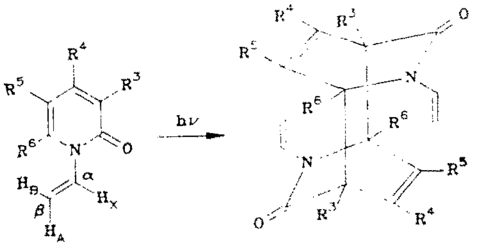
PHOTODIMERS OF 1-VINYL-2-PYRIDONES; SYNTHESIS AND STUDY OF THE STRUCTURE BY THE METHOD OF ^{1}H AND ^{13}C NMR

A. V. Afonin, M. A. Andriyankov, and M. V. Nikitin

UDC 543.422.25:547.823

The action of natural light on 1-vinyl-2-pyridone and a series of its substituted compounds gave the corresponding photodimers with the retention of the vinyl group. The steric and electronic structure of the substances obtained was studied by the method of ^{1}H and ^{13}C NMR by comparison with the structure of the initial monomers. It was established that the stereoorientation of the vinyl group depends on the position of the substituent in the ring.

The irradiation of 2-pyridone and its 1-methyl-substituted derivative leads to their dimerization [1, 2]. We studied the conversions of 1-vinyl-2-pyridone and a series of its substituted compounds under the action of natural light, and investigated the structure of the products by the method of ^{1}H and ^{13}C NMR.



Ia-VIa Ib-VIb

I $R^3=R^4=R^5=R^6=H$; II $R^3=CH_3$, $R^4=R^5=R^6=H$; III $R^4=CH_3$, $R^3=R^5=R^6=H$, IV $R^5=CH_3$, $R^3=R^4=R^6=H$; V $R^6=CH_3$, $R^3=R^4=R^5=H$; VI $R^5=Cl$, $R^3=R^4=R^6=H$

The PMR spectral parameters of the initial 1-vinyl-2-pyridones (Ia)-(VIa) and their dimers (Ib)-(VIb) were determined (Table 1). The signals of the protons of the vinyl group (H_A, H_B, and H_X; see Table 1) are preserved in the PMR spectra of the substances (Ib)-(VIb). At the same time, the chemical shifts of the protons of the heterocycle undergo marked changes. The signals of the $H_{(3)}$ and $H_{(6)}$ protons are displaced especially strongly (~3 ppm; see Table 1). The PMR spectra of the products of the irradiation of the 1-vinyl-2-pyridones (Ib)-(VIb) show the characteristic appearance of the large SSCC (10.1-10.3 Hz) between the $H_{(3)}$ and $H_{(6)}$ protons of the ring (see Table 1). These changes are in accord with the formation of the dimers (Ib)-(VIb) on account of the addition of the rings at the positions 3 and 6.

It follows from the PMR spectrum of the photodimer (Ib) in the presence of the paramagnetic amplifying reagent $Gd(fod)_3$ (Fig. 1) that the carbonyl groups in compound (Ib) have the anti-orientation. The reagent $Gd(fod)_3$ forms a coordination bond with the molecule of (Ib) at the oxygen atom, since the unshared pair of the nitrogen atom is delocalized onto the vinyl and carbonyl groups [3]. The broadenings induced by the $Gd(fod)_3$ and the ^{1}H NMR spectrum are determined by the formula [3]

$$\Delta\nu = A \cdot r^{-6},$$

where $\Delta\nu$ is the broadening, A is a constant, and r is the distance from the paramagnetic center to the resonating proton.

The presence of $Gd(fod)_3$ in the solution leads to a significantly larger broadening of the signal of the $H_{(5)}$ proton than that of $H_{(4)}$; the disappearance of the multiplicity of the $H_{(4)}$ signal after the addition of $Gd(fod)_3$ is explained by the effect of the removal of the spin–spin interaction by the chemical exchange [4]. Consequently, the $H_{(5)}$ proton is disposed significantly closer to the coordination center (the O atom). This is possible in the case where the anti-form of the disposition of the carbonyl group is realized, and the $H_{(5)}$ proton is found "over" ("under") the oxygen atom of the second pyridine ring.

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 942-946, July, 1990. Original article submitted November 10, 1988; revision submitted July 11, 1989.

0009-3122/90/2607-0785$12.50

TABLE 1. Parameters of the PMR Spectra of 1-Vinyl-2-pyridones (Ia)-(VIa) and Their Photodimers (Ib)-(VIb)

Compound	Chemical shifts, ppm								J, Hz										
	$H_{(3)}$	$H_{(4)}$	$H_{(5)}$	$H_{(6)}$	H_A	H_B	H_X	CH_3	$H_{(3)}H_{(4)}$	$H_{(3)}H_{(5)}$	$H_{(3)}H_{(6)}$	$H_{(4)}H_{(5)}$	$H_{(4)}H_{(6)}$	$H_{(5)}H_{(6)}$	H_AH_B	H_AH_X	H_BH_X	H_5H_X	H_6H_B
Ia	6,51	7,27	6,16	7,46	5,03	5,25	7,50	—	9,3	1,4	0,8	6.6	2,0	7,1	—1,7	8,8	15,9	0,45	0,35
Ib	3,72	6,20	6,56	4,54	4,46	4,34	7,19	—	7.0	1,6	10,2	8,1	1,2	6,7	—1,6	9,2	16,1	0,35	0,5
IIa	—	7,18	6,14	7,42	5,01	5,25	7,60	2,12	—	—	—	6,9	1,6	6,9	—1,6	9,0	16,0	0,45	0,35
IIb	—	5,86	6,48	4,08	4,46	4,44	7,28	1,59	—	—	—	8,3	1,2	7,0	—1,4	9,1	16,2	0,35	0,5
IIIa	6,34	—	6,05	7,40	4,99	5,22	7,51	2,16	—	1,6	0,8	—	—	7,0	—1,65	9,1	16,1	0,45	0,35
IIIb	3,54	—	6,18	4,67	4,44	4,44	7,17	1,79	—	2,2	10,3	—	—	7,1	—1,5	9,1	16,1	0,35	0,5
IVa	6,49	7,19	—	7,27	5,00	5,24	7,53	2.09	9,2	—	0,8	—	2,0	—	—1,65	9,1	16,1	—	0,35
IVb	3,63	5,71	—	4,20	4,39	4,24	7,19	1,90	7,1	—	10,1	—	1,8	—	—1,5	9,3	16,0	—	0,5
Va	6,39	7,22	6,05	—	5,57	5,42	6,63	2,18	9,1	0,8	—	6,8	—	—	—0,4	8,3	15,8	0	—
Vb	3,33	6,21*	6,21*	—	5,07	5,24	6,00	2,16	6,1	2,9	—	*	—	—	0	9,0	15,7	0	—
VIa	6,35	7,29	—	7,59	5,08	5,31	7,48	—	9,8	—	0,6	—	2,8	—	—2,0	9,0	16,0	—	0,35
VIb	3,87	6,12	—	4,60	4,51	4,27	7,21	—	7,6	—	10,1	—	2,0	—	—2,0	9,3	16,0	—	0,5

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*The chemical shifts of the signals of $H_{(4)}$ and $H_{(5)}$ of the photodimer (Vb) represent multiplets not of the first order, and practically coincide with each other.

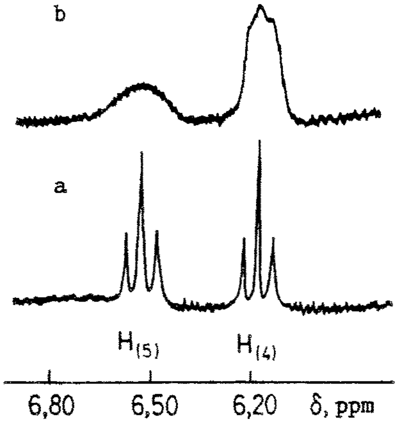

Fig. 1. A fragment of the PMR spectrum of the photodimer of 1-vinyl-2-pyridone (Ib). a) Signals of the $H_{(4)}$ and $H_{(5)}$ protons; b) the same signals after the addition of Gd(fod)$_3$.

Two types of distant spin–spin interaction between the protons of the ring and the vinyl group are observed in the PMR spectra of the molecules (I)-(IVa) and (VIa) (Table 1). The distant interaction between the $H_{(5)}$ and H_X protons in the compounds (Ia)-(IIIa), occurring through five bonds (${}^5J_{H_{(3)}H_X}$ = 0.45 Hz), is mainly transmitted by the σ-system through the zigzag type of fragment (see the conformation A), which is only realized by the s-trans-(O)-conformation of the vinyl group [5-8]. There is also the distant spin–spin interaction in compounds (Ia)-(IVa) and (VIa), which occurs formally through five bonds between the $H_{(6)}$ ring proton and the H_B proton of the vinyl group, and is transmitted through space [7, 9]. Such an interaction is only possible with the steric proximity of the protons, i.e., also in the close-to-planar s-trans-(O)-conformation A.

The chemical shifts of the proton signals of the vinyl group in the PMR spectra of compounds (Ia)-(IVa) and (VIa) differ insignificantly. The small high-field shifts of the signals of the H_A and H_B protons (0.02-0.04 ppm) occurring with the introduction of the donor methyl group into the ring correspond with some increase of the conjugation with the vinyl group [10]. The small low-field shift of these signals (0.05-0.06 ppm) occurring with the introduction of the acceptor atom of chlorine indicates the weakening of the conjugation with the vinyl fragment [10]. Consequently, the transfer of the electronic effect of the substituent takes place across the ring to the vinyl group; this is in accord with the conclusion on the close-to-coplanar structure of the molecules (Ia)-(IVa) and (VIa). Therefore, molecules (Ia)-(IVa) and (VIa) have a structure which is close to planar (the planar structure of the pyridone ring in the crystals was shown in [11]) with the s-trans-(O) steric orientation of the vinyl group.

The distant spin–spin interaction between the ring protons $H_{(5)}$ and $H_{(6)}$ and the H_X and H_B protons of the vinyl group is preserved correspondingly in the PMR spectra of the photodimers (Ib)-(IVb) and (VIb) ((${}^5J_{H_{(3)}H_X}$ = 0.35 Hz and (${}^5J_{H_{(6)}H_B}$ = 0.5 Hz). Consequently, the vinyl group retains its steric orientation [s-trans-(O)] in the process of the photodimerization of the molecules (Ia)-(IVa) and (VIa), and the photodimers (Ib)-(IVb) and (VIb) are conformationally uniform. In conformity with this, close values of the chemical shifts of all the protons of the vinyl group are preserved in the series (Ib)-(IVb) and (VIb) (Table 1), and the low-field disposition of the H_X signal (7.17-7.28 ppm), which is due to the steric proximity of the H_X proton to the oxygen atom, is preserved.

The distant spin–spin interaction between the $H_{(5)}$ and H_X protons in the molecule of (Va) disappears. Moreover, the sharp low-field shift of the chemical shifts of the signals of the vinyl group H_A and H_B takes place in the spectrum of compound (Va) (owing to the breaking of the conjugation with the vinyl group [10]), as well as the increase of the geminal SSCC ${}^2J_{AB}$ (Table 1), which is sensitive to the torsional angle at the N–C_α bond [12]. The observed effects indicate the emergence of the vinyl group from the plane of the heterocycle (by means of the rotation at the N–C_α bond and the breaking of the conjugation with it) in the molecule of (Va) on account of the steric influence of the methyl group at position 6.

The emergence of the vinyl group from the plane of the heterocycle in the molecule of (Va) is accompanied by the large high-field shift (0.9-1.0 ppm, Table 1) of the H_X signal in regard to compounds (Ia)-(IVa) and (VIa). This is explained by the fact that the H_X proton in compounds (Ia)-(IVa) and (VIa) occurs in steric proximity to the oxygen atom (see the conformation A). On account of this, its signal in the PMR spectrum is anomalously displaced to low field [10, 13, 14]. With the emergence of the vinyl group from the plane of the heterocycle, the H_X proton is removed sterically from the oxygen atom; this leads to the removal of the influence of the steric proximity of the heteroatom on the signal of the H_X proton, and its high-

TABLE 2. Parameters of the ^{13}C NMR Spectra of the 1-Vinyl-2-pyridones (IIa) and (IIIa) and Their Photodimers (IIb) and (IIIb)

Compound	Chemical shifts, ppm							
	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	CH_3	C_α	C_β
IIa	161,65	130,47	136,78	106,31	129,65	17,23	132,46	103,47
IIIa	161,06	119,53	151,60	109,26	131,10	21,29	131,75	102,93
IIb	—*	—*	136,86	132,43	60,45	23,86	132,37	93,57
IIIb	172,36	51,11	142,04	126,10	55,81	22,17	130,56	93,08

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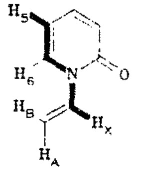
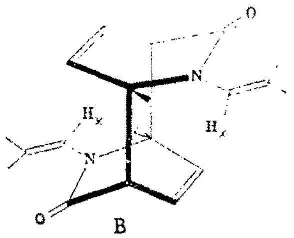
*The signals of the quaternary carbon atoms in the ^{13}C NMR spectrum of the photodimer (IIb) were not registered due to the low concentration.

field shift. Proceeding from these assumptions, it can be concluded that the disposition of the unsaturated fragments in 1-vinyl-6-methyl-2-pyridone (Va) is nonplanar.



A



B

In the transition to the photodimer of 1-vinyl-6-methyl-2-pyridone (Vb), the change of the parameters of the vinyl group in relation to dimers (Ib)-(IVb) and (VIb) takes place again (Table 1). The increase of the geminal SSCC $^2J_{AB}$ (1.4-2.0 Hz) and the disappearance of the distant spin–spin interaction of the $H_{(5)}$ and H_X protons correspond with the removal of the vinyl group from the plane passing through the N and C=O atoms (conformation B); this is caused by the steric influence of the CH_3 group at position 6 of the ring. The breaking of the conjugation with the vinyl group, which is expressed by the large low-field shift of the signals of the H_A and H_B protons (0.6-1.0 ppm), accompanies this [10]. The marked high-field shift of the H_X signal should especially be distinguished in the spectrum of the photodimer (Vb) in relation to compounds (Ib)-(IVb) and (VIb). A similar shift for compound (Va) in relation to the series (Ia)-(IVa) and (VIa) is significantly less (by 0.3-0.4 ppm). This may be associated with the presence of two factors. First, the effect of the steric proximity of the oxygen atom disappears in the molecule of the dimer (Vb). Second, in the case of the s-trans-orientation of the vinyl group in relation to the $C_{(4)}$–$C_{(5)}$ fragment (conformation B), the H_X proton falls into the region of shielding of the double bond [15] and undergoes additional high-field displacement. Therefore, the steric orientation of the vinyl group is also preserved in the photodimerization of 1-vinyl-6-methyl-2-pyridone (Va).

Regrettably, the very limited solubility of compounds (Ib)-(VIb) only allowed the ^{13}C NMR spectra of two molecules – (IIb) and (IIIb) – to be obtained (Table 2). An interesting feature of these spectra is the strong shielding of the C_β atom of the vinyl group (~93 ppm) which testifies to the effectiveness of the conjugation of the unshared electron pair of the nitrogen atom with the vinyl group [16] in the photodimers. In the initial compounds (IIa) and (IIIa), the shielding of the C_β atom is significantly less (by 10 ppm). This means that the strengthening of the conjugation of the unshared electron pair of the nitrogen atom with the vinyl group proceeds in the process of the photodimerization on account of the loss of its conjugation with the heterocycle.

EXPERIMENTAL

The impulse spectrometers Tesla BS-567A (100 MHz) and Bruker WP-200 SY (200 MHz) were utilized to register the PMR spectra. The time for the reading of the decrease of the signal of the free induction comprised 5 sec; the total time for the buildup of one spectrum comprised from 5 to 40 min. The ^{13}C NMR spectra were registered on a Tesla BS-567A spectrometer (25.1 MHz). The time for the buildup of one ^{13}C NMR spectrum was 2-3 h. The solvent utilized was $CDCl_3$. The internal standard was HMDS. The measurements were performed at room temperature (25 ± 2°C).

trans-3,7-Diazatricyclo[4.2.2.2^{2,5}]dodeca-9,11-diene-3,7-divinyl-4,8-dione (Ib). This was obtained by maintaining the solution of 0.6 g (0.05 mole) of the compound (Ia) [17] in 2 ml of ethanol in the course of 70 h in the light and at room temperature. The precipitated crystals are washed with ethanol and dried. The yield was 0.15 g (25%); mp 216°C.

By analogy, the monomers (IIa)-(VIa) [18] yielded the dimers (IIb) (mp 184-186°C), (IIIb) (mp 235-236°C), (IVb) (mp 233-234°C), (Vb) (mp 184-186°C), and (VIb) (mp 213-215°C).

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