Modified *Riemschneider* Reaction of 3-Thiocyanatoquinolinediones

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The *Riemschneider* reaction of 3-thiocyanatoquinoline-2,4(1*H*,3*H*)-diones with conc. H_2SO_4 was investigated. Using different reaction conditions, 13 types of reaction products were isolated. Compounds bearing a Me, Et, or Bu group at C(3) afforded mainly [1,3]thiazolo[5,4-*c*]quinoline-2,4-diones and 1,9b-dihydro-9b-hydroxythiazolo[5,4-*c*]quinoline-2,4-diones. In the case of the 3-Bu derivatives of the starting compounds, *C*-debutylation was also observed. If a Bn group is present at C(3), rapid *C*-debenzylation of the starting thiocyanates occurred, yielding [1,3]oxathiolo[4,5-*c*]quinoline-2,4-diones, and mixtures of mono-, di-, and trisulfides derived from 4-hydroxy-3-sulfanylquinoline-2-ones. The reaction mechanism of all of the transformations is discussed. All new compounds were characterized by IR, ^{1}H- and ^{13}C-NMR, and EI and ESI mass spectra, and in some cases, ^{15}N-NMR spectra were also used to characterize new compounds.

1. Introduction. – One of the most important families of naturally occurring sulfur compounds is the glucosinolate family, which occurs in cruciferous vegetables. By enzymatic hydrolysis, this class of compounds affords glucose, HSO_4^- ions, and aglycone derivatives, as well as isothiocyanates, thiocyanates, and nitriles [1].

Some aglycones such as thiocyanates act as chemoprotective agents against chemically induced carcinogenesis by blocking the initiation of tumors in a variety of rodent tissues [2]. Thiocyanates are also important starting compounds for the synthesis of various heterocyclic compounds that possess important biological activities [3][4].

Several methods are known for the introduction of S functionalities into molecules [5][6]. We found that 3-chloro- and 3-bromoquinoline-2,4-diones react with some S reagents (NaSH, AcSH, KSCN, thiourea) to give 4-hydroxy-1*H*-quinoline-2-ones **1** [7]. In this reaction, the 3-halogenoquinoline-2,4-diones, which bear a 'positive charged' halogen atom, exhibit a strong oxidative effect on all of the compounds that have a free SH group. Therefore, the preparation of their 3-sulfanyl or 3-thiocyanato analogs by a nucleophilic substitution route is impossible. However, we have prepared 3-thiocyanatoquinoline-2,4-diones **2** *via* the reaction of 4-hydroxy-1*H*-quinoline-2-ones **1** with an *in situ* prepared $(SCN)_2$ in AcOH [7].

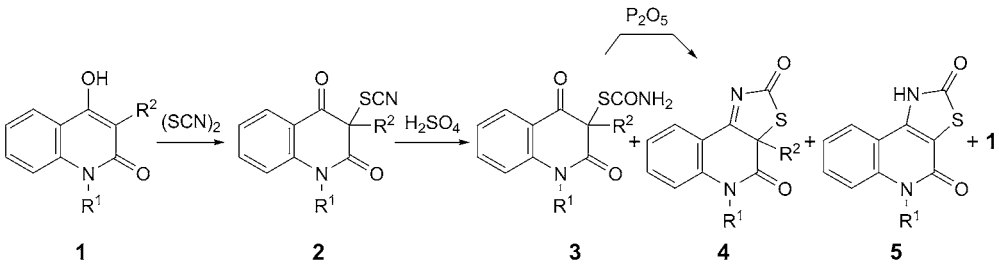
Although the non-enolizable α-thiocyanato derivatives of β-dicarbonyl compounds should be relatively stable [6], compounds **2** are only stable in the crystalline form. In protic solvents, they readily undergo nucleophilic attack by H_2O on the S-atom to form the starting 4-hydroxy-1*H*-quinoline-2-ones **1** [7]. This reaction is analogous to the reactions of α-thiocyanato β-diketones with aqueous alkali or with NH_4OH [8][9]. We

also found that the thiocyanato (SCN) group can be selectively transferred from **2** to some nucleophiles (amines, activated aromatic compounds, thioles, *Wittig* reagents) [10].

The SCN group can be transformed to the thiocarbamate group *via* the *Riemschneider* reaction by treatment with conc. H_2SO_4 [11][12]. The reaction of α-thiocyanato ketones with H_2SO_4, most frequently carried out in the presence of AcOH, usually does not stop at the formation of the carbamates but continues through a dehydration process to form thiazol-2(3*H*)-ones [13–15].

In a previous report [16], we described the reaction of 3-thiocyanatoquinoline-2,4-diones **2** in conc. H_2SO_4, or in its mixture with AcOH, to give a mixture of hydrolytically unstable thiocarbamates **3** and [1,3]thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-diones **4** (*Scheme 1*). Compounds **3** were cyclodehydrated to **4** by treatment with P_2O_5 in AcOH. In two cases, the *C*(*3*)-dealkylated products, which were identified as thiazoloquinolinediones **5**, were also isolated. The extent of this reaction substantially increases, when excess of P_2O_5 was added to the mixture.

Scheme 1



Therefore, we decided to study the modified *Riemschneider* reaction in detail under different reaction conditions and using compounds that bear varying substituents at C(3). Owing to the high reactivity of quinoline-2,4-dione derivatives and our experiences in this area, we anticipated the isolation of novel compounds in this process.

2. Results and Discussion. – To determine the influence of the R^2 substituent (*cf. Scheme 1*) on the transformation of compounds **2**, we chose the Me, Et, Bu, and Bn groups, and H, Me, and Ph were selected as R^1. The starting compounds **2** were prepared by the reaction of 4-hydroxy-1*H*-quinolin-2-ones **1** with $(SCN)_2$ according to [7][16]. By this process, seven novel compounds were prepared. Although two new methods for the α-thiocyanation of ketones and β-dicarbonyl compounds were recently described [17][18], we were unable to use them, because 4-hydroxy-1*H*-quinolin-2-ones **1** were insoluble in the procedure's requisite solvents. The starting compound **1l** was almost insoluble even in AcOH. Thus, we carried out the thiocyanation of **1l** in a DMF solution. The ^{1}H- and ^{13}C-NMR spectra of the new compounds **2** are presented in *Table 1*.

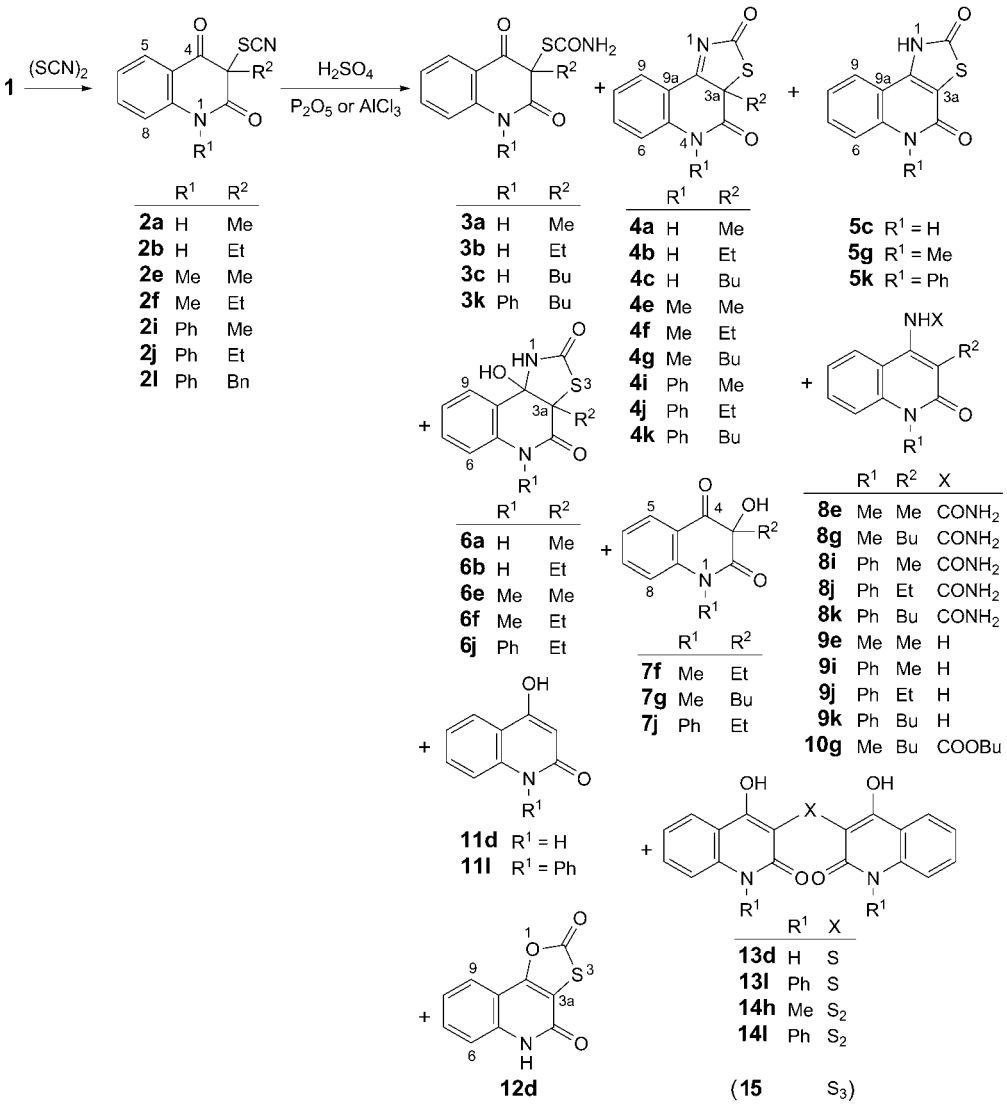
Because the composition of the mixture for the reaction of thiocyanates **2** substantially influences the ratio of the reaction products [16], we carried out the reaction under three different reaction conditions. In the first method, P_2O_5 was added

Table 1. *^{1}H- and ^{13}C-NMR Data* ($CDCl_3$) *of New Compounds* **2** (δ in ppm)

Position	**2a**		**2b**		**2e**		**2f**		**2i**		**2j**		**2l**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
2	–	168.7	–	168.5	–	166.8	–	166.2	–	166.9	–	166.7	–	166.4
3	–	59.7	–	64.8	–	59.8	–	65.6	–	59.0	–	65.1	–	63.4
4	–	188.5	–	188.7	–	188.6	–	188.8	–	188.7	–	189.1	–	189.2
4a	–	118.0	–	118.5	–	119.5	–	119.9	–	119.0	–	119.4	–	119.4
5	8.01	128.7	8.02	128.5	8.06	129.0	8.07	128.9	8.10	128.8	8.11	128.6	8.06	128.5
6	7.25	124.8	7.26	124.8	7.29	124.3	7.27	124.1	7.24	124.4	7.25	124.3	7.13	124.2
7	7.67	137.5	7.67	137.6	7.73	137.3	7.73	137.4	7.48	136.9	7.49	137.0	7.37	137.0
8	7.15	117.0	7.13	117.0	7.24	115.4	7.23	115.4	6.52	117.4	6.52	117.4	6.28	117.2
8a	–	139.9	–	139.9	–	142.3	–	142.4	–	143.5	–	143.5	–	143.3
Substituent at N(1)														
1	10.08	–	9.97	–	3.55	30.8	3.56	30.6	–	136.5	–	136.5	–	136.2
2,6	–	–	–	–	–	–	–	–	7.24, 7.62	129.0, 128.4	7.24, 7.62	129.0, 128.6	6.83, 7.53	129.0, 128.3
3,5	–	–	–	–	–	–	–	–	7.42, 7.57	130.7, 130.4	7.40, 7.59	130.7, 130.4	7.36, 7.58	130.6, 130.4
4	–	–	–	–	–	–	–	–	7.54	129.6	7.55	129.6	7.52	129.5
Substituent at C(3)														
1	2.01	20.9	2.52	30.0	1.97	21.0	2.44	30.0	2.01	20.1	2.53	29.7	3.77	42.4
			2.45				2.43				2.46			
2	–	–	1.02	9.8	–	–	0.96	9.9	–	–	1.08	10.0	–	133.1
3	–	–	–	–	–	–	–	–	–	–	–	–	7.19	128.6
4	–	–	–	–	–	–	–	–	–	–	–	–	7.19	130.7
5	–	–	–	–	–	–	–	–	–	–	–	–	7.19	129.5
SCN	–	108.3	–	108.6	–	108.3	–	108.8	–	108.3	–	108.8	–	108.6

to the solution of **2** in a 1:9 mixture AcOH conc. H_2SO_4 (*Method A*), in the second one, P_2O_5 was added to the solution of **2** in conc. H_2SO_4 (*Method B*), and in the third method (*Method C*), $AlCl_3$ was added to the solution of **2** in conc. H_2SO_4. The results of these experiments are compiled in *Scheme 2* and *Table 2*.

Scheme 2



To our surprise, thiocarbamates **3** were isolated in only four cases, *i.e.* **3a**, **3b**, **3c**, and **3g**. Thiazoloquinolinediones **4** were found as products from all of the starting

Table 2. *Results of Modified* Riemschneider *Reaction of 3-Thiocyanatoquinoline-2,4-diones* **2**

Entry	**2**	R^1	R^2	*Method*[a])	Time [min]	Product(s) (Yield [%])[b])[c])
1	**a**	H	Me	*A*	60	**6a** (46)
2				*B*	30	**3a** (35), **4a** (7)
3				*C**	50	**1a** (52)[b]), **6a** (8)
4	**b**	H	Et	*A*	180	**4b** (7), **6b** (40)
5				*B*	60	**3b** (42), **4b** (18)
6				*C*	60	**1b** (26), **4b** (18)
7	**c**	H	Bu	*A*	10	**3c** (52), **4c** (10)
8				*A*	30	**1c** (33), **4c** (14)
9				*A*	21 h	**5c** (43)
10				*B**	30	**1c** (30)
11				*B**	40	**1c** (47)
12				*C*	21 h	**5c** (34)
13	**d**	H	Bn	*A*	180	**12d** (48), **Md** (4)[d])
14				*B*	30	**11d** (6), **12d** (5), **Md**[d]) (55)
15				*B**		**Md**[d]) (22)
16				*C**	30	**Md**[d]) (35)
17	**e**	Me	Me	*A*	150	**1e** (5), **4e** (18), **6e** (63)
18				*B**	60	**1e** (27), **4e** (8), **8e** (29)
19				*C**	60	**1e** (24), **4e** (4), **6e** (3), **8e** (23)
20	**f**	Me	Et	*A*	17 h	**4f** (41), **6f** (16), **7f** (4)
21				*B**	40	**1f** (13), **4f** (53)
22				*C*	60	**1f** (5), **4f** (42)
23	**g**	Me	Bu	*A*	180	**5g** (63)
24				*B*	60	**1g** (14), **4g** (21), **5g** (1)
25				*B**	90	**1g** (10), **4g** (18), **5g** (3), **7g** (4), **8g** (18)
26				*C**	90	**1g** (38), **4g** (4), **8g** (10)
27	**h**	Me	Bn	*A*	60	**Mh**[d]) (33)
28				*B*	30	**Mh**[d]) (46)
29				*C*	60	**Mh**[d]) (33)
30	**i**	Ph	Me	*A*	120	**1i** (7), **4i** (69)
31				*B**	60	**1i** (36), **4i** (4), **8i** (25)
32				*C**	60	**1i** (59), **4i** (2), **8i** (22)
33	**j**	Ph	Et	*A*	60	**1j** (7), **4j** (61), **6j** (8)
34				*B**	40	**1j** (30), **4j** (12), **7j** (7)
35				*C**	30	**1j** (30), **4j** (35)
36	**k**	Ph	Bu	*A*	60	**1k** (22), **4k** (54)
37				*A*	21 h	**1k** (6), **4k** (15), **5k** (34)
38				*A**	45	**1k** (14), **4k** (23), **8k** (26), **9k** (4)
39				*B*	25	**3k** (40), **4k** (23)
40				*C*	45	**3k** (23), **4k** (51)
41	**l**	Ph	Bn	*A*	45	**11l** (9)[b], **12l** (7), **Ml**[d]) (30)
42				*A**	45	**Ml**[d]) (44)
43				*B*	45	**11l** (4), **12l** (26), **Ml**[d]) (25)
44				*B**	30	**11l** (3), **Ml**[d]) (32)
45				*C**	60	**11l** (5), **Ml**[d]) (42)

[a]) *Methods: A:* H_2SO_4 96%/AcOH, 9:1, P_2O_5; *B:* H_2SO_4 96%, P_2O_5; *C:* H_2SO_4 96%, $AlCl_3$. In experiments designated with asterisk, for alkalization of the crude mixture, NH_4OH was used. [b]) All isolated compounds **1** and **7** were identical to authentic samples. [c]) In most cases, elemental sulfur was also isolated. [d]) Mixtures of compounds **13**, **14**, and **15**, yields were calculated to pure compound **14**.

compounds **2** with the exception of **2d**, **2h**, and **2l**, which bear a Bn group at C(3). In the reactions in which **4a**, **4b**, **4e**, **4f**, and **4j** were formed, their hydrated analogs **6a**, **6b**, **6e**, **6f**, and **6j**, none of which has been reported previously, arose from their corresponding starting materials. The structures of studied compounds were based on standard 1D ^{1}H- and ^{13}C-NMR spectra, and on several 2D experiments (gradient-selected (gs)-COSY, gs-HMQC, gs-HMBC). The presence of one sp^3 C-atom (C(3)) and ^{13}C signals resonating at 194 ppm (C(4)) was a typical feature of compounds **3**, whereas compounds **4** showed one sp^3 C-atom resonance (C(3a)), and compounds **6** displayed two sp^3 C-atom resonances (C(3a) and C(9b); *cf. Tables 3–5*).

Table 3. *^{1}H- and ^{13}C-NMR Data* ($CDCl_3$) *of Compounds* **3** (δ in ppm)

Position	**3a**		**3b**		**3c**		**3k**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
2	–	171.7	–	171.0	–	171.1	–	170.8
3	–	61.9	–	66.3	–	65.5	–	65.8
4	–	193.8	–	193.7	–	193.7	–	193.2
4a	–	117.8	–	119.0	–	119.0	–	119.8
5	7.82	127.3	7.80	126.8	7.80	126.8	7.98	127.2
6	7.15	122.5	7.14	122.4	7.13	122.4	7.24	123.0
7	7.66	136.1	7.64	136.0	7.64	136.0	7.56	136.0
8	7.18	116.4	7.16	116.4	7.16	116.4	6.38	116.6
8a	–	141.6	–	141.6	–	141.6	–	143.5
Substituent at N(1)								
1	11.01	–	11.05	–	11.04	–	–	138.0
2,6	–	–	–	–	–	–	7.42, 7.16	130.4, 128.6
3,5	–	–	–	–	–	–	7.67, 7.42	130.3, 129.4
4	–	–	–	–	–	–	7.56	128.9
Substituent at C(3)								
1	1.46	21.7	1.92	29.8	1.86	36.0	1.99	36.2
			1.87		1.82			
2	–	–	0.83	9.0	1.22	26.2	1.39	26.3
					1.12		1.24	
3	–	–	–	–	1.19	22.1	1.24	22.1
4	–	–	–	–	0.78	13.6	1.07	13.6
$SCONH_2$	7.90, 7.41	166.4	7.86, 7.39	166.4	7.82, 7.38	166.4	7.97, 7.45	166.5

Unfortunately, we have found that the dealkylated products **5** were formed only in cases in which the starting compounds contained a Bu group at C(3) (*i.e.,* **5c**, **5g**, and **5k**), and prolonged reaction times were employed (*Table 2*). In some cases, nucleophilic substitution was found to proceed in thiocyanates **2**, and small quantities of known 3-hydroxyquinoline-2,4-diones **7f**, **7g**, and **7j** were isolated.

In several cases, conc. NH_4OH was used during the isolation of the reaction product with the aim to basify the crude extract after the reaction (*Methods A**, *B**, and *C**). Under these conditions, side-products **8i**, **8k** and **9e**, **9g**, and **9k** were isolated (*Table 2*). We propose that compounds **8** and **9** arise from the nucleophilic ring opening of the thiazolones **4** with NH_4OH and subsequent desulfuration (*Scheme 3*). The presence of the $CONH_2$ group at the N-atom in compounds **8** implies that the C(O)–S bond in

Table 4. *^{1}H- and ^{13}C-NMR Data* ((D_6)DMSO) *of Compounds* **4** (δ in ppm)

Position	**4a**		**4b**		**4e**		**4f**		**4g**		**4i**		**4j**		**4k**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
2	–	184.9	–	185.3	–	184.7	–	185.1	–	185.2	–	184.9	–	185.3	–	185.4
3a	–	72.5	–	78.2	–	72.6	–	78.3	–	77.8	–	72.9	–	78.6	–	78.1
4	–	167.9	–	167.3	–	167.2	–	166.5	–	166.5	–	167.4	–	166.7	–	166.7
5a	–	141.1	–	141.1	–	142.2	–	142.2	–	142.3	–	143.3	–	143.3	–	143.3
6	7.24	117.1	7.24	117.0	7.56	116.8	7.55	116.9	7.55	116.8	6.51	117.4	6.50	117.4	6.50	117.4
7	7.76	137.1	7.76	137.0	7.88	137.1	7.88	137.1	7.87	137.1	7.88	136.6	7.67	136.6	7.67	136.6
8	7.31	123.7	7.30	123.7	7.40	123.9	7.39	123.9	7.39	124.0	7.40	123.9	7.36	123.9	7.36	124.0
9	8.00	128.2	7.98	128.0	8.07	128.2	8.05	128.0	8.05	128.1	8.13	128.4	8.11	128.1	8.10	128.2
9a	–	114.7	–	115.0	–	116.3	–	116.5	–	116.6	–	115.9	–	116.1	–	116.2
9b	–	193.2	–	192.3	–	192.6	–	191.7	–	191.9	–	192.7	–	191.8	–	191.9
Substituent at N(1)																
1	11.30	–	11.30	–	3.44	30.4	3.45	30.4	3.44	30.5	–	137.0	–	137.0	–	137.1
2,6	–	–	–	–	–	–	–	–	–	–	7.55, 7.40	129.5, 128.9	7.54, 7.38	129.5, 128.9	7.54, 7.38	129.5, 128.9
3,5	–	–	–	–	–	–	–	–	–	–	7.67, 7.63	130.4, 130.1	7.67, 7.63	130.4, 130.1	7.65, 7.61	130.4, 130.2
4	–	–	–	–	–	–	–	–	–	–	7.40	129.3	7.56	128.9	7.55	129.3
Substituent at C(3)																
1	1.91	31.0	2.24	36.0	1.89	30.7	2.20	35.8	2.16	41.7	2.07	30.8	2.42	36.0	2.38	41.7
			1.98						1.91				2.20		2.11	
2	–	–	0.93	9.6	–	–	0.91	9.5	1.37	27.3	–	–	0.99	9.8	1.45	27.3
									1.14						1.23	
3	–	–	–	–	–	–	–	–	1.21	21.4	–	–	–	–	1.31	21.4
4	–	–	–	–	–	–	–	–	0.79	13.6	–	–	–	–	0.85	13.6
5	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

Table 5. *^{1}H- and ^{13}C-NMR Data* ((D_6)DMSO) *of Compounds* **6** (δ in ppm)

Position	**6a**		**6b**		**6e**		**6f**		**6j**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
1	9.06	–	8.91a)	–	9.08b)	–	8.95c)	–	9.13	–
2	–	170.5	–	171.1	–	170.7	–	171.2	–	171.2
3a	–	63.7	–	69.2	–	64.5	–	69.8	–	70.5
4	–	169.6	–	169.4	–	169.3	–	169.0	–	168.9
5a	–	134.9	–	134.9	–	136.8	–	136.7	–	137.9
6	6.99	115.2	6.97	115.1	7.26	114.9	7.23	114.8	6.25	115.8
7	7.37	130.1	7.35	130.0	7.50	130.4	7.50	130.3	7.30	129.9
8	7.14	122.8	7.11	122.7	7.26	123.3	7.23	123.2	7.21	123.3
9	7.71	127.8	7.69	127.0	7.82	127.7	7.81	126.9	7.86	127.5
9a	–	122.1	–	122.6	–	123.4	–	124.1	–	123.5
9b	–	87.3	–	86.7	–	86.6	–	85.6	–	86.1
Substituent at N(1)										
1	10.72	–	10.75c)		3.39	30.5	3.43	30.4	–	137.7
2,6	–	–	–	–	–	–	–	–	7.35	129.0
3,5	–	–	–	–	–	–	–	–	7.65	130.2
4	–	–	–	–	–	–	–	–	7.56	128.7
Substituent at C(3a)										
1	1.54	18.9	2.04	26.1	1.51	18.9	2.04	26.2	2.16	26.0
			1.96				1.95		2.12	
2	–	–	0.78	10.1	–	–	0.68	10.1	0.88	10.3
3	–	–	–	–	–	–	–	–	–	–
4	–	–	–	–	–	–	–	–	–	–
5	–	–	–	–	–	–	–	–	–	–
OH	7.00	–	7.08	–	7.07	–	7.22	–	7.25	–

a) ^1J (^{15}N, ^{1}H) = 90.8. b) ^1J (^{15}N, ^{1}H) = 90.9. c) ^1J (^{15}N, ^{1}H) = 90.2.

compounds **4** must be primarily attacked during the formation of intermediate **A**. We confirmed our assumption by carrying out the reactions of compounds **4e**, **4g**, **4i**, and **4j** with NH_4OH in EtOH (*Method D*), and these reactions yielded compounds **8e**, **8g**, **8j** and **9e**, **9i**, **9j**, respectively. In all cases, elemental S arises simultaneously. The analogous reaction proceeds also with **6e**, but does not occur with compounds **5**. The most characteristic ^{13}C resonance in compounds **9** was that of C(3), which reflected the strong donor effect of the amino group at C(4) (*Table 6*). The presence of the

Scheme 3

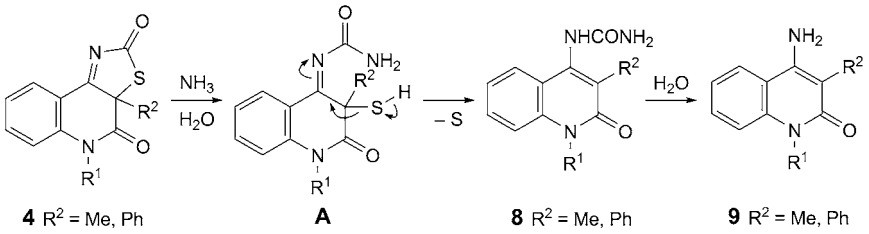


Table 6. *^{1}H- and ^{13}C-NMR Data* ((D_6)DMSO) *of Compounds* **8**, **9,** *and* **10** (δ in ppm)

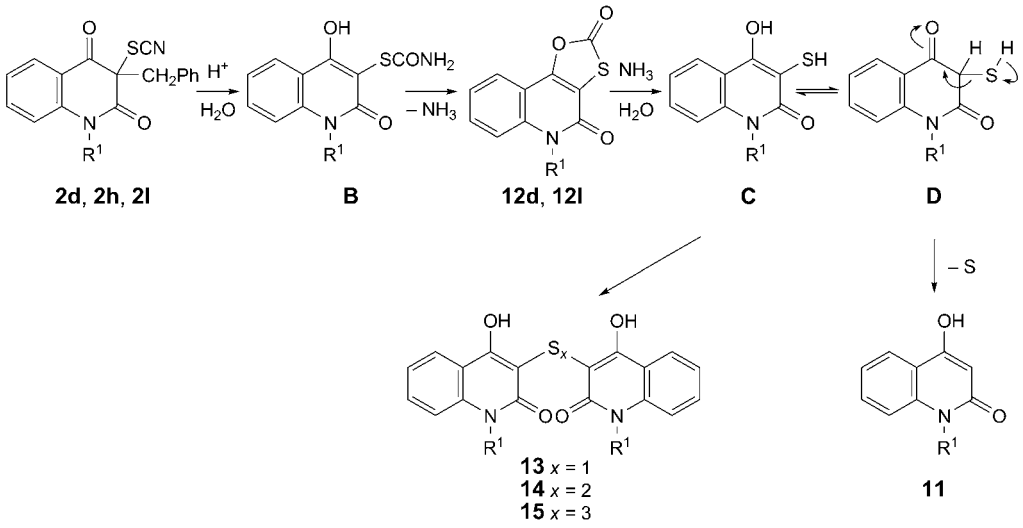
Position	**8e**		**8g**		**8i**		**8j**		**8k**		**9e**		**9i**		**9j**		**10g**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
2	–	163.2	–	161.9	–	163.2	–	161.9	–	162.0	–	162.1	–	162.2	–	161.8	–	161.7
3	–	106.6	–	119.8	–	106.6	–	119.7	–	119.6	–	99.5	–	99.3	–	105.6	–	119.2
4	–	156.1	–	140.8	–	156.1	–	141.5	–	141.6	–	147.4	–	148.2	–	147.4	–	139.5
4a	–	116.4	–	129.3	–	116.2	–	130.8	–	129.7	–	114.6	–	114.4	–	114.6	–	130.4
5	8.01	123.0	7.70	125.0	8.05	123.0	7.74	125.1	7.72	125.1	8.06	122.8	8.10	122.8	8.10	123.0	7.65	124.4
6	7.28	121.4	7.30	121.6	7.26	121.6	7.28	121.9	7.26	121.9	7.22	120.6	7.20	121.0	7.19	120.9	7.32	122.0
7	7.61	130.3	7.61	129.8	7.40	129.9	7.40	128.8	7.38	128.8	7.56	129.7	7.35	129.4	7.34	129.4	7.63	130.2
8	7.50	114.4	7.55	114.4	6.51	115.1	6.54	115.2	6.53	115.1	7.43	114.4	6.46	115.4	6.46	115.3	7.58	114.7
8a	–	138.3	–	138.2	–	139.2	–	139.3	–	139.2	–	138.5	–	139.5	–	139.6	–	138.3
Substituent at N(1)																		
1	3.63	29.3	3.69	29.6	–	138.5	–	138.2	–	138.1	3.59	29.0	–	139.3	–	139.0	3.71	29.7
2,6	–	–	–	–	7.30	129.5	7.35	129.2	7.33	129.1	–	–	7.25	129.7	7.26	129.7	–	–
3,5	–	–	–	–	7.64	130.0	7.68	130.2	7.67	130.2	–	–	7.61	130.9	7.61	129.8	–	–
4	–	–	–	–	7.57	128.5	7.60	129.6	7.29	129.6	–	–	7.53	128.2	7.53	128.1	–	–
Substituent at C(3)																		
1	2.09	10.4	2.61	26.4	2.11	10.1	2.64	20.0	2.62	30.0	2.03	11.0	2.03	10.7	2.60	17.6	2.60	26.3
2	–	–	1.47	30.0	–	–	1.12	12.8	1.50	26.2	–	–	–	–	1.06	12.4	1.46	29.8
3	–	–	1.35	22.6	–	–	–	–	1.38	22.6	–	–	–	–	–	–	1.34	22.5
4	–	–	0.94	14.0	–	–	–	–	0.93	14.0	–	–	–	–	–	–	0.93	13.9
Substituent at C(4)																		
1	10.2	–	8.16[a])	–[b])	10.3	–	8.30	–	8.30	–	6.21	–	6.40	–	6.40	–	9.42	–
2	–	158.8	–	156.7	–	158.7	–	156.8	–	156.8	–	–	–	–	–	–	–	154.8
3	5.50	–	6.06[c])	–[d])	5.48[e])	–[f])	6.16	–	6.16	–	–	–	–	–	–	–	–	[g])

[a]) $^1J(^{15}N,^1H) = 88.9$. [b]) $\delta(^{15}N) = -243.7$. [c]) $^1J(^{15}N,^1H) = 86.6$. [d]) $\delta(^{15}N) = -245.3$. [e]) $^1J(^{15}N,^1H) = 85.6$. [f]) $\delta(^{15}N) = -245.5$. [g]) 4.13/64.3 (CH_2(1)), 1.64/30.8 (CH_2(2)), 1.46 and 1.34/18.6 (CH_2(3)), 0.95/13.7 (Me(4)).

$NHCONH_2$ fragment in compounds **8g** was clearly demonstrated by using ^{15}N-NMR spectra (*Table 6*). Surprisingly, the corresponding carbamate **10g** was obtained after recrystallization of **8g** from BuOH. Compared with the NMR data of compound **8g**, a second set of Bu group signals appeared in the spectrum of compound **10g**, and the typical ^{13}C resonance of the carbamate COO group (154.8 ppm) was observed (*Table 6*).

The reaction of compounds **2** with the Bn group at C(3), *i.e.*, **2d**, **2h**, and **2l**, proceeds differently. A minute quantity of compound **11l** was obtained from the reaction of **2l**. In two cases, novel dealkylated compounds **12d** and **12l** were obtained. The presence of an oxathiolone ring in these compounds indicated a rapid debenzylation of compounds **2** under the formation of intermediate **B**, followed by closure of the oxathiolone ring to give compounds **12** (*Scheme 4*). However, compounds **12** behave unlike their aza analogs **5**. Whereas compounds **5** did not react with NH_4OH, compounds **12d** and **12l** yielded (*Method D*) 4-hydroxyquinoline-2-ones **11d** and **11l**, respectively (*Scheme 4*). Compounds **12** were possibly transformed to compounds **11** through intermediates **C** and their tautomers **D**.

Scheme 4



The main products of the reaction of **2d**, **2h**, and **2l** are poorly soluble fractions designated as **Md**, **Mh**, and **Ml** (*Table 2*). In both their ^{1}H- and ^{13}C-NMR spectra, the signals corresponding to the Bn group are not present, *i.e.*, the debenzylation of starting compounds **2** took place during the formation of compounds **12**. The molecular peak corresponding to sulfides **13** appears in EI-MS of fractions **M**. However, the results of elemental analyses are not in accord with those expected for structure **13**. They show considerable higher levels of S and more likely correspond to disulfides **14**. Therefore, we used ESI-MS, a process with milder conditions. The results of these recordings provided evidence that fractions **M** are mixtures of sulfides **13**, disulfides **14**, and

trisulfides **15**. However, the dominant compound in mixtures **M** was always disulfide **14**. The origin of this compound can be explained by the dehydrogenation of intermediate **C** (*Scheme 4*). The formation of compounds **13** and **15** can be rationalized by the disproportionation of disulfide **14**. Another possibility is the formation of **15** by the reaction of **14** with elemental S, which was isolated in most cases from the mixture, and the formation of **13** by the reaction of disulfide **14** with **11**, similar to that which was described for the reaction of **11** with disulfides [19].

All of our attempts to isolate pure individual compounds from the mixtures **M** by column chromatography failed. In particular, this failure was due to their poor solubility and very similar chromatographic characteristics. Therefore, we tried to separate the mixtures **M** by repeated fractional crystallization. By this method, albeit in poor yields, pure compounds **13d**, **13l**, **14h**, and **14l** were obtained (see *Table 7*, *Exper. Part*, for NMR data for these compounds).

3. Conclusions. – The the *Riemschneider* reaction of thiocyanates **2** under classical conditions in H_2SO_4 or its mixture with AcOH provide only compounds **3** and **4** [16]. In conclusion, we would like to emphasize that the addition of P_2O_5 or $AlCl_3$ to the mixture leads, according to presumption, to the formation of other new compounds, mainly **6** (*Table 2*). In addition, compounds **8** and **9** can be obtained by modifying the procedure treating the crude reaction product with NH_4OH. The best results for these experiments were obtained by *Method A*, where the smallest quantities of **1** as degradation products were produced. *Method C* was found to be inconvenient in the majority of cases. The exceptionally easy *C*-debenzylation of compounds **2** enabled the desired preparation of novel [1,3]oxathiolo[4,5-*c*]quinoline-2,4-diones **12** by a simple procedure. Because many biologically active compounds contain a S-atom [20][21], compounds **12** could also be interesting structures to be studied in further investigations.

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Experimental Part

1. *General.* TLC: *Alugram®-SIL-G/UV$_{254}$* foils (*Macherey-Nagel*); elution with benzene/AcOEt 4:1, $CHCl_3$/EtOH 9:1 and/or 19:1, $CHCl_3$/AcOEt 7:3, and $CHCl_3$/AcOH 9:1. Column chromatography (CC): silica gel (SiO_2; *Merck*, grade *60*, 70–230 mesh); elution with $CHCl_3$, then $CHCl_3$/EtOH 99:1 → 8:2, or benzene, and then benzene/AcOEt 99:1 → 8:2. M.p.: *Kofler* block or *Gallencamp* apparatus. IR Spectra: *Nicolet iS10* spectrophotometer; KBr pellets; ν in cm^{-1}. NMR Spectra: *Bruker Avance* spectrometer at 500.13 (^1H) and 125.76 MHz (^{13}C), and *Bruker Avance II 400* spectrometer at 400.13 (^1H), 100.56 (^{13}C), and 40.55 MHz (^{15}N); (D_6)DMSO soln.; δ in ppm rel. to Me_4Si as internal or ^{15}N-enriched $MeNO_2$ as external (in a co-axial capillary) standard; *J* in Hz; manufacturer's software for all 2D experiments (gradient-selected (gs)-COSY, gs-NOESY, gs-HMQC, and gs-HMBC). EI-MS (pos.): *Shimadzu QP-2010* instrument within *m*/*z* 50–600 using direct inlet probe (DI); analysis of samples in CH_2Cl_2 (30 µg/ml), 10 µl of the soln. was evaporated in DI cuvette at 50°; ion-source temp., 200°; the energy of electrons, 70 eV; only signals exceeding rel. abundance of 5% are listed. ESI-MS (pos. as well as neg.): *amaZon X* ion-trap mass spectrometer (*Bruker Daltonics*, D-Bremen) equipped with an ESI source; individual samples infused into the ion source as MeOH/H_2O 1:1 (*v*/*v*) solns. *via* a syringe pump

at a constant flow rate of 4 µl/min; other instrumental conditions: m/z range 50–1500; electrospray voltage, ±4.2 kV; drying gas temp., 220 , drying gas flow, 6.0 dm^3/min; nebulizer pressure, 55.16 kPa; cap. exit ±140 V; N_2 used as nebulizing as well as drying gas. Elemental analysis (C, H, N, S): *Flash EA 1112* elemental analyzer (*Thermo Fisher Scientific*).

2. *Starting 3-Thiocyanatoquinoline-2,4-(1*H,3H*)-diones* (*=1,2,3,4-Tetrahydro-2,4-dioxoquinolin-3-yl Thiocyanates*; **2**). Compounds **2** were prepared according to the procedure described in [7][16]. Seven new derivatives, **2a**, **2b**, **2e**, **2f**, **2i**, **2j**, **2l**, were prepared. Compound **2l** was also prepared by a modification of this method, using DMF as solvent instead of AcOH.

1,2,3,4-Tetrahydro-3-methyl-2,4-dioxoquinolin-3-yl Thiocyanate (**2a**). Prepared from **1a** in 46% yield. Yellowish oil. IR 3084, 2989, 1920, 2156, 1709, 1674, 1612, 1597, 1500, 1485, 1441, 1377, 1350, 1321, 1277, 1232, 1159, 1101, 1057, 1009, 964, 908, 872, 760, 665, 579, 525. ^{1}H- and ^{13}C-NMR: see *Table 1*. EI-MS: 232 (35, M^+), 204 (20), 176 (7), 175 (64), 174 (11), 147 (11), 146 (65), 128 (22), 120 (58), 119 (100), 118 (11), 117 (16), 93 (12), 92 (44), 91 (20), 90 (16), 77 (22), 76 (12), 65 (24), 64 (20), 63 (18), 59 (28), 55 (21), 51 (12). ESI-MS (pos.): 486.9 (37, $[2\,M + Na]^+$), 430.0 (25, $[2\,M + Na - SCN + H]^+$), 368.0 (33, $[3\,M + Ca]^{2+}$), 270.9 (44, $[M + K]^+$), 255.0 (100, $[M + Na]^+$), 250.0 (14, $[M + NH_4]^+$), 233.0 (5, $[M + H]^+$), 198.0 (5, $[M + Na - SCN + H]^+$), 176.0 (25, $[M + H - SCN + H]^+$). ESI-MS (neg.): 230.9 (100, $[M - H]^-$), 173.9 (17, $[M - SCN]^-$).

3-Ethyl-1,2,3,4-tetrahydro-2,4-dioxoquinolin-3-yl Thiocyanate (**2b**). Prepared from **1b** in 68% yield. Yellow crystals. M.p. 103–107° (benzene/hexane). IR: 3217, 3141, 3085, 2987, 2933, 2874, 2738, 2156, 1709, 1659, 1614, 1597, 1506, 1485, 1458, 1434, 1374, 1318, 1299, 1252, 1232, 1156, 1060, 1000, 959, 909, 870, 842, 807, 773, 745, 684, 663, 617, 528, 516. ^{1}H- and ^{13}C-NMR: see *Table 1*. EI-MS: 246 (4, M^+), 190 (10), 189 (76), 188 (33), 187 (5), 186 (9), 175 (13), 174 (100), 161 (15), 156 (5), 146 (14), 128 (8), 127 (5), 120 (27), 119 (11), 115 (9), 113 (7), 99 (7), 93 (6), 92 (26), 91 (7), 90 (8), 87 (12), 85 (12), 77 (15), 71 (24), 69 (13), 65 (18), 64 (11), 63 (9), 59 (29), 58 (6), 57 (39), 56 (5), 55 (26), 43 (21), 41 (19). Anal. calc. for $C_{12}H_{10}N_2O_2S$ (246.29): C 58.52, H 4.09, N 11.37, S 13.02; found: C 58.34, H 4.11, N 11.27, S 12.92.

1,2,3,4-Tetrahydro-1,3-dimethyl-2,4-dioxoquinolin-3-yl Thiocyanate (**2e**). Prepared from **1e** in 90% yield. Yellow oil. IR: 3087, 2988, 2944, 2893, 2360, 2342, 2155, 1704, 1667, 1603, 1493, 1473, 1419, 1373, 1357, 1301, 1258, 1177, 1120, 1092, 1046, 969, 903, 761, 664, 613, 584, 530. ^{1}H- and ^{13}C-NMR: see *Table 1*. EI-MS: 246 (11, M^+), 190 (12), 189 (100), 188 (7), 161 (8), 160 (44), 147 (8), 146 (52), 144 (7), 134 (24), 133 (23), 132 (20), 130 (8), 118 (6), 117 (12), 116 (9), 106 (9), 105 (27), 104 (24), 103 (5), 95 (6), 92 (5), 91 (12), 90 (7), 79 (8), 78 (12), 77 (37), 76 (7), 65 (8), 64 (7), 63 (9), 59 (15), 51 (12). ESI-MS (pos.): 515.1 (14, $[2\,M + Na]^+$), 458.2 (9, $[2\,M + Na - SCN + H]^+$), 389.2 (15, $[3\,M + Ca]^{2+}$), 285.1 (20, $[M + K]^+$), 269.2 (100, $[M + Na]^+$), 265.2 (17, $[M + NH_4]^+$), 247.2 (32, $[M + H]^+$), 228.2 (13, $[M + K - SCN + H]^+$), 212.2 (5, $[M + Na - SCN + H]^+$), 190.3 (30, $[M + H - SCN + H]^+$), 188.3 (21, $[M - SCN]^+$). ESI-MS (neg.): 188.1 (100),$[M - SCN]^-$).

3-Ethyl-1,2,3,4-tetrahydro-1-methyl-2,4-dioxoquinolin-3-yl Thiocyanate (**2f**). Prepared from **1f** in 67% yield. Yellowish crystals. M.p. 62–65° (benzene/cyclohexane). IR: 2992, 2971, 2936, 2155, 1698, 1668, 1603, 1473, 1355, 1242, 1159, 1186, 1031, 818, 778, 755, 660, 462. ^{1}H- and ^{13}C-NMR: see *Table 1*. EI-MS: 219 (13), 204 (11), 203 (81), 202 (13), 189 (13), 188 (100), 175 (9), 163 (29), 162 (54), 160 (13), 149 (14), 147 (6), 146 (9), 135 (6), 134 (47), 132 (13), 130 (11), 117 (9), 116 (11), 115 (7), 106 (16), 105 (13), 104 (18), 103 (6), 102 (7), 97 (9), 95 (6), 94 (7), 92 (9), 91 (14), 90 (8), 89 (7), 85 (10), 83 (10), 81 (8), 79 (12), 78 (15), 77 (43), 76 (9), 71 (18), 69 (23), 67 (6), 65 (10), 64 (8), 63 (10), 57 (41). ESI-MS (pos.): 543.1 (14, $[2\,M + Na]^+$), 486.2 (5, $[2\,M + Na - SCN + H]^+$), 410.2 (10, $[3\,M + Ca]^{2+}$), 299.2 (23, $[M + K]^+$), 283.2 (100, $[M + Na]^+$), 278.2 (7, $[M + NH_4]^+$), 261.2 (16, $[M + H]^+$), 242.2 (5, $[M + K - SCN + H]^+$), 226.2 (5, $[M + Na - SCN + H]^+$), 204.3 (9, $[M + H - SCN + H]^+$), 202.3 (8, $[M - SCN]^+$). ESI-MS (neg.): 202.1 (100, $[M - SCN]^-$). Anal. calc. for $C_{13}H_{12}N_2O_2S$ (260.31): C 59.98, H 4.65, N 10.76, S 12.32; found: C 60.25, H 4.72, N 10.60, S 12.12.

1,2,3,4-Tetrahydro-3-methyl-2,4-dioxo-1-phenylquinolin-3-yl Thiocyanate (**2i**). Prepared from **1i** in 71% yield. Yellow crystals. M.p. 132–135° (benzene/hexane). IR: 3065, 3015, 2363, 2154, 1701, 1667, 1601, 1583, 1491, 1464, 1370, 1340, 1304, 1256, 1132, 1166, 1157, 1103, 1071, 1055, 1026, 961, 895, 843, 795, 769, 759, 744, 703, 657, 602, 554, 537. ^{1}H- and ^{13}C-NMR: see *Table 1*. EI-MS: 308 (9, M^+), 251 (19), 250 (20), 222 (11), 195 (11), 167 (10), 126 (10), 114 (24), 112 (9), 104 (17), 98 (7), 97 (6), 95 (7), 86 (9), 83 (11), 81 (6), 77 (8), 74 (100), 72 (47), 69 (16), 67 (8), 62 (7), 60 (15), 59 (82), 57 (10), 56 (7), 55 (34), 44

(15), 43 (24), 41 (17). Anal. calc. for $C_{17}H_{12}N_2O_2S$ (308.35): C 66.22, H 3.92, N 9.08, S 10.40; found: C 66.19, H 3.88, N 9.08, S 10.28.

3-Ethyl-1,2,3,4-tetrahydro-2,4-dioxo-1-phenylquinolin-3-yl Thiocyanate (**2j**). Prepared from **1j** in 67% yield. Yellowish crystals. M.p. 110–113° (benzene). IR: 3067, 2977, 2934, 2162, 1708, 1673, 1599, 1491, 1464, 1346, 1397, 1249, 1100, 1013, 813, 777, 767, 751, 704, 660, 603, 512. ^{1}H- and ^{13}C-NMR: see *Table 1*. EI-MS: 281 (6), 266 (19), 265 (100), 264 (51), 251 (17), 250 (89), 237 (11), 225 (12), 224 (9), 196 (28), 195 (19), 168 (9), 167 (29), 166 (11), 149 (20), 140 (7), 139 (9), 127 (10), 124 (11), 115 (8), 114 (6), 111 (10), 99 (6), 98 (9), 97 (16), 95 (8), 85 (11), 84 (7), 83 (19), 81 (8), 77 (25), 74 (10), 72 (9), 71 (22), 70 (11), 69 (29), 67 (8), 59 (17), 57 (36). ESI-MS (pos.): 667.1 (6, $[2\,M+Na]^+$), 610.2 (5, $[2\,M+Na-SCN+H]^+$), 553.3 (5, $[2\,M+Na-2\cdot SCN+2\cdot H]^+$), 503.2 (6, $[3\,M+Ca]^{2+}$), 361.2 (26, $[M+K]^+$), 345.2 (100, $[M+Na]^+$), 340.3 (6, $[M+NH_4]^+$), 323.2 (19, $[M+H]^+$), 304.2 (7, $[M+K-SCN+H]^+$), 288.3 (18, $[M+Na-SCN+H]^+$), 266.3 (22, $[M+H-SCN+H]^+$). ESI-MS (neg.): 264.1 (100, $[M-SCN]^-$). Anal. calc. for $C_{18}H_{14}N_2O_2S$ (322.38): C 67.06, H 4.38, N 8.69, S 9.95; found: C 66.91, H 4.39, N 8.60, S 9.74.

3-Benzyl-1,2,3,4-tetrahydro-2,4-dioxo-1-phenylquinolin-3-yl Thiocyanate (**2l**). *a*) Prepared from **1l** in 7% yield according to the procedure described in [7]. Yellowish crystals. M.p. 141–144° (benzene/hexane). IR: 3080, 3028, 2958, 2924, 2859, 2157, 1708, 1677, 1598, 1492, 1461, 1331, 1298, 1245, 1213, 1183, 1160, 1086, 1071, 1045, 1030, 1002, 957, 944, 923, 806, 765, 750, 703, 661, 611, 581, 502. ^{1}H- and ^{13}C-NMR: see *Table 1*. EI-MS: 384 (7, M^+), 328 (12), 327 (49), 326 (18), 256 (6), 222 (8), 196 (10), 167 (10), 140 (7), 127 (9), 126 (19), 125 (11), 124 (6), 114 (21), 113 (11), 112 (17), 111 (18), 110 (8), 109 (10), 97 (29), 91 (31), 85 (21), 83 (30), 74 (100), 69 (31), 59 (92), 57 (45), 55 (51), 43 (56). Anal. calc. for $C_{23}H_{16}N_2O_2S$ (384.45): C 71.85, H 4.19, N 7.29, S 8.34; found: C 71.70, H 4.24, N 7.11, S 8.18.

b) A soln. of **1l** (2.45 g, 7.5 mmol) in DMF (37.5 ml) was added in one portion to the stirred soln. of $(SCN)_2$, prepared by adding Br_2 (0.42 ml, 8.25 mmol) to the soln. of KSCN (1.75 g, 18 mmol) in DMF (38 ml). The stirring was continued for 5 min, and then the mixture was poured into a well-stirred mixture of H_2O (260 ml) and benzene (110 ml). The benzene layer was separated, and the aq. layer was extracted with benzene (6×50 ml). The collected extracts were washed with H_2O (3×40 ml), dried (anh. Na_2SO_4), and evaporated to dryness *in vacuo*. The residue was separated by CC (SiO_2; benzene) and crystallized from benzene/hexane. Yield of **2l**: 50%.

3. *Modified* Riemschneider *Reaction of Compounds* **2**. *General Methods. Method A*. Compound **2** (2 mmol) was added under vigorous stirring at 0° to a mixture of 96% H_2SO_4 and AcOH (40 ml, 9:1 (*v*/*v*)). After dissolution of the starting compounds, P_2O_5 (4 g, 28 mmol) was added in two portions, and the mixture was stirred at r.t. The course of the reaction was monitored with TLC. After disappearance of the spot corresponding to **2** (for reaction time, see *Table 2*), the mixture was poured onto crushed ice (400 ml). Deposited precipitate was filtered with suction and washed with H_2O. The filtrate was extracted several times with AcOEt; the soln. was dried (anh. Na_2SO_4) and evaporated to dryness. The residue was dissolved in EtOH and filtered. The filtrate was evaporated to dryness, and the residue was crystallized from the appropriate solvent or separated by CC (SiO_2). In some cases, designated with asterisk in *Table 2*, the EtOH soln. was alkalized with NH_4OH (25%) before filtration.

Method B. The reaction was carried out as in *Method A*, but 96% H_2SO_4 (36 ml) was used instead of its mixture with AcOH.

Method C. The reaction was carried out as in *Method B*, anh. $AlCl_3$ (3.7 g, 14 mmol) was added instead of P_2O_5.

S-*(1,2,3,4-Tetrahydro-3-methyl-2,4-dioxoquinolin-3-yl) Carbamothioate* (**3a**). Prepared from **2a** in 35% yield (*Method B*). Colorless crystals. M.p. 172–174° and then 266–272° (AcOEt). IR: 3400, 3227, 3174, 3067, 2927, 2867, 1698, 1662, 1610, 1597, 1486, 1446, 1380, 1354, 1324, 1230, 1103, 969, 806, 786, 751, 676, 623, 529. ^{1}H- and ^{13}C-NMR: see *Table 3*. EI-MS: 176 (11), 175 (100, $[M-SCONH]^+$), 174 (11), 147 (9), 146 (32), 129 (5), 128 (5), 120 (70), 119 (38), 118 (8), 117 (6), 104 (9), 93 (17), 92 (34), 91 (10), 90 (6), 88 (6), 77 (15), 76 (6), 74 (14), 65 (24), 64 (5), 63 (10), 59 (7), 55 (14), 51 (10). ESI-MS (pos.): 373.2 (100, $[2\,M+Na-2\cdot SCONH]^+$), 198.2 (46, $[M+Na-SCONH]^+$), 176.2 (46, $[M+H-SCONH]^+$). ESI-MS (neg.): 174.1 (100, $[M-H-SCONH]^-$). Anal. calc. for $C_{11}H_{10}N_2O_3S$ (250.27): C 52.79, H 4.03, N 11.19, S 12.81; found: C 52.88, H 4.03, N 11.17, S 12.65.

S-*(3-Ethyl-1,2,3,4-tetrahydro-2,4-dioxoquinolin-3-yl) Carbamothioate* (**3b**). Prepared from **2b** in 42% yield (*Method B*). Colorless crystals. M.p. 173–179° (AcOEt). IR: 3407, 3382, 3302, 3254, 3184,

2974, 1678, 1667, 1653, 1612, 1598, 1488, 1362, 1296, 1160, 848, 776, 753, 678, 667, 622, 594, 528. ^{1}H- and ^{13}C-NMR: see *Table 3*. EI-MS: 221 (30, $[M - CONH]^+$), 206 (15), 193 (24), 190 (9), 189 (76, $[M - SCONH]^+$), 188 (38), 175 (11), 174 (100), 170 (6), 161 (15), 149 (6), 148 (10), 146 (19), 132 (6), 130 (10), 128 (9), 120 (47), 119 (17), 117 (7), 116 (5), 115 (11), 93 (6), 92 (34), 91 (9), 90 (13), 89 (6), 87 (12), 77 (18), 76 (7), 74 (15), 73 (20), 69 (14), 66 (7), 65 (21), 64 (42), 63 (12), 59 (6), 55 (18), 50 (5). ESI-MS (pos.): 551.1 (5, $[2\,M + Na]^+$), 476.2 (25, $[2\,M + Na - SCONH]^+$), 401.2 (91, $[2\,M + Na - 2 \cdot SCONH]^+$), 303.2 (20, $[M + K]^+$), 287.2 (100, $[M + Na]^+$), 212.2 (56, $[M + Na - SCONH]^+$), 190.2 (56, $[M + H - SCONH]^+$). ESI-MS (neg.): 188.1 (100, $[M - H - SCONH]^-$). Anal. calc. for $C_{12}H_{12}N_2O_3S$ (264.30): C 54.53, H 4.58, N 10.60, S 12.13; found: C 54.48, H 4.56, N 10.53, S 11.86.

S-*(3-Butyl-1,2,3,4-tetrahydro-2,4-dioxoquinolin-3-yl) Carbamothioate* (**3c**). Prepared from **2c** by *Method A* in 52% yield. Colorless crystals. M.p. 163–165° (AcOEt/benzene). Identical in all respects to an authentic sample [16]. ^{1}H- and ^{13}C-NMR: see *Table 3*.

S-*(3-Butyl-1,2,3,4-tetrahydro-2,4-dioxo-1-phenylquinolin-3-yl) Carbamothioate* (**3k**). Prepared from **2k** in 40 (*Method B*) and 23% yield (*Method C*), resp. Yellowish crystals. M.p. 177–182° (benzene/hexane). IR: 3395, 3202, 2955, 2872, 1684, 1667, 1655, 1601, 1491, 1464, 1346, 1303, 761, 749, 701, 687, 662. ^{1}H- and ^{13}C-NMR: see *Table 3*. EI-MS: 368 (1, M^+), 293 (18, $[M - SCONH]^+$), 264 (33), 252 (18), 251 (100), 250 (53), 237 (9), 196 (16), 195 (11), 168 (8), 167 (12), 166 (5), 77 (14), 51 (7). Anal. calc. for $C_{20}H_{20}N_2O_3S$ (368.45): C 65.20, H 5.47, N 7.60, S 8.70; found: C 65.38, H 5.48, N 7.51, S 8.57.

3a-Methyl[1,3]thiazolo[5,4-c]quinoline-2,4(3aH,5H)-dione (**4a**). Prepared from **2a** in 7% yield (*Method B*). Yellow crystals. M.p. 187–189° and then 274–280° (benzene/hexane). IR: 3215, 3164, 3111, 3060, 2993, 2921, 2856, 1724, 1700, 1610, 1589, 1574, 1503, 1475, 1379, 1344, 1275, 1239, 1155, 1132, 1106, 1077, 1028, 972, 960, 780, 755, 674, 643, 288, 526. ^{1}H- and ^{13}C-NMR: see *Table 4*. EI-MS: 234 (6), 233 (13), 232 (100, M^+), 204 (7), 203 (31), 175 (30), 174 (7), 171 (11), 160 (6), 146 (15), 145 (23), 144 (7), 120 (25), 119 (13), 118 (15), 117 (14), 116 (8), 102 (15), 93 (6), 92 (12), 91 (7), 90 (13), 89 (7), 77 (7), 76 (7), 75 (7), 65 (9), 64 (9), 63 (10), 60 (13), 59 (52), 58 (6), 51 (9). Anal. calc. for $C_{11}H_8N_2O_2S$ (232.26): C 56.88, H 3.47, N 12.06, S 13.81; found: C 56.81, H 3.31, N 12.03, S 13.65.

3a-Ethyl[1,3]thiazolo[5,4-c]quinoline-2,4(3aH,5H)-dione (**4b**). Prepared from **2b** in 7 (*Method A*), 18 (*Method B*), and 18% yield (*Method C*), resp. Yellow crystals. M.p. 186–198° (AcOEt). IR: 3209, 3152, 3056, 2978, 2965, 2927, 2857, 1721, 1698, 1609, 1567, 1505, 1476, 1435, 1360, 1336, 1266, 1242, 1155, 1137, 1081, 1035, 1011, 978, 960, 926, 873, 804, 772, 745, 694, 674, 642, 590, 526. ^{1}H- and ^{13}C-NMR: see *Table 4*. EI-MS: 247 (14), 246 (100, M^+), 232 (7), 231 (44), 217 (8), 204 (5), 203 (47), 185 (12), 184 (6), 175 (9), 171 (11), 145 (8), 129 (8), 128 (6), 127 (7), 126 (6), 125 (7), 123 (7), 118 (6), 117 (11), 116 (10), 115 (6), 114 (5), 113 (6), 112 (5), 111 (10), 110 (6), 109 (8), 102 (12), 101 (7), 100 (24), 99 (7), 98 (8), 97 (14), 96 (7), 95 (11), 87 (7), 86 (7), 85 (14), 84 (10), 83 (20), 82 (8), 81 (12), 79 (9), 74 (21), 73 (24), 72 (20), 71 (29), 70 (12), 69 (26), 67 (9), 60 (6), 59 (23), 58 (16), 57 (34), 56 (9), 55 (28). Anal. calc. for $C_{12}H_{10}N_2O_2S$ (246.29): C 58.52, H 4.09, N 11.37, S 13.02; found: C 58.20, H 4.12, N 11.21, S 12.86.

3a-Butyl[1,3]thiazolo[5,4-c]quinoline-2,4(3aH,5H)-dione (**4c**). Prepared from **2c** in 10 and 14% yield (*Method A*), resp. Yellow crystals. M.p. 180–185° (AcOEt/benzene). Identical in all respects to the authentic sample [16].

3a,5-Dimethyl[1,3]thiazolo[5,4-c]quinoline-2,4(3aH,5H)-dione (**4e**). Prepared from **2e** in 18 (*Method A*), 8 (*Method B**), and 4% yield (*Method C**), resp. Yellow crystals. M.p. 147–149° (benzene/hexane). IR: 3083, 2985, 2929, 1724, 1685, 1592, 1571, 1470, 1420, 1382, 1351, 1292, 1176, 1133, 1095, 1061, 1042, 970, 933, 867, 774, 755, 690, 663, 643, 601, 549, 525. ^{1}H- and ^{13}C-NMR: see *Table 4*. EI-MS: 247 (15), 246 (100, M^+), 214 (15), 189 (8), 188 (24), 187 (6), 186 (6), 185 (10), 160 (14), 143 (7), 132 (9), 131 (6), 116 (7), 109 (6), 102 (11), 89 (5), 77 (10), 76 (6), 75 (6), 63 (5), 59 (53), 51 (6). Anal. calc. for $C_{12}H_{10}N_2O_2S$ (246.29): C 58.52, H 4.09, N 11.37, S 13.02; found: C 58.37, H 4.06, N 11.29, S 12.82.

3a-Ethyl-5-methyl[1,3]thiazolo[5,4-c]quinoline-2,4(3aH,5H)-dione (**4f**). Prepared from **2f** in 41 (*Method A*), 53 (*Method B**), and 42% yield (*Method C*), resp. Yellow crystals. M.p. 111–113° (benzene/hexane). IR: 2973, 1717, 1679, 1601, 1583, 1472, 1356, 1291, 1128, 1094, 1068, 1038, 1009, 953, 784, 768,748, 694, 683. ^{1}H and ^{13}C-NMR: see *Table 4*. EI-MS: 261 (12), 260 (70, M^+), 245 (16), 232 (42), 231 (9), 228 (24), 227 (19), 217 (12), 213 (17), 200 (20), 199 (20), 189 (6), 188 (27), 187 (26), 185 (12), 173 (7), 167 (33), 163 (8), 162 (6), 160 (10), 159 (7), 155 (6), 150 (12), 149 (100), 145 (6), 142 (8), 141 (9), 131 (6), 127 (12), 125 (11), 116 (11), 113 (18), 111 (16), 109 (10), 105 (13), 104 (11), 102 (12), 100

(80), 97 (19), 95 (11), 85 (16), 83 (29), 81 (18), 77 (16), 76 (12), 73 (12), 72 (33), 71 (66), 70 (26), 69 (38), 59 (37), 57 (70). Anal. calc. for $C_{13}H_{12}N_2O_2S$ (260.31): C 59.98, H 4.65, N 10.76, S 12.32; found: C 60.18, H 4.64, N 10.75, S 12.04.

*3a-Butyl-5-methyl[1,3]thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-dione* (**4g**). Prepared from **2g** in 21 (*Method B*), 18 (*Method B**), and 4% yield (*Method C**), resp. Yellow crystals. M.p. 109–110° (benzene/hexane). ^{1}H- and ^{13}C-NMR: see *Table 4*. Identical in all respects to an authentic sample [16].

*3a-Methyl-5-phenyl[1,3]thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-dione* (**4i**). Prepared from **2i** in 69 (*Method A*), 4 (*Method B*), and 2% yield (*Method C**), resp. Yellow crystals. M.p. 206–209° (benzene/hexane). IR: 3383, 3088, 3049, 3036, 2998, 2938, 1712, 1698, 1603, 1587, 1491, 1465, 1381, 1340, 1296, 1273, 1252, 1161, 1122, 1079, 1041, 1009, 966, 931, 868, 852, 768, 755, 745,723, 703, 691, 644, 616, 512. ^{1}H- and ^{13}C-NMR: see *Table 4*. EI-MS: 309 (19), 308 (92, M^+), 307 (14), 278 (6), 277 (35), 276 (86), 275 (100), 251 (7), 250 (31), 249 (23), 248 (8), 247 (12), 221 (6), 219 (11), 205 (11), 204 (12), 194 (10), 193 (5), 192 (6), 167 (10), 151 (5), 150 (6), 149 (49), 140 (10), 139 (6), 138 (5), 128 (11), 127 (5), 125 (8), 111 (12), 109 (11), 103 (11), 102 (19), 97 (17), 95 (11), 85 (15), 83 (22), 81 (11), 77 (42), 71 (35), 70 (14), 69 (26), 60 (15), 59 (42), 57 (46), 56 (13), 55 (22), 51 (20), 45 (29), 43 (61), 41 (32). Anal. calc. for $C_{17}H_{12}N_2O_2S$ (308.35): C 66.22, H 3.92, N 9.08, S 10.40; found: C 65.97, H 3.86, N 8.99, S 10.23.

*3a-Ethyl-5-phenyl[1,3]thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-dione* (**4j**). Prepared from **2j** in 61 (*Method A*), 12 (*Method B**), and 35% yield (*Method C**), resp. Yellow crystals. M.p. 191–193° (benzene/AcOEt). IR: 3079, 3051, 2979, 2966, 2932, 2874, 1719, 1688, 1603, 1584, 1491, 1462, 1380, 1349, 1328, 1299, 1283, 1266, 1246, 1162, 1153, 1098, 1076, 1038, 1027, 993, 955, 919, 805, 782, 764, 754, 732, 704, 682, 644, 619, 534, 516. ^{1}H- and ^{13}C-NMR: see *Table 4*. EI-MS: 324 (7), 323 (22), 322 (100, M^+), 307 (22), 294 (21), 293 (10), 289 (11), 279 (11), 262 (8), 261 (8), 250 (25), 249 (10), 203 (6), 194 (8), 188 (9), 109 (5), 102 (6), 77 (35), 73 (39), 71 (7), 57 (8), 51 (17). Anal. calc. for $C_{18}H_{14}N_2O_2S$ (322.38): C 67.06, H 4.38, N 8.69, S 9.95; found: C 67.11, H 4.34, N 8.63, S 9.75.

*3a-Butyl-5-phenyl[1,3]thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-dione* (**4k**). Prepared from **2k** in 15 and 54 (*Method A*), 23 (*Method A**), 23 (*Method B*), and 51% yield (*Method C*), resp. Yellow crystals. M.p. 158–160° (benzene/hexane). ^{1}H- and ^{13}C-NMR: see *Table 4*. Identical in all respects to an authentic sample [16].

*[1,3]Thiazolo[5,4-*c*]quinoline-2,4(1*H*,5*H*)-dione* (**5c**). Prepared from **2c** in 43 (*Method A*) and 34% yield (*Method C*), resp., using prolonged reaction times. Beige crystals. M.p. >320° (DMF). IR: 3150, 3111, 3000, 2970, 2883, 2850, 2693, 1665, 1646, 1600, 1543, 1424, 1387, 1277, 1175, 1138, 917, 859, 755, 727, 680, 622, 506. ^{1}H- and ^{13}C-NMR: see *Table 7*. EI-MS: 219 (13), 218 (100, M^+), 162 (23), 157 (14), 146 (6), 145 (6), 129 (20), 118 (11), 109 (9), 103 (7), 102 (9), 91 (7), 81 (8), 76 (9). Anal. calc. for $C_{10}H_6N_2O_2S$ (218.23): C 55.04, H 2.77, N 12.84, S 14.69; found: C 55.07, H 2.75, N 12.69, S 14.51.

*5-Methyl[1,3]thiazolo[5,4-*c*]quinoline-2,4(1*H*,5*H*)-dione* (**5g**). Prepared from **2g** in 63 (*Method A*), 1 (*Method B*), and 3% yield (*Method B**), resp. Colorless crystals. M.p. >330° (DMF). IR: 3113, 3050, 2986, 2893, 2819, 1712, 1627, 1617, 1585, 1564, 1528, 1464, 1451, 1429, 1374, 1347, 1216, 1187, 1156, 1118, 1079, 1047, 978, 946, 846, 751, 726, 691, 664, 653, 622, 556, 542. ^{1}H- and ^{13}C-NMR: see *Table 7*. EI-MS: 233 (14), 232 (100, M^+), 189 (6), 176 (12), 175 (6), 171 (8), 161 (7), 132 (9), 131 (9), 117 (6), 115 (11), 104 (6), 102 (12), 77 (7), 76 (7). Anal. calc. for $C_{11}H_8N_2O_2S$ (232.26): C 56.88, H 3.47, N 12.06, S 13.81; found: C 56.86, H 3.57, N 11.87, S 13.57.

*5-Phenyl[1,3]thiazolo[5,4-*c*]quinoline-2,4(1*H*,5*H*)-dione* (**5k**). Prepared from **2k** in 34% yield (*Method A*; prolonged reaction time). Colorless crystals. M.p. 329–331° (AcOEt). ^{1}H- and ^{13}C-NMR: see *Table 7*. Identical in all respects to an authentic sample [16].

*5,9b-Dihydro-9b-hydroxy-3a-methyl[1,3]thiazolo[5,4-*c*]quinoline-2,4(1*H*,3a*H*)-dione* (**6a**). Prepared from **2a** in 46 (*Method A*) and 8% yield (*Method C**), resp. Colorless crystals. M.p. 179–183° and then 227–236° (THF/hexane). IR: 3297, 3238, 3064, 2984, 2929, 1677, 1667, 1600, 1497, 1439, 1393, 1378, 1352, 1258, 1197, 1161, 1140, 1122, 1098, 1072, 1053, 1039, 951, 926, 828, 776, 757, 717, 704, 680, 643, 608, 567, 535, 501. ^{1}H- and ^{13}C-NMR: see *Table 5*. EI-MS: 250 (5, M^+), 207 (21), 176 (10), 175 (92), 174 (13), 159 (19), 157 (9), 149 (11), 148 (9), 147 (9), 146 (33), 142 (11), 141 (100), 140 (11), 139 (7), 130 (6), 129 (7), 128 (11), 123 (7), 121 (6), 120 (71), 119 (42), 118 (8), 104 (6), 98 (8), 97 (95), 95 (6), 93 (18), 92 (35), 91 (10), 90 (7), 85 (7), 84 (6), 81 (7), 77 (14), 76 (5), 70 (12), 69 (10), 66 (6), 65 (20), 64 (36), 63

Table 7. *^{1}H- and ^{13}C-NMR Data* ((D_6)DMSO) *of Compounds* **5** *and* **12** (δ in ppm)

Position	**5c**		**5g**		**5k**		**12d**		**12l**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
1	13.0	–	13.01	–	13.12	–	–	–	–	–
2	–	156.3	–	155.7	–	155.7	–	156.1	–	155.6
3a	–	108.7	–	108.6	–	108.6	–	110.4	–	110.4
4	–	171.8	–	171.1	–	171.7	–	168.5	–	168.4
5a	–	137.8	–	138.6	–	139.8	–	137.7	–	139.8
6	7.45	116.4	7.72	116.1	6.66	116.7	7.51	116.4	6.73	116.7
7	7.60	130.5	7.72	131.0	7.52	130.7	7.69	131.6	7.62	131.4
8	7.32	122.3	7.45	122.6	7.37	122.8	7.38	123.1	7.46	123.6
9	8.03	122.7	8.11	123.3	8.14	123.2	7.80	121.8	7.96	122.5
9a	–	110.2	–	111.1	–	110.9	–	109.2	–	110.1
9b	–	140.3	–	139.3	–	140.0	–	150.6	–	150.4
Substituent at N(1)										
1	12.05	–	3.73	29.5	–	137.2	12.46	–	–	136.7
2	–	–	–	–	7.41	129.4	–	–	7.44	129.2
3	–	–	–	–	7.68	130.2	–	–	7.71	130.4
4	–	–	–	–	7.63	129.1	–	–	7.66	129.5

(8), 59 (10), 55 (12), 51 (9), 44 (8), 43 (43), 42 (22), 41 (11). Anal. calc. for $C_{11}H_{10}N_2O_3S$ (250.27): C 52.79, H 4.03, N 11.19, S 12.81; found: C 52.81, H 4.21, N 11.03, S 12.65.

*3a-Ethyl-5,9b-dihydro-9b-hydroxy[1,3]thiazolo[5,4-*c*]quinoline-2,4(1*H*,3a*H*)-dione* (**6b**). Prepared from **1b** in 40% yield (*Method A*). Colorless crystals. M.p. 175–179° (AcOEt). IR: 3481, 3193, 3075, 2981, 2933, 1689, 1667, 1599, 1497, 1440, 1376, 1315, 1291, 1251, 1212, 1132, 1108, 1076, 1046, 998, 947, 893, 849, 755, 680, 655, 630, 609, 567, 542. ^{1}H- and ^{13}C-NMR: see *Table 5*. EI-MS: 264 (1, M^+), 246 (1), 221 (17), 206 (10), 193 (15), 189 (76), 188 (36), 175 (12), 174 (100), 170 (6), 161 (15), 149 (11), 148 (6), 146 (17), 132 (5), 130 (9), 128 (8), 120 (39), 119 (14), 117 (6), 115 (10), 100 (7), 93 (6), 92 (29), 91 (8), 90 (10), 89 (6), 87 (7), 86 (6), 77 (18), 76 (7), 73 (7), 71 (6), 69 (14), 65 (19), 64 (37), 63 (10), 55 (21), 51 (8). Anal. calc. for $C_{12}H_{12}N_2O_3S$ (264.30): C 54.53, H 4.58, N 10.60, S 12.13; found: C 54.67, H 4.61, N 10.55, S 12.05.

*5,9b-Dihydro-9b-hydroxy-3a,5-dimethyl[1,3]thiazolo[5,4-*c*]quinoline-2,4(1*H*,3a*H*)-dione* (**6e**). Prepared from **2e** in 63 (*Method A*) and 3% yield (*Method C**), resp. Colorless crystals. M.p. 172–176° (AcOEt). IR: 3318, 3216, 3079, 2996, 2924, 2830, 1680, 1640, 1605, 1597, 1504, 1471, 1445, 1414, 1382, 1367, 1298, 1258, 1206, 1185, 1135, 1103, 1090, 1070, 1054, 948, 919, 870, 841, 770, 759, 727, 690, 650, 589, 553, 511. ^{1}H- and ^{13}C-NMR: see *Table 5*. EI-MS: 264 (18, M^+), 246 (5), 222 (6), 221 (46), 190 (12), 189 (89), 188 (10), 177 (6), 165 (6), 164 (27), 163 (53), 162 (58), 161 (21), 160 (50), 147 (10), 146 (45), 145 (6), 144 (8), 134 (37), 133 (28), 132 (27), 131 (8), 130 (12), 127 (5), 125 (5), 123 (7), 117 (19), 105 (35), 104 (34), 97 (15), 91 (17), 85 (20), 83 (18), 78 (19), 77 (56), 71 (33), 64 (22), 57 (38), 55 (28), 43 (100). Anal. calc. for $C_{12}H_{12}N_2O_3S$ (264.30): C 54.53, H 4.58, N 10.60, S 12.13; found: C 54.35, H 4.61, N 10.49, S 11.93.

*3a-Ethyl-5,9b-dihydro-9b-hydroxy-5-methyl[1,3]thiazolo[5,4-*c*]quinoline-2,4(1*H*,3a*H*)-dione* (**6f**). Prepared from **2f** in 16% yield (*Method A*). Colorless crystals. M.p. 104–106° and then 118–123° ($CHCl_3$). IR: 3293, 3179, 1680, 1647, 1604, 1478, 1372, 1251, 1209, 1181, 1164, 1116, 1078, 1056, 977, 861, 817, 766, 687, 622, 471, 459. ^{1}H- and ^{13}C-NMR: see *Table 5*. EI-MS: 279 (5), 278 (33, M^+), 235 (17), 208 (8), 207 (61), 204 (11), 203 (80), 202 (44), 189 (13), 188 (100), 178 (15), 175 (11), 174 (6), 163 (32), 162 (30), 161 (8), 160 (16), 147 (7), 146 (16), 135 (7), 134 (64), 133 (10), 132 (17), 131 (7), 130 (14), 117 (11), 116 (13), 115 (8), 106 (14), 105 (18), 104 (25), 103 (7), 102 (9), 94 (8), 92 (8), 91 (13), 90 (9), 89 (7), 79 (12), 78 (18), 77 (49), 76 (10), 75 (6), 73 (19), 69 (20), 66 (5), 65 (9), 64 (17), 55 (7), 51 (15). Anal. calc. for $C_{13}H_{14}N_2O_3S$ (278.33): C 56.10, H 5.07, N 10.06, S 11.52; found: C 55.81, H 5.07, N 9.82, S 11.29.

3a-Ethyl-5,9b-dihydro-9b-hydroxy-5-phenyl[1,3]thiazolo[5,4-c]quinoline-2,4(1H,3aH)-dione (**6j**). Prepared from **2j** in 8% yield by *Method A*. Colorless crystals. M.p. 250–256° (AcOEt). IR: 3369, 3187, 3073, 2976, 2876, 1682, 1657, 1602, 1497, 1466, 1456, 1354, 1328, 1305, 1262, 1206, 1131, 1073, 1049, 1004, 978, 927, 852, 805, 767, 753, 724, 701, 636, 621, 574, 516. ^{1}H- and ^{13}C-NMR: see *Table 5*. EI-MS: 340 (1, M^+), 322 (5), 269 (10), 266 (18), 265 (100), 264 (50), 251 (16), 250 (88), 237 (11), 196 (25), 195 (22), 167 (27), 166 (12), 92 (8), 77 (31), 69 (12), 64 (20), 51 (16). Anal. calc. for $C_{18}H_{16}N_2O_3S$ (340.40): C 63.51, H 4.74, N 8.23, S 9.42; found: C 63.42, H 4.74, N 8.19, S 9.21.

3-Ethyl-3-hydroxy-1-methylquinoline-2,4(1H,3H)-dione (**7f**). Prepared from **2f** in 4% yield (*Method A*). M.p. 145–146° (AcOEt/benzene). Identical in all respects to the authentic sample, prepared according to [22].

3-Butyl-3-hydroxy-1-methylquinoline-2,4(1H,3H)-dione (**7g**). Prepared from **2g** in 4% yield (*Method B**). Colorless crystals. M.p. 123–125° (hexane). Identical in all respects to an authentic sample [23].

3-Ethyl-3-hydroxy-1-phenylquinoline-2,4(1H,3H)-dione (**7j**). Prepared from **2j** in 7% yield (*Method B**). Colorless crystals. M.p. 196–201° (EtOH/AcOEt). Identical in all respects to an authentic sample [23].

1-(1,2-Dihydro-1,3-dimethyl-2-oxoquinolin-4-yl)urea (**8e**). Prepared from **2e** in 29% yield (*Method B**) and 23% yield (*Method C**), resp., from **4e** in 20% yield (*Method D*), and from **6e** (*Method D*) in 79% yield (*Method D*), resp. Colorless crystals. M.p. 197–200° (AcOEt). IR: 3398, 3190, 2943, 1673, 1642, 1607, 1577, 1506, 1462, 1420, 1401, 1372, 1343, 1290, 1216, 1183, 1165, 1120, 1096, 1045, 982, 945, 902, 832, 817, 753, 678, 655, 621, 605, 562, 460. ^{1}H- and ^{13}C-NMR: see *Table 6*. EI-MS: 232 (10), 231 (73, M^+), 230 (9), 216 (32), 215 (29), 214 (100), 189 (7), 188 (43), 187 (23), 186 (12), 185 (33), 173 (16), 172 (8), 161 (9), 160 (20), 159 (48), 158 (12), 156 (10), 145 (20), 144 (16), 143 (20), 132 (10), 131 (13), 130 (17), 129 (12), 128 (12), 117 (17), 116 (13), 115 (14), 103 (14), 102 (17), 89 (12), 77 (27), 76 (11), 63 (10), 51 (14), 44 (14), 43 (12). ESI-MS (pos.): 463.2 (13, $[2\,M+H]^+$), 401.2 (100, $[2\,M+Na-2\cdot NCO]^+$), 212.2 (41, $[M+Na-NCO]^+$), 190.2 (41, $[M+H-NCO]^+$). ESI-MS (neg.): 188.1 (100, $[M-H-NCO]^-$). Anal. calc. for $C_{12}H_{13}N_3O_2$ (231.25): C 62.33, H 5.67, N 18.17; found: C 62.39, H 5.81, N 18.19.

1-(3-Butyl-1,2-dihydro-1-methyl-2-oxoquinolin-4-yl)urea (**8g**). Prepared from **2g** in 18 (*Method B**) and 10% yield (*Method C**), resp., and from **4g** in 50% yield (*Method D*). Colorless crystals. M.p. 250–258° (EtOH). IR: 3418*s*, 3293, 3246, 2956, 2934, 2869, 1665, 1633, 1593, 1573, 1528, 1499, 1463, 1413, 1386, 1354, 1295, 1227, 1164, 1123, 1098, 753, 672, 634, 597, 572, 541. ^{1}H- and ^{13}C-NMR: see *Table 6*. EI-MS: 273 (24, M^+), 256 (18), 244 (19), 241 (8), 232 (10), 231 (71), 230 (28), 227 (27), 216 (31), 215 (29), 214 (100), 213 (53), 201 (52), 199 (16), 188 (71), 187 (79), 185 (16), 184 (11), 159 (20), 144 (12), 143 (10), 132 (9), 131(11), 130 (15), 117 (14), 116 (11), 115 (14), 103 (10), 77 (20), 44 (14), 43 (14). ESI-MS (pos.): 569.3 (37, $[2\,M+Na]^+$), 429.8 (10, $[3\,M+Ca]^{2+}$), 312.2 (29, $[M+K]^+$), 296.3 (100, $[M+Na]^+$), 293.3 (12, $[2\,M+Ca]^{2+}$), 274.3 (53, $[M+H]^+$). ESI-MS (neg.): 581.0 (5, $[2\,M+Cl]^-$), 545.2 (21, $[2\,M-H]^-$), 308.2 (26, $[M+Cl]^-$), 272.2 (100, $[M-H]^-$), 229.2 (35, $[M-NH_2CO]^-$). Anal. calc. for $C_{15}H_{19}N_3O_2$ (273.33): C 65.91, H 7.01, N 15.37; found: C 65.80, H 7.06, N 15.52.

1-(1,2-Dihydro-3-methyl-2-oxo-1-phenylquinolin-4-yl)urea (**8i**). Prepared from **2i** in 25 (*Method B**) and 22% yield (*Method C**), resp. Colorless crystals. M.p. 275–278° (AcOEt). IR: 3489, 3454, 3325, 3199, 3055, 1678, 1628, 1601, 1587, 1562, 1496, 1452, 1377, 1356, 1334, 1304, 1288, 1228, 1182, 1135, 1113, 1043, 1003, 964, 901, 754, 696, 661, 651, 617, 546, 515. ^{1}H- and ^{13}C-NMR: see *Table 6*. EI-MS: 252 (17), 251 (100, $[M-NCO]^+$), 250 (90), 222 (8), 196 (9), 195 (31), 194 (8), 167 (23), 166 (9), 146 (9), 126 (8), 92 (6), 84 (11), 77 (20), 51 (11). ESI-MS (pos.): 525.2 (56, $[2\,M+Na-2\cdot NCO]^+$), 396.7 (18, $[3\,M+Ca-3\cdot NCO]^{2+}$), 290.2 (10, $[M+K-NCO]^+$), 274.2 (65, $[M+Na-NCO]^+$), 252.3 (100, $[M+H-NCO]^+$). ESI-MS (neg.): 250.1 (100, $[M-H-NCO]^-$). Anal. calc. for $C_{17}H_{15}N_3O_2$ (293.32): C 69.61, H 5.15, N 14.33; found: C 69.55, H 4.86, N 14.12.

1-(3-Butyl-1,2-dihydro-2-oxo-1-phenylquinolin-4-yl)urea (**8k**). Prepared from **2k** in 26% yield (*Method A**). Colorless needles. M.p. 228–230° (EtOH). IR: 3436, 3214, 2954, 2924, 2857, 1670, 1630, 1601, 1570, 1521, 1492, 1454, 1359, 1228, 1174, 1115, 748, 698, 648, 592, 526. ^{1}H- and ^{13}C-NMR: see *Table 6*. EI-MS: 335 (1, M^+), 318 (8), 303 (6), 290 (10), 289 (21), 277 (21), 276 (100), 275 (51), 263 (6), 262 (5), 261 (23), 204 (9), 77 (15), 51 (7). Anal. calc. for $C_{20}H_{21}N_3O_2$ (335.40): C 71.62, H 6.31, N 12.53; found: C 71.37, H 6.34, N 12.49.

*4-Amino-3-butyl-1-phenylquinolin-2(1*H*)-one* (**9k**). Prepared from **2k** in 4% yield (*Method A**). Colorless crystals. M.p. 263–270° (AcOEt). Identical in all respects to an authentic compound [24].

Butyl (3-Butyl-1,2-dihydro-1-methyl-2-oxoquinolin-4-yl)carbamate (**10g**). Prepared in 75% yield by boiling a soln. of **8g** in BuOH for 2 h. Colorless crystals. M.p. 108–112° (cyclohexane). IR: 3265, 2958, 2931, 2871, 1716, 1695, 1637, 1591, 1572, 1508, 1498, 1460, 1414, 1381, 1315, 1277, 1244, 1167, 1101, 1086, 1063, 1037, 1007, 943, 906, 874, 775, 754, 746, 683, 658, 638, 567, 544. ^{1}H- and ^{13}C-NMR: see *Table 6*. EI-MS: 331 (7), 330 (32, M^+), 313 (14), 301 (10), 289 (19), 288 (100), 259 (6), 257 (7), 246 (19), 245 (35), 232 (13), 231 (20), 229 (8), 227 (7), 215 (17), 214 (49), 213 (58), 201 (20), 199 (11), 189 (9), 188 (61), 187 (28), 185 (8), 130 (7), 159 (11), 149 (18), 145 (6), 144 (7), 131 (7), 130 (8), 77 (9), 57 (24), 55 (12). Anal. calc. for $C_{19}H_{26}N_2O_3$ (330.42): C 69.06, H 7.93, N 8.48; found: C 68.83, H 7.83, N 8.45.

*4-Hydroxyquinolin-2(1*H*)-one* (**11d**). Prepared from **2d** (*Method B*) in 6 and from **12d** (*Method D*) in 50% yield. Colorless crystals. M.p. >350°. Identical in all respects to an authentic compound (*Aldrich 86-59-9*).

*4-Hydroxy-1-phenylquinolin-2(1*H*)-one* (**11l**). Prepared from **2l** in 9 (*Method A*), 4 (*Method B*), 3 (*Method B**), and 5% yield (*Method C**), and from **12l** in 61% yield (*Method D*), resp. Colorless crystals. M.p. >350°. Identical in all respects to an authentic compound prepared in 51% yield from Ph_2NH and malonic acid according to [25].

*[1,3]Oxathiolo[4,5-*c*]quinoline-2,4(5*H*)-dione* (**12d**). Prepared from **2d** in 48 (*Method A*) and 5% yield (*Method B*), resp. Beige crystals. M.p. 344–348° (AcOH). IR: 3001, 2956, 2925, 2843, 1762, 1735, 1650, 1622, 1602, 1567, 1501, 1477, 1442, 1386, 1332, 1271, 1165, 1149, 1128, 1095, 992, 912, 896, 869, 757, 729, 676, 657, 635, 603, 536. ^{1}H- and ^{13}C-NMR: see *Table 7*. EI-MS: 220 (12), 219 (100, M^+), 192 (5), 191 (47), 163 (22), 146 (33), 141 (8), 136 (6), 135 (60), 130 (6), 120 (7), 119 (18), 109 (9), 108 (15), 104 (9), 97 (15), 92 (21), 91 (8), 90 (12), 85 (9), 83 (7), 76 (17), 75 (5), 74 (10), 71 (31), 70 (11), 69 (15), 64 (20), 63 (16), 57 (17), 55 (9), 50 (10), 43 (18). Anal. calc. for $C_{10}H_5NO_3S$ (219.22): C 54.79, H 2.30, N 6.39, S 14.63; found: C 54.75, H 2.38, N 6.22, S 14.52.

*5-Phenyl[1,3]oxathiolo[4,5-*c*]quinoline-2,4(5*H*)-dione* (**12l**). Prepared from **2l** in 7 (*Method A*) and 26% yield (*Method B*), resp. Colorless needles. M.p. 243–247° (benzene). IR: 3058, 1780, 1757, 1662, 1595, 1558, 1496, 1489, 1446, 1388, 1329, 1296, 1259, 1219, 1153, 1105, 1088, 1036, 997, 949, 883, 810, 769, 754, 744, 731, 702, 656, 627, 611, 548, 511. ^{1}H- and ^{13}C-NMR: see *Table 7*. EI-MS: 297 (7), 296 (19), 295 (100, M^+), 267 (12), 240 (11), 239 (64), 238 (25), 211 (12), 210 (14), 195 (10), 167 (21), 166 (12), 146 (17), 140 (8), 139 (9), 121 (17), 92 (9), 84 (27), 77 (32), 76 (16), 75 (5), 71 (6), 63 (8), 51 (25), 50 (10). Anal. calc. for $C_{16}H_9NO_3S$ (295.31): C 65.07, H 3.07, N 4.74, S 10.86; found: C 64.88, H 2.95, N 4.75, S 10.65.

4. *Purification of the Crude Mixtures* **Md**, **Mh**, *and* **Ml**. Mixtures of compounds **13**, **14**, and **15** were obtained from compounds **2d**, **2h**, and **2l** in yields given in *Table 2*. After separation by fractional crystallization, the following pure compounds were isolated.

*3,3′-Sulfanediylbis(4-hydroxyquinolin-2(1*H*)-one)* (**13d**). Isolated from **Md**. Yellowish crystals. M.p. >320° (DMF). For **13d**, a m.p. of 370° (dec.) was reported in [26]. IR: 3138, 3072, 2949, 2860, 2742, 1649, 1604, 1541, 1494, 1477, 1421, 1367, 1350, 1313, 1263, 1163, 1147, 1109, 1080, 1028, 947, 870, 785, 750, 717, 671, 644, 542, 468. ^{1}H- and ^{13}C-NMR: see *Table 8*. EI-MS: 353 (11), 352 (51, M^+), 335 (6), 334 (28, $[M-H_2O]^+$), 319 (11), 162 (34), 161 (100), 146 (10), 133 (16), 120 (52), 119 (49), 105 (11), 104 (12), 92 (45), 77 (19), 76 (9), 65 (22), 64 (19), 63 (12), 51 (11). ESI-MS (pos.): 391.0 (27, $[M+K]^+$), 375.0 (100, $[M+Na]^+$), 353.1 (40, $[M+H]^+$). ESI-MS (neg.): 351.0 (100, $[M-H]^-$). Anal. calc. for $C_{18}H_{12}N_2O_4S$ (352.36): C 61.35, H 3.43, N 7.95, S 9.10; found: C 61.12, H 3.23, N 8.15, S 8.84.

*3,3′-Sulfanediylbis(4-hydroxy-1-phenylquinolin-2(1*H*)-one)* (**13l**). Isolated from **Ml**. Beige crystals. M.p. 325–326° (benzene/hexane). IR: 3034, 2925, 2848, 2713, 2578, 1620, 1568, 1552, 1491, 1454, 1442, 1350, 1321, 1284, 1248, 1213, 1171, 1103, 1072, 1036, 1003, 955, 910, 860, 802, 756, 698, 677, 631, 567, 550, 513, 469. ^{1}H- and ^{13}C-NMR: see *Table 8*. EI-MS: 487 (19), 486 (57, $[M-H_2O]^+$), 322 (6), 281 (9), 267 (5), 242 (12), 238 (16), 237 (100), 236 (82), 208 (13), 207 (55), 196 (15), 195 (61), 180 (9), 168 (8), 167 (17), 166 (15), 140 (8), 98 (19), 92 (13), 77 (23), 73 (13), 64 (18), 63 (7), 54 (9), 51 (21). ESI-MS (pos.): 543.1 (28, $[M+K]^+$), 527.1 (81, $[M+Na]^+$), 505.1 (100, $[M+H]^+$). ESI-MS (neg.): 1029.2 (17, $[2\,M-2\cdot H+Na]^-$), 503.1 (100, $[M-H]^-$). Anal. calc. for $C_{30}H_{20}N_2O_4S$ (504.56): C 71.41, H 4.00, N 5.55, S 6.36; found: C 71.67, H 4.26, N 5.37, S 6.20.

Table 8. *^{1}H- and ^{13}C-NMR Data* ((D_6)DMSO) *of Compounds* **13** *and* **14** (δ in ppm)

Position	**13d**		**13l**		**14h**		**14l**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
2	–	165.3	–	165.0	–	162.6	–	162.8
3	–	103.0	–	103.7	–	100.3	–	100.1
4	–	172.5[a])	–	166.7	–	168.3	–	169.4
4a	–	118.2	–	115.3	–	119.7	–	119.5
5	7.96	124.6	8.07	124.2	8.16	124.6	8.17	125.3
6	7.14	120.9	7.39	123.2	7.24	120.8	7.18	121.1
7	7.48	130.8	7.60	133.0	7.60	131.0	7.36	130.7
8	7.26	115.0	6.67	116.3	7.41	114.1	6.40	115.1
8a	–	138.5	–	140.4	–	139.7	–	140.9
OH	n.o.		11.87	–	n.o.	–	n.o.	–
Substituent at N(1)								
1	11.06		–	137.4	3.58	29.3	–	139.3
2,6	–		7.44	129.1	–	–	7.29	129.8
3,5	–		7.69	130.3	–	–	7.62	130.0
4	–		7.62	129.2	–	–	7.53	128.2

*3,3′-Disulfanediylbis(4-hydroxy-1-methylquinolin-2(1*H*)-one)* (**14h**). Isolated from **Mh**. Yellowish crystals. M.p. 261–263° (AcOEt). IR: 3094, 2945, 2904, 1617, 1607, 1574, 1540, 1504, 1446, 1419, 1401, 1337, 1316, 1269, 1248, 1208, 1170, 1118, 1077, 1041, 971, 944, 860, 834, 755, 686, 662, 618, 587, 537. ^{1}H- and ^{13}C-NMR: see *Table 8*. EI-MS: 381 (15), 380 (65, $[M-S]^+$), 207 (23), 176 (18), 175 (100), 174 (8), 162 (12), 147 (14), 146 (30), 134 (37), 133 (12), 132 (23), 116 (10), 105 (17), 104 (18), 91 (11), 78 (10), 77 (29), 64 (16), 51 (8). ESI-MS (pos.): 847.0 (21, $[2M+Na]^+$), 451.1 (18, $[M+K]^+$), 435.1 (100, $[M+Na]^+$), 413.1 (24, $[M+H]^+$). ESI-MS (neg.): 411.0 (100, $[M-H]^-$). Anal. calc. for $C_{20}H_{16}N_2O_4S_2$ (412.48): C 58.24, H 3.91, N 6.79, S 15.55; found: C 58.04, H 3.93, N 6.95, S 15.27.

*3,3′-Disulfanediylbis(4-hydroxy-1-phenylquinolin-2(1*H*)-one)* (**14l**). Isolated from **Ml**. Yellow crystals. M.p. 241–246° and then 320–328° (benzene). IR: 3140, 3010, 2814, 1597, 1587, 1560, 1498, 1452, 1414, 1377, 1319, 1257, 1218, 1174, 1109, 1070, 1038, 910, 860, 835, 798, 766, 754, 700, 690, 671, 627, 580, 546. ^{1}H- and ^{13}C-NMR: see *Table 8*. EI-MS: 505 (22), 504 (62, $[M-S]^+$), 385 (6), 269 (22), 238 (25), 237 (100), 236 (68), 209 (7), 208 (10), 197 (10), 196 (84), 195 (37), 180 (11), 168 (7), 167 (32), 166 (9), 139 (6), 102 (6), 77 (30), 73 (15), 64 (66), 61 (11), 60 (18), 51 (16), 45 (15), 44 (38), 43 (26). ESI-MS (pos.): 575.1 (28, $[M+K]^+$), 559.1 (100, $[M+Na]^+$), 537.1 (81, $[M+H]^+$). ESI-MS (neg.): 1093.1 (5, $[2M-2\cdot H+Na]^-$), 535.1 (100, $[M-H]^-$). Anal. calc. for $C_{30}H_{20}N_2O_4S_2$ (536.62): C 67.15, H 3.76, N 5.22, S 11.95; found: C 67.26, H 3.68, N 5.31, S 11.63.

5. *General Procedure for the Reaction of Compounds* **4**, **6**, *and* **12** *with NH$_4$OH* (*Method D*). To a soln. of compound **4**, **6**, or **12** (50 mg) in EtOH (5 ml), 0.3 ml of NH_4OH (35%) was added, and the mixture was heated to 70° for 1 h. The solvent was evaporated, and the residue was crystallized from an appropriate solvent or separated by CC. The following compounds were obtained: *a*) from **4e**, compounds **8e** and **9e** were obtained in yields of 20 and 31%, resp.; *b*) from **4g**, compound **8g** was obtained in 50% yield; *c*) from **4i**, compound **9i** was obtained in 27% yield; *d*) from **4j**, compounds **8j** and **9j** were obtained in yields 28 and 23%, resp.; *e*) from **6e**, compound **8e** was obtained in 79% yield; *f*) from **12d**, compound **11d** was prepared in 50% yield; *g*) from **12l**, compound **11l** was prepared in 61% yield. Compounds **8j**, **9e**, **9i**, and **9j** were prepared merely by *Method D*. Compounds **8e**, **8g**, **9e**, **11d**, and **11l** were prepared also by *Methods A*, *B*, *C*, and are described in *Sect. 3* of the *Exper. Part*.

1-(3-Ethyl-1,2-dihydro-2-oxo-1-phenylquinolin-4-yl)urea (**8j**). Prepared from **4j** by *Method D* in 28% yield. Colorless crystals. M.p. 222–225° and then 294–297° (EtOH). IR: 3431, 3292, 3246, 2962, 2931, 2871, 1668, 1637, 1601, 1568, 1529, 1493, 1450, 1387, 1358, 1323, 1299, 1279, 1250, 1215, 1171, 1138, 1113, 1047, 881, 752, 700, 673, 642, 517. ^{1}H- and ^{13}C-NMR: see *Table 6*. EI-MS: 307 (5, M^+), 291 (20), 290

(95), 289 (41), 275 (23), 264 (17), 263 (29), 262 (96), 261 (100), 249 (18), 247 (12), 236 (7), 235 (32), 234 (7), 218 (6), 217 /5), 205 (9), 204 (17), 167 (9), 140 (7), 137 (10), 131 (7), 116 (9), 115 (10), 109 (9), 103 (7), 102 (16), 96 (6), 91 (7), 77 (35), 65 (6), 58 (6), 51 (25). Anal. calc. for $C_{18}H_{17}N_3O_2$ (307.35): C 70.34, H 5.58, N 13.67; found: C 70.23, H 5.74, N 13.51.

*4-Amino-1,3-dimethylquinolin-2(1*H*)-one* (**9e**). Prepared from **4e** by *Method D* in 31% yield. Colorless crystals. M.p. 168–179° (AcOEt). For **9e**, an m.p. of 185° was reported in [27]. IR: 3413, 3363, 3244, 1655, 1624, 1599, 1564, 1421, 1342, 1228, 1132, 1095, 1049, 1034, 980, 939, 752, 746, 677, 625, 536, 459. ^{1}H- and ^{13}C-NMR: see *Table 6*. EI-MS: 189 (17), 188 (100, M^+), 173 (19), 161 (10), 160 (17), 159 (51), 146 (9), 145 (22), 144 (8), 132 (8), 131 (9), 130 (10), 118 (8), 117 (9), 115 (6), 104 (7), 103 (6), 80 (15), 77 (16), 51 (8). Anal. calc. for $C_{11}H_{12}N_2O$ (188.23): C 70.19, H 6.43, N 14.88; found: C 69.95, H 6.40, N 14.71.

*4-Amino-3-methyl-1-phenylquinolin-2(1*H*)-one* (**9i**). Prepared from **4i** by *Method D* in 27% yield. Colorless crystals. M.p. 254–255° (AcOEt). IR: 3469, 3332, 3224, 3070, 2912, 2854, 1655, 1603, 1577, 1558, 1504, 1491, 1448, 1421, 1358, 1333, 1319, 1307, 1286, 1234, 1198, 1167, 1124, 1111, 1074, 1003, 951, 918, 841, 796, 758, 702, 673, 652, 623, 592, 546, 515. ^{1}H- and ^{13}C-NMR: see *Table 6*. EI-MS: 251 (13), 250 (81, M^+), 249 (100), 221 (11), 125 (8), 103 (5), 77 (12), 51 (7). Anal. calc. for $C_{16}H_{14}N_2O$ (250.30): C 76.78, H 5.64, N 11.19; found: C 76.83, H 5.44, N 11.29.

*4-Amino-3-ethyl-1-phenylquinolin-2(1*H*)-one* (**9j**). Prepared from **4j** by *Method D* in 23% yield. Colorless crystals. M.p. 297–299° (AcOEt). IR: 3463, 3329, 3222, 3062, 2960, 2949, 2924, 2864, 1655, 1620, 1603, 1577, 1558, 1504, 1444, 1419, 1360, 1340, 1323, 1284, 1261, 1230, 1155, 1117, 1074, 1063, 1022, 1003, 943, 858, 821, 781, 764, 752, 700, 677, 654, 619, 552, 517. ^{1}H- and ^{13}C-NMR: see *Table 6*. EI-MS: 265 (18), 264 (92, M^+), 263 (50), 250 (19), 149 (100), 235 (9), 221 (10), 219 (6), 204 (6), 132 (8), 124 (12), 116 (5), 110 (11), 103 (5), 77 (13), 51 (7). Anal. calc. for $C_{17}H_{16}N_2O$ (264.32): C 77.25, H 6.10, N 10.60; found: C 76.98, H 6.10, N 10.51.

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