ADDITION OF HETEROCYCLIC CH ACIDS TO THE C=N BOND OF AZOMETHINES

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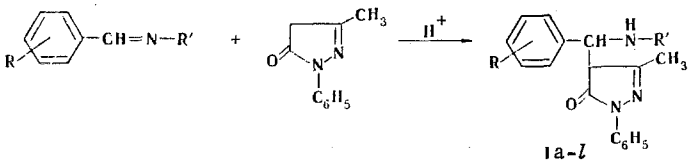
The aminomethylation of oxindole, 1-phenyl-3-methyl-5-pyrazolone, and N-phenylrhodanine was studied. Derivatives of these CH acids were obtained as a result of aminomethylation. The addition products were subjected to acid and base hydrolysis; the corresponding arylidene derivatives are formed in the case of the products of aminomethylation of oxindole and 1-phenyl-3-methyl-5-pyrazolone, while thioglycolic acids are formed in the case of N-phenylrhodanine derivatives.

The reactions of azomethines with various compounds that contain a labile hydrogen atom have been studied quite thoroughly. Ketones and β-dicarbonyl compounds [1, 2], as well as some unsaturated compounds [3], react readily with azomethines to give addition products. Up until now the reaction has not been extended to heterocyclic CH acids such as 1-phenyl-3-methyl-5-pyrazolone, which is the basic structural fragment of many medicinal agents with antiphlogistic, antipyretic, and analgetic activity [4, 5].

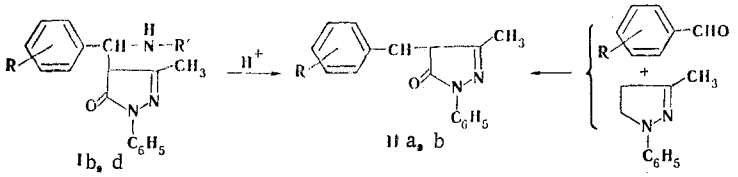
In the present research we studied the aminomethylation of some heterocyclic CH acids by means of Schiff bases. We found that 1-phenyl-3-methyl-5-pyrazolone readily reacts with various Schiff bases in the presence of catalytic amounts of hydrochloric acid to give addition products Ia-*l*:*



Ia-*l*

a R=H, R′=4-I—C_6H_5; b R=H, R′=4-Br—C_6H_5; c R=3-OH, R′=3-Br—C_6H_5; d R=4-OCH_3, R′=C_6H_5; e R=2-OCH_3, R′=C_6H_5; f R=4-CH_3, R′=C_6H_5; g R=2-OCH_3, R′=CH_3; h R=2-OH, R′=CH_3; i R=4-Cl, R′=CH_3; j R=H, R′=CH_3; k R=O—C_6H_5, R′=C_6H_5; *l* R=3-NO_2, R′=7-quinolyl

Aminomethyl derivatives I are rather unstable compounds and readily split out alkylamino or arylamino groups when they are refluxed briefly in dilute solutions of mineral acids to give arylidene derivatives (II), the structures of which were proved by alternative synthesis by direct condensation of 1-phenyl-3-methyl-5-pyrazolone with the corresponding aldehydes:



Ib, d IIa, b

An amino group is also detached in the case of alkaline hydrolysis, but a longer time is required for this.

Compounds I are white crystalline substances, and an intense absorption band at 1700-1710 cm^{-1} (pyrazolone $\nu_{C=O}$) and a broad absorption band centered at 3200 cm^{-1} (ν_{NH}) are observed in their IR spectra.

*The stereochemistry of the process will be investigated in the future.

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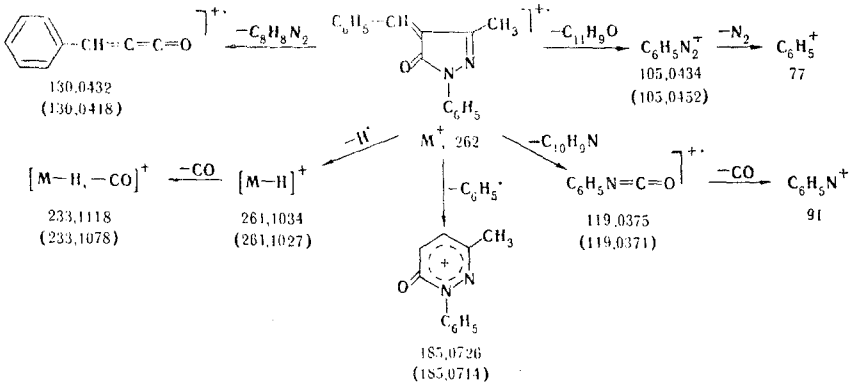
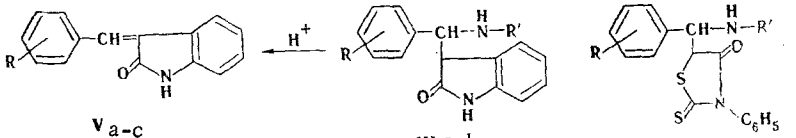
An M^+ peak is not recorded in the mass spectrum of Ia. The ion peak with the highest m/e value corresponds to the corresponding arylidene derivative IIa; this was confirmed rigorously by data from the high-resolution mass spectrum (HRMS) (the value determined from the spectrum was 262.1115, as compared with the value of 262.1106 calculated form the empirical composition $C_{17}H_{14}N_2O$).

The character of the fragmentation of substituted 5-pyrazolones has been studied quite thoroughly [6-8]. We determined the compositions of the fragment ions for II by means of the high-resolution mass spectra. The mass-spectrometric fragmentation corresponds completely to the IIa structure.*



In addition to the common ions indicated in the scheme, peaks of ions with m/e 92† ($[C_6H_5N]^+$), 127 ($[I]^+$), 192 ($[C_5H_5]^+$), 203 ($[IC_6H_4]^+$), and 219 ($[IC_6H_4NH_2]^+$), which are formed as a result of fragmentation of p-iodoaniline, are observed in the mass spectrum of Ia. It may be assumed that a rearrangement process associated with the elimination of the amine component from Ia also takes place under the elevated temperature conditions during vaporization of the substance into the ion source.

Other heterocyclic CH acids, viz., oxindole and N-phenylrhodanine, also add readily to the double bond of azomethines to give III and IV. Product III undergoes acid hydrolysis to give arylidene derivative V. Some compounds of the V type were obtained by alternative synthesis:



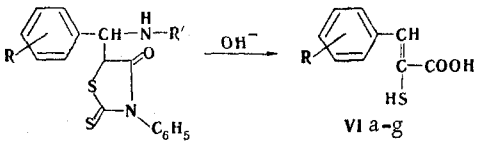
V a-c III a-k IV a-k

III a R=2-OH, R′=C_2H_5; b R=4-OH, R′=C_6H_5; c R=4-CH_3, R′=C_6H_5; d R=4-OCH_3, R′=C_6H_5; e R=4-NO_2, R′=C_6H_5; f R=4-NO_2, R′=4-NO_2—C_6H_5; g R=4-F, R′=C_6H_5; h R=4-Cl, R′=C_6H_5; i R=H, R′=4-Cl—C_6H_5; j R=H, R′=4-Br—C_6H_5; k R=H, R′=4-I—C_6H_5; IV a R=3-NO_2, R′=C_6H_5; b R=4-OH, R′=C_6H_5; c R=4-$(CH_3)_2N$, R′=C_6H_5; d R=4-Br, R′=C_6H_5; e R=4-F, R′=C_6H_5; f R=2-OH, 5-NO_2, R′=C_6H_5; g R=4-Br, R′=3-NO_2—C_6H_5; h R=4-F, R′=3-NO_2—C_6H_5; i R=4-NO_2, R′=C_6H_5—O—C_6H_5; j R=4-$(CH_3)_2N$, R′=C_6H_5—O—C_6H_5; k R=H, R′=CH_3; V a R=H; b R=4-Cl; c R=4-Br

It is known that the thiazolidine ring in the N-phenylrhodanine molecule is extremely unstable in alkaline media and undergoes cleavage to give thioglycolic acids. We investigated the behavior of aminomethyl derivatives IV under alkaline-hydrolysis conditions and observed that they are converted to the sodium salts of mercaptocinnamic acids VI. Simultaneous cleavage of the thiazolidine ring and elimination of the amine component occur in this case under the influence of alkali:

*The accurately measured and calculated masses (in parentheses) of the ions for the indicated compositions are presented under the formulas.

†Here and subsequently, the numbers that characterize the ions are the mass-to-charge ratios.



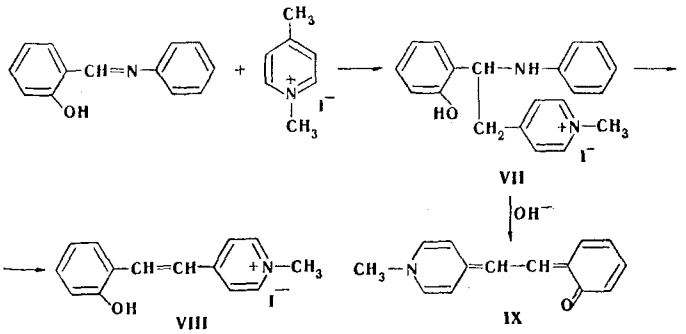
IV b, d-i, k VI a-g

VI a R=4-OH; b R=4-N$(CH_3)_2$; c R=4-Br; d R=4-F; e R=2-OH, 5-NO_2; f R=4-NO_2; g R=H

The IR spectra of IV contain intense absorption bands at 1700-1720 cm^{-1} corresponding to the C=O group of the thiazoline ring, a band at 1160 cm^{-1} ($\nu_{C=S}$), and a weak absorption band with a maximum at 3200 cm^{-1} (ν_{NH}). An M^+ peak is not recorded in the mass spectrum of IVd (as in the case of Ia). Thermal destruction of this compound during vaporization of the sample into the ion source of the mass spectrometer evidently also occurs in this case, and two substances, viz., aniline (m/e 93) and a substance corresponding to an arylidene derivative (m/e 375 and 377 with an ion-peak intensity ratio of 1:1, which is characteristic for the presence of one Br atom in the molecule), are recorded in the mass spectrum.

β-Cleavage relative to the rhodanine ring, which is associated with the elimination of a C_6H_4Br particle (the 220 ion), occurs in the first step of the fragmentation of the M^+ ion of the corresponding arylidene derivative. The formation of 119 ($[C_6H_5NCO]^+$), 135 ($[C_6H_5NCS]^+$), and 167 ($[C_6H_5NCS_2]^+$) ions is characteristics for rhodanine structures [9].

It is known that the methyl groups in quaternary α- and γ-picolinium and α- and γ-methylquinolinium salts have a certain degree of CH acidity, and this made it possible to introduce their residues in the acridine molecule [10]. It seemed to us that the introduction of residues of α- and γ-methylpyridines and quinolines in various azomethine molecules, which would lead to an easy method for the synthesis of aminoethylpyridine derivatives, would be similarly possible. However, we were unable to isolate the corresponding addition products (VII) in all of these cases — they immediately split out an arylamino group and were converted to quaternary α- and γ-styrylpyridinium and quinolinium salts (VIII), except for the product (VII) of addition of γ-picolinium methiodide to a Schiff base:



However, even this product proved to be extremely unstable and was converted to 1-methyl-4-(2-hydroxystyryl)pyridinium iodide (VIII) when it was allowed to stand for a long time. Product VII was converted to anhydro base IX, which we obtained by an independent method, when it was treated with ammonium hydroxide.

EXPERIMENTAL

The IR spectra of solutions of the compounds in chloroform and suspensions in mineral oil (l = 0.15-0.6 mm, C = 0.5-1.0 mole/liter) were recorded with an IK-20 spectrometer. The mass spectra were obtained with a Varian MAT-311A spectrometer at an accelerating voltage of 3 kV, a cathode emission current of 300 μA, an ionizing voltage of 70 V, and an ion-source temperature of 250-300°C. Chromatography in a loose thin layer of aluminum oxide (Brockmann activity II) was realized by elution with a chloroform–benzene–hexane–methanol system (30:6:1:1) with development by iodine vapors and in UV light.

1-Phenyl-3-methyl-4-[(4-iodophenylamino)phenyl]methyl-5-pyrazolone (Ia). A mixture of 1.5 g (0.005 mole) of benzal-4-iodoaniline, 0.85 g (0.005 mole) of 1-phenyl-3-methyl-5-pyrazolone, and a drop of concentrated HCl in 15 ml of ethanol was refluxed for 5 min, after which it was cooled, and the precipitate was removed by filtration and recrystallized from

TABLE 1. Aminomethyl and Arylidene Derivatives of Heterocyclic CH Acids

Compound	mp,* °C	R_f†	Found, %				Empirical formula	Calculated, %				Yield, %
			C	H	N	S		C	H	N	S	
Ia	165—167	0,46	57,3	4,1	8,6	—	$C_{23}H_{20}IN_3O$	57,4	4,2	8,7	—	20
Ib	135—137	0,44	63,4	4,8	9,9	—	$C_{23}H_{20}BrN_3O$	63,6	4,6	9,7	—	60
Ic	203—205	0,42	61,2	4,6	9,3	—	$C_{23}H_{20}BrN_3O_2$	61,3	4,5	9,3	—	10
Id	125—127	0,44	74,7	6,1	10,7	—	$C_{24}H_{23}N_3O_2$	74,8	6,0	10,9	—	70
Ie	200—202	0,48	74,7	6,1	10,7	—	$C_{24}H_{23}N_3O_2$	74,8	6,0	10,9	—	27
If	166—168	0,47	77,9	6,4	11,2	—	$C_{24}H_{23}N_3O$	78,0	6,3	11,4	—	45
Ig	83—85	0,49	70,5	6,6	13,1	—	$C_{19}H_{21}N_3O_2$	70,6	6,5	13,0	—	48
Ih	225—227	0,45	70,0	6,4	13,7	—	$C_{18}H_{19}N_3O_2$	69,9	6,2	13,6	—	40
Ii	173—175	0,34	66,1	5,4	12,6	—	$C_{18}H_{18}ClN_3O$	65,9	5,5	12,8	—	11
Ij	170—172	0,41	73,6	6,4	14,4	—	$C_{18}H_{19}N_3O$	73,7	6,5	14,3	—	42
Ik	136—137	0,34	77,7	5,5	9,6	—	$C_{29}H_{25}N_3O_2$	77,8	5,6	9,4	—	38
Il	156—158	0,40	69,1	4,4	15,3	—	$C_{26}H_{20}N_5O_3$	69,3	4,5	15,5	—	38
IIIa	199—201	0,41	72,0	6,3	10,0	—	$C_{17}H_{18}N_2O_2$	72,3	6,4	9,9	—	71
IIIb	197—199	0,41	76,2	5,6	8,4	—	$C_{21}H_{18}N_2O_2$	76,3	5,5	8,5	—	51
IIIc	205—207	0,50	80,7	6,3	8,3	—	$C_{22}H_{20}N_2O$	80,5	6,1	8,5	—	31
IIId	195—197	0,55	76,5	5,7	8,3	—	$C_{22}H_{20}N_2O_2$	76,7	5,9	8,1	—	92
IIIe	186—188	0,55	70,0	5,0	11,5	—	$C_{21}H_{17}N_3O_3$	70,2	4,8	11,7	—	58
IIIf	248—250	0,50	62,6	4,2	13,7	—	$C_{21}H_{16}N_4O_5$	62,4	4,0	13,9	—	52
IIIg	192—194	0,50	76,0	5,5	8,2	—	$C_{21}H_{17}FN_2O$	75,9	5,2	8,4	—	36
IIIh	200—201	0,50	72,2	4,8	8,2	—	$C_{21}H_{17}ClN_2O$	72,3	4,9	8,0	—	69
IIIi	215—217	0,74	72,1	4,8	8,1	—	$C_{21}H_{17}ClN_2O$	72,3	4,9	8,0	—	45
IIIj	210—212	0,74	64,3	4,3	7,0	—	$C_{21}H_{17}BrN_2O$	64,1	4,4	7,1	—	81
IIIk	220—222	0,73	57,2	4,1	6,3	—	$C_{21}H_{17}IN_2$	57,3	3,9	6,4	—	49
IIa	210—212	0,33	77,6	5,3	10,8	—	$C_{17}H_{14}N_2O$	77,8	5,4	10,7	—	40
IIb	217—219	0,33	74,1	5,7	9,5	—	$C_{18}H_{16}N_2O_2$	74,0	5,5	9,6	—	53
IVa	246—248	0,89	60,5	4,0	9,9	14,5	$C_{22}H_{17}N_3O_3S_2$	60,7	3,9	9,7	14,7	50
IVb	290—292	0,89	67,5	4,6	7,4	16,3	$C_{22}H_{18}N_2OS_2$	67,7	4,7	7,1	16,4	42
IVc	234—235	0,90	66,2	5,3	9,9	14,9	$C_{24}H_{23}N_3OS_2$	66,5	5,4	9,7	14,8	31
IVd	210—212	0,89	56,1	3,9	6,2	13,4	$C_{22}H_{17}BrN_2OS_2$	56,3	3,7	6,0	13,7	67
IVe	230—232	0,89	64,7	4,2	6,5	15,8	$C_{22}H_{17}FN_2OS_2$	64,7	4,2	6,7	15,7	62
IVf	202—204	0,89	58,5	3,6	9,5	14,0	$C_{22}H_{17}N_3O_4S_2$	58,5	3,8	9,3	14,2	35
IVg	178—180	0,89	51,3	3,3	8,5	12,3	$C_{22}H_{16}BrN_3O_3S_2$	51,4	3,1	8,2	12,5	43
IVh	150—152	0,89	58,5	3,4	9,1	14,4	$C_{22}H_{16}FN_3O_3S_2$	58,3	3,6	9,3	14,1	39
IVi	198—200	0,89	63,5	4,1	8,2	12,3	$C_{28}H_{21}N_3O_4S_2$	63,7	4,0	8,0	12,2	40
IVj	222—224	0,89	68,4	5,5	8,2	12,1	$C_{30}H_{27}N_3O_2S_2$	68,5	5,2	8,0	12,2	32
IVk	192—194	0,89	62,4	5,0	8,3	19,4	$C_{17}H_{16}N_2OS_2$	62,2	4,9	8,5	19,5	67
VIa	182—184	0,89	54,4	4,5	—	16,7	$C_9H_9O_3S$	54,8	4,6	—	16,5	34
VIb	238—240	0,89	58,7	6,2	6,5	14,4	$C_{11}H_{14}NO_2S$	58,9	6,3	6,2	14,3	24
VIc	170—172	0,89	41,4	3,2	—	12,5	$C_9H_8BrO_2S$	41,6	3,1	—	12,3	75
VId	150—152	0,89	54,5	4,3	—	16,0	$C_9H_8FO_2S$	54,3	4,1	—	16,1	30
VIe	118—120	0,89	44,7	3,5	5,6	13,4	$C_9H_8NO_5S$	44,6	3,3	5,8	13,2	17
VIf	160—162	0,89	48,0	3,5	6,4	14,0	$C_9H_8NO_4S$	47,8	3,6	6,2	14,2	17
VIg	124—126	0,89	59,9	4,9	—	17,6	$C_9H_9O_2S$	59,7	5,0	—	17,7	15
Va	170—172	0,40	81,3	5,2	6,4	—	$C_{15}H_{11}NO$	81,4	5,0	6,3	—	25
Vb	179—181	0,32	70,2	4,1	5,5	—	$C_{15}H_{10}ClNO$	70,4	3,9	5,5	—	49
Vc	168—170	0,42	60,2	3,2	4,8	—	$C_{15}H_{10}BrNO$	60,0	3,4	4,7	—	52
VII	139—140	—	55,7	4,7	6,7	—	$C_{20}H_{21}IN_2O$	55,6	4,9	6,5	—	10
VIII	232—234	—	49,5	4,4	4,3	—	$C_{14}H_{14}INO$	49,6	4,2	4,1	—	50
IX	255—257	—	79,7	6,1	6,3	—	$C_{14}H_{13}NO$	79,6	6,2	6,6	—	85

*From ethanol. †In a chloroform—benzene—hexane—methanol system (30:6:1:1).

ethanol to give 0.5 g (20%) of a product with mp 165-167°C and R_f 0.46. IR spectrum: 1710 (C=O) and 3200 cm^{-1} (N—H). Mass spectrum, m/e (intensity, %):* 55 (15.6), 57 (13.2), 63 (31.9), 64 (35.7), 65 (18.1), 74 (10.0), 75 (13.2), 76 (18.9), 77 (95.3), 78 (18.3), 89 (20.4), 90 (13.2), 91 (87.1), 92 (13.2), 93 (6.9), 102 (22.0), 103 (16.1), 105 (31.4), 116 (15.1), 119 (5.0), 127 (34.1), 128 (23.1), 129 (14.5), 130 (14.8), 185 (100.0), 186 (18.3), 192 (15.6), 194 (10.1), 203 (5.0), 219 (5.4), 232 (18.1), 233 (10.0), 261 (55.4), 262 (95.5), 263 (20.8). Found: C 57.3; H 4.1; I 26.7; N 8.6%. $C_{23}H_{20}IN_3O$. Calculated: C 57.4; H 4.2; I 26.4; N 8.7%.

3-Phenyl-5-[(4-bromophenyl)phenylamino]methylrhodanine (IVd). A mixture of 1.3 g (0.005 mole) of p-bromobenzalaniline, 1.0 g (0.005 mole) of N-phenylrhodanine, and a drop of concentrated HCl in 20 ml of ethanol was refluxed for 4-5 h, after which the precipitate was removed by filtration and recrystallized from ethanol to give 1.53 g (67%) with mp 210-212°C. IR spectrum: 1710 (C=O), 3200 (N—H), and 1160 cm^{-1} (C=S). Mass spectrum, m/e (intensity, %): 55 (23.6), 56 (10.8), 57 (26.8), 62 (10.4), 63 (30.5), 64 (16.5), 65 (10.6),

*The ion peaks with intensities ≥3% of the maximum ion peak are indicated.

69 (15.9), 70 (9.1), 71 (17.4), 74 (12.6), 75 (20.9), 76 (12.0), 77 (62.0), 79 (6.0), 81 (6.1), 83 (11.0), 89 (46.5), 90 (14.4), 91 (11.8), 93 (17.3), 94 (6.3), 105 (21.4), 119 (4.5), 133 (49.0), 134 (9.6), 135 (14.4), 167 (5.3), 194 (21.2), 220 (5.6), 375 (100.0), 376 (13.6), 377 (98.8), 378 (12.8). Found: C 56.3; H 3.7; Br 17.0; N 6.0; S 13.7%. $C_{22}H_{17}BrN_2OS_2$. Calculated: C 56.2; H 3.9; Br 17.3; N 6.1; S 13.5%. Other aminomethyl derivatives of heterocyclic CH acids, the principal characteristics of which are presented in Table 1, were similarly obtained.

1-Phenyl-3-methyl-3-benzylidene-5-pyrazolone (IIa). A) A 2.4-g (0.005 mole) sample of 1-phenyl-3-methyl-4-[(4-iodophenylamino)phenyl]methyl-5-pyrazolone was refluxed in 20 ml of dilute HCl (1:1) for 1 h, after which the precipitate was removed by filtration and recrystallized from ethanol to give 0.9 g (40%) of a product with mp 210-212°C and R_f 0.33. Found: C 77.6; H 5.5; N 10.6%. $C_{17}H_{14}N_2O$. Calculated: C 77.8; H 5.4; N 10.7%. Other arylidene derivatives of heterocyclic CH acids, the principal characteristics of which are presented in Table 1, were similarly obtained.

B) A mixture of 1.17 g (0.01 mole) of 1-phenyl-3-methyl-5-pyrazolone and 1.06 g (0.01 mole) of benzaldehyde in 10 ml of ethanol was refluxed for 5 h, after which it was cooled, and the precipitate was removed by filtration and recrystallized from ethanol to give 1.26 g (45%) of a product with mp 211-213°C. No melting-point depression was observed for a mixture of this product with a sample of the compound obtained by method A.

1-Mercapto-2-(p-bromophenyl)cinnamic Acid (VIc). A 0.2-g (0.0004 mole) sample of N-phenyl-5-[(4-bromophenyl)phenylamino]methylrhodanine was refluxed in 20 ml of a 5% solution of KOH for 4-5 h, after which the mixture was cooled and neutralized with concentrated HCl, and the precipitate was removed by filtration and recrystallized from ethanol to give 0.15 g (75%) of a product with mp 160-162°C. Found: C 41.6; H 3.4; Br 30.6; S 12.3%. $C_9H_8BrO_2S$. Calculated: C 41.6; H 3.1; Br 30.8; S 12.4%.

1-Methyl-4-[2-anilino-2-(2-hydroxyphenyl)ethyl]pyridinium Iodide (VII). A mixture of 1.97 g (0.01 mole) of o-hydroxybenzalaniline, 2.35 g (0.01 mole) of γ-picoline methiodide, and 15 ml of ethanol was refluxed for 10 min, after which it was cooled, and the precipitate was removed by filtration and recrystallized from ethanol to give 0.43 g (10%) of a product with mp 139-140°C. IR spectrum: 1650 (C=N), 3320 (N–H), and 3600 cm^{-1} (OH). Found: C 55.7; H 4.7; I 29.2; N 6.7%. $C_{20}H_{21}IN_2O$. Calculated: C 55.6; H 4.9; I 29.4; N 6.5%.

Workup of the combined filtrates gave 1.7 g (50%) of 1-methyl-4-(2-hydroxystyryl)-pyridinium iodide (VIII) with mp 232-234°C (from ethanol), which did not depress the melting point of a genuine sample obtained by the method described in [11].

1-Methyl-4-[2-(2-oxophenylidene)ethylidene]-1,4-dihydropyridine (IX). A suspension of 0.2 g (0.0006 mole) of 1-methyl-4-(2-hydroxystyryl)pyridinium iodide was maintained at 20°C for 1-2 min, after which it was worked up to give 0.17 g (85%) of IX with mp 255-257°C.

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