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Novel Tandem Hydration/Cyclodehydration of α-Thiocyanatoketones to 2-Oxo-3-thiazolines. Application to Thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-dione Synthesis

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Novel tandem hydration of α-thiocyanatoketones to thiocarbamates followed by in situ cyclodehydration to fused 2-oxo-3-thiazolines is described. The reaction is applied to the synthesis of [1,3]-thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-diones (**4**). Concentrated sulfuric acid was found to be critical for the reaction as both corresponding 2,3-dioxo-1,2,3,4-tetrahydroquinolin-3-yl thiocyanates (**2**) and *S*-(2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl) thiocarbamates (**3**) rapidly hydrolyze in the presence of water to 4-hydroxyquinolin-2(1*H*)-ones (**1**).

Introduction

A broad range of fascinating pharmacological activities has been associated with 2-quinolone derivatives. For example, they are potent antagonists of several receptors such as the *N*-methyl-D-aspartate and the *γ*-aminobutyric acid (GABA) receptor.[1] Very recently, novel 2-quinolones fused to sulfur-containing heterocycles have received attention. Benzo[*b*]thieno[2,3-*c*]quinolones have been proposed to exert cytostatic activity against a broad range of malignant cell lines.[2] Syntheses of 2-arylthiazolo[4,5-*c*]quinolin-4(5*H*)-ones, 1-thia analogues of 2-aryloxazolo[4,5-*c*]quinolin-4(5*H*)-ones[1b] that possess high affinity for the GABA receptor, have been disclosed.[3]

Although thiazole ring construction has been reviewed, reports on 2-oxo-3-thiazolines are few.[4] In combination, the above facts prompted us to develop a new approach to 2-oxo-3-thiazolines fused to 2-quinolones. Having recently published the synthesis of fused 2-oxo-3-imidazolines via cyclodehydration of the corresponding α-ureidocarbonyls,[5] we surmised that the cyclodehydration protocol could also be applied to the synthesis of [1,3]-thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-diones **4** with *S*-(2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl) thiocarbamates **3** as intermediates.

For the preparation of N,N-unsubstituted thiocarbamates **3**, comprehensive approaches[6] involving manipulations of a thiol group are not applicable as no synthesis of 3-sulfanylquinoline-2,4(1*H*,3*H*)-diones has been described yet. Alternatively, thiocarbamates were prepared by acidic hydration of organic thiocyanates,[7] which, so far, has only been applied to the examples where both thiocyanates and thiocarbamates are relatively stable. Not surprisingly, hydration of α-thiocyanato-*β*-dicarbonyls to α-carbamoylsulfanyl-*β*-dicarbonyls is as yet to be reported, due to the fact that the former are unstable and readily decompose to a mixture of products.[8]

Results and Discussion

We recently reported[9] the high reactivity of 2,3-dioxo-1,2,3,4-tetrahydroquinolin-3-yl thiocyanates[10] **2** toward

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(1) For recent related references, see: (a) Rowley, M.; Kulagowski, J. J.; Watt, A. P.; Rathbone, D.; Stevenson, G. I.; Carling, R. W.; Baker, R.; Marshall, G. R.; Kemp, J. A.; Foster, A. C.; Grimwood, S.; Hargreaves, R.; Hurley, C.; Saywell, K. L.; Tricklebank, M. D.; Leeson P. D. *J. Med. Chem.* **1997**, *40*, 4053−4068. (b) Albaugh, P. U.S. Patent 5 182 290, 1993; *Chem. Abstr.* **1993**, *119*, 49380. (c) Hayashi, H.; Miwa, Y.; Ichikawa, S.; Yoda, N.; Miki, I.; Ishii, A.; Kono, M.; Yasuzawa, T.; Suzuki, F. *J. Med. Chem.* **1993**, *36*, 617−626. (d) DeVita, R. J.; Hollings, D. D.; Goulet, M. T.; Wyvratt, M. J.; Fisher, M. H.; Lo, J.-L.; Yang, Y. T.; Cheng, K.; Smith, R. G. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 2615−2620.

(2) Koružnjak, J. D.; Grdiša, M.; Slade, N.; Zamola, B.; Pavelić, K.; Karminski-Zamola, G. *J. Med. Chem.* **2003**, *46*, 4516−4524.

(3) Hodgetts, K. J.; Kershaw, M. T. *Org. Lett.* **2003**, *5*, 2911−2914.

(4) Dondoni, A.; Merino, P. Thiazoles. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Shinkai, I., Eds.; Elsevier Science: New York, 1996; Vol. 3, pp 373−474.

(5) (a) Klásek, A.; Kořistek, K.; Lyčka, A.; Holčapek, M. Tetrahedron **2003**, *59*, 1283−1288. (b) Klásek, A.; Kořstek, K.; Lyčka, A.; Holčapek, M. *Tetrahedron* **2003**, *59*, 5279−5288.

(6) For examples, please see: (a) Jones, W. D.; Reynolds, K. A.; Sperry, C. K.; Lachicotte, R. J.; Godleski, S. A.; Valente, R. R. *Organometallics* **2000**, *19*, 1661−1669. (b) Mizuno, T.; Takahashi, J.; Ogawa, A. *Tetrahedron* **2003**, *59*, 1327−1331. (c) Wynne, J. H.; Jensen, S. D.; Snow, A. W. *J. Org. Chem.* **2003**, *68*, 3733−3735 and references therein.

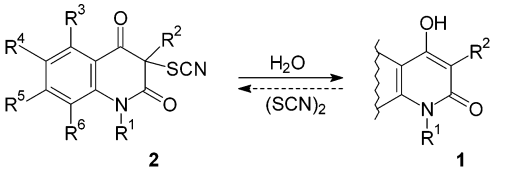
(7) Hydrochloric acid: (a) Zil'berman, E. N.; Lazaris, A. Y. *J. Gen. Chem. USSR* **1963**, *33*, 1012−1014. *Advanced Organic Chemistry*, 5th ed.; Smith, M. B., March, J., Eds.; Wiley-Interscience: New York, 2001; p 1179. Sulfuric acid: (b) Sápi, A.; Fetter, J.; Lempert, K. Kajtár-Peredy, M.; Czira, G. *Tetrahedron* **1997**, *53*, 12729−12738. (c) Riemschneider, R.; Orlick, G. *Monatsch. Chem.* **1953**, *84*, 313−318 and ref 1 cited therein. Trifluoroacetic acid: (d) LeMaréchal, A. M.; Robert, A.; Leban, I. *J. Chem. Soc., Perkin Trans. 1* **1993**, 351−356.

(8) For examples see: (a) Atkins, E. F.; Dabbs, S.; Guy, R. G.; Mahomed, A. A.; Mountford, P. *Tetrahedron* **1994**, *50*, 7253−7264. (b) Prakash, O.; Kaur, H.; Batra, H.; Rani, N.; Singh, S. P.; Moriarty, R. M. *J. Org. Chem.* **2001**, *66*, 2019−2023.

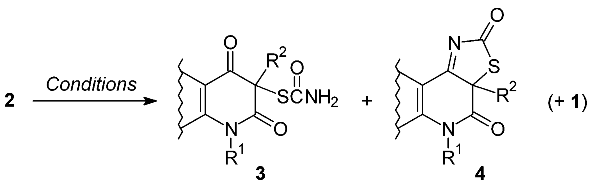
(9) Klásek, A.; Mrkvička, V. *J. Heterocycl. Chem.* **2003**, *40*, 747−752.

10.1021/jo0493370 CCC: $27.50

SCHEME 1

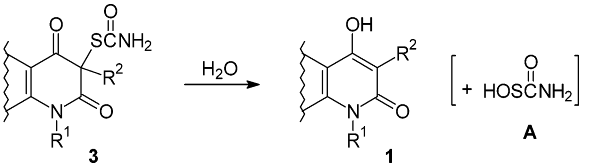


SCHEME 2[a]

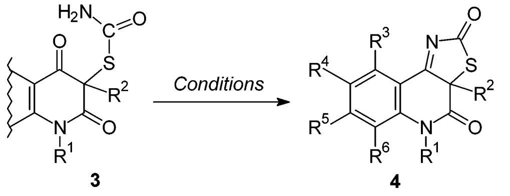


[a] For conditions, see Table 1. The formation of **1** is due to decomposition of **3** during the isolation workup.

SCHEME 3



SCHEME 4. Independent Transformation of 3 to 4[a]



4	yield (%)
a	67
b	63
c	61
d	79
e	14
f	73
g	70
h	21

[a] Conditions: **3a−d,f,g**, P_2O_5/HOAc, 50 °C, 4 h; **3e,h**, 60 °C, 6 h (see Experimental Section).

water leading to **1** (Scheme 1), and as noted in this paper, the same applies to the thiocarbamates **3**. This high water sensitivity renders the hydration of **2** to **3** nontrivial, and we anticipated it could only be accomplished using a "water-containing water-reactive" agent. Thus, the hydration was attempted and proved to work upon exposure of **2** to neat concentrated (96%) sulfuric acid at room temperature, usually within 5−10 min (Scheme 2, Table 1, reaction conditions A). In some cases these reaction conditions gave dark-colored reaction mixtures, which we were able to avoid by diluting the 96% sulfuric acid with glacial acid (Table 1, reaction conditions B). Unfortunately, the dilution did not increase the yield of **3**, which we isolated along with 4-hydroxyquinolin-2(1*H*)-ones **1** and thiazoloquinolones **4** (Scheme 2, Table 1).

In solution, thiocarbamates **3** in the presence of water rapidly transform to **1** (Scheme 3). For example, slow transformation of **3** to **1** takes place in cold dimethyl sulfoxide and warm absolute ethanol solutions, whereas in aqueous ethanol this transformation proceeds within minutes. Relatively stable are compounds **3** in glacial acid, but even trace amounts of water cause an instant reaction. Slow transformation of **3** to **1** also takes place in an ethyl acetate/benzene/silica gel mixture, the chromatographic system used for product isolation. Hence, decomposition of **3** on silica gel is the major cause for the low isolated yields of **3** and the appearance of **1**. Ironically, chromatographic separation of **3** from **1** proved to be even more troublesome as both compounds possess similar chromatographic properties, and the isolation of **3** from the crude reaction mixture by repeated crystallization from a suitable dry solvent usually worked best.

In the presence of sulfuric acid as water scavenger the thiocarbamates **3** in situ cyclodehydrate to **4**. Transformation of **3** to **4** was confirmed by independent experiments where acetic acid solutions of **3a−h** were treated with phosphorus pentoxide to give **4a−h** (Scheme 4). In comparison with **3a−d** and **3f−g**, the cyclodehydration of **3e,h** proved to be sluggish and required a higher temperature and a prolonged reaction time to be completed. It appears that **3e,h** are less prone to cyclodehydration, which corresponds to the modest yields of **4e,h** in the one pot hydration/cyclodehydration, as shown in Table 1.

Attempts have been made at increasing the yields of **4** by changing the composition of the hydration medium and the reaction time. Prolonged reaction times (compare entries 2 to 3, 11 to 12, and 16 to 17 and 18, Table 1) as well as an addition of phosphorus pentoxide to the reaction mixture proved beneficial. For example, the yield of **4b** doubled from a modest 26%, for a reaction in a sulfuric acid/acetic acid mixture (Table 1, entry 5), to a good 56% by the addition of phosphorus pentoxide (entry 6). Interestingly however, if the amount of phosphorus pentoxide was too high, a new compound resulted (entry 7), the structure of which has been assigned as 6-methyl-[1,3]thiazolo[5,4-*c*]quinoline-2,4(1*H*,5*H*)-dione (**5b**, Figure S1).[11]

An analogous debutylated compound **5g** was obtained in small amounts from **2g** upon conducting the reaction in the absence of P_2O_5 (Table 1, entries 19 and 20). The structure of **5g** was confirmed by X-ray diffraction analysis (Figures S1 and S2).[11] We were successful in isolating two other minor side products: 4-imino-1-methyl-3-phenyl-3-sulfanyl-3,4-dihydroquinolin-2(1*H*)-one (**6**) from **2f** and acridin-9(10*H*)-one (**7**) from **2h** (Figure S1,[11] Table 1).

Thiocarbamates **3** were characterized by IR, MS, and NMR spectroscopy. Despite the very short lifetimes (from minutes to several hours) of **3** in DMSO-d_6 and their low solubility in other NMR solvents, in some cases we were able to acquire satisfactory carbon spectra. Four carbon resonances are characteristic for **3**: C-3 (δ 65−72 ppm); C-4 (δ 192−194 ppm); C-2 and SCON (δ 166−171 ppm). The thiocarbamate carbon resonance is in good agreement with the literature reports for N-substituted analogues.[6b,c] The disappearance of **3** and subsequent appearance of carbon resonances of **1** concurred with the appearance of one additional carbon resonance at δ 149.8 ppm. Although it is reasonable to assume that amino(oxo)methansulfenic acid (**A**, Scheme 3) initially forms in this reaction,[12] the resonance at δ 149.8 ppm most likely corresponds to its decomposition product.[13]

The composition and structure of **4** were established by CHNS elemental analysis,[14] IR, NMR, and mass

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(10) Compounds **2** are easily prepared by thiocyanation of 4-hydroxyquinolin-2(1*H*)-ones **1** (Scheme 1): Klásek, A.; Polis, J.; Mrkvička, V.; Košmrlj, J. *J. Heterocycl. Chem.* **2002**, *39*, 1315−1320.

(11) Please see Supporting Information.

TABLE 1. Hydration/Cyclodehydration Experiments with 2a−h

		substituents								product, yield[b]			
entry	educt **2**	R^1	R^2	R^3	R^4	R^5	R^6	reacn conditns[a]	reacn time	**1**	**3**	**4**	other
1	**a**	H	n-C_4H_9	H	H	H	H	A	10 min	6	27	24	
2	**a**							B	5 min	32		6	
3	**a**							B	10 min	21		38	
4	**b**	H	n-C_4H_9	H	H	H	CH_3	A	10 min	7	32	22	
5	**b**							B	10 min	10	8	26	
6	**b**							B + P_2O_5[c]	10 min			56	
7	**b**							B + P_2O_5[d]	10 min				**5b**, 59
8	**c**	H	n-C_4H_9	H	Cl	H	H	A	5 min	5	49	7	
9	**c**							B	5 min	5	10	18	
10	**d**	CH_3	n-C_4H_9	H	H	H	H	A	10 min	8	34	29	
11	**d**							B	5 min	28		29	
12	**d**							B	10 min	17		35	
13	**e**	CH_3	n-C_4H_9	CH_3	H	CH_3	H	C	15 min		58	3	
14	**f**	CH_3	C_6H_5	H	H	H	H	A	40 min		25	24	
15	**f**							B	40 min	4	37	28	
16	**f**							C	1 min		33	20	
17	**f**							C	40 min		23	37	**6**, 6
18	**f**							C	1.5 h			58	
19	**g**	C_6H_5	n-C_4H_9	H	H	H	H	A	5 min	20	12	32	**5g**, 4
20	**g**							B	5 min	26	6	46	**5g**, 2
21	**h**	C_6H_5	C_6H_5	H	H	H	H	A	10 min	7	29	9	**7**, 8
22	**h**							B	10 min	24	1	22	

[a] Room temperature, 6 mL/mmol of **2** for conditions A (96% H_2SO_4), B (96% H_2SO_4/HOAc (9/1, v/v)), and C (96% H_2SO_4/HOAc (85/15, v/v)). [b] Percent yields of isolated pure products are given. [c] P_2O_5 (0.6 g/mmol of **2b**) was added after the addition of **2b**. [d] P_2O_5 (2 g/mmol of **2b**) was added after the addition of **2b**.

spectra. The base peaks in electron-impact mass spectra for 3-phenyl derivatives **4f,h** corresponded to their molecular ions or, in the case of 3-butyl derivatives (**4a−e,h**), to m/z M − 56 (M − Bu). Characteristic fragment ions were found at m/z M − 28 (M − CO), M − 42 (M − NCO), and M − 33 (M − SH). In the ^{13}C NMR spectra of **4**, four characteristic resonances appeared in the ranges of 77.2−79.5 ppm (C-3a), 165.1−168.8 ppm (C-9b), 184.9−185.9 ppm (C-4), and 189.7−191.7 ppm (C-2). In one instance, that of **4g**, the structure was confirmed by single-crystal X-ray diffraction (Figure S3).[11]

Interestingly, the aromatic region of the ^{13}C NMR spectrum of **4g** recorded at 302 K exhibits some additional broad resonances, which we assigned to nonequivalent *ortho*- and *meta*-protons of the *N*-phenyl ring, restricted in its rotation about the C−N bond (Figure S4).[11] This has been confirmed by variable-temperature ^{13}C NMR measurements, showing coalescence below 323 K. A similar behavior was observed in the ^{13}C NMR spectra of **2g**, **3h**, and **4h**. To the best of our knowledge, this is the first report on such an anisotropic effect in quinolinone derivatives.

Conclusions

In summary, we have reported a novel hydration/cyclodehydration procedure of 3-substituted 2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl thiocyanates **2** to 3a-substituted [1,3]thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-diones **4** via thiocarbamates **3**. Concentrated sulfuric acid, though hazardous and not compatible with many functional groups, is indispensable for the hydration step, as both **2** and **3** in the presence of water rapidly transform to **1**. Future endeavors will focus on exploring chemical and pharmacological applications of **3** and **4**, as well as on extending the scope to the synthesis of other 3-thiazolin-2-ones. Experiments on the rearrangement of **4** to the isomeric [1,3]thiazolo[3,4-*c*]quinazoline-3,5(6*H*)-diones are currently underway in our laboratories.

Experimental Section

General Experimental Methods. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded at 302 K (unless otherwise indicated). Chemical shifts are in ppm (δ) and are referenced to internal TMS. Coupling constants (J) are given in Hz. High-resolution mass spectra were obtained using EI ionization at 70 eV. Data are reported as m/z (intensity relative). For column chromatography, Merck Silica gel 60, 70−230 mesh, was used with benzene and then successive mixtures of benzene−ethyl acetate (ratios from 99:1 to 4:1) (solvent system S1) or with chloroform and then successive mixtures of chloroform−ethanol (ratios from 99:1 to 4:1) (solvent system S2) as eluents. Reactions and the course of separation were monitored by TLC (eluent systems: benzene−ethyl acetate, 4:1; chloroform−ethanol, 9:1 or 19:1; chloroform−ethyl acetate, 4:1) on Alugram SIL G/UV$_{254}$ foils (Macherey-Nagel). **Caution!** *Sulfuric acid causes severe burns and should be handled with care.* **Caution!** *Benzene is flammable, may cause cancer, and should be handled with care.*

4-Hydroxyqunolin-2(1*H*)-ones (**1a−h**) were prepared according to the general procedures reported in the literature.[15] For physical and spectroscopic data for compounds **1b**,**c**,**e**, see ref 15. Physical data (without NMR data) for compounds **1a**,**d**,**g**,**h** are reported in the literature.[16]

3-Butyl-4-hydroxyquinolin-2(1*H*)-one (1a): yield 67%; mp 199−200 °C (ethanol), lit.[16a] mp 190−192 °C (ethanol); ^{1}H NMR (DMSO-d_6) δ 0.91 (t, J = 7.1 Hz, 3H), 1.28−1.50 (m, 4H),

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(12) Huffman, J. W. *J. Org. Chem.* **1961**, *26*, 1470−1474.

(13) We were not able to confirm the proposed structure of the byproduct **A** by means of isolation or spectroscopic characterization. It is noteworthy that sulfenic acids are extremely reactive species: Davis, F. A.; Jenkins, R. H., Jr.; Rizvi, S. Q. A.; Yocklovich, S. G. *J. Am. Chem. Soc.* **1981**, *46*, 3467−3474.

(14) All synthesized [1,3]thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-diones **4** gave satisfactory elemental analysis with the range of C ± 0.28%, N ± 0.29%, and S ± 0.30%.

(15) Klásek, A.; Koristek, K.; Polis, J.; Košmrlj, J. *Tetrahedron* **2000**, *56*, 1551−1560.

2.58 (t, J = 7.8 Hz, 2H), 7.14 (ddd, J = 8.0, 8.0, 1.0 Hz, 1H), 7.26 (d, J = 8.0 Hz, 1H), 7.43 (ddd, J = 8.0, 8.0, 1.3 Hz, 1H), 7.89 (dd, J = 8.0, 1.0 Hz, 1H), 9.97 (br s, 1H), 11.28 (br s, 1H); ^{13}C NMR (DMSO-d_6) δ 14.0, 22.2, 22.7, 30.4, 111.8, 114.7, 115.4, 120.8, 122.4, 129.5, 137.3, 156.8, 163.5.

3-Butyl-4-hydroxy-1-methylquinolin-2(1*H*)-one (1d): yield 73%; mp 143−145 °C (ethanol), lit.[16b] mp 141 °C (ethanol); ^{1}H NMR (DMSO-d_6) δ 0.91 (t, J = 7.1 Hz, 3H), 1.28−1.50 (m, 4H), 2.64 (t, J = 7.7 Hz, 2H), 7.22 (ddd, J = 8.0, 7.1, 1.4 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.57 (ddd, J = 8.0, 7.1, 1.4 Hz, 1H), 8.01 (dd, J = 8.0, 1.4 Hz, 1H), 10.00 (br s, 1H); ^{13}C NMR (DMSO-d_6) δ 14.0, 22.2, 23.6, 29.0, 30.4, 111.4, 114.1, 116.2, 121.0, 122.9, 130.0, 138.2, 155.7, 162.7.

3-Butyl-4-hydroxy-1-phenylquinolin-2(1*H*)-one (1g): yield 85%; mp 208−210 °C (ethanol), lit.[16b] mp 250 °C; ^{1}H NMR (DMSO-d_6) δ 0.91 (t, J = 7.1 Hz, 3H), 1.29−1.52 (m, 4H), 2.64 (t, J = 7.7 Hz, 2H), 6.48 (d, J = 8.1 Hz, 1H), 7.18−7.29 (m, 4H), 7.31−7.38 (m, 1H), 7.48−7.55 (m, 1H), 7.55−7.63 (m, 2H), 8.04 (dd, J = 8.0, 1.3 Hz, 1H), 10.22 (br s, 1H); ^{13}C NMR (DMSO-d_6) δ 13.9, 22.2, 23.3, 30.3, 111.5, 114.9, 121.3, 122.9, 128.3, 129.3, 129.7, 129.8, 138.3, 139.2, 156.4, 162.8.

4-Hydroxy-1,3-diphenylquinolin-2(1*H*)-one (1h): yield 85%; mp 232−233 °C (ethanol), lit.[16c] mp 218 °C (ethanol); ^{1}H NMR (DMSO-d_6) δ 6.52 (d, J = 8.3 Hz, 1H), 7.21−7.28 (m, 1H), 7.29−7.46 (m, 8H), 7.48−7.55 (m, 1H), 7.55−7.63 (m, 2H), 8.11 (dd, J = 8.0, 1.3 Hz, 1H), 10.29 (br s, 1H); ^{13}C NMR (DMSO-d_6) δ 112.3, 115.0, 116.1, 121.5, 123.5, 126.9, 127.6, 128.3, 129.3, 129.8, 130.6, 131.2, 133.2, 138.1, 139.8, 156.9, 161.9.

3-Alkyl/aryl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl thiocyanates (2a−h) were prepared according to the procedure in the ref 10. For physical and spectroscopic data for compounds **2a**−**c**,**e**−**f**,**h**, see ref 10.

3-Butyl-1-methyl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl thiocyanate (2d): yellow oil; yield 87% (after chromatography); IR 2958, 2932, 2867, 2154, 1698, 1664, 1601, 1471, 1427, 1356, 1299, 1251, 1171, 1108, 1088, 1049, 1034, 951, 810, 765, 663, 526 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.85 (t, J = 7.2 Hz, 3H), 1.18−1.38 (m, 4H), 2.33−2.40 (m, 2H), 3.56 (s, 3H), 7.27 (d, J = 7.9 Hz, 1H), 7.28 (t, J = 8.1 Hz, 1H), 7.74 (ddd, J = 8.1, 7.9, 1.5 Hz, 1H), 8.06 (dd, J = 8.1, 1.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 13.4, 22.4, 27.2, 30.5, 36.0, 64.5, 108.6, 115.3, 119.6, 124.0, 124.3, 128.6, 137.3, 142.2, 166.5, 188.7; EIMS *m*/*z* (%) 288 (M$^+$, 13), 245 (20), 232 (74), 216 (11), 212 (19), 202 (48), 189 (100), 176 (26), 160 (15), 146 (14), 134 (33), 117 (7), 104 (19), 91 (7), 77 (26), 59 (22), 55 (13); HRMS (*m*/*z*) calcd for $C_{15}H_{16}N_2O_2S$ 288.0933, found 288.0938.

3-Butyl-1-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl thiocyanate (2g): colorless crystals, mp 96−97 °C (hexane−cyclohexane); yield 83%; IR 2961, 2932, 2872, 2167, 1707, 1677, 1601, 1491, 1465, 1340, 1330, 1295, 1244, 1222, 1165, 1114, 1069, 1041, 974, 930, 839, 758, 746, 704, 665, 602 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 0.85 (t, J = 7.1 Hz, 3H), 1.22−1.48 (m, 4H), 2.20−2.38 (m, 2H), 6.40 (d, J = 8.3 Hz, 1H), 7.20−7.70 (m, 7H), 7.95 (dd, J = 7.8, 1.5 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 13.5, 13.9, 21.7, 26.6, 36.2, 68.5, 110.4, 116.9, 119.0, 123.8, 127.6, 128.3, 128.7, 129.2, 129.8, 130.2, 136.7, 137.0, 143.2, 166.9, 189.2 (some additional resonances in the aromatic region of ^{13}C NMR spectra appear due to a restricted rotation of the *N*-phenyl group about the C−N bond); EIMS *m*/*z* (%) 350 (M$^+$, 10), 294 (33), 264 (48), 251 (100), 237 (17), 195 (40), 167 (37), 139 (7), 115 (6), 92 (11), 77 (32), 69 (8), 59 (23). Anal. Calcd for $C_{20}H_{18}N_2O_2S$: C, 68.55; H, 5.18; N, 7.99; S, 9.15. Found: C, 68.26; H, 5.22; N, 7.79; S, 9.01.

General Procedure for the Reaction of 3-Alkyl/Aryl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl Thiocyanates (2a−h) with Sulfuric Acid. To an ice-cooled 96% sulfuric acid (30 mL) or a mixture of 96% sulfuric acid and glacial acid (30 mL, for volume ratio, see Table 1) was added thiocyanate **2** (5 mmol) in small portions during 5 min under stirring at 0 °C. After dissolution of **2**, the resulting deep red mixture was stirred at room temperature for the time indicated in Table 1 and then poured onto crushed ice. The yellow precipitate was filtered off with suction, dried, and crystallized from a solvent indicated below to give compound **3**. The aqueous portions were extracted with benzene (3 × 20 mL) or chloroform (3 × 20 mL). These collected organic layers were dried over sodium sulfate, combined with mother liquors after crystallization, and subjected to column chromatography using solvent system S1 or S2 to afford products **1**, **3**, and **4**−**7**. Reaction conditions and the yields of isolated thiocarbamates **3a**−**h** (combined yields from crystallization and column chromatography are given), thiazoloquinolones **4a**−**h**, and 4-hydroxyquinolin-2(1*H*)-ones **1a**−**h** are given in Table 1.

Physical and spectroscopic data for thiocarbamates **3a**−**h**, [1,3]thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-diones **4a**−**h**, [1,3]-thiazolo[5,4-*c*]quinoline-2,4(1*H*,5*H*)-diones **5a**,**g**, and 4-imino-1-methyl-3-phenyl-3-sulfanyl-3,4-dihydroquinolin-2(1*H*)-one (**6**) are given below. Spectral data for compound **7** are identical with those of authentic acridin-9(10*H*)-one. Thiocarbamates **3** are thermally unstable, and their thermal decomposition could be the reason that some of them melt in a relatively wide temperature range, despite being chromatographically pure.

***S*-(3-Butyl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl) thiocarbamate (3a):** colorless crystals; mp 165−167 °C (tetrahydrofuran−cyclohexane); IR 3438, 3241, 3162, 2957, 2930, 2871, 1708 sh, 1663, 1610, 1600, 1487, 1433, 1371, 1312, 1158, 781, 754, 682, 666, 613 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 0.73 (t, J = 6.5 Hz, 3H), 1.02−1.25 (m, 4H), 1.72−1.88 (m, 2H), 7.08−7.17 (m, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.78 (d, J = 7.7 Hz, 1H), 10.98 (br s, 1H); ^{13}C NMR (DMSO-d_6) δ 13.4, 21.9, 26.0, 35.8, 65.4, 116.2, 118.9, 122.2, 126.6, 135.8, 141.4, 166.2, 170.9, 193.6; FABMS *m*/*z* (%) 293 (MH$^+$, 100), 250, (55), 218 (18), 193 (27), 71 (58); EIMS *m*/*z* (%) 292 (M$^+$, 1), 274 (4), 256 (5), 231 (6), 231 (6), 217 (25), 193 (42), 188 (46), 175 (100), 161 (31), 146 (20), 120 (35), 92 (16), 77 (8), 64 (8), 55 (5). Anal. Calcd for $C_{14}H_{16}N_2O_3S$: C, 57.52; H, 5.52; N, 9.58; S, 10.97. Found: C, 57.80; H, 5.79; N, 9.37; S, 10.71.

***S*-(3-Butyl-8-methyl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl) thiocarbamate (3b):** colorless crystals; mp 166−167 °C (tetrahydrofuran−cyclohexane); IR 3390, 3220, 2957, 2933, 2871, 1696, 1664, 1599, 1499, 1469, 1353, 1314, 1239, 952, 797, 749, 695, 612, 550 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.81 (t, J = 7.0 Hz, 3H), 1.17−1.44 (m, 4H), 1.98−2.06 (m, 2H), 2.31 (s, 3H), 5.39 (br s, 2H), 7.06 (dd, J = 7.7, 7.7 Hz, 1H), 7.40 (d, J = 7.7 Hz, 1H), 7.85 (br s, 1H), 7.88 (d, J = 7.7 Hz, 1H); ^{13}C NMR δ (CDCl$_3$) 13.5, 16.6, 22.6, 26.5, 36.4, 67.1, 119.4, 123.0, 123.1, 126.2, 137.3, 138.2, 167.6, 171.3, 193.1; EIMS *m*/*z* 306 (M$^+$, 5), 263 (14), 245 (7), 231 (28), 220 (54), 207 (100), 202 (46), 189 (98), 160 (19), 144 (7), 134 (44), 130 (12), 115 (8), 104 (27), 91(18), 77 (22), 64 (25). Anal. Calcd for $C_{15}H_{18}N_2O_3S$: C, 58.80; H, 5.92; N, 9.14. Found: C, 58.94; H, 5.86; N, 8.97.

***S*-(3-Butyl-6-chloro-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl) thiocarbamate (3c):** colorless crystals; mp 174−176 °C (tetrahydrofuran−cyclohexane); IR 3426, 3225, 3163, 2959, 2931, 2872, 1707, 1664, 1608, 1597, 1492, 1407, 1351, 1328, 1258, 1204, 827, 687, 664, 622, 560 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 0.75 (t, J = 6.7 Hz, 3H), 1.08−1.25 (m, 4H), 1.75−1.88 (m, 2H), 7.16 (d, J = 8.6 Hz, 1H), 7.66 (dd, J = 2.4, 7.7 Hz, 1H), 7.71 (d, J = 2.4 Hz, 1H), 11.14 (br s, 1H); ^{13}C NMR (DMSO-d_6) δ 13.9, 21.9, 26.0, 35.7, 65.1, 118.4, 119.9, 125.5, 126.2, 135.4, 140.2, 166.2, 170.8, 192.9; EIMS *m*/*z* (%) 326 (M$^+$, 2), 283 (5), 251 (26), 227 (64), 222 (33), 209 (100), 195 (15), 154 (21), 126 (13), 90 (5), 64 (19). Anal. Calcd for $C_{14}H_{15}ClN_2O_3S$: C, 51.45; H, 4.63; N, 8.57; S, 9.81. Found: C, 51.22; H, 4.42; N, 8.47; S, 9.57.

***S*-(3-Butyl-1-methyl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl) thiocarbamate (3d):** colorless crystals; mp 117−

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[16] (a) Ukrainets, I. V.; Taran, S. G.; Evtifeeva, O. A.; Gorokhova. O. V.; Bezugly. P. A.; Turov, A. V.; Voronina, L. N.; Filimonova, N. I. *Chem. Heterocycl. Compd. (Engl. Transl.)* **1994**, *30*, 591−595. (b) Stadlbauer, W.; Laschober, R.; Lutschounig, H.; Schindler. G.; Kappe. T. *Monatsh. Chem.* **1992**, *123*, 617−636. (c) Pfister, R.; Hafliger, F., U.S. Patent 3 025 299, 1962; *Chem. Abstr.* **1962**, *57*, 12444e.

130 °C (tetrahydrofuran−cyclohexane); IR 3331, 3171, 2957, 2927, 2869, 1694, 1672, 1649, 1599, 1472, 1360, 1306, 1244, 1173, 1148, 1111, 1034, 752, 708, 664 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.74−0.83 (m, 3H), 1.13−1.29 (m, 4H), 1.96−2.05 (m, 2H), 3.55 (s, 3H), 5.34 (br s, 2H), 7.13−7.24 (m, 2H), 7.60−7.68 (m, 1H), 8.09 (dd, J = 7.7, 1.5 Hz, 1H); ^{13}C NMR (CH$_3$CO$_2$H) δ 13.8, 23.3, 27.3, 31.2, 37.7, 67.6, 116.6, 122.0, 124.4, 128.9, 137.4, 143.7, 171.8, 173.0, 194.5; EIMS m/z 306 (M$^+$, 4), 272 (2), 263 (3), 256 (6), 247 (6), 231 (20), 207 (100), 202 (36), 189 (62), 176 (13), 162 (28), 146 (13), 134 (32), 117 (7), 104 (15), 91 (6), 77 (19), 64 (12). Anal. Calcd for $C_{15}H_{18}N_2O_3S$: C, 58.80; H, 5.92; N, 9.14. Found: C, 58.73; H, 6.12; N, 8.97.

***S*-(3-Butyl-1,5,7-trimethyl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl) thiocarbamate (3e):** colorless crystals; mp 183−187 °C (benzene); IR 3330, 3171, 2957, 2929, 2870, 1701 sh, 1672, 1645, 1607, 1573, 1493, 1461, 1351, 1298, 1240, 1172, 841, 708, 610 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.78 (t, J = 7.0 Hz, 3H), 1.11−1.28 (m, 4H), 1.88−2.01 (m, 2H), 2.39 (s, 3H), 2.63 (s, 3H), 3.52 (s, 3H), 5.64 (br s, 2H), 6.81 (s, 1H), 6.89 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 13.5, 22.1, 22.6, 23.1, 26.8, 31.3, 36.6, 68.8, 113.9, 117.3, 127.9, 142.8, 143.7, 145.3, 167.6, 170.7, 192.7; EIMS m/z 334 (M$^+$, 8), 290 (16), 258 (13), 248 (6), 235 (100), 230 (16), 216 (31), 203 (27), 190 (55), 174 (20), 162 (22), 133 (13), 105 (8), 91 (16), 77 (9), 64 (9), 55 (13). Anal. Calcd for $C_{17}H_{22}N_2O_3S$: C, 61.05; H, 6.63; N, 8.38; S, 9.59. Found: C, 61.08; H, 6.59; N, 8.16; S, 9.60.

***S*-(1-Methyl-3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl) thiocarbamate (3f):** colorless crystals; mp 192−193 °C (benzene); IR 3393, 3302, 3265, 3177, 1706 sh, 1682, 1649, 1597, 1472, 1358, 1308, 1241, 1140, 1035, 827, 775, 757, 714, 697, 681, 664, 528 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.62 (s, 3H), 5.42 (br s, 2H), 7.11−7.17 (m, 2H), 7.25−7.31 (m, 4H), 7.35−7.40 (m, 2H), 7.58 (ddd, J = 8.0, 7.5, 1.6 Hz, 1H), 8.06 (dd, J = 8.0, 1.6 Hz, 1H). All attempts to record carbon spectra failed. As soon as **3f** is dissolved in DMSO-d_6 it decomposes to 3-butyl-4-hydroxy-1-phenylquinolin-2(1*H*)-one (**1f**). EIMS (m/z): 326 (M$^+$, 2), 308 (1), 283 (83), 266 (15), 250 (100), 222 (33), 208 (17), 194 (12), 162 (22), 152 (12), 134 (72), 121 (45), 116 (12), 104 (23), 91 (15), 77 (48), 64 (27). Anal. Calcd for $C_{17}H_{14}N_2O_3S$: C, 62.56; H, 4.32; N, 8.58; S, 9.83. Found: C, 62.73; H, 4.18; N, 8.39; S, 9.54.

***S*-(3-Butyl-1-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl) thiocarbamate (3g):** colorless crystals; mp 95−97 °C (ethyl acetate); IR 3349, 3255, 3183, 2954, 2927, 2869, 1701sh, 1672, 1599, 1492, 1463, 1341, 1299, 1252, 1161, 753, 702, 693, 662, 620, 579, 514 cm^{-1}; EIMS m/z (%) 368 (M$^+$, 48), 352 (18), 334 (9), 317 (30), 309 (35), 293 (37), 278 (33), 2645 (30), 251 (51), 237 (17), 222 (14), 204 (13), 196 (37), 167 (100), 160 (22), 128 (20), 115 (9), 96 (10), 83 (11), 77 (26), 64 (22), 55 (25); HRMS m/z calcd 368.1195, found 368.1203. All attempts to record proton and carbon spectra failed. As soon as **3g** is dissolved in DMSO-d_6, it decomposes to 3-butyl-4-hydroxy-1-phenylquinolin-2(1*H*)-one (**1g**).

***S*-(1,3-Diphenyl-2,4-dioxo-1,2,3,4-tetrahydroquinolin-3-yl) thiocarbamate (3h):** colorless crystals; mp 192−194 °C (tetrahydrofuran−cyclohexane); IR 3444, 3285, 3204, 3159, 1703, 1674, 1598, 1491, 1462, 1331, 1302, 1243, 1162, 858, 769, 743, 701, 663, 619, 583 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 6.38 (d, J = 8.3 Hz, 1H), 7.10−7.20 (m, 1H), 7.27−7.76 (m, 11 H), 8.10 (d, 1H); ^{13}C NMR (CH$_3$CO$_2$H) δ 74.1, 118.1, 121.4, 124.7, 129.2, 129.5, 130.0, 130.2, 130.5, 131.0, 131.1, 131.7, 132.4, 136.8, 139.1, 144.1, 171.1, 172.4, 191.4 (additional resonances in the aromatic region of ^{13}C NMR spectra are due to a restricted rotation of the *N*-phenyl group about the C−N bond); EIMS m/z (%) 388 (M$^+$, 1), 370 (0.2), 345 (1.5), 313 (100), 284 (6), 256 (10), 196 (54), 180 (6), 167 (36), 160 (15), 121 (11), 105 (7), 89 (15), 77 (37), 64 (34); HRMS m/z calcd 388.0882, found 388.0890. Anal. Calcd for $C_{22}H_{16}N_2O_3S$: C, 68.02; H, 4.15; N, 7.21; S, 8.26. Found: C, 68.13; H, 4.32; N, 7.17; S, 8.03.

3a-Butyl[1,3]thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-dione (4a): yellow crystals; mp 180−187 °C (benzene−hexane); IR 3219, 3165, 2963, 2924, 2853, 1719, 1700, 1607, 1588, 1568, 1502, 1475, 1430, 1347, 1274, 1240, 1221, 1155, 1092, 1050, 776, 754, 732, 587 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.87 (t, J = 7.1 Hz, 3H), 1.19−1.37 (m, 3H), 1.44−1.60 (m, 1H), 1.87−1.90 (m, 1H), 2.21−2.33 (m, 1H), 7.13 (d, J = 8.0 Hz, 1H), 7.28 (ddd, J = 7.8, 7.6, 0.8 Hz, 1H), 7.65 (ddd, J = 8.0, 7.6, 1.3 Hz, 1H), 8.09 (dd, J = 7.8, 1.3 Hz, 1H), 9.38 (br s, 1H); ^{13}C NMR (CDCl$_3$) δ 13.6, 22.0, 27.4, 42.6, 77.3, 115.8, 116.8, 124.9, 128.8, 136.8, 139.2, 168.8, 185.2, 190.6. Anal. Calcd for $C_{14}H_{14}N_2O_2S$: C, 61.29; H, 5.14; N, 10.21; S, 11.69. Found: C, 61.49; H, 4.77; N, 9.94; S, 11.41.

3a-Butyl-6-methyl[1,3]thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-dione (4b): yellow crystals; mp 215−218 °C (benzene−hexane); IR 3264, 2951, 2930, 2869, 1704, 1599, 1573, 1496, 1461, 1347, 1273, 1232, 1219, 1143, 1101, 1071, 793, 751, 729, 595 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.83 (t, J = 7.0 Hz, 3H), 1.19−1.35 (m, 3H), 1.42−1.60 (m, 1H), 1.83−1.96 (m, 1H), 2.20−2.31 (m, 1H), 2.42 (s, 3H), 7.18 (dd, J = 7.6, 7.6 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.93 (d, J = 7.6 Hz, 1H), 8.58 (br s, 1H); ^{13}C NMR (CDCl$_3$) δ 13.6, 17.1, 22.0, 27.4, 42.4, 77.2, 115.8, 124.3, 124.7, 126.7, 137.5, 138.1, 168.4, 185.2, 191.1. Anal. Calcd for $C_{15}H_{16}N_2O_2S$: C, 62.48; H, 5.59; N, 9.71; S, 11.12. Found: C, 62.55; H, 5.50; N, 9.49; S, 10.97.

3a-Butyl-8-chloro[1,3]thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-dione (4c): yellow crystals; mp 144−149 °C (benzene−hexane); IR 3202, 3142, 3057, 2953, 1733, 1719, 1699, 1607, 1589, 1476, 1422, 1328, 1237, 1116, 1080, 1016, 903, 826, 608, 538, 492 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 0.78 (t, J = 6.9 Hz, 3H), 1.10−1.28 (m, 3H), 1.28−1.48 (m, 1H), 1.80−1.93 (m, 1H), 2.19−2.21 (m, 1H), 7.22 (d, J = 8.7 Hz, 1H), 7.75 (dd, J = 8.7, 2.2 Hz, 1H), 7.91 (d, J = 2.2 Hz, 1H), 11.34 (br s, 1H); ^{13}C NMR (DMSO-d_6) δ 13.5, 21.3, 27.2, 41.5, 77.3, 116.2, 118.9, 126.7, 127.2, 136.2, 139.8, 167.0, 184.9, 191.0; EIMS m/z (%) 308 (M$^+$, 100), 275 (7), 265 (95), 252 (25), 247 (15), 237 (74), 230 (19), 209 (20), 179 (12), 151 (10), 124 (7), 100 (7), 59 (5). Anal. Calcd for $C_{14}H_{13}ClN_2O_2S$: C, 54.46; H, 4.24; N, 9.07; S, 10.38. Found: C, 54.74; H, 4.49; N, 8.78; S, 10.63.

3a-Butyl-5-methyl[1,3]thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-dione (4d): yellow crystals; mp 109−110 °C (benzene−hexane); IR 2965, 2927, 2872, 1720, 1684, 1589, 1468, 1351, 1301, 1287, 1128, 1109, 1044, 964, 765, 693, 600, 502 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.81 (t, J = 7.0 Hz, 3H), 1.14−1.30 (m, 3H), 1.38−1.52 (m, 1H), 1.79−1.92 (m, 1H), 2.13−2.26 (m, 1H), 3.49 (s, 3H), 7.26 (d, J = 8.5 Hz, 1H), 7.30 (dd, J = 8.5, 8.5 Hz, 1H), 7.73 (ddd, J = 8.5, 7.7, 1.5 Hz, 1H), 8.10 (dd, J = 7.7, 1.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 13.6, 22.0, 27.2, 30.5, 42.4, 77.8, 115.6, 117.2, 124.2, 128.8, 136.6, 141.8, 166.9, 185.3, 190.5. Anal. Calcd for $C_{15}H_{16}N_2O_2S$: C, 62.48; H, 5.59; N, 9.71; S, 11.12. Found: C, 62.31; H, 5.80; N, 9.73; S, 10.85.

3a-Butyl-5,7,9-trimethyl[1,3]thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-dione (4e): yellow crystals; mp 129−134 °C (benzene−hexane); IR 2960, 2934, 2864, 1716, 1687, 1605, 1581, 1495, 1455, 1333, 1327, 1310, 1173, 1144, 1087, 1047, 843, 763, 685, 619, 584 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.80 (t, J = 7.2 Hz, 3H), 0.99−1.23 (m, 3H), 1.39−1.51 (m, 1H), 1.75−1.88 (m, 1H), 2.06−2.18 (m, 1H), 2.45 (s, 3H), 2.67 (s, 3H), 3.46 (s, 3H), 6.89 (s, 1H), 6.97 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 13.6, 21.9, 22.1, 22.3, 27.2, 31.0, 41.3, 79.0, 114.1, 114.4, 128.2, 141.7, 142.4, 146.1, 166.6, 186.0, 190.1; EIMS m/z (%) 316 (M$^+$, 52), 283 (27), 273 (22), 260 (100), 255 (12), 241 (30), 231 (24), 216 (30), 199 (16), 188 (12), 171 (5), 159 (18), 144 (4), 130 (6), 115 (4), 101 (10), 77 (6), 67 (7), 55 (8); HRMS (m/z) calcd for $C_{17}H_{20}N_2O_2S$ 316.1246, found 316.1231.

5-Methyl-3a-phenyl[1,3]thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-dione (4f): yellow crystals; mp 239−243 °C (benzene−cyclohexane); IR 2940, 2884, 1695, 1684, 1592, 1580, 1486, 1468, 1447, 1350, 1286, 1144, 1130, 1116, 1054, 963, 770, 750, 712, 695, 611 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.52 (s, 3H), 7.07−7.16 (m, 3H), 7.20−7.30 (m, 4H), 7.60 (ddd, J = 7.7, 7.6, 1.5 Hz, 1H), 8.13 (dd, J = 7.7, 1.5 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 30.8, 79.6, 115.8, 118.5, 124.3, 125.6, 128.7, 129.3, 129.6, 136.2, 136.3, 141.5, 165.6, 185.3, 188.8; EIMS m/z (%) 308 (M$^+$, 100), 291 (16), 280 (10), 275 (34), 266 (53), 251 (15), 219 (8), 205 (9), 190 (4), 121 (54), 102 (9), 77 (27), 63 (7); HRMS (*m*/*z*) calcd for $C_{17}H_{12}N_2O_2S$ 308.0620, found 308.0609. Anal. Calcd for $C_{17}H_{12}N_2O_2S$: C, 66.22; H, 3.92; N, 9.08; S, 10.40. Found: C, 66.11; H, 4.00; N, 9.07; S, 10.12.

3a-Butyl-5-phenyl[1,3]thiazolo[5,4-*c*]quinoline-2,4-(3a*H*,5*H*)-dione (4g): yellow crystals; mp 161−162 °C (benzene−hexane); IR 2956, 2936, 2869, 1722, 1695, 1590, 1491, 1460, 1345, 1290, 1270, 1242, 1159, 1110, 1080, 1034, 1013, 1002, 770, 757, 699, 616, 507, 481 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 0.80 (t, J = 7.0 Hz, 3H), 1.15−1.32 (m, 3H), 1.32−1.47 (m, 1H), 2.01−2.13 (m, 1H), 2.28−2.40 (m, 1H), 6.47 (d, J = 8.4 Hz, 1H), 7.27−7.69 (m, 7H), 8.06 (dd, J = 7.7, 1.2 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 13.6, 21.4, 27.4, 41.7, 77.9, 116.1, 117.2, 123.8, 128.0, 128.8, 129.1, 129.4, 130.0, 130.2, 136.5, 136.9, 143.2, 166.5, 185.2, 191.7. Additional resonances in the aromatic region of ^{13}C NMR spectra appear due to a restricted rotation of the *N*-phenyl group about the C−N bond. This has been confirmed by variable-temperature ^{13}C NMR measurements; see Figure S4.[11] EIMS *m*/*z* (%): 350 (34), 317 (58), 308 (25), 294 (100), 289 (19), 276 (54), 266 (13), 250 (17), 237 (11), 204 (11), 188 (11), 101 (7), 77 (22), 67 (6). Anal. Calcd for $C_{20}H_{18}N_2O_2S$: C, 68.55; H, 5.18; N, 7.99; S, 9.15. Found: C, 68.28; H, 5.40; N, 8.16; S, 8.91.

3a,5-Diphenyl[1,3]thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-dione (4h): yellow crystals; mp 207−210 °C (benzene−hexane); IR 3067, 3033, 2965, 2940, 2865, 1715, 1688, 1588, 1493, 1459, 1340, 1296, 1274, 1252, 1158, 1037, 1018, 777, 745, 697, 679, 613 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 6.34 (d, J = 8.4 Hz, 1H), 7.20−7.68 (m, 12H), 8.13 (dd, J = 7.7, 1.3 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 79.5, 117.2, 117.4, 124.0, 125.3, 128.1, 128.3, 128.7, 129.2, 129.4, 129.6, 130.0, 131.0, 136.1, 136.3, 136.9, 142.5, 165.2, 185.2, 189.7 (some additional resonances in the aromatic region of ^{13}C NMR spectra appear due to a restricted rotation of the *N*-phenyl group about the C−N bond); EIMS *m*/*z* (%) 370 (M$^+$, 100), 337(22), 328 (44), 311 (17), 281 (4), 251 (7), 223 (6), 205 (7), 190 (4), 121 (54), 97 (6), 77 (36), 69 (16), 57 (15); HRMS (*m*/*z*) calcd for $C_{22}H_{14}N_2O_2S$ 370.0776, found 370.0786. Anal. Calcd for $C_{22}H_{14}N_2O_2S$: C, 71.33; H, 3.81; N, 7.56; S, 8.66. Found: C, 71.07; H, 3.68; N, 7.29; S, 8.35.

6-Methyl[1,3]thiazolo[5,4-*c*]quinoline-2,4(1*H*,5*H*)-dione (5b): colorless crystals; mp >350 °C; yield 59%; IR 3224, 3035, 3012, 2967, 2686, 1692, 1679, 1638, 1601, 1560, 1513, 1480, 1425, 1409, 1389, 1198, 1136, 1027, 841, 753, 673, 635, 553; ^{1}H NMR (CF_3CO_2D) δ 7.57 (dd, J = 7.8, 7.8 Hz, 1H, H-8), 7.73 (d, J = 7.8 Hz, 1H, H-7), 7.88 (d, J = 7.8 Hz, 1H, H-9); ^{13}C NMR (CF_3CO_2D) δ 17.7 (CH_3), 109.3, 113.0 (C-9a), 122.0 (C-9), 128.3 (C-8), 129.2 (C-6), 136.5 (C-7), 136.9 (C-5a), 146.0 (C-9b), 160.8, 179.6; EIMS *m*/*z* 232 (M$^+$, 100), 204 (6), 189 (7), 176 (13), 143 (22), 131 (12), 116 (12), 89 (8), 81 (6), 69 (12), 57 (10). Anal. Calcd for $C_{11}H_8N_2O_2S$: C, 56.88; H, 3.47; N, 12.06; S, 13.81. Found: C, 56.67; H, 3.22; N, 11.97; S, 13.72.

5-Phenyl[1,3]thiazolo[5,4-*c*]quinoline-2,4(1*H*,5*H*)-dione (5g): colorless crystals; mp 327−331 °C (ethyl acetate); IR 3062, 3010, 2965, 2884, 2819, 2745, 1705, 1679, 1651, 1631, 1561, 1517, 1455, 1322, 1228, 1166, 1110, 1089, 757, 699, 654, 632, 514 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 6.62 (d, J = 8.5 Hz, 1H, H-6), 7.30−7.40 (m, 3H, 2 × *o*-Ph, H-8), 7.47 (dd, J = 7.7, 7.8 Hz, 1H, H-7), 7.52−7.69 (m, 3H, 2 × *m*-Ph, *p*-Ph), 8.11 (d, J = 7.8 Hz, 1H, H-9), 13.07 (br s, 1H); ^{13}C NMR (DMSO-d_6) δ 108.5, 110.8 (C-9a), 116.5 (C-6), 122.6 (C-8), 123.1 (C-9), 128.9 (C-4 of phenyl), 129.2 (C-2 and C-6 of phenyl), 130.0 (C-3 and C-5 of phenyl), 130.5 (C-7), 137.1 (C-1 of phenyl), 139.6 (C-5a), 139.9 (C-9b), 155.5, 171.5; EIMS *m*/*z* (%) 294 (100), 266 (41), 237 (23), 221 (14), 205 (13), 161 (6), 102 (9), 77 (23), 66 (6); HRMS (*m*/*z*) calcd for $C_{16}H_{10}N_2O_2S$ 294.0463, found 294.0464.

4-Imino-1-methyl-3-phenyl-3-sulfanyl-3,4-dihydroquinolin-2(1*H*)-one (6): colorless crystals; mp 202−204 °C (benzene); IR 3422, 3146, 3028, 2816, 1646, 1607, 1574, 1509, 1490, 1455, 1441, 1422, 1315, 1285, 1171, 869, 756, 688, 646, 585 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.68 (s, 3H), 3.90 (s, 1H), 6.64 (d, J = 8.2 Hz, 1H), 6.70 (ddd, J = 7.5, 7.5, 0.6 Hz, 1H), 7.08−7.22 (m, 6H), 7.28 (ddd, J = 8.2, 7.5, 1.6 Hz, 1H), 8.89 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 30.4, 110.8, 115.0, 116.5, 117.2, 126.3, 127.0, 127.7, 128.6, 130.5, 131.1, 131.5, 146.9, 172.1; EIMS *m*/*z* (%) 282 (M$^+$, 95), 249 (100), 234 (45), 223 (11), 207 (26), 164 (8), 132 (17), 121 (23), 119 (23), 91 (10), 77 (24), 69 (11), 57 (7). Anal. Calcd for $C_{16}H_{14}N_2OS$: C, 68.06; H, 5.00; N, 9.92; S, 11.36. Found: C, 68.16; H, 4.91; N, 9.78; S, 11.11.

General Procedure for the Conversion of Thiocarbamates 3 to [1,3]Thiazolo[5,4-*c*]quinoline-2,4(3a*H*,5*H*)-diones 4. To a stirred solution of **3** (0.3 mmol) in acetic acid (3 mL) was added 45 mg (0.3 mmol) of P_2O_5 at room temperature. After 5 min of stirring, the reaction temperature was increased to 50 °C (for **3a**−**d**,**f**,**g**) or 60 °C (for **3e**,**h**) and kept at this temperature for 60 min. The additional quantity of P_2O_5 (45 mg, 0.3 mmol) was added. The reaction was monitored by TLC, and after the starting material disappeared (after about 3 h for **3a**−**d**,**f**,**g**; 5 h for **3e**,**h**) the reaction mixture was cooled and poured onto crushed ice. The precipitate was filtered off with suction and recrystallized from appropriate solvent to give compounds **4**. For the yields of **4a**−**h**, see Scheme 4, and for physical and spectroscopic data, see above.

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Supporting Information Available: X-ray crystallographic data for **4g** and **5g** in CIF format and Figures S1 (structures of **5**−**7**), S2 (partial packing diagram for 5**g** from the X-ray crystal structure), S3 (ORTEP view of **4g**), and S4 (VT ^{13}C NMR spectra of **4g**). This material is available free of charge via the Internet at http://pubs.acs.org.

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