1-Methyl-2(3,4)-(1-vinylpyrrol-2-yl)pyridinium iodides: some structural features revealed by ^{1}H and ^{13}C NMR spectroscopy

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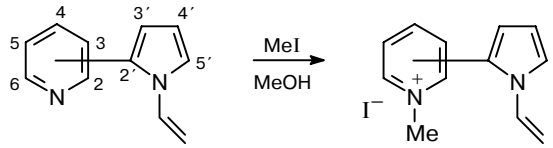
The reactions of 2-, 3-, and 4-(1-vinylpyrrol-2-yl)pyridines with methyl iodide afford the corresponding quaternary salts. Analysis of their ^{1}H and ^{13}C NMR spectra showed that the quaternization of the nitrogen atom considerably enhances the π-acceptor effect of the pyridine ring on the pyrrole ring and on the vinyl group. 1-Methyl-2-(1-vinylpyrrol-2-yl)pyridinium iodide contains no weak intramolecular C—H...N hydrogen bond present in the starting compound.

Key words: (1-vinylpyrrol-2-yl)pyridines, quaternization, 1-methyl-(1-vinylpyrrol-2-yl)pyridinium iodides, ^{1}H NMR spectra, ^{13}C NMR spectra.

It is known that 2-(pyrrol-2-yl)pyridine[1] and indolylpyridines[2—4] react with alkyl halides to form pyridinium salts, whose properties are well known. However, (1-vinylpyrrol-2-yl)pyridines (**1a—c**) have not been previously quaternized because of their unavailability.

The goal of the present work was to synthesize this series of new quaternary salts and study their electronic and spatial structures. 2-(1-Vinylpyrrol-2-yl)pyridine (**1a**), 3-(1-vinylpyrrol-2-yl)pyridine (**1b**), and 4-(1-vinylpyrrol-2-yl)pyridine (**1c**) are prepared by the Trofimov reaction from methyl pyridyl ketone oximes and acetylene[5,6] and easily react with methyl iodide to give the corresponding iodides **2a—c** in up to 90% yields.



1a—c **2a—c**

In anhydrous methanol at room temperature, the reaction is completed within 2—3 h. Compounds **2a—c** are crystalline substances soluble in chloroform, ethanol, acetone, and water. The structures of salts **2a—c** were examined by ^{1}H and ^{13}C NMR spectroscopy. The corresponding spectral characteristics of quaternary salts **2a—c**, the starting pyrrolylpyridines **1a—c**, pyridine (**3**), and 1-methylpyridinium iodide (**4**) are given in Tables 1 and 2, respectively.

The chemical shifts of all protons and carbon atoms in the quaternary salt are different significantly from those for the starting pyrrolylpyridines **1a—c**. Most of the signals are shifted downfield, because the positive charge becomes delocalized over the vinylpyrrole fragment upon the addition of methyl iodide (Tables 1 and 2). The quaternization of the nitrogen atom in pyridine (**3**) causes the signals for the C(3) (C(5)) and C(4) atoms to shift downfield by 5.5 and 10.8 ppm, while a signal for the C(2) (C(6)) atom is shifted upfield by 3 ppm (Table 2). Similar shifts were noted for signals of the pyridine C atoms in salts (**2a—c**) compared to the corresponding signals for pyrrolylpyridines **1a—c**.

The pyrrole ring in pyrrolylpyridines functions as a π-donor for the pyridine ring. As a result, all ^{13}C signals for the pyridine ring in salts **2b**,**c** are additionally shifted upfield by 1—6 ppm, as compared to 1-methylpyridinium iodide (**4**) (Table 2). In the case of salt **2a**, the effect of the pyrrole ring decreases the chemical shifts of the C(4) and C(5) atoms by 1.8 and 2.4 ppm, respectively, while the signals for the C(3) and C(6) atoms are shifted downfield by 1.6 and 1.2, respectively.

By contrast, the pyridine ring is a π-acceptor for the pyrrole ring. For salts **2a—c**, signals for the pyrrole C(3′) and C(5′) atoms experience additional upfield shifts of 4.5—7.0 and 4.1—7.7 ppm, respectively, because the pyridine ring becomes a stronger acceptor upon its quaternization. This enhanced withdrawing effect of the quaternized pyridine ring is transferred through the pyrrole ring to the vinyl group, which increases the chemical shifts of the β-C atom by 4.1—6.6 ppm in iodides **2a—c** compared to the starting compounds **1a—c** (Table 2).

Changes in the chemical shifts for the protons mostly follow changes in the shifts for the corresponding carbon atoms.[9] However, for the quaternized pyridine ring, a signal for its C(2) (C(6)) atom is shifted upfield, while a signal for the H(2) (H(6)) atom is shifted downfield (compounds **3** and **4**, Tables 1 and 2). Interestingly, a

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Table 1. ^{1}H NMR spectra (δ) of (1-vinylpyrrol-2-yl)pyridines (**1a—c**), their quaternary salts (**2a—c**), pyridine (**3**)[a], and 1-methylpyridinium iodide (**4**)[b]

Compound	δ											
	H(3′)	H(4′)	H(5′)	H(2)	H(3)	H(4)	H(5)	H(6)	H_a	H_b	H_x	Me
1a	6.57	6.27	7.18	—	7.45	7.60	7.05	8.58	4.72	5.16	7.90	—
1b	6.31	6.31	7.14	8.64	—	7.66	7.31	8.53	4.76	5.20	6.82	—
1c	6.38	6.25	7.09	8.52	7.23	—	7.23	8.52	4.77	5.19	6.85	—
2a	6.73	6.50	7.33	—	7.86	8.42	8.09	9.07	5.07	5.28	6.92	4.47
2b	6.79	6.35	7.16	8.95	—	8.27	8.04	9.18	5.07	5.34	7.00	4.72
2c	6.94	6.42	7.24	9.02	7.87	—	7.87	9.02	5.24	5.47	7.01	4.55

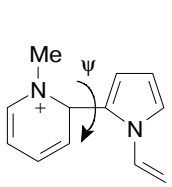
[a] **3**: 8.61 (H(2), H(6)), 7.27 (H(3), H(5)), 7.67 (H(4)).
[b] **4**: 9.22 (H(2), H(6)), 8.08 (H(3), H(5)), 8.46 (H(4)), 4.72 (Me).

Table 2. ^{13}C NMR spectra of (1-vinylpyrrol-2-yl)pyridines (**1a—c**), their quaternary salts (**2a—c**), pyridine (**3**)[a], and 1-methylpyridinium iodide (**4**)[b]

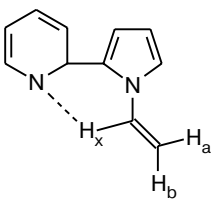
Compound	δ											
	C(2′)	C(3′)	C(4′)	C(5′)	C(2)	C(3)	C(4)	C(5)	C(6)	C_α	C_β	Me
1a	131.40	111.78	109.56	119.66	151.27	121.59	135.78	120.10	148.04	133.04	98.00	—
1b	130.33	111.13	110.31	119.49	149.60	128.41	136.10	123.14	148.02	131.35	100.19	—
1c	130.88	112.09	110.37	121.05	149.49	122.25	139.70	122.25	149.49	131.56	101.02	—
2a	120.89	118.01	111.55	123.76	146.76	130.80	144.94	126.84	148.02	130.94	104.41	48.02
2b	125.21	115.58	111.43	124.01	143.02	133.15	142.40	128.08	142.40	131.43	105.31	49.98
2c	127.22	119.13	112.17	128.73	144.58	122.90	146.20	122.90	144.58	131.67	107.62	47.80

[a] **3**: 149.88 (C(2), C(6)), 123.72 (C(3), C(5)), 135.93 (C(4)).
[b] **4**: 146.85 (C(2), C(6)), 129.24 (C(3), C(5)), 146.71 (C(4)), 49.38 (Me) (in CD_3OD).

downfield shift of a signal for the H(3′) atom of the pyrrole ring is smaller in methyl derivative **2a** compared to **2b** and **2c** (0.16, 0.48, and 0.56 ppm, respectively), whereas changes in the chemical shifts of signals for the C(3′) atom in these compounds are one order of magnitude. Salt **2a** contains two bulky substituents near the bridging C(2′)—C(2) bond. As a result, the torsion angle ψ between the heterocycles has to increase (see structure **A**).[7] In this case, the H(3′) proton becomes shielded by the pyridine ring, and its signals is shifted upfield. In compound **2a**, the pyrrole ring causes an upfield shift (0.22 ppm) of a signal for the pyridine H(3) proton and a downfield shift (1.56 ppm) of a signal for the C(3) atom (Tables 1 and 2). Apparently, this is due to a shielding effect of the pyrrole ring on the H(3) proton.



A



B

Finally, unlike iodides **2b**,**c**, a signal for H_x of the vinyl group in salt **2a** is strongly shifted upfield compared to pyrrolylpyridine **1a** (0.98 ppm). At the same time, the downfield shifts of signals for the H_a and H_b protons in all compounds **2a—c** are roughly equal (0.12—0.28 and 0.31—0.47 ppm, respectively, see Table 1).

In 2-(vinylpyrrol-2-yl)pyridine (**1a**), a signal for the H_x proton is shifted downfield by nearly 1.1 ppm compared to 3- and 4-substituted pyridines **2b**,**c** (see Table 1). This can be due to the existence of an unusual C—H...N hydrogen bond between the vinyl H_x proton and the pyridine N atom (**B**).[8,9] Quaternization of the nitrogen atom in salt **2a** precludes this interaction (**A**), and the chemical shift of the H_x signal takes a standard value (the δH_x values for iodides **2a—c** are virtually the same (see Table 1)).

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-250 spectrometer (250.1 and 62.9 MHz, respectively) in $CDCl_3$ with HMDS as the internal standard. The concentration of ^{13}C and ^{1}H NMR samples was 5—10 and 1—2 wt. %, respectively. Signals for the carbon atoms were assigned using two-dimensional heteronuclear NMR spectroscopy with the HMQC [10] and HMBC procedures.[11]

IR spectra of the compounds obtained were recorded on a Bruker ISF 25 instrument (KBr).

Quaternization of (1-vinylpyrrol-2-yl)pyridines 1a—c. A mixture of compound **1a**, **1b**, or **1c** (1.02 g, 6 mmol) and methyl iodide (0.40 mL, 6 mmol) in 6 mL of anhydrous methanol was stirred at ~20 °C for 2—3 h. Removal of the solvent *in vacuo* (15 Torr) gave the corresponding iodides **2a—c**.

The yields, melting points, and elemental analysis and IR data are presented below.

1-Methyl-2-(1-vinylpyrrol-2-yl)pyridinium iodide (2a). Yield 1.70 g (91%), m.p. 104—105 °C (from ethanol). IR, ν/cm^{-1}: 436, 506, 547, 589, 658, 737, 775, 796, 885, 899, 965, 992, 1065, 1087, 1164, 1175, 1257, 1273, 1292, 1329, 1400, 1421, 1430, 1456, 1469, 1500, 1543, 1563, 1622, 1639, 2960, 2980, 3026, 3065, 3094, 3110. Found (%): C, 46.25; H, 4.53; N, 9.04; I, 40.18. $C_{12}H_{13}N_2I$. Calculated (%): C, 46.17; H, 4.20; N, 8.97; I, 40.65.

1-Methyl-3-(1-vinylpyrrol-2-yl)pyridinium iodide (2b). Yield 1.56 g (85%), m.p. 137—138 °C (from ethanol). IR, ν/cm^{-1}: 428, 508, 535, 600, 661, 683, 693, 764, 800, 818, 884, 932, 956, 1003, 1027, 1045, 1066, 1085, 1166, 1200, 1210, 1258, 1287, 1324, 1342, 1412, 1427, 1449, 1476, 1502, 1546, 1584, 1640, 2949, 2986, 3020, 3083, 3090. Found (%): C, 45.84; H, 4.52; N, 8.88; I, 40.76.

1-Methyl-4-(1-vinylpyrrol-2-yl)pyridinium iodide (2c). Yield 1.65 g (88%), m.p. 114—115 °C (from ethanol). IR, ν/cm^{-1}: 505, 591, 608, 638, 692, 723, 764, 837, 892, 970, 986, 1049, 1073, 1092, 1200, 1227, 1257, 1285, 1300, 1332, 1414, 1442, 1480, 1505, 1543, 1560, 1639, 2923, 3011, 3079. Found (%): C, 45.97; H, 4.58; N, 8.78; I, 40.57.

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