Chemistry of Heterocyclic Compounds, Vol. 36, No. 3, 2000

SYNTHESIS OF SCHIFF'S BASES FROM FURYLACROLEINS AND AMINOPYRIDINES IN THE PRESENCE OF MOLECULAR SIEVES*

I. Iovel, L. Golomba, J. Popelis, A. Gaukhman, and E. Lukevics

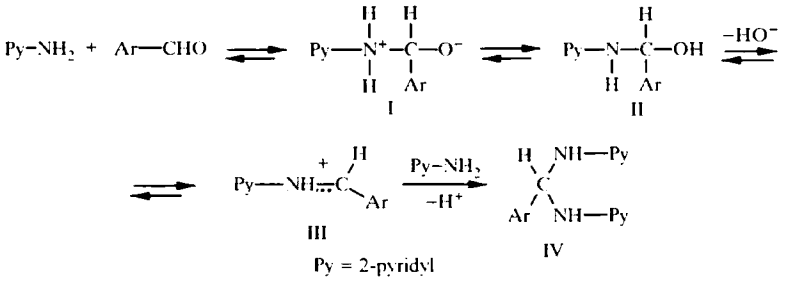
We have studied the reactions of (hetero)aromatic aldehydes with 2-aminopyridines. The results obtained suggest that molecular sieves play a role in these processes not only as a dehydrating agent but also as an acid catalyst. We have synthesized a series of novel heterocyclic azomethines.

Keywords: 2-aminopyridine, furylacrolein, Schiff's bases, catalysis by zeolites.

Schiff's bases, obtained by condensation of nitrofurylacrolein with aniline derivatives, exhibit pesticidal action [1]. It seems promising to develop methods for synthesis of azomethines by reactions of furylacrolein and its derivatives (some conversions of which we studied recently [2]) with heterocyclic amines (in particular, 2-aminopyridines).

Concerning synthesis of imines based on 2-aminopyridines, it is known that reaction of benzaldehyde with 2-aminopyridine, catalyzed by *para*-toluenesulfonic acid, leads to formation of the corresponding aldimine (N-benzylidene-2-aminopyridine) [3]. In the absence of a catalyst, the product of this reaction was unexpectedly the aminal N,N'-benzylidene-bis(2-aminopyridine) [4]. This type of reactivity for 2-aminopyridine suggests a rather high mobility of the first proton and a complicated elimination scheme for the second proton in the NH_2 group of this compound.

Usually aldehydes react easily with nucleophilic primary amines without addition of acids with formation of azomethines [5]. The basicity of 2-aminopyridine is characterized by $pK_a = 6.86$ [6], and it obviously forms a carbonium-immonium ion III. Most primary amines then convert to the imine, spliting out a proton from the nitrogen atom in this intermediate form. But 2-aminopyridine reacts differently, forming the aminal IV:



* Dedicated to Professor M. A. Yurovskaya on her Jubilee.

Latvian Institute of Organic Synthesis, Riga LV-1006; e-mail: iovel@osi.lv. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 324-335, March, 2000. Original article submitted May 20, 1999.

Obviously, the elimination scheme for the second proton from the NH_2 group of 2-aminopyridine is complicated because of the nature of the pyridine ring: the presence of a pair of electrons on the nitrogen atom, which makes it necessary to use an acid catalyst for synthesis of aldimines from this compound. But in our work, it was not possible to use strong acids because of the acidophobicity of the aldehyde substrates. We hypothesized that in this case, it would be optimal to use molecular sieves (MS), which as it is known are dehydrating agents and contain surface Brønsted and Lewis acid centers [7, 8]. The latter may react with pyridines through the nitrogen atom of the ring, resulting in a catalytic effect. Reaction of the amino group with the zeolite is less likely, since it is a less basic center in aminopyridines than the ring nitrogen [6].

In this work, we have studied reactions of three furylacroleins and also cinnamic aldehyde with three 2-aminopyridines and two anilines. We used the following aldehydes and amines: *trans*-3-(2-furyl)acrolein (**1a**), *trans*-3-(5-methyl-2-furyl)acrolein (**2a**), *trans*-3-(5-methyl-2-furyl)acrolein (**3a**), cinnamic aldehyde (**4a**); 2-aminopyridine (**1b**), 2-amino-3-methylpyridine (**2b**), 2-amino-6-methylpyridine (**3b**), aniline (**4b**), 3-trifluoromethylaniline (**5b**). In addition, we studied the reaction of benzaldehyde (**5a**) with amines **1b-3b** in the presence of zeolite 4 A.

The reactions of aldehydes with amines, used in equimolar amounts, were carried out in dry benzene at room temperature (the products obtained from aminopyridines are thermally unstable), periodically withdrawing samples and analyzing them by GLC and GLC-MS.

In Fig. 1, we present the results of an investigation of the reaction of furylacrolein with amine **3b** at room temperature in the presence of molecular sieves (for a concentration of 0.6 g per mmol substrate), and also anhydrous sodium sulfate (10 mmol/mmol substrate, 1.4 g/mmol). In the presence of zeolite, the target product is formed in up to 94% yield with practically complete conversion of both substrates (GLC), while in the presence of anhydrous sodium sulfate, although the product is formed, its yields and the conversion rates of the starting compounds are very low. We studied the effect of the zeolite concentration on this reaction. The curves presented in Fig. 2 are typical for catalytic processes. In the interval 0.4-1.4 g/mmol, the product yield is practically proportional to the amount of the molecular sieves; in this case, even low concentrations of such molecular sieves ensure complete conversion over the course of an appropriate time period.

In Table 1, we present the basic results for all the investigated reactions. Furylacrolein (**1a**) in the presence of sieves (1 g/mmol) reacts with all three studied aminopyridines **1b-3b** , forming the corresponding aldimines **1-3**. The derivatives **4, 5** of anilines **4b, 5b** were synthesized from this aldehyde using sodium sulfate. Similar results were obtained when carrying out the reactions of the methyl derivative **2a** with the indicated amines

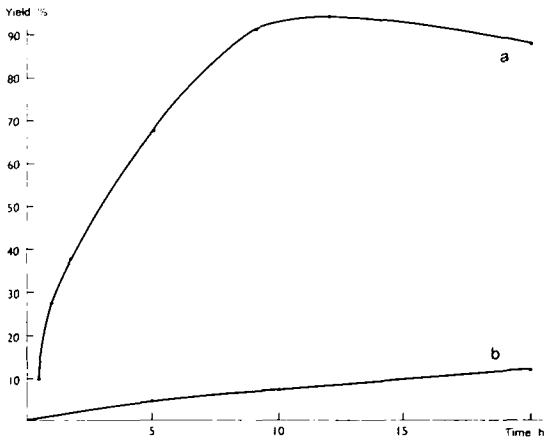


Fig. 1. Time dependence of the yield of N-[3-(2-furyl)-2-propenylidene]-2-amino-6-methylpyridine (**3**) in the reaction of furylacrolein (**1a**) with 2-amino-6-methylpyridine (**3b**) in the presence of: *a*) zeolite 4 A (0.6 g/mmol); *b*) anhydrous sodium sulfate (1.4 g/mmol).

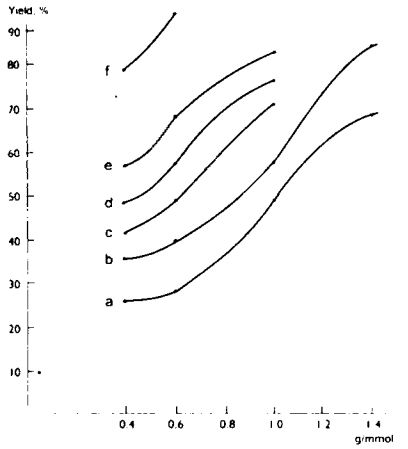
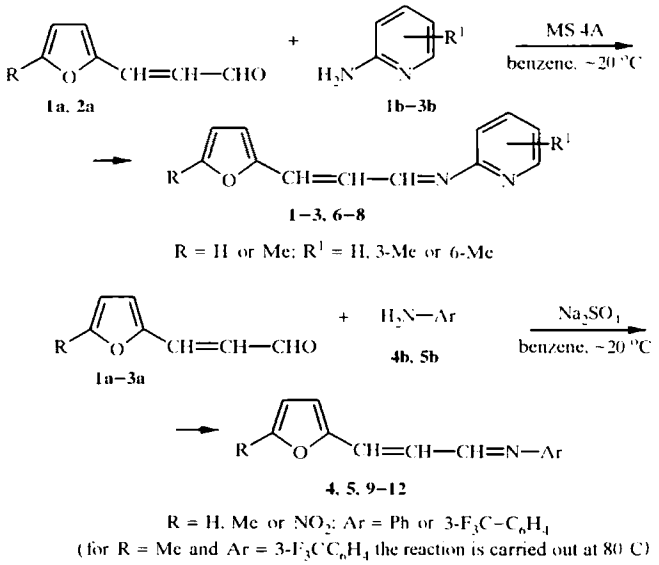


Fig. 2. Yield of N-[3-(2-furyl)-2-propenylidene]-2-amino-6-methylpyridine (**3**) in the reaction of furylacrolein (**1a**) with 2-amino-6-methylpyridine (**3b**) as a function of the concentration of zeolite 4 A for reaction times of 1-5, 9 h (a-e, f respectively).

1b-5b: in this case, the imines **6-10** are synthesized. The corresponding products **11, 12** are formed from nitrofurylacrolein (**3a**) only on reaction with aromatic amines (**4b, 5b**); reactions with aminopyridines **1b-3b** lead to rapid appearance of unidentified black substances similar to rubber.



The reaction time (Table 1) mainly correlates with the electrophilicity of the aldehydes (which among the studied furylacroleins, is maximum for the nitro derivative and minimum for the methyl substituted derivative) and the basicity of the amines. The latter have the following pK_a values: **1b** - 6.86, **2b** - 7.24, **3b** - 7.41 [6]; **4b** - 27.08, **5b** - 25.40 [9].

In studying the reactions of aldehyde **4a**, we obtained the corresponding azomethines **13-16** with participation of the amines **1b, 2b, 4b, 5b**. Amine **3b**, reacting with this aldehyde, gives a complicated mixture of products which could not be separated. As in the case of furylacrolein, the phenyl derivative of acrolein reacts with aminopyridines **1b, 2b** when treated with sieves, and anils may be synthesized in the presence of sodium sulfate.

TABLE 1. Characteristics of the Reactions* and the Synthesized Products

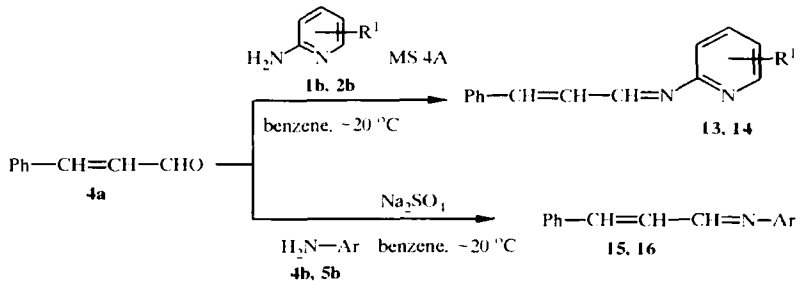
Starting		Reaction time, h	Product	Yield*[2], %	mp, °C	Color
aldehyde	amine					
1a	**1b**	35	1	62	64-66 (subl. 60-70°C/0.1 mm)	Yellow
	2b	14	2	64		Dark red
	3b	5	3	79	46-47 (subl. 60-70°C/0.1 mm)	Yellow
	4b	24	4	66	55-56	Brown
	5b	120	5	58	75-76	Yellow
2a	**1b**	69	6	44	73-75	Orange
	2b	45	7	62	-*[1]	Dark red
	3b	22	8	54	41-42	Orange
	4b	44	9	78	77-78	Yellow
	5b	12*[4]	10	75	-*[1]	Dark red
3a	**4b**	4	11	50	140-141	Yellow
	5b	12	12	45	118-119	Brown
4a	**1b**	46	13	53	73-74	Orange
	2b	34	14	43	-*[1]	Dark red
	4b	6	15	84	101-102	Orange
	5b	12	16	57	92-93	Yellow
5a	**1b**	30	17	66	-*[1]	Yellow
	2b	30	18	71	-*[1]	Yellow
	3b	30	19	70	-*[1]	Yellow

* The reactions with aminopyridines were carried out in the presence of molecular sieves 4 A (1 g/mmol), the dehydrating agent during synthesis of anils was anhydrous sodium sulfate (10 mmol/mmol substrate), the reactions were carried out at room temperature.

*[2] Yield of isolated products.

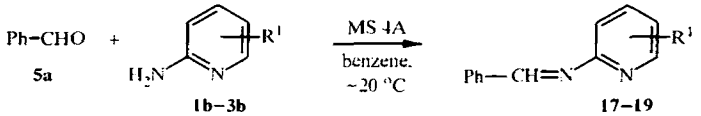
*[1] Oily substance.

*[4] With boiling in benzene.



R^1 = H or 3-Me; Ar = Ph or 3-F_3C-C_6H_4

The reactions of benzaldehyde with aminopyridines **1b-3b** in the presence of sieves 4 A lead to the corresponding benzylidene aminopyridines **17-19** and up to 100% yields (GLC) (Fig. 3). Some decrease in these values in the final stage of the processes is due to the instability of the indicated products. Formation of azomethines in high yield rather than aminals confirms the acid catalytic action of the zeolite.



R^1 = H, 3-Me or 6-Me

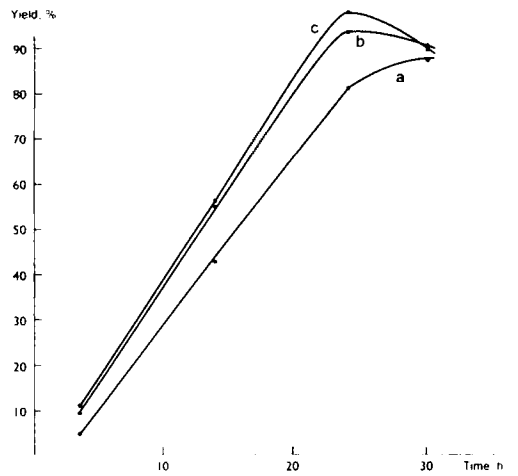


Fig. 3. Yield of N-benzylidene-2-aminopyridines **17-19** (a-c respectively) in the reaction of benzaldehyde (**5a**) with 2-aminopyridines **1b-3b** *vs.* the reaction time in the presence of zeolite 4 A (1.0 g/mmol).

After completion of the reaction, the sieve (or the sodium sulfate) was filtered off, the benzene was evaporated on a rotary evaporator, and the residues of the substrates were removed under vacuum (45-50°C/0.1 mm).

TABLE 2. Characteristics of Synthesized Compounds*

Compound	Empirical formula	Found, % / Calculated, %		
		C	H	N
1	$C_{12}H_{10}N_2O$	72.61 / 72.71	5.08 / 5.08	14.13 / 14.13
3	$C_{11}H_{12}N_2O$	72.98 / 73.58	5.67 / 5.66	13.40 / 13.20
4	$C_{13}H_{11}NO$	78.98 / 79.15	5.63 / 5.58	7.06 / 7.09
5	$C_{14}H_{10}NF_3$	63.34 / 63.39	3.78 / 3.77	5.23 / 5.28
6	$C_{13}H_{12}N_2O$	73.52 / 73.57	5.69 / 5.69	13.20 / 13.20
8	$C_{14}H_{14}N_2O$	74.22 / 74.31	6.22 / 6.24	12.34 / 12.38
9	$C_{14}H_{13}NO$	79.49 / 79.60	6.31 / 6.20	6.57 / 6.63
10	$C_{15}H_{12}NOF_3$	64.09 / 64.52	4.33 / 4.33	5.06 / 5.02
11	$C_{13}H_{10}N_2O_3$	64.09 / 64.39	4.04 / 4.13	11.45 / 11.56
12	$C_{14}H_9N_2O_3F_3$	54.34 / 54.20	2.86 / 2.92	8.91 / 9.03
13	$C_{11}H_{12}N_2$	80.81 / 80.74	5.94 / 5.81	13.24 / 13.45
15	$C_{15}H_{13}N$	86.75 / 86.83	6.46 / 6.27	6.55 / 6.75
16	$C_{16}H_{12}NF_3$	69.79 / 69.81	4.38 / 4.39	5.08 / 5.09

* Analysis for solid and viscous compounds.

TABLE 3. ^{1}H NMR Spectra of N-[3-(2-Furyl)-2-propenylidene]-2-aminopyridines **1-3** ($CDCl_3$, TMS, δ (ppm), *J* (Hz), 200 MHz)

Imine	Furyl			Pyridine ring				CH=CH m	CH=N m	CH_3 s
	H-3 d	H-4 dd	H-5 d	H-4	H-6 dd	H-3	H-5			
1	6.59, J = 3.6	6.47, J_1 = 3.6, J_2 = 1.8	7.50, J = 1.8	7.71 td, J_1 = 7.6, J_2 = 1.8	8.45, J_1 = 4.8, J_2 = 1.8	7.26 d, J = 7.6	7.13 m, J_1 = 7.6, J_2 = 4.8	6.7-7.1	8.93, J_1 = 6.0, J_2 = 3.1	---
2	6.58, J = 3.4	6.47, J_1 = 3.4, J_2 = 1.2	7.49, J = 1.2	7.51 d, J = 7.0	8.26, J_1 = 4.6, J_2 = 1.2	--	7.96 d J = 7.0	6.9-7.2	8.80, J_1 = 6.0, J_2 = 3.0	2.40
3	6.58, J = 3.4	6.47, J_1 = 3.4, J_2 = 1.8	7.50, J = 1.8	7.59, J = 7.7	--		6.8-7.2 (4H)		8.90, J_1 = 6.6, J_2 = 3.0	2.54

TABLE 4. ^{1}H NMR Spectra of N-[3-(2-Furyl)-2-propenylidene]anilines **4, 5** ($CDCl_3$, TMS, δ (ppm), *J* (Hz), 200 MHz)

Imine	Furyl			Aromatic ring, m	CH=CH m	CH=N m
	H-3 d	H-4 dd	H-5 d			
4	6.55, J = 3.0	6.46, J_1 = 3.0, J_2 = 1.2	7.48, J = 1.2	7.1-7.4 (5H)	6.8-7.1	8.18, J_1 = 7.4, J_2 = 1.1
5	6.60, J = 3.5	6.49, J_1 = 3.5, J_2 = 1.6	7.51, J = 1.6	7.3-7.5 (4H)	6.9-7.0	8.18, J_1 = 4.4, J_2 = 4.4

TABLE 5. ^{1}H NMR Spectra of N-[3-(5-Methylfur-2-yl)-2-propenylidene]-2-aminopyridines **6-8** ($CDCl_3$, TMS, δ (ppm), *J* (Hz), 200 MHz)

Imine	Furan ring		Pyridine ring				CH=CH m	CH=N m	CH_3 s	
	H-3 d	H-4 d	H-4	H-6 dd	H-3 d	H-5			Fur	Py
6	6.49	6.07	7.69 td	8.44,	7.24, *J* = 8.2	7.10 m,	6.8-7.2	8.90,	2.34	—
	J = 2.8		J_1 = 7.6, J_2 = 1.6	J_1 = 4.6, J_2 = 1.8		J_1 = 7.6, J_2 = 4.6		J_1 = 5.8, J_2 =3.3		
7	6.48	6.07	7.50 d, *J* = 7.0	8.26,	—	7.06 dd,	6.8-7.2	8.78,	2.35	2.39
	J = 3.6			J_1 = 4.6, J_2 = 1.2		*J* = 7.0, J_2 = 4.6		J_1 = 6.4, J_2 = 2.6		
8	6.47	6.07	7.58 t, *J* = 7.6	—	7.02 m		6.8-7.2	8.87,	2.35	1.53
	J = 3.0							J_1 = 6.4, J_2 = 2.5		

TABLE 6. ^{1}H NMR Spectra of N-[3-(5-Methylfur-2-yl)-2-propenylidene]anilines **9, 10** ($CDCl_3$, TMS, δ (ppm), *J* (Hz), 200 MHz)

Imine	Furan ring		Aromatic ring m	CH_α	CH_β	CH=N	CH_3 s
	H-3 d	H-4 d					
9	6.44, *J* = 2.9	6.06, *J* = 2.9	7.08-7.44 (5H)	6.81 d, *J*= 15.2	6.90 dd, J_1 = 15.2, J_2 = 7.6	8.16 d, *J* = 7.6	2.34
10	6.49, *J* = 2.8	6.09, *J* = 2.8	7.18-7.56 (4H)	6.7-7.1 m (2H)		8.15 m, J_1 = 4.9, J_2 = 3.9	2.36

TABLE 7. ^{1}H NMR Spectra of N-[3-(5-Nitrofur-2-yl)-2-propenylidene]anilines **11, 12** ($CDCl_3$, TMS, δ (ppm), *J* (Hz), 200 MHz)

Imine	Furan ring		Aromatic ring m	CH_α d	CH_β dd	CH=N d
	H-3 d	H-4 d				
11	6.73, *J* = 3.6	7.36, *J* = 3.6	7.1-7.5 (5H)	6.93, *J* = 15.8	7.23, J_1 = 15.8, J_2 = 8.8	8.25, *J* = 8.8
12	6.76, *J* = 3.4	7.34, *J* = 3.4	7.3-7.5 (4H)	6.98, *J* = 16.0	7.27, J_1 = 16.0, J_2 = 8.8	8.24, *J* = 8.8

TABLE 8. ^{1}H NMR Spectra of N-[3-Phenyl-2-propenylidene]-2-aminopyridines **13, 14** and N-[3-Phenyl-2-propenylidene]anilines **15, 16** ($CDCl_3$, TMS, δ (ppm), *J* (Hz), 200 MHz)

Imine	Ph m	Ar m	Pyridine ring				CH_α	CH_β	CH=N d	CH_3 s
			H-4	H-6 dd	H-3 d	H-5				
13	7.3-7.6 (5H)		7.72 td, J_1 = 7.6, J_2 = 1.7	8.47 J_1 = 4.8, J_2 = 1.7	7.38 *J* =7.6	7.15 ddd, J_1 = 7.6, J_2 = 4.8, J_3 = 1.2	7.30 dd, *J* = 15.8	7.14 dd, J_1 = 15.8, J_2 = 8.6	9.00, *J* = 8.6	—
14	7.3-7.7 (5H)		7.55 d, *J* = 7.0	8.28 J_1 = 4.6, J_2 = 1.0	—	7.05 dd J_1 = 7.0, J_2 = 4.6	7.28 dd, *J* = 15.2	7.16 dd, J_1 = 15.2, J_2 = 8.2	8.87, *J* = 8.2	2.41
15	7.0-7.6 (10H)		—	—			7.1-7.2 m (2H)		8.25, J_1 = 5.2, J_2 = 3.0	—
16	7.3-7.6 (9H)		—	—	—		7.22 d, *J* =15.8	7.09 dd, J_1 = 15.8, J_2 = 8.2	8.26, *J* = 8.2	—

TABLE 9. ^{1}H NMR Spectra of N-benzylidene-2-aminopyridines **17-19** ($CDCl_3$, TMS, δ (ppm), *J* (Hz), 200 MHz)

Imine	Ph		Pyridine ring				CH=N s	CH_3 s
	3H m	2H m	H-4	H-6 dd	H-3 d	H-5		
17	7.49	7.98	7.74 td, J_1 = 8.1, J_2 = 2.2	8.49, J_1 = 5.0, J_2 = 2.2	7.32, *J* = 8.1	7.15 m, J_1 = 8.1, J_2 = 5.0	9.14	-
18	7.48	8.01	7.53 br. s, J_1 = 7.7	8.29, J_1 = 4.6, J_2 = 1.8	—	7.15 dd, J_1 = 7.7, J_2 = 4.6	9.06	2.45
19	7.46	7.97	7.69 dd, J_1 = 8.2, J_2 = 7.6		7.8, *J* = 8.2	7.01 d, *J* = 7.6	9.06	2.56

TABLE 10. Mass Spectra of Synthesized Aldimines

Imine	m/z (I_{rel}, %)
1	198 (16, M$^+$), 197 (8, M$^+$-H), 170 (16), 169 (100, M$^+$-OCH), 143 (5), 120 (7, M$^+$-Py), 118 (13), 79 (24, PyH$^+$),78 (22, Py), 65 (7), 52 (17), 51 (18), 39 (15)
2	212 (39, M$^+$), 211 (12, M$^+$-H), 184 (16), 183 (100, M$^+$-OCH), 169 (7), 157 (6), 132 (18), 131 (13), 120 (10,M$^+$-MeC$_5$H$_4$N), 119 (8, M$^+$-FurCHCH), 93 (36, FurCHCH), 92 (23, MeC$_5$H$_4$N), 78 (7, Py), 65 (31), 51 (12), 39 (20)
3	212 (17, M$^+$), 211 (6, M$^+$-H), 184 (14), 183 (100, M$^+$-OCH), 168 (5), 156 (4), 132 (11), 131 (9), 120 (10, M$^+$-MeC$_5$H$_4$N), 119 (7, M$^+$-FurCHCH), 93 (32, FurCHCH), 92 (14, MeC$_5$H$_4$N), 78 (7, Py), 65 (31), 51 (12), 39 (20)
4	197 (38, M$^+$), 196 (19, M$^+$-H), 180 (4), 169 (19), 168 (100, M$^+$-OCH), 167 (37), 156 (19), 143 (23), 115 (10), 104 (5, PhNCH), 77 (46, Ph), 65 (12), 51 (30), 39 (15)
5	265 (45, M$^+$), 264 (26, M$^+$-H), 246 (6, M$^+$-F) 237 (22), 236 (100, M$^+$-OCH), 235 (15), 224 (38), 211 (32), 196 (5, M$^+$-CF$_3$), 185 (4), 172 (9, M$^+$-FurCHCH), 168 (17), 167 (35), 145 (50), 125 (11), 115 (7), 95 (18), 75 (17), 65 (19), 51 (16), 39 (26)
6	212 (7, M$^+$), 211 (5, M$^+$-H), 197 (2, M$^+$-Me), 183 (2, M$^+$-OCH), 170 (13), 169 (100, M$^+$-OCCH$_3$), 134 (4), 118 (7), 105 (3, PyNCH), 91 (2), 79 (17, PyH$^+$), 78 (10, Py), 65 (3), 51 (14), 43 (9), 39 (7)
7	226 (12, M$^+$), 225 (9, M$^+$-H), 184 (15), 183 (100, M$^+$-OCCH$_3$), 169 (15), 132 (16), 93 (21), 92 (12), 78 (6, Py), 77 (8), 65 (17), 51 (7), 43 (17), 39 (13)
8	226 (6, M$^+$), 225 (9, M$^+$-H), 184 (15), 183 (100, M$^+$-OCCH$_3$), 169 (15), 132 (16), 93 (21), 92 (12), 78 (6, Py), 77 (8), 65 (17), 51 (7), 43 (17), 39 (13)
9	211 (19, M$^+$), 210 (17, M$^+$-H), 196 (29, M$^+$-Me), 169 (14), 168 (100, M$^+$-OCCH$_3$), 167 (53), 154 (5), 115 (5), 104 (5, PhNCH), 77 (39, Ph), 65 (7), 51 (27), 43 (18), 39 (11)
10	279 (39, M$^+$), 278 (37, M$^+$-H), 264 (79, M$^+$-Me), 260 (5, M$^+$-F), 237 (17), 236 (100, M$^+$-OCCH$_3$), 235 (23), 216 (12), 196 (4), 168 (10), 167 (62), 145 (42), 125 (9), 107 (8), 95 (17), 77 (18), 65 (12), 51 (17), 43 (45), 39 (2)
11	242 (18, M$^+$), 210 (12, M$^+$-O$_2$), 196 (95, M$^+$-NO$_2$), 181 (15), 168 (55, M$^+$-OCNO$_2$), 167 (100, M$^+$-OCHNO$_2$), 166 (28), 154 (18), 130 (30, M$^+$-C$_4$H$_2$O-NO$_2$), 115 (18), 104 (5, PhNCH), 77 (100, Ph), 71 (33), 69 (38), 57 (55), 55 (60), 51 (90), 43 (53), 41 (62), 39 (50)
12	310 (23, M$^+$), 291 (3, M$^+$-F), 278 (10, M$^+$-O$_2$), 264 (100, M$^+$-NO$_2$), 236 (28, M$^+$-OCNO$_2$), 235 (33, M$^+$-OCHNO$_2$), 216 (15), 198 (16, M$^+$-C$_4$H$_2$O-NO$_2$), 172 (18, F$_3$CC$_6$H$_4$N=CH), 168 (15), 167 (100, M$^+$-CF$_3$-OCNO$_2$), 166 (22), 145 (71, F$_3$CC$_6$H$_4$), 125 (13), 121 (15), 95 (21), 75 (11), 65 (16), 64 (8), 63 (11), 39 (50)
13	208 (38, M$^+$), 207 (59, M$^+$-H), 180 (7), 132 (9), 131 (100, M$^+$-Ph), 130 (65, M$^+$-Py), 115 (13), 103 (9, PhCHCH), 102 (11), 93 (5), 89 (6), 79 (59, PyH$^+$), 78 (46, Py), 77 (17, Ph), 63 (9), 52 (27), 51 (32), 50 (9), 39 (11)
14	222 (39, M$^+$), 221 (50, M$^+$-H), 207 (4, M$^+$-Me), 194 (4), 146 (11), 145 (100, M$^+$-Ph), 131 (9), 130 (44, M$^+$-Ph-Me), 115 (15), 103 (7, PhCHCH), 93 (45), 92 (29), 77 (14, Ph), 65 (29), 63 (11), 51 (12), 39 (24)
15	207 (29, M$^+$), 206 (100, M$^+$-H), 130 (5, M$^+$-Ph), 128 (10), 115(10), 104 (5, PhNCH), 103 (7, PhCHCH), 89 (4), 78 (7), 77 (40, Ph), 63 (6), 51 (25), 39 (7)
16	275 (28, M$^+$), 274 (100, M$^+$-H), 256 (4, M$^+$-F), 178 (2, M$^+$-H-F-Ph), 145 (16, F$_3$CC$_6$H$_4$), 128 (9), 115 (10), 103 (6, PhCHCH), 95 (6), 77 (Ph), 63 (5), 51 (6), 39 (4)
17	182 (15, M$^+$), 181 (39, M$^+$-H), 154 (6), 104 (2, M$^+$-Py), 103 (2, M$^+$-Ph), 89 (5), 79 (100, PyH$^+$), 78 (46, Py), 63 (5), 52 (21), 51 (24), 39 (7)
18	196 (16, M$^+$), 195 (33, M$^+$-H), 181 (2, M$^+$-Me), 168 (6), 119 (5, M$^+$-Ph), 93 (100, CH$_3$C$_5$H$_3$NH$^+$), 92 (19), 77 (8, Ph), 66 (13), 65 (22), 51 (13), 39 (23)
19	196 (8, M$^+$), 195 (5, M$^+$-H), 168 (3), 154 (2), 119 (2, M$^+$-Ph), 103 (2), 93 (100, CH$_3$C$_5$H$_3$NH$^+$), 77 (8, Ph), 66 (17), 65 (16), 51 (8), 39 (14)

Thus we have developed a simple and convenient method for synthesis of the target products and we have obtained a series of the corresponding azomethines **1-19**, which are crystalline or oily substances ranging from light yellow to brown in color. The solid samples were additionally purified by recrystallization or vacuum sublimation. Column chromatography proved to be quite unsuitable for the imines **1-19**, since they decompose on reaction with silica gel.

The synthesized compounds were identified by various physicochemical methods (Table 1). Elemental analysis was performed for the solid or sufficiently viscous samples (Table 2). The ^{1}H NMR spectra and mass spectra (Tables 3-10) correspond to the structure of compounds **1-19**. Molecular ion peaks are present in the mass

spectra of all the azomethines. A characteristic feature of the spectra of the furyl derivatives **1-5** is the presence of a maximum peak corresponding to the [M^+-HCO] ion; the [M^+-CH_3CO] peak of the methylfuryl derivatives **6-10** is characterized by 100 percent intensity, and in the spectra of the nitrofuryl derivatives **11, 12**, in addition to the [M^+-NO_2] peaks there are intense signals from [M^+-O_2NCO] ions. Elimination of the formyl radical and its derivatives is observed in mass spectra of many furan compounds [10]. For the spectra of azomethines **13, 14**, obtained from cinnamic aldehyde and aminopyridines, the [M^+-Ph] peaks are typically most intense; for imines **15, 16**, the reaction products of this aldehyde with anilines, the [M^+-H] ion peaks are the most intense. In the spectra of benzylidene aminopyridine **17** and its methyl derivatives **18, 19**, the [C_5H_4N-H^+] or [$CH_3C_5H_3N$-H^+] signals respectively are maximum.

In the ^{1}H NMR spectra of azomethines (Tables 5-9), we see two major groups of signals: signals from protons of the chain CH=CH–CH=N (or the CH=N moiety of the benzylidene derivatives), and signals from (hetero)aryl substituents. The three protons of the propenylidene moiety in the imines **9, 11-14**, and **16** form multiplets of the AMX type in which the chemical shifts and the spin-spin coupling constants can be directly measured. The values of the vicinal constants ^3J = 15.7 (±0.5) Hz suggest a *trans* arrangement of the protons at the double bond C=C, while ^3J = 18.2 (±0.6) Hz is typical for protons of the moiety =CH–CH= with rotation about the C–C bond. Signals from the most shielded protons of the –CH=N– moieties are doublets only in the spectra of the indicated compounds. For other imines, signals from the –CH=N– protons are observed as doublets of doublets (**1-4, 6-8, 15**) or triplets (**5, 10**), despite the fact that one of the constants J_{AX} or J_{BX} is equal to zero. This is typical for ABX or AA'X spin systems [11]. As shown by two dimensional COSY spectra and the results of iteration of the spectra, splitting of the X parts of the spectra is determined to a large degree by the differences in shielding of the remaining two protons, while the spin-spin coupling constants vary little: 8.4 (±0.2) Hz.

The chemical shifts and the nature of the splitting of the signals from aryl and heteroaryl protons are determined by the site of addition of the rest of the substituents. The numerical values of δ and J are predicted satisfactorily by the familiar additivity schemes in [12].

EXPERIMENTAL

The ^{1}H NMR spectra were studied on a Varian Mercury spectrometer (200 MHz) for solutions in $CDCl_3$, internal standard TMS. For interpretation of the spectra, we used a modification of the program LAOCOON installed in the spectrometer. The mass spectra were obtained on an MS-50 instrument (70 eV) and an HP 6890 GC/MS chromatograph/mass spectrometer, equipped with an HP-5 MS column (30.0 m × 250 μm × 0.25 μm), with temperature programming from 70°C to 260°C (10°C/min). The reaction mixtures were analyzed on a Chrom-4 chromatograph equipped with a flame ionization detector and a glass column (1.2 m × 3 mm) filled with 5% OV-17 phase on Chromosorb W-AW (60-80 mesh), column temperature of 120-250°C, carrier gas nitrogen (60 ml/min).

The benzene was distilled over CaH_2 before use. Aldehydes **1a** and **2a** were synthesized according to the procedure in [13]. Benzyl and cinnamic aldehydes, aniline, and 3-trifluoromethylaniline were purified by vacuum distillation, after which their properties corresponded to the literature values. The nitro derivative **3a** (Reakhim) and the aminopyridines **1b-3b** (Fluka and Merck) where recrystallized from benzene. In this work, we used the molecular sieves 4 A (VEB Laborchemie Apolda).

General Procedure for Synthesis of Azomethines 1-19. Dry benzene (10 ml) and each of the starting aldehyde (5 mmol) and amine were placed in a flask followed by 5 g of freshly calcined molecular sieves (or 7 g anhydrous sodium sulfate). The reaction mixture was held at room temperature, periodically withdrawing samples and analyzing them by GLC and GLC-MS. Depending on the substrates, their practically complete conversion to the corresponding products occurred over a certain time period (Table 1). At the end of the reaction, the dehydrating agents were filtered off, washed with benzene, the filtrate was evaporated at reduced pressure (40°C/50 mm), and slight residues of the starting compounds were removed under vacuum (45-50°C/0.1 mm). We obtained oily materials or crystalline compounds (ranging from light yellow to brown in color). The solid products

were additionally purified by vacuum sublimation or recrystallization from petroleum ether, benzene, or a mixture of the two, after which we determined the characteristics of the compounds obtained (Tables 1, 2) and recorded their spectra (Tables 3-9); the mass spectra are presented in Table 10.

We would like to thank the Latvian Science Council for financing this work (Grant No. 707).

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