3-Phenylbenzo[c]pyrido[1,2-f]phenanthridinium perchlorate (VII). A solution of 0.5 g of the perchlorate II in 0.5 liter of ethanol was irradiated for 6 h. The reaction mixture was evaporated to 50 ml and 0.38 g (76%) of compound VII was filtered off. Mp 300-302°C (dec.), from acetonitrile. Found: C 71.2; H 4.0; Cl 7.9; N 3.1%. $C_{27}H_{18}ClNO_4$. Calculated: C 71.2; H 4.0; Cl 7.8; N 3.1%.

6-Phenylbenzo[b]pyrido[1,2-f]phenanthridinium perchlorate (VIII). A solution of 0.35 g of the perchlorate IV in 0.5 liter of a 1:1 mixture of ethanol and chloroform was irradiated for 8 h. The reaction mixture was evaporated to 50 ml, and 0.22 g (63%) of compound VIII was obtained. Mp 263-265°K (dec.), from a 1:1 mixture of acetonitrile and ethanol. Found: C 71.2; H 3.9; Cl 7.6; N 3.2%. $C_{27}H_{18}ClNO_4$. Calculated: C 71.2; H 4.0; Cl 7.8; N 3.1%.

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THERMAL DECOMPOSITION OF 1,2-DIMETHYL-3(5)-(4-R-STYRYL)-PYRAZOLIUM IODIDES

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The reaction of 1,2,3(5)-trimethylpyrazolium iodide with aromatic aldehydes yielded the series of 1,2-dimethyl-3(5)-(4-R-styryl)pyrazolium iodides (R = H, NMe_2, NO_2). The quantitative ratio of 1-methyl-3- and -5-(4-R-styryl)pyrazoles formed in the thermal decomposition of the above-mentioned pyrazolium iodides depends on steric factors in the initial compounds and on the electronic influence of the substituent R. A simple method was proposed for the production of trans,trans-1,4-bis(1-methyl-3-pyrazolylvinyl)benzene and 1-methyl-3,5-distyrylpyrazole, which possess fluorescent properties.

Earlier we described the synthesis of trans-1-methyl-3- and -5-(4-R-styryl)pyrazoles (R = NO_2, NH_2) and trans,trans-1,4-bis(1-methyl-3- (I) and -5-pyrazolylvinyl)benzenes (II). However, the multistep nature of the synthesis and the low yields hinder searches for ways of practical utilization of compounds I and II, which possess intense fluorescence in solutions and in the solid state [1]. The methyl group in the 3(5)- position of 1,2,3(5)-trimethylpyrazolium iodide (III) is active in the reaction of condensation with aldehydes, and certain 1,2-dimethyl-3(5)-(R-styryl)pyrazolium iodides have been produced by the reaction of compound III with aromatic aldehydes [2]. Thus, we synthesized 1,2-dimethyl-3(5)-(4-R-

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styryl)pyrazolium iodides (IVa, b; *a* R = H, b R = NMe_2), as well as 1,2-dimethyl-3(5)-(4-nitrostyryl)pyrazolium iodide (IVc) and 1,4-bis[1,2-dimethylpyrazolium-3(5)vinyl]benzene diiodide (V), which have not been described in the literature. The styrylpyrazolium iodides IVa-c exist in the form of trans-isomers; compound V has a trans,trans-configuration of the ethylene fragments, which is confirmed by the position and intensity of the long-wave band in the electronic absorption spectra of these compounds, sensitive to the geometrical configuration of the molecules [1, 3]. The hyposochromic shift of the long-wave band in the spectrum of compound IVc relative to the similar band in the spectra of trans-1-methyl-3- and -5-(4-nitrostyryl)pyrazoles [1] is due to a decrease in the π-donor pyrazolium residue in comparison with 3- and 5-pyrazolyl radicals [4], leading to a weakening of the interaction of the heterocycle with the electron acceptor 4-nitrostyryl substituent. In the thermal decomposition of 1,2,3(5)-trimethylpyrazolium iodide III, a mixture of 1,3- and 1,5- dimethylpyrazoles is obtained [5]; in the mass spectra of compounds IVa-c the peak of the molecular ions (M^+) is absent, while in the region of high values of m/z the peak of the ions $[M - CH_3I]^+$ is observed. Stripping of methyl iodide from 1,2-dimethyl-3(5)-(4-R-styryl)pyrazolium iodides leads to the formation of the corresponding 1-methyl(4-R-styryl)pyrazoles.

On the basis of the aforementioned, we conducted the thermal decomposition of compounds IVa-c in order to obtain styrylpyrazoles. The initial pyrazolium iodides were heated to the decomposition point, exposed until methyl iodide ceased to be distilled off, and the products obtained in the extraction of the residue were analyzed. It was established that in the thermolysis of 1,2-dimethyl-3(5)-(4-nitrostyryl)pyrazolium iodide IVc, only trans-1-methyl-3-(4-nitrostyryl)pyrazole (VI), obtained previously by directed synthesis from 1,3-dimethylpyrazole, is formed [1]. Under the same conditions a mixture of 1-methyl-3-styryl- (VII) and 1-methyl-5-styrylpyrazole (VIII) is obtained in a 3:1 ratio from 1,2-dimethyl-3(5)-styrylpyrazolium iodide, while a mixture of 1-methyl-3-(4-dimethylaminostyryl)pyrazole (IX) and its 1,5-isomer (X) in a 2:1 ratio is obtained from 1,2-dimethyl-3(5)-(4-dimethylaminostyryl)pyrazolium iodide. To determine the ratio of the isomers VII and VIII and IX and X in the mixtures we used the PMR spectra, recorded in DMSO-D_6. In this solvent, as is shown by a comparison of the spectra of individual trans-1-methyl-3- and -5-(4-R-styryl)-pyrazoles (R = NO_2, NH_2) [1] and compounds I and II (Table 1), the signals of the protons of the methyl group in the 1-position and the 4-H proton of the pyrazole ring in 1,3-isomers are shifted into a stronger field in comparison with the 1,5-isomers. Moreover, in the spectra of 3-substituted 1-methylpyrazole derivatives, the signal of the 5-H proton lies in a weaker field than the signal of the 3-H proton in the spectra of the corresponding 5-substituted compounds, regardless of the electronic effect of the substituent [6].

As is shown by the data of thermal decomposition of 1,2-dimethyl-3(5)-(4-R-styryl)-pyrazolium iodides IVa-c, elimination of a methyl group from the 2-N atom, leading to the formation of 1-methyl-3-(4-R-styryl)pyrazoles, is promoted by two factors: greater steric hindrances in comparison with the methyl group at the 1-N atom and an increase in the electron acceptor capacity of the substituent R, increasing the partial positive charge on the 1-N and 2-N atoms and facilitating stripping of a methyl group.

This conclusion is confirmed by the results of thermolysis of bis(1,2-dimethylpyrazolium)diiodide V. In the molecule of compound V the pyrazolium residues contain a substituted 4-vinylstyryl radical in the 3-position, the electron acceptor capacity of which should be higher than in the styryl radical. As a result, in the thermal decomposition of compound V there is an elimination of methyl groups only from the 2-position, and one of three possible isomers is formed: trans,trans-1,4-bis(1-methyl-3-pyrazolylvinyl)benzene I, the individuality of which was confirmed by the data of the PMR spectrum. The proposed method of synthesis of derivatives of styrylpyrazoles permitted the production of 1,2-dimethyl-3,5-distyrylpyrazolium iodide (XII) from 1,2,3,5-tetramethylpyrazolium iodide (XI), and the thermal decomposition of XII led to trans,trans-1-methyl-3,5-distyrylpyrazole (XIII).

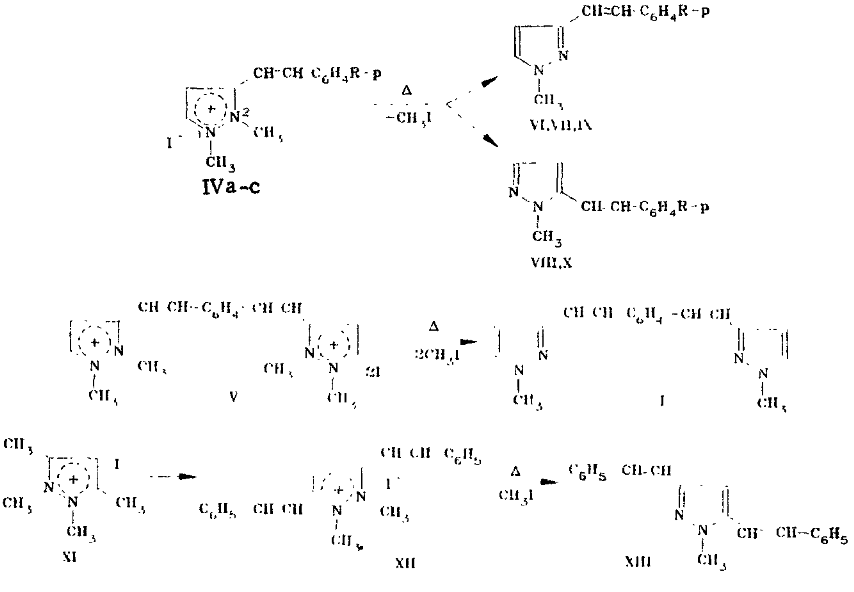
EXPERIMENTAL

The electronic absorption spectra of the compounds synthesized were recorded on a Specord UV spectrophotometer in ethanol, the PMR spectra on a Varian instrument with a working frequency of 100 MHz at 25°C in DMSO-D_6, internal standard TMS. The mass spectra were recorded on a MX-1303 instrument at an energy of ionizing electrons 70 eV. The data of the PMR spectra of styrylpyrazoles are cited in Table 1; the characteristics and yield of the compounds obtained are cited in Table 2.

TABLE 1. Data of the PMR Spectra of Styrylpyrazoles

Compound	Chemical shifts, ppm, and SSCC, Hz								
	1-CH$_3$ (s)	protons of pyrazole			4—3 (5)	olefinic protons (CH= CH)	J, trans	aromatic protons	J, ortho
		4-H, d	5-H, d	3-H, d					
I	3,84	6,54	7,67	—	2,5	7,12, s	—	7,55, s	—
II	3,92	6,61	—	7,37	2,0	7,16, d; 7,24, d	16,0	7,65, s	
VI	3,84	6,58	7,67	—	2,2	7,24, d; 7,33, d	16,0	7,79, d; 8,17, d	8,8
VII	3,82	6,50	7,61	—	2,5	7,12,s	—	7,3—7,8, m[a]	
VIII	3,91	6,58	—	Overlaps	2,0	7,15, d; 7,23, d	16,0		
IX[b]	3,80	6,42	7,60	—	2,5	6,86, d; 6,96, d	16,0	6,68, d; 7,34, d	8,7
X[c]	3,86	6,50	—	7,30	2,0	6,98, s	—	6,69; d; 7,43, d	8,7
XIII	3,95	6,94	—	—	—	7,11, s 7,16, d, 7,22, d	16,0	7,3—7,8, m[d]	

[a] The multiplet of the protons of the phenyl residues of isomers VII and VIII. [b] Chemical shift of the protons of $N(CH_3)_2$ 2.90 ppm (s). [c] Chemical shift of the protons of $N(CH_3)_2$ 2.93 ppm (s). [d] Multiplet of the protons of the two phenyl residues.



IV a R=H, b R=N(CH$_3$)$_2$, c R=NO$_2$; VI R=NO$_2$; VII, VIII R=H; IX, X R=N(CH$_3$)$_2$

1,2,3(5)-Trimethylpyrazolium iodide (III) was produced in the reaction of 1,3-dimethylpyrazole with methyl iodide at 125-130°C for 6 h, mp 254-256°C; according to the data of [2], mp 256°C.

1,2,3,5-Tetramethylpyrazolium iodide (XI) was synthesized from 1,3,5-trimethylpyrazole [5] analogously to compound III.

1,2-Dimethyl-3(5)-styrylpyrazolium iodide (IVa) was produced by the reaction of compound III with benzaldehyde, using sodium ethylate instead of sodium methylate [2].

1,2-Dimethyl-3(5)-(4-dimethylaminostyryl)pyrazolium iodide (IVb) was produced by the reaction of compound III with 4-dimethylaminobenzaldehyde analogously to compound IVa [2].

1,2-Dimethyl-3(5)-(4-nitrostyryl)pyrazolium iodide (IVc). A solution of sodium ethylate, prepared from 1.4 g of sodium and 70 ml of abs. ethanol, and a solution of 4.1 g (26.5 mmoles) 4-nitrobenzaldehyde in 80 ml abs. ethanol were added dropwise to a solution of 7.0 g (29 mmoles) of the pyrazolium iodide III in 80 ml of abs. ethanol, mixed at 20°C until a precipitate appeared, and exposed for 1 h. The precipitate of compound IVc was filtered off. Conducting the reaction at 60-70°C leads to strong resinification of the reaction mass.

1,4-Bis[1,2-dimethyl-3(5)-pyrazoliumvinyl]benzene diiodide (V). A solution of sodium ethylate, produced from 2.4 g sodium and 120 ml abs. ethanol, and a solution of 3.35 g (25

TABLE 2. Characteristics of the Compounds I, IV-XIII

Compound[a]	Mp, °C (ethanol)	Maximum value of m/z in mass spectrum	UV spectrum, λ_{max}, nm (ε)	N found, %	Gross formula	N calc., %	Yield, %
I	229—230	M^+ 290	344 (63 400)	—	—	—	53
IVa	236—238	$[M-CH_3I]^+$ 184	306 (26 600)	—	—	—	80
IV b	245—247	$[M-CH_3I]^+$ 227	391 (33 000)	—	—	—	86
IVc	223—226	$[M-CH_3I]^+$ 229	327 (24 300)	10,98	$C_{13}H_{14}IN_3O_2$	11,32	18
V	277—279	$[M-CH_3I]^+$ 290	362 (50 500)	10,07	$C_{20}H_{24}I_2N_4$	9,75	60
VI	145—147	M^+ 229	351 (20 500)	—	—	—	60
VII VIII	35—52[b]	M^+ 184	—	14,96	$C_{12}H_{12}N_2$	15,21	56
IX X	105—115[b]	M^+ 227	—	18,58	$C_{14}H_{17}N_3$	18,50	66
XI	230—235	—	—	11,00	$C_7H_{13}IN_2$	11,11	72
XII	225—228[c]	$[M-CH_3I]^+$ 286	305—315 (45 000)	6,88	$C_{21}H_{21}IN_2$	6,55	50
XIII	127—128[c]	M^+ 286	310 (47 800)[d]	9,61	$C_{20}H_{18}N_2$	9,79	29

[a] Compounds I, IVa, c, and VI were described in the literature. [b] Mixture of isomers. [c] Ethanol—water, 1:1. [d] Fluorescence spectrum (toluene): λ_{max} 395 nm, η = 0.36.

mmoles) terephthalic aldehyde in 100 ml abs. ethanol were added to a solution of 11.9 g (50 mmoles) pyrazolium iodide III in 170 ml abs. ethanol, heated to boiling, exposed for 3 h, cooled, and the precipitate of compound V filtered off.

1,2-Dimethyl-3,5-distyrylpyrazolium iodide (XII). A solution of sodium ethylate, produced from 2.0 g sodium and 50 ml abs. ethanol, was added to a solution of 5.04 g (20 mmoles) 1,2,3,5-tetramethylpyrazolium iodide XI and 4.24 g (40 mmoles) benzaldehyde in 50 ml abs. ethanol, heated to boiling, exposed for 6 h, left overnight, and the precipitate of compound XII filtered off.

Thermal decomposition of pyrazolium iodides IVa-c, V, and XII. A 2.0 g portion (6.1 mmoles) of 1,2-dimethyl-3(5)-styrylpyrazolium iodide IVa was heated until the salt melted and exposed until the evolution of methyl iodide ceases (2 min). After cooling the mass was treated with ether (4 × 5 ml), and the solvent was distilled off from the extract. A mixture of trans-1-methyl-3-styrylpyrazole VII and trans-1-methyl-5-styrylpyrazole VIII was obtained in a 3:1 ratio (according to the data of the PMR spectrum).

When 1,2-dimethyl-3(5)-(4-nitrostyryl)pyrazolium iodide IVc, 1,2-dimethyl-3(5)-(4-dimethylaminostyryl)pyrazolium iodide IVb, and 1,2-dimethyl-3,5-distyrylpyrazolium iodide XII were treated analogously to compound IVa, trans-1-methyl-3-(4-nitrostyryl)pyrazole VI [1], a mixture of trans-1-methyl-3-(4-dimethylaminostyryl)pyrazole IX with trans-1-methyl-5-(4-dimethylaminostyryl)pyrazole X, 2:1, and trans,trans-1-methyl-3,5-distyrylpyrazole XIII were obtained, respectively.

A 3.0 g portion (5.2 mmoles) of compound V was heated until the salt melted, exposed for 2 min, the solid residue pulverized after cooling, 2 ml of ethanol was added, filtered off, and the residue recrystallized from ethanol. Trans,trans-1,4-bis(1-methyl-3-pyrazolylvinyl)benzene (I) was obtained [1].

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