Reaction of a Mixture of (IX) and (X) with Methanolic Potassium Hydroxide. Similarly, from 1.1 g (0.02 mole) of KOH in 30 ml of methanol and 2.9 g (0.02 mole) of a mixture of (IX) and (X) (9:1), there was obtained 2.3 g (80%) of (IX), bp 86-87°C (3 mm),  $n_D^{2^\circ}$  1.4910.

Reaction of 4-Acetoxy-4-nitromethyltetrahydropyran with Potassium Carbonate. A mixture of 2 g (0.01 mole) of 4-acetoxy-4-nitromethyltetrahydropyran and 2.8 g (0.02 mole) of  $K_2CO_3$  was heated at 100°C with simultaneous removal of the reaction products, to give 1.1 g (78%) of a mixture of (IX) and (X) (9:1), bp 85-88°C (3 mm),  $n_D^{2°}$  1.4910. PMR spectrum: 1.9-2.35 (m, CH<sub>2</sub>C); 3.6-3.9 (t, CH<sub>2</sub>OC); 4.0-4.25 (m, OCH<sub>2</sub>C=); 4.83 (s, CH<sub>2</sub>NO<sub>2</sub>); 5.85-6.1 (m, CH=); 6.9-7.0 ppm (=CHNO<sub>2</sub>).

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REACTIONS OF HETEROCYCLIC CATIONS WITH N-CONTAINING NUCLEOPHILES.

17.\* SYNTHESIS OF PYRYLIUM SALTS WITH THREE-RING AZOLE SUBSTITUENTS<sup>†</sup>

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2,6-Diphenylpyrylium perchlorate was hetarylated with imidazo- and pyrrolo-[1,2-a]benzimidazoles, and deeply colored 4-azolylpyrylium perchlorates were obtained.

We have described a method for the introduction of monocyclic pyrazole substituents into the pyrylium ring and have found that imidazole, in view of its insufficient local  $\pi$ surplus character, does not hetarylate pyrylium salts [1]. In the present research we investigated the possibility of the introduction into the pyrylium ring of three-ring azole substituents, viz., imidazo- and pyrrolo[1,2-a]benzimidazoles I and II, in which the external imidazole and pyrrole rings are  $\pi$ -surplus rings. The calculated and experimental data provide evidence for high nucleophilicity of the 3 position in imidazo[1,2-a]benzimidazoles I [3, 4]. Quantum-mechanical calculations of the electron-density distribution in pyrrolo[1,2-a]benzimidazole molecules II indicate the presence in them of two nucleophilic centers, viz., the C<sub>(1)</sub> and C<sub>(3)</sub> atoms [4, 5]. It was demonstrated experimentally that in these molecules the 1 position, which is adjacent to the bridge nitrogen atom, initially undergoes electrophilic attack; if the 1 position is occupied, the 3 position then undergoes attack [4, 5].

Refluxing 2,6-diphenylpyrylium perchlorate (III) with I and II in freshly distilled dimethylformamide (DMF) leads to dark-crimson and dark-violet 4-imidazo- and 4-pyrrolo[1,2a]benzimidazolyl-2,6-diphenylpyrylium perchlorates IV and V. The addition of salt III to azoles I and II proceeds via the same mechanism as in the case of methylpyrazoles [1], viz., through a step involving the formation of a 4H-4-hetaryl-2,6-diphenylpyran, which is then converted to pyrylium salt IV or V by the action of starting perchlorate III. However, the liberated perchloric acid does not react with the solvent but rather with azoles I and II, converting them to salts. In these reactions, in contrast to the reactions with pyrrole, indole, methylpyrazoles, and pyrazolones [1], one must therefore introduce equimolar amounts

\*See [1] for communication 16. †Communication 24 from the series "Research on imidazo[1,2- $\alpha$ ]benzimidazole derivatives." See [2] for communication 23.

Scientific-Research Institute of Physical and Organic Chemistry, M. A. Suslov Rostov State University, Rostov-on-Don 344090. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 309-313, March, 1987. Original article submitted August 23, 1985. of the starting compounds. Partial hydrolysis of salt III under the influence of the "pyridine" nitrogen atom of azoles I with the formation of pyranylidenepentenedione VIII proceeds simultaneously with the hetarylation reaction. Owing to the absence of a "pyridine" nitrogen atom in azoles II, salt III does not undergo hydrolysis, and the yields of perchlorates Va, b are quantitative. The addition of salt III to 2-phenyl- and 2,3-diphenyl-4-methylpyrrolo[1,2-a]benzimidazoles (IIa, b) takes place in the l position of the latter; this follows from the literature data. The identical character of the UV and IR spectra of salts Va, b and their identical color constitute additional proof for this.



I, IV, VI a R=H,  $R^{1}=CH_{3}$ ; b  $R=CH_{3}$ ,  $R^{1}=C_{2}H_{5}$ ; c R=H,  $R^{1}=CH(CH_{3})_{2}$ ; II, V, VII a R=H; b  $R=C_{6}H_{5}$ 

Salts IV and V can exist in three resonance forms A, B, and C. Their dark color can be explained by the large contribution of structures C, which contain the longest conjugation chain. The structures of salts IV and V were confirmed by the presence in the IR spectra of absorption bands of a heteroaromatic cation (1580, 1600, 1620 cm<sup>-1</sup>) and a perchlorate ion  $(1100 \text{ cm}^{-1})$ . Intense absorption at 380 and 530 nm is observed in the UV spectra of perchlorates Va, b. Two three-proton singlets of methyl groups at 2.30 and 2.37 ppm, a three-proton triplet at 1.50 ppm and a two-proton quartet at 4.42 ppm, which correspond to an ethyl group, and a multiplet of 19 aromatic and heteroaromatic protons at 7.47-8.22 ppm are present in the PMR spectrum of perchlorate IVb. Perchlorate IVa was obtained by alternative synthesis. For this, from 2-phenyl-3-formyl-9-methylimidazo[1,2- $\alpha$ ]benzimidazole (IX) and acetophenone via the method in [6] we synthesized 1,5-diketone X, which was then subjected to cyclization to 4-hetaryl-4H-pyran XI by treatment with polyphosphoric ester.



Perchlorates of the starting heterocycles, which we obtained by an independent method, are secondary products of each hetarylation reaction. The protonation of pyrrolo[1,2-a]-

TABLE 1. Characteristics of the Synthesized Compounds

Y ield,	al I	65	66	67	100	100	92 96	67	78 75 96 100
	z	7,3	6,8	6'9	4,9	4,3	12,1 10,8	11,2	8,55 8,55 10,8 8,55 10,8 8,55
d/o	cı	6,2	5,7	5,9	6,2	5,4	10,2 9,1	9,5	10,3 8,2
Calc.,	н	4,2	4,8	4,6	4,3	4,4	4,0 5,1	4,8	5,4,4,0 8,2,4,4,0 8,5,4,4,0
	c	68,6	69,7	69,4	70,8	73,6	55,3 58,5	57,5	58,9 63,8 79,7 82,7 83,4
Empirical formula	5	C <sub>38</sub> H <sub>24</sub> CIN <sub>3</sub> O <sub>5</sub>	C <sub>36</sub> H <sub>30</sub> ClN <sub>3</sub> O <sub>5</sub>	C <sub>35</sub> H <sub>28</sub> CIN <sub>3</sub> O <sub>3</sub>	C <sub>34</sub> H <sub>25</sub> CIN <sub>2</sub> O <sub>5</sub>	C40H29CIN2O5	C <sub>16</sub> H <sub>14</sub> CIN <sub>3</sub> O <sub>4</sub> C <sub>19</sub> H <sub>20</sub> CIN <sub>3</sub> O <sub>4</sub>	C <sub>18</sub> H <sub>18</sub> CIN <sub>3</sub> O <sub>4</sub>	C <sub>17</sub> H <sub>15</sub> CIN <sub>2</sub> O, C <sub>23</sub> H <sub>19</sub> CIN <sub>2</sub> O, C <sub>33</sub> H <sub>27</sub> N <sub>5</sub> O C <sub>33</sub> H <sub>25</sub> N <sub>5</sub> O C <sub>35</sub> H <sub>26</sub> N, C <sub>36</sub> H <sub>36</sub> N,
	z	7,6	6,8	7,2	5,0	4,6	1,11 1,11	11,2	8,4 6,6 8,5 10,8
96	ci	5,9	. 6,0	6,1	5,9	5,2	9,9 9,1	9,2	10,0 8,1
Found	н	4,1	5,1	4,4	4,5	4,7	4,3 5,1	5,1	4,4 5,53 0,03 0,03 0,03 0,03 0,03 0,03 0,03
	ပ	68,3	70,0	69,1	71,1	73,8	55,6 58,4	57,5	58,6 63,5 79,4 83,6 83,6
UV spectrum, $\lambda$ , nm	(10g c)	380 (4,3257), 530 (4,4030)	385 (4,4130), 585 (4,4130), 595 (4,1059)	380 (4,2688), 520 (4,2688),	365 (4,2200), 550 (4,2200),	360 (4,1300), 550 (4,4310)	(11011) 000		
		600,	610,	1625	1620,	1610,	3125 1660,	1650,	1620
um, cm <sup>-1</sup>		1580, 1	1580,	1600,	1595,	1575,	1620, 1630,	1610,	1590, 1580, 1670 1630
		, 1540,	, 1540,	, 1565,	, 1540,	, 1545,	1570, 1575,	, 1570,	), 1520 ), 1520 1610, 1630
shect	, abee	), 1500	), 1510	5, 1515	), 1520	), 1510	0, 1525 0, 1525	), 1515	0, 1500 11490 1585 1585
Ĕ	1	0, 126(	0, 125(	0, 124	0, 122(	0, 121( 0, 121( 121(	000° 1488 1488	0, 150	0, 135 0, 135 0, 1540 0, 1570
		110		100	011	011			110
mp, °C		216	267.	259-260	144-145	185186	226-227 $252-253$	247248	235-236 217-218 178-179 139-140 215-216
Com-	hund	IVa	IVb**	IVc	Va	$v_{b}$	VIa VIb	VIc	VII a VII b*** X XI XII XII

ethanol, and XI successively from heptane and ether. \*\*PMR spectrum (d<sub>7</sub>-DMF): 1.50 (t, 3H, NCH<sub>2</sub>CH<sub>3</sub>), 2.30 (s, 3H, CH<sub>3</sub>), 2.37 (s, 3H, CH<sub>3</sub>), 4.42 (q, 2H, NCH<sub>2</sub>CH<sub>3</sub>), 7.47-8.22 \*The compounds were recrystallized: IV and V from butanol, VIa-c, VIIa, b, and XII from ethanol-acetonitrile, X from

ppm (m, 19H, H<sub>arom</sub>). \*\*\*PMR spectrum (d,-DMF): 3.63 (s, 3H, NCH<sub>3</sub>), 5.90 (s, 2H, CH<sub>2</sub>), 7.13-7.78 (m, 14H, H<sub>arom</sub>).

benzimidazoles takes place at the  $C_{(1)}$  atom [7]. In fact, the PMR spectrum of perchlorate VIIb contains a singlet of a CH<sub>2</sub> group at 5.90 ppm, as well as a singlet of a methyl group at 3.63 ppm and a multiplet of aromatic and heteroaromatic protons at 7.13-7.78 ppm. The ratio of the integral intensities is 2:3:14.

In attempts to obtain pyridines from salts IVa, c and Va, b the latter undergo decomposition, and distinct products cannot be isolated from the reaction mixtures. Primarily the azole fragments of the molecules, the stabilities of which are reduced significantly under the influence of the acceptor pyrylium cation, evidently undergo decomposition. The presence of two donor methyl groups in the imidazo[1,2-a]benzimidazole substituent of salt IVb increases the stability of the latter and makes it possible to convert perchlorate IVb to pyridine XII.

Thus we have developed a method for the direct introduction of three-ring azole substituents into the 4 position of 2,6-diphenylpyrylium perchlorate.

## EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord 71-IR spectrometer. The UV spectra were obtained with a Specord-M40 spectrophotometer from solutions of the compounds in CHCl<sub>3</sub>. The PMR spectra of solutions in  $d_7$ -DMF were obtained with a Tesla BS-487C spectrometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The purity of the compounds obtained was monitored by thin-layer chromatography on silicon dioxide or aluminum oxide plates with elution by benzene or chloroform. Data on the synthesized compounds are presented in Table 1.

<u>9-Methyl-2-phenylimidazo[1,2-a]benzimidazole</u> was synthesized by the method in [8], and 6,7-dimethyl-2-phenyl-9-ethylimidazo[1,2-a]benzimidazole was synthesized by the method in [9]; 2-phenyl- and 2,3-diphenyl-4-methylpyrrolo[1,2-a]benzimidazole were obtained by the method in [10]; 9-methyl-2-phenyl-3-formylimidazo[1,2-a]benzimidazole was synthesized by the method in [4]. We obtained 9-isopropyl-2-phenylimidazo[1,2-a]benzimidazole for the first time by the method presented below.

<u>2-Amino-l-isopropyl-3-phenacylbenzimidazolium Bromide.</u> A 4 g (20 mmole) sample of phenacyl bromide was added to a hot solution of 3.5 g (20 mmole) of 2-amino-l-isopropyl-benzimidazole [11] in 80 ml of acetone, after which the mixture was stirred thoroughly until the phenacyl bromide had dissolved, and the solution was allowed to stand at 20°C for 3-4 h. The precipitated large cubic crystals of the bromide were removed by filtration and washed thoroughly with acetone and ether to give 6.85 g (91.5%) of a product with mp 208°C (from alcohol). IR spectrum: 1685 cm<sup>-1</sup> (C=0). Found, %: C 57.6, H 5.6, Br 21.0, N 11.4. C<sub>18</sub>H<sub>19</sub>N<sub>3</sub>O+HBr. Calculated, %: C 57.8, H 5.4, Br 21.3, N 11.2.

<u>9-Isopropyl-2-phenylimidazo[1,2-a]benzimidazole (Ic).</u> A 3.75 g (10 mmole) sample of 2-aminobenzimidazolium bromide was refluxed in 150 ml of concentrated HCl for 3 h, during which we observed initially dissolving of the starting salt, followed by the precipitation of a snow-white imidazo[1,2-a]benzimidazole salt. The mixture was cooled, and the salt was removed by filtration and washed with a small amount of water and acetone. It was then dried and treated with 22% ammonium hydroxide, and the precipitated base was removed by filtration, washed with water, and air dried to give 2.73 g (almost quantitative) of snowwhite plates with mp 127°C (from petroleum ether). IR spectrum (chloroform): 1505, 1605, 1615 cm<sup>-1</sup> (C=C, C=N). Found, %: C 78.6, H 6.1, N 15.3. C1eH1,N3. Calculated, %: C 78.5, H 6.2, N 15.3.

<u>4-(6,7-Dimethyl-2-phenyl-9-ethylimidazo[1,2- $\alpha$ ]-3-benzimidazolyl)-2,6-diphenylpyrylium</u> <u>Perchlorate (IVb).</u> A solution of 0.7 g (2.4 mmole) of 6,7-dimethyl-2-phenyl-9-ethylimidazo-[1,2- $\alpha$ ]Benzimidazole and 0.66 g (2 mmole) of salt III in 10 ml of freshly distilled DMF was refluxed for 40 min, after which it was cooled and diluted with excess petroleum and diethyl ethers, and the crimson precipitate (0.9 g) was removed by filtration. Treatment of the precipitate with 10 ml of chloroform left 0.44 g (93% of the theoretically possible amount) of the colorless perchlorate (VIb) of the starting heterocycle. Dilution of the chloroform solution with excess petroleum and diethyl ethers gave 0.41 g (66% of the theoretically possible amount) of pyrylium perchlorate IVb, which was purified by means of TLC on silicon dioxide plates (with chloroform as the solvent and benzene as the eluent) with subsequent crystallization from butanol. The mother liquors were combined and evaporated, and the residue was dissolved in benzene and separated with a column packed with aluminum oxide (layer height 30 cm) by elution with benzene-chloroform (2:1) to give 0.17 g (18%) of VIII.

Perchlorates IVa, c and Va, b were obtained by a similar method from salt III and 2-phenyl-9-methylimidazo-, 2-phenyl-9-isopropylimidazo-, 2-phenyl-4-methylpyrrolo-, and 2,3-diphenyl-4-methylpyrrolo[1,2- $\alpha$ ]benzimidazole (Ia, c, IIa, b), respectively. Only perchlorate Vb was separated from the perchlorate (VIIb) of the starting heterocycle by reprecipitation from acetone solution by the addition of water.

<u>1,5-Diphenyl-3-(2-phenyl-9-methylimidazo[1,2- $\alpha$ ]-3-benzimidazolyl)pentane-1,5-dione (X).</u> A solution of 0.1 g (2.5 mmole) of NaOH in 1 ml of water was added to a solution of 0.28 g (1 mmole) of aldehyde IX and 0.35 ml [0.36 g (3 mmole)] of acetophenone in 10 ml of ethanol, after which the reaction mixture was refluxed on a water bath for 1.5 h. It was then cooled and filtered to give 0.35 g of X.

 $\frac{4-(2-\text{Phenyl-9-methylimidazo[1,2-a]-3-benzimidazolyl)-2,6-diphenyl-4H-pyran (XI).}{g (1 mmole) sample of diketone X was stirred for 2 h in 5 g of polyphosphoric ester at 80°C, after which the mixture was cooled and dissolved in 15 ml of chloroform. The chloroform solution was passed through a column packed with aluminum oxide (layer height 20 cm) by elution with chloroform. The first yellow fraction was collected, and the solvent was removed by distillation to give 0.46 g of pyran XI.$ 

Reaction of Pyran XI with Salt III. A mixture of 0.14 g (0.3 mmole) of XI and 0.13 g (0.4 mmole) of salt III was refluxed for 30 min in DMF, after which it was cooled and treated with ether to give 0.1 g (60%) of precipitated salt IVa.

2,3-Diphenyl-4-methylpyrrolo[1,2- $\alpha$ ]benzimidazole Perchlorate (VIIb). A 0.046 g (0.31 mmole) sample of 70% perchloric acid was added with stirring and cooling to a suspension of 0.1 g (0.31 mmole) of IIb in 3 ml of ethanol, after which the mixture was diluted with ether and filtered to give 0.13 g (quantitative) of perchlorate VIIb.

Perchlorates VIa-c and VIIa were similarly obtained from 2-phenyl-9-methylimidazo-, 2-phenyl-6,7-dimethyl-9-ethylimidazo-, 2-phenyl-9-isopropylimidazo-, and 2-phenyl-4-methyl-pyrrolo[1,2-a]benzimidazole (Ia-c, IIa), respectively.

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