# VINYLOGS OF 4-PYRIDINALDEHYDE

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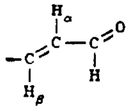
*Condensation of 4-pyridinaldehyde and 3-(4'-pyridyl)acrolein with acetaldehyde in the presence of morpholine acetate has given their vinylogs. These compounds have been shown to exist mainly in the trans-configurations.*

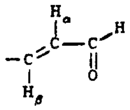
Unlike unsaturated aromatic carbonyl compounds, the study of the structural features of which has formed the subject of several reports [1-7], the corresponding pyridine compounds have received little attention.

Unsaturated aromatic aldehydes are usually obtained by aldol condensation of carbonyl derivatives of benzene with acetaldehyde in the presence of KOH, followed by dehydration of the resulting aldol [5, 7]. The condensation of pyridinaldehydes with acetaldehyde is more selective when the salt of an organic base, morpholine acetate, is used as catalyst. This afforded the crotonic condensation products 4-pyrinaldehyde (I) with acetaldehyde giving 3-(4'-pyridyl)acroline (II), and (II) with acetaldehyde giving 5-(4'-pyridyl)penta-2,4-dienal (III). The latter compound (III) was new.

The initial rate of reaction of (I) was 0.15, and of (II) 0.46 mole/(liter·h). It is assumed that in this instance the rate of reaction is limited by fission of the C=O bond in the pyridinaldehyde, the lower rate of reaction of (I) being attributed to the polarizing influence of the carbonyl oxygen in this product being neutralized to a greater extent by the electron-acceptor influence of the pyridine ring. That the C=O bond in (I) is stronger is also shown by the higher frequency of $\nu_{C=O}$ vibrations in (I) as compared with (II) (Table 1).

Compounds II and III may have two isomeric forms:


s-trans


s-cis

Comparison of the stereospecific coupling constants between the protons of the carbonyl group and $H_{(\alpha)}$ for (II) and (III) (Table 2) with those for the cis- (2-3 Hz) and trans-conformations (4-9 Hz) of α,β-unsaturated aldehydes and ketones suggests that the aldehydes obtained exist primarily in the s-trans-conformations. This conclusion is supported by the nature of the changes in the screening effects of the α-protons in the aldehyde (II) on changing from the solution in chloroform (ε 4.8) to aqueous solution (ε 78.5). The difference in the $H_{(\alpha)}$ chemical shifts for solutions with low and high dielectric permeability amounts to 0.32 pm. By analogy with the specific effect of the reaction field of the solvent on the corresponding protons in α,β-unsaturated aromatic carbonyl compounds [4, 9], it may be concluded that such descreening can only occur for the s-trans-conformer. If the other isomer predominated, then a similar change of solvent should result in the difference in chemical shifts being a negative one. Splitting of the band for the carbonyl group in the IR spectrum of (III) suggests the presence of a certain amount of the s-cis-isomer. With respect to stereoisomerism relative to the double bonds, the $H_{(\alpha)}$–$H_{(\beta)}$ and $H_{(\gamma)}$–$H_{(\beta)}$ coupling constants for the aldehydes (II) and (III) (14.5-16.1 Hz) (Table 2) indicate that the crotonic condensation used in the present investigation is stereospecific, leading to the formation of the E-isomers almost exclusively [10]. However, 5-(3'-pyridyl)penta-2,4-dienal obtained, for example, by condensation of 3-pyridinaldehyde with formylallyltriphenylarsonium bromide [11], is a mixture of the (2E, 4E)- and (2E, 4Z)-isomers.

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TABLE 1. IR and UV Spectra of (I-III)

| Compound | IR spectrum, cm$^{-1}$ | | | | UV spectrum, $\lambda_{max}$, nm (lg ε) |
|---|---|---|---|---|---|
| | $\nu_{C=O}$ | $\nu_{C=C}$ | $\nu_{C=O}-\nu_{C=C}$ | $\delta_{=CH}$* | |
| I | 1710 | — | — | — | 258 (2,85) |
| II | 1680 | 1600 | 80 | 990 | 208 (2,15), 269 (3,4) |
| III | 1685, 1670** | 1605, 1625 | 80 | 1015, 990 | 295 p. 310 (3,5), 320 sh. |

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*Assigned as in [5].

**Assignment of the $\nu_{C=O}$ band was based on the absence from the spectrum of the thiosemicarbazone of aldehyde (III) of absorption at these frequencies.

TABLE 2. PMR Spectra of (II) and (III)

| Compound | Solvent | Chemical shifts, ppm* | | | | | SSCC, Hz | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $H_{(2,6)}$ | $H_{(3,5)}$ | $H_{(\beta)}$ | $H_{(\alpha)}$ | CHO | $H_{(\alpha)}-H_{(\beta)}$ | $H_{(\beta)}-H_{(\gamma)}$ | $H_{(\gamma)}-H_{(\delta)}$ |
| II** | $D_2O$ | 8,86 | 8,29 | 7,90 | 7,16 | 9,81 | 16,1 | — | — |
| | $CDCl_3$ | 8,73 | 7,43 | 7,47 | 6,84 | 9,80 | 16,0 | — | — |
| III*** | $CDCl_3$ | 8,65 | 7,35 | 7,28 | 6,37 | 9,68 | 14,5 | 11,0 | 15,0 |

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*For (III): 7.17 ($H_\gamma$), 6.95 ppm ($H_\delta$).

**$-CH_{(\beta)}=CH_{(\alpha)}-CHO$.

***$-CH_{(\delta)}=CH_{(\gamma)}-CH_{(\beta)}=CH_{(\alpha)}-CHO$.

TABLE 3. Characteristic Ions in the Mass Spectra of Unsaturated Pyridine Aldehydes

| Compound | m/z ($I_{rel}$, %)* | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $M^{+\cdot}$ | $M-(H)^+$ | $M-(CO)^+$ | $M-(CHO)^+$ | $Py^+$ | A | B | $M-Py^+$ | C |
| II | 133<br>(100) | 132<br>(38) | 105<br>(25) | 104<br>(56) | 79<br>(40) | 78<br>(54) | — | — | — |
| III | 159<br>(67) | 158<br>(16) | 131<br>(16) | 130<br>(100) | — | — | 103,0540<br>(29)<br>$C_8H_7$** | 81,0356<br>(54)<br>$C_5H_5O$** | 77,0400<br>(41)<br>$C_8H_5$** |

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*A = $M-(CH=CHCHO)^+$, B = $M-(CHO)-(CHN)^+$, C = $M-(CHO)-(CHN)-(C_2H_2)^+$.

**The exact masses of these ions were measured.

As a result of the polarization of the double bond by the carbonyl group, and the reduction in electron density at the β-carbon atom, $H_{(\beta)}$ in (II) and (III) resonates at lower field than $H_{(\alpha)}$, as is also the case with cinnamaldehyde [4]. As far as the protons at the second double bond in the aldehyde (III) are concerned, $H_{(\gamma)}$, which is furthest from the ring, resonates at lower field, apparently as a result of the polarizing effect of the heteratomic nitrogen. In (III), in which the double bond experiences simultaneously the opposing effects of the two electron-acceptor groups, the carbonyl group is the stronger.

It has been shown for aliphatic [2] and aromatic [3] compounds that isomers of this type may be distinguished by the positions of the absorption for C=O and C=C stretching vibrations, the $\nu_{C=O}-\nu_{C=C}$ value being >75 cm$^{-1}$ for the cis-isomer, while that for the trans-isomer is usually <75 cm$^{-1}$. The results shown in Table 1 indicate that the criteria for assessing isomerism in unsaturated heterocyclic aldehydes must be different. In aldehydes (II) and (III), which according to their PMR spectra are the trans-isomers, the differences in these absorptions is 80.

Examination of the UV spectra of the aldehydes (I-III) (Table 1) shows that the introduction of one vinyl group into the molecule results in a bathochromic shift of the absorption maximum by 11 nm, and of the second by 40 nm with a concomitant increase in the intensity of absorption. For their benzene analogs, these values are 38-48 and 30 nm, respectively [3].

The mass spectra of (II) and (III) show strong molecular ions (100 and 67%) (Table 3). The first step in the breakdown of these unsaturated aldehydes under electron impact is removal of an H· radical, with ejection of a CO molecules and concomitant removal of a CHO· radical. Fragmentation of (II) is similar to that of 3-phenylacrolein [12], but that of (III) differs considerably. For example, the ion with m/z 130 arising on fragmentation of this compound, formed by removal of the aldehyde group, then successively loses HCN (m* = 81.6) and $C_2H_2$ (m* = 57.6) fragments. Another mode of fragmentation results from rupture of the α-bond in the molecular ion, with the formation of an ion with m/z 81 (m* = 41.26). This indicates that the charge is preferentially located in the side chain of the molecular ion. The absence of nitrogen from the ions with m/z 103.81 and 77 was shown by measurement of their precise masses.

Hence, the redistribution of electron density in the unsaturated pyridinaldehyde with two double bonds substantially affects its mode of fragmentation.

## EXPERIMENTAL

The condensations were followed by GLC [13]. Preparative isolation of (III) from the reaction mixture was accomplished by HPLC on a Du Pont 830 chromatograph with a column (150 × 4.6 mm) packed with Silasorb LC-18. The mobile phase was methanol–water (1:1), and the flow rate 2 ml/min. IR spectra were obtained on a Perkin–Elmer 580 B (in Nujol), UV spectra on a Specord UV-VIS (in ethanol), and $^1$H NMR spectra on a WH-90/DS (90 MHz). Mass spectra were obtained on a KRATOS MS-25 GC-MS. The precise masses of the ions and metastable ions were measured with a KRATOS MS-50. The ionizing electron energy was 70 eV, and the temperature of the ionizing chamber 200°C.

4-Pyridinaldehyde (I) was obtained by vapor-phase oxidation of 4-methylpyridine [14]. 3-(4'-Pyridyl)acrolein (II) was synthesized as described in [13].

**5-(4'-Pyridyl)penta-2,4-dienal (III, $C_{10}H_9NO$).** A solution of 1.4 g (10.5 mmoles) of (II) and 0.16 g (1.1 mmoles) of morpholine acetate in 44 ml of benzene was flushed out for 10 min with an inert gas, and heated to 77-79°C. A solution of 0.7 g (16 mmoles) of acetaldehyde in 3 ml of benzene was added dropwise. The resulting mixture was kept at the temperature indicated for 3 h, then the solvent was removed. The residue was subjected to preparative liquid chromatography to give 0.42 g (25%) of (III) as a yellow crystalline solid, mp 53-55°C.

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