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NEW METHOD FOR THE ANNELATION OF A PYRIDINE RING ON DERIVATIVES OF IMIDAZOLE AND BENZIMIDAZOLE

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The interaction of (Z)-1,3-diaryl-4-bromo-2-buten-1-ones with 1-substituted (benz)imidazoles in benzene gave (Z)-1-R-3-(2,4-diaryl-4-oxo-2-butenyl)-1H-imidazolium bromides and (Z)-1-R-3-(2,4-diaryl-4-oxo-2-butenyl)-1H-benzimidazolium bromides which readily cyclize in the presence of base to form derivatives of 7,9-diarylpyrido[1,2-a]benzimidazole and 6,8-diarylpyrimidazo[1,2-a]pyridine. The effects of the nature of substituents in the benzene ring of the diarylbutenones and the substituent at N(1) in the (benz)imidazoles on the alkylation and cyclization reactions has been studied. The optimum conditions for the synthesis of the 5-R-4-hydroxy-2,4-diphenyl-4,5-dihydro-1H-pyrido[1,2-a]benz-imidazol-10-ium, 5-R-2,4-diaryl-4-hydroxy-4,5-dihydro-3H-pyrido[1,2-a]benzimidazol-10-ium, and 5-R-2,4-diaryl-5H-pyrido[1,2-a]benzimidazol-10-ium have been found.

Keywords: γ-bromodypnone, imidazo[1,2-*a*]pyridine, pyrido[1,2-*a*]benzimidazole, cyclization of azolium ylides.

The imidazo[1,2-*a*]pyridine system has been studied very actively recently, in connection with the introduction into the practice of medicine of preparations of the type of *zolpidem* [3], *fazadinium* [4], and others. The basic method for the construction of imidazo[1,2-*a*]pyridine system consists of the construction of the imidazole part of the bicycle. An alternative possibility is annelation, when the final closing of the imidazo[1,2-*a*]pyridine or pyrido[1,2-*a*]imidazole system is carried out during the construction of the pyridine ring, has been insufficiently studied [5-7].

In the present work a simple variant of the construction of the pyridine ring on the imidazole or benzimidazole structure is proposed, based on the "inversion" of the A. E. Chichibabin reaction [8]. The formation of imidazo[1,2-*a*]pyridines according to Chichibabin consists of the interaction of α-halo ketones with 2-aminopyridine, which proceeds *via* the initial formation of a quaternary salt, its deprotonation, and intramolecular attack on the carbonyl group by a nucleophile. The intermediate carbinolamine is readily converted into an imidazo[1,2-*a*]pyridine by dehydration, but it may be isolated in pure form [9]. Our proposed inverted variant consists, in the first place, in replacing the α-halo ketones by their vinylogs (in this work we refer to γ-bromodypnone) and secondly, in using imidazole or benzimidazole without substitutions in position 2. The sequence of conversions in these reactions is identical to the stages of the Chichibabin reaction.

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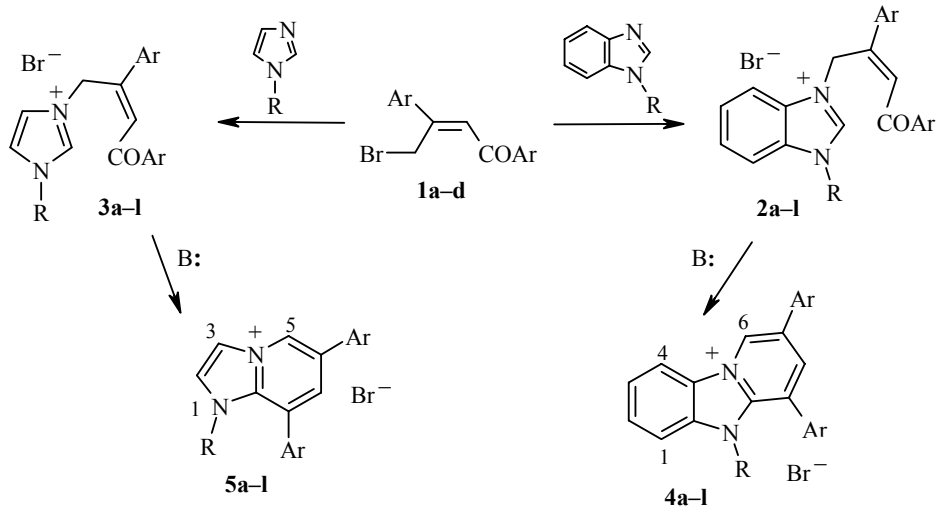


1 a Ar = Ph, **b** Ar = 4-$MeOC_6H_4$, **c** Ar = 4-ClC_6H_4, **d** Ar = BrC_6H_4; **2**, **4** **a**–**e** Ar = Ph, **a** R = Me, **b** R = Et, **c** R = $(CH_2)_2CN$, **d** R = Bn, **e** R = Ph; **f**, **g** Ar = 4-$MeOC_6H_4$, **f** R = Me, **g** R = Bn; **h**–**j** Ar = 4-ClC_6H_4, **h** R = Me, **i** R = Bn, **j** R = Ph; **k**, **l** Ar = 4-BrC_6H_4, **k** R = Me, **l** R = Bn; **3**, **5** **a**–**e** Ar = Ph, **a** R = Me, **b** R = Et, **c** R = CH_2Vin, **d** R = Bn, **e** R = Vin; **f**, **g** Ar = 4-$MeOC_6H_4$, **f** R = Me, **g** R = Bn; **h**, **i** Ar = 4-ClC_6H_4, **h** R = Me, **i** R = Bn; **j–l** Ar = 4-BrC_6H4, **j** R = Et, **k** R = Me, **l** R = Bn

Recently [10] we found that 1-alkyl-1H-benzimidazoles and imidazoles interact with (*Z*)-4-bromo-1,3-diphenyl-2-buten-1-one (γ-bromodypnone, **1a**) to form quaternary (*Z*)-1-alkyl-3-(2,4-diaryl-4-oxo-2-butenyl)-1H-benzimidazol-3-ium **2a,b** and (*Z*)-1-alkyl-3-(2,4-diaryl-4-oxo-2-butenyl)-1H-imidazol-3-ium **3a,b** salts. Subsequent heating them in the presence of base cyclized them into derivatives of the 2,4-diphenylpyrido-[1,2-*a*]benzimidazole (**4**) and 6,8-diphenylimidazo[1,2-*a*]pyridine (**5**) systems respectively (Table 1). It was shown that the structures of the reaction products were determined by the nature of the substituent at N(1) atom of azole and the conditions of the reaction. These results encouraged us to study in more detail the process of cyclization of salts of types **2** and **3**. For this we chose to use 1-substituted diazoles and derivatives of γ-bromodypnone.

The γ-bromodypnones **1b-d** with N-substituents in the benzene ring, like unsubstituted **1a**, form quaternary salts with structures **2** and **3** with 1-alkyl-1H-imidazoles and -benzimidazoles on maintaining of benzene solutions of the starting materials at room temperature. The influence of the nature of the substituents in γ-bromodypnone **1** on the reaction time for conversion to the products of alkylation and their yields was negligible. There was a more notable change in the rate of formation of the quaternary salts in changing from 1-alkyl-1H-benzimidazoles to 1-alkyl-1H-imidazoles. For example, the time for the formation of products of type **2** was 6-12 h, but for products of type **3** was 1-4 h.

The nature of the substituent at atom N(1) showed a considerable influence on the rate of reaction only in the case of 1-phenyl-1H-benzimidazole: to obtain the salts **2e** and **2j** required respectively 8 days (48% yield) and 10 days (43% yield). Also a quaternary salt of type **2** was not obtained with compound **1d**. The structures of compounds **2c-l** and **3c-l** were determined from their ^{1}H NMR and IR spectra (Table 2), which corresponded with data for compounds **2a,b** and **3a,b** [10]

Intramolecular cyclization into the 5R-2,4-diaryl-5H-pyrido[1,2-*a*]benzimidazol-10-ium bromides **4a-l** and 1-R-6,8-diaryl-1H-imidazo[1,2-*a*]pyridin-4-ium bromides **5a-l** occurred when salts **2** and **3** were heated in the presence of a base. We found that products **4** and **5** were formed in high yield and high purity on heating salts **2** and **3** in ethanol in the presence of morpholine, independent of the structure of the initial quaternary salt

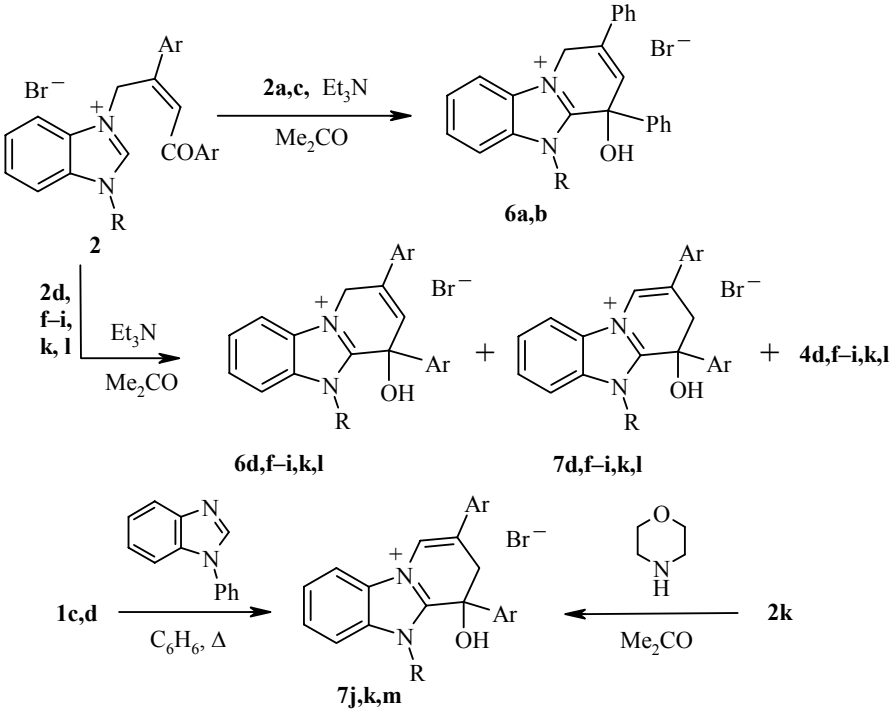
TABLE 1. Physicochemical Properties of the Compounds Synthesized

Compound	Empirical formula	Found, % / Calculated, %					mp, °C*	Yield, %*[2]
		C	H	Br	Cl	N		
1	2	3	4	5	6	7	8	9
2c	$C_{26}H_{22}BrN_3O$	66.08 / 66.11	4.60 / 4.69	16.91 / 16.92		8.92 / 8.90	186-187[a]	56
2d	$C_{30}H_{25}BrN_2O$	70.65 / 70.73	4.91 / 4.95	15.70 / 15.68		5.51 / 5.50	117-118[a]	76
2e	$C_{29}H_{23}BrN_2O$	70.25 / 70.31	4.61 / 4.68	16.16 / 16.13		5.69 / 5.65	145-148[b]	48
2f	$C_{26}H_{25}BrN_2O_3$	63.23 / 63.29	5.10 / 5.11	16.22 / 16.19		5.67 / 5.68	200-203[a]	88
2g	$C_{32}H_{29}BrN_2O_3$	67.45 / 67.49	5.07 / 5.13	14.09 / 14.03		4.96 / 4.92	170-172[a]	74
2h	$C_{24}H_{19}BrCl_2N_2O$	57.34 / 57.40	3.75 / 3.81	15.89 / 15.91	14.16 / 14.12	5.60 / 5.58	173-175[a]	87
2i	$C_{30}H_{23}BrCl_2N_2O$	62.31 / 62.30	3.92 / 4.01	13.85 / 13.82	12.21 / 12.26	4.83 / 4.84	191-193[a]	72
2j	$C_{29}H_{21}BrCl_2N_2O$	61.66 / 61.72	3.70 / 3.75	14.17 / 14.16	12.57 / 12.57	4.99 / 4.96	172-173[b]	43
2k	$C_{24}H_{19}Br_3N_2O$	48.70 / 48.76	3.19 / 3.24	40.53 / 40.55		4.77 / 4.74	173-175[a]	86
2l	$C_{30}H_{23}Br_3N_2O$	53.97 / 54.00	3.40 / 3.47	35.97 / 35.93		4.23 / 4.20	209-211[a]	73
3c	$C_{22}H_{21}BrN_2O$	64.49 / 64.55	5.11 / 5.17	19.56 / 19.52		6.84 / 6.84	186-188[a]	91
3d	$C_{26}H_{23}BrN_2O$	67.91 / 67.98	5.00 / 5.05	17.42 / 17.39		6.15 / 6.10	167-169[a]	87
3e	$C_{21}H_{19}BrN_2O$	63.77 / 63.81	4.79 / 4.84	20.24 / 20.21		7.11 / 7.09	210-212[a]	89
3f	$C_{22}H_{23}BrN_2O_3$	59.56 / 59.60	5.18 / 5.23	18.07 / 18.02		6.33 / 6.32	124-126[a]	93
3g	$C_{28}H_{27}BrN_2O_3$	64.70 / 64.74	5.25 / 5.24	15.41 / 15.38		5.41 / 5.39	159-161[a]	82
3h	$C_{20}H_{17}BrCl_2N_2O$	53.06 / 53.12	3.74 / 3.79	17.68 / 17.67	15.67 / 15.68	6.23 / 6.20	186-188[a]	90
3i	$C_{26}H_{21}BrCl_2N_2O$	59.05 / 59.11	3.98 / 4.01	15.11 / 15.13	13.45 / 13.42	5.31 / 5.30	142-145[a]	74
3j	$C_{21}H_{19}Br_3N_2O$	45.40 / 45.44	3.41 / 3.45	43.21 / 43.18		5.09 / 5.05	202-204[a]	76
3k	$C_{20}H_{17}Br_3N_2O$	44.37 / 44.40	3.12 / 3.17	44.34 / 44.30		5.19 / 5.18	199-201[a]	88
3l	$C_{26}H_{21}Br_3N_2O$	50.58 / 50.60	3.45 / 3.43	38.85 / 38.84		4.51 / 4.54	157-159[a]	72
4c	$C_{26}H_{20}BrN_3$	68.70 / 68.73	4.38 / 4.44	17.60 / 17.59		9.25 / 9.25	274-276[a]	84
4d	$C_{30}H_{23}BrN_2$	73.25 / 73.32	4.66 / 4.72	16.25 / 16.26		5.73 / 5.70	235-237[c]	89
4e	$C_{29}H_{21}BrN_2$	72.91 / 72.96	4.46 / 4.43	16.75 / 16.74		5.89 / 5.87	361-362[c]	83
4f	$C_{26}H_{23}BrN_2O_2$	65.60 / 65.69	4.82 / 4.88	16.83 / 16.81		5.92 / 5.89	268-271[a]	91
4g	$C_{32}H_{27}BrN_2O_2$	69.64 / 69.69	4.87 / 4.93	14.50 / 14.49		5.10 / 5.08	251-253[a]	82
4h	$C_{24}H_{17}BrCl_2N_2$	59.47 / 59.53	3.50 / 3.54	16.51 / 16.50	14.64 / 14.64	5.82 / 5.79	305-307[a]	88
4i	$C_{30}H_{21}BrCl_2N_2$	64.27 / 64.31	3.70 / 3.78	14.28 / 14.26	12.66 / 12.65	5.01 / 5.00	264-266[c]	87
4j	$C_{29}H_{19}BrCl_2N_2$	63.70 / 63.76	3.46 / 3.51	14.61 / 14.63	13.00 / 12.98	5.15 / 5.13	352-354[c]	79
4k	$C_{24}H_{17}Br_3N_2$	50.28 / 50.30	2.90 / 2.99	41.85 / 41.83		4.90 / 4.89	289-291[a]	91
4l	$C_{30}H_{21}Br_3N_2$	55.45 / 55.50	3.22 / 3.26	36.91 / 36.92		4.35 / 4.31	252-254[c]	86
5c	$C_{22}H_{19}BrN_2$	67.49 / 67.53	4.85 / 4.89	20.44 / 20.42		7.20 / 7.16	232-234[a]	84

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9
								86
5d	$C_{26}H_{21}BrN_2$	70.70 70.75	4.76 4.80	18.13 18.10		6.37 6.35	273-275 [c]	
5e	$C_{21}H_{17}BrN_2$	66.80 66.85	4.48 4.54	21.20 21.18		7.41 7.43	269-271 [a]	81
5f	$C_{22}H_{21}BrN_2O_2$	62.08 62.13	4.91 4.98	18.80 18.79		6.61 6.59	227-229 [a]	89
5g	$C_{28}H_{25}BrN_2O_2$	67.00 67.07	4.98 5.03	15.95 15.94		5.59 5.59	242-245 [a]	80
5h	$C_{20}H_{15}BrCl_2N_2$	55.26 55.33	3.40 3.48	18.02 18.04	16.30 16.33	6.49 6.45	299-301 [a]	86
5i	$C_{26}H_{19}BrCl_2N_2$	61.17 61.20	3.70 3.75	15.66 15.66	13.93 13.90	5.51 5.49	239-241 [a]	77
5j	$C_{21}H_{17}Br_3N_2$	46.91 46.96	3.15 3.19	44.73 44.69		5.23 5.22	268-270 [a]	78
5k	$C_{20}H_{15}Br_3N_2$	45.87 45.92	2.81 2.89	45.81 45.83		5.39 5.36	317-319 [a]	85
5l	$C_{26}H_{19}Br_3N_2$	52.09 52.12	3.15 3.20	40.05 40.01		4.71 4.68	257-258 [c]	82
6b	$C_{26}H_{22}BrN_3O$	66.15 66.11	4.92 4.69	16.95 16.92		8.90 8.90	228-231 [a]	73
7j	$C_{29}H_{21}BrCl_2N_2O$	61.68 61.72	3.73 3.75	14.17 14.16	12.56 12.57	4.98 4.96	292-294 [a]	81
7k	$C_{24}H_{19}Br_3N_2O$	48.70 48.76	3.18 3.24	40.56 40.55		4.76 4.74	288-289 [c]	92
7m	$C_{29}H_{21}Br_3N_2O$	53.24 53.32	3.17 3.24	36.71 36.70		4.30 4.29	282-283 [c]	83

* Solvents for recrystallization: 2-PrOH (a), $MeNO_2$ (b), and AcOH (c).
*[2] The yields of compounds **4**, **5** made by method A.



6 a R = Me, **b** R = $(CH_2)_2CN$; **7 j** Ar = 4-ClC_6H_4, R = Ph; **k**, **m** Ar = 4-BrC_6H_4, **k** R = Me, **m** R = Ph

TABLE 2. Spectral Characteristics of [(*Z*)-2,4-diaryl-4-oxo-2-butenyl]azolium Bromides **2** and **3**

Compound	IR spectrum, ν, cm^{-1}	^1H NMR spectrum, δ, ppm (*J*, Hz)			
		1H, s, H-2	Aromatic protons+ H-3'*	2H, s, $C(1')H_2$	Other protons
1	2	3	4	5	6
2c	3014, 2247 (CN), 1648 (C=O), 1600, 1555, 1449, 1371, 1222, 1189, 1029, 769, 691	9.88	8.16 (2H, d, ^3J = 8.5, H-2'",6'"); 8.08 (2H, m, H-4,7); 7.75 (1H, s, H-3'); 7.71 (3H, m, H-2",6",4"); 7.66 (2H, m, H-5,6); 7.60 (2H, t, ^3J = 8.5, H-3'",5'"); 7.35 (3H, m, H-3"–5")	6.15	4.81 (2H, t, ^3J = 6.5, $–CH_2CN$); 3.17 (2H, t, ^3J = 6.5, $NCH_2–$)
2d	3064, 1659 (C=O), 1614, 1555, 1449, 1373, 1222, 1177, 761, 705	10.03	8.17 (2H, d, ^3J = 8.0, H-2'",6'"); 8.04 (1H, d, ^3J = 8.0, H-4); 7.80 (1H, d, ^3J = 8.0, H-7); 7.73 (1H, t, ^3J = 8.0, H-6); 7.68 (3H, m, H-3',2",6"); 7.61 (3H, m, H-5,3'",5'"); 7.56 (1H, t, ^3J = 8.0, H-4'"); 7.35 (3H, m, H-3"-5"); 7.31 (3H, m, H-3""-5""); 7.11 (2H, m, H-2"",6"")	6.22	5.71 (2H, s, CH_2)
2e	2997, 1653 (C=O),1614, 1552, 1217, 752, 696, 683	10.36	8.18 (3H, m, H-4,2'",6'"); 7.78 (2H, m, H-6,7); 7.74-7.58 (12H, m, H-5,3',2",6", H-3'"-5'", H-2'"-6'"); 7.37 (3H, m, H-3"-5")	6.27	—
2f	2924, 1644 (C=O),1600, 1569, 1267, 1228, 1186, 1169, 1029, 833, 761, 612	9.73	8.14 (2H, d, ^3J = 8.5, H-2'",6'"); 8.08 (1H, m, H-4); 7.94 (1H, m, H-7); 7.74 (3H, m, H-3',2",6"); 7.66 (2H, m, H-5,6); 7.10 (2H, d, ^3J = 8.5, H-3'",5'"); 6.92 (2H, d, ^3J = 8.5, H-3",5")	6.05	4.03 (3H, s, NCH_3); 3.87 (3H, s, 4'"-OCH_3); 3.73 (3H, s, 4"-OCH_3)
2g	3008, 1653 (C=O), 1600, 1510, 1258 (C–O), 1225, 1166, 1026, 839, 769	10.04	8.15 (2H, d, ^3J = 8.0, H-2'",6'"); 8.04 (1H, d, ^3J = 8.0, H-4); 7.84 (1H, d, ^3J = 8.0, H-7); 7.67 (2H, d, ^3J = 8.5, H-2",6"); 7.62 (2H, m, H-6,3'); 7.57 (1H, t, ^3J = 8.0, H-5); 7.29 (3H, m, H-3""-5""); 7.15 (2H, d, ^3J = 8.0, H-2"",6""); 7.10 (2H, d, ^3J = 8.5, H-3'",5'"); 6.90 (2H, d, ^3J = 8.0, H-3",5")	6.19	5.73 (2H, s, CH_2); 3.88 (3H, s, 4'"-OCH_3); 3.74 (3H, s, 4"-OCH_3)
2h	3019, 1653 (C=O), 1591, 1482, 1219, 1091, 1010, 833, 750, 677	9.70	8.18 (2H, d, ^3J = 8.0, H-2'",6'"); 8.04 (1H, m, H-4); 8.93 (1H, m, H-7); 7.77 (3H, m, H-3',2",6"); 7.66 (4H, m, H-5,6,3'",5'"); 7.43 (2H, d, ^3J = 8.0, H-3",5")	6.06	4.01 (3H, s, NCH_3)
2i	3014, 1656 (C=O), 1589, 1558, 1216, 1192, 1091, 1007, 833, 750	9.99	8.20 (2H, d, ^3J = 8.5, H-2'",6'"); 8.02 (1H, d, ^3J = 8.0, H-4); 7.82 (1H, d, ^3J = 8.0, H-7); 7.70 (4H, m, H-2",6",2'",6'"); 7.67 (1H, s, H-3'); 7.63 (1H, t, ^3J = 8.0, H-6); 7.57 (1H, t, ^3J = 8.0, H-5); 7.41 (2H, d, ^3J = 8.5, H-3",5"); 7.33 (3H, m, H-3'"-5'"); 7.13 (2H, m, H-2'",6'")	6.19	5.71 (2H, s, CH_2)
2j	3014, 1656 (C=O), 1608, 1589, 1555, 1494, 1214, 1091, 1010, 817, 755	10.22	8.17 (3H, m, H-4,2'",6'"); 7.81 (2H, d, ^3J = 8.0, H-2",6"); 7.76-7.65 (11H, m, H-5-7, H-3',3'",5'", H-2'"-6'"); 7.37 (2H, d, ^3J = 8.0, H-3",5")	6.19	—
2k	3019, 2913, 1653 (C=O), 1591, 1580, 1220, 1066, 1007, 831, 758, 677	9.74	8.10 (2H, d, ^3J = 8.5, H-2'",6'"); 8.04 (1H, m, H-4); 7.94 (1H, m, H-7); 7.81 (2H, d, ^3J = 8.0, H-2",6"); 7.76 (1H, s, H-3'); 7.71 (2H, d, ^3J = 8.5, H-3'",5'"); 7.66 (2H, m, H-5,6); 7.56 (2H, d, ^3J = 8.0, H-3",5")	6.07	4.02 (3H, s, NCH_3)

TABLE 2 (continued)

1	2	3	4	5	6
2l	3008, 1656 (C=O), 1605, 1583, 1213, 1071, 1007, 831, 750	10.00	8.11 (2H, d, ^3J = 8.0, H-2'",6'"); 8.02 (1H, d, ^3J = 8.0, H-4); 7.82 (3H, m, H-7,2",6"); 7.68 (1H, s, H-3'); 7.63 (3H, m, H-6,3'",5'"); 7.57 (1H, t, ^3J = 8.0, H-5); 7.54 (2H, d, ^3J = 8.0, H-3",5"); 7.33 (3H, m, H-3""-5""); 7.14 (2H, m, H-2"",6"")	6.19	5.71 (2H, s, CH_2)
3c	3025, 1656 (C=O), 1617, 1222 1150, 783, 705	9.19	8.13 (2H, d, ^3J = 7.5, H-2'",6'"); 7.70 (5H, m, H-4,5,2",6",4"); 7.59 (3H, m, H-3',3'",5'"); 7.43 (3H, m, H-3"–5")	5.79	5.93 (1H, m, –CH=); 5.22 (1H, d, ^3J = 10.0, =C$\underline{H}_A$H$_B$); 4.90 (1H, d, ^3J = 17.0, =CH$_A$$\underline{H}_B$); 4.77 (2H, d, ^3J = 5.5, NCH_2)
3d	3047, 1658 (C=O), 1606, 1563, 1449, 1222, 1149, 699	9.42	8.13 (2H, d, ^3J = 7.5, H-2'",6'"); 7.71 (4H, m, H-2",6",3'",5'"); 7.68 (1H, s, H-4); 7.65 (1H, s, H-5); 7.59 (2H, t, ^3J = 7.5, H-3",5"); 7.41 (3H, m, H-3',4",4'"); 7.34 (3H, m, H-3""-5""); 7.10 (2H, m, H-2",6")	5.85	5.37 (2H, s, CH_2)
3e	3036, 1656 (C=O), 1608, 1552, 1449, 1220, 1169, 951, 778, 738, 697	9.47	8.14 (2H, d, ^3J = 7.5, H-2'",6'"); 8.11 (1H, m, H-4); 7.83 (1H, m, H-5); 7.72 (4H, m, H-3',2",6",4'"); 7.59 (2H, t, H-3'",5'"); 7.45 (3H, m, H-3"-5")	5.79	7.24 (1H, dd, ^3J = 15.5, ^3J = 8.5, NCH=); 5.89 (1H, dd, ^3J = 15.5, ^2J = 2.5, =C$\underline{H}_A$H$_B$); 5.37 (1H, dd, ^3J = 8.5, ^2J = 2.5, =CH$_A$$\underline{H}_B$)
3f	3047, 1653 (C=O), 1600, 1513, 1259, 1225, 1175 (C–O), 844	9.12	8.11 (2H, d, ^3J = 9.0, H-2'",6'"); 7.72 (2H, d, ^3J = 8.5, H-2",6"); 7.68 (1H, s, H-4); 7.66 (1H, s, H-5); 7.61 (1H, s, H-3'); 7.09 (2H, d, ^3J = 9.0, H-3'",5'"); 6.98 (2H, d, ^3J = 8.5, H-3",5")	5.70	3.86 (3H, s, 4'"-OCH_3); 3.79 (6H, s, NCH_3, 4"-OCH_3)
3g	3047, 1653 (C=O), 1606, 1513, 1258, 1225, 1163 (C–O), 825, 713	9.33	8.10 (2H, d, ^3J = 9.0, H-2'",6'"); 7.67 (3H, m, H-4,2",6"); 7.59 (1H, s, H-5); 7.34 (4H, m, H-3', H-3""–5""); 7.14 (2H, m, H-2"",6""); 7.08 (2H, d, ^3J = 9.0, H-3'",5'"); 6.96 (2H, d, ^3J = 9.0, H-3",5")	5.77	5.36 (2H, s, CH_2); 3.87 (3H, s, 4'"-OCH_3); 3.79 (3H, s, 4"-OCH_3)
3h	3070, 1659 (C=O), 1600, 1589, 1216, 1160, 1091, 833, 816, 624	9.14	8.16 (2H, d, ^3J = 8.0, H-2'",6'"); 7.78 (2H, d, ^3J = 8.0, H-2",6"); 7.72 (1H, s, H-4); 7.66 (3H, m, H-5,3'",5'"); 7.61 (1H, s, H-3'); 7.51 (2H, d, ^3J = 8.0, H-3",5")	5.73	3.78 (3H, s, NCH_3)
3i	3081, 1653 (C=O), 1589, 1216, 1150, 1094, 1007, 830, 685	9.31	8.15 (2H, d, ^3J = 8.0, H-2'",6'"); 7.71-7.65 (6H, m, H-4,5,2",6",3'",5'"); 7.47 (2H, d, ^3J = 7.5, H-3",5"); 7.36 (4H, m, H-3', H-3""-5""); 7.10 (2H, m, H-2"",6"")	5.81	5.34 (2H, s, CH_2)
3j	3053, 1653 (C=O), 1606, 1583, 1216, 1161, 1068, 1007, 831, 769	9.22	8.07 (2H, d, ^3J = 8.5, H-2'",6'"); 7.80 (2H, d, ^3J = 8.5, H-2",6"); 7.71 (1H, m, H-4); 7.69 (1H, m, H-5); 7.68 (3H, m, H-3',3'",5'"); 7.63 (2H, d, ^3J = 8.5, H-3",5")	5.76	4.12 (2H, q, ^3J = 7.0, NCH_2); 1.30 (3H, t, ^3J = 7.0, CH_3)
3k	3048, 1653 (C=O), 1611, 1583, 1217, 1169, 1068, 1007, 831, 769	9.14	8.07 (2H, d, ^3J = 8.5, H-2'",6'"); 7.80 (2H, d, ^3J = 8.5, H-2",6"); 7.71 (3H, m, H-4,3'",5'"); 7.67 (1H, s, H-5); 7.63 (2H, d, ^3J = 8.5, H-3",5"); 7.61 (1H, s, H-3')	5.73	3.78 (3H, s, NCH_3)
3l	3040, 1650 (C=O), 1603, 1583, 1214, 1155, 1071, 1007, 822, 699	9.36	8.07 (2H, d, ^3J = 8.5, H-2'",6'"); 7.80 (2H, d, ^3J = 8.5, H-2",6"); 7.70 (1H, s, H-4); 7.66-7.59 (6H, m, H-5,3',3",5",3'",5'"); 7.35 (3H, m, H-3""-5""); 7.10 (2H, m, H-2"",6"")	5.82	5.36 (2H, s, CH_2)

* Signals of the protons of the benzene rings 2'-Ar (for **2c-l** and **3c-l**) are designated H-2"-6", those for 4' (for **2c-l** and **3c-l**) are designated H-2'"-6'", and for 1-Ph and 1-CH_2Ph (for **2d,g,i,j,l** and **3d,g,i,l**) are designated H-2""-6"".

TABLE 3. Spectral Characteristics of 10H-pyrido[1,2-*b*]benzimidazol-5-ium and 1H-imidazolo[1,2-*a*]pyridin-4-ium Bromides

Compound	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm (*J*, Hz)		
		Signals of the pyridine ring	Aromatic protons*	Other protons
1	2	3	4	5
4c	3019, 2247 (CN), 1524, 1502, 1477, 766, 752, 705	10.08 (1H, s, H-6); 8.54 (1H, s, H-8)	8.96 (1H, d, ^3J = 8.0, H-4); 8.28 (1H, d, ^3J = 8.0, H-1); 8.07 (2H, d, ^3J = 7.5, H-2',6'); 7.94 (1H, t, ^3J = 8.0, H-2); 7.83 (1H, t, ^3J = 8.0, H-3); 7.75 (2H, m, H-2",6"); 7.69 (3H, m, H-3"-5"); 7.61 (2H, t, ^3J = 7.5, H-3',5'); 7.53 (1H, t, ^3J = 7.5, H-4')	4.41 (2H, t, ^3J = 7.0, –CH_2CN); 2.77 (2H, t, ^3J = 7.0, NCH_2–)
4d	3042, 1518, 1494, 1480, 1441, 761, 705	10.12 (1H, s, H-6); 8.48 (1H, s, H-8)	9.01 (1H, d, ^3J = 8.0, H-4); 8.07 (2H, d, ^3J = 8.0, H-2',6'); 7.90 (1H, d, ^3J = 8.0, H-1); 7.83 (2H, m, H-2,3); 7.61 (2H, t, ^3J = 8.0, H-3',5'); 7.54 (4H, m, H-4',2",4",6"); 7.42 (2H, t, ^3J = 8.5, H-3",5"); 7.22 (3H, m, H-3"'–5"'); 6.82 (2H, m, H-2"',6"')	5.44 (2H, s, CH_2)
4e	1500, 1475, 1375, 750	10.17 (1H, s, H-6); 8.56 (1H, s, H-8)	9.06 (1H, d, ^3J = 8.0, H-4); 8.11 (2H, d, ^3J = 8.0, H-2',6'); 7.86 (2H, m, H-2,3); 7.62 (2H, m, H-3',5'); 7.56 (1H, m, H-4'); 7.50 (1H, m, H-1); 7.36 (3H, m, H-2"',6"',4"'); 7.27 (4H, m, H-2",6",3"',5"'); 7.19 (1H, m, H-4"); 7.09 (2H, m, H-3",5")	–
4f	3008, 2964, 1611 (C=N), 1510, 1248 (C–O), 1192, 1029 (C–O), 848, 766	9.90 (1H, s, H-6); 8.40 (1H, s, H-8)	8.90 (1H, d, ^3J = 8.0, H-4); 8.09 (1H, d, ^3J = 8.0, H-1); 8.00 (2H, d, ^3J = 8.0, H-2',6'); 7.90 (1H, m, H-2); 7.79 (1H, m, H-3); 7.64 (2H, d, ^3J = 8.0, H-2",6"); 7.19 (2H, d, ^3J = 8.0, H-3",5"); 7.14 (2H, d, ^3J = 8.0, H-3',5')	3.87 (3H, s, 4"'-OCH_3); 3.84 (3H, s, 4"-OCH_3); 3.59 (3H, s, NCH_3)
4g	3030, 1608 (C=N), 1505, 1477, 1253 (C–O), 1186, 1027 (C–O), 839, 755, 699	9.99 (1H, s, H-6); 8.40 (1H, s, H-8)	8.96 (1H, d, ^3J = 8.0, H-4); 8.01 (2H, d, ^3J = 8.5, H-2',6'); 7.90 (1H, d, ^3J = 8.0, H-1); 7.84 (1H, t, ^3J = 8.0, H-2); 7.81 (1H, t, ^3J = 8.0, H-3); 7.43 (2H, d, ^3J = 8.5, H-3',5'); 7.19 (3H, m, H-3"'-5"'); 7.15 (2H, d, ^3J = 8.5, H-2",6"); 6.97 (2H, d, ^3J = 8.5, H-3",5"); 6.84 (2H, d, ^3J = 8.0, H-2"',6"')	5.47 (2H, s, CH_2); 3.85 (3H, s, 4"'-OCH_3); 3.81 (3H, s, 4"-OCH_3)
4h	3014, 1527, 1494, 1480, 1091, 833, 758	10.07 (1H, d, ^4J = 1.0, H-6); 8.53 (1H, d, ^4J = 1.0, H-8)	8.93 (1H, d, ^3J = 8.0, H-4); 8.12 (3H, m, H-1,2',6'); 7.93 (1H, t, ^3J = 8.0, H-2); 7.81 (1H, t, ^3J = 8.0, H-3); 7.74 (4H, m, H-2",3",5",6"); 7.67 (2H, d, ^3J = 8.0, H-3',5')	3.60 (3H, s, NCH_3)
4i	3025, 1477, 1457, 1088, 867, 831, 758	10.15 (1H, s, H-6); 8.52 (1H, s, H-8)	8.98 (1H, d, ^3J = 8.0, H-4); 8.11 (2H, d, ^3J = 8.0, H-2',6'); 7.96 (1H, d, ^3J = 8.0, H-1); 7.85 (2H, m, H-2,3); 7.69 (2H, d, ^3J = 8.0, H-3',5'); 7.47 (4H, m, H-2",3",5",6"); 7.19 (3H, m, H-3"'-5"'); 6.80 (2H, d, ^3J = 8.0, H-2"',6"')	5.48 (2H, s, CH_2)
4j	1640 (C=N), 1500, 1475, 1090, 821, 750	10.19 (1H, s, H-6); 8.61 (1H, s, H-8)	9.02 (1H, d, ^3J = 8.0, H-4); 8.16 (2H, d, ^3J = 8.0, H-2',6'); 7.87 (2H, m, H-2,3); 7.71 (2H, d, ^3J = 8.0, H-3',5'); 7.52 (1H, d, ^3J = 8.0, H-1); 7.43 (1H, t, ^3J = 8.0, H-4"'); 7.35 (4H, m, H-2"',3"',5"',6"'); 7.26 (2H, d, ^3J = 8.0, H-2",6"); 7.15 (2H, d, ^3J = 8.0, H-3",5")	—
4k	2997, 1527, 1491, 1477, 1074, 1007, 839, 755	10.04 (1H, s, H-6); 8.53 (1H, s, H-8)	8.89 (1H, d, ^3J = 8.0, H-4); 8.13 (1H, d, ^3J = 8.0, H-1); 8.03 (2H, d, ^3J = 8.0, H-2',6'); 7.93 (1H, t, ^3J = 8.0, H-2); 7.82 (5H, m, H-3,2",3",5",6"); 7.68 (2H, d, ^3J = 8.0, H-3',5')	3.60 (3H, s, NCH_3)
4l	3025, 1516, 1477, 1068, 1010, 831, 755	10.15 (1H, s, H-6); 8.51 (1H, s, H-8)	8.98 (1H, d, ^3J = 8.0, H-4); 8.04 (2H, d, ^3J = 8.0, H-2',6'); 7.97 (1H, d, ^3J = 8.0, H-1); 7.84 (4H, m, H-2,3,3',5'); 7.59 (2H, d, ^3J = 8.0, H-2",6"); 7.41 (2H, d, ^3J = 8.0, H-3",5"); 7.20 (3H, m, H-3"'-5"'); 6.80 (2H, d, ^3J = 8.0, H-2"',6"')	5.49 (2H, s, CH_2)

TABLE 3 (continued)

1	2	3	4	5
5c	3053, 1521, 1494, 1421, 1287, 1273, 934, 758, 738, 710, 697	9.43 (1H, s, H-5); 8.17 (1H, s, H-7)	8.50 (1H, s, H-3); 8.24 (1H, s, H-2); 7.88 (2H, d, ^3J = 8.0, H-2',6'); 7.64-7.57 (7H, m, H-3',5', H-2"-6"); 7.50 (1H, m, H-4')	5.63 (1H, m, –CH=); 5.09 (1H, d, ^3J = 10.0, =C$\underline{H}_A$H$_B$); 4.77 (1H, d, ^3J = 17.0, =CH$_A$$\underline{H}_B$); 4.51 (2H, d, ^3J = 4.5, NCH$_2$)
5d	3037, 1527, 1499, 1284, 1206, 892, 761, 738, 716, 705	9.53 (1H, d, ^4J = 1.0, H-5); 8.12 (1H, d, ^4J = 1.0, H-7)	8.60 (1H, s, H-3); 8.37 (1H, s, H-2); 7.88 (2H, d, ^3J = 8.0, H-2',6'); 7.55 (3H, m, H-3'-5'); 7.44 (5H, m, H-2"-6"); 7.21 (3H, m, H-3'"-5'"); 6.65 (2H, d, ^3J = 7.5, H-2'",6'")	5.24 (2H, s, CH$_2$)
5e	3031, 1645 (C=C), 1513, 1488, 1272, 1245, 895, 878, 760, 741, 699, 629	9.51 (1H, s, H-5); 8.27 (1H, s, H-7)	8.67 (1H, d, ^3J = 1.5, H-3); 8.64 (1H, d, ^3J = 1.5, H-2); 7.90 (2H, d, ^3J = 8.0, H-2',6'); 7.61 (5H, m, H-2"-6"); 7.56 (2H, t, ^3J = 8.0, H-3',5'); 7.51 (1H, m, H-4')	6.36 (1H, dd, ^3J = 15.5, ^3J = 9.0, NCH=); 5.77 (1H, dd, ^3J = 15.5, ^2J = 2.5, =C$\underline{H}_A$H$_B$); 5.10 (1H, dd, ^3J = 9.0, ^2J = 2.5, =CH$_A$$\underline{H}_B$)
5f	3047, 1611 (C=N), 1510, 1289, 1253 (C–O), 1188, 1029 (C–O), 836, 733	9.31 (1H, d, ^4J = 1.0, H-5); 8.06 (1H, d, ^4J = 1.0, H-7)	8.41 (1H, d, ^3J = 1.5, H-3); 8.21 (1H, d, ^3J = 1.5, H-2); 7.81 (2H, d, ^3J = 8.5, H-2',6'); 7.57 (2H, d, ^3J = 8.5, H-2",6"); 7.12 (4H, m, H-3',5',3",5")	3.85 (3H, s, 4'"-OCH$_3$); 3.82 (3H, s, 4"-OCH$_3$); 3.48 (3H, s, NCH$_3$)
5g	3036, 2997, 1608 (C=N), 1508, 1250 (C–O), 1183, 1032 (C–O), 833, 716	9.37 (1H, d, ^4J = 1.0, H-5); 8.04 (1H, d, ^4J = 1.0, H-7)	8.50 (1H, d, ^3J = 1.5, H-3); 8.30 (1H, d, ^3J = 1.5, H-2); 7.80 (2H, d, ^3J = 8.5, H-2',6'); 7.36 (2H, d, ^3J = 8.5, H-2",6"); 7.21 (3H, m, H-3'"-5'"); 7.10 (2H, d, ^3J = 8.5, H-3',5'); 6.98 (2H, d, ^3J = 8.5, H-3",5"); 6.68 (2H, d, ^3J = 8.0, H-2'",6'")	5.24 (2H, s, CH$_2$); 3.82 (6H, s, OCH$_3$)
5h	3036, 1491, 1295, 1090, 830, 733	9.46 (1H, s, H-5); 8.18 (1H, s, H-7)	8.45 (1H, s, H-3); 8.27 (1H, s, H-2); 7.91 (2H, d, ^3J = 8.0, H-2',6'); 7.69-7.63 (6H, m, H-3',5',2",3",5",6")	3.49 (3H, s, NCH$_3$)
5i	3031, 1491, 1091, 828, 724	9.57 (1H, d, ^4J = 1.0, H-5); 8.15 (1H, d, ^4J = 1.0, H-7)	8.58 (1H, s, H-3); 8.38 (1H, s, H-2); 7.91 (2H, d, ^3J = 8.0, H-2',6'); 7.63 (2H, d, ^3J = 8.0, H-3',5'); 7.43 (4H, m, H-2",3",5",6"); 7.20 (3H, m, H-3'"-5'"); 6.64 (2H, m, H-2'",6'")	5.28 (2H, s, CH$_2$)
5j	3036, 1485, 1292, 1071, 1007, 839, 825, 814	9.48 (1H, d, ^4J = 1.5, H-5); 8.17 (1H, d, ^4J = 1.5, H-7)	8.50 (1H, s, H-3); 8.37 (1H, s, H-2); 7.83 (4H, m, H-2',6',2",6"); 7.77 (2H, d, ^3J = 8.0, H-3',5'); 7.65 (2H, d, ^3J = 8.0, H-3",5")	3.88 (2H, q, ^3J = 7.0, NCH$_2$); 1.09 (3H, t, ^3J = 7.0, CH$_3$)
5k	3025, 2980, 1483, 1287, 1007, 828, 730, 713, 699	9.44 (1H, d, ^4J = 1.0, H-5); 8.18 (1H, d, ^4J = 1.0, H-7)	8.44 (1H, d, ^3J = 1.0, H-3); 8.26 (1H, d, ^3J = 1.0, H-3); 7.84 (2H, d, ^3J = 8.0, H-2',6'); 7.79 (4H, m, H-3',5',2",6"); 7.62 (2H, d, ^3J = 8.0, H-3",5")	3.48 (3H, s, NCH$_3$)
5l	3025, 2980, 1524, 1482, 1449, 1287, 1007, 828, 730, 713, 699	9.54 (1H, s, H-5); 8.15 (1H, s, H-7)	8.56 (1H, d, ^3J = 1.0, H-3); 8.36 (1H, d, ^3J = 1.0, H-2); 7.84 (2H, d, ^3J = 8.0, H-2',6'); 7.77 (2H, d, ^3J = 8.0, H-3',5'); 7.59 (2H, d, ^3J = 8.0, H-2",6"); 7.35 (2H, d, ^3J = 8.0, H-3",5"); 7.19 (3H, m, H-3'"-5'"); 6.64 (2H, m, H-2'",6'")	5.27 (2H, s, CH$_2$)

* The signals of the benzene rings 7-Ar (for **4c-l**) and 6-Ar (for **5c-l**) are designated H-2'-6', 9-Ar (for **4c-l**) and 8-Ar (for **5c-l**) H-2"-6", and for N-Ph and N-CH$_2$Ph (for **4d**,**g**,**i**,j,**l** and **5d**,**g**,**i**,**l)** are designated H-2'"-6'".

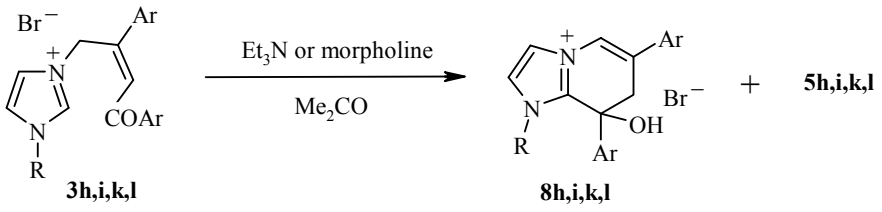
(method A). The spectral data (^{1}H NMR and infrared spectra, Table 3) of the products of cyclization agreed with those of compounds **4a,b** and **5a,b** [10], on the basis of which we assumed the structures of compounds **4c-l** and **5c-l**.

Cyclization of salts **2** in acetone gave nondehydrated products and their mixtures with salts of type **4**. Heating of bromide **2a** in acetone with Et_3N (method B) gave 4-hydroxy-5-methyl-2,4-diphenyl-4,5-dihydro-1H-pyrido[1,2-*a*]benzimidazol-10-ium bromide (**6a**) [10]. The structure of compound **6a** was reliably found by two-dimensional NMR spectroscopy (Fig. 1, **A**). The reaction of benzimidazolium bromide **2c** led to a compound with a similar structure (**6b**). 1-Ethyl- (**2b**) and 1-phenylbenzimidazolium bromides (**2e,j**) formed the aromatic salts **4b** [10] and **4e,j** under similar conditions. From the remaining benzimidazolium salts a mixture of cyclization products was obtained (according to ^{1}H NMR data), the composition of which depended on the nature of the substituents in the benzene ring of the dypnone and the substituent at atom N(1) in the benzimidazole. For example, 1-methylbenzimidazolium bromides **2f,h,k** gave mixtures (Table 4) containing ~50% of products of type **6**, while in the products of cyclization of 1-benzylimidazolium bromide **2d** (Ar = Ph) the amount of the product of type **6** was 70%.

The second component of the mixture – compound of previously unknown structure – is also present in the mixture of products from the cyclization of 1-benzylbenzimidazolium bromides **2i** and **2l** (Ar = 4-ClC_6H_4, 4-BrC_6H_4). The basic component of the mixtures in these cases are pyrido[1,2-*a*]benzimidazolium salt of type **4**, but compounds of type **6** and the unknown (in a ratio of ~1:1) did not exceed 30%. The presence of the unknown compound and its content in the product mixture was determined from the characteristic signals in the 3.50-3.54 ppm region of the ^{1}H NMR spectrum of the methylene group as a broadened two-proton multiplet or doublet of doublets of the AB-system with ^2J = 17.0 Hz. The presence of such a signal at higher field than for compounds of type **6** ($C(6)H_2$ 5.67-5.83 ppm), and the signal of a methyne proton in the 8.32-8.54 ppm region – at weaker field in comparison with compounds of type **6**, provides a basis for suggesting that the structure of the unknown compound corresponds to that of the 5-R-2,4-diaryl-4-hydroxy-4,5-dihydro-3H-pyrido[1,2-*a*]benzimidazol-10-ium cation (**7**).

When morpholine was used in boiling acetone (method C) the 1-methylbenzimidazolium salts **2a** and **2f** (Ar = Ph, 4-$MeOC_6H_4$) and 1-benzylimidazolium salts **2d**,**g**,**i,** and **l** were converted into aromatic salts of type **4**. 1-Methylbenzimidazolium bromide **2h** (Ar = 4-ClC_6H_4) gave a mixture consisting of 30% bromide **4h** and a compound of type **7**, which, in the case of 1-methylbenzimidazolium bromide **2k** (Ar = 4-BrC_6H_4), was the basic reaction product (Table 4).

To confirm the structure of compounds **7** we studied the IR, ^{1}H and ^{13}C NMR spectra of pyrido-[2,1-*a*]benzimidazolium bromide **7k**, and also its 2D HMQC, HMBC, and NOESY spectra. A correlation was found in the HMBC and NOESY spectra (Fig 1, **B**) which indicates the connectivity of the methylene group at 3.54 and the methyne proton at 8.53 ppm to the pyridine unit of the 2,4-diaryl-4,5-dihydro-3H-pyrido-[1,2-*a*]benz-imidazol-10-ium condensed system. The presence of the OH group in **7k** is shown by the presence of a signal at 7.73 ppm which exchanges with D_2O, and by the presence of the signal in the 3166 cm^{-1} in the IR spectrum. The presence of the OH group in the molecule is confirmed from its 2D NOESY spectrum: a negative NOE value is observed for the water signals and the proton at 7.73 ppm (as in the case of compound **6a** [10]) which showed the exchange process. The basic difference in the correlation diagrams for the isomers **6** and **7** consists in the observed correlations of the protons of the methylene group. In the case of the 6H isomer



3h,i,k,l **8h,i,k,l**

(compound **6a**, Fig 1., **A**) there is a cross-peak in the HMBC spectrum at 130.7 ppm which corresponds to the quaternary atom C(4a) of the benzimidazolium unit. Whereas in the spectrum of the 8H isomer (compound **7k**), the cross-peak is at 71.8 ppm for the quaternary atom C(9) of the pyridine unit bonded to the OH group.

On alkylation of the γ-bromodypnones **1c** and **1d** with an excess of 1-phenylbenzimidazole in benzene heated to 50-60°C, cyclic products are obtained: 2,4-diaryl-4-hydroxy-5-phenyl-4,5-dihydro-3H-pyrido-[1,2-*a*]benzimidazol-10-ium bromides **7j,m**. It should be noted that formation of the cyclic product **7j** was observed even during the isolation of the quaternary salt **2j** (~8-10% in the crude product according to ^{1}H NMR data). This shows that the nature of the substituents in the benzene rings and at atom N(1) in benzimidazolium salts **2** affect the rate of cyclization – the increased electronegativity of the substituents facilitates the reaction.

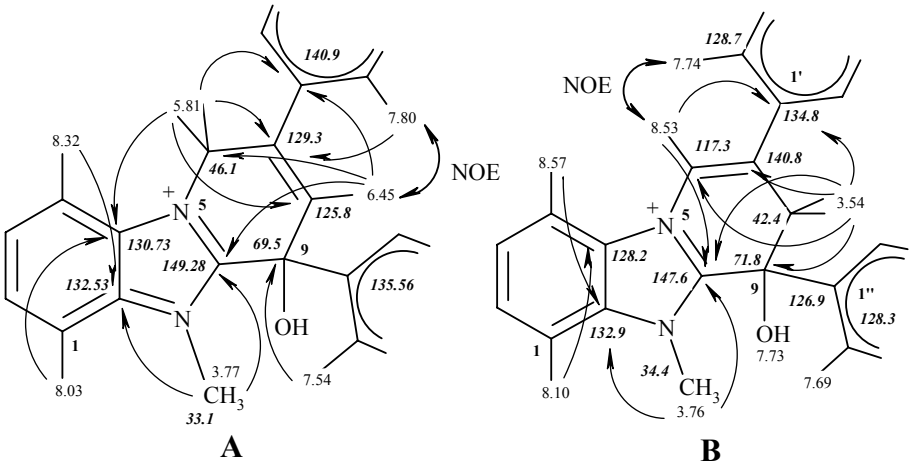


Fig. 1 Structure significant HMBC and NOESY Correlations for Compounds **6a** (**A**) and **7k** (**B**)

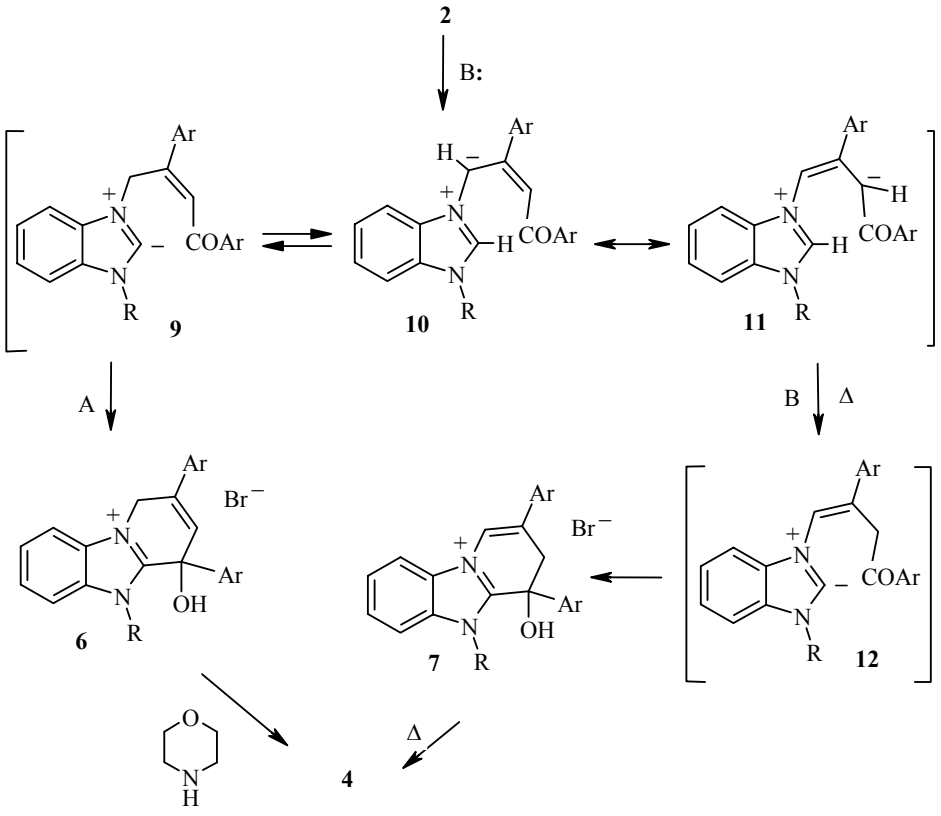
TABLE 4. Results of the Cyclization Reactions of Salts **2**

Com-pound	Base	Reaction conditions (method)	Result of reaction
2a	Et_3N	B	**6**
	Morpholine	B	**4**
2f	Et_3N	B	**6f** + **7f** (1.5 : 1)
	Morpholine	B	**4f**
2h	Et_3N	B	**6h** +**7h** (1 : 1.3)
	Morpholine	B	**7h** + **4h** (2 : 1)
	Morpholine	A	**4h**
2k	Et_3N	B	**6k** + **7k** (1 : 1)
	Morpholine	B	**7k**
	Morpholine	A	**4k**
2d	Et_3N	B	**6d** + **7d** (2 : 1)
	Et_3N	Acetone, Δ, 3.5 h	**6d** + **4d** (1 : 1.4)
	Morpholine	B	**4d**
2g	Et_3N	B	**6g** + **7g** + **4g** (1:1:1)
	Morpholine	B	**4g**
2i	Et_3N	B	**6i** + **7i** + **4i** (1.3:1:4)
	Morpholine	B	**4i**
2l	Et_3N	B	**6l** + **7l** + **4l** (1.8:1: 6)
	Morpholine	B	**4l**
2e	Et_3N	B	**4e**
2j	Et_3N	B	**4j**

The dependence of the results of the cyclization imidazolium salts **3** on the nature of substituents in varying conditions is not as well expressed. The formation of 1-R-6,8-diaryl-8-hydroxy-7,8-dihydro-1H-imidazo[1,2-*a*]pyridin-4-ium bromides (**8**) in mixtures with aromatic products **5** (method C) was recorded by ^{1}H NMR spectroscopy only in the case of the imidazolium bromides **3h**,**i**, **k**, **l** (Ar = 4-ClC_6H_4, BrC_6H_4): the signals of the protons of the C(7)H_2 were observed at 3.44 ppm as a multiplet or as a doublet of doublets with ^2J = 17.0 Hz. The formation of 5H-derivatives of type **6** was not observed. The content of products **8** in the mixtures decreased with increasing electronegativity of the substituents in the initial salts **3** (from 60% for R = Me to 30% for R =Bn). When using Et_3N (method B) the amount of hydroxy derivatives **8** did not exceed 10-15%.

The observed regularities of the cyclization reaction may be explained as follows. The quaternary azolium salts are capable of forming ylide structures in the presence of bases [6, 11, 12) with participation of cyclic (structure **9**) or acyclic (structure **10**) anionic molecular fragments. The latter mechanism (with participation of intermediate structures of type **11**) are realized, for example in reactions with the formation of indolizines by the reaction of 1-(4-oxo-2,4-diphenyl-2-butenyl)pyridinium salts with bases [13, 14], and also in the synthesis of some derivatives of pyrrolo[1,2-*a*]benzimidazole and pyrrole[1,2-*a*]imidazole [15,16].

In our case, it is evident that conversion of salts **2** into 4-hydroxy-4,5-dihydro-1H-pyrido[1,2-*a*]benz-imidazol-10-ium bromides **6** includes a stage of formation of structure **9** (route A). Compounds **6** may be converted into isomers **7** as a result of tautomeric transfer of a hydrogen atom. However we consider this route to be less likely since heating compound **6** in acetone with morpholine (in conditions in which formation of isomers of type **7** are observed) led to aromatic products **4**. Moreover 4-hydroxy-4,5-dihydro-3H-pyrido[1,2-*a*]benz- imidazol-10-ium bromides **7** are less stable to heat than salts of type **6**: prolonged heating (2-2.5 h) of a mixture of compounds **6d** + **7d** (2:1, obtained from salt **2d** by method B) in acetone with Et_3N led to the formation of a mixture of compounds **6d** + **4d** (1:1.4). Evidently the mechanism for the conversion of salt **2** into **7** includes a stage for the intermediate formation of structure **11** (route B). When a stronger base is used (morpholine),



the proportion of structures of type **10** and **11** among the products of the reaction of **2** with bases increases. Further attack of the anionic center C(3')$^-$ at the methyne group C(2)H ensures the elimination of the proton on heating to give product **12**.

The observed dependence of the content of compound **7** in the reaction products on the nature of the substituents in the quaternary azolium salts confirms the correctness of the proposed scheme for the formation of compounds of types **6** and **7**. Increasing electronegativity of the substituents in the benzene rings of the dypnone units facilitates the formation of structures of type **10** and realization of route B, for both benzimidazolium salts **2** and imidazolium salts **3**. The possibility of reaction *via* route A is determined in large degree by the properties of azole unit: with increased electronegativity of the substituent at atom N(1), the acidity of proton H-2 increases and consequently the probability of formation of structure **9** increases. Consequently the fraction of compounds of type **7** (and type **8** for imidazoles) in the mixture of products from the conversion of benzimidazolium bromides **2** (and imidazolium bromides **3**) is decreased.

The general tendency for hydroxy derivatives of imidazo[1,2-*a*]pyridinium and pyrido[1,2-*a*]benzimidazolium, expressed as a decrease in their stability with increased acceptor properties of their substituents, does not depend on their position. For example, the greater stability of derivatives of 4-hydroxypyrido[1,2-*a*]benzimidazolium **7** in comparison with derivatives of imidazo[1,2-*a*]pyridine **8** is evidently explained by the known effect [17] of the decreased difference in the energy of formation of dihydro derivatives on going from bicyclic to tricyclic aromatic systems. In the case of 9-hydroxy derivatives of imidazo[1,2-*a*]pyridine, the relative stability of compounds of type **7** is increased by the effect of the increased chain of conjugation in the molecule, which allows for their formation and their isolation in pure form.

EXPERIMENTAL

IR spectra of KBr tablets were recorded with a Perkin-Elmer "Spectrum BX". ^{1}H NMR spectra were recorded with a Bruker AVANCE DRX 500 (500 MHz) instrument. Two dimension correlation spectroscopy was carried out with a Varian Mercury 400 instrument (400 and 100 MHz respectively for ^{1}H and ^{13}C), in DMSO-d_6 with TMS as internal standard. Melting points were measured on a Boetius block. Purity of the products was monitored by TLC on Silufol UV-254 plates and mass-spectrometric HPLC on an Agilent 1100 series with an Agilent LC/MSD SL selective detector (samples were introduced in a CF_3CO_2H matrix, with EI ionization).

(*Z*)-4-Bromo-1,3-diphenyl-2-buten-1-one (**1a**) was prepared by method [18], (*Z*)-1,3-diaryl-4-bromo-2-buten-1-ones **1b-d** by method [19]. 1-R-1H-Benzimidazoles and 1-R-1H-imidazoles were products of the company "Enamine".

(*Z*)-1-R-3-(2,4-diaryl-4-oxo-2-butenyl)-1H-benzimidazol-3-ium Bromides 2c-l were prepared by the synthetic method used for **2a,b**, described in paper [10].

(*Z*)-1-R-3-(2,4-diaryl-4-oxo-2-butenyl)-1H-imidazol-3-ium Bromides 3c-l were prepared by the method for the synthesis of products **3a,b** described in paper [10].

5-R-2,4-diaryl-5H-pyrido[1,2-*a*]benzimidazol-10-ium Bromides 4c-l. A. A mixture of salt **2** (1.15 mmol) and morpholine (2 ml) in ethanol (10 ml) was heated for 2 h. After cooling, the precipitate formed was filtered off and washed with acetone to give the pyridobenzimidazolium bromides **4c-l**.

B. An analogous method to A, using acetone as solvent and Et_3N as base, gave pyridobenzimidazolium bromides **4c-j** (yields 74-88%).

C. An analogous method to B, using morpholine as base, gave pyridobenzimidazolium bromides **4c,f,g,i** and **l** (yields 78-94%).

1-R-6,8-diaryl-1H-imidazo[1,2-*a*]pyridin-4-ium Bromides 5c-l. A. Imidazopyridinium bromides **5c-l** were obtained.

B. Imidazopyridinium bromides **5c-g, j** were obtained (yields 81-93%).

5-(2-Cyanoethyl)-4-hydroxy-2,4-diphenyl-4,5-dihydro-1H-pyrido[1,2-*a*]benzimidazol-10-ium bromide (6b) was obtained from salt **2c** by method C for the synthesis of products **4**. IR spectrum, ν, cm^{-1}: 3100 (OH), 3031, 2252 (CN), 1485, 1449, 1136, 1063 (C–O), 750, 702. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.32 (1H, d, ^3J = 8.0, H-4); 8.22 (1H, d, ^3J = 8.0, H-1); 7.94 (1H, s, OH); 7.81 (2H, m, H-2,3); 7.74 (2H, d, ^3J = 8.0, H-2',6'); 7.57 (2H, d, ^3J = 8.0, H-2",6"); 7.47 (6H, m, H-3'-5', H-3"-5"); 6.47 (1H, s, H-8); 5.84 (2H, s, C(6)H_2); 4.85 (1H, m, –C$\underline{H}_A$$H_B$CN); 4.51 (1H, m, –C$H_AC\underline{H}_B$CN); 2.62 (1H, m, NC$\underline{H}_A$$H_B$–); 2.56 (1H, m, NC$H_AC\underline{H}_B$–).

2,4-Bis(4-chlorophenyl)-4-hydroxy-5-phenyl-4,5-dihydro-3H-pyrido[1,2-*a*]benzimidazol-10-ium Bromide (7j). 1-Phenyl-1H-benzimidazole (0.97 g, 5 mmol) was added to a solution of γ-bromodypnone **1c** (1.31 g, 3.55 mmol) in benzene (50 ml). The mixture was kept at room temperature for a week. The solution was then heated at 50-60°C for 10 min. The precipitate was filtered off and washed with acetone. IR spectrum, ν, cm^{-1}: 3166 (OH), 3019, 1511, 1474, 1091 (C–O), 747, 661. ^{1}H NMR spectrum, δ, ppm (*J,* Hz): 8.70 (1H, d, ^3J = 8.0, H-4); 8.53 (1H, d, ^4J = 1.5, H-6); 7.88 (3H, m, H-2,2',6'); 7.73 (2H, m, H-3, 9-OH); 7.57 (2H, d, ^3J = 8.0, H-3',5'); 7.49-4.41 (5H, m, H-2",6",2"',6"',4"'); 7.33 (2H, m, H-3"',5"'); 7.12 (3H, m, H-1,3",5"); 3.61 (1H, dd, ^4J = 1.5, ^2J = 18.0, H_A-8); 3.37 (1H, d, ^2J =18.0, H_B-8).

2,4-Bis(4-bromophenyl)-4-hydroxy-5-methyl-4,5-dihydro-3H-pyrido[1,2-*a*]benzimidazol-10-ium Bromide (7k) was obtained from salt **2** by method C for the synthesis of products **4**. IR spectrum, ν, cm^{-1}: 3100 (OH), 3025, 1547, 1482, 1074 (C–O), 1007, 825, 749. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.57 (1H, d, ^3J = 8.0, H-4), 8.53 (1H, s, H-6), 8.10 (1H, d, ^3J = 8.0, H-1), 7.84 (1H, m, H-2), 7.81 (1H, m, H-3), 7.74 (3H, m, H-2',6', 9-OH), 7.69 (4H, m, H-3',5',2",6"), 7.62 (2H, d, ^3J = 8.0, H-3",5"), 3.76 (3H, s, CH_3), 3.54 (2H, s, CH_2). ^{13}C NMR spectrum, δ, ppm: 147.6 (C-9a), 140.8 (C-7), 134.8 (C-1'), 132.9 (C-10a), 132.7 (C-3',5'), 132.4 (C-3",5"), 129.0 (C-3), 128.7 (C-2',6'), 128.3 (C-2",6"), 128.2 (C-4a), 128.1 (C-2), 126.9 (C-1"), 123.1 (C-4'), 123.0 (C-4"), 117.3 (C-6), 114.5 (C-1), 114.3 (C-4), 71.8 (C-9), 42.4 (C-8), 34.4 (CH_3).

2,4-Bis(4-bromophenyl)-4-hydroxy-5-phenyl-4,5-dihydro-3H-pyrido[1,2-*a*]benzimidazol-10-ium Bromide (7m) was made by the method for the synthesis of product **7j**, using γ-bromodypnone **1d** (1.63 g, 3.55 mmol). IR spectrum, ν, cm^{-1}: 3154 (OH), 3025, 1516, 1477, 1077 (C–O), 1007, 816, 750, 694. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.65 (2H, m, H-4,6), 7.88 (1H, t, ^3J = 8.0, H-2), 7.78 (2H, d, ^3J = 8.0, H-2',6'), 7.72 (4H, m, H-3,3',5', 9-OH), 7.48-4.40 (5H, m, H-2",6",2"',6"',4"'), 7.33 (2H, m, H-3"',5"'), 7.28 (2H, d, ^3J = 8.0, H-3",5"), 7.10 (1H, d, ^3J = 8.0, H-1), 3.61 (1H, dd, ^4J = 1.5, ^2J = 18.0, H_A -8), 3.37 (1H, d, ^2J = 18.0, H_B -8).

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