

A STUDY OF REACTIONS OF 5-SUBSTITUTED FURFURYLIDENE DERIVATIVES WITH SECONDARY AMINES*

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The paper describes preparation of 5-bromo-, 5-nitro-, 5-phenylsulphonyl-, and 5-phenylthio-2-furfurylidene derivatives and investigation of their reactions with N-phenylpiperazine, morpholine, piperidine, and pyrrolidine. Kinetics of the reactions have been followed, and UV, IR, and ^1H NMR spectra of the compounds produced are interpreted.

Our previous papers dealt with nucleophilic substitution of arylthio, heteroarylthio, arylsulphonyl, and aryloxy groups in 2-cyano-3-(5-X-2-furyl)-2-propenenitriles and acrylates¹⁻⁵. It was shown that the S_{N} reaction only took place if there was a strong electron-acceptor group at 2-position of the furane.

The present paper continues this research, following the reactivity of condensation products of 5-X-2-furanecarbaldehydes (X = nitro, bromo, phenylthio, phenylsulphonyl substituents) with diethyl propanedioate, ethyl 3-oxobutanoate, and 2,5-pentanedione at the conditions of S_{N} reactions.

The condensation products were prepared by the Lehnert method^{6,7}. Their reactions with nucleophilic reagents were carried out in absolute ethanol at various temperatures and at various molar ratios of the reacting components. N-Phenylpiperazine, morpholine, piperidine, and pyrrolidine were used as the nucleophilic reagents. The individual substrates show different behaviour in the reactions studied: either with respect to the reaction course or from the point of view of formation of final products (Table I).

In the reactions of the condensation products with nucleophilic reagents at room temperature, the nucleophilic adducts were isolated in the case of 5-bromo-, 5-nitro-, and 5-phenylthio-2-furfurylidene propanedioate with N-phenylpiperazine, 5-nitro-2-furfurylidene-3-oxobutanoate and -propanedioate with morpholine, and 5-phenylsulphonyl-2-furfurylidene propanedioate with all the given amines. If the reactions were carried out at the boiling point of the solvent, substitution reaction took place in the case of 5-bromo-2-furfurylidene-3-oxobutanoate and -propanedioate with N-phenylpiperazine and morpholine.

* Part CLXXXIV in the series on Furane derivatives; Part CLXXXIII: This Journal 50, (1985).

TABLE I
Analytical data of the compounds synthesized

No	Formula (mol. wt.)	M.p., °C yield, %	Calculated/Found				
			% C	% H	% N	% S	% Br
<i>I</i>	$C_{17}H_{16}O_4S$ (316.4)	80–81	63.54	5.10	—	10.14	—
		50	63.38	4.95	—	10.03	—
<i>II</i>	$C_{16}H_{14}O_3S$ (286.4)	^a	67.11	4.93	—	11.20	—
		55	69.58	4.90	—	10.88	—
<i>III</i>	$C_{18}H_{18}O_5S$ (346.4)	63–64	62.41	5.24	—	9.26	—
		70	62.24	5.15	—	8.83	—
<i>IV</i>	$C_{11}H_{11}NO_6$ (253.2)	124–125	52.18	4.38	5.53	—	—
		74	52.20	4.25	5.70	—	—
<i>V</i>	$C_{10}H_9NO_5$ (223.2)	119–120	53.82	4.06	6.28	—	—
		42	53.69	4.01	6.42	—	—
<i>VI</i>	$C_{12}H_{13}NO_7$ (283.2)	109–110	50.88	4.63	4.94	—	—
		77	50.25	4.68	5.28	—	—
<i>VII</i>	$C_{11}H_{11}BrO_4$ (287.1)	92–93	46.02	3.86	—	—	27.83
		63	45.93	3.87	—	—	28.02
<i>VIII</i>	$C_{10}H_9BrO_3$ (257.1)	85–86	46.72	3.53	—	—	31.08
		32	46.24	3.49	—	—	31.71
<i>IX</i>	$C_{12}H_{13}BrO_5$ (317.1)	77–78	45.45	4.13	—	—	25.20
		72	45.43	4.05	—	—	25.83
<i>X</i>	$C_{17}H_6O_6S$ (348.3)	135–137	58.62	4.63	—	9.20	—
		36	58.47	4.54	—	9.14	—
<i>XI</i>	$C_{16}H_{14}O_5S$ (318.3)	113–114	60.37	4.43	—	10.07	—
		55	60.06	4.27	—	9.94	—
<i>XII</i>	$C_{18}H_{18}O_7S$ (378.4)	83–84	57.14	4.79	—	8.47	—
		60	56.92	4.68	—	8.38	—
<i>XIII</i>	$C_{28}H_{32}N_2O_5S$ (508.6)	126–127	66.13	6.34	5.51	6.30	—
		72	66.06	6.33	5.63	6.18	—
<i>XIV</i>	$C_{22}H_{27}BrN_2O_5$ (479.4)	124–125	55.17	5.68	5.84	—	16.67
		61	54.95	5.54	5.95	—	17.01
<i>XV</i>	$C_{22}H_{27}N_3O_7$ (445.5)	113–114	59.32	6.11	9.43	—	—
		87	59.08	6.10	9.55	—	—
<i>XVI</i>	$C_{16}H_{22}N_2O_8$ (370.4)	89–90	51.89	5.99	7.65	—	—
		79	51.90	5.78	7.85	—	—
<i>XVII</i>	$C_{15}H_{20}N_2O_7$ (340.3)	92–93	52.93	5.92	8.23	—	—
		61	53.01	5.77	8.20	—	—

TABLE I
(Continued)

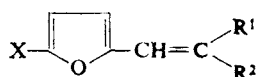
No	Formula (mol.wt.)	M.p., °C yield, %	Calculated/Found				
			% C	% H	% N	% S	% Br
XVIII	C ₂₃ H ₂₉ NO ₇ S (463.6)	107—109	59.59	6.31	3.02	6.92	—
		36	59.13	6.08	2.87	6.83	—
XIX	C ₂₂ H ₂₇ NO ₈ S (465.5)	109—110	56.76	5.85	3.01	6.89	—
		54	56.49	5.71	2.85	6.68	—
XX	C ₂₆ H ₃₂ N ₂ O ₇ S (516.6)	138—140	60.45	6.24	2.71	6.21	—
		86	60.23	6.03	2.53	6.08	—
XXI	C ₂₂ H ₂₇ NO ₇ S (449.5)	136—138	58.78	6.05	3.12	7.13	—
		89	58.49	5.86	2.87	6.91	—
XXII	C ₁₅ H ₁₉ NO ₅ (293.3)	116—117	61.42	6.53	4.78	—	—
		53	61.42	6.51	4.70	—	—
XXIII	C ₁₆ H ₂₁ NO ₆ (323.4)	76—77	59.43	6.55	4.33	—	—
		68	59.51	6.38	4.42	—	—
XXIV	C ₂₁ H ₂₄ N ₂ O ₄ (368.4)	84—85	68.46	6.57	7.60	—	—
		51	68.33	6.58	7.42	—	—
XXV	C ₂₅ H ₂₉ BrN ₄ O (481.5)	151—152	62.37	6.07	11.64	—	16.60
		88	62.32	6.12	11.28	—	16.39
XXVI	C ₃₁ H ₃₄ NO ₄ S (510.7)	153—154	72.91	6.71	10.97	6.28	—
		85	72.90	6.69	11.04	6.18	—
XXVII	C ₃₁ H ₃₄ N ₄ O ₃ S (542.7)	151—152	68.61	6.32	10.32	—	—
		86	68.48	6.18	10.09	—	—
XXVIII	C ₂₅ H ₂₉ BrNO ₄ (481.5)	246—247	62.37	6.07	11.64	—	16.60
		90	62.41	6.08	11.34	—	16.62

^a Yellow oil, $n_D^{20} = 1.406$.

An unexpected reaction course was found in the case of 5-X-2-furfurylidene-3-oxobutanoate and -propanedioate (X = bromo, phenylthiol and phenylsulphonyl group) with N-phenylpiperazine, the amins of 2-[bis(N-phenylpiperaziny)]methyl-5-X-furanes being formed in ethanol at room temperature. Whereas amins of 5-phenylsulphonyl- and 5-phenylthio-2-furaldehyde were stable during crystallization from boiling ethanol, 2-[bis(N-phenylpiperaziny)]methyl-5-bromofurane underwent a rearrangement at the said conditions and gave [5-(4-phenyl-1-piperaziny)]-2-furfurylidene-4-phenylpiperazinium bromide (XXVIII). Further reaction of the ammonium salt with excess N-phenylpiperazine gave a mixture of products wherefrom

N-phenylpiperazinium bromide was isolated. The presumed reaction product 2-[bis(3-phenylpiperaziny)]methyl-5-(4-phenylpiperaziny)furan was not isolated, although its formation is indicated by kinetic study of this reaction.

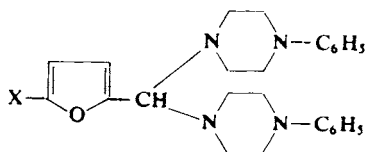
The other reactions of the 5-X-2-furfurylidene derivatives were unsuccessful: either the original condensation products were isolated in 70–80% yields or tarry non-identified products were formed.



- I, X = C₆H₅S, R¹ = COCH₃, R² = COOC₂H₅
 II, X = C₆H₅S, R¹ = R² = COCH₃
 III, X = C₆H₅S, R¹ = R² = COOC₂H₅
 IV, X = NO₂, R¹ = COCH₃, R² = COOC₂H₅
 V, X = NO₂, R¹ = R² = COCH₃
 VI, X = NO₂, R¹ = R² = COOC₂H₅
 VII, X = Br, R¹ = COCH₃, R² = COOC₂H₅
 VIII, X = Br, R¹ = R² = COCH₃
 IX, X = Br, R¹ = R² = COOC₂H₅
 X, X = C₆H₅SO₂, R¹ = COCH₃, R² = COOC₂H₅
 XI, X = C₆H₅SO₂, R¹ = R² = COCH₃
 XII, X = C₆H₅SO₃, R¹ = R² = COOC₂H₅
 XXII, X = morpholinyl, R¹ = COCH₃, R² = COOC₂H₅
 XXIII, X = morpholinyl, R¹ = R² = COOC₂H₅
 XXIV, X = 4-phenylpiperaziny, R¹ = COCH₃, R² = COOC₂H₅
 XIII, X = C₆H₅S, R¹ = R² = COOC₂H₅, B = 4-phenylpiperaziny
 XIV, X = Br, R¹ = R² = COOC₂H₅, B = 4-phenylpiperaziny
 XV, X = NO₂, R¹ = R² = COOC₂H₅, B = 4-phenylpiperaziny
 XVI, X = NO₂, R² = COOC₂H₅, B = morpholinyl
 XVII, X = NO₂, R¹ = COCH₃, R² = COOC₂H₅, B = morpholinyl
 XVIII, X = C₆H₅SO₂, R¹ = R² = COOC₂H₅, B = piperidinyl
 XIX, X = C₆H₅SO₂, R¹ = R² = COOC₂H₅, B = morpholinyl
 XX, X = C₆H₅SO₂, R¹ = R² = COOC₂H₅, B = 4-phenylpiperaziny
 XXI, X = C₆H₅SO₂, R¹ = R² = COOC₂H₅, B = pyrrolidinyl

Structure of the compounds prepared was confirmed by IR, UV, and ¹H NMR spectra. The UV spectra of the 5-X-2-furfurylidene derivatives I–III, VII–XII exhibit three absorption maxima in the regions 206–212 nm, 233–243 nm, and 320 to 362 nm. The nitro derivatives IV–VI show a bathochromic shift of the absorption bands to higher wavelengths, the absorption maxima being in the regions 242 nm, 281–284 nm, and 348–349 nm. The first two can be assigned respectively to the n→π* and π→π* electronic transitions localized in the 5-X-furan section of the molecule, the third band corresponds to oscillations of electrons along the whole

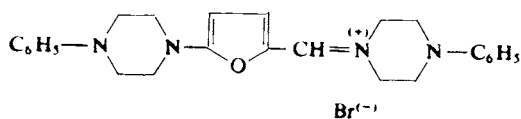
conjugated system of the molecule (K-band). The Michael adducts *XIII*, *XVI*–*XXI* show 2 absorption maxima in their UV spectra which can be assigned to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions localized in the furane, 5-X-furane, or benzene section of the molecule. The compounds *XIV* and *XV* show three absorption bands: the first two bands were assigned to the $\pi \rightarrow \pi^*$ electronic transitions localized in benzene and furane rings, and the longest-wave band to the $n \rightarrow \pi^*$ electronic transition of the 5-nitrofurane section of the molecule. The substitution products *XXII*–*XXIV* exhibit a bathochromic shift of the last band of the original condensation compounds up to the visible part of spectrum, which corresponds to the extension of the conjugated system by the free p electrons at nitrogen atom. Three absorption maxima correspond to the $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ electronic transitions in the furane and benzene nucleus, resp., the last band is due to the electron oscillation along the whole conjugated system of the molecule. UV spectrum of the imonium salt *XXVIII* is interpreted similarly.



XXV, X = Br

XXVI, X = C₆H₅S

XXVII, X = C₆H₅SO₂



XXVIII

The IR spectra of the 5-X-2-furfurylidene derivatives were particularly examined in the regions 1 705–1 725 cm⁻¹ (the wave numbers of C=O bond) and 1 600 to 1 640 cm⁻¹ (the C=C valence vibrations). The IR spectra of the addition products are characterized by the disappearing of the C=C bond vibrations and the shift of C=O vibrations towards higher wave numbers (1 725–1 735 cm⁻¹), which is due to perturbation of conjugation. The IR spectra of amins are characterized by disappearance of the C=C valence vibrations as well as of C=O bond vibrations. The lengthening of conjugated system in the substitution products is manifested by lowering of wave numbers of both C=C and C=O bonds (Table II).

The ¹H NMR spectra of the 5-X-2-furfurylidene derivatives exhibit the singlet

of the olefinic proton in the region of 7.17–7.45 ppm, doublets of the furane protons in the regions of 6.41–6.65 ppm and 6.73–6.80 ppm. The highest δ values were found with the nitro derivatives (6.88–6.93 ppm and 7.32–7.36 ppm). The addition products show a shift of the δ values of the doublets of the furane protons towards lower ppm values as well as a decrease in the values of coupling constants. The coupling constants $J_{\alpha,\beta}$ have the values of 11–12 Hz, which indicates *trans* configuration of the adducts. The substitution products, having extended conjugated

TABLE II
Spectral characteristics of the compounds synthesized (cm^{-1} , nm)

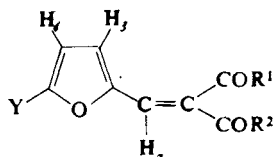
No	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{C})$	λ_{max}	$\log \epsilon$	λ_{max}	$\log \epsilon$	λ_{max}	$\log \epsilon$
I	1 720	1 625	209	3.23	242	3.03	342	2.27
II	1 715	1 630	209	3.26	243	3.05	338	3.26
III	1 725	1 630	210	3.32	243	3.15	335	3.37
IV	1 705	1 630	242	3.09	282	3.11	348	3.24
V	1 710	1 640	242	3.10	284	3.11	348	3.25
VI	1 720	1 635	241	3.08	281	2.81	349	3.25
VII	1 710	1 635	211	2.96	235	2.76	327	3.42
VIII	1 711	1 630	212	3.00	233	2.78	329	3.48
IX	1 725	1 630	210	3.08	235	2.86	325	3.47
X	1 700	1 650	206	3.19	238	3.16	320	3.62
XI	1 720	1 600	207	3.27	236	3.24	321	3.36
XII	1 719	1 625	206	3.14	230	3.07	317	3.38
XIII	1 735	—	209	3.42	246	3.48	—	—
XIV	1 728	—	209	3.25	249	3.23	285	2.20
XV	1 725	—	209	3.30	249	3.19	329	3.08
XVI	1 735	—	210	2.90	319	3.09	—	—
XVII	1 725	—	209	2.88	325	3.08	—	—
XVIII	1 733	—	209	3.08	261	3.03	—	—
XIX	1 735	—	217	3.60	264	3.52	—	—
XX	1 731	—	207	3.43	253	3.39	—	—
XXI	1 735	—	212	3.20	257	3.19	—	—
XXII	1 700	1 615	209	2.96	238	3.04	410	3.42
XXIII	1 705	1 615	210	2.90	231	3.07	405	3.41
XXIV	1 700	1 610	207	3.02	247	3.04	419	3.20
XXV	—	—	208	3.46	251	3.42	—	—
XXVI	—	—	209	3.45	248	3.50	—	—
XXVII	—	—	211	3.26	259	3.35	—	—
XXVIII	—	—	215	3.45	249	3.42	405	3.79
					284	2.48		

system, showed a lowering of δ values of the doublet of H_3 proton and increase of the δ values of the H_4 proton. Also the coupling constants increased by 0.3 Hz in average. Especially high δ values of the furane protons, the δ value of the olefinic proton, and of the coupling constant between the furane protons are observed with the imonium salt XXIV. The reason lies in the positive charge of the nitrogen atom (Tables III and IV).

A number of kinetic measurements were carried out by the spectrophotometric method with the aim of elucidation of the mechanism of both formation of the ami-

TABLE III

^1H NMR data of the 5-X-2-furfurylidene derivatives (δ , ppm)



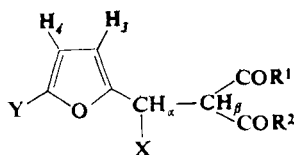
No	Ethyl				COCH_3 s	H_x s	H_3 d	H_4 d	$J_{3,4}$, Hz
	CH_3	t	CH_2	q					
I ^a	1.20		4.20		2.31	7.20	6.64	6.80	3.45
II ^b	—		—		2.28	7.17	6.60	6.76	3.45
III ^c	1.21	1.29	4.15	4.31	—	7.37	6.65	6.76	3.55
IV	1.34		4.46		2.40	7.31	6.91	7.32	4.05
V	—		—		2.43	7.35	6.88	7.35	4.00
VI	1.35	1.40	4.32	4.50	—	7.45	6.93	7.36	4.05
VII	1.41		4.41		2.35	7.26	6.41	6.73	3.50
VIII	—		—		2.33	7.20	6.42	6.71	3.45
IX	1.30	1.40	4.28	4.40	—	7.32	6.41	6.70	3.50
X ^d	1.40		4.51		2.39	7.23	6.79	7.20	3.25
XI ^e	—		—		2.35	7.08	6.75	7.19	3.75
XII ^f	1.32	1.40	4.30	4.50	—	7.36	6.74	7.17	3.70
XXII ^g	1.36		4.29		3.28	7.27	5.30	6.97	3.75
XXIII ^h	1.27	1.32	4.21	4.29	—	7.10	5.25	6.86	3.77
XXIV ⁱ	1.28	1.35	4.22	4.35	2.28 2.45	7.24	6.56	7.05	3.80

^a 7.25 s (phenyl); ^b 7.26 s (phenyl); ^c 7.26 s (phenyl); ^d 7.41 — 8.18 m (phenyl); ^e 7.50 — 8.13 m (phenyl); ^f 7.45 — 8.12 m (phenyl); ^g 3.79 t, 3.28 t (morpholine); ^h 3.76 t, 3.26 t (morpholine); ⁱ 3.25 t, 3.44 t (piperazine), 6.87 — 7.37 m (phenyl).

nals and formation of the S_N reaction products at 5-position of the furane ring. The reaction course of the amination was followed in the reaction of 5-bromo-2-furfurylidene-3-oxobutanoate *VII* with N-phenylpiperazine at the conditions

TABLE IV

^1H NMR data of the addition products (δ , ppm)



No	Ethyl		H_α d	H_β d	H_3 d	H_4 d	$J_{3,4}$, Hz	$J_{\alpha,\beta}$, Hz
	CH_3 t	CH_2 q						
<i>XIII</i> ^a	1.10 1.28	4.06 4.21	4.17	4.47	6.29	6.68	3.50	11.50
<i>XIV</i> ^b	1.16 1.29	4.10 4.22	4.12	4.43	6.18	6.23	3.43	11.75
<i>XV</i> ^c	1.31 1.19	4.12 4.25	4.22	4.55	6.45	7.31	3.65	12.00
<i>XVI</i> ^d	1.23 1.38	4.18 4.27	4.18	4.45	6.45	7.30	3.68	11.75
<i>XVII</i> ^e	1.33	4.18	4.35	4.52	6.40	7.31	3.66	11.50
<i>XVIII</i> ^f	1.04 1.32	3.99 4.23	4.10	4.37	6.26	7.15	3.50	12.00
<i>XIX</i> ^g	1.02 1.31	4.24 4.27	4.10	4.36	6.31	7.16	3.00	11.75
<i>XX</i> ^h	1.05 1.29	4.25 4.69	4.34	4.72	6.31	6.80	3.50	12.00
<i>XXI</i> ⁱ	1.01 1.28	3.95 4.26	4.07	4.36	6.27	7.13	3.50	11.00

^a 6.78–7.35 m (phenyl); 3.09 t, 2.25–2.88 m (N-phenylpiperazine); ^b 6.75–7.33 m (phenyl); 3.10 t, 2.32–2.88 m (N-phenylpiperazine); ^c 6.74–7.25 m (phenyl); 3.13 t, 2.34–2.88 m (N-phenylpiperazine); ^d 3.63 t, 2.13–2.88 m (morpholine); ^e 2.30 s (COCH_3), 3.61 t, 2.18–2.70 m (morpholine); ^f 7.38–8.13 m (phenyl), 1.83–2.68 m (piperidine); ^g 7.33–8.13 m (phenyl), 3.53 t, 1.88–2.75 m (morpholine); ^h 6.68–7.41 m (phenyl), 3.02 t, 2.28–2.88 m (N-phenylpiperazine); ⁱ 7.43–8.10 m (phenyl), 2.02–2.70 m (pyrrolidine).

of pseudomonomolecular reaction (excess nucleophilic reagent) at the $\lambda_{\max}$ of the absorption band of the condensation product. The reaction kinetics could not be followed at $\lambda_{\max}$ of the aminal formed, because N-phenylpiperazine itself absorbs as far as to $\lambda \sim 300$ nm. Therefore, from the calculated rate constant $k_2 = 1.72 \cdot 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ we can only estimate the overall rate of conversion of the condensation product and not the rate of the aminal formation. The rate constant of the 1,5-sigmatropic rearrangement to the corresponding imonium salt is $k' = 6.87 \cdot 10^{-5} \text{ s}^{-1}$. The time dependence of UV spectrum at the $\lambda_{\max}$ of imonium salt showed an abrupt extinction decrease within about 15 min of the reaction of the imonium salt with excess N-phenylpiperazine, whereafter the UV spectrum remained unchanged. Linear dependence was obtained from the kinetic equations. We suppose that the reaction only proceeds partially, and that an equilibrium is established, which agrees with ref.⁸. Finally we also followed the kinetics of S_N reaction of compound VII with N-phenylpiperazine in methanol (at the boiling temperature) and with morpholine at various temperatures. The data found indicate that the S_N reaction proceeds through an intermediate M probably adduct – which could not be trapped synthetically and identified.

With the aim of elucidation of the influence of the condensation residue bound at 2-position of the furane ring on the course of the S_N reaction, we carried out kinetic measurements to compare reactivities of compounds VII and IX in their reactions with morpholine. It was shown that the substituted ethyl 2-oxobutanoate VII is more reactive by the factor of 3.34, which is connected with its stronger electron-acceptor character.

EXPERIMENTAL

5-X-2-Furfurylidene Derivatives I–XII

A solution of 16.5 ml (0.15 mol) TiCl_4 in 400 ml CCl_4 was added dropwise to 250 ml tetrahydrofuran, and the mixture was treated with 0.075 mol 5-X-2-furaldehyde in 30 ml tetrahydrofuran.

TABLE V

The rate constants k_2 ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) of the S_N reactions in methanol

Substrate	Reagent	Temperature °C	$\lambda_{\max}$ nm	k' s^{-1}	$k_2 \cdot 10^{-2}$
VII	N-phenylpiperazine	B.p.	419	—	1.21
VII	morpholine	25°	410	$1.66 \cdot 10^{-4}$	1.66
VII	morpholine	B.p.	410	$9.59 \cdot 10^{-5}$	1.91
VIII	morpholine	B.p.	405	$2.87 \cdot 10^{-5}$	0.57

and with 0.075 mol of the respective 1,3-dicarbonyl compound. Within further 2 h, 24 ml (0.3 mol) pyridine in 25 ml tetrahydrofuran was added drop by drop with stirring and cooling at -5°C . The mixture was then kept at -5°C for 24 h and decomposed with 75 ml water. The aqueous layer was extracted with ether, the organic portions were combined, dried, concentrated, and left to crystallize. The raw product was recrystallized from ethanol. Compound *V* (oil) was isolated chromatographically (silica gel; benzene–2-propanone 4 : 1).

Addition Products *XIII*–*XXI*

A solution of 0.003 mol of the respective 5-X-2-furfurylidene derivative in 20 ml ethanol was treated with 0.006 mol secondary amine. The mixture was stirred at room temperature until precipitation of the raw product which was collected by suction and recrystallized from ethanol.

Products of Nucleophilic Substitution *XXII*–*XXIV*

A solution of 0.03 mol 5-bromo-2-furfurylidene derivative in 20 ml ethanol was treated with 0.009 mol secondary amine. The mixture was boiled 2–3 h and stirred at room temperature 12 h. During the reaction a precipitate was formed (hydrobromide of unreacted reagent) which was removed by filtration; the filtrate was concentrated, and the products were isolated by column chromatography (silica gel, benzene–2-propanone 3 : 2).

Aminals *XXV*–*XXVII*

A solution of 0.003 mol ethyl 2-(5-X-2-furfurylidene)-3-oxobutanoate and 3-(5-X-furfurylidene)-2,4-pentanedione ($\text{X} = \text{Br}, \text{C}_6\text{H}_5\text{S}, \text{C}_6\text{H}_5\text{SO}_2$) in 20 ml ethanol was treated with 0.009 mol N-phenylpiperazine. The mixture was stirred at room temperature until separation of a precipitate. The raw product was purified by crystallization from ethanol. ^1H NMR spectra: *XXV*: 6.22 d (H_3); 6.28 d (H_4); 3.84 s (H_2); 2.40 t, 3.19 t (piperazine); 6.75–7.38 m (phenyl); $J_{3,4} = 3.50$ Hz. *XXVI*: 6.31 d (H_3); 6.70 d (H_4); 3.89 s (H_2); 2.68 t, 3.16 t (piperazine); 6.80–7.37 m (phenyl); $J_{3,4} = 3.25$ Hz. *XXVII*: 6.36 d (H_3); 6.65 d (H_4); 3.90 s (H_2); 3.11 t, 2.19–2.80 m (piperazine); 6.68–7.40 m (phenyl); $J_{3,4} = 3.25$ Hz.

[5-(4-Phenyl-1-piperazinyl)-2-furfurylidene]-4-phenyl-piperazinium Bromide (*XXVIII*)

A solution of 0.003 mol 2-[bis(4-phenylpiperazino)]methyl-5-bromofurane in 20 ml ethanol was heated on water bath 10 min. The imonium salt was obtained by cooling. ^1H NMR spectrum: 8.84 s (H_α); 8.81 d (H_3); 6.16 d (H_4); 3.25–4.32 m (piperazine); 6.78–7.40 (phenyl); $J_{3,4} = 4.56$ Hz.

Spectral Measurements

The IR spectra were measured with a UR-20 apparatus (Zeiss, Jena) in a 0.26 mm cell in chloroform. The apparatus was calibrated with a polystyrene film of 25 μm thickness. The accuracy of the frequency readings was $\pm 3 \text{ cm}^{-1}$. The ^1H NMR spectra were measured with an 80 MHz NMR spectrometer BS 587 C Tesla in C_2HCl_3 using tetramethylsilane as the internal standard. The UV absorption spectra of the synthesized compounds were measured with Specord UV VIS apparatus, (Zeiss, Jena) in 10 mm cell; concentration of the methanolic solutions was (2 to 5) $\cdot 10^{-5} \text{ mol dm}^{-3}$. The kinetic measurements of the S_N reactions were carried out with a recording spectrophotometer Specord UV VIS (Zeiss, Jena) in 1 cm tempered cells. The measured mixture was composed of 0.3–0.7 ml substrate in methanol and 0.3–9.9 ml solution of the secondary

amine. The resulting concentrations of the substrate and nucleophile were $(3-7) \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$ and $1 \cdot 10^{-1} \text{ mol dm}^{-3}$, respectively. The apparent rate constants k' were calculated from the slope of the dependence $\log(a - x) = f(t)$, and the rate constants k_2 were obtained by dividing k' by concentration of the nucleophilic reagent. The values obtained are given in Table V.

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