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INTERACTION OF (*Z*)-4-BROMO-1,3-DI(2-THIENYL)-2-BUTEN-1-ONE WITH AMINES, SYNTHESIS OF DI(2-THIENYL)AZOLO[*a*]PYRIDINES

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(Z)-4-Bromo-1,3-di(2-thienyl)-2-buten-1-one was obtained by the bromination of 1,3-di(2-thienyl)-2-buten-1-one by NBS in anhydrous CCl_4. The starting butanone was obtained by the condensation of 1-(2-thienyl)-1-ethanone by the action of $SOCl_2$. The reaction of (Z)-4-bromo-1,3-di(2-thienyl)-2-buten-1-one with tertiary amines such as Et_3N, pyridine, 1-alkyl-1,3-diazole, 1-alkylbenzimidazole, and 1-alkyl-1,2,4-triazole leads to quaternary salts. The azolium salts cyclize by the action of base to give di(2-thienyl)azolo[a]pyridinium derivatives. 3-Methyl-6,8-di(2-thienyl)[1,3]thiazolo[3,2-a]pyridin-4-ium and 2,4-di(2-thienyl)pyrido[2,1-b]benzothiazol-10-ium bromides were obtained by the same procedure but without separating the intermediate quaternary salts.

Keywords: 4-bromo-1,3-di(2-thienyl)-2-buten-1-one, imidazo[1,2-*a*]pyridine, pyrido[1,2-*a*]benzimidazole, pyrido[2,1-*b*]benzothiazole, [1,3]benzothiazolo[3,2-*a*]pyridine, [1,2,4]triazolo[4,3-*a*]pyridine.

The continued interest in the azolo[*a*]pyridine system is due to the discovery of compounds in this class with a high level of biological activity and a broad range of action mechanisms [1-3]. The introduction of additional heterocyclic fragments into this system may lead to the appearance of new and useful properties of such compounds. Two common methods have been reported for hetaryl-substituted azolo[*a*]pyridines: 1) Condensation of 2,3-dialkylazolium salts with heterocyclic α-diketones [4] and 2) Condensation of N-hetarylmethylpyridinium salt with isocyanates [5].

In recent work [6, 7], we found a convenient method for the synthesis of diarylazolo[*a*]pyridinium salts, which involves the base-initiated cyclization of quaternary [(*Z*)-2,4-diaryl-4-oxo-2-butenyl]azolium salts obtained by the alkylation of 1,3-diazoles unsubstituted at the C-2 position using derivatives of 4-bromo-1,3-diphenyl-2-buten-1-one (γ-bromodypnone). In the present work, (*Z*)-4-bromo-1,3-di(2-thienyl)-2-buten-1-one (**1**) was used for the synthesis of azolo[1,2-*a*]pyridinium derivatives.

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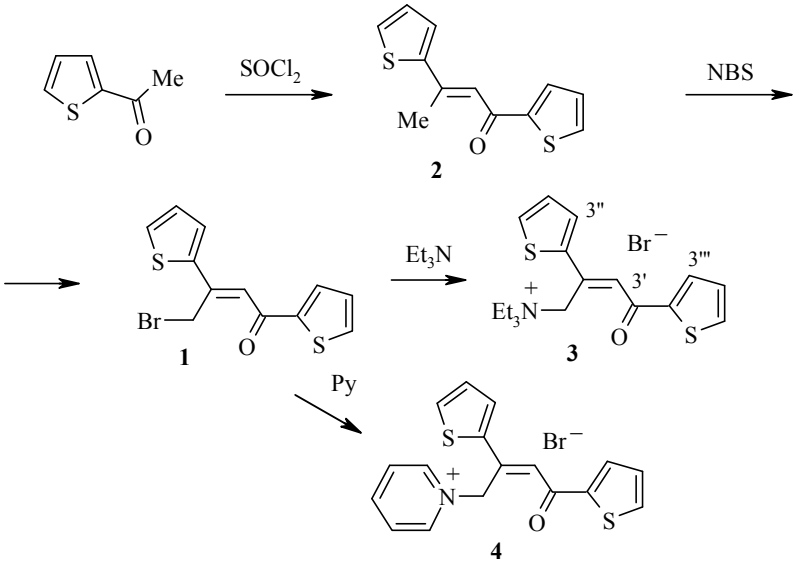
The information in the literature on the properties of bromo ketone **1** is limited to a synthesis of this compound in 26% yield as a by-product in the reaction of 1-(2-thienyl)-1-ethanone (methyl thienyl ketone) and 2-bromo-1-(2-thienyl)-1-ethanone [8]. Kulinkovich et al. [8] did not discuss the three-dimensional structure of this compound. We have found a convenient method for the synthesis of bromo ketone **1** involving the bromination of 1,3-di(2-thienyl)-2-buten-1-one (**2**) using N-bromosuccinimide in carbon tetrachloride. The reaction product, bromo ketone **1**, is formed in 88% yield and in high purity. Starting dithienyl-2-buten-1-one **2** was obtained in 60% yield by the condensation of methyl thienyl ketone by the action of thionyl chloride.



Since the spatial structure of unsaturated 1,4-dielectrophiles significantly affects the time required for their reaction with various nucleophiles, we undertook to establish the configuration of bromo ketone **1**.

The results of an X-ray diffraction study indicated the formation of the (*Z*)-isomer of bromo ketone **1** (Fig. 1*a*, Tables 1-3). The central conjugated segment of the molecule connecting the two thiophene rings is virtually planar. The mean-square deviation of O(1), C(4), C(5), C(6), C(7), C(8), and C(9) from their mean plane is 0.04 Å. The thiophene rings are slightly twisted relative to this fragment; the torsion angle C(7)–C(8)–C(9)–C(10) is -11.0(6)°, while C(3)–C(4)–C(5)–C(7) is -174.2(4)°. The C–Br bond is oriented almost perpendicularly to this fragment; the torsion angle C(4)–C(5)–C(6)–Br(1) is 83.7(4)°. The planar conformation of the conjugated fragment is additionally stabilized by formation of a weak intramolecular hydrogen bond C(6)–H(6B)···O(1) (H···O, 2.22 Å; C-H···O, 122°).

Dithienyl bromo ketone **1**, similar to its carbocyclic analog, γ-bromodypnone, is susceptible to the action of acids and bases. However, in contrast to γ-bromodypnone, which is converted under these conditions primarily into 2,4-diphenylfuran [9, 10], bromo ketone **1** forms a complex mixture of products, which could not be identified. Bromo ketone **1** demonstrates the same behavior with formation of complex reaction mixtures in its reaction with primary or secondary amines (anilines and morpholine were tested). However, the reaction with triethylamine yielded its quaternary salt, (*E*)-N,N,N-triethyl-4-oxo-2,4-di(2-thienyl)-2-butene-1-amonium bromide (**3**). Maintaining a solution of diethyl bromo ketone **1** and triethylamine in benzene at room temperature gave salt **3** in 44% yield. Under similar conditions, quaternary pyridinium, imidazolium, benzimidazolium, and 1,2,4-triazolium salts were obtained but with higher yields: 1-[(*E*)-4-oxo-2,4-di(2-thienyl)-2-butenyl]pyridinium (**4**), 1-R-3-[(*E*)-4-oxo-2,4-di(2-thienyl)-2-butenyl]-1H-imidazol-3-ium **5a-e**, 3-R-1-[(*E*)-4-oxo-2,4-di(2-thienyl)-2-butenyl]-3H-benzimidazol-1-ium **6a**,**b**, and 1-methyl-4-[(*E*)-4-oxo-2,4-di-(2-thienyl)-2-butenyl]-1H-1,2,4-triazol-4-ium (**7**) bromides, respectively. The structure of salts **3-7** was supported by their ^{1}H NMR and IR spectral data (Tables 4 and 5), which are in accord with the results for the corresponding quaternary

salts obtained in the reactions of azoles with γ-bromodypnones [6, 7]. The precise assignment of the signals of the aromatic protons in the ^{1}H NMR spectra of salts **3-7** was made on the basis of data from the 2D COSY HH spectrum of salt **7**.

The reaction of 1-(4-oxo-2,4-diphenyl-2-butenyl)pyridinium salts with bases gives 1,2-disubstituted indolizines [11, 12]. A similar transformation apparently occurs in our case as well. Heating pyridinium salt **4** in ethanol in the presence of potassium carbonate or triethylamine leads to intramolecular cyclization. However, the ^{1}H NMR spectrum of the reaction product and the GC/MS data indicate the formation of a mixture, which could not be separated either by recrystallization or chromatography.

TABLE 1. Coordinates ($\times 10^4$) and Equivalent Isotropic Characteristics ($Å^2 \times 10^3$) of Non-Hydrogen Atoms in the Structures of **1** and **8c**

Compound	Atom	*x/a* (σ)	*y/b* (σ)	*z/c* (σ)	U_{eq}
1	Br(1)	1821(1)	3894(1)	4475(1)	117(1)
	S(1)	1158(1)	2235(1)	7293(1)	92(1)
	S(2)	4490(1)	9990(3)	8208(1)	100(1)
	O(1)	3606(2)	6266(7)	6649(3)	97(1)
	C(1)	471(3)	-88(13)	6879(5)	99(2)
	C(2)	563(4)	-1481(11)	6175(6)	113(2)
	C(3)	1191(3)	-784(7)	5950(3)	66(1)
	C(4)	1609(2)	1414(7)	6553(3)	60(1)
	C(5)	2293(2)	2809(7)	6548(3)	55(1)
	C(6)	2534(3)	2081(9)	5737(3)	73(1)
	C(7)	2670(2)	4695(8)	7214(3)	59(1)
	C(8)	3331(3)	6356(8)	7264(3)	65(1)
	C(9)	3675(2)	8199(7)	8100(3)	57(1)
	C(10)	3410(2)	8989(7)	8816(3)	58(1)
	C(11)	3878(3)	10939(9)	9412(4)	82(1)
	C(12)	4485(4)	11668(10)	9195(4)	92(2)
8c	Br(1)	3931(1)	4303(1)	6998(1)	50(1)
	S(1)	1188(1)	-887(1)	5627(1)	65(1)
	S(2)	569(1)	2903(1)	3472(1)	56(1)
	N(1)	3271(1)	1636(1)	6205(2)	33(1)
	N(2)	3607(1)	250(1)	6811(2)	38(1)
	N(3)	3942(2)	-2929(2)	6110(4)	95(1)
	C(1)	1303(2)	-1804(2)	4271(4)	67(1)
	C(2)	1902(2)	-1692(2)	3138(4)	63(1)
	C(3)	2295(1)	-852(1)	3311(3)	50(1)
	C(4)	1978(1)	-332(1)	4643(3)	42(1)
	C(5)	2240(1)	587(1)	5169(3)	36(1)
	C(6)	3005(1)	767(1)	6038(2)	33(1)
	C(7)	1766(1)	1314(1)	4686(3)	38(1)
	C(8)	2037(1)	2215(1)	4960(2)	34(1)
	C(9)	2805(1)	2355(1)	5665(2)	36(1)
	C(10)	1523(1)	3006(1)	4523(3)	41(1)
	C(11)	1698(1)	3890(1)	4921(3)	48(1)
	C(12)	1042(2)	4462(2)	4370(4)	67(1)
	C(13)	405(2)	4027(2)	3587(4)	67(1)
	C(14)	4049(1)	1642(1)	7010(3)	41(1)
	C(15)	4245(1)	797(1)	7389(3)	42(1)
	C(16)	3596(1)	-724(1)	7135(3)	45(1)
	C(17)	4096(1)	-1212(1)	5751(3)	49(1)
	C(18)	4012(2)	-2175(1)	5937(4)	61(1)

TABLE 2. Some Valence (ω) and Torsion Angles (φ) for Molecules of **1** and **8c**

Com-pound	Angle	ω, deg	Angle	φ, deg
1	C(7)–C(5)–C(4)	121.9(3)	C(3)–C(4)–C(5)–C(7)	-174.2(4)
	C(7)–C(5)–C(6)	122.0(4)	S(1)–C(4)–C(5)–C(7)	7.3(5)
	C(4)–C(5)–C(6)	116.1(4)	C(3)–C(4)–C(5)–C(6)	7.7(5)
	C(5)–C(6)–Br(1)	108.4(3)	S(1)–C(4)–C(5)–C(6)	-170.9(3)
	C(5)–C(7)–C(8)	121.1(4)	C(7)–C(5)–C(6)–Br(1)	-94.4(4)
	O(1)–C(8)–C(9)	118.8(4)	C(4)–C(5)–C(6)–Br(1)	83.7(4)
	O(1)–C(8)–C(7)	123.2(4)	C(4)–C(5)–C(7)–C(8)	-176.2(4)
	C(9)–C(8)–C(7)	118.0(3)	C(5)–C(7)–C(8)–C(9)	-176.8(3)
	C(5)–C(4)–S(1)	123.0(3)	O(1)–C(8)–C(9)–C(10)	169.3(4)
	C(3)–C(4)–C(5)	128.2(4)	C(7)–C(8)–C(9)–C(10)	-11.0(6)
	C(10)–C(9)–C(8)	131.3(3)	O(1)–C(8)–C(9)–S(2)	-4.0(5)
	C(8)–C(9)–S(2)	118.1(3)	C(7)–C(8)–C(9)–S(2)	175.8(3)
			C(8)–C(9)–C(10)–C(11)	-174.5(4)
8c	C(1)–N(1)–C(5)	122.82(16)	C(1)–C(2)–C(8)–C(9)	-7.4(3)
	C(1)–N(1)–C(7)	127.85(16)	C(1)–C(2)–C(8)–S(1)	175.2(2)
	C(5)–N(1)–C(7)	109.32(16)	C(3)–C(4)–C(12)–C(13)	106.2(2)
	C(5)–N(2)–C(6)	108.83(16)	C(3)–C(4)–C(12)–S(2)	-71.9(2)
	C(3)–C(4)–C(5)	116.83(17)	C(5)–N(2)–C(16)–C(17)	104.5(2)
	N(2)–C(5)–N(1)	105.93(16)	C(6)–N(2)–C(16)–C(17)	-80.1(2)
	N(2)–C(5)–C(4)	134.36(18)	N(2)–C(16)–C(17)–C(18)	-173.6(2)
	N(1)–C(5)–C(4)	119.71(16)		
	C(5)–C(4)–C(12)	122.42(17)		
	C(1)–C(2)–C(3)	118.50(17)		
	C(2)–C(1)–N(1)	119.35(17)		
	C(7)–C(6)–N(2)	108.84(18)		
	C(6)–C(7)–N(1)	107.02(17)		

The cyclization of azolium salts **5-7** upon heating them with morpholine in ethanol occurs virtually without the formation of side products. The reaction products are 1-R-6,8-di(2-thienyl)-1H-imidazo[1,2-*a*]-pyridin-4-ium **8a-e**, 10-R-7,9-di(2-thienyl)-10H-pyrido[1,2-*a*]benzimidazol-5-ium **9a,b**, and 1-methyl-6,8-di-(2-thienyl)-1H-[1,2,4]triazolo[4,3-*a*]pyridin-4-ium (**10**) bromides, respectively. The structure of bromides **8-10**

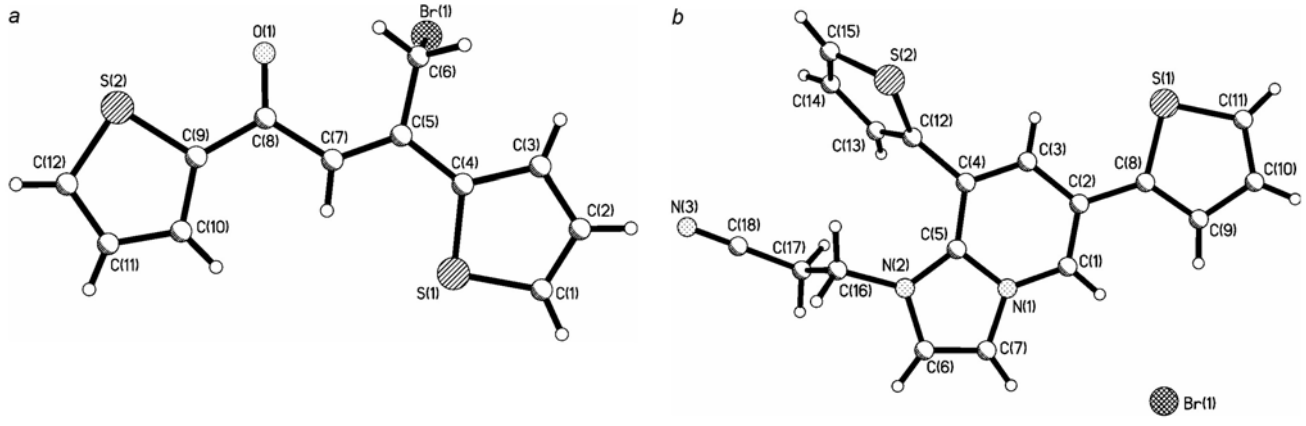


Fig. 1. Structure of molecules of **1** (*a*) and **8c** (*b*).

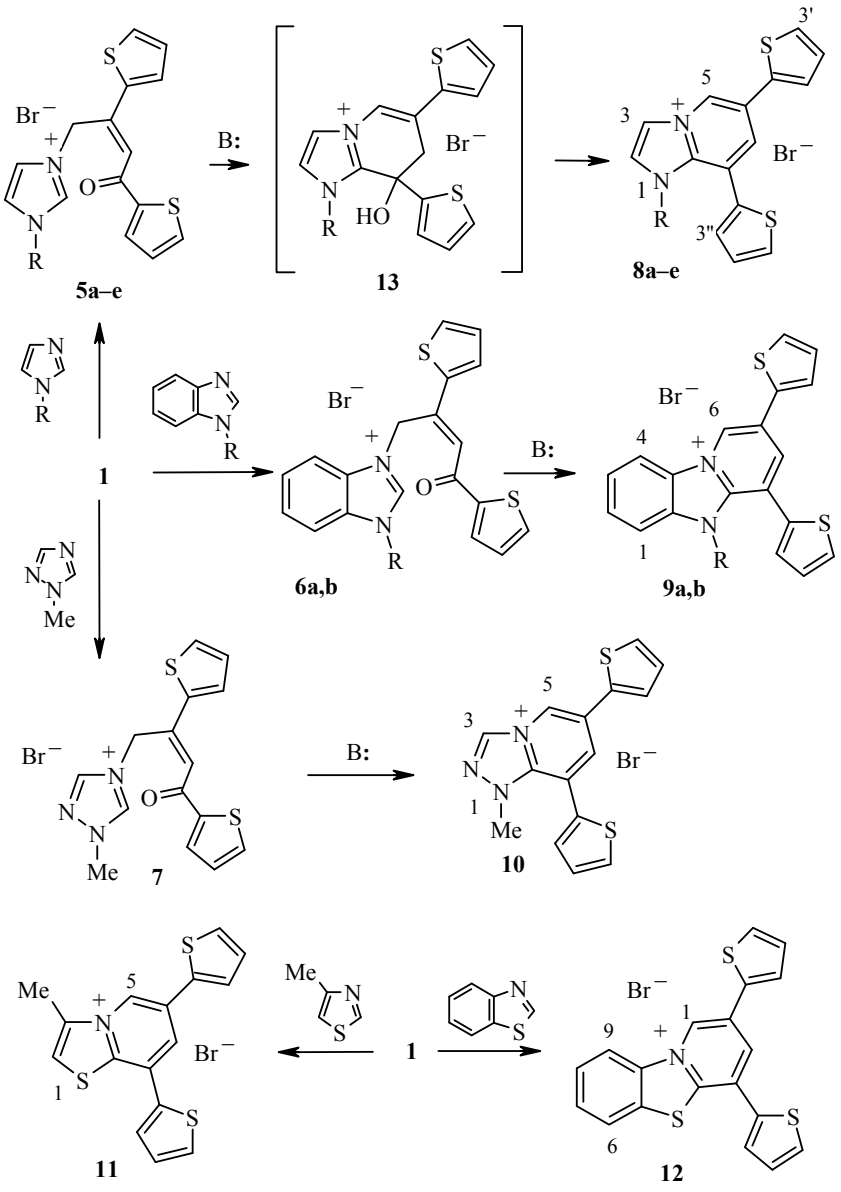
TABLE 3. Some Bond Lengths (*l*) in Molecules of **1** and **8c**

Bond	*l*, nm	Bond	*l*, nm
Compound **1**		Compound **8c**	
Br(1)–C(6)	1.964(4)	N(1)–C(1)	1.363(2)
O(1)–C(8)	1.216(5)	N(1)–C(5)	1.367(2)
C(4)–C(5)	1.454(6)	N(1)–C(7)	1.380(2)
C(5)–C(7)	1.346(5)	N(2)–C(5)	1.354(2)
C(5)–C(6)	1.493(5)	N(2)–C(6)	1.376(3)
C(7)–C(8)	1.468(6)	C(1)–C(2)	1.355(3)
C(8)–C(9)	1.464(6)	C(2)–C(3)	1.423(3)
S(1)–C(1)	1.661(7)	C(2)–C(8)	1.474(3)
S(1)–C(4)	1.689(4)	C(3)–C(4)	1.369(3)
S(2)–C(12)	1.700(6)	C(4)–C(5)	1.406(3)
S(2)–C(9)	1.710(4)	C(4)–C(12)	1.478(3)
		C(6)–C(7)	1.324(3)

was determined using their IR and ^{1}H NMR spectra (Tables 4 and 6), in which a series of analogies was found with the spectra of the corresponding diaryl derivatives [6, 7], specifically, the positions of the aromatic (H-5 and H-7 for **8a-e, 10** and H-6 and H-8 for **9a,b** and aliphatic protons of the aliphatic substituents at N-1 in the azolopyridinium fragment in the ^{1}H NMR spectra. Two-dimensional COSY HH, NOESY, HMQC, and HMBC spectra for salt **8a** were taken for the precise assignment of the aromatic proton signals and confirmation of the structure of salts **8-10**. The signals for the carbon atoms of the imidazolo[1,2-*a*]pyridine fragment in 1-methyl-6,8-di(2-thienyl)imidazopyridinium bromide (**8a**) are seen in the same regions as for the corresponding 6,8-diphenyl-substituted derivative [6]. Final confirmation of the structure of cyclic products **8-10** is found in the X-ray diffraction structural data for 1-(2-cyanoethyl)-6,8-di(2-thienyl)-1H-imidazo[1,2-*a*]-pyridin-4-ium bromide (**8c**) (Fig. 1*b*, Tables 2 and 3).

TABLE 4. IR Spectra of Compounds **3-12**

Com-pound	ν, cm^{-1}
3	3080, 2974, 2941, 1630 (C=O), 1565, 1413, 1242, 770, 736
4	3025, 1634 (C=O), 1586, 1575, 1409, 1231, 1071, 817, 761, 677
5a	3048, 1631 (C=O), 1580, 1415, 1242, 1155, 744, 732, 629
5b	3058, 2986, 1633 (C=O), 1583, 1407, 1239, 1225, 816, 755, 713
5c	3031, 2252 (CN), 1631 (C=O), 1572, 1410, 1234, 1158, 727
5d	3064, 1639 (C=O), 1580, 1415, 1234, 1152, 845, 820, 708, 638
5e	3081, 3031, 1625 (C=O), 1561, 1410, 1242, 1175, 1071, 993, 747, 724
6a	3014, 1625 (C=O), 1572, 1410, 1245, 741
6b	3014, 1631 (C=O), 1575, 1415, 1253, 1192, 825, 744, 713, 699
7	3008, 1631 (C=O), 1578, 1410, 1242, 1150, 816, 705, 624
8a	3036, 2986, 1541, 1301, 884, 850, 820, 733, 705
8b	3036, 2958, 1580, 1513, 1290, 1248, 887, 853, 758, 708
8c	3081, 3048, 2963, 2902, 2247 (CN), 1538, 1510, 1290, 1248, 850, 733, 713, 699
8d	3042, 1536, 1505, 1446, 1273, 1242, 733, 719, 705
8e	3036, 2975, 1653 (C=C), 1533, 1505, 1284, 1245, 951, 730, 702
9a	3014, 1536, 1516, 1483, 1312, 1239, 844, 755, 744, 699
9b	3019, 1508, 1480, 1454, 1441, 1225, 741, 685
10	3036, 2969, 1555, 1435, 1287, 1245, 829, 822, 738, 708
11	2975, 2678, 1435, 1399, 1169, 1035, 817, 716
12	2975, 1594, 1547, 1471, 1429, 1399, 848, 761, 713



5, **8 a** R = Me, **b** R = Et, **c** R = $(CH_2)_2CN$, **d** R = Bn, **e** R = Vin;
6, **9 a** R = Me, **b** R = Bn

Crystals of compound **8c** is a of an organic cation and bromide anion. Analysis of the bond lengths in the bicyclic fragment suggests that the positive charge is localized predominantly on N(2). This is indicated by the alternation of C–C bonds in the pyridine ring (the C(1)–C(2) 1.355(3) Å and C(3)–C(4) bonds 1.369.3 Å are much shorter than the C(2)–C(3) 1.423(3) Å and C(4)–C(5) bonds 1.406(3) Å) as well as by some shortening of the N(2)–C(5) bond to 1.354(2) Å in comparison with the N(2)–C(6) bond 1.376(3) Å. The S(1)···C(11) thiophene ring lies virtually in the plane of the bicyclic fragment (the C(1)–C(2)–C(8)–C(9) torsion angle is -7.4(3)°). The cyanomethyl substituent has *ap*-conformation (the N(2)–C(16)–C(17)–C(18) torsion angle is -173.56(19)°), which leads to a strong rotation of the S(2)···C(12) thiophene ring relative to the bicycle (the C(5)–C(4)–C(12)–C(13) torsion angle is -68.4(3)°) due to steric hindrance (shortening of the intramolecular C(16A)···C(12) 2.57 Å and H(17A)···C(13) contacts 2.78 Å, while the sum of the van der Waals radii is

TABLE 5. ^{1}H NMR Spectra of Quaternary Salts **3-7**

Compound	Chemical shifts (DMSO-d_6), δ, ppm (*J*, Hz)			
	1H (s)	Aromatic protons + H-3'	2H, s, C(1')H_2	Other signals
3*	—	8.15 (1H, d, ^3J = 3.2, H-3'"); 8.07 (1H, d, ^3J = 4.5, H-5'"); 7.86 (1H, d, ^3J = 3.5, H-3"); 7.79 (1H, d, ^3J = 4.8, H-5"); 7.52 (1H, s, H-3'); 7.27 (1H, m, H-4'"); 7.22 (1H, m, H-4")	5.06	3.39 (6H,q, ^3J = 6.6, CH_2); 1.28 (9H, t, ^3J = 6.6, CH_3)
4*		9.28 (2H, d, ^3J = 6.0, H-2,6); 8.64 (1H, t, ^3J = 8.0, H-4); 8.20-8.15 (3H, m, H-3,5,3'"); 8.03 (1H, d, ^3J = 4.8, H-5'"); 7.96 (1H, d, ^3J = 3.5, H-3"); 7.72 (1H, d, ^3J = 5.0, H-5"); 7.70 (1H, s, H-3'); 7.28 (1H, m, H-4'"); 7.16 (1H, m, H-4")	6.33	—
5a	9.25 (H-2)	8.25 (1H, d, ^3J = 3.5, H-3'"); 8.12 (1H, d, ^3J = 5.0, H-5'"); 7.88 (1H, d, ^3J = 3.5, H-3"); 7.83 (1H, d, ^3J = 5.0, H-5"); 7.82 (1H, s, H-4); 7.68 (1H, s, H-5); 7.64 (1H, s, H-3'); 7.32 (1H, m, H-4'"); 7.21 (1H, m, H-4")	5.75	3.83 (3H, s, NCH_3)
5b	9.33 (H-2)	8.25 (1H, d, ^3J = 3.5, H-3'"); 8.12 (1H, d, ^3J = 5.0, H-5'"); 7.87 (1H, d, ^3J = 3.5, H-3"); 7.83 (1H, d, ^3J = 5.0, H-5"); 7.81 (2H, s, H-4,5); 7.64 (1H, s, H-3'); 7.32 (1H, m, H-4'"); 7.21 (1H, m, H-4")	5.75	4.19 (2H,q ^3J = 7.5, NCH_2); 1.37 (3H, t, ^3J = 7.5, CH_3)
5c	9.40 (H-2)	8.28 (1H, d, ^3J = 3.5, H-3'"); 8.14 (1H, d, ^3J = 5.0, H-5'"); 7.90 (1H, d, ^3J = 3.5, H-3"); 7.87 (1H, d, ^3J = 5.0, H-5"); 7.85 (2H, m, H-4,5); 7.67 (1H, s, H-3'); 7.34 (1H, m, H-4'"); 7.23 (1H, m, H-4")	5.80	4.52 (2H, t, ^3J = 6.5, –CH_2CN); 3.20 (2H, t, ^3J = 6.5, NCH_2–)
5d	9.49 (H-2)	8.25 (1H, d, ^3J = 3.5, H-3'"); 8.12 (1H, d, ^3J = 5.0, H-5'"); 7.84 (2H, m, H-3",5"); 7.81 (1H, s, H-4); 7.77 (1H, s, H-5); 7.64 (1H, s, H-3'); 7.37 (3H, m, H-3""-5""); 7.31 (3H, m, H-4'",2"",6""); 7.21 (1H, m, H-4")	5.78	5.42 (2H, s, NCH_2)
5e	9.58 (H-2)	8.27 (1H, m, H-3'"); 8.23 (1H, s, H-4); 8.13 (1H, d, ^3J = 5.0, H-5'"); 7.95 (1H, s, H-5); 7.87 (1H, m, H-3"); 7.84 (1H, d, ^3J = 5.0, H-5"); 7.66 (1H, s, H-3'); 7.32 (1H, m, H-4'"); 7.22 (1H, m, H-4")	5.78	7.30 (1H, m, NCH=); 5.89 (1H, dd, ^3J = 16.0, ^2J = 1.5, =C$\underline{H}_A$$H_B$); 5.37 (1H, dd, ^3J = 8.5, ^2J = 1.5, =$CH_A$$\underline{H}_B$)
6a	9.76 (H-2)	8.31 (1H, d, ^3J = 3.5, H-3'"); 8.19 (1H, d, ^3J = 8.0, H-4); 8.13 (1H, d, ^3J = 5.0, H-5'"); 8.00 (1H, d, ^3J = 8.0, H-7); 7.86 (1H, d, ^3J = 3.5, H-3"); 7.80 (1H, d, ^3J = 5.0, H-5"); 7.77 (1H, s, H-3'); 7.72 (2H, m, H-5,6); 7.33 (1H, m, H-4'"); 7.17 (1H, m, H-4")	6.06	4.06 (3H, s, NCH_3)
6b	10.08 (H-2)	8.29 (1H, d, ^3J = 3.5, H-3'"); 8.13 (1H, d, ^3J = 5.0, H-5'"); 8.10 (1H, d, ^3J = 8.0, H-4); 7.91 (1H, d, ^3J = 8.0, H-7); 7.84 (1H, d, ^3J = 3.5, H-3"); 7.80 (1H, d, ^3J = 5.0, H-5"); 7.75 (1H, s, H-3'); 7.68 (1H, t, ^3J = 8.0, H-6); 7.62 (1H, t, ^3J = 8.0, H-5); 7.32 (6H, m, H-4'",H-2""-H-6""); 7.18 (1H, m, H-4")	6.14	5.76 (2H, s, NCH_2)
7	9.36 (H-5)	10.17 (1H, s, H-3); 8.27 (1H, d, ^3J = 3.5, H-3'"); 8.13 (1H, d, ^3J = 5.0, H-5'"); 7.93 (1H, d, ^3J = 3.5, H-3"); 7.87 (1H, d, ^3J = 5.0, H-5"); 7.66 (1H, s, H-3'); 7.32 (1H, m, H-4'"); 7.24 (1H, m, H-4")	5.80	4.04 (3H, s, NCH_3)

* The ^{1}H NMR spectrum was taken in 1:1 DMSO-d_6 on a Varian Mercury 400 spectrometer at 400 MHz.

TABLE 6. ^{1}H NMR Spectra of Azolo[*a*]pyridinium Bromides **8-12**

Compound	Chemical shifts (DMSO-d_6), δ, ppm (*J*, Hz)		
	Pyridine ring signals	Aromatic protons	Other signals
8a*	9.45 (1H, d, ^3J = 1.7, H-5); 8.26 (1H, d, ^3J = 1.7, H-7)	8.49 (1H, d, ^3J = 2.2, H-3); 8.28 (1H, d, ^3J = 2.2, H-2); 7.92 (1H, d, ^3J = 5.2, H-5"); 7.84 (1H, d, ^3J = 3.7, H-3'); 7.75 (1H, d, ^3J = 5.0, H-5'); 7.49 (1H, d, ^3J = 3.5, H-3"); 7.30 (1H, dd, ^3J = 3.5, ^3J = 5.2, H-4"); 7.23 (1H, dd, ^3J = 3.7, ^3J = 5.0, H-4')	3.54 (3H, s, NCH_3)
8b	9.41 (1H, s, H-5); 8.25 (1H, s, H-7)	8.49 (1H, d, ^3J = 1.5, H-3); 8.34 (1H, d, ^3J = 1.5, H-2); 7.92 (1H, d, ^3J = 4.0, H-5"); 7.83 (1H, m, H-3'); 7.74 (1H, d, ^3J = 4.0, H-5'); 7.51 (1H, m, H-3"); 7.30 (1H, m, H-4"); 7.22 (1H, m, H-4')	3.94 (2H, q, ^3J = 7.5, NCH_2); 1.60 (3H, t, ^3J = 7.5, CH_3)
8c	9.46 (1H, s, H-5); 8.33 (1H, m, H-7) *2	8.53 (1H, d, ^3J = 1.5, H-3); 8.33 (1H, m, H-2) *2, 7.97 (1H, m, H-5"); 7.86 (1H, s, H-3'); 7.78 (1H, m, H-5'); 7.56 (1H, s, H-3"); 7.33 (1H, m, H-4"); 7.25 (1H, m, H-4')	4.22 (2H, t, ^3J = 6.5, –CH_2CN); 2.91 (2H, t, ^3J = 6.5, NCH_2–)
8d	9.48 (1H, s, H-5); 8.24 (1H, s, H-7)	8.57 (1H, d, ^3J = 1.5, H-3); 8.31 (1H, d, ^3J = 1.5, H-2); 7.83 (1H, m, H-3'); 7.80 (1H, d, ^3J = 4.0, H-5"); 7.75 (1H, d, ^3J = 4.0, H-5"); 7.30 (1H, m, H-3"); 7.24 (4H, m, H-4',4",3'",5'"); 7.18 (1H, m, H-4'"); 6.80 (2H, m, H-2'",6'")	5.31 (2H, s, NCH_2)
8e	9.43 (1H, s, H-5); 8.37 (1H, s, H-7)	8.63 (1H, s, H-3); 8.57 (1H, s, H-2); 7.93 (1H, d, ^3J = 5.0, H-5"); 7.87 (1H, m, H-3'); 7.77 (1H, d, ^3J = 5.0, H-5'); 7.42 (1H, m, H-3"); 7.30 (1H, m, H-4"); 7.24 (1H, m, H-4')	6.43 (1H, dd, ^3J = 15.5, ^3J = 8.5, NCH=); 5.79 (1H, d, ^3J = 15.5, =C$\underline{H}_A$H$_B$); 5.19 (1H, d, ^3J = 8.5, =CH$_A$$\underline{H}_B$)
9a	9.95 (1H, s, H-6); 8.51 (1H, s, H-8)	8.93 (1H, d, ^3J = 8.0, H-4); 8.12 (1H, d, ^3J = 8.0, H-1); 7.96 (2H, m, H-5",3'); 7.92 (1H, t, ^3J = 8.0, H-2); 7.80 (2H, m, H-3,5'); 7.51 (1H, m, H-3"); 7.34 (1H, m, H-4"); 7.28 (1H, m, H-4')	3.64 (3H, s, NCH_3)
9b	10.04 (1H, s, H-6); 8.52 (1H, s, H-8)	8.99 (1H, d, ^3J = 8.0, H-4); 7.98 (1H, m, H-3'); 7.83 (5H, m, H-1–H-3, H-5',5"); 7.28 (2H, m, H-3",4"); 7.23 (3H, m, H-4',3'",5'"); 7.15 (1H, m, H-4'"); 6.96 (2H, m, H-2'",6'")	5.49 (2H, s, NCH_2)
10	9.40 (1H, s, H-5); 8.53 (1H, s, H-7)	9.76 (1H, s, H-3); 7.96 (1H, d, ^3J = 4.0, H-5"); 7.92 (1H, m, H-3'); 7.79 (1H, d, ^3J = 4.0, H-5'); 7.52 (1H, m, H-3"); 7.33 (1H, m, H-4"); 7.25 (1H, m, H-4')	3.76 (3H, s, NCH_3)
11	9.23 (1H, d, ^3J = 1.0, H-5); 8.26 (1H, d, ^3J = 1.0, H-7)	8.70 (1H, s, H-2); 8.14 (1H, d, ^3J = 2.5, H-3"); 8.07 (1H, d, ^3J = 4.5, H-5"); 8.03 (1H, d, ^3J = 2.5, H-3'); 7.92 (1H, d, ^3J = 5.0, H-5'); 7.45 (1H, m, H-4"); 7.35 (1H, m, H-4')	2.89 (3H, s, CH_3)
12	10.23 (1H, s, H-1); 8.86 (1H, s, H-3)	9.27 (1H, d, ^3J = 8.0, H-9); 8.58 (1H, d, ^3J = 8.0, H-6); 8.22 (1H, m, H-3'); 8.12-7.95 (5H, m, H-7,8,5',3", 5"); 7.48 (1H, m, H-4"); 7.38 (1H, m, H-4')	—

* The ^{1}H NMR spectra were taken in 1:1 DMSO–CCl_4 on a Varian Mercury 400 spectrometer at 400 MHz.

*2 Superposition of the signals for H-7 and H-2.

2.87 Å [9]). The marked extrusion of the C(4)-C(12) and N(2)-C(16) bonds from the plane of the bicycle is also a consequence of considerable steric strain (torsion angles N(1)-C(5)-C(4)-C(12) 168.59(18)°; N(1)–C(5)–N(2)–C(16), 174.04(16)°). The bromide anion in the crystal is bound to the cations by a series of attractive shortened intermolecular contacts: Br(1)···H(1), 2.66 Å; Br(1)···H(9), 3.04 Å; Br(1)···H(6) [1-*x*, 0.5+*y*, 1.5-*z*], 2.92 Å; Br(1)···H(13) [*x*, 0.5-*y*, 0.5+*z*] 2.90 Å, and Br(1)···H(17B) [1-*x*, 0.5+*y*, 1.5-*z*] 2.74 Å (the sum of the corresponding van der Waals radii is 3.13 Å [13]).

A change in the conditions of cyclization of imidazolium salts **5**, specifically, replacement of the ethanol solvent by acetone or replacement of the morpholine base by triethylamine leads to the formation of mixtures of products of intramolecular condensation: crotonic type **8** and aldol type **13**. ^{1}H NMR spectroscopy indicated the presence of hydroxy derivatives **13** in the product mixture by finding characteristic methylene group signals at 3.61-3.76 ppm as two AB-spin doublets with ^2J = 17.0 Hz. Similar to the corresponding aryl derivatives [7], products **13** are unstable and very readily lose a water molecule.

TABLE 7. Physicochemical and Elemental Analysis Data for Compounds **3-12**

Compound	Empirical formula	Found, % / Calculated, %			mp, °C*	Yield, %
		Br	N	S		
3	$C_{18}H_{24}BrNOS_2$	19.35 / 19.28	3.41 / 3.38	15.42 / 15.47	115-118 (dec.)	44
4	$C_{17}H_{14}BrNOS_2$	20.30 / 20.37	3.59 / 3.57	16.40 / 16.35	191-192	61
5a	$C_{16}H_{15}BrN_2OS_2$	20.23 / 20.21	7.12 / 7.09	16.20 / 16.22	192-195	90
5b	$C_{17}H_{17}BrN_2OS_2$	19.51 / 19.52	6.86 / 6.84	15.65 / 15.67	173-175	86
5c	$C_{18}H_{16}BrN_3OS_2$	18.35 / 18.40	9.68 / 9.67	14.80 / 14.76	155-156	51
5d	$C_{22}H_{19}BrN_2OS_2$	16.98 / 16.95	5.97 / 5.94	13.59 / 13.60	158-160	81
5e	$C_{17}H_{15}BrN_2OS_2$	19.65 / 19.62	6.89 / 6.88	15.75 / 15.74	174-176	88
6a	$C_{20}H_{17}BrN_2OS_2$	17.93 / 17.94	6.32 / 6.29	14.43 / 14.40	203-205	79
6b	$C_{26}H_{21}BrN_2OS_2$	15.34 / 15.32	5.38 / 5.37	12.31 / 12.30	191-193	76
7	$C_{15}H_{14}BrN_3OS_2$	20.15 / 20.16	10.63 / 10.60	16.20 / 16.18	187-189	75
8a	$C_{16}H_{13}BrN_2S_2$	21.20 / 21.18	7.45 / 7.42	17.03 / 17.00	344-347 (dec.)	92
8b	$C_{17}H_{15}BrN_2S_2$	20.41 / 20.42	7.18 / 7.16	16.41 / 16.39	238-241	88
8c	$C_{18}H_{14}BrN_3S_2$	19.22 / 19.19	10.08 / 10.09	15.45 / 15.40	239-241	63
8d	$C_{22}H_{17}BrN_2S_2$	17.64 / 17.62	6.18 / 6.18	14.13 / 14.14	233-235 (dec.)	85
8e	$C_{17}H_{13}BrN_2S_2$	20.55 / 20.52	7.22 / 7.20	16.45 / 16.47	288-291	90
9a	$C_{20}H_{15}BrN_2S_2$	18.74 / 18.70	6.54 / 6.55	15.06 / 15.01	269-271	87
9b	$C_{26}H_{19}BrN_2S_2$	15.89 / 15.87	5.59 / 5.56	12.73 / 12.74	243-245	80
10	$C_{15}H_{12}BrN_3S_2$	21.14 / 21.12	11.13 / 11.11	16.96 / 16.95	252-254 (dec.)	84
11	$C_{16}H_{12}BrNS_3$	20.22 / 20.26	3.57 / 3.55	24.41 / 24.39	219220	63
12	$C_{19}H_{12}BrNS_3$	18.52 / 18.56	3.26 / 3.25	22.36 / 22.35	282-284	67

* Recrystallization solvents: acetone for **3**, acetonitrile for **4**, $MeNO_2$ for **5a-e, 6a,b,** and **7**, acetic acid for **8a-e, 9a,b,** and **10-12**.

Less basic 2-methyl-1,3-thiazole and 1,3-benzthiazole react less rapidly with dithienyl bromo ketone **1**. The reaction takes 96 h in contrast to the reactions of salts **3-7**, which require only 24-48 h. On the other hand, quaternary thiazolium and benzthiazolium salts are converted more readily into cyclic products. The ^{1}H NMR spectra show the presence of 3-methyl-6,8-di(2-thienyl)[1,3]thiazolo[3,2-*a*]pyridin-4-ium bromide (**11**) and 2,4-di(2-thienyl)pyrido[2,1-*b*]benzothiazol-10-ium bromide (**12**), respectively, even in the alkylation step. Thus, bromides **11** and **12** were prepared without isolation of the intermediates.

EXPERIMENTAL

The IR spectra were taken on a Perkin-Elmer Spectrum BX spectrometer for KBr pellets. The UV spectrum of bromo ketone **1** was obtained on a Lambda 20 UV-vis spectrometer in methanol. The ^{1}H NMR spectra were taken on a Bruker Avance DRX 500 spectrometer at 500 MHz. The two-dimensional correlation spectra were taken on a Varian Mercury 400 spectrometer at 400 MHz for ^{1}H NMR signals and 100 MHz for ^{13}C NMR signals in DMSO-d_6 with TMS as the internal standard. The purity of the products was monitored by thin-layer chromatography on Silufol UV-254 plates and HPLC/MS on an Agilent 1100 Series with an Agilent LC/MSD SL detector. The sample was introduced in a CF_3CO_2H matrix. Electron impact ionization was employed. The physicochemical characteristics and elemental analysis data of the products are given in Table 7.

1,3-Di(2-thienyl)-2-buten-1-one (2). Thionyl chloride (14.4 ml, 200 mmol) was added dropwise with stirring to a solution of methyl thienyl ketone (19 g, 150 mmol) in absolute ethanol (50 ml) at room temperature. Stirring was continued for 30 min. Then, 100 ml water and 50 ml 50% aq. sodium carbonate were added. Chloroform (100 ml) was added and the lower layer was separated. The chloroform solution was dried over sodium sulfate and the solvent was distilled off. The residue was fractionated in vacuum to give 21 g (60%) butanone **2**; bp 215-220°C (15 mm Hg) (bp 180°C (3 mm Hg) [14]). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.03 (1H, d, ^3J = 4.0, H-3'); 7.96 (1H, d, ^3J = 5.0, H-5'); 7.72 (2H, m, H-3", H-5"); 7.34 (1H, s, H-2); 7.23 (1H, m, H-4'); 7.18 (1H, m, H-4"); 2.59 (3H, s, CH_3).

(*Z*)-4-Bromo-1,3-di(2-thienyl)-2-buten-1-one (1). N-Bromosuccinimide (8.9 g, 50 mmol) was added to a solution of 2-buten-1-one **2** (11.7 g, 50 mmol) in anhydrous carbon tetrachloride (50 ml). The mixture was heated to reflux and benzoyl peroxide (0.3 g) was added and heating at reflux was continued for 1.0-1.5 h. The mixture was cooled and succinimide was filtered off. The solvent was evaporated off and the residue was recrystallized from 2-propanol to give 13.8 g (88%) bromo ketone **1**; mp 102-103°C (2-propanol) (mp 98°C [8]). UV spectrum, λ_{max}, nm ($\varepsilon\cdot10^{-3}$): 264 (24.63), 280 (23.54), 348 (12.84). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 8.15 (1H, d, ^3J = 3.0, H-3'); 8.05 (1H, d, ^3J = 4.0, H-5'); 7.83 (1H, d, ^3J = 3.5, H-3"); 7.80 (1H, d, ^3J = 4.0, H-5"); 7.41 (1H, s, H-2); 7.28 (1H, m, H-4'); 7.23 (1H, m, H-4"); 5.08 (2H, s, CH_2).

Crystallographic Data. The unit cell parameters for monoclinic crystals of bromo ketone **1**, $C_{12}H_9BrOS_2$ at 293 K are as follows: a = 18.283(2), b = 5.2739(4), c = 14.6632(11) Å, β = 116.883(9)°, V = 1261.09(19) Å^3, M_r = 313.22, Z = 4, space group *Cc*, d_{calc} = 1.650 g/cm^3, μ(MoKα) = 3.565 mm^{-1}, F(000) = 624. The unit cell parameters and intensities of 6251 reflections (3062 independent reflections, R_{int} = 0.032) were measured on an Xcalibur 3 diffractometer using MoKα radiation, CCD detector, graphite monochromator, and ω-scanning, $2\theta_{max}$ = 60°. The structure was solved by the direct method using the *SHELTXL* program package [15]. The positions of the hydrogen atoms were found from the electron density difference map and refined by the "horse rider" model with U_{iso}= 1.2 U_{eq} of the non-hydrogen atom bound to the given hydrogen. The structure was refined relative to F^2 by the full-matrix method of least squares for the non-hydrogen atoms to wR_2 = 0.071 using 3022 reflections (R_1 = 0.036 using 1396 reflections with $F > 4\sigma(F)$, S = 0.77). Some of the valence and torsion angles and bond lengths are given in Tables 2 and 3. The registration number in the Cambridge Crystallographic Data Center is CCDC 740758.

(*E*)-4-Oxo-N,N,N-triethyl-2,3-di(2-thienyl)-2-butene-1-ammonium Bromide (3). Triethylamine (0.3 ml, 2.1 mmol) was added to a solution of bromoketone **2** (0.5 g, 1.6 mmol) in benzene (20 ml) and maintained at room temperature for 24 h. The precipitate formed was filtered off and washed with acetone.

1-[(*E*)-4-Oxo-2,4-di(2-thienyl)-2-butenyl]pyridinium Bromide (4), 1-R-3-[(*E*)-4-Oxo-2,4-di(2-thienyl)-2-butenyl]-1H-imidazol-3-iuim Bromides 5a-e, 3-R-1-[(*E*)-4-Oxo-2,4-di(2-thienyl)-2-butenyl]-3H-benzimidazol-1-ium Bromides 6a,b, and 1-Methyl-4-[(*E*)-4-oxo-2,4-di(2-thienyl)-2-butenyl]-1H-1,2,4-triazol-4-ium Bromide (7) were obtained according to the procedure for the synthesis of bromide **3** using pyridine or 1-alkylazole (2.0 mmol). The reaction time was 48 h.

1-R-6,8-Di(2-thienyl)-1H-imidazo[1,2-*a*]pyridin-4-ium Bromides 8a-e. A mixture of salt **5a-e** (1.0 mmol) and morpholine (2 ml) in ethanol (10 ml) was heated at reflux for 1 h. After cooling, the precipitate formed was filtered off and washed with acetone.

Bromide 8a. ^{13}C NMR spectrum, δ, ppm: 137.1 (C-8a), 136.9 (C-2'), 134.6 (C-7), 132.6 (C-2"), 132.3 (C-3"), 130.1 (C-5"), 129.6 (C-4'), 129.3 (C-2), 128.8 (C-5'), 128.2 (C-4"), 127.9 (C-3'), 125.5 (C-5), 124.2 (C-6), 120.95 (C-8), 115.9 (C-3), 37.4 (CH_3).

Crystallographic Data. The unit cell parameters of monoclinic crystals of bromide **8c**, $C_{18}H_{14}BrN_3S_2$ at 293 C are as follows: $a = 16.4323(3)$, $b = 14.8654(3)$, $c = 7.3236(2)$ Å, $\beta = 92.853(2)°$, $V = 1786.74(7)$ Å^3, $M_r = 416.35$, $Z = 4$, space group $P2_1/c$, $d_{calc} = 1.548$ g/cm^3, μ(MoKα) = 2.538 mm^{-1}, $F(000) = 840$. The unit cell parameters and intensities of 25,680 reflections (5713 independent reflections, $R_{int} = 0.042$) were measured on an Xcalibur 3 diffractometer using MoKα radiation, CCD detector, graphite monochromator, and ω-scanning, $2\theta_{max} = 60°$. The structure was solved by the direct method using the *SHELX-97* program package [15]. The positions of the hydrogen atoms were found from the electron density difference map and refined by the "horse rider" model with $U_{iso} = 1.2U_{eq}$ of the non-hydrogen atom bound to the given hydrogen. The structure was refined relative to F^2 by the full-matrix method of least squares for the non-hydrogen atoms to $wR_2 = 0.0637$ for 5153 reflections ($R_1 = 0.036$ for 2993 reflections with $F > 4\sigma(F)$, $S = 0.860$). Some valence and torsion angles and bond lengths are given in Tables 2 and 3. The registration number in the Cambridge Crystallographic Center is CCDC 740757.

10-R-7,9-Di(2-thienyl)-10H-pyrido[1,2-*a*]benzimidazol-5-ium Bromides 9a,b and 1-Methyl-6,8-di-(2-thienyl)-1H-[1,2,4]triazolo[4,3-*a*]pyridin-4-ium Bromide (10) were obtained according to the procedure for the synthesis of bromides **5** using benzimidazolium bromide **6a** or **6b** or triazolium bromide **7**.

Bromide 9a. ^{13}C NMR spectrum, δ, ppm: 140.1 (C-9a), 139.2 (C-8), 136.2 (C-2'), 134.1 (C-10a), 132.3 (C-2"), 131.9 (C-3"), 130.2 (C-5"), 129.8 (C-4'), 129.1 (C-5'), 128.4 (C-4a), 128.0 (C-4"), 127.8 (C-3'), 126.7 (C-2), 125.4 (C-6), 125.2 (C-3), 123.9 (C-7), 120.3 (C-9), 115.3 (C-4), 113.2 (C-1), 33.6 (CH_3).

Bromide 10. ^{13}C NMR spectrum, δ, ppm: 140.9 (C-8a), 138.2 (C-7), 136.6 (C-3), 135.7 (C-2'), 132.1 (C-3"), 131.0 (C-2"), 130.1 (C-5"), 129.2 (C-4'), 128.8 (C-5'), 128.2 (C-4"), 128.0 (C-3'), 125.2 (C-6), 122.7 (C-5), 119.7 (C-8), 40.0 (CH_3).

3-Methyl-6,8-di(2-thienyl)[1,3]thiazolo[3,2-*a*]pyridin-4-ium Bromide (11) and 2,4-Di(2-thienyl)-pyrido[2,1-*b*][1,3]benzothiazol-10-ium Bromide (12). 2-Methyl-1,3-thiazole or 1,3-benzothiazole (2.0 mmol) was added to a solution of bromo ketone **1** (0.5 g, 1.6 mmol) in benzene (20 ml). The mixture was maintained for four days at room temperature. The precipitate formed was filtered off and washed with acetone. Triethylamine (2 ml) was added to a suspension of the solid precipitate in acetone (15 ml) and heated at reflux for 1 h. After cooling, the precipitate formed was filtered off and washed with acetone.

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