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SYNTHESIS OF DIARYLAZOLO[*a*]PYRIDINES FROM [(*Z*)-2,4-DIARYL-4-OXO-2-BUTENYL]AZOLIUM SALTS

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A method for the synthesis of derivatives of [1,3]thiazolo[3,2-a]pyridines, pyrido[2,1-b][1,3]benzothiazole, [1,3,4]thiadiazolo[3,2-a]pyridine, and [1,2,4]triazolo[4,3-a]pyridine, which includes base initiated cyclization of quaternary azolium salts, formed by the interaction of (Z)-1,3-diaryl-4-bromo-2-buten-1-ones with 1-alkyl-1H-1,2,4-triazoles, 4-methyl-1,3-thiazole, 1,3-benzothiazole, and N-phenyl-1,3,4-thiadiazole-2-amine. Derivatives of 2-chloroimidazo[1,2-a]pyridine were obtained when 5-chloro-1-methyl-1H-imidazole was used.

Keywords: γ-bromodypnone, imidazo[1,2-*a*]pyridine, pyrido[2,1-*b*][1,3]benzothiazole, [1,3,4]thiadiazolo[3,2-*a*]pyridine, [1,3]thiazolo[3,2-*a*]pyridine, [1,2,4]triazolo[4,3-*a*]pyridine, cyclization of azolium ylides.

Some examples of azolo[*a*]pyridine system construction are known in which heterocyclization based on azoles unsubstituted at position 2 is used as a method of annelation of the pyridine ring [1-4]. Only one of these [2] has a general nature and was extended to different azoles. We have previously [5, 6] found a suitable method for the synthesis 1-R-6,8-diaryl-1H-imidazo[1,2-*a*]pyridin-4-ium (**1**) and 5-R-2,4-diaryl-5H-pyrido[1,2-*a*]benzimidazol-1-ium bromides (**2**) which include base initiated cyclization of (*Z*)-3-R-1-[2,4-diaryl-4-oxo-2-butenyl]-3H-benz-imidazol-1-ium and (*Z*)-1-R-3-[2,4-diaryl-4-oxo-2-butenyl]-1H-imidazol-3-ium quaternary salts. The latter were obtained by alkylation of 1-alkyl-1H-imidazoles and -benzimidazoles with derivatives of 4-bromo-1,3-diphenyl-2-buten-1-one (γ-bromodypnone) **3a-d**. In this work we extend the range of azoles used in these conversion schemes.

It was shown earlier [6] that the structure of the azole the stage of the formation of the quaternary salts preeminently affected the effectivness of the conversion of the azoles into the polycyclic systems **1** and **2**. For example the rates of alkylation and the yields of reaction products decreased on going from 1-alkyl-1H-imidazoles (80-90%, 1-4 h) to 1-alkyl-1H-benzimidazoles (60-80%, 6-12 h). On introducing electron-acceptor substituents into the imidazole ring a still larger decrease in rate and yield of reaction products was observed. Thus on subjecting solutions of 5-chloro-1-methyl-1H-imidazole with derivatives of γ-bromodypnone **3a-c** in benzene at room temperature [6] (*Z*)-3-[2,4-bis(aryl)-4-oxo-2-buten-yl]-5-chloro-1-methyl-1H-imidazol-3-ium bromides **4a-c**

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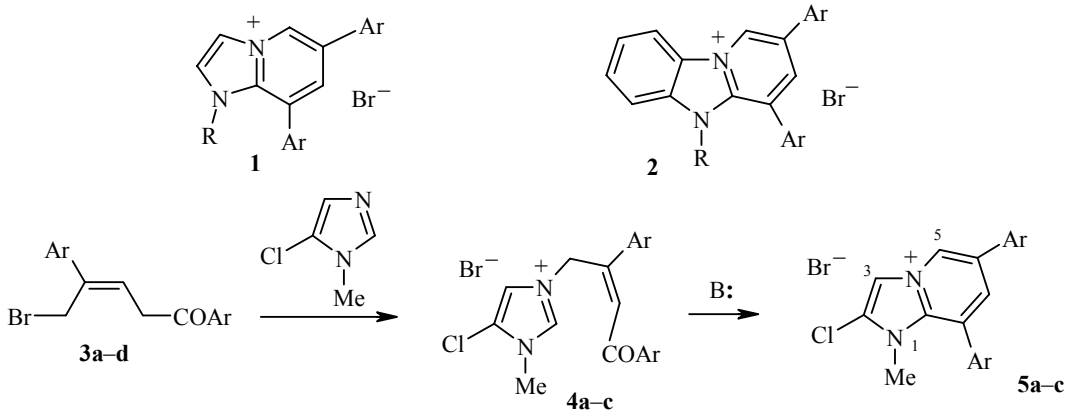
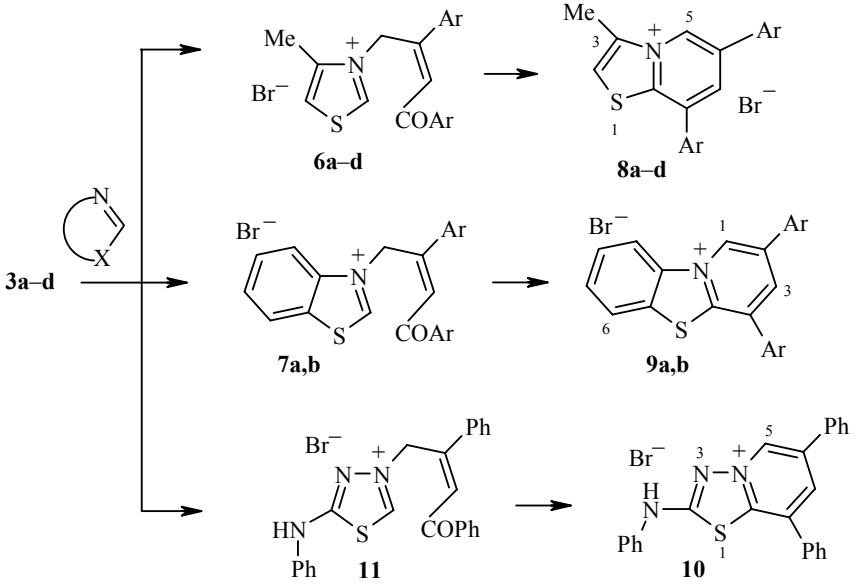
were formed in 2-3 days in yields of 40-55%. Under these conditions 5-chloro-1-methyl-4-nitro-1H-imidazole did not form a quaternary salt and heating the mixture of reagents led to products of the intramolecular cyclization of the γ-bromodypnones **3** – 2,4-diarylfurans [7]. 6,8-Diaryl-2-chloro-1-methyl-1H-imidazo-[1,2-*a*]pyridin-4-ium bromides **5a-c** were formed in high yields (75-82%) on heating the salts **4a-c** in acetone in the presence of morpholine.



3, 4 a Ar = Ph, **b** Ar = 4-MeOC$_6$H$_4$, **c** Ar = 4-ClC$_6$H$_4$; **3d** Ar = 4-BrC$_6$H$_4$

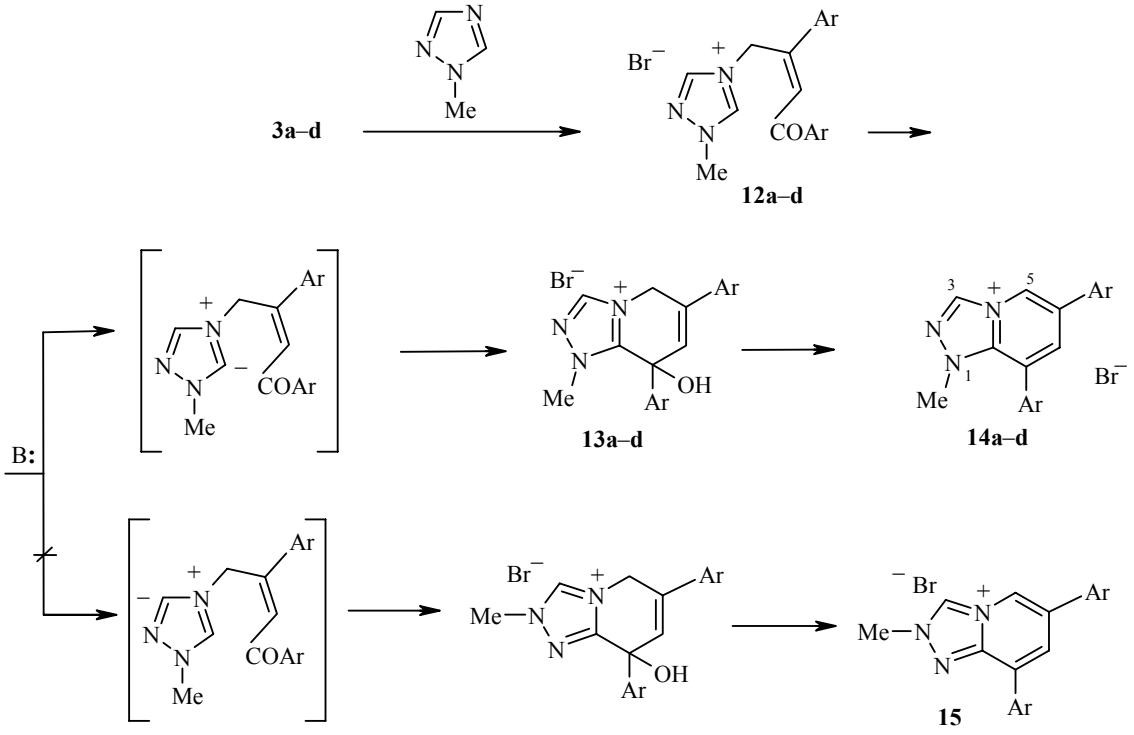
Reactions of derivatives of γ-bromodypnones **3a-d** with other azoles were then studied. Quaternary azolium salts – (*Z*)-3-[2,4-diaryl-4-oxo-2-butenyl]-4-methyl-1,3-thiazol-3-ium bromides **6a-d** and (*Z*)-3-[2,4-diaryl-4-oxo-2-butenyl]-1,3-benzothiazol-3-ium bromides **7a,b** (Table 1) were formed from 4-methyl-1,3-thiazole and 1,3-benzothiazole and the γ-bromodypnones in benzene at room temperature. The times necessary for conversion into salts **6** and **7** at 25°C was 3-4 d. Heating the solutions lead to an increased rate of alkylation but intramolecular cyclization of the γ-bromodypnone starting materials into 2,4-diarylfurans. 6,8-Diaryl-3-methyl[1,3]thiazolo-[3,2-*a*]pyridin-4-ium bromides **8a-d** and 2,4-diarylpyrido[2,1-*b*]benzothiazol-10-ium bromides **9a,b** were formed in high yields (80-82%) on heating the quaternary salts **6a-d** and **7a,b** in acetone with triethylamine.



6, **8 a** Ar = Ph, **b** Ar = 4-MeOC$_6$H$_4$, **c** Ar = 4-ClC$_6$H$_4$, **d** Ar = 4-BrC$_6$H$_4$;
7, **9 a** Ar = Ph, **b** Ar = 4-ClC$_6$H$_4$

The structures of the reaction products **6-9** were established by spectroscopic methods (IR, ^{1}H NMR), the results of which corresponded with those obtained earlier for derivatives of 1-alkyl-1H-benzimidazoles and -imidazoles **1, 2** [5, 6] and **4, 5** (Tables 2 and 3).

2-Anilino-6,8-diphenyl[1,3,4]thiadiazolo[3,2-*a*]pyridine-4-ium bromide (**10**) was synthesized by the same scheme. In contrast to the reaction with thiazoles, it was not possible to isolate the quaternary salt with structure **11** in pure form. The product of the alkylation of N-phenyl-1,3,4-thiadiazole-2-amine with γ-bromodypnone **3a** (in benzene at room temperature for 4 d) gave the starting materials, salts **11** and **10**, but attempts to purify quaternary salt **11** by recrystallization from nitromethane or 2-propanol led only to an increase in the content of the cyclic product **10** in the mixture.



12–14 a Ar = Ph, **b** Ar = 4-MeOC$_6$H$_4$, **c** Ar = 4-ClC$_6$H$_4$, **d** Ar = 4-BrC$_6$H$_4$

(*Z*)-4-[2,4-Diaryl-4-oxo-2-butenyl]-1-methyl-1H-1,2,4-triazol-4-ium bromides **12b-d** were formed in yields of 53-61% from the reaction of 1-methyl-1H-1,2,4-triazole with the γ-bromodypnones **3b-d** under the same conditions (benzene, room temperature, 24 h). In the reaction of γ-bromodypnone **3a** with 1-methyl-1H-1,2,4-triazole a mixture of products of alkylation (salts of type **12**) and further cyclization were obtained – 1-alkyl-6,8-diaryl-8-hydroxy-5,8-dihydro-1H-[1,2,4-triazolo[4,3-*a*]pyridin-4-ium bromide (**13**) – in a ratio of 1:4 (**12a** + **13a**). The composition of the mixture was determined by ^{1}H NMR spectroscopy. The presence of the 8-hydroxy-5,8-dihydro-1H-[1,2,4]triazolo[4,3-*a*]pyridin-4-ium cation in the mixture was confirmed by the signals of the protons of the dihydropyridine fragment: 2H-5 in the 5.64 ppm region as an AB spin system with J = 18.5 Hz, H-7 (s, 6.40), and OH (s, 7.79 ppm). We had observed a similar resonance pattern previously [5, 6] for 4-hydroxy-4,5-dihydro-1H-pyrido[1,2-*a*]benzimidazol-10-ium salts which allowed us to determine the structure of product **13a**. Further heating of the quaternary salts **12b-d** or the mixture **12a** + **13a** in acetone in the presence of triethylamine led to the 6,8-diaryl-1R-1H-[1,2,4]triazolo[4,3-*a*]pyridin-4-ium bromides **14a-d**.

Table 1. Physicochemical Properties and Elemental Analyses

Compound	Empirical formula	Found, % / Calculated, %						mp, °C*	Yield, %
		C	H	Br	Cl	N	S		
4a	$C_{20}H_{18}BrClN_2O$	57.45 / 57.51	4.28 / 4.34	19.15 / 19.13	8.48 / 8.49	6.73 / 6.71	—	152-154	48
4b	$C_{22}H_{22}BrClN_2O_3$	55.25 / 55.31	4.60 / 4.64	16.70 / 16.72	7.44 / 7.42	5.88 / 5.86	—	172-174	52
4c	$C_{20}H_{16}BrCl_3N_2O$	49.30 / 49.36	3.24 / 3.31	16.43 / 16.42	21.88 / 21.86	5.75 / 5.76	—	216-217	47
5a	$C_{20}H_{16}BrClN_2$	60.06 / 60.10	3.95 / 4.03	19.96 / 19.99	8.88 / 8.87	7.05 / 7.01	—	248-250	77
5b	$C_{22}H_{20}BrClN_2O_2$	57.39 / 57.47	4.30 / 4.38	17.40 / 17.38	7.70 / 7.71	6.09 / 6.09	—	229-231	82
5c	$C_{20}H_{14}BrCl_3N_2$	51.21 / 51.26	2.95 / 3.01	17.06 / 17.05	22.71 / 22.70	6.00 / 5.98	—	262-263	75
6a	$C_{20}H_{18}BrNOS$	59.96 / 60.00	4.48 / 4.53	19.97 / 19.96		3.53 / 3.50	8.00 / 8.01	170-172 (decomp)	62
6b	$C_{22}H_{22}BrNO_3S$	57.32 / 57.39	4.75 / 4.82	17.38 / 17.36		3.05 / 3.04	6.95 / 6.97	152-153	48
6c	$C_{20}H_{16}BrCl_2NOS$	51.12 / 51.19	3.39 / 3.44	17.05 / 17.03	15.13 / 15.11	3.01 / 2.99	6.84 / 6.83	203-205	58
6d	$C_{20}H_{16}Br_3NOS$	42.92 / 43.04	2.81 / 2.89	42.97 / 42.95		2.54 / 2.51	5.78 / 5.75	174-176 (decomp)	50
7a	$C_{23}H_{18}BrNOS$	63.24 / 63.31	4.10 / 4.16	18.30 / 18.31		3.22 / 3.21	7.38 / 7.35	156-158	42
7b	$C_{23}H_{16}BrCl_2NOS$	54.59 / 54.67	3.09 / 3.19	15.84 / 15.81	14.00 / 14.03	2.77 / 2.77	6.36 / 6.35	186-188	38
8a	$C_{20}H_{16}BrNS$	62.76 / 62.83	4.15 / 4.22	20.93 / 20.90		3.65 / 3.66	8.40 / 8.39	262-265	88
8b	$C_{22}H_{20}BrNO_2S$	59.66 / 59.73	4.50 / 4.56	18.09 / 18.06		3.16 / 3.17	7.28 / 7.25	251-252	86
8c	$C_{20}H_{14}BrCl_2NS$	53.16 / 53.24	3.05 / 3.13	17.73 / 17.71	15.70 / 15.71	3.12 / 3.10	7.14 / 7.11	272-274	79
8d	$C_{20}H_{14}Br_3NS$	44.42 / 44.48	2.57 / 2.61	44.40 / 44.38		2.60 / 2.59	5.92 / 5.94	302-304	83
9a	$C_{23}H_{16}BrNS$	65.95 / 66.03	3.79 / 3.85	19.12 / 19.10		3.38 / 3.35	7.65 / 7.66	319-321	80
9b	$C_{23}H_{14}BrCl_2NS$	56.65 / 56.70	2.86 / 2.90	16.42 / 16.40	14.53 / 14.55	2.88 / 2.87	6.61 / 6.58	279-282	82
10	$C_{24}H_{18}BrN_3S$	62.58 / 62.61	3.88 / 3.94	17.37 / 17.36		9.15 / 9.13	6.98 / 6.96	364-365	57
12b	$C_{21}H_{22}BrN_3O_3$	56.71 / 56.77	4.93 / 4.99	18.00 / 17.98		9.48 / 9.46	—	192-194	56
12c	$C_{19}H_{16}BrCl_2N_3O$	50.30 / 50.36	3.51 / 3.56	17.65 / 17.63	15.67 / 15.65	9.29 / 9.27	—	209-211	61
12d	$C_{19}H_{16}Br_3N_3O$	42.06 / 42.10	2.93 / 2.98	44.23 / 44.22		7.73 / 7.75	—	208-210	53
14a	$C_{19}H_{16}BrN_3$	62.25 / 62.31	4.38 / 4.40	21.84 / 21.82		11.49 / 11.47	—	261-263	81
14b	$C_{21}H_{20}BrN_3O_2$	59.10 / 59.17	4.68 / 4.73	18.75 / 18.74		9.88 / 9.86	—	222-224	80
14c	$C_{19}H_{14}BrCl_2N_3$	52.40 / 52.44	3.26 / 3.24	18.38 / 18.36	16.27 / 16.29	9.67 / 9.66	—	239-241	77
14d	$C_{19}H_{14}Br_3N_3$	43.50 / 43.55	2.63 / 2.69	45.76 / 45.74		8.05 / 8.02	—	249-251 (decomp)	83

* Recrystallization solvent: $MeNO_2$ (compounds **4a-c**, **6d**, **7a,b**, **10**, **12c,d**), AcOH (compounds **5a-c, 6b**, **8a-d**, **9a,b**, **14c,d**) and 2-PrOH (compounds **6a,c**, **12b**, **14a,b**).

Table 2. Spectral Characteristics of 3(4)-[(*Z*)-2,4-Diaryl-4-oxo-2-butenyl]azolium Bromides **4**, **6**, **7**, and **12**

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 signals
4a	2997, 1667 (C=O), 1656, 1611, 561, 1449, 1217, 1141, 699	9.36	8.14 (2H, d, ^3J = 8.0, H-2'",6'"); 8.07 (1H, s, H-4); 7.78 (3H, m, H-3',2",6"); 7.70 (1H, t, ^3J = 8.0, H-4'"); 7.59 (2H, t, ^3J = 8.0, H-3'",5'"); 7.47 (3H, m, H-3"-5")	5.74	3.74 (3H, s, NCH_3)
4b	2997, 1639 (C=O), 1603, 1586, 1572, 1292, 1250, 1225, 1189, 1169 (C–O), 1147, 1024, 836	9.30	8.12 (2H, d, ^3J = 9.0, H-2'",6'"); 8.05 (1H, s, H-4); 7.75 (2H, d, ^3J = 8.5, H-2",6"); 7.72 (1H, s, H-3'); 7.09 (2H, d, ^3J = 9.0, H-3'",5'"); 7.00 (2H, d, ^3J = 8.5, H-3",5")	5.69	3.87 (3H, s, 4'"-OCH_3); 3.80 (3H, s, 4"-OCH_3); 3.74 (3H, s, NCH_3)
4c	2975, 1656 (C=O), 1603, 1589, 1217, 1144, 1091, 1007, 831	9.32	8.16 (2H, d, ^3J = 8.0, H-2'",6'"); 8.04 (1H, s, H-4); 7.81 (2H, d, ^3J = 8.0, H-2",6"); 7.78 (1H, s, H-3'); 7.66 (2H, d, ^3J = 8.0, H-3'",5'"); 7.52 (2H, d, ^3J = 8.0, H-3",5")	5.72	3.74 (3H, s, NCH_3)
6a	2992, 1656 (C=O), 1603, 1443, 1225, 962, 769, 699	10.05	8.14 (2H, d, ^3J = 8.0, H-2'",6'"); 7.88 (1H, s, H-5); 7.70 (3H, m, H-2",6",4'"); 7.66 (1H, s, H-3'); 7.59 (2H, t, ^3J = 8.0, H-3'",5'"); 7.42 (3H, m, H-3"–H-5")	6.12	2.45 (3H, s, 4-CH_3)
6b	3104, 2958, 1641 (C=O), 1600, 1513, 1264, 1222, 1189, 1169 (C–O), 1029, 836, 691, 607	10.02	8.11 (2H, d, ^3J = 8.5, H-2'",6'"); 7.92 (1H, s, H-5); 7.70 (2H, d, ^3J = 8.5, H-2",6"); 7.62 (1H, s, H-3'); 7.08 (2H, d, ^3J = 8.5, H-3'",5'"); 6.96 (2H, d, ^3J = 8.5, H-3",5")	6.06	3.86 (3H, s, 4'"-OCH_3); 3.77 (3H, s, 4"-OCH_3)
6c	3120, 1670 (C=O), 1611, 1589, 1217, 1091, 839, 806	10.03	8.15 (2H, d, ^3J = 8.5, H-2'",6'"); 7.91 (1H, s, H-5); 7.75 (2H, d, ^3J = 8.5, H-2",6"); 7.67 (1H, s, H-3'); 7.65 (2H, d, ^3J = 8.5, H-3'",5'"); 7.49 (2H, d, ^3J = 8.5, H-3",5")	6.08	2.46 (3H, s, 4-CH_3)
6d	3008, 1656 (C=O), 1600, 1583, 1206, 1007, 967, 811	10.07	8.07 (2H, d, ^3J = 8.5, H-2'",6'"); 7.92 (1H, s, H-5); 7.79 (2H, d, ^3J = 8.5, H-2",6"); 7.69 (2H, d, ^3J = 8.5, H-3'",5'"); 7.66 (1H, s, H-3'); 7.62 (2H, d, ^3J = 8.5, H-3",5")	6.10	2.44 (3H, s, 4-CH_3)
7a	3014, 2840, 1640 (C=O), 1594, 1569, 1427, 1214, 957, 763, 691	10.64	8.42 (1H, d, ^3J = 8.0, H-4); 8.34 (1H, d, ^3J = 8.0, H-7); 8.16 (2H, d, ^3J = 8.0, H-2'",6'"); 7.89 (1H, t, ^3J = 8.0, H-6); 7.79 (1H, t, ^3J = 8.0, H-5); 7.72 (2H, m, H-3',4'"); 7.65 (2H, m, H-2",6"); 7.60 (2H, t, ^3J = 8.0, H-3'",5'"); 7.33 (3H, m, H-3"–5")	6.51	—
7b	3008, 1656 (C=O), 1589, 1220, 1091, 831, 755	10.60	8.42 (1H, d, ^3J = 8.0, H-4); 8.32 (1H, d, ^3J = 8.0, H-7); 8.18 (2H, d, ^3J = 8.5, H-2'",6'"); 7.89 (1H, t, ^3J = 8.0, H-6); 7.80 (1H, t, ^3J = 8.0, H-5); 7.73 (1H, s, H-3'); 7.67 (4H, m, H-2",6",3'",5'"); 7.41 (2H, d, ^3J = 8.5, H-3",5")	6.46	—
12b	3014, 1645 (C=O), 1597, 1569, 1513, 1222, 1169 (C–O), 1144, 1021, 830, 609	10.09*[2]	9.22 (1H, s, H-3); 8.13 (2H, d, ^3J = 8.5, H-2'",6'"); 7.77 (2H, d, ^3J = 8.5, H-2",6"); 7.73 (1H, s, H-3'); 7.09 (2H, d, ^3J = 8.5, H-3'",5'"); 7.01 (2H, d, ^3J = 8.5, H-3",5")	5.76	3.87 (3H, s, 4'"-OCH_3); 3.80 (3H, s, 4"-OCH_3)
12c	2958, 1656 (C=O), 1586, 1216, 1155, 1091, 833	10.07*[2]	9.20 (1H, s, H-3); 8.16 (2H, d, ^3J = 8.5, H-2'",6'"); 7.81 (2H, d, ^3J = 8.5, H-2",6"); 7.79 (1H, s, H-3'); 7.66 (2H, d, ^3J = 8.5, H-3'",5'"); 7.53 (2H, d, ^3J = 8.5, H-3",5")	5.78	4.00 (3H, s, NCH_3)
12d	3003, 1653 (C=O), 1583, 1144, 1004, 828, 811	10.08*[2]	9.20 (1H, s, H-3); 8.08 (2H, d, ^3J = 8.5, H-2'",6'"); 7.81 (2H, d, ^3J = 8.5, H-2",6"); 7.79 (1H, s, H-3'); 7.74 (2H, d, ^3J = 8.5, H-3'",5'"); 7.66 (2H, d, ^3J = 8.5, H-3",5")	5.78	4.00 (3H, s, NCH_3)

* Signals of the benzene rings protons: 2'-Ar are designated H-2"-6", 4'-Ar are designated H-2'"-6'".

*[2] 1H, s, H-5.

Table 3. Spectral Characteristics of Azolo[*a*]pyridinium Bromides **5**, **8**, **9**, **10**, and **14**

Compound	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm (*J*, Hz)		
		Signals of pyridine ring	Aromatic protons*	Other signals
5a	3031, 1527, 1491, 892, 775, 741, 699	9.41 (1H, d, ^4J = 1.5, H-5), 8.24 (1H, d, ^4J = 1.5, H-7)	8.80 (1H, s, H-3); 7.89 (2H, d, ^3J = 7.5, H-2',6'); 7.66 (2H, m, H-2",6"); 7.61 (3H, m, H-3"–5"); 7.57 (2H, t, ^3J = 7.5, H-3',5'); 7.52 (1H, m, H-4')	3.35 (3H, s, NCH_3)
5b	3092, 1611, 1513, 1250 (C–O), 1175, 1035, 816	7.76 (1H, s, H-5), 7.30 (1H, s, H-7)	8.28 (1H, s, H-3); 7.52 (2H, d, ^3J = 8.5, H-2',6'); 7.46 (2H, d, ^3J = 8.5, H-2",6"); 6.99 (4H, d, ^3J = 8.5, H-3',5',3",5")	3.78 (3H, s, 4"'-OCH_3); 3.76 (3H, s, 4"-OCH_3); 3.43 (3H, s, NCH_3)
5c	3070, 1527, 1494, 1094, 828	9.43 (1H, s, H-5), 8.28 (1H, s, H-7)	8.79 (1H, s, H-3); 7.93 (2H, d, ^3J = 8.0, H-2',6'); 7.64 (2H, d, ^3J = 8.0, H-2",6"); 7.56 (2H, d, ^3J = 8.0, H-3',5'); 7.51 (2H, d, ^3J = 8.0, H-3",5")	3.37 (3H, s, NCH_3)
8a	3031, 1611, 1491, 1449, 1412, 1130, 766, 705	9.36 (1H, s, H-5), 8.32 (1H, s, H-7)	8.68 (1H, s, H-2); 8.09 (2H, d, ^3J = 8.0, H-2',6'); 7.91 (2H, d, ^3J = 8.0, H-2",6"); 7.68 (3H, m, H-3"–5"); 7.64 (2H, t, ^3J = 8.0, H-3',5'); 7.58 (1H, m, H-4')	2.90 (3H, s, 3-CH_3)
8b	3036, 2930, 1605, 1508, 1435, 1248 (C–O), 1172, 1021, 836	9.26 (1H, s, H-5), 8.32 (1H, s, H-7)	8.59 (1H, s, H-2); 8.06 (2H, d, ^3J = 8.5, H-2',6'); 7.87 (2H, d, ^3J = 8.5, H-2",6"); 7.25 (2H, d, ^3J = 8.5, H-3",5"); 7.19 (2H, d, ^3J = 8.5, H-3',5')	3.89 (3H, s, 4"'-OCH_3); 3.87 (3H, s, 4"-OCH_3)
8c	3019, 1597, 1491, 1432, 1393, 1091, 1012, 825, 813	9.40 (1H, s, H-5), 8.35 (1H, s, H-7)	8.70 (1H, s, H-2); 8.14 (2H, d, ^3J = 8.0, H-2',6'); 7.94 (2H, d, ^3J = 8.0, H-2",6"); 7.78 (2H, d, ^3J = 8.0, H-3",5"); 7.71 (2H, d, ^3J = 8.0, H-3',5')	2.90 (3H, s, 3-CH_3)
8d	3025, 1488, 1432, 1390, 1077, 1007, 825, 811	9.39 (1H, s, H-5), 8.35 (1H, s, H-7)	8.69 (1H, s, H-2); 8.06 (2H, d, ^3J = 8.0, H-2',6'); 7.91 (2H, m, H-2",6"); 7.85 (4H, m, H-3',5',3",5")	2.90 (3H, s, 3-CH_3)
9a	3047, 2986, 1448, 1448, 1427, 783, 760, 708, 685	10.33 (1H, s, H-1), 8.88 (1H, s, H-3)	9.24 (1H, d, ^3J = 8.0, H-9); 8.51 (1H, d, ^3J = 8.0, H-6); 8.17 (2H, d, ^3J = 8.0, H-2',6'); 7.98 (H-7,8,2",6"); 7.73 (3H, m, H-3"–5"); 7.68 (2H, t, ^3J = 8.0, H-3',5'); 7.61 (1H, m, H-4')	—
9b	3008, 2986, 1597, 1494, 1471, 1438, 1396, 1091, 1012, 839, 769	10.35 (1H, s, H-1), 8.91 (1H, s, H-3)	9.19 (1H, d, ^3J = 8.0, H-9); 8.50 (1H, d, ^3J = 8.0, H-6); 8.21 (2H, d, ^3J = 8.0, H-2',6'); 7.98 (4H, m, H-7,8,2",6"); 7.81 (2H, d, ^3J = 8.0, H-3",5"); 7.75 (2H, d, ^3J = 8.0, H-3',5')	—
10	3058, 2778, 1619, 1569, 1550, 1452, 761, 691	9.94 (1H, s, H-5), 8.68 (1H, s, H-7)	8.07 (2H, d, ^3J = 8.0, H-2',6'); 7.88 (2H, d, ^3J = 8.0, H-2",6"); 7.74 (2H, d, ^3J = 8.0, H-2"',6"'); 7.68 (3H, m, H-3"–5"); 7.60 (3H, m, H-3'–5'); 7.50 (2H, t, ^3J = 8.0, H-3"',5"'); 7.24 (1H, t, ^3J = 8.0, H-4"')	11.72 (1H, s, NH)
14a	3031, 2958, 1547, 1499, 1295, 769, 705	9.53 (1H, s, H-5), 8.40 (1H, s, H-7)	9.92 (1H, s, H-3); 7.91 (2H, d, ^3J = 8.0, H-2',6'); 7.71 (2H, m, H-2",6"); 7.63 (3H, m, H-3"–5"); 7.58 (2H, t, ^3J = 8.0, H-3',5'); 7.52 (1H, m, H-4')	3.68 (3H, s, NCH_3)
14b	3008, 2840, 1608, 1513, 1295, 1259 (C–O), 1180, 1029, 845, 831	9.35 (1H, s, H-5), 8.34 (1H, s, H-7)	9.81 (1H, s, H-3); 7.88 (2H, d, ^3J = 8.5, H-2',6'); 7.65 (2H, d, ^3J = 8.5, H-2",6"); 7.20 (2H, d, ^3J = 8.5, H-3",5"); 7.15 (2H, d, ^3J = 8.5, H-3',5')	3.88 (3H, s, 4"'-OCH_3); 3.85 (3H, s, 4"-OCH_3); 3.73 (3H, s, NCH_3)
14c	3058, 1546, 1491, 1088, 1013, 825	9.49 (1H, s, H-5), 8.44 (1H, s, H-7)	9.85 (1H, s, H-3); 7.96 (2H, d, ^3J = 8.0, H-2',6'); 7.72 (4H, m, H-2",3",5",6"); 7.67 (2H, d, ^3J = 8.0, H-3',5')	3.73 (3H, s, NCH_3)
14d	3058, 1550, 1488, 1292, 1080, 1010, 819	9.49 (1H, s, H-5), 8.44 (1H, s, H-7)	9.84 (1H, s, H-3); 7.86 (4H, m, H-2',6',2",6"); 7.80 (2H, d, ^3J = 8.0, H-3",5"); 7.67 (2H, d, ^3J = 8.0, H-3',5')	3.72 (3H, s, NCH_3)

* Signals of the protons of the benzene rings: 6-Ar (for **5**, **8**, **10**, and **14**) and 2-Ar (for **9**) are designated H-2'-6'; 8-Ar (for **5**, **8**, **10**, and **14**) and 4-Ar (for **9**) are designated H-2"-6".

From the interaction of triazolium salts of type **12** with bases (Et_3N or 1-alkyl-1H-1,2,4-triazole) two different ylides may be formed, cyclization of which leads to two isomeric triazolopyridines, **14** and/or **15**. According to NMR and mass chromatography of the raw reaction products, only one final product was formed. The choice from the alternative structures was decided on the basis of experiments with HMQC, HMBC, and NOESY two-dimensional correlation spectroscopy using compound **14a** as an example. The coordinates of the cross-peaks found in the two-dimensional spectra are given in Table 3, while the Figure 1 shows the assignments of the signals and the NOESY and HMBC correlations which served as bases for the assignments. In the spectrum of compound **14a** there are three singlets of aromatic protons bonded to the heterocyclic nucleus of the molecule. The presence of a NOE correlation of the signal at 8.40 ppm with the signals of the *ortho* protons of both phenyl substituents shows that this proton is between the phenyl nuclei. The other singlet with no correlation with the phenyl protons is found at 9.92 ppm. This indicates that it is far from the phenyls which gives its correct assignment as the proton of the thiazole ring.

Thus the signal at 9.55 ppm is of the proton of the pyridine ring, α to the nitrogen atom. The presence of an HMBC correlation of the signal of the protons of the methyl group (3.68 ppm) with the signal of the quaternary C-8a at 141.4 ppm and the NOE correlation with the *ortho* protons of the phenyl substituent shows unambiguously that the methyl group is located on N-1.

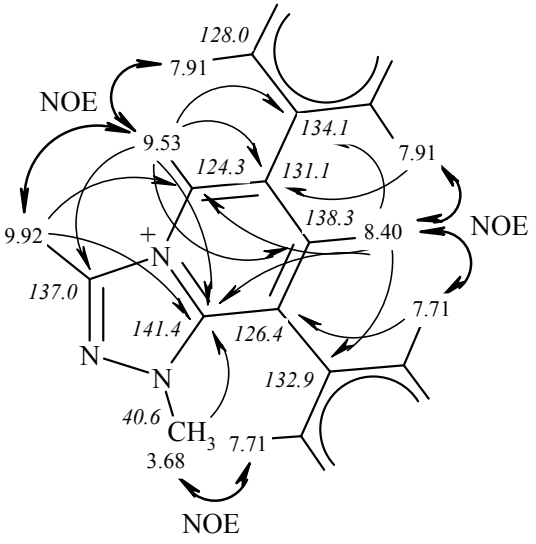


Fig. 1. Structurally significant HMBC and NOESY correlations for compound **14a**.

TABLE 4. ^{1}H-^{1}H and ^{1}H-^{13}C Correlations for Compound **14a**

^{1}H signal, δ, ppm	Positions of the cross-peaks in the ^{13}C measurements, δ, ppm		NOESY, δ, ppm
	HMQC	HMBC	
9.92	136.9	141.4, 124.3	9.53
9.53	124.3	141.4, 138.8, 137.0, 134.1, 131.1, 126.4	9.92, 7.91
8.41	138.3	141.4, 134.1, 132.9, 124.3	7.91, 7.71
7.92	128.0	130.7, 130.2, 128.0	9.53, 8.40, 7.58
7.71	130.7	132.9, 130.7, 129.4, 128.0, 126.4	8.40, 7.63, 3.68
7.63	129.4	132.9, 130.7, 129.4	7.71
7.58	130.2	134.1, 130.2, 128.0	7.92, 7.53
7.53	130.7	130.2, 128.0	7.58
3.68	40.6	141.4	7.71

Summing up the results of the reactions of derivatives of γ-bromodypnone with azoles, one can conclude that the rate of formation of the quaternary salts of the azoles is determined by the basicity of the azole and decreases in the series: 1-alkyl-1H-imidazoles > 1-alkyl-1H-benzimidazoles > 1-alkyl-1H-1,2,4-triazoles > 5-chloro-1-methyl-1H-imidazole > 4-methyl-1,3-thiazole > 1,3-benzothiazole > N-phenyl-1,3,4-thiadiazole-2-amine. The influence of the structure of the azole and the nature of the substituents in the benzene rings of the dypnone unit on the rate of cyclization of the quaternary salts is nonexistent, but results in the lower stability of the intermediate hydroxy derivatives of dihydroazolo[*a*]pyridines with increasing acceptor properties of the substituents on the pyridine ring [6].

EXPERIMENTAL

IR spectra (KBr tablets) were recorded on a Perkin-Elmer Spectrum BX instrument. ^{1}H NMR spectra were recorded in DMSO-d_6 with TMS as internal standard on a Bruker AVANCE DRX-500 (500 MHz) instrument. Two-dimensional correlation experiments were carried out with Varian Mercury 400 (^{1}H and ^{13}C, 400 and 100 MHz respectively), with TMS as internal standard, chemical shifts on the δ scale. Control of the purity of the compounds synthesized was by TLC on Silufol UV-254 plates and HPLC mass-spectroscopic method with an Agilent 1100 series instrument with an Agilent LC/MSD SL selective detector (samples were introduced in a CF_3CO_2H matrix, EI ionization).

(*Z*)-4-Bromo-1,3-diphenyl-2-buten-1-one **3a** was prepared by method [7], (*Z*)-1,3-diaryl-4-bromo-2-buten-1-ones **3b-d** were made by method [8].

5-Chloro-1-methyl-1H-imidazole, 4-methyl-1,3-thiazole, 1,3-benzothiazole, N-phenyl-1,3,4-thiadiazole-2-amine, and 1-methyl-1H-1,2,4-triazole were commercial products of the "Enamine" company.

(*Z*)-3-[2,4-diaryl-4-oxo-2-butenyl]-5-chloro-1-methyl-1H-imidazol-3-ium Bromides 4a-c. 5-Chloro-1-methyl-1H-imidazole (0.41 g, 3.55 mmol) was added to a solution of γ-bromodypnone **3** (1.07 g, 3.55 mmol) in benzene (30 ml). The mixture was kept for 1-2 d at room temperature. The precipitate was filtered off, washed with acetone, and recrystallized from nitromethane.

6,8-Diaryl-2-chloro-1-methyl-1H-imidazo[1,2-*a*]pyridine-4-ium Bromides 5a-c. A mixture of salt **4a-c** (1.15 mmol) and morpholine (2 ml) in acetone (10 ml) was heated for 2h. After cooling, the precipitate was filtered off and washed with acetone.

(*Z*)-3-[2,4-Diaryl-4-oxo-2-butenyl]-4-methyl-1,3-thiazol-3-ium Bromides 6a-d and (*Z*)-3-[2,4-Diaryl-4-oxo-2-butenyl]-1,3-benzothiazol-3-ium Bromides 7a,b were prepared by the method used to synthesize products **4a-c**. Reaction time 2-3 d.

6,8-Diaryl-3-methyl[1,3]thiazolo[3,2-*a*]pyridine-4-ium Bromides 8a-d and 2,4-Diarylpyrido-[2,1-*b*][1,3]benzothiazol-10-ium Bromides 9a,b. A mixture of salts **6a-d** or **7a,b** (1.15 mmol) and triethylamine (2 ml) in acetone (10 ml) was heated for 2 h. After cooling, the precipitate was filtered off and washed with acetone.

2-Anilino-6,8-diphenyl[1,3,4]thiadiazolo[3,2-*a*]pyridin-4-ium Bromide (10). N-phenyl-1,3,4-thiadiazole-2-amine (0.63 g, 3.55 mmol) was added to a solution of γ-bromodypnone **3a** (1.07 g, 3.55 mmol) in benzene (30 ml). The mixture was kept for 4 d at room temperature. The precipitate formed was filtered off and washed with acetone. Triethylamine (2 ml) was added to a suspension of the solid substance in acetone (15 ml) and the mixture was heated for 2 h. After cooling, the precipitate was filtered off and washed with acetone.

(*Z*)-4-[2,4-diaryl-4-oxo-2-butenyl]-1-methyl-1H-1,2,4-triazol-4-ium Bromides 12b-d were prepared by the method used for the synthesis of products **4a-c**. Reaction time 24 h.

1-Methyl-6,8-diphenyl-1H-[1,2,4]triazolo[4,3-*a*]pyridin-4-ium Bromide (14a). 1-Methyl-1H-1,2,4-triazole (0.3 g, 3.55 mmol) was added to a solution of γ-bromodypnone **3a** (1.07 g, 3.55 mmol) in benzene (30 ml). The mixture was kept at room temperature for 24 h, the precipitate was filtered off and washed with

acetone. Triethylamine (2 ml) was added to the solid substance, a mixture of **12a** + **13a**, in acetone (15 ml), and the mixture was heated for 2 h. After cooling, the precipitate was filtered off and washed with acetone. ^{13}C NMR spectrum, δ, ppm: 141.4 (C-8a), 138.2 (C-7), 137.0 (C-3), 134.1 (C-1'), 132.9 (C-1"), 131.1 (C-6), 130.7 (C-4',2",6"), 130.2 (C-3',5'), 129.4 (C-3",5"), 128.0 (C-4"), 126.4 (C-8), 124.3 (C-5), 40.6 (CH_3).

6,8-Diaryl-1-methyl-1H-[1,2,4]triazolo[4,3-*a*]pyridin-4-ium Bromides 14b-d were made by the method used to synthesize **8a-d**, using the salts **12b-d**.

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