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ACYLATION AND CYCLODEHYDRATION OF BENZOFURAN-, BENZOTHIOPHENE-, AND INDOLYL-3-ACETIC ACID ARYLAMIDES. SYNTHESIS OF NOVEL BENZOFURO[2,3-*c*]-, BENZOTHIENO[2,3-*c*], AND INDOLO[2,3-*c*]-PYRILIUM AND PYRIDINE DERIVATIVES

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The acylation of benzo[b]furan-, benzo[b]thiophene, and indolyl-3-acetic acid arylamides using acetic anhydride in the presence of 70% perchloric acid occurs at the α-position of the heterocycle to give 2-acetylbenzo[b]furan-, 2-acetylbenzo[b]thiophene, and 2-acetylindolyl-3-acetic acid arylamides. Depending on the amount of perchloric used in the reaction they undergo cyclodehydration to 3-arylamino-1-methylhetero[2,3-c]pyrilium salts and to N-aryl-1-methyl-3(2H)hetero[2,3-c]pyridones.

Keywords: 2-acetylbenzo[*b*]thiophene-3-acetic acid arylamides, 2-acetylbenzo[*b*]furan-3-acetic acid arylamides, 2-acetylindolyl-3-acetic acid arylamides, 3-arylamino-1-methylhetero[2,3-*c*]pyrilium, N-aryl-1-methyl-3(2H)hetero[2,3-*c*]pyridones, cyclodehydration.

o-Acylation and subsequent dehydration of β-oxoalkyl derivatives of aromatic and heterocyclic systems give condensed pyrilium salts [1]. This reaction has been used by us previously in the benzofuran, benzothiophene, and indole series [2-4]. The acylation and cyclodehydration of benzofuran-, benzothiophene-, and indolyl-3-acetic acid arylamides has not been studied previously. This reaction is of interest since the amides described above have two reactive nucleophilic centers (CO and NH) and hence acylation-cyclodehydration can occur by two routes to yield pyrilium salts and pyridine bases.

We have studied the acylation of the arylamides of the benzo[*b*]furan-3-acetic acid **1a-e**, benzo[*b*]thiophene-3-acetic acids **2a,b**, and indolyl-3-acetic acids **3a-c** in the system acetic anhydride–70% perchloric acid with different perchloric acid content. The acylation takes place at the α-position of the heterocycle. The intermediately formed 2-acetylheteryl-3-acetic acid arylamides **4-6** are cyclodehydrated to the corresponding 3-arylamino-1-methylpyrilium perchlorates **7-9**. We have found that the yields of the pyrilium salts **7-9** depend on the amount of perchloric acid taken in the reaction. The maximal yields for the pyrilium salt (90%) are observed with a two fold excess of perchloric acid. It was interesting to find that the NH group in the 3-arylaminopyrilium salts is not acylated, even upon prolonged holding of compounds **7-9** in the acylating mixture.

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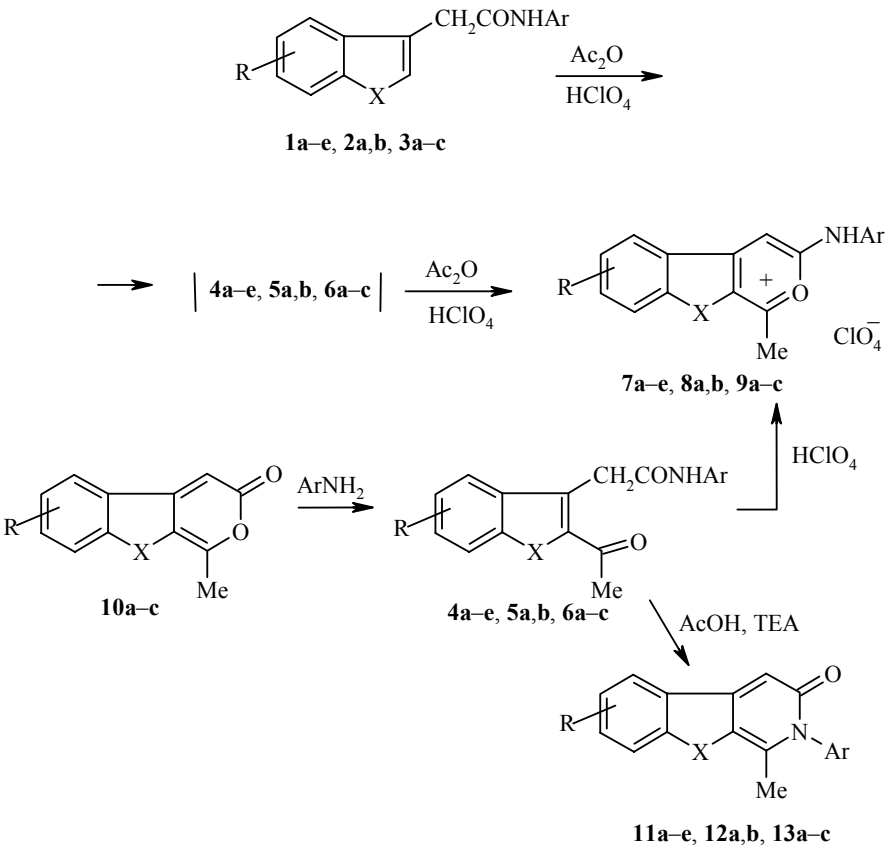

1, **4** X = O, R = 6-Me; **a** Ar = Ph, **b** Ar = 4-MeC_6H_4, **c** Ar = 4-ClC_6H_4, **d** Ar = 4-BrC_6H_4, **e** Ar = 4-$CH_3OC_6H_4$; **2**, **5**, X = S, R = 5-Me, **a** Ar = 4-MeC_6H_4, **b** Ar = 4-$MeOC_6H_4$; **3**, **6**, **9** X = NH, R = H; **a** Ar = Ph; **b** Ar = 4-MeC_6H_4; **c** Ar = 4-$MeOC_6H_4$; **7, 11** X = O, R = 7-Me, **a** Ar = Ph, **b** Ar = 4-MeC_6H_4, **c** Ar = 4-ClC_6H_4, **d** Ar = 4-BrC_6H_4, **e** Ar = 4-$CH_2OC_6H_4$; **8**, **12** X = S, R = 6-Me, **a** Ar = 4-MeC_6H_4, **b** Ar = 4-$MeOC_6H_4$; **10 a** X = O, R = 7-Me, **b** X = S, R = 6-Me, **c** X = NH, R = H; **13** X = NH, R = H; **a** Ar = Ph, **b** Ar = 4-MeC_6H_4, c Ar = 4-$MeOC_6H_4$

In contrast to the acylation of the benzo[*b*]furan-3-acetic acid arylamides **1a-e** and the benzo[*b*]thiophene-3-acetic acid arylamides **2a,b** that of the indolyl-3-acetic acid arylamides occurs with significant tarring. Since we could not prepare the corresponding pyrilium salts in the pure state, we carried out an alternative method for their synthesis consisting of the cyclization of the 2-acetylindolyl-3-acetic acid arylamides **6a-c** in a mixture of acetic anhydride and 70% perchloric acid. The 2-acetylheteryl-3-acetic acid arylamides **4-6** were prepared by the reaction of the 1-methylhetero[2,3-*c*]pyrones **10a-c** with anilines in DMF. Cyclodehydration of the keto amides **4a-e, 5a,b, 6a-c** in an acylating mixture with an excess of 70% perchloric acid gave the corresponding pyrilium salts **7a-e, 8a,b, 9a-c** in greater than 90% yield. The pyrilium perchlorates **7-9** synthesized by this method were identical to the pyrilium salts obtained by the acylation of the benzofuran- and benzothiophene-3-acetic acid arylamides. The structure of the 3-arylamino-1-methylpyrilium perchlorates **7-9** was confirmed using elemental analytical analysis and from their ^{1}H NMR spectra (Tables 1 and 2).

A study of the cyclodehydration of the keto amides **4a-e, 5a,b, 6a-c** in the acylating mixture with an equivalent amount of 70% perchloric acid showed that, along with the pyrilium salts **7a-e, 8a,b, 9a-c**, the reaction mixture contained the corresponding N-aryl-1-methyl-3(2H)hetero[2,3-*c*]pyridones **11-13**. Thus a chromatographic investigation of the composition of the reaction mixture (after separation of the pyrilium salt) showed that the product of cyclodehydration of the 2-acetyl-6-methyl-(4-methylphenyl)amide of benzo[*b*]furan-3-acetic acid (**4b**) using 70% perchloric acid in acetic anhydride gave both the pyrilium salt **7b** (yield 40%)

TABLE 1. Characteristics of the Compounds Synthesized

Compound	Empirical formula	Found, % / Calculated, %					mp, °C	R_f	Yield, % (method)
		C	H	Hal	N	S			
1	2	3	4	5	6	7	8	9	10
1a	$C_{17}H_{15}NO_2$	76.80 / 76.96	5.79 / 5.70	—	5.32 / 5.28	—	159-160	—	75 (A), 77 (B)
1b	$C_{18}H_{17}NO_2$	77.28 / 77.40	6.21 / 6.13	—	5.15 / 5.01	—	149-150	—	76 (A), 76 (B)
1c	$C_{17}H_{14}ClNO_2$	68.00 / 68.12	4.62 / 4.71	11.65 / 11.83	4.55 / 4.67	—	172-173	0.55	70 (A), 75(B)
1d	$C_{17}H_{14}BrNO_2$	59.15 / 59.32	4.29 / 4.10	23.38 / 23.21	4.21 / 4.07	—	180-181	—	76 (A), 75 (B)
1e	$C_{18}H_{17}NO_3$	73.00 / 73.20	5.67 / 5.80	—	4.59 / 4.74	—	173-174	—	67 (A), 68 (B)
2a	$C_{18}H_{17}NOS$	73.05 / 73.19	5.70 / 5.80	—	4.51 / 4.74	10.69 / 10.85	157-158	0.75	65 (A) 67 (B)
2b	$C_{18}H_{17}NO_2S$	69.62 / 69.43	5.67 / 5.50	—	4.61 / 4.50	10.56 / 10.30	171-172	—	63 (A), 69 (B)
3a	$C_{16}H_{14}N_2O$	77.56 / 76.78	5.57 / 5.64	—	11.31 / 11.19	—	186-187	—	75 (B)
3b	$C_{17}H_{16}N_2O$	77.38 / 77.25	6.21 / 6.10	—	10.69 / 10.60	—	187-188	—	80 (B)
3c	$C_{17}H_{16}N_2O_2$	72.65 / 72.84	5.67 / 5.75	—	9.83 / 9.99	—	184-185	—	78 (B)
4a	$C_{19}H_{17}NO_3$	74.37 / 74.25	5.63 / 5.58	—	4.41 / 4.56	—	187-188	—	88
4b	$C_{20}H_{19}NO_3$	74.86 / 74.75	5.83 / 5.96	—	4.21 / 4.36	—	173	0.81	95
4c	$C_{19}H_{16}ClNO_3$	66.85 / 66.77	4.63 / 4.72	10.45 / 10.37	4.17 / 4.10	—	175-176	0.64	80
4d	$C_{19}H_{16}BrNO_3$	58.95 / 59.08	4.12 / 4.18	20.56 / 20.69	3.67 / 3.63	—	192-193	0.57	83
4e	$C_{20}H_{19}NO_4$	71.36 / 71.20	5.56 / 5.68	—	4.25 / 4.15	—	193	0.93	93
5a	$C_{20}H_{19}NO_2S$	71.28 / 71.19	5.53 / 5.68		4.21 / 4.15	9.36 / 9.50	205-206	0.86	80
5b	$C_{20}H_{19}NO_3S$	67.81 / 67.97	5.35 / 5.42	—	4.10 / 3.96	9.26 / 9.07	198-200	—	87
6a	$C_{18}H_{16}N_2O_2$	73.81 / 73.96	5.67 / 5.52	—	9.42 / 9.58	—	235-237	0.42	95
6b	$C_{19}H_{18}N_2O_2$	74.40 / 74.49	6.02 / 5.92	—	9.03 / 9.14	—	229-230	0.43	98
6c	$C_{19}H_{18}N_2O_3$	70.65 / 70.79	5.74 / 5.63	—	8.78 / 8.69	—	224-225	—	93
7a	$C_{19}H_{16}ClNO_6$	58.51 / 58.55	4.24 / 4.14	9.11 / 9.10	3.45 / 3.59	—	224-225 (with dec.)	—	90
7b	$C_{20}H_{18}ClNO_6$	59.43 / 59.49	4.58 / 4.49	8.69 / 8.78	3.57 / 3.47	—	240 (with dec.)	—	86
7c	$C_{19}H_{15}Cl_2NO_6$	53.67 / 53.79	3.68 / 3.56	16.63 / 16.71	3.44 / 3.30	—	227-228 (with dec.)	—	83
7d	$C_{19}H_{15}BrClNO_6$	48.56 / 48.69	3.37 / 3.23	17.13 / 17.05	3.14 / 2.99	—	248-249 (with dec.)	—	90
7e	$C_{20}H_{18}ClNO_7$	57.34 / 57.22	4.48 / 4.32	8.35 / 8.44	3.28 / 3.34	—	223-224 (with dec.)	—	85
8a	$C_{20}H_{18}ClNO_5S$	57.32 / 57.21	4.48 / 4.32	8.38 / 8.44	3.25 / 4.34	7.58 / 7.64	240 (with dec.)	—	90
8b	$C_{20}H_{18}ClNO_6S$	55.23 / 55.11	4.02 / 4.16	8.21 / 8.13	3.15 / 3.21	7.28 / 7.36	232-233 (with dec.)	—	97
9a	$C_{18}H_{15}ClN_2O_5$	57.55 / 57.69	4.17 / 4.03	9.33 / 9.46	7.51 / 7.47	—	235 (with dec.)	—	80

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10
9b	$C_{19}H_{17}ClN_2O_5$	58.76 / 58.69	4.52 / 4.41	8.98 / 9.12	7.13 / 7.20	—	254-255 (with dec.)	—	90
9c	$C_{19}H_{17}ClN_2O_6$	56.29 / 56.38	4.15 / 4.23	8.91 / 8.76	7.10 / 6.92	—	233-234 (with dec.)	—	96
10a	$C_{19}H_{15}NO_2$	78.73 / 78.87	5.35 / 5.23	—	4.66 / 4.84	—	192-193	0.36	100
10b	$C_{20}H_{17}NO_2$	79.25 / 79.19	5.47 / 5.65	—	4.57 / 4.62	—	193-194	0.33	100
10c	$C_{19}H_{14}ClNO_2$	70.33 / 70.48	4.23 / 4.36	10.78 / 10.95	4.45 / 4.33	—	226-227	0.45	100
10d	$C_{19}H_{14}BrNO_2$	61.83 / 61.97	3.98 / 3.83	21.61 / 21.70	3.68 / 3.80		229-230	0.38	100
10e	$C_{20}H_{17}NO_3$	75.37 / 75.22	5.51 / 5.37	—	4.27 / 4.39	—	191-192	0.31	100
11a	$C_{20}H_{17}NOS$	75.06 / 75.20	5.49 / 5.36	—	4.52 / 4.38	9.95 / 10.04	214-215	—	100
11b	$C_{20}H_{17}NO_2S$	71.45 / 71.62	5.04 / 5.11	—	4.31 / 4.18	9.42 / 9.56	254-255 (with dec.)	0.27	100
12a	$C_{18}H_{14}N_2O$	78.65 / 78.81	5.27 / 5.14	—	10.34 / 10.21	—	284-285 (with dec.)	—	100
12b	$C_{19}H_{16}N_2O$	79.26 / 79.14	5.68 / 5.59	—	9.56 / 9.71	—	290 (with dec.)	0.41	100
12c	$C_{19}H_{16}N_2O_2$	75.14 / 74.98	5.47 / 5.30	—	9.18 / 9.20	—	288-289 (with dec.)	0.32	100
13a	$C_{13}H_{10}O_3$	72.78 / 72.89	4.63 / 4.71	—	—	—	160	0.50	100
13b	$C_{13}H_{10}O_2S$	67.71 / 67.80	4.44 / 4.38	—	—	13.85 / 13.92	187-188	0.44	100

together with 16.5% of the starting keto amide **4b** and 26% of the 1,7-dimethyl-2-N-(4-methylphenyl)-3(2H)benzofuro[2,3-*c*]pyridone (**11b**). The alternative direction of cyclodehydration of the keto amides **4-6** is achieved by heating them in acetic acid in the presence of triethylamine. In this way the N-aryl-1-methyl-3(2H)hetero[2,3-*c*]pyridones **11-13** are formed in good yields.

EXPERIMENTAL

^{1}H NMR spectra were taken on a Gemini-200 instrument (200 MHz) using DMSO-d_6 as solvent and TMS as internal standard. Monitoring of the purity of the products obtained was carried out using TLC on Silufol UV-254 plates and the system toluene–ethanol (4:1). Analysis of the reaction products was performed by HPLC on a Laboratory pristroje chromatograph (Prague) with an RIDK-102 differential refractometer detector and 3 × 150 mm column using Separon C_{18} stationary phase and methanol–water (7:3) mobile phase.

The parameters for the compounds synthesized are given in Tables 1 and 2.

6-Methylbenzo[*b*]furan-3-acetic acid and 5-methylbenzo[*b*]thiophene-3-acetic acids were prepared by the methods [5, 6].

Preparation of the Arylamides (1a-e, 2a,b, 3a-c) (General Method). A. Pyridine (1 ml) and the corresponding arylamine (0.01 mol) were added with cooling to a benzene solution (20 ml) of the 6-methylbenzo[*b*]furan-3-acetic acid chloride or 5-methylbenzo[*b*]thiophene-3-acetic acid chloride which had been obtained from the corresponding acid (0.01 mol) and PCl_5 by the standard method. The product was held at room temperature for 4 h. The precipitate was filtered off and washed with aqueous alcohol and hexane. Crystallization from isopropanol gave the arylamides **1a-e, 2a,b**.

TABLE 2. ^{1}H NMR Spectra of Compounds Synthesized

Com-pound	Chemical shift, δ, ppm (spin spin coupling, *J*, Hz)					
	R, substituent in Ar (3H, s) (3H, s)	CH_3 (3H, s)	CH_2 (2H, s)	H arom. in Het	H arom. in Ar	NH (NH in Het); (1H, s)
1	2	3	4	5	6	7
1a	2.41 (6-CH_3)	—	3.73	7.08 (1H, d, *J* = 8.0, 5-H); 7.37 (1H, s, 2-H); 7.54 (1H, d, *J* = 8.0, 4-H); 7.81 (2H, s, 7-H)	7.00 (1H, t, *J* = 8.0, 4'-H); 7.28 (2H, t, *J* = 8.0, 3',5'-H); 7.60 (2H, d, *J* = 8.0, 2',6'-H)	10.12
1b	2.20 (4'-CH_3); 2.42 (6-CH_3)	—	3.71	7.14 (1H, d, *J* = 8.0, 5-H); 7.36 (1H, s, 2-H); 7.56 (1H, d, *J* = 8.0, 4-H); 7.80 (1H, s, 7-H)	7.04 (2H, d, *J* = 8.0, 3',5'-H); 7.52 (2H, d, *J* = 8.0, 2',6'-H)	10.06
1c	2.42 (6-CH_3)	—	3.72	7.08 (1H, d, *J* = 8.0, 5-H); 7.36 (1H, s, 2-H); 7.60 (1H, d, *J* = 8.0, 4-H); 7.81 (1H, s, 7-H)	7.34 (2H, d, *J* = 8.0, 2',6'-H); 7.61 (2H, d, *J* = 8.0, 3',5'-H)	10.37
1d	2.40 (6-CH_3)	—	3.72	7.08 (1H, d, *J* = 8.0, 5-H); 7.37 (1H, s, 2-H); 7.57 (1H, d, *J* = 8.0, 4-H); 7.81 (1H, s, 7-H)	7.52 (2H, d, J = 8.0, 2',6'-H); 7.54 (2H, d, *J* = 8.0, 3',5'-H)	10.41
1e	2.41 (6-CH_3); 3.71 (4'-OCH_3)	—	3.68	7.08 (1H, d, *J* = 8.0, 5-H); 7.36 (1H, s, 2-H); 7.54 (1H, d, *J* = 8.0, 4-H); 7.80 (1H, s, 7-H)	6.87 (2H, d, *J* = 8.9, 3',5'-H); 7.51 (2H, d, *J* = 8.9, 2',6'-H)	10.12
2a	2.23 (4'-CH_3); 2.42 (5-CH_3)	—	3.86	7.20 (1H, d, *J* = 8.2, 6-H); 7.53 (1H, s, 2-H); 7.69 (1H, s, 4-H); 7.83 (1H, d, *J* = 8.2, 7-H)	7.09 (2H, d, *J* = 8.2, 3',5'-H); 7.48 (2H, d, *J* = 8.2, 2',6'-H)	10.14
2b	2.43 (5-CH_3); 3.71 (4'-OCH_3)	—	3.85	7.21 (1H, d, *J* = 8.2, 6-H); 7.53 (1H, s, 2-H); 7.70 (1H, s, 4-H); 7.85 (1H, d, *J* = 8.2, 7-H)	6.88 (2H, d, *J* = 8.6, 3',5'-H); 7.51 (2H, d, *J* = 8.6, 2',6'-H)	10.11

TABLE 2 (continued)

1	2	3	4	5	6	7
3a	—	—	3.69	6.98 (1H, t, *J* = 7.5, 6-H); 7.07 (1H, t, *J* = 7.5, 5-H); 7.24 (1H, d, *J* = 2.0, 2-H); 7.36 (1H, d, *J* = 8.0, 7-H); 7.62 (1H, d, *J* = 8.0, 4-H)	7.10 (1H, t, *J* = 8.0, 4'-H); 7.30 (2H, t, *J* = 8.0, 3',5'-H); 7.56 (2H, d, *J* = 8.0, 2',6'-H)	9.95 (10.92)
3b	2.20 (4'-CH_3)	—	3.69	6.98 (1H, t, *J* = 7.5, 6-H); 7.07 (1H, t, *J* = 7.5, 5-H); 7.24 (1H, d, *J* = 2.0, 2-H); 7.36 (1H, d, *J* = 8.0, 7-H); 7.62 (1H, d, *J* = 8.0, 4-H)	7.09 (2H, d, *J* = 8.4, 3',5'-H); 7.53 (2H, d, *J* = 8.4, 2',6'-H)	9.95 (10.92)
3c	3.70 (4'-OCH_3)	—	3.69	6.98 (1H, t, *J* = 7.5, 6-H); 7.07 (1H, t, *J* = 7.5, 5-H); 7,24 (1H, d, *J* = 2.0, 2-H); 7.35 (1H, d, *J* = 8.0, 7-H); 7.61 (1H, d, *J* = 8.0, 4-H)	6.85 (2H, d, *J* = 9.0, 3',5'-H); 7.51 (2H, d, *J* = 9.0, 2',6'-H)	9.93 (10.90)
4a	2.46 (6-CH_3)	2.57	4.19	7.17 (1H, d, *J* = 8.0, 5-H); 7.47 (1H, s, 7-H); 7.68 (1H, d, *J* = 8.0, 4-H)	7.02 (1H, t, *J* = 8.0, 4'-H); 7.27 (2H, t, *J* = 8.0, 3',5'-H); 7.57 (2H, d, *J* = 8.0, 2',6'-H)	10.16
4b	2.20 (4'-CH_3); 2.42 (6-CH_3)	2.53	4.15	7.14 (1H, d, *J* = 8.0, 5-H); 7.45 (1H, s, 7-H); 7.66 (1H, d, *J* = 8.0, 4-H)	7.04 (2H, d, *J* = 8.0, 3',5'-H); 7.42 (2H, d, *J* = 8.0, 2',6'-H)	10.06
4c	2.45 (6-CH_3)	2.56	4.12	7.18 (1H, d, *J* = 8.1, 5-H); 7.36 (1H, s, 7-H); 7.70 (1H, d, *J* = 8.1, 4-H)	7.34 (2H, d, *J* = 8.0, 2',6'-H); 7.61 (2H, d, *J* = 8.0, 3',5'-H)	10.37
4d	2.45 (6-CH_3)	2.57	4.12	7.16 (1H, d, *J* = 8.1, 5-H); 7.40 (1H, s, 7-H); 7.70 (1H, d, *J* = 8.1, 4-H)	7.34 (2H, d, *J* = 8.0, 2',6'-H); 7.55 (2H, d, *J* = 8.0, 3',5'-H)	10.20
4e	2.48 (6-CH_3); 3.71 (4'-OCH_3)	2.57	4.14	7.16 (1H, d, *J* = 8.1, 5-H); 7.44 (1H, s, 7-H); 7.66 (1H, d, *J* = 8.1, 4-H)	6.82 (2H, d, *J* = 8,9, 3',5'-H); 7.46 (2H, d, *J* = 8.9, 2',6'-H)	9.95
5a	2.22 (4'-CH_3); 2.43 (5-CH_3)	2.61	4.36	7.38 (1H, d, *J* = 8.3, 6-H); 7.86 (1H, d, *J* = 8.3, 7-H); 7.92 (2H, s, 4-H)	7.08 (2H, d, *J* = 8.0, 3',5'-H); 7.46 (2H, d, *J* = 8.0, 2',6'-H)	10.19
5b	2.43 (5-CH_3); 3.70 (4'-OCH_3)	2.61	4.32	7.37 (1H, d, *J* = 8.4, 6-H); 7.84 (1H, d, *J* = 8.4, 7-H); 7.90 (1H, s, 4-H)	6.86 (2H, d, *J* = 8.8, 3',5'-H); 7.44 (2H, d, *J* = 8.8, 2',6'-H)	10.15

TABLE 2 (continued)

1	2	3	4	5	6	7
6a	—	2.63	4.18	7.04 (1H, t, *J* = 8.0, 6-H); 7.24 (1H, t, *J* = 8.0, 5-H); 7.46 (1H, d, *J* = 8.0, 7-H); 7.75 (1H, d, *J* = 8.0, 4-H)	7.10 (1H, t, *J* = 8.0, 4'-H); 7.30 (2H, t, *J* = 8.0, 3',5'-H); 7.56 (2H, d, *J* = 8.0, 2',6'-H)	10.07, (10.64)
6b	2.22 (4'-CH_3)	2.63	4.18	7.06 (1H, t, *J* = 8.0, 6-H); 7.28 (1H, t, *J* = 8.0, 5-H); 7.46 (1H, d, *J* = 8.0, 7-H); 7.75 (1H, d, *J* = 8.0, 4-H)	7.08 (2H, d, *J* = 8.0, 3',5'-H); 7.46 (2H, d, *J* = 8.0, 2',6'-H)	10.07, (10.64)
6c	3.70 (4'-OCH_3)	2.63	4.16	7.07 (1H, t, *J* = 8.0, 6-H); 7.29 (1H, t, *J* = 8.0, 5-H); 7.45 (1H, d, *J* = 8.0, 7-H); 7.75 (1H, d, *J* = 8.0, 4-H)	6.85 (2H, d, *J* = 8.7, 3',5'-H); 7.48 (2H, d, *J* = 8.7, 2',6'-H)	10.03 (11.62)
7b	2.35 (4'-CH_3); 2.50 (7-CH_3)	2.74	—	7.45 (1H, d, *J* = 8.0, 6-H); 7.48 (1H, s, 8-H); 7.58 (1H, s, 4-H); 8.29 (1H, d, *J* = 8.0, 5-H)	7.34 (2H, d, *J* = 8.0, 3',5'-H); 7.45 (2H, d, *J* = 8.0, 2',6'-H)	12.23
7c	2.54 (7-CH_3)	2.79	—	7.40 (1H, d, *J* = 8.0, 6-H); 7.61 (2H, m, 4,8-H); 8.34 (1H, d, *J* = 8.0, 5-H)	7.61 (4H, m, 2',3',5',6'-H)	12.38
7e	2.52 (7-CH_3); 3.80 (4'-OCH_3)	2.74	—	7.36 (1H, d, *J* = 8.0, 6-H); 7.47 (1H, s, 8-H); 7.60 (1H, s, 4-H); 8.31 (1H, d, *J* = 8.0, 5-H)	7.10 (2H, d, *J* = 8.8, 3',5'-H); 7.49 (2H, d, *J* = 8.8, 2',6'-H)	12.19
8a	2.41 (4'-CH_3); 2.52 (6-CH_3)	2.81	—	7.49 (1H, d, *J* = 8.0, 7-H); 7.75 (1H, s, 4-H); 8.07 (1H, d, *J* = 8.0, 8-H); 8.44 (1H, s, 5-H)	7.40 (2H, d, 3',5'-H *J* = 8.0); 7.54 (2H, d, *J* = 8.0, 2',6'-H)	12.38
8b	2.46 (6- CH_3); 3.81 (4'-OCH_3)	2.75	—	7.46 (1H, d, *J* = 8.0, 7-H); 7.70 (1H, s, 4-H); 8.00 (1H, d, *J* = 8.0, 8-H); 8.36 (1H, s, 5-H)	7.10 (2H, d, *J* = 8.6, 3',5'-H); 7.50 (2H, d, *J* = 8.6, 2',6'-H)	12.25
9a	—	2.91	—	7.21 (1H, t, *J* = 8.0, 7-H); 7.31 (1H, d, *J* = 8.0, 8-H); 7.60 (1H, s, 4-H); 7.73 (1H, t, *J* = 8.0, 6-H); 8.31 (1H, d, *J* = 7.8, 5-H)	7.45–7.53 (5H, m, 2',3',4',5',6-H)	11.56 (11.85)
9b	2.34 (4'-CH_3)	2.86	—	7.21 (1H, t, *J* = 8.0, 7-H); 7.49 (1H, d, *J* = 8.0, 8-H); 7.56 (1H, s, 4-H); 7.74 (1H, t, *J* = 8.0, 6-H); 8.31 (1H, d, *J* = 7.8, 5-H)	7.29 (2H, d, *J* = 8.6, 3',5'-H); 7.42 (2H, d, *J* = 8.6, 2',6'-H)	11.59 (11.90)

TABLE 2 (continued)

1	2	3	4	5	6	7
10a	2.42 (7-CH_3)	2.42	—	6.56 (1H, s, 4-H); 7.50 (1H, s, 8-H); 7.61 (1H, d, *J* = 8.2, 6-H); 7.93 (1H, d, *J* = 8.2, 5-H)	—	—
10b	2.40 (6-CH_3)	2.40	—	6.78 (1H, s, 4-H); 7.42 (1H, d, *J* = 8.2, 7-H); 7.63 (1H, d, *J* = 8.2, 8-H); 7.96 (1H, s, 5-H)	—	—
11a	2.48 (7-CH_3)	2.12	—	6.74 (1H, s, 4-H); 7.14 (1H, d, *J* = 8.0, 6-H); 7.59 (1H, s, 8-H); 7.88 (1H, d, *J* = 8.0, 5-H)	7.24-7.55 (5H, m, 2',3',4',5',6'-H)	—
11b	2.39 (4'-CH_3); 2.47 (7-CH_3)	2.10	—	6.80 (1H, s, 4-H); 7.19 (1H, s, 8-H); 7.34 (1H, d, *J* = 8.0, 6-H); 7.94 (1H, d, *J* = 8.0, 5-H)	7.16 (2H, d, *J* = 8.0, 3',5'-H); 7.34 (2H, d, *J* = 8.0, 2',6'-H)	—
11c	2.46 (7-CH_3)	2.10	—	6.82 (1H, s, 4-H); 7.17 (1H, d, *J* = 8.0, 6-H); 7.39 (1H, s, 8-H); 7.95 (1H, d, *J* = 8.0, 5-H)	7.37 (2H, d, *J* = 8.6, 3',5'-H); 7.61 (2H, d, *J* = 8.6, 2',6'-H)	—
11d	2.47 (7-CH_3)	2.11	—	6.83 (1H, s, 4-H); 7.18 (1H, d, *J* = 8.0, 6-H); 7.39 (1H, s, 8-H) 7.95 (1H, d, *J* = 8.0, 5-H)	7.31 (2H, d, *J* = 7.5, 3',5'-H); 7.75 (2H, d, *J* = 7.5, 2',6'-H)	—
11e	2.45 (7-CH_3); 3.81 (4'-OCH_3)	2.09	—	6.79 (1H, s, 4-H); 7.16 (1H, d, *J* = 7.8, 6-H); 7.37 (1H, s, 8-H); 7.94 (1H, d, *J* = 7.8, 5-H)	7.06 (2H, d, *J* = 8.4, 3',5'-H); 7.20 (2H, d, *J* = 8.4, 2',6'-H)	—
12a	2.38 (4'-CH_3); 2.42 (6-CH_3)	2.08	—	7.10 (1H, s, 4-H); 7.38 (1H, d, *J* = 8.0, 7-H); 7.72 (1H, d, *J* = 8.0, 8-H); 8.02 (1H, s, 5-H)	7.15 (2H, d, *J* = 8.0, 3',5'-H); 7.33 (2H, d, *J* = 8.0, 2',6'-H)	—
12b	2.43 (6-CH_3); 3.82 (4'-OCH_3)	2.12	—	7.03 (1H, s, 4-H); 7.42 (1H, d, *J* = 8.0, 7-H); 7.76 (1H, d, *J* = 8.0, 8-H); 8.04 (1H, s, *J* = 8.0, 5-H)	7.10 (2H, d, *J* = 8.8, 3',5'-H); 7.22 (2H, d, *J* = 8.8, 2',6'-H)	—
13b	2.36 (4'-CH_3)	2.14	—	6.82 (1H, s, 4-H); 7.00 (1H, t, *J* = 8.0, 7-H); 7.25 (1H, d, *J* = 8.0, 8-H); 7.44 (1H, t, *J* = 8.0, 6-H); 7.87 (1H, d, *J* = 8.0, 5-H)	7.10 (2H, d, *J* = 8.0, 3',5'-H); 7.29 (2H, d, *J* = 8.0, 2',6'-H)	(10.41)
13c	3.84 (4'-OCH_3)	2.20	—	6.87 (1H, s, 4-H); 7.03 (1H, t, *J* = 7.6, 7-H); 7.29 (1H, d, *J* = 8.0, 8-H); 7.48 (1H, t, *J* = 7.6, 6-H); 8.02 (1H, d, *J* = 8.0, 5-H)	7.08 (2H, d, *J* = 8.8, 3',5'-H); 7.20 (2H, d, *J* = 8.8, 2',6'-H)	(10.53)

B. Carbonyldiimidazole (1.62 g, 0.01 mol) was added to a solution of the corresponding heteryl-3-acetic acid (0.01 mol) in anhydrous dioxane. The solution was stirred for 1.5 h at room temperature and the arylamine (0.01 mol) was added. The mixture was stirred for 4 h and poured into a 5% aqueous solution of $NaHCO_3$ (50 ml). The precipitated crystals were filtered off, washed with water, and crystallized from isopropanol to give the arylamides **1a-e, 2a,b, 3a-c**.

Preparation of the Pyrilium Salts (7a-e, 8a,b, 9a-c) (General Method). Perchloric acid (70%, 2 ml) was added with cooling to a solution of the arylamides **1a-e, 2a,b** or the corresponding keto amide **4-6** (0.01 mol) in acetic anhydride (10 ml). The mixture was held at room temperature for 2 h. The precipitate formed was filtered off, washed with acetic acid and then water, dried, and crystallized from acetic acid to give the pyrilium salts **7a-e, 8a,b, 9a-c**.

1,7-Dimethylbenzofuro[2,3-*c*]-3-pyrone (10a) was prepared from 1,7-dimethyl-3-hydroxybenzofuro-[2,3-*c*]pyrilium fluoroborate [7] by a method similar to that for **10c** [8].

1,6-Dimethylbenzothieno[2,3-*c*]-3-pyrone (10b) was prepared from 1,6-dimethyl-3-hydroxybenzothieno[2,3-*c*]pyrilium fluoroborate [7] by a method similar to that for **10c** [8].

Preparation of 2-Acetylheteryl-3-acetic Acid Arylamides (4a-e, 5a,b, 6a-c) (General Method). The arylamine (0.15 mol) was added to a solution of the pyrone **10a** (0.01 mol) in isopropanol (for pyrones **10b,c** in DMF). The mixture was refluxed for 0.5 h (for **10b,c** refluxed for 2 h), cooled, and poured into water. The precipitate formed was filtered off, washed with water, and dried to give the arylamides **4a-e, 5a,b, 6a-c**. Compounds **4a-e** were crystallized from isopropanol and **5a,b, 6a-c** were crystallized from aqueous DMF.

Preparation of N-Aryl-1-methyl-3(2H)hetero[2,3-*c*]pyrid-3-ones (11a-e, 12a,b, 13a-c) (General Method). Triethylamine (0.05 mol) was added to a solution of the 2-acetylheteryl-3-acetic acid arylamides **4a-e, 5a,b, 6a-c** (0.01 mol) in acetic acid. The mixture was refluxed for 1.5 h, cooled, poured into water, and a solution of ammonia was added to pH ≥ 7. The precipitate was filtered off, washed with water, dried, and crystallized from alcohol to give the pyridones **11a-e, 12a,b, 13a-c**.

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