

Table 1
 Physical and Analytical Data of Compounds **2**, **4**, and **5**

Compound No.	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	Method Yield (%)	Mp (°C) (Solvent)	Formula M.W.	Analysis (%)		
										Calcd./Found	C	H N
2a	H	<i>n</i> -C ₄ H ₉	H	H	H	H	61	76-9 (hexane)	C ₁₄ H ₁₄ N ₂ O ₂ S 274.34	61.29 61.47	5.14 5.19	10.21 9.95
2b	H	C ₆ H ₅ CH ₂	H	H	H	H	77	120-2 (benzene – <i>c</i> -C ₆ H ₁₂)	C ₁₇ H ₁₂ N ₂ O ₂ S 308.36	66.22 65.98	3.92 3.93	9.08 8.29
2c	H	C ₆ H ₅	H	H	H	H	0	-	-	-	-	-
2d	CH ₃	C ₆ H ₅ CH ₂	H	H	H	H	47	105-7 (benzene)	C ₁₈ H ₁₄ N ₂ O ₂ S 322.38	67.06 67.12	4.38 4.35	8.69 8.72
2e	CH ₃	C ₆ H ₅	H	H	H	H	52	169-71 (benzene – <i>c</i> -C ₆ H ₁₂)	C ₁₇ H ₁₂ N ₂ O ₂ S 308.36	66.22 66.47	3.92 3.83	9.08 8.86
2f	C ₆ H ₅	C ₆ H ₅	H	H	H	H	26	167-70 (benzene – <i>c</i> -C ₆ H ₁₂)	C ₂₂ H ₁₄ N ₂ O ₂ S 370.42	71.33 71.48	3.81 3.91	7.56 7.27
2g	H	<i>n</i> -C ₄ H ₉	H	CH ₃	H	H	72	85-9 (hexane)	C ₁₅ H ₁₆ N ₂ O ₂ S 288.37	62.48 62.63	5.59 5.53	9.71 9.76
2h	H	<i>n</i> -C ₄ H ₉	H	Cl	H	H	65	102-7 (hexane)	C ₁₄ H ₁₃ ClN ₂ O ₂ S 308.78	54.46 54.82	4.24 4.38	9.07 8.70
2i	H	<i>n</i> -C ₄ H ₉	H	H	H	CH ₃	59	68-72 (<i>c</i> -C ₆ H ₁₂)	C ₁₅ H ₁₆ N ₂ O ₂ S 288.37	62.48 62.76	5.59 5.48	9.71 9.58
2j	H	<i>n</i> -C ₄ H ₉	CH ₃	H	CH ₃	H	85	127-9 (<i>c</i> -C ₆ H ₁₂)	C ₁₆ H ₁₈ N ₂ O ₂ S 302.39	63.55 63.67	6.00 6.16	9.26 9.12
2k	H	C ₆ H ₅ CH ₂	CH ₃	H	CH ₃	H	85	66-74 (benzene – <i>c</i> -C ₆ H ₁₂)	C ₁₉ H ₁₆ N ₂ O ₂ S °0.2 C ₆ H ₅ 351.83	68.96 68.69	4.93 5.26	7.96 7.71
2l	H	C ₆ H ₅	CH ₃	H	CH ₃	H	25	200-10 (benzene-hexane)	C ₁₈ H ₁₄ N ₂ O ₂ S 322.38	67.06 67.31	4.38 4.28	8.69 8.51
2m	CH ₃	<i>n</i> -C ₄ H ₉	CH ₃	H	CH ₃	H	74	104-5 (<i>c</i> -C ₆ H ₁₂)	C ₁₇ H ₂₀ N ₂ O ₂ S 316.42	64.53 64.58	6.37 6.52	8.85 8.62
2n	H	C ₆ H ₅ CH ₂	Cl	H	H	CH ₃	26	162-5 (benzene – <i>c</i> -C ₆ H ₁₂)	C ₁₈ H ₁₃ ClN ₂ O ₂ S 356.83	60.59 60.41	3.67 3.57	7.85 7.79
2o	H	C ₆ H ₅ CH ₂	H	H	Cl	CH ₃	71	175-8 (benzene – <i>c</i> -C ₆ H ₁₂)	C ₁₈ H ₁₃ ClN ₂ O ₂ S 356.83	60.59 60.89	3.67 3.73	7.85 7.71
4g	H	<i>n</i> -C ₄ H ₉	H	CH ₃	H	H	A: 11 B: 92	136-8 (hexane- <i>c</i> -C ₆ H ₁₂)	C ₁₄ H ₁₆ BrNO ₂ 310.19	54.21 53.91	5.20 5.44	4.52 4.44
4h	H	<i>n</i> -C ₄ H ₉	H	Cl	H	H	A: 3 B: 65	146-50 (hexane- <i>c</i> -C ₆ H ₁₂)	C ₁₃ H ₁₃ BrClNO ₂ 330.60	47.23 47.10	3.96 4.03	4.24 4.13
4i	H	<i>n</i> -C ₄ H ₉	H	H	H	CH ₃	A: 3 B: 68	123-6 (hexane- <i>c</i> -C ₆ H ₁₂)	C ₁₄ H ₁₆ BrNO ₂ 310.19	54.21 53.84	5.20 5.55	4.52 4.42
4j	H	<i>n</i> -C ₄ H ₉	CH ₃	H	CH ₃	H	A: 6 C: 12	149-52 (<i>c</i> -C ₆ H ₁₂)	C ₁₅ H ₁₈ BrNO ₂ 324.21	55.57 55.34	5.60 5.65	4.32 4.36
4m	CH ₃	<i>n</i> -C ₄ H ₉	CH ₃	H	CH ₃	H	A: 7 C: 16	74-5 (methanol)	C ₁₆ H ₂₀ BrNO ₂ 338.24	56.82 57.06	5.96 6.26	4.14 4.00
5j	H	<i>n</i> -C ₄ H ₉	CH ₃	-	CH ₃	H	B: 65 C: 28	194-7 (benzene)	C ₁₅ H ₁₇ Br ₂ NO ₂ 403.11	44.69 44.97	4.25 4.38	3.47 3.39
5m	CH ₃	<i>n</i> -C ₄ H ₉	CH ₃	-	CH ₃	H	B: 62 C: 31	128-31 (methanol)	C ₁₆ H ₁₉ Br ₂ NO ₂ 417.14	46.07 45.95	4.59 4.89	3.36 3.19

anilines with substituted diethyl malonates, according to known procedures [9-11]. In our preliminary experiment we found that the reaction of compound **1e** with excess of thiocyanogen, *in situ* generated by the addition of bromine to a solution of **1e** and potassium thiocyanate in acetic

acid, results in a mixture of two products. The minor reaction product was isolated and identified as the expected thiocyanato derivative **2e**. The major reaction product was identified as 3-bromo derivative **4e**. This indicates that both **1e** and potassium thiocyanate react with bromine with

a comparable rate. Therefore, in further experiments, we first prepared the solution of thiocyanogen (by adding bromine to the excess of potassium thiocyanate in acetic acid) to which the solution of starting compound **1** in acetic acid was added in the next step. Under these conditions the conversion of **1** to **2** proceeded nearly quantitatively (according to tlc). However, compounds **2** are sensitive to hydrolysis and workup, such as dilution of the reaction mixture with water, resulted in a rapid conversion of **2** to the starting material **1** and a polymeric yellow substance. A similar formation of the yellow polymeric material during the decomposition of α -thiocyanato- α -ketoesters has already been described by Prakash *et al.* [7]. The conversion of **2** to **1** can be explained by nucleophilic

attack of a water molecule at the "positive charged" sulfur atom of the thiocyanato group (Scheme 2). An analogous transformation has been described [12] for 3-bromo-1*H*,3*H*-quinoline-2,4-diones (**3**), which in the presence of potassium hydroxide in methanol reacted to 4-hydroxy-(1*H*)-quinolin-2-ones **1** and hypobromite.

Scheme 2

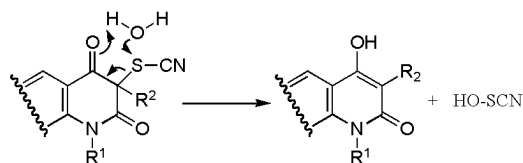


Table 2
IR and NMR Data of Compounds **2**, **4** and **5**

Compound No.	R (cm ⁻¹)	¹ H and ¹³ C NMR (in d ₆ -DMSO) (ppm)
2a	3190, 3115, 3069, 3002, 2959, 2934, 2675, 2153, 1702, 1665, 1611, 1594, 1484, 1440, 1439, 1424, 1375, 1323, 1313, 1252, 1237, 1157, 876, 839, 769, 749, 731, 687, 618	¹ H NMR: 0.81 (t, <i>J</i> = 6.5 Hz, 3H, CH ₃), 1.15-1.33 (m, 4H, H-2 and H-3 of butyl), 2.12-2.28 (m, 2H, H-1 of butyl), 7.17 (d, <i>J</i> = 8.3 Hz, 1H, H-8), 7.21 (t, <i>J</i> = 7.9 Hz, 1H, H-6), 7.71 (dt, <i>J</i> = 7.7 and 1.4 Hz, 1H, H-7), 7.86 (dd, <i>J</i> = 7.7 and 1.1 Hz, H-5), 11.49 (s, 1H, NH). ¹³ C NMR: 13.39, 21.82, 26.65, 35.54, 65.21, 109.76, 116.82, 117.79, 123.50, 127.35, 137.26, 141.13, 166.88, 189.46.
2b	3190, 3064, 2997, 2934, 2153, 1702, 1665, 1612, 1594, 1485, 1440, 1430, 1374, 1324, 1256, 1242, 1225, 1159, 1033, 940, 869, 826, 759, 745, 707, 664, 654	¹ H NMR: 3.56 (s, 2H, PhCH ₂), 7.03-7.09 (m, 2H, <i>m</i> -H of Ph), 7.13-7.24 (m, 3H, <i>o</i> - and <i>p</i> -H of Ph), 7.02 (d, <i>J</i> = 8.1 Hz, 1H, H-8), 7.15 (dt, <i>J</i> = 7.5 and 0.8 Hz, 1H, H-6), 7.61 (dt, <i>J</i> = 7.7 and 1.5 Hz, 1H, H-7), 7.78 (dd, <i>J</i> = 7.8 and 1.4 Hz, H-5), 11.50 (s, 1H, NH). ¹³ C NMR: 64.77, 109.78, 116.69, 117.84, 123.55, 127.18, 127.60, 128.23, 129.90, 133.16, 137.41, 140.89, 166.45, 189.35.
2d	3113, 3082, 3062, 3032, 2152, 1689, 1658, 1598, 1493, 1473, 1437, 1361, 1305, 1245, 1141, 1062, 1038, 982, 920, 907, 856, 774, 748, 702, 662	¹ H NMR: 3.36 (s, 3H, N-CH ₃), 3.52 and 3.57 (two d, 2H, CH ₂), 6.95-7.05 (m, 2H, <i>m</i> -H of Ph), 7.13-7.20 (m, 3H, <i>o</i> - and <i>p</i> -H of phenyl), 7.20-7.32 (m, 2H, H-6 and H-8), 7.72 (dt, <i>J</i> = 7.8 and 1.0 Hz, 1H, H-7), 7.87 (dd, <i>J</i> = 7.7 and 1.0 Hz, H-5). ¹³ C NMR: 30.28, 43.29, 67.45, 110.45, 116.07, 119.57, 123.71, 127.35, 127.68, 128.06, 129.80, 132.77, 137.25, 141.91, 166.18, 189.02.
2e	3116, 3086, 3033, 2986, 2940, 2887, 2151, 1710, 1667, 1603, 1494, 1471, 1446, 1418, 1361, 1298, 1240, 1145, 1035, 957, 923, 866, 805, 778, 754, 750, 695, 667	¹ H NMR: 3.49 (s, 3H, CH ₃), 7.21 (t, <i>J</i> = 7.7 Hz, 1H, H-6), 7.22-7.28 (m, 2H, <i>m</i> -H of Ph), 7.33 (d, <i>J</i> = 8.3 Hz, 1H, H-8), 7.35-7.44 (m, 3H, <i>o</i> - and <i>p</i> -H of Ph), 7.67 (dt, <i>J</i> = 7.8 and 1.6 Hz, 1H, H-7), 7.86 (dd, <i>J</i> = 7.7 and 1.6 Hz, H-5). ¹³ C NMR: 30.91, 75.84, 111.44, 116.10, 120.67, 123.59, 127.10, 127.41, 129.47, 129.95, 132.89, 136.42, 141.42, 165.88, 187.88.
2f	3101, 3067, 3018, 2152, 1713, 1678, 1596, 1492, 1463, 1449, 1342, 1300, 1238, 1170, 1120, 1069, 1001, 952, 847, 775, 764, 749, 736, 719, 707, 690, 665, 605	¹ H NMR: 6.29 (d, <i>J</i> = 8.3 Hz, 1H, H-8), 7.18 (t, <i>J</i> = 7.5 Hz, 1H, H-6), 7.32-7.70 (m, 11H, H-7 and two Ph), 7.92 (d, <i>J</i> = 7.6 Hz, 1H, H-5). ¹³ C NMR: 76.02, 111.31, 116.78, 120.46, 123.63, 127.22, 127.43, 128.21, 128.62, 129.16, 129.68, 130.08, 130.39, 132.69, 135.91, 137.16, 142.29, 165.93, 187.72.
2g	3191, 3067, 2956, 2933, 2871, 2153, 1709, 1698, 1666, 1615, 1503, 1426, 1358, 1318, 1233, 1151, 1096, 961, 909, 828, 748, 731, 656	¹ H NMR: 0.81 (t, <i>J</i> = 6.6 Hz, 3H, CH ₃ of butyl), 1.11-1.32 (m, 4H, H-2 and H-3 of butyl), 2.13-2.23 (m, 2H, H-1 of butyl), 2.32 (s, 3H, Ar-CH ₃), 7.07 (d, <i>J</i> = 8.2 Hz, 1H, H-8), 7.53 (d, <i>J</i> = 8.2 Hz, 1H, H-7), 7.65 (s, 1H, H-5), 11.42 (s, 1H, NH). ¹³ C NMR: 13.39, 19.94, 21.82, 26.67, 35.51, 64.90, 109.71, 116.79, 117.58, 126.87, 132.87, 138.17, 138.95, 166.70, 189.48.
2h	3117, 3063, 2961, 2932, 2905, 2873, 2152, 1704, 1667, 1608, 1595, 1497, 1480, 1412, 1116, 1088, 908, 889, 844, 738, 706, 1360, 1311, 1261, 1205, 663, 600	¹ H NMR: 0.81 (t, <i>J</i> = 6.9 Hz, 3H, CH ₃ of butyl), 1.18-1.33 (m, 4H, H-2 and H-3 of butyl), 2.09-2.25 (m, 2H, H-1 of butyl), 7.19 (d, <i>J</i> = 8.5 Hz, 1H, H-8), 7.72-7.79 (m, 2H, H-5 and H-7), 11.57 (s, 1H, NH). ¹³ C NMR: 13.39, 21.78, 26.52, 35.54, 65.90, 109.89, 118.91, 119.06, 126.19, 127.31, 136.61, 140.00, 166.91, 188.61.
2i	3252, 2961, 2932, 2663, 2157, 1697, 1672, 1597, 1498, 1465, 1354, 1312, 1262, 1236, 1222, 1143, 1059, 1025, 951, 906, 800, 784, 752, 715, 674	¹ H NMR: 0.81 (t, <i>J</i> = 6.9 Hz, 3H, CH ₃ of butyl), 1.19-1.35 (m, 4H, H-2 and H-3 of butyl), 2.11-2.25 (m, 2H, H-1 of butyl), 2.35 (s, 3H, Ar-CH ₃), 7.13 (t, <i>J</i> = 7.6 Hz, 1H, H-6), 7.56 (d, <i>J</i> = 7.0 Hz, 1H, H-7), 7.70 (d, <i>J</i> = 7.6 Hz, 1H, H-5), 10.59 (s, 1H, NH). ¹³ C NMR: 13.40, 17.28, 21.74, 26.62, 35.64, 66.28, 109.93, 118.21, 123.21, 125.17, 125.43, 128.22, 138.43, 139.11, 167.23, 189.68.
2j	3036, 3012, 2961, 2929, 2871, 2154, 1703, 1664, 1616, 1578, 1526, 1463, 1428, 1380, 1367, 1291, 1251, 1228, 1216, 1172, 1037, 930, 885, 851, 824, 769, 740, 687, 655	¹ H NMR: 0.81 (t, <i>J</i> = 6.8 Hz, 3H, CH ₃ of butyl), 1.18-1.30 (m, 4H, H-2 and H-3 of butyl), 2.12-2.20 (m, 2H, H-1 of butyl), 2.31 (s, 3H, Ar-CH ₃), 2.50 (s, 3H, Ar-CH ₃), 6.82 (s, 1H, H-8), 6.87 (s, 1H, H-6), 11.33 (s, 1H, NH). ¹³ C NMR: 13.41, 21.30, 21.43, 21.77, 26.74, 35.67, 67.54, 110.09, 114.29, 114.95, 127.57, 141.48, 141.76, 146.61, 166.61, 189.69.

Table 2 (continued)

Compound No.	R (cm ⁻¹)	¹ H and ¹³ C NMR (in d ₆ -DMSO) (ppm)
2k	3150, 3068, 3034, 2922, 2844, 2153, 1710, 1701, 1670, 1618, 1578, 1522, 1458, 1437, 1427, 1354, 1320, 1288, 1230, 1032, 915, 909, 852, 754, 704, 681	¹ H NMR: 2.26 (s, 3H, Ar-CH ₃), 2.46 (s, 3H, Ar-CH ₃), 3.50 and 3.56 (two d, <i>J</i> = 13.5 Hz, 2H, CH ₂), 6.72 (s, 1H, H-8), 6.82 (s, 1H, H-6), 7.02-7.08 (m, 2H, <i>m</i> -H of Ph), 7.17-7.25 (m, 3H, <i>o</i> - and <i>p</i> -H of Ph), 7.36 (s, 1.2 H, benzene), 11.35 (s, 1H, NH). ¹³ C NMR: 21.27, 21.52, 42.01, 67.79, 110.39, 114.50, 114.89, 127.61, 128.20, 128.22, 129.82, 133.26, 141.41, 141.66, 146.80, 166.39, 189.43.
2l	3216, 3157, 3016, 2921, 2158, 1712, 1703, 1675, 1663, 1616, 1580, 1518, 1461, 1449, 1426, 1358, 1320, 1166, 1036, 851, 813, 750, 694, 553	¹ H NMR: 2.21 (s, 3H, Ar-CH ₃), 2.50 (s, 3H, Ar-CH ₃), 6.67 (s, 1H, H-8), 6.77 (s, 1H, H-6), 7.26-7.32 (m, 2H, <i>m</i> -H of Ph), 7.38-7.48 (m, 3H, <i>o</i> - and <i>p</i> -H of Ph), 11.46 (s, 1H, NH). ¹³ C NMR: 20.63, 21.16, 76.57, 111.53, 114.74, 115.54, 126.77, 127.15, 129.54, 129.94, 133.25, 140.49, 140.51, 146.02, 165.66, 188.59.
2m	3032, 2962, 2934, 2875, 2159, 1701, 1665, 1605, 1572, 1491, 1459, 1343, 1320, 1301, 1243, 1167, 1092, 1041, 1023, 921, 845, 809, 785, 749, 735, 688	¹ H NMR: 0.80 (t, <i>J</i> = 7.0 Hz, 3H, CH ₃ of butyl), 1.10-1.38 (m, 4H, H-2 and H-3 of butyl), 2.13 (t, <i>J</i> = 7.9 Hz, 2H, H-1 of butyl), 2.39 (s, 3H, Ar-CH ₃), 2.49 (s, 3H, Ar-CH ₃), 3.42 (s, 3H, N-CH ₃), 6.98 (s, 1H, H-6), 7.17 (s, 1H, H-8). ¹³ C NMR: 13.38, 21.32, 21.52, 21.65, 26.72, 31.04, 36.29, 70.33, 110.53, 114.93, 115.92, 127.85, 141.06, 142.87, 146.29, 166.07, 189.77.
2n	3233, 3158, 3088, 2156, 1720, 1677, 1597, 1580, 1486, 1460, 1362, 1335, 1255, 1211, 1032, 969, 820, 772, 708, 662	¹ H NMR: 2.27 (s, 3H, Ar-CH ₃), 3.46 and 3.60 (two d, <i>J</i> = 14.0 Hz), 7.05-7.10 (m, 2H, <i>m</i> -H of Ph), 7.18 (d, <i>J</i> = 8.1 Hz, 1H, H-7), 7.22-7.28 (m, 3H, <i>o</i> - and <i>p</i> -H of Ph), 7.43 (d, <i>J</i> = 8.1 Hz, 1H, H-6), 10.61 (s, 1H, NH). ¹³ C NMR: 17.42, 42.59, 72.42, 111.13, 116.32, 124.82, 125.59, 127.78, 128.06, 129.90, 130.46, 132.51, 137.34, 140.28, 166.25, 187.65.
2o	3230, 3154, 3067, 3026, 2951, 2924, 2158, 1719, 1674, 1595, 1582, 1491, 1453, 1400, 1368, 1340, 1311, 1248, 1216, 1199, 1142, 1081, 1068, 1035, 967, 956, 912, 825, 804, 789, 774, 754, 714, 701, 678, 617	¹ H NMR: 2.31 (s, 3H, Ar-CH ₃), 3.54 (s, 2H, CH ₂), 7.02-7.09 (m, 2H, <i>m</i> -H of Ph), 7.16-7.23 (m, 3H, <i>o</i> - and <i>p</i> -H of Ph), 7.26 (d, <i>J</i> = 8.5 Hz, 1H, H-6), 7.65 (d, <i>J</i> = 8.5 Hz, 1H, H-5), 10.77 (s, 1H, NH). ¹³ C NMR: 14.07, 42.16, 66.96, 110.31, 117.48, 123.28, 124.09, 125.84, 127.65, 128.07, 129.99, 132.85, 140.27, 141.80, 167.08, 188.86.
4g	3187, 3064, 2958, 2928, 2871, 1702, 1665, 1615, 1508, 1428, 1417, 1365, 1326, 1236, 1158, 1123, 1099, 1030, 915, 856, 826, 742, 702, 655, 612	¹ H NMR: 0.83 (t, <i>J</i> = 7.2 Hz, 3H, CH ₃ of butyl), 0.98-1.22 (m, 2H, H-3 of butyl), 1.22-1.35 (m, 2H, H-2 of butyl), 2.31 (s, 3H, Ar-CH ₃), 2.41 (t, <i>J</i> = 7.9 Hz, 2H, H-1 of butyl), 7.06 (d, <i>J</i> = 8.2 Hz, 1H, H-8), 7.50 (dd, <i>J</i> = 8.2 and 1.4 Hz, 1H, H-7), 7.66 (s, 1H, H-5), 11.20 (s, 1H, NH). ¹³ C NMR: 13.51, 19.94, 21.92, 27.81, 33.58, 56.46, 116.52, 116.87, 127.23, 132.59, 137.61, 138.45, 166.73, 187.91.
4h	3185, 3122, 3065, 2968, 2927, 2909, 2869, 1708, 1667, 1608, 1593, 1487, 1477, 1427, 1414, 1358, 1316, 1261, 1236, 1217, 1161, 1128, 1097, 964, 916, 843, 730, 652	¹ H NMR: 0.75 (t, <i>J</i> = 7.1 Hz, 3H, CH ₃ of butyl), 1.11-1.25 (m, 2H, H-3 of butyl), 1.25-1.37 (m, 2H, H-2 of butyl), 2.39 and 2.42 (two d, <i>J</i> = 7.0 Hz, 2H, H-1 of butyl), 7.19 (d, <i>J</i> = 8.7 Hz, 1H, H-8), 7.72 (dd, <i>J</i> = 8.7 and 2.5 Hz, 1H, H-7), 7.81 (d, <i>J</i> = 2.5 Hz, 1H, H-5), 11.40 (s, 1H, NH). ¹³ C NMR: 13.53, 22.38, 27.87, 33.14, 56.56, 118.44, 118.68, 126.48, 127.13, 136.20, 139.51, 166.77, 186.83.
4i	3108, 3086, 2963, 2929, 2859, 1703, 1667, 1595, 1496, 1466, 1424, 1366, 1311, 1260, 1237, 1175, 1031, 965, 902, 794, 740, 679. ¹³ C NMR: 13.53, 17.26	¹ H NMR: 0.85 (t, <i>J</i> = 7.2 Hz, 3H, CH ₃ of butyl), 1.07-1.22 (m, 2H, H-3 of butyl), 1.22-1.38 (m, 2H, H-2 of butyl), 2.35 (s, 3H, Ar-CH ₃), 2.43 (t, <i>J</i> = 7.9 Hz, 2H, H-1 of butyl), 7.12 (t, <i>J</i> = 7.6 Hz, 1H, H-6), 7.53 (d, <i>J</i> = 7.3 Hz, 1H, H-7), 7.74 (d, <i>J</i> = 7.6 Hz, 1H, H-5), 10.39 (s, 1H, NH). ¹³ C NMR: 22.35, 27.87, 33.52, 56.01, 117.51, 122.94, 125.09, 125.50, 138.04, 138.64, 167.22, 188.15.
4j	3145, 3112, 3070, 3015, 2953, 2930, 2869, 1702, 1667, 1615, 1578, 1524, 1463, 1428, 1403, 1378, 1290, 1223, 1145, 1099, 1028, 926, 883, 857, 735, 671	¹ H NMR: 0.85 (t, <i>J</i> = 7.2 Hz, 3H, CH ₃ of butyl), 1.06-1.18 (m, 2H, H-3 of butyl), 1.22-1.38 (m, 2H, H-2 of butyl), 2.30 (s, 3H, Ar-CH ₃), 2.38 (t, <i>J</i> = 6.7 Hz, 2H, H-1 of butyl), 2.51 (s, 3H, Ar-CH ₃), 6.81 (s, 1H, H-8), 6.85 (s, 1H, H-6), 11.13 (s, 1H, NH). ¹³ C NMR: 13.52, 21.21, 21.61, 22.37, 27.82, 33.61, 57.28, 113.82, 114.71, 127.36, 141.31, 141.83, 145.93, 166.60, 187.92.
4m	2973, 2954, 2918, 2872, 1697, 1660, 1609, 1572, 1496, 1458, 1434, 1345, 1328, 1302, 1250, 1181, 1148, 1106, 1073, 1033, 928, 846, 719, 655, 607	¹ H NMR: 0.85 (t, <i>J</i> = 7.3 Hz, 3H, CH ₃ of butyl), 1.09-1.22 (m, 2H, H-3 of butyl), 1.22-1.37 (m, 2H, H-2 of butyl), 2.34-2.47 (m, 2H, H-1 of butyl), 2.39 (s, 3H, Ar-CH ₃), 2.52 (s, 3H, Ar-CH ₃), 3.43 (s, 3H, N-CH ₃), 6.97 (s, 1H, H-6), 7.15 (s, 1H, H-8). ¹³ C NMR: 13.54, 21.45, 21.75, 22.42, 27.91, 30.77, 34.24, 57.23, 114.66, 115.85, 127.72, 141.59, 142.39, 145.70, 166.00, 187.69.
5j	3187, 3119, 3056, 2955, 2871, 1704, 1673, 1603, 1571, 1503, 1454, 1426, 1392, 1269, 1206, 1145, 1101, 992, 927, 871, 845, 739, 678, 650	¹ H NMR: 0.86 (t, <i>J</i> = 7.2 Hz, 3H, CH ₃ of butyl), 1.12-1.24 (m, 2H, H-3 of butyl), 1.24-1.38 (m, 2H, H-2 of butyl), 2.32-2.42 (m, 2H, H-1 of butyl), 2.41 (s, 3H, Ar-CH ₃), 2.64 (s, 3H, Ar-CH ₃), 7.00 (s, 1H, H-8), 11.25 (s, 1H, NH). ¹³ C NMR: 13.55, 20.92, 22.44, 24.67, 27.89, 33.25, 57.75, 116.37, 122.73, 128.22, 139.75, 140.52, 145.40, 166.24, 187.48.
5m	2951, 2934, 2869, 1702, 1672, 1587, 1473, 1458, 1411, 1327, 1309, 1278, 1252, 1225, 1159, 1143, 1071, 1022, 929, 845, 722, 670, 622	¹ H NMR: 0.87 (t, <i>J</i> = 7.1 Hz, 3H, CH ₃ of butyl), 1.16-1.28 (m, 2H, H-3 of butyl), 1.28-1.39 (m, 2H, H-2 of butyl), 2.37 (t, <i>J</i> = 7.7 Hz, 2H, H-1 of butyl), 2.51 (s, 3H, Ar-CH ₃), 2.63 (s, 3H, Ar-CH ₃), 3.42 (s, 3H, N-CH ₃), 7.39 (s, 1H, H-8). ¹³ C NMR: 13.57, 21.07, 22.47, 24.73, 27.96, 30.90, 33.98, 57.93, 116.43, 118.70, 123.49, 139.93, 140.73, 145.16, 165.60, 187.47.

The undesired hydrolysis of **2** was successfully eliminated when we diluted the reaction mixture with aqueous sodium acetate instead of water. Hence the strong hypothiocyanous acid (HOSCN), which probably catalyzes hydrolytic cleavage of 3-thiocyanato derivatives **2** to **1**, is neutralized. However, even under these reaction condi-

tions, we were not successful in isolating compound **2c**, which was according to tlc monitoring formed, but rapidly decomposed to the initial compound **1c** during the isolation.

In the crystalline form compounds **2** are relatively stable. In their infrared spectra, a characteristic sharp absorp-

tion band of the -SCN group appears in the narrow region of 2151-2154 cm^{-1} . In the cases of 8-methyl substituted derivatives (**2i**, **n**, **o**) this absorption band is shifted to the region of 2156-2158 cm^{-1} . Other characteristic bands for **2** occur at 1689-1720 cm^{-1} (keto group) and 1664-1677 cm^{-1} (lactam).

In some cases the crude products of the thiocyanation reactions contained small amounts of 3-bromo derivatives **4**, which we isolated by column chromatography. Their structures were confirmed by an independent bromination of **1** with bromine in acetic acid. However, the bromination of some compounds **1** did not only take place at the 3 position but also at the fused benzene ring. For example, the bromination of **1h** resulted in a mixture of 3-bromo and 3,6-dibromo derivatives **4h** and **5h** even when 0.5 molar equivalent of bromine was employed in the reaction. By screening over several different solvents we learned that both **4h** and **5h** possess similar chromatographic properties, not allowing us to isolate the products by column chromatography. Thus from the crude reaction product, consisting of **4h**, **5h**, and unreacted starting material **1h**, the 3-bromo derivative **4h** was obtained by repeated crystallization. A similar observation was found for the bromination of **1n**.

Besides with water, we found out that thiocyanates **2** also react with nitrogen nucleophiles such as aliphatic amines and anilines. In all the examined cases of this preliminary research the reactions preceded at the sulfur atom with migration of -SCN group to the nucleophile, analogously to that reported in the literature [13-19]. In conclusion it seems that the thiocyanato derivatives **2** may not serve as suitable intermediates for the synthesis of 3-sulfanyl-1*H*,3*H*-quinoline-2,4-diones. On the other hand, these can potentially be utilized as thiocyanation agents. The reactions of **2** with nucleophiles will be the subject of our forthcoming investigation.

EXPERIMENTAL

The melting points were determined on a Kofler block or Gallenkamp apparatus and are uncorrected. The IR spectra were recorded on a Perkin-Elmer 421 and 1310 and Mattson 3000 spectrophotometers using samples in potassium bromide disks. The NMR spectra were recorded on a Bruker DPX-300 spectrometer at 302 K in hexadeuteriodimethyl sulfoxide (unless otherwise indicated). Chemical shifts are given on the δ scale (ppm) and are referenced to internal TMS. Some ^{13}C chemical shifts are referenced to deuteriochloroform. The column chromatography was carried out on silica gel 70-230 mesh, 60 Å (Aldrich) using benzene and then successive mixtures of benzene - ethyl acetate (in ratios from 99:1 to 8:2) as eluent (solvent system S). The course of separation and also the purity of substances were monitored by TLC (elution systems benzene-ethyl acetate, 4:1 and chloroform-ethanol, 9:1) on Alugram® SIL G/UV₂₅₄ foils (Macherey-Nagel). Elemental analyses (C, H, N) were performed with a

Perkin-Elmer 2400 CHN Analyser and EA 1108 Elemental Analyser (Fisons Instrument). The physical and analytical data of compounds under investigation are given in Table 1, spectral data are given in Table 2.

Reaction of 4-Hydroxy-1-methyl-3-phenyl-1*H*-quinolin-2-one (**1e**) with Diacetyl Disulfide.

A mixture of **1e** (2.51 g, 10 mmol), diacetyl disulfide (1.50 g, 10 mmol), and potassium carbonate (2.76 g, 20 mmol) in dimethyl formamide (20 ml) was stirred for 6 hrs at room temperature. After addition of cold water (100 ml) the precipitate was collected by suction filtration. After crystallization from ethanol, 1.85 g (63%) of 4-acetoxy-1-methyl-3-phenyl-1*H*-quinolin-2-one (**6e**), mp 188-90 °C, was obtained. Isolated compound was identical (IR, mixed mp) with that prepared from **1e** by usual procedure with acetic anhydride in pyridine. For **6e**, m.p. 184-7 °C was reported [20].

Anal. Calcd. for $\text{C}_{18}\text{H}_{15}\text{NO}_3$ (293.32): C, 73.71; H, 5.15; N, 4.78. Found: C, 73.58; H, 5.27; N, 4.56.

General Procedure for the Preparation of 3-Alkyl/aryl-3-thiocyanato-1*H*,3*H*-quinoline-2,4-diones (**2**).

A solution of appropriate 4-hydroxy-1*H*-quinolin-2-one **1** [8-11] (10 mmol) in acetic acid (50 ml) was added in one portion to the stirred solution of $(\text{SCN})_2$ prepared by adding bromine (0.56 ml, 11 mmol) to the solution of potassium thiocyanate (2.33 g, 24 mmol) in acetic acid (50 ml). The stirring was continued for 2 min and then the reaction mixture was poured into a well-stirred mixture of sodium acetate (1.98 g, 24 mmol) in water (350 ml) and benzene (150 ml). The benzene layer was separated and the aqueous layer was extracted with benzene (twice 20 ml). The collected benzene extracts were washed three times with 50 ml of 5% solution of sodium hydrogen carbonate or 3% solution of potassium carbonate, respectively, dried with anhydrous sodium sulfate and evaporated to dryness *in vacuo*. The residue was crystallized from an appropriate solvent (Table 1). In the cases when 3-bromo-1*H*,3*H*-quinoline-2,4-dione **4** was present (according to TLC), the crude product was purified by column chromatography on silica gel using solvent system S as eluent. The course of separation and also the purity of isolated substances were monitored by TLC. Isolated yields of 3-bromo-1*H*,3*H*-quinoline-2,4-diones **4** are given in Table 1 (Method A).

General Procedure for the Preparation of 3-Alkyl/aryl-3-bromo-1*H*,3*H*-quinoline-2,4-diones (**4**) (Method B).

To the stirred solution of initial compound **1** (0.4 mmol) in acetic acid (3 ml), bromine (0.042 ml, 0.82 mmol) was added. After 5 min, the red solution was poured into water (25 ml) and the yellow suspension was extracted twice with benzene (each portion 20 ml). The collected extracts were dried with sodium sulfate, evaporated to dryness *in vacuo* and crystallized to give compounds **4** (Table 1). In the case of compounds **1j** and **1m**, compounds **5j** and **5m**, respectively, were obtained by this procedure (Table 1).

General Procedure for the Bromination of 4-Hydroxy-1*H*-quinolin-2-ones **1j** and **1m** (Method C).

The procedure was the same as in method A, but only one half of theoretical quantity of bromine was used. The benzene solution of crude reaction product was twice washed with potassium carbonate solution (5%) to eliminate unreacted compound **1**. The

solution was dried with sodium sulfate, evaporated to dryness and repeatedly crystallized to obtain pure 3-bromo-1*H*-quinoline-2,4-diones (**4j** and **4m**), and 3,6-dibromo-1*H*-quinoline-2,4-diones (**5j** and **5m**), respectively (Table 1).

General Procedure for the Reaction of 3-Benzyl-3-halogeno-1*H*,3*H*-quinoline-2,4-diones (**3b** and **4b**) and 3-Halogeno-1-methyl-3-phenyl-1*H*,3*H*-quinoline-2,4-diones (**3e** and **4e**) with Sodium Hydrogen Sulfide.

To the stirring solution of 3-bromo/chloro-1*H*,3*H*-quinoline-2,4-dione **3** or **4** (5 mmol) in dimethyl formamide (15 ml), 0.55 g (6 mmol) of NaSH·2H₂O was added in small portions during 2 hours. The reaction mixture was poured onto crushed ice (100 ml), precipitated product **1** was collected by filtration with suction and crystallized from the appropriate solvent. Compounds **1b** (benzene, 81% from **3b** and 83% from **4b**) or **1e**, (methanol-ethyl acetate, 73% from **3e** and 74% from **4e**), respectively, were obtained. The identity of isolated compounds was proved by comparison of their IR spectra with that of authentic specimens prepared by condensation of diethyl malonates with corresponding anilines [7,12]. The mother liquors after crystallization of **1** were evaporated and extracted three times with methanol (5 ml each). The insoluble portion was crystallized from benzene-hexane to give pale yellow crystals, mp 110–2 °C, identified as elemental sulfur (yields 69% from **3b**, 62% from **4b**, 57% from **3e**, and 58% from **4b**).

General Procedure for the Reaction of 3-Chloro-1-methyl-3-phenyl-1*H*,3*H*-quinoline-2,4-dione (**3e**) with Some Sulfur Reagents.

To the stirring solution of 3-chloro-1-methyl-3-phenyl-1*H*,3*H*-quinoline-2,4-dione (**3e**) (1.42 g, 5 mmol) in dimethyl formamide (15 ml), appropriate sulfur reagent (thiourea, sodium thiosulfate, potassium thioacetate, or potassium thiocyanate, respectively) (6 mmol) was added in small portions during 2 hours. The reaction mixture was diluted with water (100 ml), precipitated compound **1e** was collected by filtration with suction and crystallized from benzene. Yields: (%/sulfur reagent): 85%/thiourea, 56%/sodium thiosulfate, 79%/sodium thioacetate, or 59%/potassium thiocyanate, respectively. In the case where potassium thioacetate was used, 30% of the side product **6e** was isolated by repeated crystallization from benzene–cyclohexane.

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