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PHENYLFURYLTHIENO[2,3-*b*]PYRIDYL-METHANES. SYNTHESIS AND REACTIONS OF THE FURAN RING TRANSFORMATION

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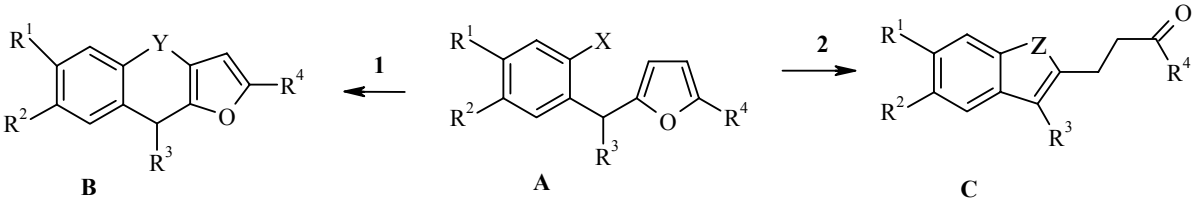
Triarylmethane derivatives with various substituents, phenyl, 5-methyl-2-furyl, and 3-acylamino-thieno[2,3-b]pyrid-2-yl have been obtained for the first time. The behavior of these compounds under protolytic conditions has been studied. It was shown that the character of the protection of the amino group of the thienopyridine fragment affects the type of transformation of the furan ring.

Keywords: 3-amino-2-benzoylthieno[2,3-*b*]pyridines, N-[2-(2,5-dioxo-1-phenylhexyl)thieno[2,3-*b*]pyrid-3-yl]benzamides, (phenyl)(2-acylaminothieno[2,3-*b*]pyrid-2-yl)carbinols, (phenyl)(5-methylfur-2-yl)-(2-acylaminothieno[2,3-*b*]pyrid-2-yl)methanes, 4-(3-phenyl-1H-pyrrolo[2',3':4,5]thieno[2,3-*b*]pyrid-2-yl)-butan-2-ones, alkylation, acylation, reduction, transformation of the furan ring.

Derivatives of benzylfuran of type **A** containing a functional group X in the *ortho* position of the benzene ring, are attractive as intermediates for obtaining the most varied condensed carbo- and heterocyclic compounds [1]. Depending on the character of substituent X two routes of conversion are possible in principle: 1) closing of the hetero- or carbocycle between the furan and benzene rings with the formation of a product of type **B** [2, 3] or 2) cleavage of the heterocycle and annelation of the benzene nucleus with the formation of a product of type **C** (Scheme 1).

Scheme 1



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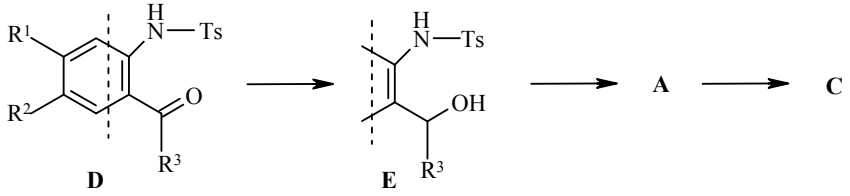
From the second route, named by us "furan ring opening – heterocyclic ring closing" [4], derivatives of benzofuran [5, 6], indole [4, 7], isochromone [8], isoquinolone [9, 10], benzopyran [11], and cinnoline [12] were obtained. In particular, derivatives of indole of type **C** (Z = NTs) were synthesized by us starting from *ortho*-acylaminoarenes **D** (Scheme 2), converted through carbinols **E** into compounds of type **A** (X = NHTs).

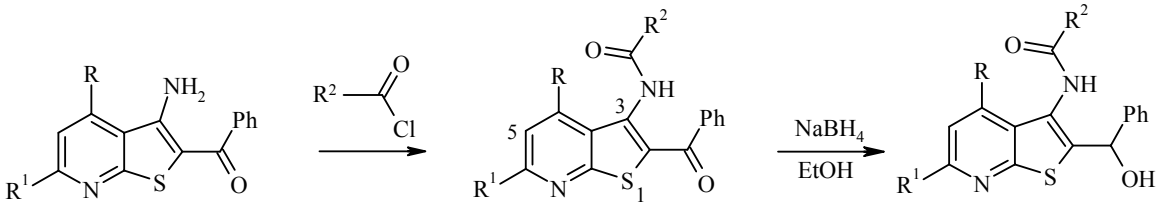
Scheme 2



The problem of the present work was to show the possibility of using analogs of compounds **A** with a heterocyclic acylamino-substituted fragment in transformations according to pathway 2. To solve this, readily available analogs of compounds **D** were selected as starting materials, *viz.* derivatives of 2-acyl-3-amino-thieno[2,3-*b*]pyridine **1** obtained by the Torp reaction from the appropriate 3-cyanopyridine-2-thiones [13].

We showed in [14] that the direct conversion of amino ketones **1** into the corresponding alcohols by the action of $NaBH_4$ was not possible. In their place derivatives of 6-phenyl-7,12-dithia-1,5,8-triaza-indeno[1,2-*a*]fluorene were formed, products of intermolecular dimerization accompanied by the elimination of benzonitrile. Consequently acyl protection of the amino group of compounds **1** was carried out before reduction of the carbonyl group. It is known [4, 7] that such protection is also necessary at the following stage of alkylation of the furan by carbinols. The acylamino derivatives **2** were obtained in high yield (70-95%, Table 1) by boiling amino ketones **1** with the appropriate acid chlorides of carboxylic acids in dioxane or toluene by the procedure of [15] (Scheme 3).

Scheme 3



1 a R = R^1 = Me, **b** R = CH_2OMe, R^1 = Me, **c** R = R^1 = Ph, **d** R = 5-methyl-2-furyl, R^1 = Ph, **e** R = C_6H_4Br-4, R^1 = Ph; **2, 3 a–e** R^2 = Ph, **a** R = R^1 = Me, **b** R = CH_2OMe, R^1 = Me, **c** R = R^1 = Ph, **d** R = 5-methyl-2-furyl, R^1 = Ph, **e** R = C_6H_4Br-4, R^1 = Ph, **f** R = R^1 = Me, R^2 = 2-furyl, **g** R = CH_2OMe, R^1 = Me, R^2 = 2-furyl, **h** R = CH_2OMe, R^1 = Me, R^2 = 2-thenoyl, **i** R = R^1 = R^2 = Me, **j** R = CH_2OMe, R^1 = R^2 = Me

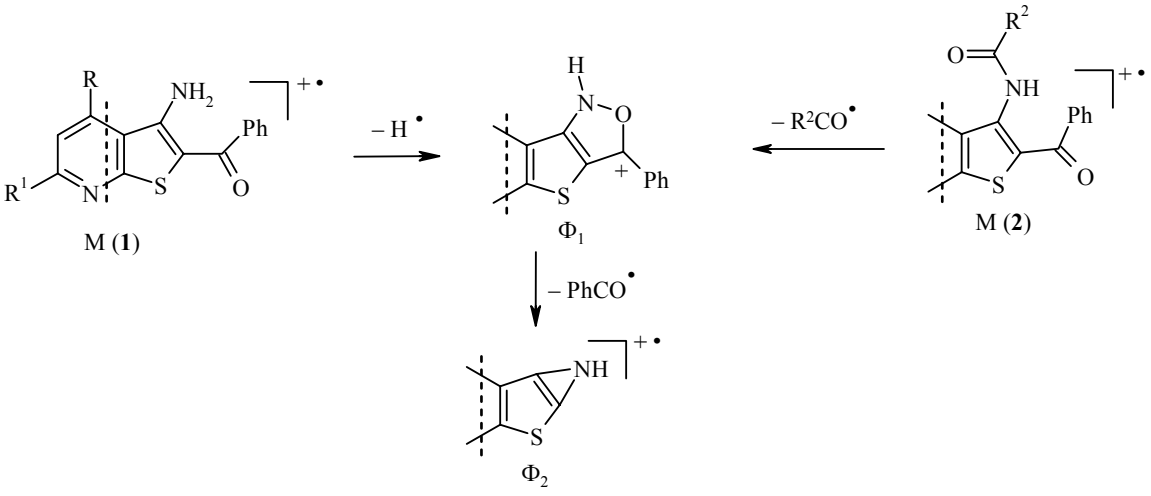
We note that amino ketones **1** do not react with carboxylic acid anhydrides. For example, boiling compounds **1** with an excess of acetic anhydride for 5-6 h does not lead to the formation of appreciable quantities of products of type **2**.

The acyl derivatives **2a-j** are colorless crystalline substances with sharp melting points (Table 1). In the IR spectra of these compounds (Table 2) there are two narrow intense absorption bands in the region of 1630-1635 and 1670-1680 cm^{-1} corresponding to the stretching vibrations of the amide and ketone carbonyl groups. A broad absorption band is also present in the region of 3230-3360 cm^{-1} corresponding to the stretching

vibrations of the amide N–H bond. In the ^{1}H NMR spectra of compounds **2** (Table 3), together with signals for H_{Ph} and H_{Het}, there are signals for the protons of the introduced N-acyl fragment and a one-proton singlet for the NHCO group.

The formation of cation **Φ$_1$** at the first stage of fragmentation (electron impact, 70 eV) is general for the molecular ions of compounds **1, 2** (Scheme 4). This has maximum intensity in the mass spectra of amino ketones **1**, but in the spectra of their acyl derivatives **2** is 60-80% of maximum, which in these cases is the intensity of the peak of cation R^2CO^+.

Scheme 4



The second step of the fragmentation, the thermodynamically unfavorable process of removing a PhCO radical from cation **Φ$_1$**, leads to the odd-electron fragment **Φ$_2$**.

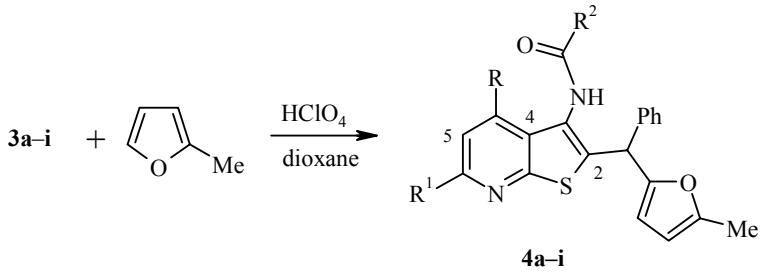
Reduction of the carbonyl group of compounds **2** with sodium borohydride in ethanol at 40-60°C leads to the corresponding alcohol **3** in 75-90% yield (Scheme 3, Table 1). Products **3a-j** were colorless crystalline substances with sharp melting points. In the IR spectra of alcohols **3** there were bands for the stretching vibrations of the OH group at 3381-3245 cm^{-1}, but the band for the amide NH group at 3380-3417 cm^{-1} was displaced towards long wave in comparison with the analogous band in the spectra of the corresponding ketones **2**. The ^{1}H NMR spectra also indicate the presence of the CH–OH grouping, the protons of which have coupling constants ~3.0-4.5 Hz (Table 3). The singlet signal of the CONH group is found at low field in the region of 9.4-10.1 ppm. Reduction of the ketone group to alcohol leads to the formation of an asymmetric center in the alcohol molecules, which is clearly displayed in the spectra of compounds **3b,g,h,j**, having a CH_2OCH_3 group. The prochiral methylene protons in the alcohol molecules become diastereotopic and resonate as pairs of one-proton doublets with a common geminal coupling constant J = 14.5 Hz.

The molecular ions of alcohols **3** are extremely unstable and are not found when using standard values for the energy of the ionizing electrons. The first step of their fragmentation, the rearrangement with elimination of a water molecule, is common to all the series of compounds investigated. The [M-18] cation-radical formed is decomposed in two directions, with cleavage of molecules of R^2CN and R^2NCO. When R^2 = Alk (compounds **3i,j**) simple removal of radical R^2 occurs in parallel.

Furylhetarylmethanes **4a-i** were obtained by the alkylation of 2-methylfuran with alcohols **3a-i** by boiling equimolar quantities of reactants in dioxane (3-12 h) in the presence of catalyst, which was a mixture of 70% perchloric acid, acetic anhydride, and glacial acetic acid (Scheme 5).

The carrying out of the reaction with the aid of the indicated catalytic system makes possible, even on extended contact with the acid catalyst, a reduction in resinification of the furan substrate and prevent side conversions of both the initial methylfuran and of the reaction products **4** containing the acidophobic furan ring.

Scheme 5



4a–i

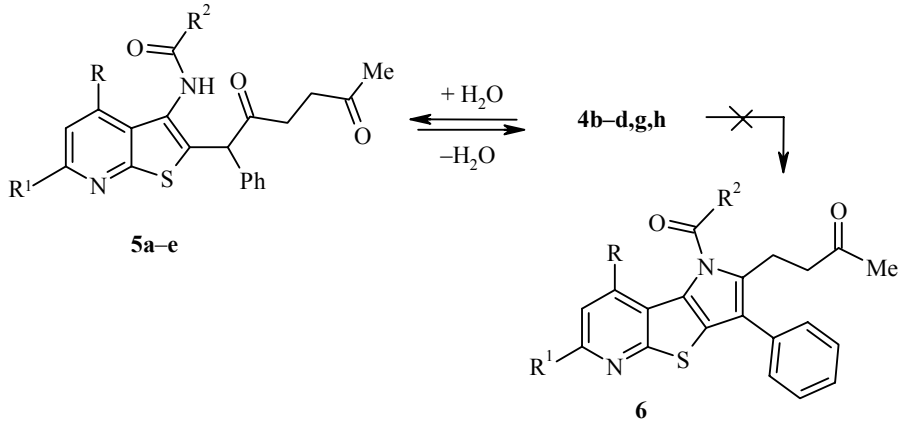
Products **4**, isolated from the reaction mixture in 65-95% yield, were colorless crystalline compounds, soluble in methylene chloride, ethyl acetate, and alcohol (Table 1).

In the ^{1}H NMR spectra of methanes **4** (Table 3) signals were present for the two β-protons of the furan ring as a pair of doublets at 6.0-6.1 ppm with coupling constant typically ^3J = 2.8-3.3 Hz and a singlet signal for the protons of the methyl group in position 5 of the furan fragment. The methine proton at the central sp^3-hybridized carbon atom resonates as a singlet in the 5.8-6.0 ppm region. The diastereotopic protons of the methylene unit of the CH_2OCH_3 group of compounds **4b,g,h**, as in the spectra of the corresponding alcohols **3b,g,h**, also resonate as a pair of one-proton doublets with ^2J = ~14 Hz.

The molecular ions of methanes **4** had low intensities, but for compounds **4b,g**, having a methoxymethyl fragment, were generally absent. Peaks of cation radicals [M-CH_3OH] had the greatest value of *m/z*. The typical sequence of fragmentation reactions of the molecular ion (or [M-CH_3OH] ion) was separation of a R^2CO radical and subsequent rearrangement with extrusion of a ketene molecule. We note in all mass spectra of this series of compounds the presence of a characteristic peak of the (phenyl)(5-methyl-2-furyl)-methyl cation with *m/z* 171.

Investigation of the behavior of methanes **4** in acidic medium (acetic acid with added perchloric acid or ethanol saturated with dry HCl) showed that the character of the proceeding reactions depended on the type of acyl substituent at the nitrogen atom. Extended boiling (up to 8 h) of compounds **4b-d,g,h**, having an aryl or hetaryl substituent R^2, leads only to the products of hydrolytic breakdown of the furan ring **5a-e**, without the formation of recyclization products of type **6** (Scheme 6). It should be noted that in the reaction mixture an equilibrium was established between the initial furans **4** and diketones **5** significantly more rapidly in acetic acid than in ethanol.

Scheme 6



5a–e

6

5 a R = CH_2OMe, R^1 = Me, R^2 = Ph, **b** R = R^1 = R^2 = Ph, **c** R = 5-methyl-2-furyl, R^1 = R^2 = Ph, **d** R = CH_2OMe, R^1 = Me, R^2 = 2-furyl, **e** R = CH_2OMe, R^1 = Me, R^2 = 2-thenoyl

The fact of the equilibrium between the initial and final reaction products was confirmed by us experimentally. Under the same conditions diketone **5b** forms an analogous equilibrium mixture (~2:3) of compounds **4c** and **5b** after a short time (~1 h), according to data of ^{1}H NMR spectra.

TABLE 1. Physicochemical Characteristics of the Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %			mp, °C	Yield, %
		C	H	N		
2c	$C_{33}H_{22}N_2O_2S$	77.55 / 77.62	4.33 / 4.34	5.53 / 5.49	153-154	85
2d	$C_{32}H_{22}N_2O_3S$	74.63 / 74.69	4.25 / 4.31	5.54 / 5.44	185-186	60
2e	$C_{33}H_{21}BrN_2O_2S$	67.33 / 67.24	3.50 / 3.59	4.58 / 4.75	203-204	80
2h	$C_{22}H_{18}N_2O_3S_2$	62.67 / 62.54	4.37 / 4.29	6.54 / 6.63	169-170	70
2i	$C_{18}H_{16}N_2O_2S$	66.75 / 66.64	5.06 / 4.97	8.77 / 8.64	161-162	50
2j	$C_{19}H_{18}N_2O_3S$	64.47 / 64.39	4.98 / 5.12	7.82 / 7.90	166-167	45
3c	$C_{33}H_{24}N_2O_2S$	77.43 / 77.32	4.58 / 4.72	5.39 / 5.46	257-258	90
3d	$C_{32}H_{24}N_2O_3S$	74.52 / 74.40	4.81 / 4.68	5.56 / 5.42	200-201	70
3e	$C_{33}H_{23}BrN_2O_2S$	67.13 / 67.01	3.99 / 3.92	4.59 / 4.74	222-223	90
3f	$C_{21}H_{18}N_2O_3S$	66.57 / 66.65	4.91 / 4.79	7.50 / 7.40	137-138	85
3h	$C_{22}H_{20}N_2O_3S_2$	62.33 / 62.24	4.68 / 4.75	6.68 / 6.60	165-166	80
3i	$C_{18}H_{18}N_2O_2S$	66.27 / 66.23	5.66 / 5.58	8.66 / 8.58	178-179	73
3j	$C_{19}H_{20}N_2O_3S$	64.07 / 64.02	5.56 / 5.66	7.75 / 7.86	133-134	72
4a	$C_{28}H_{24}N_2O_2S$	74.25 / 74.31	5.21 / 5.35	6.30 / 6.19	229-230	80
4b	$C_{29}H_{26}N_2O_3S$	72.22 / 72.17	5.52 / 5.43	5.93 / 5.80	204-205	75
4c	$C_{38}H_{28}N_2O_2S$	79.27 / 79.14	4.85 / 4.89	4.71 / 4.86	198-199	71
4d	$C_{37}H_{28}N_2O_3S$	76.64 / 76.53	4.76 / 4.86	4.86 / 4.82	218-219	60
4e	$C_{38}H_{27}BrN_2O_2S$	69.73 / 69.62	4.02 / 4.15	4.37 / 4.27	>135 (decomp.)	65
4f	$C_{26}H_{22}N_2O_3S$	70.71 / 70.57	5.13 / 5.01	6.40 / 6.33	229-230	95
4g	$C_{27}H_{24}N_2O_4S$	68.57 / 68.62	5.01 / 5.12	5.83 / 5.93	144-145	80
4h	$C_{27}H_{24}N_2O_3S_2$	66.49 / 66.37	4.84 / 4.95	5.81 / 5.73	197-198	82
4i	$C_{23}H_{22}N_2O_2S$	70.65 / 70.74	5.78 / 5.68	7.26 / 7.17	187-188	30
5a	$C_{29}H_{28}N_2O_4S$	69.69 / 69.58	5.55 / 5.64	5.69 / 5.60	132-133	27
5b	$C_{38}H_{30}N_2O_3S$	76.78 / 76.74	4.99 / 5.08	4.63 / 4.71	169-170	32
5c	$C_{37}H_{30}N_2O_4S$	74.33 / 74.23	4.97 / 5.05	4.81 / 4.68	181-182	25
5d	$C_{27}H_{26}N_2O_5S$	66.22 / 66.10	5.23 / 5.34	5.64 / 5.71	121-122	35
5e	$C_{27}H_{26}N_2O_4S_2$	63.93 / 64.01	5.27 / 5.17	5.59 / 5.53	171-172	40
7a	$C_{21}H_{20}N_2OS$	72.49 / 72.38	5.91 / 5.79	7.94 / 8.04	178-179	67
7b	$C_{22}H_{22}N_2O_2S$	69.88 / 69.81	5.77 / 5.86	7.48 / 7.40	>230 (sublimed)	40

TABLE 2. IR Spectra of the Synthesized Compounds

Compound	IR spectrum, ν, cm^{-1}	Compound	IR spectrum, ν, cm^{-1}
2c	3230 (NH), 1645 (C=O)	**4c**	3272 (NH), 1652 (C=O)
2d	3369 (NH), 1676 (C=O)	**4d**	3267 (NH), 3147-3029 (C–H arom.), 1645 (C=O)
2e	3209 (NH), 1651 (C=O)	**4e**	3636–3100 (NH), 3057 (C–H arom.), 1665 (C=O)
2h	3354 (NH), 1666 (C=O), 1625 (C=O)	**4f**	3471–3150 (NH), 3028 (C–H arom.), 1650 (C=O)
2i	3245 (NH), 1662 (C=O), 1645 (C=O)	**4g**	3251 (NH), 3058 (C–H arom.), 1672 (C=O)
2j	3431, 3134 (NH), 1697 (C=O), 1635 (C=O)	**4h**	3286 (NH), 3093-3027 (C–H arom.), 1637 (C=O)
3c	3232 (OH), 1630 (C=O)	**4i**	3272 (NH), 1654 (C=O)
3d	3380 (OH), 1647 (C=O)	**5a**	3330 (NH), 1710 (C=O ketone), 1668 (C=O amide)
3e	3384 (OH), 3217, 3185 (NH), 1626 (C=O)	**5b**	3423 (NH), 1716 (C=O ketone), 1701 (C=O ketone), 1682 (C=O amide)
3f	3245 (NH), 1655 (C=O)	**5c**	3305 (NH), 1710 (C=O ketone), 1647 (C=O amide)
3h	3240 (OH), 1633 (C=O)	**5d**	3270 (NH), 1714 (C=O ketone), 1673 (C=O amide)
3i	3280–3120 (br. peak, NH and OH), 1652 (C=O)	**5e**	3373 (NH), 1701 (C=O ketone), 1655 (C=O amide)
3j	3384 (OH), 3230, 3185 (NH), 1654 (C=O)	**7a**	3262 (NH), 1715 (C=O)
4a	3278 (NH), 3122-3093 (C–H arom.), 1648 (C=O)	**7b**	3485 (NH), 1712 (C=O)
4b	3278 (NH), 3122-3062 (C–H arom.), 1654 (C=O)		

Diketones **5a-e** were colorless crystalline substances (Table 1). Bands were present in the IR spectra of these compounds for the stretching vibrations of three carbonyl groups, two ketones at 1701-1716 and an amide in the region of 1647-1682 cm^{-1} (Table 2). In the ^{1}H NMR spectra there were two triplet signals for methylene protons at 2.6-2.9 ppm having a vicinal coupling constant ^3J = 5.8-6.4 Hz, and a singlet signal for the protons of the acetyl group at 2.0-2.1 ppm (Table 3). Formally the diastereotopic protons of the methylene unit of the methoxymethyl group of compounds **5a,d,e** resonate in NMR spectra as homotopic as a two-proton singlet at 4.7-4.8 ppm. It is possible that this is due to a rapidly proceeding inversion of the asymmetric center as a result of keto-enol tautomerism involving the hydrogen atom of the methine unit and the carbonyl group neighboring it.

The molecular ions of compounds **5** are unstable and are not confirmed in the mass spectra (Table 4). They are decomposed by two routes (Scheme 7) at the one bond between the methine carbon atom and the neighboring carbonyl group, which indicates the localization of charge and spin precisely on the oxygen atom of the "inner" carbonyl group.

Scheme 7

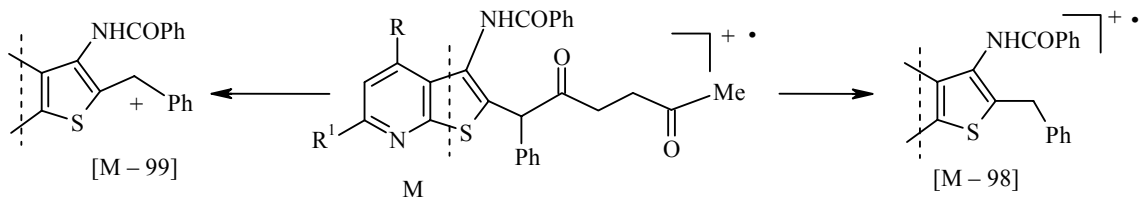


TABLE 3. ^{1}H NMR Spectra of the Synthesized Compounds

Com-pound	Chemical shifts, δ, ppm, SSCC (*J*, Hz)
1	2
2c	6.95 (4H, d, *J* = 7.3, *o*-H 4-, 6-Ph); 7.11-7.60 (12H, m, *m*-, *p*-H 4-, 6-Ph, PhCO, PhCN); 7.75 (2H, d, *J* = 6.8, *o*-H PhCO); 7.92 (1H, s, H-5); 8.30 (2H, d, *J* = 7.8, *o*-H PhCON); 9.56 (1H, s, NH)
2d	1.81 (3H, s, CH_3); 6.09 (1H, d, *J* = 2.9, H-4 methylfuryl); 7.02 (1H, d, *J* = 2.9, H-3 methylfuryl); 7.25-7.65 (11H, m, H arom); 7.78 (2H, d, *J* = 2.8, *o*-H PhCON); 8.13 (1H, s, H-5); 8.30 (2H, d, *J* = 8.3, *o*-H PhCO); 10.14 (1H, s, NH)
2e	6.96 (2H, d, *J* = 7.3, *o*-H C_6H_4Br-4); 7.22 (2H, t, *J* = 8.1, *m*-H 6-Ph); 7.30-7.46 (9H, m, H arom); 7.55 (2H, d, *J* = 7.3, *m*-H C_6H_4Br-4); 7.74 (2H, d, *J* = 7.3, *m*-H PhCO); 7.95 (1H, s, H-5); 8.30 (2H, d, *J* = 7.3, *o*-H PhCON); 9.70 (1H, s, NH)
2h	2.50 (3H, s, 4-CH_3); 3.32 (3H, s, OCH_3); 4.92 (2H, s, OCH_2); 7.10 (1H, t, *J* = 3.9, H-3 thenoyl); 7.32-7.49 (5H, m, 2 *m*-H, *p*-H PhCO, H-5, H-4 thenoyl); 7.57 (1H, d, *J* = 3.4, H-5 thenoyl); 7.77 (2H, d, *J* = 7.8, *o*-H PhCON); 10.24 (1H, s, NH)
2i	1.50 (3H, s, CH_3CO); 2.57 (3H, s, 4-CH_3); 2.62 (3H, s, 6-CH_3); 7.19 (1H, s, H-5); 7.52 (2H, t, *J* = 7.3, C_6H_5); 7.62-7.74 (3H, m, C_6H_5); 9.76 (1H, s, NH)
2j	1.52 (3H, s, CH_3CO); 2.63 (3H, s, 6-CH_3); 3.95 (3H, s, OCH_3); 4.92 (2H, s, OCH_2); 7.43 (1H, s, H-5); 7.52 (2H, t, *J* = 8.1, C_6H_5); 7.60-7.70 (3H, m, C_6H_5); 9.82 (1H, s, NH)
3c	6.12 (1H, d, *J* = 4.4, C<u>H</u>OH); 6.44 (1H, d, *J* = 4.4, OH); 7.06-7.54 (18H, m, H arom); 7.74 (1H, s, H-5); 8.15-8.26 (2H, m, H PhCO); 9.54 (1H, s, NH)
3d	1.96 (3H, s, CH_3 methylfuryl); 6.00 (1H, d, *J* = 4.39, C<u>H</u>OH); 6.22 (1H, br. s, OH); 6.50 (1H, d, *J* = 2.4, H-4 methylfuryl); 6.88 (1H, d, *J* = 2.4, H-3 methylfuryl); 7.25 (2H, d, *J* = 7.3, *m*-H PhCON); 7.36-7.65 (9H, m, H arom); 7.80 (2H, d, *J* = 7.3, *o*-H <u>Ph</u>CH)); 7.96 (1H, s, H-5); 8.20 (2H, d, *J* = 6.8, *m*-H 6-Ph); 9.97 (1H, s, NH)
3e	6.13 (1H, d, *J* = 4.4, C<u>H</u>OH); 6.50 (1H, d, *J* = 4.4, OH); 7.15-7.56 (17H, m, H arom); 7.76 (1H, s, H-5); 8.19 (2H, d, *J* = 6.6, *m*-H PhCO); 9.62 (1H, s, NH)
3f	2.47 (6H, s, 4-, 6-CH_3); 6.02 (1H, d, *J* = 4.4, C<u>H</u>OH); 6.36 (1H, d, *J* = 4.4, OH); 6.72 (1H, s, H-3 furoyl); 7.02 (1H, s, H-5); 7.17-7.34 (4H, m, 3H Ph, H-4 furoyl); 7.37 (2H, d, *J*= 6.6, *o*-H arom); 7.95 (1H, s, H-2 furoyl); 9.97 (1H, br. s, NH)
3h	2.6 (3H, s, 6-CH_3); 3.27 (3H, s, OCH_3); 4.74 (1H, d, *J* = 14.4, OCH_2); 4.76 (1H, d, *J* = 14.4, OCH_2); 6.03 (1H, d, *J* = 2.9, C<u>H</u>OH); 6.51 (1H, d, *J* = 2.9, OH); 7.21-7.41 (7H, m, 5 H Ph, <u>H</u>-5, H-4 thenoyl); 7.91 (1H, d, *J* = 4.4, H-3 thenoyl); 7.96 (1H, d, *J* = 3.4, H-5 thenoyl); 10.04 (1H, s, NH)
3i	2.03 (3H, s, CH_3CO); 3.35 (6H, s, 4-, 6-CH_3); 5.98 (1H, d, *J* = 3.7, C<u>H</u>OH); 6.36 (1H, d, *J* = 3.7, OH); 7.00 (1H, s, H-5); 7.2 -7.4 (5H, m, C_6H_5); 9.51 (1H, s, NH)
3j	2.04 (3H, s, CH_3CO); 2.55 (3H, s, 6-CH_3); 3.35 (3H, s, OCH_3); 4.75 (1H, d, *J* = 14.7, OCH_2); 4.77 (1H, d, *J* = 14.7, OCH_2); 5.96 (1H, d, *J* = 3.7, C<u>H</u>OH); 6.40 (1H, d, *J* = 3.7, OH); 7.22-7.42 (6H, m, C_6H_5, H-5); 9.44 (1H, s, NH)
4a	2.21 (3H, s, CH_3 methylfuryl); 2.5 (6H, s, 4-, 6-CH_3); 5.85 (1H, s, PhC<u>H</u>); 6.01 (1H, d, *J* = 3.1, H-4 methylfuryl); 6.06 (1H, d, *J* = 3.1, H-3 methylfuryl); 7.06 (1H, s, H-5); 7.26 (2H, d, *J* = 7.94, *o*-H PhCON); 7.30-7.35 (3H, m, *o*-, *p*-H PhCH); 7.51-7.65 (3H, m, *m*-, *p*-H PhCON); 7.97 (2H, d, *J* = 7.9, *m*-H <u>Ph</u>CH); 10.13 (1H, s, NH)
4b	2.22 (3H, s, CH_3 methylfuryl); 2.58 (3H, s, 6-CH_3); 3.28 (3H, s, OCH_3); 4.76 (1H, d, *J* = 14.0, OCH_2); 4.79 (1H, d, *J* = 14.0, OCH_2); 5.86 (1H, s, PhC<u>H</u>); 6.0 (1H, d, *J* = 2.8, H-4 methylfuryl); 6.10 (1H, d, *J* = 2.8, H-3 methylfuryl); 7.3 (6H, m, C_6H_5, H-5); 7.52-7.66 (3H, m, *m*-, *p*-H PhCON); 7.97 (2H, d, *J* = 7.4, *o*-H PhCH); 10.02 (1H, s, NH)
4c	2.2 (3H, s, CH_3 methylfuryl); 5.92 (1H, s, PhC<u>H</u>); 6.04 (1H, d, *J* = 2.9, H-4 methylfuryl); 6.10 (1H, d, *J* = 2.9, H-3 methylfuryl); 7.02-7.55 (18H, m, H arom); 7.76 (1H, s, H-5); 8.19 (2H, d, *J* = 6.4, *o*-H <u>Ph</u>CH); 9.65 (1H, s, NH)
4d	1.89 (3H, s, CH_3 methylfuryl-CH); 2.23 (3H, s, CH_3 4-methylfuryl); 6.02 (1H, s, PhC<u>H</u>); 6.10 (2H, d, *J* = 2.9, methylfuryl-CH); 6.90 (2H, d, *J* = 2.9, CH_3 4-methylfuryl); 7.21-7.35 (5H, m, H arom); 7.41-7.59 (6H, m, H arom); 7.77 (2H, d, *J* = 7.3, *o*-H <u>Ph</u>CH); 7.97 (1H, s, H-5); 8.18 (2H, d, *J* = 6.6, *o*-H PhCON); 10.08 (1H, s, NH)
4e	2.23 (3H, s, CH_3 methylfuryl); 5.94 (1H, s, PhC<u>H</u>); 6.02 (1H, d, *J* = 2.9, H-4 methylfuryl); 6.10 (1H, d, *J* = 2.9, H-3 methylfuryl); 7.22-7.58 (17H, m, H arom); 7.75 (1H, s, H-5); 8.18 (2H, d, *J* = 5.9, *o*-H PhCON); 9.57 (1H, s, NH)

TABLE 3 (continued)

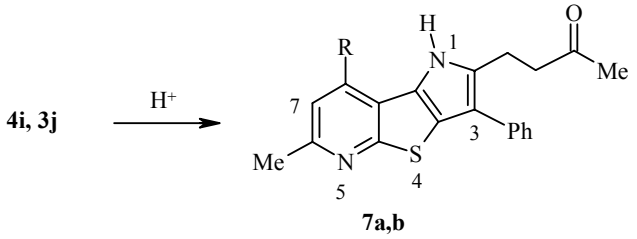
1	2
4f	2.2 (3H, s, CH_3 methylfuryl); 2.5 (6H, s, 4,6-CH_3); 5.81 (1H, s, PhC<u>H</u>); 6.02 (1H, d, *J* = 2.9, H-4 methylfuryl); 6.06 (1H, d, *J* = 2.9, H-3 methylfuryl); 6.71 (1H, d, *J* = 3.5, H-4 furoyl); 7.05 (1H, dd, *J* = 3.5, *J* = 1.9, H-3 furoyl); 7.20-7.38 (6H, m, C_6H_5, H-5); 7.94 (1H, d, *J* = 1.9, H-5 furoyl); 10.03 (1H, s, NH)
4g	2.22 (3H, s, CH_3 methylfuryl); 2.6 (3H, s, 6-CH_3); 3.27 (3H, s, OCH_3); 4.74 (1H, d, *J* = 14.2, OCH_2); 4.78 (1H, d, *J* = 14.2, OCH_2); 5.82 (1H, s, PhC<u>H</u>); 6.00 (1H, d, *J* = 2.9, H-4 methylfuryl); 6.06 (1H, d, *J* = 2.9, H-3 methylfuryl); 6.73 (1H, dd, *J* = 1.5, *J* = 3.9, H-4 furoyl); 7.21-7.36 (7H, m, 5H Ph, H-5, H-3 furoyl); 7.96 (1H, d, *J* = 1.5, H-5 furoyl); 9.98 (1H, s, NH)
4h	2.22 (3H, s, CH_3 methylfuryl); 2.6 (3H, s, 6-CH_3); 3.27 (3H, s, OCH_3); 4.76 (1H, d, *J* = 14.2, OCH_2); 4.78 (1H, d, *J* = 14.2, OCH_2); 5.82 (1H, s, PhC<u>H</u>); 6.03 (1H, d, *J* = 2.9, H-4 methylfuryl); 6.07 (1H, d, *J* = 2.9, H-3 methylfuryl); 7.21-7.37 (7H, m, C_6H_5, H-5, H-4 thenoyl); 7.88 (1H, d, *J* = 4.9, H-3 thenoyl); 7.97 (1H, d, *J* = 3.9, H-5 thenoyl); 10.08 (1H, s, NH)
4i	2.04 (6H, s, CH_3CO, CH_3 methylfuryl); 2.23 (6H, s, 4-, 6-CH_3); 5.77 (1H, s, PhC<u>H</u>); 6.02 (1H, d, *J* = 3.2, H-4 methylfuryl); 6.04 (1H, d, *J* = 3.2, H-3 methylfuryl); 7.03 (1H, s, H-5); 7.21-7.38 (5H, m, C_6H_5); 9.57 (1H, s, NH)
5a	2.07 (3H, s, CH_3CO); 2.63 (2H, t, *J* = 6.4, CH_2CO); 2.82 (2H, t, *J* = 6.4, C<u>H</u>$_2$$CH_2CO$); 3.3 (3H, s, OCH_3); 4.76 (2H, s, OCH_2); 5.71 (1H, s, PhC<u>H</u>); 7.31 (2H, d, *J* = 10.9, *o*-H <u>Ph</u>CH); 7.55-7.71 (6H, m, H arom); 8.07 (2H, d, *J* = 6.4, *o*-H PhCO); 10.09 (1H, s, NH)
5b	2.07 (3H, s, CH_3); 2.64 (2H, t, *J* = 6.4, CH_2CO); 2.84 (2H, t, *J* = 6.4, C<u>H</u>$_2$$CH_2CO$); 5.74 (1H, s, C<u>H</u>Ph); 7.02-7.58 (18H, m, H arom); 7.75 (1H, s, H-5); 8.20 (2H, d, *J* = 6.4, *o*-H PhCO); 9.63 (1H, s, NH)
5c	1.86 (1H, s, CH_3 methylfuryl); 2.07 (3H, s, CH_3CO); 2.65 (2H, t, *J* = 5.9, CH_2CO); 2.85 (2H, t, *J* = 5.9, C<u>H</u>$_2$$CH_2CO$); 5.85 (1H, s, PhC<u>H</u>); 6.01 (1H, d, *J* = 3.7, H-4 methylfuryl); 6.9 (1H, d, *J* = 3.7, H-3 methylfuryl); 7.28-7.37 (2H, m, *o*-H <u>Ph</u>CH); 7.44-7.63 (9H, m, H arom); 7.87 (2H, d, *J* = 6.6, *o*-H 6-Ph); 7.95 (1H, s, H-5); 8.18 (2H, d, *J* = 7.3, *o*-H PhCO); 10.07 (1H, s, NH)
5d	2.07 (3H, s, CH_3CO); 2.63 (2H, t, *J* = 6.9, CH_2CO); 2.81 (2H, t, *J* = 6.9, C<u>H</u>$_2$$CH_2CO$); 3.28 (3H, s, OCH_3); 4.74 (2H, s, OCH_2); 5.69 (1H, s, PhC<u>H</u>); 6.76 (1H, dd, *J* = 3.0, *J* = 1.5, H-4 furoyl); 7.25-7.42 (7H, m, C_6H_5, H-5, H-3 furoyl); 8.00 (1H, d, *J* = 1.5, H-5 furoyl); 9.99 (1H, s, NH)
5e	2.06 (3H, s, CH_3CO); 2.63 (2H, t, *J* = 5.9, CH_2CO); 2.78 (2H, t, *J* = 5.9, C<u>H</u>$_2$$CH_2CO$); 3.3 (3H, s, OCH_3); 4.75 (2H, s, OCH_2); 5.69 (1H, s, PhC<u>H</u>); 7.24-7.39 (7H, m, C_6H_5, H-5, H-4 thenoyl); 7.92 (1H, d, *J* = 4.4, H-3 thenoyl); 8.04 (1H, s, H-5 thenoyl); 10.09 (1H, s, NH)
7a	2.11 (3H, s, CH_3CO); 2.70 (6H, s, 6-, 8-CH_3); 2.92 (2H, t, *J* = 7.3, C<u>H</u>$_2$$CH_2CO$); 3.12 (2H, t, *J* = 7.3, CH_2CO); 7.06 (1H, s, H-7); 7.25-7.29 (2H, m, C_6H_5); 7.43-7.57 (3H, m, C_6H_5); 11.46 (1H, s, NH)
7b	2.13 (3H, s, CH_3CO); 2.59 (3H, s, 8-CH_3); 2.94 (2H, t, *J* = 6.6, C<u>H</u>$_2$$CH_2CO$); 3.09 (2H, t, *J* = 6.6, CH_2CO); 3.46 (3H, s, OCH_3); 4.93 (2H, s, OCH_2); 7.27-7.33 (2H, m, C_6H_5); 7.45-7.53 (4H, m, 3 H arom, H-7); 11.33 (1H, s, NH)

As a result two reactions classical for mass spectrometry take place: dissociation with cleavage of an acyl radical and the formation of a cation [M-99] and rearrangement with elimination of a molecule of ketene and the formation of an odd-electron fragment [M-98]. The latter discards an acyl radical giving a stable aminohetarylphenylmethyl cation [M-98-R^2CO].

In difference to compounds **4b-d,g,h** acetylamino derivative **4i** under the same conditions is smoothly converted into the corresponding recyclization and deacetylation product, a derivative of pyrrolothienopyridine **7a** (Scheme 8). We note that a similar transformation, including the two reactions, was observed by us previously for aromatic analogs [7, 16, 17]. The conversion **4i** → **7a** occurs in ethanol in a shorter time and with a higher yield than in acetic acid.

Compound **7b** was obtained from the corresponding alcohol **3j** on attempting to synthesize methane **4j** in dioxane in the presence of $HClO_4$. A significant quantity of the recyclization and deacetylation product **7b** was rapidly formed in this way mixed with the intermediate methane **4j**, isolation of which from the reaction mixture was unsuccessful.

Scheme 8



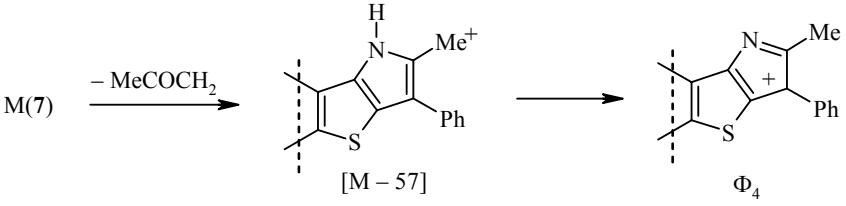
7a,b

7 a R = Me, **b** R = CH_2OMe

The pyrrolothienopyridines **7a,b** were pale-yellow crystalline substances (Table 1). In the IR spectra there was one narrow intense absorption band for the stretching vibrations of the ketonic carbonyl group at 1700-1712 cm^{-1} (Table 2). The methylene protons of the 3-oxobutyl substituent resonate as two triplets with vicinal coupling constant 5.5-7.5 Hz at 2.9-3.1 ppm, and the protons of the terminal methyl group as a singlet (2.1 ppm). The signal of the NH group proton is found at low field (11.3-11.5 ppm).

The molecular ions of compounds **7** were fairly stable (Table 4). The characteristic process of their fragmentation is simple cleavage of the β-carbon–carbon bond in the 3-oxobutyl substituent which leads to a cation of the "benzyl" type [M-57] (Scheme 9), possibly being isomerized into the even more stable ion **Φ4**.

Scheme 9



The intensity of the [M-57] ion in the spectrum was maximal, its fragmentation did not lead to any ion comparable in stability. Competing with the [M-57] ion is the acetonyl cation with *m/z* 57, which has an intensity less than 20%.

The conversions considered above of compounds **4** in acidic medium indicate that the character of the protecting acyl group at the amine nitrogen determines the possibility or impossibility of carrying out cyclization following protolytic opening of the furan ring. It is possible that in this case the difference in basicity of benzoyl- and acetylamides is displayed, which on the whole leads to a different result for the reaction.

EXPERIMENTAL

The IR spectra were recorded on a Infralyum FT-2 spectrometer (nujol suspensions), the ^1H NMR spectra on a Bruker AC 200 instrument (200 MHz) in DMSO-d_6 and $CDCl_3$, internal standard was TMS. The mass spectra were obtained on a Finnigan MAT INCO S50 instrument with direct insertion of samples into the ion source (energy of ionizing electrons was 70 eV, temperature of ionization chamber was 56-180°C).

TABLE 4. Mass Spectra of the Synthesized Compounds

Compound	m/z (I_{rel}, %)
1	2
2c	510 (32), 405 (15), 105 (100), 76 (35), 43 (27)
2d	514 (30), 409 (17), 105 (100), 101 (38), 77 (27), 59 (38) 43 (24)
2e	588* (48), 483 (28), 105 (94), 77 (100), 60 (16), 55 (22), 43 (27)
2h	422 (57), 317 (48), 311 (24), 295 (10), 285 (15), 111 (100), 105 (81), 76 (29), 59 (21), 43 (18), 42 (11)
2i	324 (29), 281 (100), 121 (11), 105 (13), 59 (25), 43 (49)
2j	354 (63), 312 (66), 311 (56), 298 (27), 297 (82), 279 (34), 249 (65), 175 (33), 105 (100), 77 (91), 59 (36), 43 (62), 42 (42)
3c	510 [M–H_2] (1), 496 [M–16] (46), 391 [M–121] (48), 389 ([M–H_2–121]), 178 (13), 105 (100), 101 (30), 77 (51), 55 (24), 43 (53), 42 (44)
3d	500 [M–16] (28), 395 [M–121] (100), 393 [M–H_2–121] (20), 105 (82), 77 (38), 59 (40), 57 (17), 55 (12), 43 (41)
3e	574* [M–16] (15), 469* [M–121] (33), 105 (100), 91 (46), 77 (95), 59 (41), 43 (64)
3f	378 (5), 360 [M–H_2O] (3), 267 [M–111] (100), 190 [M–111] (61), 105 (38), 95 (73), 77 (36), 51 (12), 39 (35)
3h	406 [M–H_2O] (27), 392 [M–CH_3OH] (14), 376 [M–CH_2O] (24), 281 [M–CH_3OH–111] (13), 111 (100), 105 (48), 95 (10), 77 (11), 57 (19), 43 (38)
3i	326 (0.7), 308 [M–H_2O] (20), 293 [M–H_2O–CH_3] (40), 267 [M–59] (100), 265 [M–59–H_2] (98), 251 [M–H_2O–CH_3NCO] (12), 105 (21), 101 (10), 80 (38), 76 (17), 59 (24), 43 (59), 42 (43)
3j	338 [M–H_2O] (15), 323 [M–H_2O–CH_3] (45), 308 [M–H_2O–CH_2O] (25), 297 [M–59] (28), 281 [M–H_2O–CH_3NCO] (100), 265 (43), 91 (45), 77 (45), 59 (71), 43 (69)
4a	452 (7), 347 (42), 332 (19), 331 (13), 305 (13), 183 (10), 171 (14), 155 (11), 141 (12), 107 (14), 105 (100), 101 (21), 83 (13), 78 (13), 77 (74), 60 (14), 57 (36), 56 (13), 55 (25), 43 (19)
4b	450 [M–CH_3OH] (50), 407 (13), 377 [M–105] (6), 345 [M–CH_3OH–105] (13), 302 (10), 171 (5), 105 (100), 77 (34), 59 (40), 43 (35)
4c	576 (46), 472 (100), 457 (11), 180 (16), 105 (27), 101 (34), 95 (27), 76 (15), 59 (35), 57 (16), 55 (15), 43 (41), 42 (21), 41 (20)
4d	580 (8), 475 (100), 433 (23), 171 (17), 141 (12), 105 (97), 101 (36), 84 (20), 83 (25), 78 (10), 77 (61), 73 (13), 70 (10), 60 (12), 59 (35), 58 (14), 57 (29), 56 (25), 55 (26), 43 (43), 42 (27), 41 (18), 39 (19), 38 (14)
4e	654* (8), 613* (17), 549* (56), 507* (9), 171 (5), 105 (100), 101 (11), 59 (30), 58 (30), 57 (13), 56 (16), 51 (13), 45 (15), 44 (36), 43 (51)
4f	442 (71), 425 (11), 399 (19), 347 (86), 332 (69), 305 (22), 272 (13), 268 (13), 171 (17), 105 (13), 101 (55), 98 (31), 95 (98), 93 (15), 82 (14), 70 (15), 69 (17), 59 (100), 57 (55), 56 (36), 55 (26), 53 (15), 45 (10), 43 (88), 41 (37), 39 (47)
4g	440 [M–CH_3OH] (100), 411 (41), 397 (27), 377 (12), 372 (17), 370 (12), 329 (13), 301 (14), 171 (9), 149 (11), 105 (29), 95 (86), 76 (12), 59 (50), 57 (31), 56 (17), 55 (22), 43 (57), 42 (36), 41 (18), 39 (30), 38 (21)
4h	488 (0.5), 456 [M–CH_3OH] (78), 413 (24), 377 (16), 345 (15), 329 (14), 301 (10), 171 (8), 111 (100), 105 (15), 82 (16), 59 (15), 39 (11)
4i	390 (82), 374 (12), 347 (100), 332 (88), 305 (49), 303 (18), 291 (28), 289 (18), 271 (11), 265 (19), 229 (12), 184 (17), 183 (10), 178 (20), 171 (37), 165 (11), 155 (12), 141 (32), 139 (10), 127 (15), 115 (13), 105 (25), 101 (16), 76 (14), 59 (21), 53 (16), 51 (10), 44 (29), 43 (54), 42 (40), 41 (26)
5a	402 [M–98] (65), 372 (12), 371 (29), 370 (16), 297 (7), 265 (13), 105 (100), 95 (21), 77 (8), 76 (75), 59 (31), 57 (13), 55 (13), 53 (12), 43 (33), 42 (11), 39 (12)
5b	496 [M–98] (44), 495 [M–99] (12), 391 [M–98–105] (22), 105 (100), 101 (15), 95 (11), 82 (16), 76 (38), 59 (24), 57 (16), 43 (35), 42 (24), 41 (18), 39 (16)
5c	500 [M–98] (12), 499 [M–99] (22), 396 (23), 395 (21), 105 (100), 101 (35), 99 (22), 83 (21), 78 (14), 77 (75), 59 (31), 57 (27), 56 (15), 55 (27), 43 (27), 42 (20), 40 (11), 39 (14), 38 (14)
5d	392 [M–98] (20), 391 [M–99] (16), 360 [M–98–CH_3OH] (100), 95 (42), 59 (13), 44 (12), 43 (16)

TABLE 4 (continued

1	2
5e	408 [M–98] (12), 377 [M–98–CH_3O] (21), 376 [M–98–CH_3OH] (36), 297 [M–98–111] (18), 265 (15), 252 (11), 181 (10), 180 (14), 179 (29), 164 (21), 113 (21), 111 (100), 101 (17), 99 (24), 91 (11), 84 (15), 83 (16), 81 (12), 77 (11), 71 (17), 59 (29), 57 (19), 56 (17), 55 (10), 53 (13), 46 (12), 45 (44), 41 (20)
7a	348 (44), 291 (100), 151 (15), 145 (15), 128 (29), 115 (30), 101 (26), 89 (11), 76 (26), 66 (11), 59 (16), 58 (40), 57 (12), 51 (24), 45 (14), 44 (12), 43 (56), 42 (29), 41 (26)
7b	378 (100), 346 (5), 321 (98), 303 (37), 289 (66), 274 (29), 101 (44), 59 (62), 43 (72)

*Peaks are given for the light ^{79}Br isotope.

A check on the progress of reactions and the homogeneity of substances was carried out by TLC on Sorbfil plates, eluent was methylene chloride–acetone–petroleum ether, 4.5:7:14. Visualization was with iodine or bromine vapor.

N-(2-Benzoyl-4,6-disubstituted[2,3-*b*]pyrid-3-yl)amides 2a,b,f,g were synthesized as described previously in [15].

N-(2-Benzoyl-4,6-diphenylthieno[2,3-*b*]pyrid-3-yl)benzamide (2c). Benzoyl chloride (1.2 g, 8.8 mmol) was added to a hot solution of amine **1c** (3 g, 7.4 mmol) in chlorobenzene (50 ml). The reaction mixture was boiled for 16 h. The crystals precipitated on cooling were filtered off, dried, and recrystallized from ethanol. Colorless crystals of compound **2c** (3.2 g) were obtained.

Compounds 2d,e were obtained analogously from amines **1d,e**, thenoyl-substituted **2h** from amine **1h** and thiophene-2-carboxylic acid chloride, and compounds **2i,j** from amines **1ij** and acetyl chloride in dioxane.

N-{2-[Hydroxy(phenyl)methyl]-4,6-disubstituted[2,3-*b*]pyrid-3-yl}amides 3a,b,g were obtained by the reduction of ketones **2a,b,g** with $NaBH_4$ by the procedure of [15].

N-{2-[Hydroxy(phenyl)methyl]-4,6-diphenylthieno[2,3-*b*]pyrid-3-yl}benzamide (3c). Compound **2c** (2.7 g, 5.3 mmol) was dissolved in ethanol (50 ml) by heating with constant stirring. $NaBH_4$ (0.24 g, 6.4 mmol) was added in portions to the obtained solution. The reaction mixture was maintained at 60-70°C for 3 h, then cooled, and poured into H_2O (250-300 ml) with vigorous stirring. The precipitated crystals were filtered off, dried, and recrystallized from ethanol. Compound **3c** (2.4 g) was obtained as colorless crystals.

Compounds 3d-f,h-j were obtained analogously from the appropriate acyl derivatives **2d-f,h-j**.

N-{2-[(5-Methyl-2-furyl)(phenyl)methyl]-4,6-dimethylthieno[2,3-*b*]pyrid-3-yl}benzamide (4a). Catalyst (0.3 ml), prepared from 70% perchloric acid (2 ml, 3.3 mmol), acetic anhydride (5.3 ml, 5.6 mmol), and acetic acid (3 ml, 5.2 mmol), was added to a solution of alcohol **3a** (0.2 g, 5 mmol) and α-methylfuran (0.67 ml, 7.5 mmol) in dioxane (20 ml). The mixture obtained was boiled for 4 h until complete consumption of the initial alcohol (check by TLC), then the mixture was poured into water (100 ml), and neutralized with dry $NaHCO_3$ to pH ≈ 7. The precipitated crystalline solid was filtered off, dried, and recrystallized with silica gel from an ethyl acetate–petroleum ether, 2:1 mixture. Compound **3a** (0.18 g) was obtained as colorless crystals.

Compounds 4b-i were obtained analogously from alcohols **3b-i**.

N-[2-(2,5-Dioxo-1-phenylhexyl)-4,6-diphenylthieno[2,3-*b*]pyrid-3-yl]benzamide (5b). Concentrated HCl (1 ml) was added to a solution of compound **4c** (1.0 g, 1.7 mmol) in glacial acetic acid (20 ml) and the mixture boiled for 3 h. After the equilibrium **4c** ↔ **5b** had been established (check by TLC) the reaction mixture was poured into water (50 ml), and neutralized with dry $NaHCO_3$ to pH ≈ 7. The precipitated crystalline solid was filtered off and dried. A mixture (0.96 g) of compounds **4c** and **5b** (according to ^1H NMR data) was obtained. Product **5b** (0.32 g) was isolated as colorless crystals by chromatography on a column (2×20 cm, silica gel 40-100 mesh, eluent acetone–petroleum ether–methylene chloride, 7:28:4.5).

Compounds 5a,c-e were obtained analogously from amides **4b,d,g,h**.

4-(6,8-Dimethyl-3-phenyl-1H-pyrrolo[2',3':4,5]thieno[2,3-*b*]pyrid-2-yl)butan-2-one (7a). A. A solution of compound **4i** (0.5 g, 1.28 mmol) in acetic acid (10 ml) and HCl (0.5 ml) was maintained at 40-50°C for 18 h (check by TLC). The reaction mass was poured into water (100 ml) and neutralized with dry $NaHCO_3$ to pH ≈ 7. The precipitated crystalline solid was filtered off, dried, and recrystallized from alcohol with the addition of activated carbon. Compound **7a** (0.2 g, 45%) was obtained as colorless crystals.

B. A solution of compound **4i** (0.7 g, 1.8 mmol) in ethyl alcohol (20 ml) saturated with dry HCl was boiled for 5 h (check by TLC), then poured into water (70 ml), and neutralized with dry $NaHCO_3$ to pH ≈ 7. The precipitated crystalline solid was filtered off, dried, and recrystallized from chloroform with addition of silica gel. Compound **7a** (0.42 g, 67%) was obtained as pale-yellow crystals.

4-(8-Methoxymethyl-6-methyl-3-phenyl-1H-pyrrolo[2',3':4,5]thieno[2,3-*b*]pyrid-2-yl)butan-2-one (7b). A solution of alcohol **3j** (0.8 g, 2.2 mmol), α-methylfuran (0.3 ml, 3.4 mmol), catalyst (see synthesis of compound **4a**) (0.3 ml) in dioxane (30 ml) was boiled for 5 h until disappearance of the initial alcohol. The reaction mass was poured into water (100 ml), and neutralized with dry $NaHCO_3$. The precipitated solid, a mixture of methane **4j** and indolothienopyridine **7b**, was dissolved in alcohol (20 ml), the solution was saturated with dry HCl, and boiled for 12 h until disappearance of methane **4j**. After cooling, the solution was poured into water (100 ml), and neutralized with dry $NaHCO_3$. The precipitated solid was filtered off, recrystallized from ethanol, and the target product **7b** (0.33 g) was obtained as pale-yellow crystals.

REFERENCES

1. A. V. Butin and V. T. Abaev, *Izv. Akad. Nauk, Ser. Khim.*, 1436 (2001).
2. A. V. Butin, T. A. Stroganova, V. T. Abaev, and V. G. Kul'nevich, *Khim. Geterotsikl. Soedin.*, 1250 (1998). [*Chem. Heterocycl. Comp.*, **34**, 1073 (1998)].
3. A. V. Butin, V. V. Mel'chin, V. T. Abaev, W. Bender, A. S. Pilipenko, and G. D. Krapivin, *Tetrahedron*, **62**, 8045 (2006).
4. A. V. Butin, T. A. Stroganova, I. V. Lodina, and G. D. Krapivin, *Tetrahedron Lett.*, **42**, 2031 (2001).
5. A. V. Butin, G. D. Krapivin, V. E. Zavodnik, and V. G. Kul'nevich, *Khim. Geterotsikl. Soedin.*, 616 (1993). [*Chem. Heterocycl. Comp.*, **29**, 524 (1993)].
6. V. T. Abaev, A. V. Gutnov, and A. V. Butin, *Khim. Geterotsikl. Soedin.*, 603 (1998). [*Chem. Heterocycl. Comp.*, **34**, 529 (1998)].
7. A. V. Butin, S. K. Smirnov, T. A. Stroganova, W. Bender, and G. D. Krapivin, *Tetrahedron*, **63**, 474 (2007).
8. V. T. Abaev, A. S. Dmitriev, A. V. Gutnov, S. A. Podelyakin, and A. V. Butin, *J. Heterocycl. Chem.*, **43**, 1195 (2006).
9. A. S. Dmitriev, V. T. Abaev, W. Bender, and A. V. Butin, *Tetrahedron*, **63**, 9437 (2007).
10. A. V. Butin, A. S. Dmitriev, O. N. Kostyukova, V. T. Abaev, and I. V. Trushkov, *Synthesis*, 2208 (2007).
11. A. V. Butin, V. T. Abaev, V. V. Mel'chin, and A. S. Dmitriev, *Tetrahedron Lett.*, **46**, 8439 (2005).
12. V. T. Abaev, A. V. Gutnov, A. V. Butin, and V. E. Zavodnik, *Tetrahedron*, **56**, 8933 (2000).
13. V. P. Litvinov, L. A. Rodinovskaya, Yu. A. Sharanin, A. M. Shestopalov, and A. Senning, *Sulfur Rep.*, **13**, 1 (1992).
14. V. K. Vasilin, M. M. Lipunov, L. D. Konyushkin, E. A. Kaigorodova, and G. D. Krapivin, *Khim. Geterotsikl. Soedin.*, 1582 (2006). [*Chem. Heterocycl. Comp.*, **42**, 1368 (2006)].
15. M. M. Lipunov, E. S. Kostenko, E. A. Kaigorodova, S. I. Firgang, and G. D. Krapivin, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **48**, 81 (2005).
16. A. V. Butin, S. K. Smirnov, and T. A Stroganova, *J. Heterocycl. Chem.*, **43**, 623 (2006).
17. A. V. Butin, S. K. Smirnov, and I. V. Trushkov, *Tetrahedron Lett.*, **49**, 20 (2008).