-4 and H-6; another very broad signal (1H) at *ca.* 7·75 δ, H-5; and finally, a doublet (1H) centred at 9·34 δ, J = 5·5 c./sec., H-1. The presence of a small peak in the middle of this doublet is discussed below.

The appearance of the +40° spectrum is interpretable on the basis of rapid rotation about both bonds (a) and (b) in the aldehyde; the coupling constant between H-1 and H-2 probably represents an averaged J value. The appearance of the aromatic protons is undoubtedly due to rapid rotation about bond (a), causing an interchange of H-3 and H-5, and of H-4 and H-6. Raising the temperature would be expected§ to produce an



(Ia) (I) (Ib)

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† All n.m.r. spectra were taken at 60 Mc./sec. in perdeuterio-acetone with Me_4Si as internal reference; the instrument used was a Varian A60A equipped with a Varian V-6040 variable temperature apparatus, and a Varian V-6058A spindecoupler.

‡ A singlet was present at *ca.* 2·98 δ due to water; this signal moved downfield on cooling and was at *ca.* 3·94 δ at −40°; the aldehyde was quite hygroscopic, and held water tenaciously so that it was not entirely removed overnight at five microns pressure over phosphorus pentoxide.

§ In analogy to *p*-nitroso-*NN*-dimethylaniline, see Ref. 4.

A_2X_2 system for the aromatic hydrogens, but experiments in this direction were frustrated by the instability of (I) above +40°.

Cooling the solution of (I) induced the transformations shown in the Figure. The results of these experiments can be explained on the basis of a higher energy barrier to rotation about bond (b) than about bond (a). Such a difference is credible in the light of the argument made earlier that resonance forms (Ia) and (Ib) should contribute substantially to the structure of the substance. Accepting this, one other significant point is needed for the interpretation, *i.e.*, that while (I) and (Ia), and (I) and (Ib) are resonance forms, (Ia) and (Ib) are not; they are *geometrical isomers*.

The low-temperature n.m.r. spectrum can thus be rationalized by assuming that the rate of rotation about bond (b) has greatly diminished at −40°, while that about bond (a) continues at a relatively rapid rate. The spectrum is therefore that of a mixture of two compounds, and displays two sets of hydrogen absorptions attributable to *cis*- and *trans*-isomers: two singlets (2 × 3H) at 3·68 and 3·77 δ, the two N-methyl groups; two overlapping doublets (2 × 1H) at *ca.* 5·03 δ, J = 3·0 c./sec., H-2,*cis*, and J = 10 c./sec., H-2,*trans*; a broadened pair of overlapping doublets (2 × 1H) centred at 6·41 δ, J = 8·0 c./sec., H-3,*trans* and H-3,*cis*; a multiplet (5H) at 7·25—7·80 δ, containing H-4,*cis*, H-4,*trans*, H-6,*cis*, H-6,*trans*, and H-5,*trans*; a broadened doublet (1H) at 8·45 δ, J = 8·0 c./sec., H-5,*cis*; a doublet (1H) at 8·98 δ, J = 3·0 c./sec., H-1,*cis*, containing a peak at its centre whose origin is discussed below; and finally, a doublet (1H) at 9·70 δ, J = 10 c./sec., H-1,*trans*, also containing a peak at its centre.

The above assignments were substantiated by spin-decoupling experiments; saturation of H-1,-*trans* (9·70 δ) and of H-1,*cis* (8·98 δ) caused collapse of the outer and inner pairs respectively of the "quartet" at 5·03 δ to singlets; saturation of H-5,*cis* (8·45 δ) caused the left pair of overlapping doublets at 6·41 δ (H-3,*cis*) to *disappear*; saturation of H-3,*cis* (and H-3,*trans*) caused the entire signal due to H-5,*cis* to *disappear*. This interesting phenomenon is presumably the result of intramolecular hydrogen exchange: rotation about bond (a) is occurring at a rate faster than the relaxation processes; saturation of H-5,*cis*, which is interchanging with H-3,*cis*, thus leads to saturation of the latter proton as well. The same behaviour has recently been observed in low-temperature spin-decoupling studies on *p*-nitroso-*NN*-dimethylaniline.[5]

The origin of the signals present at the centre of the aldehyde doublets in both the +40° and −40° spectra is a matter of some interest. The heights of these signals relative to the heights of the doublet lines varied considerably with different samples of the aldehyde. The appearance of the remainder of the spectrum under these circumstances was unchanged. The simplest explanation for these extra lines is an exchange of H-2 with the water present in the samples. Such a process could cause a collapse of the H-1 doublet in each instance to a singlet whose line position was centred between the corresponding lines of the doublet. That exchange of H-2 does indeed occur was shown by addition of D_2O to the deuterioacetone solution. The resulting room temperature n.m.r. spectrum showed a greatly broadened, but undiminished, aldehyde signal, and the signals of the aromatic protons and the *N*-methyl protons was unchanged. The doublet due to H_2 was diminished to one quarter of its former intensity. The fact that it did not entirely disappear is presumably due to the presence of some ordinary water in the sample. Addition of excess ordinary water to another sample gave a room temperature n.m.r. spectrum with the aldehyde signal greatly broadened, but undiminished, and with no change in the H-2 doublet.

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[4] D. D. MacNichol, R. Wallace, and J. C. D. Brand, *Trans. Faraday Soc.*, 1956, **61**, 1; P. K. Korver, P. J. van der Haak, and T. J. de Boer, *Tetrahedron*, 1966, **22**, 3157 (*p*-nitroso-*NN*-dimethylaniline).

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