

REACTION OF VINAMIDINIUM SALTS OF FURAN WITH ALDEHYDES

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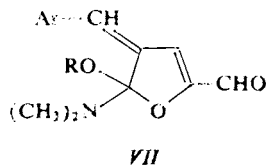
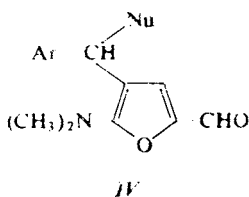
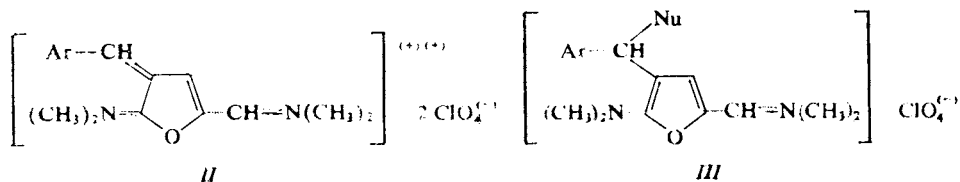
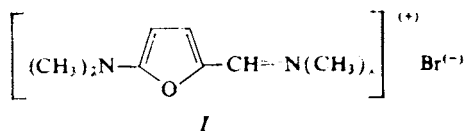
5-(N,N-dimethylamino)-2-furfurylidene-N,N-dimethylimmonium bromide (*I*) reacts with aromatic aldehydes and its vinylogues to give condensation products *II*. Addition of alkoxides, sulfinates or thiolates to *II* renews the furan ring what can be utilized for preparation of new 4-(Ar-, R-methyl)-5-(N,N-dimethylamino)-2-furancarbaldehydes *IV*.

Our preceding paper¹ presented 5-(N,N-dimethylamino)-2-furfurylidene-N,N-dimethylimmonium bromide (*I*) as a pentamethinium system with a furan ring. This compound was employed *via* electrophilic displacement for the synthesis of some new furan derivatives having substituents in β -position of the furan ring. This paper describes reactions of salts of *I* with aldehydes.

Compound *I* reacts, similarly as 1,3-bis(dimethylamino)trimethinium perchlorate^{2,3} with substituted benzaldehydes and their heterocyclic analogues in acetic anhydride-acetic acid (1 : 1) in the presence of a strong mineral acid to give 4-arylidene-5-(N,N-dimethylimmonium)-2-(4,5-dihydrofurfurylidene)-N,N-dimethylimmonium bisperchlorates *II* in high yields (Table I). Formation of condensation products *II* evidences the high reactivity of *I* in position 4 (ref.¹) towards electrophilic reagents. Compound *I* reacts in the same way with the benzaldehyde vinylogue 3-phenyl-2-propenal to afford *III*. Aliphatic aldehydes (*e.g.* formaldehyde, acetaldehyde, propionaldehyde) react with *I* under same reaction conditions primarily with acetic anhydride to yield 4-acetyl-5-(N,N-dimethylamino)-2-furfurylidene-N,N-dimethylimmonium perchlorate (*V*); the latter undergoes hydrolysis in alkaline medium to furnish 4-acetyl-5-(N,N-dimethylamino)-2-furancarbaldehyde (*VI*).

A 1,4-addition of sodium alkoxide to *II* in the corresponding anhydrous alcohol renews the furan ring under formation of 4-(1-alkoxy-1-arylmethyl)-5-(N,N-dimethylamino)-2-furfurylidene-N,N-dimethylimmonium perchlorate (*III*), which gave on hydrolysis the proper aldehyde *IV*. Formation of the furan derivative *IV* but not the dihydrofuran derivative *VII*, a product of potential 1,2-addition to the C=N bond, evidenced the absorption maxima in the UV region and chemical shifts of car-

bons in the ^{13}C NMR spectrum. The wavelength λ_{max} 366 nm of compound *IVa* is comparable with that (364 nm) of the analogous unsubstituted 5-(*N,N*-dimethylamino)-2-furancarbaldehyde⁴, whereas the longer conjugated system of *IIa* has the absorption maximum at λ_{max} 412 nm. Also the chemical shift values of furan carbons of compound *IVa* (5-(*N,N*-dimethylamino)-2,4-furandicarbaldehyde¹) are in a good agreement with those of substance *VI* (Table IV). The signal at 77.7 ppm (d, $J_{\text{CH}} = 145.2$ Hz, CH) in the ^{13}C NMR spectrum can be attributed to an alkane carbon in *IVa* and not to an olefinic one in *VII*.



	Nu	Ar
<i>a</i>	CH ₃ O	C ₆ H ₅
<i>b</i>	CH ₃ O	3,4-CH ₂ O ₂ -C ₆ H ₃
<i>c</i>	CH ₃ O	4-Br-C ₆ H ₄
<i>d</i>	CH ₃ O	4-CH ₃ O-C ₆ H ₄
<i>e</i>	CH ₃ O	4-CH ₃ -C ₆ H ₄
<i>f</i>	CH ₃ O	4-NO ₂ -C ₆ H ₄
<i>g</i>	CH ₃ O	2-furyl
<i>h</i>	CH ₃ O	5-bromo-2-furyl
<i>i</i>	CH ₃ O	5-nitro-2-furyl
<i>j</i>	CH ₃ O	5-methoxycarbonyl-2-furyl
<i>k</i>	CH ₃ O	5-methyl-2-furyl
<i>m</i>	C ₂ H ₅ O	C ₆ H ₅
<i>n</i>	C ₆ H ₅ SO ₂	C ₆ H ₅
<i>o</i>	4-CH ₃ -C ₆ H ₄ SO ₂	C ₆ H ₅
<i>p</i>	C ₆ H ₅ S	C ₆ H ₅

A like addition of sodium phenylthiolate or sodium arylsulfonates to *Ila* in acetone led to 4-(1-phenyl-1-phenylthiomethyl) (*IIIp*) or 4-(1-arylsulfonyl-1-phenylmethyl)-5-(*N,N*-dimethylamino)-2-furfurylidene-*N,N*-dimethylimmonium perchlorates *III_{n,o}*, which hydrolyzed to the corresponding aldehydes *IVp* and *IV_{n,o}*. Intermediates *III* need not be either isolated or purified; they could directly be hydrolyzed in the reaction mixture by addition of a 10% aqueous sodium hydroxide. This modification results in a higher yield of *IV*.

TABLE I

4-Arylidene-5-(*N,N*-dimethylimmonium)-2-[4,5-dihydrofurfurylidene]-*N,N*-dimethylimmonium bisperchlorates *II*

Compound	Formula (<i>M_r</i>)	M.p., °C (yield,%)	Calculated/Found			
			% C	% H	% N	% Cl
<i>Ila</i>	C ₁₆ H ₂₀ Cl ₂ N ₂ O ₉ (455·2)	183—185 (84)	42·21	4·42	6·15	15·57
			42·01	4·38	6·86	15·71
<i>Ilb</i>	C ₁₇ H ₂₀ Cl ₂ N ₂ O ₁₁ (499·2)	214—215 (91)	40·89	4·03	5·61	14·20
			40·82	4·05	5·50	14·28
<i>Ilc</i>	C ₁₆ H ₁₉ BrCl ₂ N ₂ O ₉ (534·1)	211—213 (93)	35·91	3·58	5·24	13·27
			35·07	3·02	5·71	13·87
<i>Ild</i>	C ₁₇ H ₂₂ Cl ₂ N ₂ O ₁₀ (485·2)	229—231 (96)	42·07	4·56	5·77	14·61
			42·97	4·86	5·15	14·48
<i>Ile</i>	C ₁₇ H ₂₂ Cl ₂ N ₂ O ₉ (469·2)	178—182 (92)	43·51	4·72	5·96	15·10
			44·91	5·08	5·86	14·91
<i>IIf</i>	C ₁₆ H ₁₉ Cl ₂ N ₃ O ₁₁ (499·9)	192—193 (71)	38·41	3·80	8·40	14·20
			37·83	3·92	8·78	14·14
<i>Ilg</i>	C ₁₄ H ₁₈ Cl ₂ N ₂ O ₁₀ (445·2)	238—240 (97)	37·76	4·07	6·29	15·95
			38·01	4·58	6·88	15·05
<i>Ilh</i>	C ₁₄ H ₁₇ BrCl ₂ N ₂ O ₁₀ (524·1)	198—200 (90)	32·02	3·26	5·34	13·52
			32·17	3·31	5·68	13·08
<i>Ili</i>	C ₁₄ H ₁₇ Cl ₂ N ₃ O ₁₂ (490·2)	225—227 (96)	34·30	3·49	8·59	14·46
			34·35	3·62	8·86	14·12
<i>IJj</i>	C ₁₆ H ₂₀ Cl ₂ N ₂ O ₁₂ (475·2)	240—243 (67)	40·43	4·24	5·89	14·92
			39·69	4·13	5·68	15·12
<i>IIk</i>	C ₁₅ H ₂₀ Cl ₂ N ₂ O ₁₀ (459·2)	191—194 (88)	39·23	4·38	6·14	15·43
			39·30	4·66	6·44	14·97
<i>III</i>	C ₁₈ H ₂₂ Cl ₂ N ₂ O ₉ (481·2)	220—223 (54)	44·92	4·60	5·82	14·73
			45·27	4·11	6·43	13·88

EXPERIMENTAL

Melting points were determined on a Kofler micro hot-stage, the IR spectra of chloroform solutions were measured with a Unicam SP-100 spectrophotometer in 0.5 nm-cells at a $2 \cdot 10^{-2}$ mol \cdot l^{-1} concentration. The 1H NMR spectra of deuteriochloroform solutions (unless stated otherwise) were recorded with a Tesla BS 487 C spectrometer operating at 80 MHz; internal reference was tetramethylsilane; the ^{13}C NMR spectra of deuteriochloroform solutions containing tetramethylsilane were run with a Jeol FX 60 apparatus operating at 25.04 MHz. The UV spectra of methanolic solutions were measured with a UV-VIS (Zeiss, Jena) spectrophotometer in 10 mm cells at a $5 \cdot 10^{-5}$ mol l^{-1} concentration.

TABLE II
4-(1-Alkoxy-1-arylmethyl)-5-(N,N-dimethylamino)-2-furancarbaldehydes IV

Compound	Formula (M_r)	M.p., °C (yield, %)	Calculated/Found				$\nu(C=O)$ cm^{-1}
			% C	% H	% N	% Br	
<i>IVa</i>	$C_{15}H_{17}NO_3$ (259.3)	89–90 (88)	69.47	6.60	5.40	—	1 650
			69.26	6.63	5.52	—	
<i>IVb</i>	$C_{16}H_{17}NO_5$ (303.3)	134–135 (98)	63.36	5.56	4.62	—	1 650
			63.13	5.99	4.77	—	
<i>IVc</i>	$C_{15}H_{16}BrNO_3$ (328.2)	95–96 (89)	53.27	4.76	4.14	23.62	1 650
			52.97	4.76	4.32	23.48	
<i>IVd</i>	$C_{16}H_{19}NO_4$ (275.3)	115–117 (94)	69.79	6.95	5.08	—	1 650
			69.80	6.70	5.17	—	
<i>IVe</i>	$C_{16}H_{19}NO_3$ (273.3)	70–73 (88)	70.30	7.00	5.12	—	1 649
			70.51	7.08	5.19	—	
<i>IVf</i>	$C_{15}H_{16}N_2O_5$ (304.3)	109–111 (81)	59.20	5.29	9.26	—	1 652
			59.29	5.13	9.22	—	
<i>IVg</i>	$C_{13}H_{15}NO_4$ (249.3)	112–115 (72)	62.64	6.06	5.61	—	1 654
			62.04	6.21	5.58	—	
<i>IVh</i>	$C_{13}H_{14}BrNO_4$ (328.2)	109–111 (91)	47.58	4.30	4.26	24.35	1 640
			47.49	4.35	4.30	24.03	
<i>IVi</i>	$C_{13}H_{14}N_2O_6$ (294.3)	105–108 (79)	53.06	4.79	9.51	—	1 658
			54.02	4.21	9.35	—	
<i>IVj</i>	$C_{15}H_{17}NO_6$ (307.3)	140–142 (81)	58.63	5.58	4.56	—	1 649
			58.76	4.72	4.93	—	
<i>IVk</i>	$C_{14}H_{17}NO_4$ (263.3)	115–120 (85)	63.86	6.50	5.31	—	1 651
			63.62	6.53	5.48	—	
<i>IVm</i>	$C_{16}H_{19}NO_3$ (273.3)	73–75 (74)	70.31	7.00	5.12	—	1 648
			69.73	7.12	5.61	—	

4-Arylidene-5-(N,N-dimethylimmonium)-2-(4,5-dihydrofurfurylidene)-N,N-dimethylimmonium Bisperchlorates *II*

Perchloric acid (75%, 0.64 ml), compound *I* (3 mmol, 0.795 g) and the respective aldehyde (3 mmol) were successively added to a stirred mixture of acetic anhydride (2.5 ml) and acetic acid (2.5 ml) at 5–10°C. The mixture was stirred at room temperature for 1 h, the separated compound was filtered off, washed with acetic acid and crystallized from methanol or ethanol. Data of compounds *II* are listed in Table I.

TABLE III

¹H NMR spectra of 4-(1-alkoxy-1-arylmethyl)-5-(N,N-dimethylamino)-2-furancarbaldehydes *IV*

Compound	CHO	H _f ^a	CH	N(CH ₃) ₂	OCH ₃	Others ^a
<i>IVa</i>	8.91 s	6.80 s	5.30 s	3.16 s	3.32 s	7.36 (s, 5 H, H _b)
<i>IVb</i>	8.95 s	5.85 s	5.21 s	3.15 s	3.30 s	4.02 (s, 2 H, CH ₂), 6.85 (m, 3 H, H _b)
<i>IVc</i>	8.93 s	6.77 s	5.27 s	3.13 s	3.22 s	7.22 (d, 2 H, H _b), 7.52 (d, 2 H, H _b , <i>J</i> = 8.4)
<i>IVd</i>	8.91 s	6.82 s	5.25 s	3.50 s	3.30 s	3.82 (s, 3 H, CH ₃), 6.92 (d, 2 H, <i>J</i> = 9), H _b), 7.28 (d, 2 H, <i>J</i> = 9, H _b)
<i>IVe</i>	8.90 s	6.80 s	5.26 s	3.18 s	3.22 s	2.40 (s, 3 H, CH ₃), 7.22 (s, 4 H, H _b)
<i>IVf</i>	9.00 s	6.80 s	5.40 s	3.12 s	3.37 s	7.55 (d, 2 H, <i>J</i> = 8.4, H _b), 8.25 (d, 2 H, <i>J</i> = 8.4, H _b)
<i>IVg</i>	9.07 s	7.25 s	5.40 s	3.14 s	3.48 s	6.25 (m, 3 H, H _f)
<i>IVh</i>	9.02 s	7.20 s	5.31 s	3.13 s	3.36 s	6.23 (d, 1 H, <i>J</i> = 4, H _{3f'}), 6.27 (d, 1 H, <i>J</i> = 4, H _{4f'})
<i>IVi</i>	9.07 s	7.12 s	5.41 s	3.15 s	3.40 s	6.51 (d, 1 H, <i>J</i> = 4, H _{3f'}), 7.27 (d, 1 H, <i>J</i> = 4, H _{4f'})
<i>IVj</i>	9.02 s	7.11 s	5.42 s	3.16 s	3.38 s	3.90 (s, 3 H, CH ₃), 6.41 (d, 1 H, <i>J</i> = 4, H _{3f'}), 7.15 (d, 1 H, <i>J</i> = 4, H _{4f'})
<i>IVk</i>	9.01 s	7.20 s	5.26 s	3.12 s	3.33 s	2.31 (s, 3 H, CH ₃), 6.12 (d, 1 H, <i>J</i> = 4, H _{3f'}), 5.92 (d, 1 H, <i>J</i> = 4, H _{4f'})
<i>IVm</i>	8.87 s	6.73 s	5.37 s	3.16 s	—	3.43 (q, 2 H, <i>J</i> = 7, CH ₂), 1.25 (t, 3 H, <i>J</i> = 7, CH ₃), 7.33 (s, 5 H, H _b)

^a H_b = H_{benzene}, H_f = H_{furan}.

4-(1-Alkoxy-1-arylmethyl)-5-(N,N-dimethylamino)-2-furancarbaldehydes *IVa–IVm*

Sodium methoxide (1.5 mmol) in methanol (0.5 ml) was added to a stirred solution of *II* (1 mmol) in methanol (2 ml) at 10–15°C. The solid *III*, which separated after a 1 h stirring can be either filtered off, or the reaction mixture can be concentrated under diminished pressure and hydrolyzed in 10% aqueous sodium hydroxide (15 ml). The product was extracted with benzene, dried and the solvent was distilled off. Compound *IVm* was prepared with sodium ethoxide in ethanol. Data of compounds *IVa–IVm* are presented in Tables II and III.

4-(1-Phenyl-1-methoxymethyl)-5-(N,N-dimethylamino)-2-furfurylidene-N,N-dimethylimmonium perchlorate (*IIIa*). For $C_{17}H_{23}ClN_2O_6$ (386.8) calculated: 52.87% C, 5.99% H, 9.16% Cl, 7.24% N; found: 52.84% C, 5.92% H, 9.12% Cl, 7.29% N. M.p. 164–165°C, yield 60%.

4-(1-Methoxy-1-p-nitrophenylmethyl)-5-(N,N-dimethylamino)-2-furfurylidene-N,N-dimethylimmonium perchlorate (*IIIb*). For $C_{17}H_{22}ClN_3O_8$ (431.8) calculated: 47.28% C, 5.13% H, 8.20% Cl, 9.73% N; found: 47.40% C, 5.16% H, 8.18% Cl, 9.80% N. M.p. 95–96°C, yield 70%.

4-(1-Arylsulfonyl-1-phenylmethyl)- and 4-(1-Phenyl-1-phenylthiomethyl)-5-(N,N-dimethylamino)-2-furfurylidene-N,N-dimethylimmonium Perchlorates *IIIc–IIIp*

Sodium arylsulfinate or sodium phenylthiolate (1.5 mmol) was added to *IIa* (1 mmol) in acetone at room temperature. After a 2 h-stirring a solid separated, which was filtered off.

4-(1-Benzenesulfonyl-1-phenylmethyl)-5-(N,N-dimethylamino)-2-furfurylidene-N,N-dimethylimmonium perchlorate (*IIIc*). For $C_{22}H_{25}ClN_2O_7S$ (496.9) calculated: 53.17% C, 5.07% H, 7.13% Cl, 5.63% N, 6.44% S; found: 53.41% C, 4.87% H, 6.70% Cl, 5.82% N, 6.64% S. M.p. 118–120°C, yield 68%. 1H NMR spectrum δ , ppm, (hexadeuteriodimethyl sulfoxide): 8.38 (s, 1 H, CH=N), 7.98 (s, 1 H, H_{furan}), 7.57 (m, 10 H, H_{benzene}), 5.97 (s, 1 H, CH), 3.47 (s, 6 H, CH_3), 3.36 (s, 3 H, CH_3-N), 3.18 (s, 3 H, CH_3-N).

4-(1-Phenyl-1-toluenesulfonylmethyl)-5-(N,N-dimethylamino)-2-furfurylidene-N,N-dimethylimmonium perchlorate (*IIIo*). For $C_{23}H_{23}ClN_2O_7S$ (506.9) calculated: 54.49% C, 4.57% H, 6.99% Cl, 5.52% N, 6.31% S; found: 54.28% C, 5.34% H, 6.61% Cl, 5.82% N, 6.23% S. M.p. 130 to 132°C, yield 94%. 1H NMR spectrum δ , ppm, (hexadeuteriodimethyl sulfoxide): 8.35 (s, 1 H, CH=N), 7.97 (s, 1 H, H_{furan}), 7.50 (m, 9H, H_{benzene}), 5.92 (s, 1 H, CH), 3.47 (s, 3 H, CH_3-N), 3.33 (s, 6 H, CH_3), 3.18 (s, 3 H, CH_3-N), 2.38 (s, 3 H, CH_3).

TABLE IV
 ^{13}C NMR spectra

Compound	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	CHO	CH_3
<i>IVa</i>	142.1	127.9	103.4	160.5	171.3	39.3
<i>VI</i>	141.8	129.4	104.1	162.6	173.6	40.6
^a	143.3	128.6	105.8	162.3	174.05	40.4

^a 5-(N,N-Dimethylamino)-2,4-furandicarbaldehyde.

4-(1-Phenyl-1-phenylthiomethyl)-5-(N,N-dimethylamino)-2-furfurylidene-N,N-dimethylimmonium perchlorate (IIIp). For $C_{22}H_{25}ClN_2O_5S$ (464.9) calculated: 56.83% C, 5.42% H, 7.62% Cl, 6.02% N, 6.88% S; found: 56.72% C, 5.79% H, 8.13% Cl, 6.46% N, 6.86% S. M.p. 119–120°C, yield 58%. 1H NMR spectrum, δ , ppm, (hexadeuteriodimethyl sulfoxide): 8.4 (s, 1 H, CH=N), 7.98 (s, 1 H, H_{furan}), 7.52 (m, 10 H, $H_{benzene}$), 5.95 (s, 1 H, CH), 3.47 (s, 6 H, CH_3), 3.38 (s, 3 H, CH_3-N), 3.20 (s, 3 H, CH_3-N).

4-(1-Arylsulfonyl-1-phenylmethyl)- and 4-(1-Phenyl-1-phenylthiomethyl)-5-(N,N-dimethylamino)-2-furancarbaldehydes *IVn-IVp*

Compound *III* was hydrolyzed with 10% aqueous sodium hydroxide (25 ml) and the mixture was worked up as *IVa*; n-heptane-chloroform (6 : 4) were used for crystallization.

4-(1-Benzenesulfonyl-1-phenylmethyl)-5-(N,N-dimethylamino)-2-furancarbaldehyde (*IVn*). For $C_{20}H_{19}NO_4S$ (369.4) calculated: 65.03% C, 5.18% H, 3.79% N, 8.66% S; found: 65.72% C, 5.03% H, 4.02% N, 8.73% S. M.p. 65–67°C, yield 37%. 1H NMR spectrum, δ , ppm: 9.22 (s, 1 H, CHO), 7.86 (s, 1 H, H_{furan}), 7.33 (m, 10 H, $H_{benzene}$), 5.4 (s, 1 H, CH), 2.92 (s, 6 H, CH_3). IR spectrum (cm^{-1}): 1 650 (C=O), 1 316, 1 140 (SO_2).

4-(1-Phenyl-1-toluenesulfonylmethyl)-5-(N,N-dimethylamino)-2-furancarbaldehyde (*IVo*). For $C_{21}H_{21}NO_4S$ (383.4) calculated: 65.78% C, 5.52% H, 3.65% N, 8.35% S; found: 65.31% C, 5.22% H, 4.01% N, 8.46% S. M.p. 170–171°C, yield 83%. 1H NMR spectrum, δ , ppm: 9.21 (s, 1 H, CHO), 7.83 (s, 1 H, H_{furan}), 7.36 (m, 9 H, $H_{benzene}$), 5.36 (s, 1 H, CH), 2.92 (s, 6 H, CH_3), 2.37 (s, 3 H, CH_3). IR spectrum (cm^{-1}): 1 652 (C=O), 1 315, 1 140 (SO_2).

4-(1-Phenyl-1-phenylthiomethyl)-5-(N,N-dimethylamino)-2-furancarbaldehyde (*IVp*). For $C_{20}H_{19}NO_2S$ (337.4) calculated: 71.19% C, 5.67% H, 4.15% N, 9.48% S; found: 70.89% C, 5.48% H, 4.94% N, 9.42% S. Oil, yield 64%. 1H NMR spectrum, δ , ppm: 9.22 (s, 1 H, CHO), 7.85 (s, 1 H, H_{furan}), 7.43 (m, 10 H, $H_{benzene}$), 5.37 (s, 1 H, CH), 2.92 (s, 6 H, CH_3). IR spectrum (cm^{-1}): 1 649 (C=O).

4-Acetyl-5-(N,N-dimethylamino)-2-furfurylidene-N,N-dimethylimmonium Perchlorate (*V*)

An aldehyde (formaldehyde, acetaldehyde, propionaldehyde, 3 mmol) was added to a stirred mixture consisting of acetic anhydride (2.5 ml), acetic acid (2.5 ml), 75% perchloric acid (0.64 ml) and *I* (3 mmol) at an ambient temperature. A solid separating after a 2 h-stirring was filtered off and washed with acetic acid. For $C_{11}H_{17}ClN_2O_6$ (308.7) calculated: 42.79% C, 5.55% H, 11.48% Cl, 9.07% N; found: 43.12% C, 4.71% H, 12.35% Cl, 10.65% N. M.p. 158–160°C, yield 73%. 1H NMR spectrum, δ , ppm (hexadeuteriodimethyl sulfoxide): 8.25 (s, 1 H, CH=N), 7.25 (s, 1 H, H_{furan}), 3.63 (s, 3 H, CH_3-N), 3.55 (s, 6 H, CH_3), 3.40 (s, 3 H, CH_3-N), 2.52 (s, 3 H, CH_3).

4-Acetyl-5-(N,N-dimethylamino)-2-furancarbaldehyde (*VI*)

This compound was obtained by hydrolysis of *V* by a procedure specified for *IV* and purified by chromatography on a silica gel column with benzene-ethyl acetate (1 : 1). For $C_9H_{11}NO_3$ (181.2) calculated: 59.65% C, 6.11% H, 7.73% N; found: 59.43% C, 6.19% H, 7.88% N. M.p. 78 to 79°C, yield 56%. 1H NMR spectrum, δ , ppm: 9.20 (s, 1 H, CHO), 7.45 (s, 1 H, H_{furan}), 3.28 (s, 6 H, CH_3), 2.45 (s, 3 H, CH_3). IR spectrum (cm^{-1}): 1 680 (C=O), 1 648 (CHO).

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