New Isomeric *N*-Substituted Hydrazones of 2-, 3- and 4-Pyridinecarboxaldehydes and Methyl-3-Pyridylketone

Elżbieta Wyrzykiewicz and Alfred Błaszczyk

Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Dedicated to the memory of Professor Raymond N. Castle

Twelve compounds unknown in the literature *N*-(*E*)-2-stilbenyloxymethylenecarbonyl substituted hydrazones of 2-, 3- and 4-pyridinecarboxaldehydes, as well as methyl-3-pyridylketone have been prepared. The stereochemical behavior of these compounds in dimethyl-d_6 sulfoxide solution has been studied by ^{1}H NMR technique. The *E* geometrical isomers and *cis/trans* amide conformers have been found for *N*-substituted hydrazones **1-12**. EI induced mass spectral fragmentation of these compounds were also investigated. The data obtained create the basis for distinguishing isomers.

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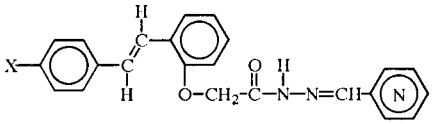
Introduction.

We have previously reported the synthesis and physicochemical properties [1] as well as results of a mass spectrometric study [2] of *N*-(*E*)-4-stilbenyloxymethylenecarbonyl substituted hydrazones of 2-, 3- and 4-pyridinecarboxaldehydes. Our studies have been recently extended to *N*-(*E*)-2-stilbenyloxymethylenecarbonyl substituted hydrazones of 2-,3- and 4-pyridinecarboxaldehydes **1-9**, as well as methyl-3-pyridylketone **10-12** (Figure 1).

This paper deals with the synthesis, physicochemical properties and mass spectral fragmentation of these compounds. The analysis of the mass spectra of **1-12** is connected with the differentiation of isomers of the hydrazones investigated in conjunction with the interpretation of the values of μ (*i.e.* the ratio of intensity of the selected fragment ion peak to that of the molecular ion peak).

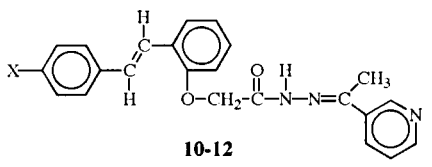
Results and Discussion.

Treatment of the corresponding 2-, 3-and 4-pyridinecarboxaldehydes and methyl-3-pyridylketone with the hydrazide of (*E*)-2-stilbenyloxyacetic acid [(*E*)-4'-chloro-2-stilbenyloxyacetic acid, or (*E*)-4'-nitro-2-stilbenyloxyacetic acid] in boiling absolute ethanol afforded **1-12** (Figure 1).



1-9

1 X = H **4** X = Cl **7** X = NO_2
2 X = H **5** X = Cl **8** X = NO_2
3 X = H **6** X = Cl **9** X = NO_2



10-12

10 X = H
11 X = Cl
12 X = NO_2

Figure 1

The hydrazones **1-12** may exist as *Z/E* geometrical isomers about the C=C bond of ethylene bridge in the stilbene portion of the molecule, *Z/E* geometrical isomers about the C=N bond of hydrazone moiety, as well as *cis/trans* amide conformers (Figure 2). According to the literature [9,10]

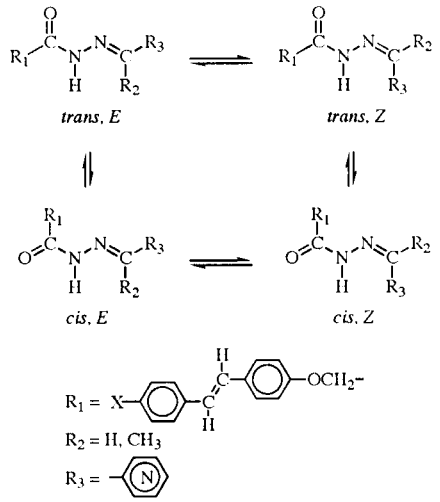
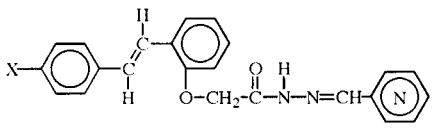


Figure 2

N-acyl substituted derivatives of hydrazones of pyridinecarboxaldehydes are present in dimethyl d_6-sulfoxide solution in the form of geometric *E* isomer about C=N double bond. In the cases of *N*-substituted hydrazones of 2-pyridylcarboxaldehydes, *Z* geometric izomers can be stabilized in less polar solvents by an intramolecular hydrogen bond [10]. The structures of all compounds synthesized were confirmed by elemental analyses, UV/VIS, IR, ^{1}H NMR and mass spectral data (Tables 1-5). (*E*)-configuration in the stilbene part of the molecules of **1-12** was determined on the basis of their UV/VIS and IR spectra.

It has been pointed out that in the UV/VIS spectra of **1-12** λ_{max} are in the range 289-357.5 nm (Table 2). According to the literature [3-5] (*E*)-stilbenes exhibited the

Table 1



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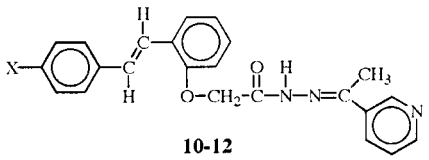


10-12

Compound	N	X	Formula (mol. weight))	M.p. [°C]	Yield [%]	R_f TLC	Reaction time hours	Crystallization solvent
1	2-	H	$C_{22}H_{19}N_3O_2$ 357.15	149-151	71.0	0.79	2.0	MeOH
2	3-	H	$C_{22}H_{19}N_3O_2$ 357.15	166-168	83.0	0.77	1.5	MeOH
3	4-	H	$C_{22}H_{19}N_3O_2$ 357.15	148-150	82.0	0.75	1.5	n-PrOH
4	2-	Cl	$C_{22}H_{18}N_3O_2Cl$ 391.11	203-205	84.0	0.89	1.5	MeOH
5	3-	Cl	$C_{22}H_{18}N_3O_2Cl$ 391.11	204-206	81.0	0.78	1.5	MeOH
6	4-	Cl	$C_{22}H_{18}N_3O_2Cl$ 391.11	192-195	85.0	0.76	1.5	MeOH
7	2-	NO_2	$C_{22}H_{18}N_4O_4$ 402.13	207-209	87.0	0.74	1.5	DMF/EtOH 1/100
8	3-	NO_2	$C_{22}H_{18}N_4O_4$ 402.13	243-245	84.0	0.68	1.0	DMF/EtOH 1/100
9	4-	NO_2	$C_{22}H_{18}N_4O_4$ 402.13	225-227	89.0	0.70	1.5	MeOH
10	3-	H	$C_{23}H_{21}O_2N_3$ 371.44	179-182	91.4	0.72	3.0	EtOH
11	3-	Cl	$C_{23}H_{20}O_2N_3Cl$ 405.88	195-198	90.7	0.74	3.0	EtOH
12	3-	NO_2	$C_{23}H_{20}O_4N_4$ 416.44	249-252	87.9	0.70	3.0	DMSO

values of λ_{max} in the range 290-360 nm and for (*Z*)-stilbenes values of λ_{max} fall in the range 260-280 nm. The infrared spectra of **1-12** show a strong band in the range 951-973 cm^{-1} which according to the literature [6,7] can be attributed to the out-of-plane deformation vibration of the C-H bond of the (*E*)-ethylene bridge of the stilbene skeletone (Table 2).

The ratio of amide *cis/trans* conformers can be easily quantified by ^1H NMR techniques. The studies were carried out in the same manner as reported previously for the cases of *N*-(*E*)-4-stilbenyloxymethylenecarbonyl substituted hydrazones of 2-, 3- and 4-pyridinecarboxaldehydes [1]. Analysis of variable temperature ^1H NMR spectra in dimethyl-d_6 sulfoxide solution of *N*-(*E*)-2-stilbenyl-

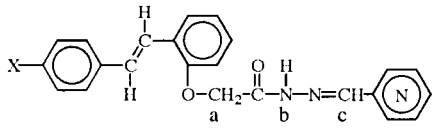
Table 2

Compound	UV/VIS λ_{max} [nm] (log ε)	IR δ_{CH} [cm^{-1}] CH=CH (*E*)	Elemental Analysis (%) Calcd. C	H	Found N	C	H	N
1	298.2 (4.58) [a]	974	73.95	5.32	11.76	73.68	5.11	11.81
2	296.0 (4.57) [a]	975	73.95	5.32	11.76	73.75	5.37	11.69
3	297.1 (4.58) [a]	975	73.95	5.32	11.76	73.89	5.20	11.57
4	291.5 (4.54) [a]	954	67.43	4.59	10.71	67.28	4.43	10.79
5	288.5 (4.65) [a]	956	67.43	4.59	10.71	67.31	4.49	10.48
6	289.7 (4.58) [a]	955	67.43	4.59	10.71	67.40	4.52	10.69
7	357.5 (4.37) [a]	964	65.66	4.51	13.92	65.70	4.46	13.98
8	351.4 (4.48) [a]	967	65.66	4.51	13.92	65.57	4.47	13.90
9	354.6 (4.39) [a]	965	65.66	4.51	13.92	65.63	4.43	13.96
10	314.0 (4.27) [a]	953	74.37	5.70	11.31	74.20	5.62	11.30
11	322.5 (4.21) [a]	959	68.06	4.97	10.35	68.00	4.90	10.12
12	375.5 (4.28) [b]	955	66.34	4.84	13.45	66.28	4.82	13.20

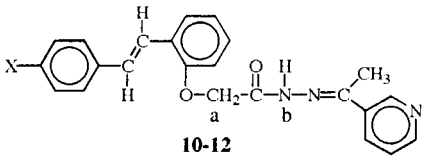
[a] MeOH. [b] DMSO.

Table 3

^{1}H-NMR Chemical Shifts of *N*-substituted Hydrazones of Pyridinecarboxaldehydes **1-12** [a].



1-9



10-12

Compound	a	c	b	Ar	Percentage of Conformer (%)
1	5.31 s	8.68 s	11.87 s	8.09-7.00 m	69.4 cis* 26.7 cis**
	4.82 s	8.36 s	11.95 s		30.6 trans* 73.3 trans**
2	5.29 s	8.90 s	11.84 s	8.63-6.98 m	70.0 cis* 23.3 cis**
	4.81 s	8.85 s	11.99 s		30.0 trans* 76.7 trans**
3	5.30 s	8.65 s	11.94 s	8.02-6.98 m	72.0 cis* 26.8 cis**
	4.82 s	8.31 s	11.98 s		28.0 trans* 73.2 trans**
4	5.30 s	8.62 s	11.85 s	8.08-6.98 m	70.6 cis* 32.2 cis**
	4.82 s	8.35 s	11.92 s		29.4 trans* 67.8 trans**
5	5.29 s	8.90 s	11.81 s	8.63-6.98 m	70.9 cis*
	4.80 s	8.85 s	11.85 s		29.1 trans*
6	5.30 s	8.65 s	11.92 s	8.01-6.98 m	73.3 cis* 32.4 cis**
	4.81 s	8.31 s	11.95 s		26.7 trans* 67.6 trans**
7	5.34 s	8.62 s	11.87 s	8.26-7.01 m	71.1 cis*
	4.86 s	8.35 s	11.94 s		28.9 trans*
8	5.49 s	9.01 s	11.78 s	8.70-7.07 m	70.6 cis*
	4.98 s	8.94 s	12.03 s		29.4 trans*
9	5.33 s	8.65 s	11.93 s	8.26-7.01 m	74.5 cis*
	4.85 s	8.31 s	11.97 s		25.5 trans*
10	5.32 s	2.32 s	11.10 s	9.04-6.95 m	81.8 cis***
	4.89 s	2.34 s	10.77 s		18.2 trans***
11	5.32 s	2.31 s	11.05 s	9.03-6.96 m	81.2 cis***
	4.89 s	2.34 s	10.76 s		18.8 trans***
12	5.48 s	2.48 s	11.05 s	9.12-7.03 m	82.6 cis***
	5.02 s	2. 46 s	10.91 s		17.4 trans***

[a] Spectra determined in *DMSO-d_6, **$CDCl_3$, ***DMF-d_7 at 25 °C and shifts are reported in ppm (δ) downfield from tetramethylsilane, s - singlet, m- multiplet.

Table 4

Elemental Composition and Relative Intensities of the Ion Peaks in the Spectra of **1-9** According to High Resolution Data

Ion	M/z	Elemental composition	Relative Intensities % **1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
$M^{+\cdot}$	357	$C_{22}H_{19}N_3O_2$	47	100	100						
a	391	$C_{22}H_{18}N_3O_2Cl$				40	100	100			
	402	$C_{22}H_{18}N_4O_4$							20	100	100
b	253	$C_{16}H_{15}NO_2$	4	4	2						
	287	$C_{16}H_{14}NO_2Cl$				9	5	3			
	298	$C_{16}H_{14}N_2O_4$							2	13	5
c	209	$C_{15}H_{13}O$	8	3	2						
	243	$C_{15}H_{12}OCl$				5	3	3			
	254	$C_{15}H_{12}NO_3$							4	5	4
d	196	$C_{14}H_{12}O$	30	41	41						
	230	$C_{14}H_{11}OCl$				21	42	43			
	241	$C_{14}H_{11}NO_3$							13	30	24
e	178	$C_{14}H_{10}$	11	7	15	11	11	10	6	19	12
f	165	$C_{13}H_9$	14	10	24	22	26	25	17	35	30
g	162	$C_8H_8N_3O$	6	9	9	7	22	17	5	85	73
h	148	$C_7H_6N_3O$	41	3	2	44	5	3	40	7	4
i	120	$C_6H_6N_3$	100	4	4	100	10	5	100	20	12
j	92	C_6H_6N	95	5	8	85	5	4	87	11	7

Table 5

Elemental Composition and Relative Intensities of the Ion Peaks in the Spectra of **10-12** According to High Resolution Data

Ion	M/z	Elemental composition	Relative Intensities % **10**	**11**	**12**
$M^{+\cdot}$ *a*	371	$C_{23}H_{21}N_3O_2$	100		
	405	$C_{23}H_{20}N_3O_2Cl$		90	
	416	$C_{23}H_{20}N_4O_4$			71
b	253	$C_{16}H_{15}NO_2$	1		
	287	$C_{16}H_{14}NO_2Cl$		1	
	298	$C_{16}H_{14}N_2O_4$			11
c	209	$C_{15}H_{13}O$	6		
	243	$C_{15}H_{12}OCl$		4	
	254	$C_{15}H_{12}NO_3$			4
d	196	$C_{14}H_{12}O$	38		
	230	$C_{14}H_{11}OCl$		25	
	241	$C_{14}H_{11}NO_3$			8
e	178	$C_{14}H_{10}$	18	14	10
f	165	$C_{13}H_{10}$	26	30	23
g	176	$C_9H_{10}N_3O$	74	100	100
h	162	$C_8H_8N_3O$	15	20	15
i	134	$C_7H_8N_3$	13	15	13
j	92	C_6H_6N	11	7	6

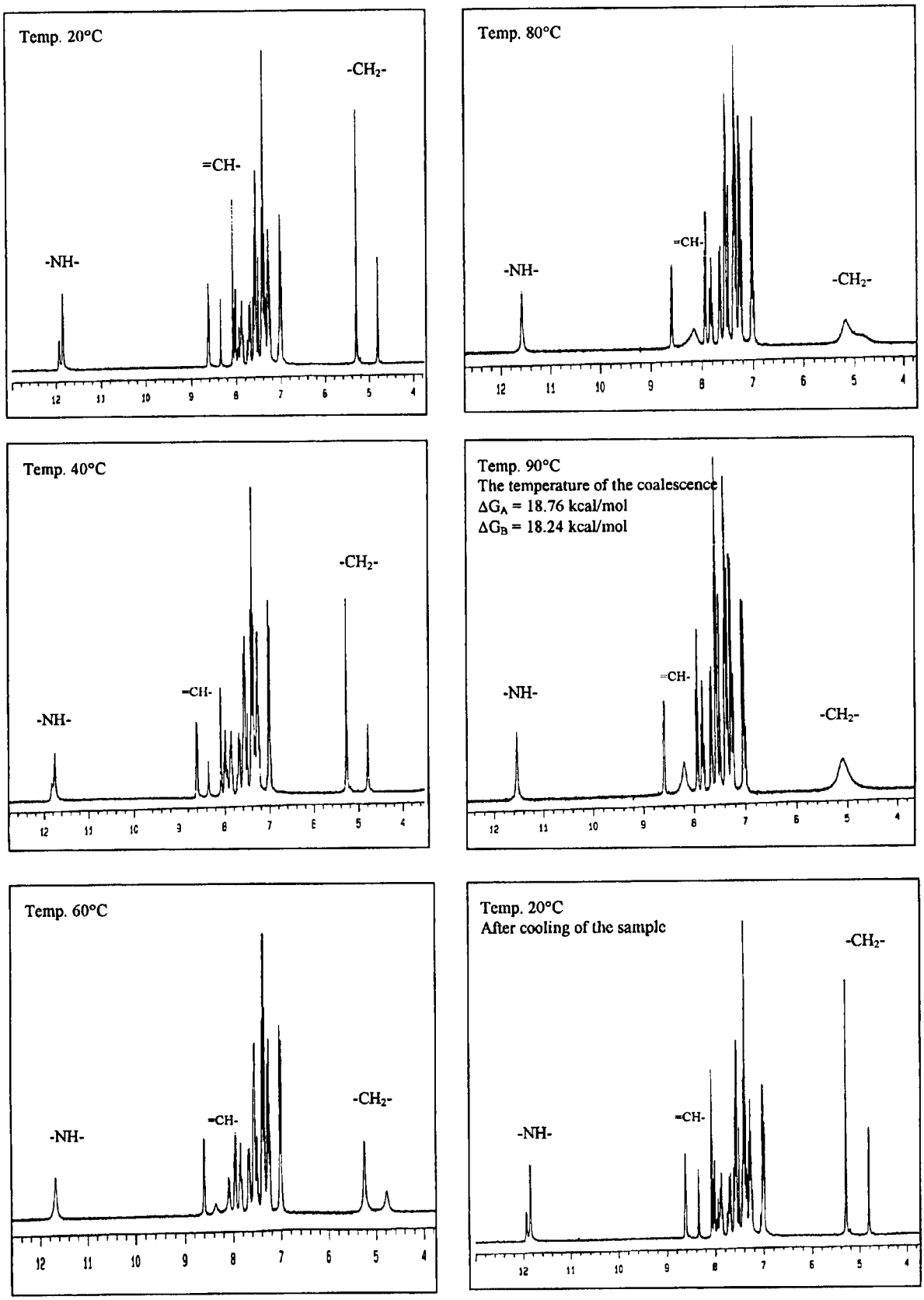
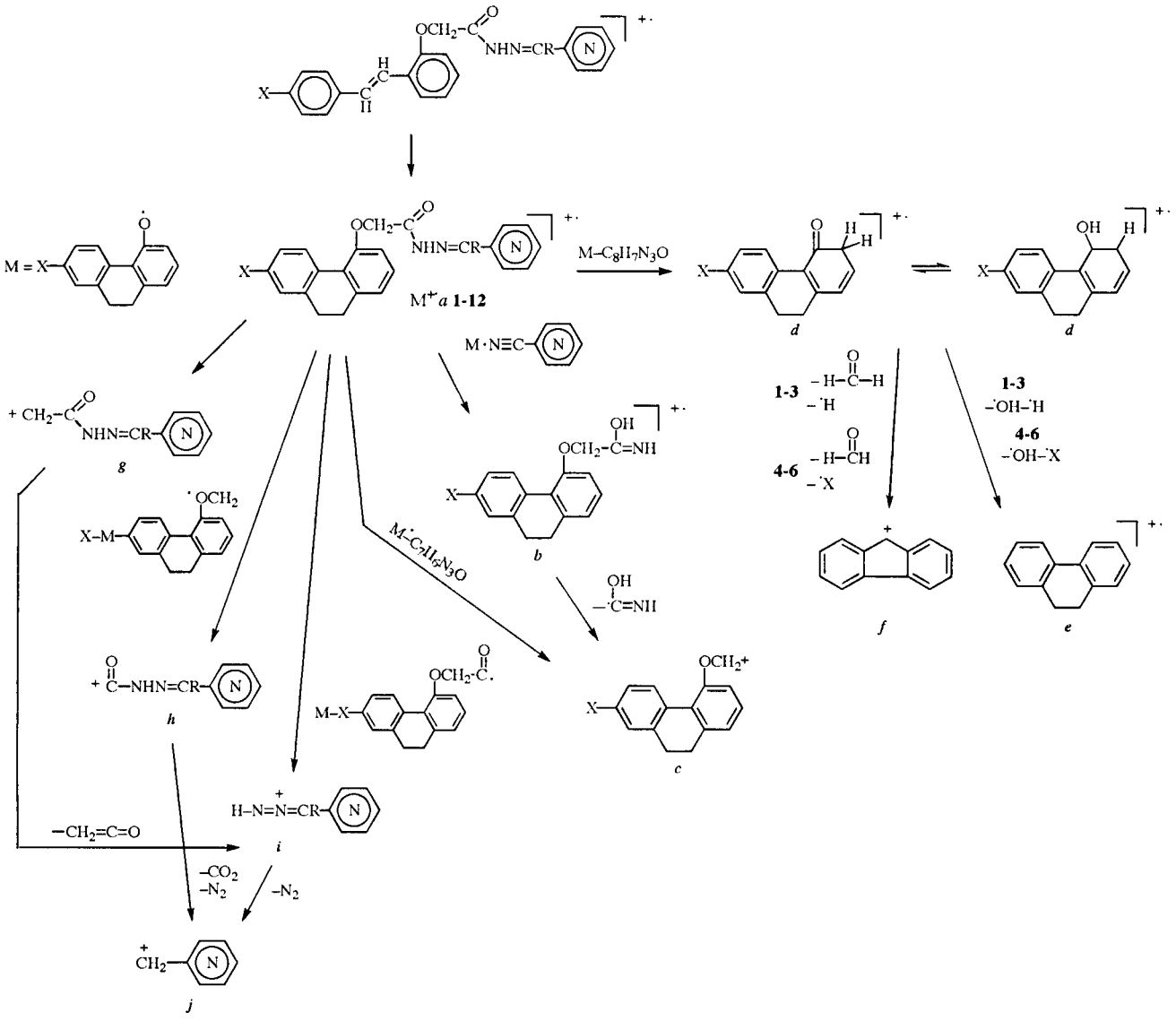


Figure 3. ^{1}H NMR spectra of **1**.

oxymethylenecarbonyl substituted hydrazone of acetone, established earlier the positions of the singlets corresponding to the methylene protons of the *cis* and *trans* amide conformers, the value of the coalescence temperature and the rate of *cis/trans* isomerization [11]. The data obtained allowed us to make measurements of the ratio of *cis/trans* amide conformers, and establish that the conversion of *cis /trans* amide conformers was the only process of isomerization. In order to acquire information about the stereochemical behavior of **1-12** in solution we have investigated ^{1}H NMR spectra of these compounds in DMSO-d_6 (**1-9**), $CDCl_3$ (**1-4,6**) and DMF-d_7 (**10-12**).

In the ^{1}H NMR spectra of **1-12** are seen two sets of singlets of methylene, imine as well as methine groups are observed (**a, b** and **c** Table 3). According to our previous data concerning *N*-(*E*)-2-stilbenyloxymethylenecarbonyl substituted hydrazone of acetone [11], the upfield lines of methylene, methine and imine protons have been assigned to *cis* amide conformers, and the downfield lines of protons of the same groups to the *trans* amide conformers. The rate of *cis/trans* isomerization of **1-3** in dimethyl-d_6 sulfoxide was followed by variable temperatures ^{1}H NMR (20, 40, 60, 80, 90°C) in order to evaluate the energy barrier of *cis/trans* conversion (Figure 3 compound **1**). The coalescence of the methylene groups of conformers **1-3** present in dimethyl-d_6 sulfoxide solution occurred at about 90 °C. The ΔG_A value 18.76 kcal/mol (*cis* amide conformer) and ΔG_B value 18.24 kcal/mol (*trans* amide conformer) were found by dynamic ^{1}H NMR using the well-known coalescence temperature method [12]. The values of ΔG_A and ΔG_B were the same for all the investigated compounds **1-3**. The intensities of the ^{1}H signals in the range of 5.29-5.49 δ and 4.80-5.02 δ allowed

Scheme 1



us to measure the ratio of the *cis/trans* amide conformers. The chemical shifts and percentage of conformers **1-12** in DMSO-d_6, $CDCl_3$ and DMF-d_7 are summarized in Table 3. It ought to be pointed out that compounds **5** and **7-12** are insoluble in $CDCl_3$, whereas compounds **10-12** are insoluble in DMSO-d_6. The ^1H NMR spectra of **1-9** demonstrated that these hydrazones behave similarly in dimethyl-d_6 sulfoxide solution as *N*-(*E*)-4-stilbenyloxymethylenecarbonyl substituted hydrazones of 2-, 3-, and 4-pyridinecarboxaldehydes **1a-6a**, (Figure 4) which were investigated by us previously [1]. When dissolved in this solvent, the *E* geometric isomers of these compounds reach a rapid *cis/trans* amide equilibrium, with the *cis* conformer predominating. The same situation is observed in the DMF-d_7 solution of **10-12**. It is clear that the position of the annular nitrogen atom in the phenyl ring of hydrazones **1-12**, as well as the position of oxymethylenecarbonylhydrazoneazabenzylidyne subsituent in the phenyl ring of the (*E*)-stilbene skeleton of **1-12**, as well as their 4-substituted counterparts **1a-6a** [1] have no influence on the ratio of *cis/trans* amide conformers of these commpounds. It should be mentioned that in compounds **1-4** and **6** in the $CDCl_3$ solution the trans conformer predominates.

The lack of influence due to a change of the position from 4- to 2- of the oxymethylenecarbonylhydrazoneazabenzylidene substituent in the phenyl ring of the (*E*)-stilbene skeleton on the stereochemical behavior of **1-12** was the driving force for the investigation of the mass fragmentation of these compounds. We wish to establish whether it would be possible to distinguish *N*-(*E*)-2-stilbenyloxymethylenecarbonyl substituted hydrazones of pyridine-carboxaldehydes **1-6** from their *N*-(*E*)-4-stilbenyloxymethylenecarbonyl substituted isomers **1a-6a**, (Figure 4) [2]. Moreover we wished to find out if it would be possible to differentiate the isomeric hydrazones derivatives of 2-, 3- and 4-pyridinecarboxaldehydes **1-12** on the basis of the differences in the values of μ (*i.e.* the ratio of intensity of the selected fragment ions peak to that of the molecular ion peak).

On the basis of low and high resolution electron ionization as well as B/E linked scan mass spectra (Tables 4-5), the principal mass spectral fragmentation routes of **1-12** are interpreted as shown in Scheme 1. It should be pointed out that 9,10-dihydrophenanthrene type structure of the molecular ions shown in Scheme 1 are conjectural, but consistent with those previously published in literature [2, 13-18]. The principal mass fragmentation pathways of **1-12** are similar to those of their isomeric *N*-(*E*)-4-stilbenyloxymethylenecarbonyl substituted hydrazones of 2-, 3- and 4-pyridinecarboxaldehydes **1a- 6a** (Figure 4) [2] but show differences in the abundances of ions. The EI–induced mass fragmentation of **1-12** begins with the cleavage of the oxymethylenecarbonylhydrazonazabenzylidene chain linking the (*E*)-stilbene and pyridine molecules of these compounds (Scheme 1). The charge-site initiated inductive cleavages *i* of O-Csp_3 , Csp_2 –N bonds (ions *g, i, c,*) as well as the radical-site initiated α-cleavage of the Csp_3 -Csp_2 bond (ion *h*), are observed as the molecular ions of these compounds decompose.

It is found that the cleavage of the O-Csp_3 bond of the methylenoxy moiety of this chain follows a Mc Lafferty rearrangement involving the migration of an hydrogen atom to the phenyl ring of (*E*)-stilbene skeleton (ions *d*). The second McLafferty rearrangement involving the cleavage of the N-N bond, with simultaneous transfer of hydrogen, producing the odd-electron fragment ion *b*.

Table 6 presents for all compounds investigated **1-12**, the ratios of the intensities of *h, i, d, g* ion peaks to those of the parent ion peak *i.e.*,

$$\mu_1 = \frac{h}{a} \quad \mu_2 = \frac{i}{a} \quad \mu_3 = \frac{d}{a} \quad \mu_4 = \frac{g}{a}$$

Because the values of μ are highly dependent on the relative intensities of the ions, results of three independent measurements were averaged. This procedure guarantees that the results with the differences of the relative intensities of the ions on level of 2-3% between each particular scan are reliable. As can be seen from the data in Table 6, the differences between the relative intensities of the peaks of the selected fragment ions *h, i , d , g* and $M^{+\cdot}$ *a* ions i. e. the values of μ_1-μ_4 for **1-12** may be sufficient to differentiate isomers. It is possible to distinguish isomeric hydrazones of 2-, 3- and 4-pyridinecarboxaldehydes with *N*-(*E*)-2- and 4-stilbenyloxymethylenecarbonyl substituent, as well as isomeric hydrazones with annular nitrogen atom situated at 2-, 3- or 4- position of the pyridine ring.

N-(*E*)-2-stilbenyloxymethylenecarbonyl substituted hydrazones derivatives of 2-pyridinecarboxaldehydes **1,4** may be distinguished from their isomeric *N*-(*E*)-4-stilbenyloxy- methylene carbonyl substituted counterparts **1a, 4a** [2], on the basis of differences in the higher values of μ_1 and μ_2 (Tables 6 and 7). *N*-(*E*)-2-stilbenyloxymethylenecarbonyl substituted hydrazones of 3-, and 4-pyridinecarboxyaldehydes **2, 5, 6** may be distinguished from their *N*-(*E*)-4-stilbenyloxymethylenecarbonyl substituted counterparts **2a, 5a, 6a** [2] on the basis of the highest values of μ_3 (Tables 6 and 7). The only exception is *N*-(*E*)-2-stilbenyloxymethylenecarbonyl substituted hydrazone of 3-pyridinecarboxaldehyde **3** because the values of μ_1, μ_2 and μ_3 of this compound are almost the same that those of *N*-(*E*)-4-stilbenyloxymethylenecarbonyl substituted isomer **3a** [2].

$$\mu_1, \mu_2 \ \mathbf{1, 4} > \mu_1, \mu_2 \ \mathbf{1a, 4a}$$
$$\mu_3 \ \mathbf{2a, 5a, 6a} > \mu_3 \ \mathbf{2, 5, 6}$$

In the series of **4-12** it is also possible to use the values of μ_2, μ_3 and μ_4 in the differentiation of the 2-, 3- or 4-position of nitrogen atom in the pyridine ring according to the following sequences:

μ_2 2 > μ_2 3 > μ_2 4	**4-9**
μ_3 2 > μ_3 3 > μ_3 4	**10-12**
μ_4 4 > μ_4 3 > μ_4 2	**10-12**

In the series of **1-3** the hydrazone **1** with the nitrogen atom in position 2 of the pyridine ring may be distinguished from isomeric hydrazones with annular nitrogen atom in positions 3- and 4- of the pyridine ring on the basis of the higher values of μ_1. In the cases of isomeric **2** and **3** all the values of μ_1, μ_2, μ_3 and μ_4 are almost the same, so it is impossible to differentiate these compounds on the basis of the differences in the values of μ.

Conclusions.

We found that, for *N*-(*E*)-2- and 4-stilbenyloxymethylene substituted hydrazones of 2-, 3- and 4-pyridinecarboxaldehydes, the ratio of *cis/trans* amide conformers in DMSO-d_6 solution is almost the same. Also the position of the oxymethylenecarbonyl substituent in the stilbene skeleton has no influence on this ratio.

The position of the annular nitrogen atom in pyridine ring of **1-12** does not affect the ratio of *cis/trans* amide conformers. The change of the polar solvent (DMSO-d_6) into the non-polar solvent ($CDCl_3$) influences the ratio of *cis/trans* amide conformers of **1-4** and **6**.

The basic mass framentation of **1-12** is due to cleavages of the O-Csp_3 , Csp_3 –Csp_2, Csp_3–N and Csp_2–N bonds of the oxymethylenecarbonylhydrazonazabenzylidene chain linking the (*E*)-stilbene and pyridine moieties of these compounds. The differences in the values μ_1- μ_4 (*i.e.* the ratio of the intensities of the selected ion peaks to the molecular ion $M^{+\cdot}$) are useful for the differentiation of isomers in the series of isomeric hydrazones **1-12**, as well as **1-12** in comparison with N-(*E*)-4-stilbenyloxymethylenecarbonyl substituted hydrazones of 2-, 3- and 4-pyridinecarboxaldehydes (**1a-6a**) [2].

EXPERIMENTAL

Purity of all described compounds was checked by m.p.'s, TLC and elemental analysis. Melting points (uncorrected) were determined on a Böetius microscope hot stage. R_f values refer to TLC silica gel F_{254} TLC plates (Merck) developed with $CHCl_3$:MeOH 5:1 and observed under UV light (λ = 254 and 366 nm). UV/VIS spectra were recorded with a Specord UV/VIS spectrophotometer in methanol. IR spectra were recorded with a FT-IR Bruker IFS-113v Spectrophotometer in KBr pellets. ^{1}H NMR spectra were determined with a Varian Gemini 300 (300 MHz) spectrophotometer in DMSO-d_6 solution with TMS as internal standard. Elemental analyses were performed with a Perkin-Elmer 240 C-CHN analyzer.

Hydrazides of (*E*)-2- stilbenyloxyacetic acid [(*E*)-4'-chloro and (*E*)-4'-nitro-2-stilbenyloxyacetic acid)] were obtained according to literature [11]. Low- and high-resolution mass spectra were recorded on an AMD-Intectra GmbH-Harpstedt D-27243 Model 402 two-sector mass spectrometer (ionizing voltage 70 eV, accelerating voltage 8 kV, resolution 10,000). Samples were introduced by a direct insertion probe at a source temperature of ~150°C. The elemental compositions of the ions were determined by the peak matching method relative to perfluorokerosene and using the same instrument. All masses measured agreed with those of the composition listed in column 3 of the Tables 4-5 to within ± 2 ppm. The B/E linked scan spectra in the first field-free region were investigated using helium as the collision gas at a pressure of 1.73×10^{-5} with the ion source temperature of 180 °C, ionization energy of 70 eV and an accelerating voltage of 8 kV. The values of μ_1, μ_2, μ_3, μ_4 were calculated as averages of three measurements.

Synthesis of 2-, 3- and 4-Pyridinecarboxaldehydes **1-9** and Methyl-3-Pyridylketone **10-12**.

General Procedure.

To a boiling solution of 1×10^{-3} mole of corresponding hydrazide of (*E*)-2-stilbenyloxyacetic acid[(*E*)-4'-chloro- or (*E*)-4'-nitro-2-stilbenyloxyacetic acid] in 50 ml of absolute ethanol the solution of 3×10^{-3} mole of corresponding 2-, 3- and 4-pyridincarboxaldehyde (or methyl-3-pyridylketone) was added dropwise. The reaction mixture was refluxed for 1-3 hours (Table 1). Then half of the volume of the solvent was evaporated on a rotatory evaporator and the residue was cooled and the precipitated solid was filtered, dried and recrystallized from a solvent selected (Table 1).

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