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SYNTHESIS OF AZOLO[*a*]PYRIDINES FROM 5-(BROMOMETHYL)HEPT-4-EN-3-ONE AND 5-BROMOPENT-3-EN-2-ONE DERIVATIVES

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Alkyl derivatives of 1H-imidazo[1,2-a]pyridin-4-ium, 5H-pyrido[1,2-a]benzimidazol-10-ium, 1H-[1,2,4]-triazolo[4,3-a]pyridin-4-ium, and 3-methylthiazolo[3,2-a]pyridin-4-ium bromides were obtained in two stages from (4Z)-5-(bromomethyl)-2,2,6,6-tetramethylhept-4-en-3-one, 5-bromo-4-methylpent-3-en-2-one, or (3E)-5-bromopent-3-en-2-one by alkylation of 1-alkyl-1H-imidazoles, 1-alkyl-1H-benzimidazoles, 1-methyl-1H-1,2,4-triazole, and 4-methylthiazole and subsequent cyclization of the quaternary azolium salts in the presence of bases.

Keywords: 5-(bromomethyl)hept-4-en-3-one, 5-bromopent-3-en-2-one, imidazo[1,2-*a*]pyridine, pyrido-[1,2-*a*]benzimidazole, thiazolo[3,2-*a*]pyridine, [1,2,4]triazolo[4,3-*a*]pyridine.

γ-Halo-substituted unsaturated ketones are highly reactive compounds and are the synthetic equivalents of 1,4-dielectrophilic synthons. On account of their relatively poor availability they were used predominantly for the production of pyrroles in reactions with primary amines [1-5]. We recently found convenient methods for the synthesis of the azolo[*a*]pyridine system derivatives on the basis of (2*Z*)-4-bromo-1,3-diphenyl-2-buten-1-one (γ-bromodypnone) and its derivatives [6-8]. While continuing investigations in this direction we turned to γ-halo ketones of the aliphatic series.

The structural features of (4*Z*)-5-(bromomethyl)-2,2,6,6-tetramethylhept-4-en-3-one (**1**) make it possible to regard it as an analog of γ-bromodypnone; there are nonenolizing groups at the carbonyl group and at the C=C double bond, and their volume leads to configurational stability for the molecule in the form of the (*Z)*-isomer [9]. Properties of this compound have hardly been studied at all, and only the formation of a quaternary triphenylphosphonium salt [9] and intramolecular cyclization to 2,4-di-*tert*-butylfuran [10] are known.

We have established that compound **1**, like γ-bromodypnone, forms quaternary azolium salts **2** with high yields when a mixture of the bromo ketone **1** and azole is kept in benzene at room temperature for several days (Scheme 1), as described in [7, 8] (Table 1). Difficulties in the isolation of the alkylation products **2b**,**e** in pure form only arose in the case of reactions with 1-benzyl-1*H*-imidazole and 1-methyl-1*H*-1,2,4-triazole. When the reaction is conducted under standard conditions (benzene, 25°, 2-3 days) the reaction mixture still contains the initial azole as impurity (15-20%), which subsequently initiates cyclization of the salts **2b**,**e** during

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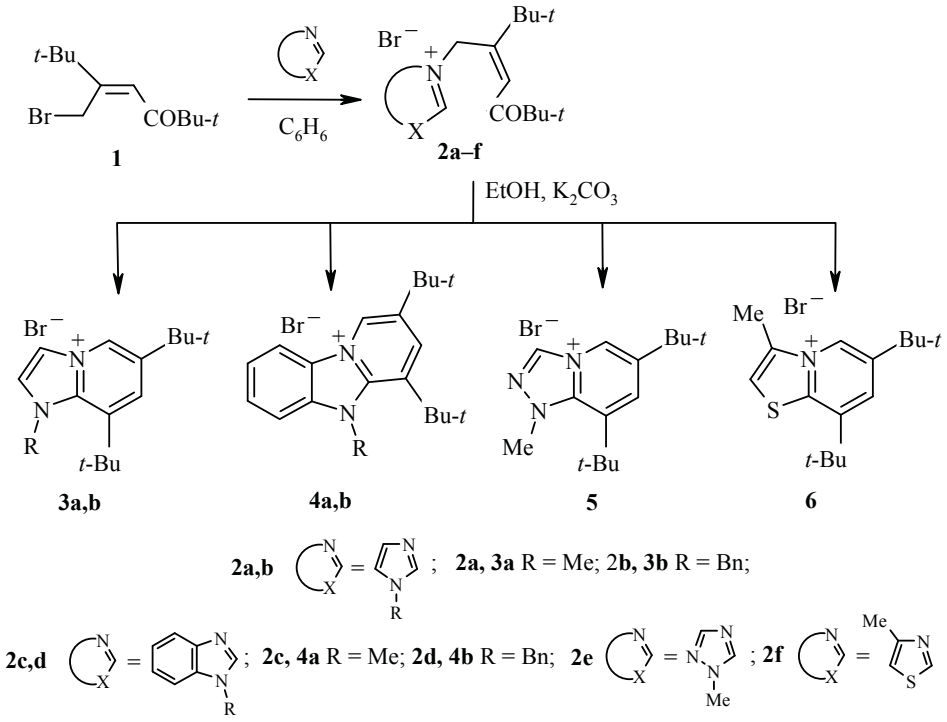
attempts of their purification by recrystallization. Increase of the reaction time or carrying out the reaction with heating also leads to appearance of cyclization products in the reaction mixture.

Scheme 1

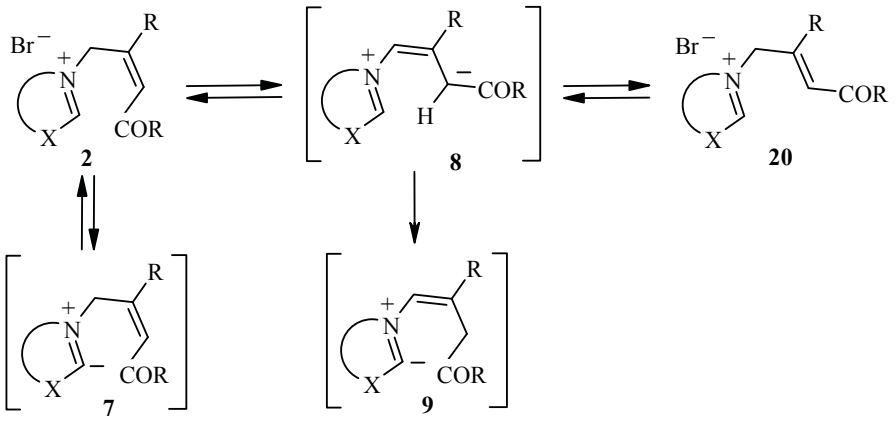


When the salts **2a-f** are heated in ethanol in the presence of K_2CO_3 intramolecular cyclization occurs with formation of 1-alkyl-6,8-di-*tert*-butyl-1*H*-imidazo[1,2-*a*]pyridin-4-ium **3a**,**b**, 5-alkyl-2,4-di-*tert*-butyl-5*H*-pyrido[1,2-*a*]benzimidazol-10-ium **4a**,**b**, 6,8-di-*tert*-butyl-1-methyl-1*H*-[1,2,4]triazolo[4,3-*a*]pyridin-4-ium (**5**), and 6,8-di-*tert*-butyl-3-methylthiazolo[3,2-*a*]pyridin-4-ium (**6**) bromides respectively. This method was the best one for production of the quaternary salts **3-6**. The use of other bases (Et_3N, morpholine, MeONa) as initiators of cyclization either reduces the yield of the desired products **5** and **6** or leads to the formation of mixtures consisting of the starting salt **2**, the desired products **3** and **4**, and hydroxy derivatives of azolo[*a*]pyridine. The structure of compounds **2a-f** and their cyclization products **3-6** was established by the data from the IR and ^{1}H NMR spectra, in which a series of analogies with the spectra of the quaternary azolium salts of γ-bromodypnone and the corresponding diarylazolo[*a*]pyridines bromides are observed [7, 8] (Table 2).

Earlier in the case of quaternary azolium salts of γ-bromodypnone it was shown that the structure of undehydrated products from their cyclization is determined by the reaction mechanism, i.e., by the structure of the ylide generated during the action of the bases [7, 8]. One of the deciding factors here was the nature of the base; the ylide **7** is formed preferentially in the presence of a relatively weak base (Et_3N) (Scheme 2), while the ylides **8** and **9** are formed in the presence of stronger bases (morpholine, MeONa).

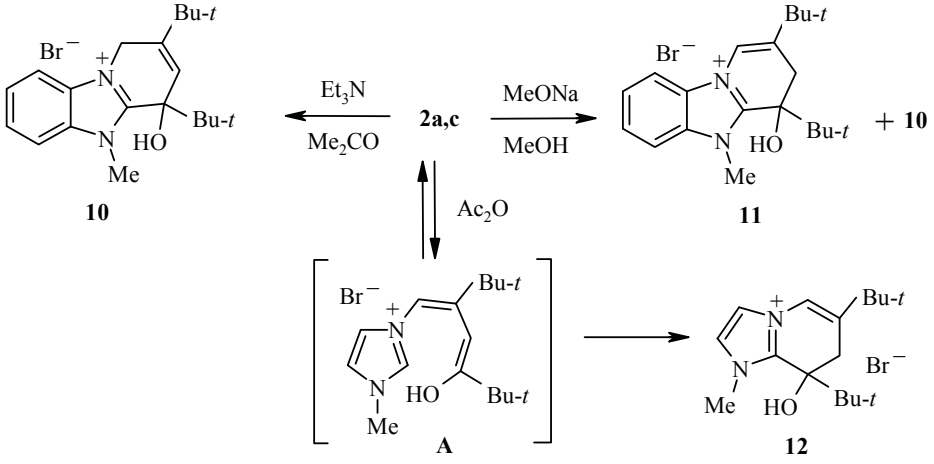
The same relationships are observed for the quaternary imidazolium and benzimidazolium salts of the bromoketone **1**. Thus, pure 2,4-di-*tert*-butyl-4-hydroxy-5-methyl-4,5-dihydro-1*H*-pyrido[1,2-*a*]benzimidazol-10-ium bromide (**10**) is formed when the salt **2c** is heated with Et_3N in acetone, while a mixture of compounds **10**+**11** (1:2), the main component of which 2,4-di-*tert*-butyl-4-hydroxy-5-methyl-4,5-dihydro-3*H*-pyrido[1,2-*a*]-benzimidazol-10-ium bromide is the product from cyclization of an ylide of type **9**, is formed in the presence of MeONa (MeOH, 0-5°C). The isomers **10** and **11** are easily identified by the data from the ^{1}H NMR spectra.

Scheme 2



Thus, in the spectrum of compound **10** the signals of the methylene group 1-CH_2 are observed in the form of an AB spin system (5.30 and 4.98 ppm) with ^2J = 18.0 Hz, and the signal of H-3 is at 5.83 ppm. For compound **11,** the signal of the 3-CH_2 group is in the region of 3.07 ppm in the form of a narrow multiplet and H-1 is at 7.35 ppm. Like its 2,4-diaryl-substituted analogs [7] 4-hydroxy-3*H*-pyridobenzimidazolium bromide **11** is unstable and loses a molecule of water when heated or during chromatographic separation of the mixture. When heated in ethanol in the presence of K_2CO_3 the hydroxy derivatives **10** and **11** are easily transformed into the corresponding pyridobenzimidazolium bromide **4a**.

Scheme 3



According to previously obtained data [7], 1-alkyl-8-hydroxy-7,8-dihydro-1*H*-imidazo[1,2-*a*]pyridin-4-ium salts are distinguished by even lower stability to heating in the presence of bases. We tried a new method for cyclization of azolium salts by heating them in Ac_2O, but it only proved moderately suitable for imidazole derivatives. Under these conditions the salt **2a** undergoes cyclization to 6,8-di-*tert*-butyl-8-hydroxy-1-methyl-7,8-dihydro-1*H*-imidazo[1,2-*a*]pyridin-4-ium bromide (**12**). It was not possible to isolate compound **12** in the pure form, and it was only characterized by the difference in ^{1}H NMR spectrum. Thus, the spectrum contained signals for the methine proton H-5 in the aromatic protons resonance region (6.70 ppm) and for the methylene group in the form of an AB system in the upfield region with $\delta < 3.0$ ppm (^2J = 15.0 Hz).

TABLE 1. Physicochemical Characteristics of the Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %				Mp*, °C	Yield, %
		C	H	Br	N		
2a	$C_{16}H_{27}BrN_2O$	55.90 / 55.98	8.05 / 7.93	23.22 / 23.28	8.18 / 8.16	132-134	86
2c	$C_{20}H_{29}BrN_2O$	60.95 / 61.07	7.40 / 7.43	20.35 / 20.31	7.10 / 7.12	188-190	77
2d	$C_{26}H_{33}BrN_2O$	66.48 / 66.52	7.18 / 7.09	17.00 / 17.02	6.00 / 5.97	210-212	73
2f	$C_{16}H_{26}BrNOS$	53.28 / 53.33	7.21 / 7.27	22.15 / 22.17	3.91 / 3.89	192-194	74
3a	$C_{16}H_{25}BrN_2$	58.90 / 59.08	7.81 / 7.75	24.55 / 24.56	8.60 / 8.61	250-252	90*[2]
3b	$C_{22}H_{29}BrN_2$	65.80 / 65.83	7.20 / 7.28	19.95 / 19.91	7.00 / 6.98	210-212	85
4a	$C_{20}H_{27}BrN_2$	63.94 / 64.00	7.21 / 7.25	21.31 / 21.29	7.48 / 7.46	315-317	87
4b	$C_{26}H_{31}BrN_2$	69.02 / 69.17	6.95 / 6.92	17.73 / 17.70	6.23 / 6.21	294-296	84
5	$C_{15}H_{24}BrN_3$	55.15 / 55.22	7.38 / 7.41	24.52 / 24.49	12.90 / 12.88	178-180	48
6	$C_{16}H_{24}BrNS$	56.10 / 56.13	7.08 / 7.07	23.36 / 23.34	4.10 / 4.09	202-204	86
10	$C_{20}H_{29}BrN_2O$	60.95 / 61.07	7.40 / 7.43	20.33 / 20.31	7.14 / 7.12	248-250	89*[2]
14a	$C_{10}H_{13}BrN_2$	49.75 / 49.81	5.40 / 5.43	33.10 / 33.14	11.65 / 11.62	216-218	63
14b	$C_{16}H_{17}BrN_2$	60.61 / 60.58	5.46 / 5.40	25.15 / 25.19	8.82 / 8.83	204-206	57
15	$C_{14}H_{15}BrN_2$	57.70 / 57.75	5.21 / 5.19	27.45 / 27.44	9.60 / 9.62	310-312	51
16	$C_9H_{12}BrN_3$	44.60 / 44.65	4.97 / 5.00	33.02 / 33.00	17.33 / 17.36	262-264	48
18	$C_9H_{11}BrN_2$	47.65 / 47.60	5.00 / 4.88	35.17 / 35.18	12.35 / 12.34	218-220	55
19	$C_8H_{10}BrN_3$	42.10 / 42.13	4.39 / 4.42	35.08 / 35.03	18.40 / 18.42	262-264	41

*Solvents: MeCN (compounds **2a**,**c**,**d**,**f**), MeOH (compounds **3a**,**b**, **4a**,**b**), $MeNO_2$ (compounds **5**, **6**), EtOH (compounds **10**, **14a**,**b**, **15**, **16**, **18**, **19**).
*[2]Yield by method A.

The mechanism of cyclization under these conditions probably includes a stage of the dienol **A** formation, and it is this that determines the structure of the reaction product as the 7,8-dihydro derivative. Heating the quaternary benzimidazolium, triazolium, and thiazolium salts **2c**,**e**,**f** in Ac_2O does not lead to cyclization. Like the salts **10** and **11**, compound **12** is easily transformed into the corresponding imidazo-pyridinium bromide **3a** when heated (EtOH, K_2CO_3).

The possibility of formation of diazolium ylides with structures **8** and **9** by the action of strong bases (Scheme 2) obviously removes restrictions of the γ-halo-substituted unsaturated ketones configuration used for synthesis of azolo[*a*]pyridines. 5-Bromo-4-methylpent-3-en-2-one (**13**) (Scheme 4) represents an equilibrium

TABLE 2. The Spectral Characteristics of the Synthesized Compounds

Compound	^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz)		IR spectrum, ν, cm^{-1}
	Protons at C-sp^2	Protons at C-sp^3 and other groups	
1	2	3	4
2a	9.01 (1H, s, H-2); 7.72 (1H, s, H-4); 7.67 (1H, s, H-5); 6.91 (1H, s, H-3')	4.97 (2H, s, 3-CH_2); 3.88 (3H, s, 1-CH_3); 1.12 (9H, s, 4'-C$(CH_3)_3$); 1.10 (9H, s, 2'-C$(CH_3)_3$)	3092, 2958, 1684 (C=O), 1614, 1474, 1158, 1091, 881, 769, 612
2b*	9.30 (1H, s, H-2); 7.83 (1H, s, H-4); 7.69 (1H, s, H-5); 7.39 (5H, m, H-2",3",4",5",6"); 6.89 (1H, s, H-3')	5.48 (2H, s, 1-CH_2); 5.02 (2H, s, 3-CH_2); 1.11 (9H, s, 4'-C$(CH_3)_3$); 1.08 (9H, s, 2'-C$(CH_3)_3$)	3064, 2964, 2874, 1681 (C=O), 1614, 1555, 1477, 1457, 1368, 1155, 1091, 713
2c	9.45 (1H, s, H-2); 8.19 (1H, d, ^3J = 8.0, H-4); 8.03 (1H, d, ^3J = 8.0, H-7); 7.73 (2H, m, H-5,6); 7.02 (1H, s, H-3')	5.14 (2H, s, 3-CH_2); 4.09 (3H, s, 1-CH_3); 1.15 (9H, s, 4'-C$(CH_3)_3$); 1.08 (9H, s, 2'-C$(CH_3)_3$)	2964, 1681 (C=O), 1611, 1572, 1474, 1454, 1211, 1091, 1004, 741
2d	9.88 (1H, s, H-2); 8.20 (1H, d, ^3J = 8.0, H-4); 8.01 (1H, d, ^3J = 8.0, H-7); 7.74 (1H, t, ^3J = 8.0, H-6); 7.69 (1H, t, ^3J = 8.0, H-5); 7.43 (2H, m, H-2",6"); 7.37 (3H, m, H-3",4",5"); 7.06 (1H, s, H-3')	5.84 (2H, s, 1-CH_2); 5.23 (2H, s, 3-CH_2); 1.23 (9H, s, 4'-C$(CH_3)_3$); 1.08 (9H, s, 2'-C$(CH_3)_3$)	2969, 1681 (C=O), 1617, 1561, 1443, 1368, 1194, 1091, 744, 702
2e*	10.09 (1H, s, H-4); 9.24 (1H, s, H-2); 6.92 (1H, s, H-3')	5.06 (2H, s, 3-CH_2); 4.11 (3H, s, 1-CH_3); 1.12 (18H, s, 2',4'-C$(CH_3)_3$)	—
2f	9.67 (1H, s, H-2); 8.08 (1H, s, H-5); 6.98 (1H, s, H-3')	5.06 (2H, s, 3-CH_2); 2.66 (3H, s, 4-CH_3); 1.16 (9H, s, 4'-C$(CH_3)_3$); 1.05 (9H, s, 2'-C$(CH_3)_3$)	3109, 2964, 1676 (C=O), 1603, 1580, 1477, 1368, 1323, 1208, 1091, 1007, 862
3a	8.82 (1H, s, H-5); 8.41 (1H, d, ^3J = 1.5, H-3); 8.18 (1H, d, ^3J = 1.5, H-2); 7.85 (1H, s, H-7)	4.28 (3H, s, 1-CH_3); 1.55 (9H, s, 6-C$(CH_3)_3$); 1.35 (9H, s, 8-C$(CH_3)_3$)	3048, 2964, 1505, 1365, 1298, 1239, 889, 797, 755
3b	8.92 (1H, s, H-5); 8.51 (1H, s, H-3); 8.03 (1H, s, H-2); 7.95 (1H, s, H-7); 7.39 (3H, m, H-3',4',5'); 7.07 (2H, d, ^3J = 7.5, H-2',6')	6.03 (2H, s, 1-CH_2); 1.53 (9H, s, 6-C$(CH_3)_3$); 1.41 (9H, s, 8-C$(CH_3)_3$)	3059, 2964, 2874, 1499, 1452, 1376, 1368, 1295, 1175, 881, 755, 733
4a	9.25 (1H, s, H-1); 8.88 (1H, d, ^3J = 8.0, H-9); 8.20 (1H, s, H-3); 8.12 (1H, d, ^3J = 8.0, H-6); 7.89 (1H, t, ^3J = 8.0, H-7); 7.75 (1H, t, ^3J = 8.0, H-8)	4.40 (3H, s, 5-CH_3); 1.65 (9H, s, 2-C$(CH_3)_3$); 1.46 (9H, s, 4-C$(CH_3)_3$)	2964, 1508, 1480, 1371, 764
4b	9.37 (1H, s, H-1); 8.96 (1H, m, H-9); 8.29 (1H, s, H-3); 7.72 (2H, m, H-7,8); 7.60 (1H, m, H-6); 7.30 (3H, m, H-3',3',5'); 7.11 (2H, d, ^3J = 6.0, H-2',6')	6.33 (2H, s, 5-CH_2); 1.61 (9H, s, 2-C$(CH_3)_3$); 1.52 (9H, s, 4-C$(CH_3)_3$)	3064, 2958, 2868, 1499, 1471, 1452, 1340, 1301, 1211, 752
5	9.86 (1H, s, H-3); 8.95 (1H, s, H-5); 8.00 (1H, s, H-7)	4.48 (3H, s, 1-CH_3); 1.58 (9H, s, 6-C$(CH_3)_3$); 1.39 (9H, s, 8-C$(CH_3)_3$)	3008, 1633 (C=N), 1538, 1457, 1295, 1197, 1007, 873, 814, 744, 733
6	8.70 (1H, s, H-5); 8.35 (1H, s, H-2); 8.21 (1H, s, H-7)	2.83 (3H, s, 3-CH_3); 1.59 (9H, s, 6-C$(CH_3)_3$) 1.48 (9H, s, 8-C$(CH_3)_3$)	3014, 2958, 1620 (C=N), 1421, 1368, 1290, 1242, 845, 727

TABLE 2 (continued)

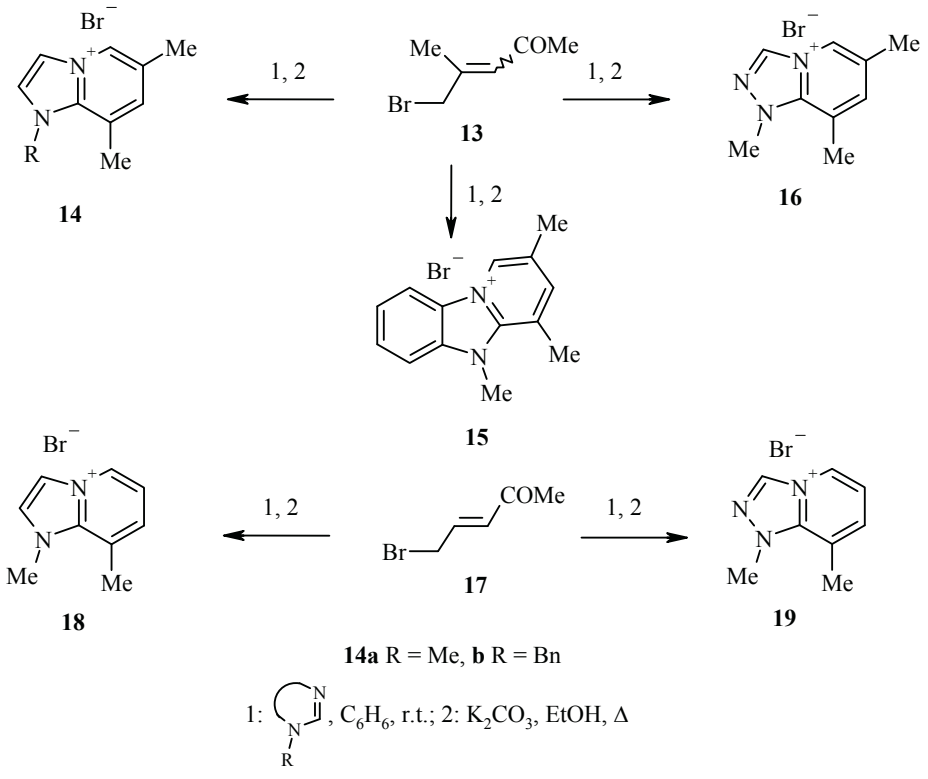
1	2	3	4
10	8.25 (1H, m, H-9); 8.04 (1H, m, H-6); 7.74 (2H, m, H-7,8); 5.83 (1H, s, H-3)	7.20 (1H, br. s, 4-OH); 5.30 (1H, d, ^2J = 18.0) and 4.89 (1H, d, ^2J = 18.0, 1-CH_2); 4.31 (3H, s, 5-CH_3); 1.24 (9H, s, 4-C(CH_3)$_3$); 0.98 (9H, s, 2-C(CH_3)$_3$)	3067 (OH), 2960, 1531, 1471, 1364, 1117 (C–O), 1001, 766
11*	8.40 (1H, m, H-9); 8.04 (1H, m, H-6); 7.74 (2H, m, H-7,8); 7.35 (1H, s, H-1)	7.20 (1H, br. s, 4-OH); 3.07 (2H, m, 3-CH_2); 1.24 (9H, s, 4-C(CH_3)$_3$); 1.05 (9H, s, 2-C(CH_3)$_3$)	—
12*	7.85 (1H, d, ^3J = 1.0, H-3); 7.76 (1H, d, ^3J = 1.0, H-2); 6.97 (1H, s, H-5)	4.06 (3H, s, 1-CH_3); 4.00 (br. s, 8-OH + H_2O); 2.92 (1H, d, ^2J = 15.0) and 2.83 (1H, d, ^2J = 15.0, 7-CH_2); 1.14 (9H, s, 8-C(CH_3)$_3$); 0.93 (9H, s, 6-C(CH_3)$_3$)	3227 (OH)
14a	8.63 (1H, s, H-5); 8.31 (1H, s, H-3); 8.17 (1H, s, H-2); 7.64 (1H, s, H-7)	4.26 (3H, s, 1-CH_3); 2.80 (3H, s, 6-CH_3); 2.35 (3H, s, 8-CH_3)	3062, 3002, 1526, 1459, 1311, 1103, 860, 742
14b	8.74 (1H, s, H-5); 8.45 (1H, s, H-3); 8.29 (1H, s, H-2); 7.68 (1H, s, H-7); 7.39 (2H, m, H-3',5'); 7.36 (1H, m, H-4'); 7.12 (2H, d, ^3J = 7.5, H-2',6')	5.93 (2H, s, 1-CH_2); 2.57 (3H, s, 6-CH_3); 2.38 (3H, s, 8-CH_3)	3053, 3001, 1632, 1515, 1452, 1415, 1281, 1198, 775, 736, 703
15	9.44 (1H, s, H-1); 8.62 (1H, d, ^3J = 8.0, H-9); 8.17 (1H, d, ^3J = 8.0, H-6); 8.00 (1H, s, H-3); 7.87 (1H, t, ^3J = 8.0, H-7); 7.72 (1H, t, ^3J = 8.0, H-8)	4.39 (3H, s, 5-CH_3); 2.93 (3H, s, 2-CH_3); 2.48 (3H, s, 4-CH_3)	3002, 1651, 1637, 1517, 1489, 1401, 1246, 833, 768, 703
16	9.77 (1H, s, H-3); 8.70 (1H, s, H-5); 7.87 (1H, s, H-7)	4.42 (3H, s, 1-CH_3); 2.81 (3H, s, 6-CH_3); 2.39 (3H, s, 8-CH_3)	3057, 2997, 1575, 1549, 1408, 1295, 867, 742, 696
18	8.82 (1H, d, ^3J = 4.0, H-5); 8.43 (1H, s, H-3); 8.23 (1H, s, H-2); 7.74 (1H, d, ^3J = 7.5, H-7); 7.41 (1H, m, H-6)	4.29 (3H, s, 1-CH_3); 2.85 (3H, s, 8-CH_3)	3071, 3030, 1634, 1519, 1457, 1418, 1399, 1306, 792, 741, 719
19	9.77 (1H, s, H-3); 8.84 (1H, d, ^3J = 4.0, H-5); 7.94 (1H, d, ^3J = 6.5, H-7); 7.51 (1H, m, H-6)	4.44 (3H, s, 1-CH_3); 2.85 (3H, s, 8-CH_3)	3008, 1634 (C=N), 1538, 1457, 1295, 1197, 1007, 873, 814, 744, 641

*The signals of the main component of the mixture are indicated: **2b** (82%), **2e** (80%), **11** (60%), **12** (78%).

mixture of the (*E)*- and (*Z)*-isomers (~56:44) [11]. From the ketone **13**, according to the scheme developed for the case of the bromo ketone **1**, high yields (48-63%) of 1-alkyl-6,8-dimethyl-1*H*-imidazo[1,2-*a*]pyridin-4-ium (**14a**,**b**), 2,4,5-trimethyl-5*H*-pyrido[1,2-*a*]benzimidazol-10-ium (**15**), and 1,6,8-trimethyl-1*H*-[1,2,4]triazolo[4,3-*a*] pyridin-4-ium (**16**) bromides were obtained. The transformation of (3*E*)-5-bromopent-3-en-2-one (**17**) into 1,8-dimethyl-1*H*-imidazo[1,2-*a*]pyridin-4-ium (**18**) and 1,8-dimethyl-1*H*-[1,2,4]triazolo[4,3-*a*]pyridin-4-ium (**19**) bromides was realized in the same way with high yields (41% and 55% respectively). The intermediate products from alkylation of the azoles by the ketones **13** and **17** were not isolated in the pure form since in addition to the quaternary salts, the reaction mixtures also contained the products from their further cyclization. The conclusion about the qualitative composition of the reaction mixtures was based on data from their ^{1}H NMR spectra and the pure cyclization products (Table 2). In our opinion the relatively high yields of compounds **14** and **15** and the fact that the products **18** and **19** are formed indicate that the mechanism of cyclization in these cases includes a stage with the formation of ylides of type **8** from salts with structure **20** ((*E)*-isomers) (Scheme 2).

It should be noted that the 1,8-dimethyl-1*H*-imidazo[1,2-*a*]pyridin-4-ium salt in the form of the iodide was described earlier [12, 13], but its method of synthesis involved alkylation of the corresponding 8-methyl-imidazo[1,2-*a*]pyridine. Thus, we have found a new method for the production of derivatives of the azolo[*a*]pyridine system alkyl-substituted in the pyridine part of the molecule by annelation of the four-carbon fragment to the azole.

Scheme 4



EXPERIMENTAL

The IR spectra were recorded using KBr pellets on a Perkin Elmer Spectrum BX instrument. The ^{1}H NMR spectra were recorded on a Bruker Avance DRX-500 instrument (500 MHz) with TMS as internal standard. The purity of the obtained compounds was monitored by HPLC mass spectrometry on an Agilent 1100

instrument with an Agilent LC/MSD SL selective detector (sample in a CF_3CO_2H matrix, EI ionization). Elemental analysis for CHNOS was conducted on a Vario Macro cube elemental analyzer, and elemental analysis for Br was done by the Schöniger flask method.

(4*Z*)-5-(Bromomethyl)-2,2,6,6-tetramethylhept-4-en-3-one (**1**) was obtained by the known method [10]. 5-Bromo-4-methylpent-3-en-2-one (**13**) (content 80%), obtained by the bromination of mesityl oxide [11], was used for the synthesis of products **14-16**. (3*E*)-5-Bromopent-3-en-2-one (**17**) (content 86%), obtained by acylation of 3-bromo-1-propene [14], was used for the synthesis of products **18** and **19**.

3-[(2*Z*)-2-*tert*-Butyl-5,5-dimethyl-4-oxohex-2-en-1-yl]-1-methyl-1*H*-imidazol-3-ium (2a), 1-Alkyl-3-[(2*Z*)-2-*tert*-butyl-5,5-dimethyl-4-oxohex-2-en-1-yl]-1*H*-benzimidazol-3-ium (2c,d), and 3-[(2*Z*)-2-*tert*-Butyl-5,5-dimethyl-4-oxohex-2-en-1-yl]-4-methyl-1,3-thiazol-3-ium (2f) Bromides (General Method). Diazole or benzimidazole (3.83 mmol) was added to a solution of bromoheptenone **1** (1.0 g, 3.83 mmol) in benzene (30 ml) . The mixture was kept at room temperature for 1-2 days. The precipitate was filtered off, washed with acetone, and recrystallized from MeCN.

6,8-Di-*tert*-butyl-1-methyl-1*H*-imidazo[1,2-*a*]pyridin-4-ium Bromide (3a). A. K_2CO_3 (0.62 g, 4.5 mmol) was added to a solution of the salt **2a** (1.03 g, 3.00 mmol) in ethanol (40 ml). The mixture was boiled for 30 min. The precipitate was filtered off, the solvent was evaporated, and hexane (30 ml) was added. The colorless precipitate was filtered off and washed with diethyl ether.

B. The salt **2a** (1.03 g, 3.00 mmol) was dissolved in Ac_2O (30 ml) and heated at 50°C for 30 min. The solvent was evaporated under vacuum, and an oily residue was obtained. It contained 78% of **6,8-di-*tert*-butyl-8-hydroxy-1-methyl-7,8-dihydro-1*H*-imidazo[1,2-*a*]pyridin-4-ium bromide** (**12**), 20% of the starting salt **2a**, and < 10% of imidazo[1,2-*a*]pyridinium bromide **3a**. The mixture was dissolved in ethanol (40 ml), and the reaction was then continued as in method A. Yield 0.79 g (81%).

1-Benzyl-6,8-di-*tert*-butyl-1*H*-imidazo[1,2-*a*]pyridin-4-ium Bromide (3b). 1-Benzyl-1*H*-imidazole (0.8 g, 3.83 mmol) was added to a solution of bromoheptenone **1** (1.0 g, 3.83 mmol) in benzene (30 ml). The mixture was kept at room temperature for two days. The precipitate was filtered off and washed with acetone. A mixture containing 82% of **1-benzyl-3-[(2*Z*)-2-*tert*-butyl-5,5-dimethyl-4-oxohex-2-en-1-yl]-1*H*-imidazol-3-ium bromide 2b** was obtained. The reaction was then continued according to method A for the synthesis of product **3a**.

5-Alkyl-2,4-di-*tert*-butyl-5*H*-pyrido[1,2-*a*]benzimidazol-10-ium (4a,b) and 6,8-Di-*tert*-butyl-3-methylthiazolo[3,2-*a*]pyridin-4-ium (6) Bromides (General Method). The compounds were obtained by method A for the synthesis of compound **3a**. The heating time was 45 min.

6,8-Di-*tert*-butyl-1-methyl-1*H*-[1,2,4]triazolo[4,3-*a*]pyridin-4-ium Bromide (5). 1-Methyl-1*H*-1,2,4-triazole (0.32 g, 3.83 mmol) was added to a solution of bromoheptanone **1** (1.0 g, 3.83 mmol) in benzene (30 ml). The mixture was kept at room temperature for four days. The solvent was evaporated, and a mixture containing 80% of **4-[(2*Z*)-2-*tert*-butyl-5,5-dimethyl-4-oxohex-2-en-1-yl]-1-methyl-1*H*-1,2,4-triazol-4-ium bromide (2e)** was obtained. The reaction was then continued according to method A for the synthesis of compound **3a**.

2,4-Di-*tert*-butyl-4-hydroxy-5-methyl-4,5-dihydro-1*H*-pyrido[1,2-*a*]benzimidazol-10-ium Bromide (10). A. A mixture of the benzimidazolium salt **2c** (1 g, 2.54 mmol) and Et_3N (4 ml) in acetone (25 ml) was heated for 45 min. After cooling, the precipitate was filtered off and washed with acetone.

B. Sodium (0.25 g, 11.0 mmol) was dissolved in MeOH (15 ml), and salt **2c** (0.45 g, 1.15 mmol) was added with stirring to the MeONa solution cooled to 0-5°C. The mixture was stirred for a further 1.5 h while the temperature was maintained at 5-10°C. The solvent was evaporated, water (20 ml) was added, and the product was extracted with chloroform. The combined extracts were dried over Na_2SO_4 (anh.), the solvent was evaporated, and a 2:1 mixture of **2,4-di-*tert*-butyl-4-hydroxy-5-methyl-4,5-dihydro-3*H*-pyrido[1,2-*a*]-benzimidazol-10-ium bromide (11)** and **2,4-di-*tert*-butyl-4-hydroxy-5-methyl-4,5-dihydro-1*H*-pyrido-[1,2-*a*]benzimidazol-10-ium bromide (10)** was obtained in the oily residue.

1-Alkyl-6,8-dimethyl-1*H*-imidazo[1,2-*a*]pyridin-4-ium Bromides 14a,b, 2,4,5-Trimethyl-5*H*-pyrido-[1,2-*a*]benzimidazol-10-ium Bromide (15), and 1,6,8-Trimethyl-1*H*-[1,2,4]triazolo[4,3-*a*]pyridin-4-ium Bromide (16) (General Method). 1-Alkyl-1*H*-imidazole, 1-methyl-1*H*-benzimidazole, or 1-methyl-1*H*-1,2,4-triazole (4.0 mmol) respectively was added to a solution of 80% 5-bromo-4-methylpent-3-en-2-one (**13)** (0.89 g, 4.0 mmol) in benzene (40 ml). The mixture was kept at room temperature for 1-2 days. The solvent was evaporated, the oily residue was dissolved in ethanol (30 ml), K_2CO_3 (0.62 g, 4.5 mmol) was added, and the mixture was boiled for 30 min. The precipitate was filtered off, the solvent was evaporated, and 30 ml of Et_2O was added. The colorless precipitate was filtered off and washed with Et_2O.

1,8-Dimethyl-1*H*-imidazo[1,2-*a*]pyridin-4-ium Bromide (18) and 1,8-dimethyl-1*H*-[1,2,4]triazolo-[4,3-*a*]pyridin-4-ium bromide (19) were obtained by the method used for the synthesis of compounds **14-16** from 86% (3*E*)-5-bromopent-3-en-2-one (**17)** (0.76 g, 4.00 mmol).

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