Molecular Rearrangement of 9b-Hydroxy-1*H*-imidazo[4,5-*c*]quinoline-2,4-diones – A Convenient Pathway to Spiro-Linked Imidazolidine – Oxindole Derivatives

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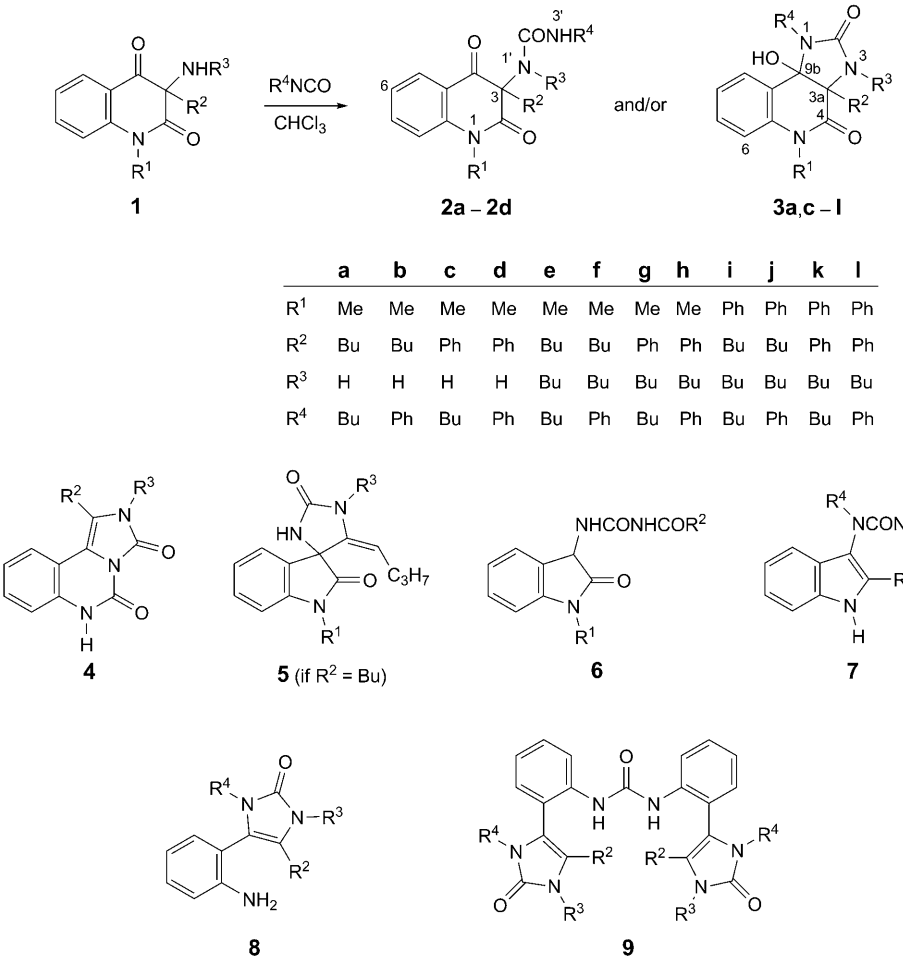
The 1-substituted 3-alkyl/aryl-3-aminoquinoline-2,4(1*H*,3*H*)-diones **1** react with alkyl/aryl isocyanates to give novel 3-alkyl/aryl-3-ureidoquinoline-2,4(1*H*,3*H*)-diones (= *N*-(3-alkyl/aryl-1,2,3,4-tetrahydro-2,4-dioxoquinolin-3-yl)ureas) **2** and/or 3a-alkyl/aryl-3,3a,5,9b-tetrahydro-9b-hydroxy-1*H*-imidazo[4,5-*c*]quinoline-2,4-diones **3** in high yields. Compounds **2** and **3** rearrange by boiling in AcOH or concentrated HCl solution to give three different types of spiro[imidazolidine-4,3′-[3*H*]indole]-2,2′(1′*H*)-diones, *i.e.*, **10**, **11**, and **12**, depending on the kind of substituents at C(3) and C(3a), respectively. All compounds were characterized by ^{1}H- and ^{13}C-NMR and IR spectroscopy as well as by atmospheric-pressure chemical-ionization (APCI) mass spectra. The structures of compounds **11c** and **12Al** were investigated by single-crystal X-ray diffraction analysis.

1. Introduction. – In our laboratory, much attention has been paid to study the reactivity of 3-alkyl/aryl-3-aminoquinoline-2,4(1*H*,3*H*)-diones **1** [1–7]. By reacting these α-amino ketones with nitrourea in dioxane, 3-ureidoquinolinediones **2** and/or imidazoquinolinediones **3** have been prepared (*Scheme 1*; $R^1 = R^4 = H$) [1][2]. Compounds **2** and **3** rearrange in boiling AcOH to give, depending on the character of substituents at positions 1 and 3, imidazoquinazolines **4** or oxindoles (=1,3-dihydro-2*H*-indol-2-ones) **5** and **6** [1][2], identical to those prepared by the reaction of **1** with urea in boiling AcOH [3][4]. With isocyanates, compounds **1** ($R^1 = H$) afford **2** and **3** ($R^1 = H$, $R^4 \neq H$) [5], which rearrange in boiling AcOH to give indolylureas **7** and/or bis[2-(imidazolyl)phenyl]ureas **9** [6][7]. Rearrangement of the same starting compounds in boiling concentrated HCl produces imidazolones **8**, which may be easily transformed into **7** by heating in AcOH [7]. Owing to simple reaction protocols, the above-mentioned transformations open an easy pathway to the preparation of new types of heterocyclic compounds.

The reaction of **1** with isocyanates has been studied so far only with 1-unsubstituted compounds (**1**; $R^1 = H$) [5–7]. For that reason, we set ourselves the objective of preparing new 1,3′-disubstituted 3-ureido derivatives **2** and their cyclic isomers **3** (*Scheme 1*; R^1, $R^4 \neq H$) and to study molecular rearrangements of these compounds in

Scheme 1



	a	b	c	d	e	f	g	h	i	j	k	l
R^1	Me	Me	Me	Me	Me	Me	Me	Me	Ph	Ph	Ph	Ph
R^2	Bu	Bu	Ph	Ph	Bu	Bu	Ph	Ph	Bu	Bu	Ph	Ph
R^3	H	H	H	H	Bu	Bu	Bu	Bu	Bu	Bu	Bu	Bu
R^4	Bu	Ph	Bu	Ph	Bu	Ph	Bu	Ph	Bu	Ph	Bu	Ph

an acid environment. We expected, by analogy to the examples presented above, the formation of novel heterocyclic systems. Results achieved in fulfilling this task are the object of this work.

2. Results and Discussion. – 2.1. *Synthesis and Spectral Properties.* By reacting 1-alkyl/aryl-3-aminoquinoline-2,4(1*H*,3*H*)-diones **1** [8] with butyl isocyanate and phenyl isocyanate, we prepared the corresponding 3-alkyl/arylureido derivatives **2a**–**2d** and their cyclic analogues **3a**,**c**–**l** (*Scheme 1*). The starting compounds **1** and the isocyanates were selected in such a way as to obtain products **2** and **3** differing mutually by the presence of aromatic (Ph) or aliphatic (Bu) substituents at positions 1 (5), 3 (3a), and 3′ (1), because the character of the substituents at these positions is decisive for the course of the following molecular rearrangement. The presence of an

H-atom or a Bu group at position 1′ (3) was chosen on the basis of our previous experiences [1–7].

The results of the experiments are presented in *Table 1*. Compounds **2** arose only from 3-aminoquinolinediones **1** that bear no substituent at their amino group ($R^3 = H$; *Entries 1–4*). But, even in these cases, compounds **3** were formed as the main product – with one exception (*Entry 2*). In the case of $R^3 \neq H$, only cyclic isomers **3** were formed in high yields (*Entries 5–12*). These results are in accord with results published for an analogous transformation of compounds **1** unsubstituted at position 1 ($R^1 = H$) [5]. Surprisingly, a side product of the reaction of **1c** with butyl isocyanate was isolated and identified as 3-hydroxy-1-methyl-3-phenylquinoline-2,4(1*H*,3*H*)-dione. Up to now, we have not observed substitution of an amino group by a hydroxy group in 3-aminoquinoline-2,4(1*H*,3*H*)-diones. ^{1}H- and ^{13}C-NMR spectra of compounds **2** and **3** are shown in *Tables 2* and *3*.

Table 1. *3-Ureidoquinoline-2,4(1*H,3H*)-diones* **2** *and 3,3a,5,9b-Tetrahydro-9b-hydroxyimidazo[4,5-*c*]quinoline-2,4-diones* **3** *from 3-Aminoquinolinediones* **1** (*Scheme 1*)

Entry	Starting compound	Substituents (R^4 from isocyanate)				Reaction time [h]	Product(s) (yield [%])
		R^1	R^2	R^3	R^4		
1	**1a**	Me	Bu	H	Bu	4	**2a** (5), **3a** (51)
2	**1a**	Me	Bu	H	Ph	3	**2b** (68)
3	**1c**	Me	Ph	H	Bu	3	**2c** (24), **3c** (45), HQD[a]) (3)
4	**1c**	Me	Ph	H	Ph	1	**2d** (22), **3d** (45)
5	**1e**	Me	Bu	Bu	Bu	3	**3e** (85)
6	**1e**	Me	Bu	Bu	Ph	2	**3f** (87)
7	**1g**	Me	Ph	Bu	Bu	3	**3g** (84)
8	**1g**	Me	Ph	Bu	Ph	2	**3h** (81)
9	**1i**	Ph	Bu	Bu	Bu	2.5	**3i** (97)
10	**1i**	Ph	Bu	Bu	Ph	2	**3j** (93)
11	**1k**	Ph	Ph	Bu	Bu	3	**3k** (86)
12	**1l**	Ph	Ph	Bu	Ph	2.5	**3l** (85)

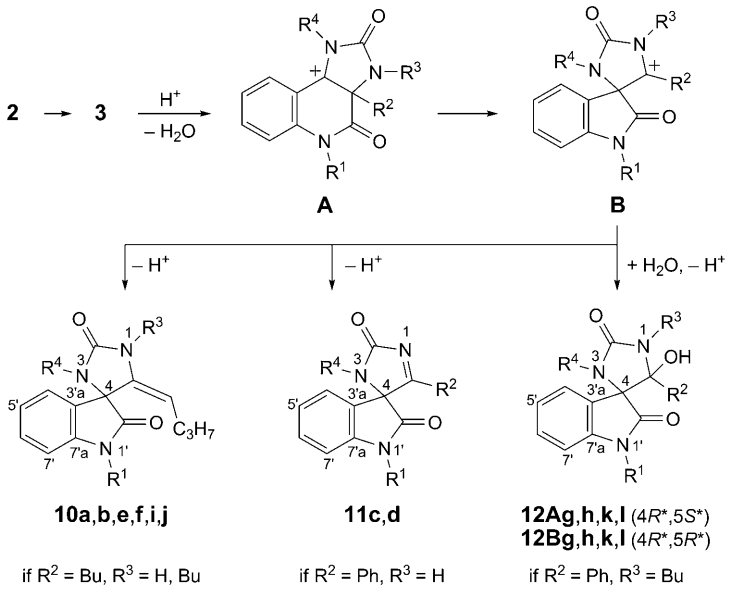
[a]) HQD = 3-Hydroxy-1-methyl-3-phenylquinoline-2,4(1*H*,3*H*)-dione, identical to the authentic compound.

Similarly to experiments performed in our earlier studies [2][6][7], we treated compounds **2** and **3** with AcOH and concentrated HCl solution. In accord with the proposed transformation mechanism of compounds **2** and **3** (R^1 = alkyl, aryl, $R^4 = H$) [2][4], we assumed the primary rearrangement intermediate would be carbocation **A** (*Scheme 2*). A migration of the amide group occurs in intermediate **A** leading to intermediate **B**. The following elimination of H^+ gives rise to spiro compounds **10** in cases where R^2 is Bu (*Table 4*). NMR Data of compounds **10a**,**b**,**e**,**f**,**i**,**j** are given in *Table 5*, the (5*E*)-configuration at the exocyclic C(5)=C bond of compounds **10** was deduced from NOE experiments confirming spatial interaction of C(5)=C*H* with the H-atoms of the CH_2(1′) and CH_2(2′) groups of the *N*-Bu group in **10e**,**f**,**i**,**j** (R^3 = Bu). Compounds **10a**,**e**,**i** are stable as crystalline materials, but they are very unstable in (D_6)DMSO solutions. Therefore, their NMR spectra were measured in $CDCl_3$ solution (*Table 5*). Unfortunately, even under these conditions, compounds **10a**,**e** decomposed

Table 2. *^{1}H- and ^{13}C-NMR Data* ((D_6)DMSO) *of Compounds* **2a**–**2d** . δ in ppm.

	2a		**2b**		**2c**		**2d**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
C(2)	–	172.1	–	171.6	–	171.0	–	170.4
C(3)	–	67.1	–	67.4	–	*71.1*	–	71.2
C(4)	–	193.7	–	193.3	–	191.3	–	191.1
C(4a)	–	120.3	–	120.1	–	120.0	–	119.9
H–C(5)	7.91	127.2	7.94	127.4	7.86	127.8	7.89	127.9
H–C(6)	7.25	122.7	7.27	122.9	7.23	123.0	7.28	123.3
H–C(7)	7.76	136.1	7.80	136.4	7.76	136.3	7.79	136.6
H–C(8)	7.42	115.6	7.45	115.8	7.46	115.9	7.49	116.1
C(8a)	–	142.8	–	142.7	–	142.4	–	142.4
N(*C*=O)N	–	157.2	–	154.6	–	157.6	–	154.8
(C=O)N*H*R^4	6.06	–	8.79	–	6.16	–	8.75	–
Me (R^1)	3.43	*29.8*	*3.47*	29.9	3.56	*30.2*	*3.58*	30.3
CH_2(1′) or C(1′) (R^2)	1.71	36.8	1.79	36.4	–	134.8	–	134.3
CH_2(2′) or H–C(2′) (R^2)	1.16	24.7	1.21	24.8	7.35	126.8	7.40	126.8
CH_2(3′) or H–C(3′) (R^2)	1.16	22.1	1.21	22.1	7.40	129.2	7.46	129.4
Me(4′) or H–C(4′) (R^2)	0.78	13.7	0.82	13.7	7.40	129.2	7.46	129.5
NH (R^3)	6.93	–	7.38	–	7.31	–	7.63	–
CH_2(1′) or C(1′) (R^4)	2.92	40.3	–	139.8	2.98	39.0	–	139.5
CH_2(2′) or H–C(2′) (R^4)	1.33	32.1	7.33	117.7	1.37	32.1	7.36	117.7
CH_2(3′) or H–C(3′) (R^4)	1.26	19.6	7.23	128.7	1.30	19.6	7.27	128.9
Me(4′) or H–C(4′) (R^4)	0.79	13.7	6.94	120.1	0.91	13.8	6.97	121.8

Scheme 2



For substituents, see *Scheme 1*

slowly, preventing the unambiguous assignment of all NMR signals. However, the assigned NMR signals of **10a**,**e** in *Footnote b* of *Table 5* were in accord with those of compounds **10b**,**f**,**i**,**j**.

An interesting result is that enamines **10a**,**b** ($R^3 = H$) also arose through rearrangement of compounds **3a** and **2b** (*Table 4*), even though, in these cases, intermediate **B** bears an H-atom at N(1) capable of deprotonation and providing the corresponding imine **11**.

If substituent R^2 in the starting compound is a Ph group (**2c**,**d**, **3c**,**d**,**g**,**h**,**k**,**l**), two different types of products arise in an acid environment. Compounds of the first type are formed by rearrangement of **2c**,**d** ($R^3 = H$) and **3c**,**d** ($R^3 = H$) to give the structures **11c** and **11d** (*Scheme 2*), deducible by deprotonation of carbocation **B**, and assigned by detailed NMR analysis (*Table 5*). The structure of **11c** was confirmed by X-ray diffraction analysis (*Fig. 1*). However, if the starting 3a-Ph derivatives **3g**,**h**,**k**,**l** bear a Bu group at position 3 ($R^3 = Bu$), carbocation **B** is stabilized by addition of H_2O and deprotonation, thus giving the products of the second type, *i.e.*, spiro compounds **12g**,**h**,**k**,**l** (*Scheme 2*). These structures are in accord with the occurrence of two signals for sp^3-C-atoms in their ^{13}C-NMR spectra at δ *ca.* 76 (C(4)) and 92 (C(5)) (*Table 6*), whereas only one signal for an sp^3-C-atom (C(4)) appears at δ *ca.* 77 ppm in the ^{13}C-NMR spectra of compounds **11c**,**d** (*Table 5*).

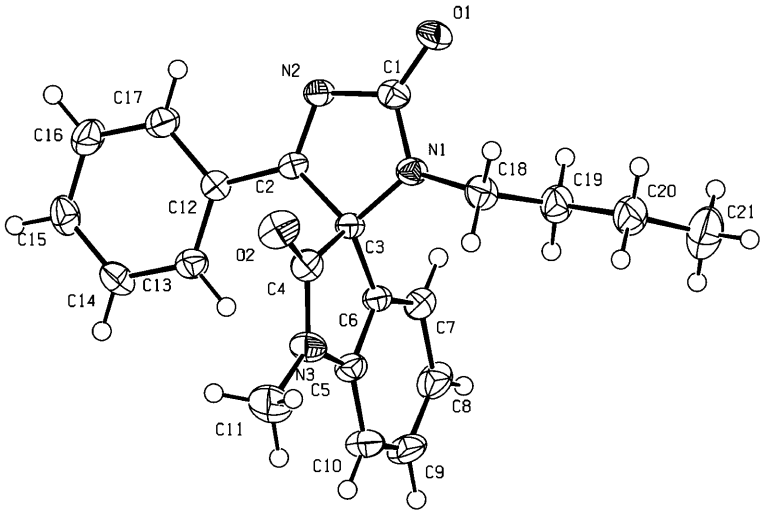


Fig. 1. *ORTEP View of compound* **11c** *showing the thermal ellipsoids at 50% probability* (arbitrary spheres for H-atoms). Arbitrary atom numbering.

Two stereogenic centers at C(4) and C(5) are present in compounds **12**. Indeed, usually two racemates **12A** and **12B** were formed after rearrangement (*Table 4*) due to nonstereospecific addition of H_2O to carbocation **B**. The NMR spectra of compound **12Al** obtained after rearrangement in HCl solution (*Method B*) show only one set of signals, indicating that the compound in question is a pure racemic diastereoisomer

Table 3. *^{1}H- and ^{13}C-Data* ((D_6)DMSO) *of Compounds* **3a**,**c**–**l**. δ in ppm.

	3a		**3c**		**3d**		**3e**		**3f**		**3g**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
C(2)	–	159.8	–	160.0	–	158.5	–	158.6	–	157.0	–	160.2
C(3a)	–	65.6	–	69.2	–	69.7	–	67.9	–	68.5	–	74.3
C(4)	–	171.2	–	170.6	–	170.4	–	170.6	–	170.4	–	170.0
C(5a)	–	137.4	–	137.6	–	137.4	–	137.1	–	136.9	–	137.4
H–C(6)	7.20	114.8	7.38	115.2	7.39	115.2	7.19	114.5	7.18	114.5	7.33	115.1
H–C(7)	7.48	130.3	7.57	130.6	7.47	130.6	7.47	130.2	7.37	130.2	7.50	130.5
H–C(8)	7.22	123.1	7.23	123.4	6.99	122.9	7.23	123.1	6.96	122.5	7.16	123.2
H–C(9)	7.83	127.1	7.75	127.7	7.21	126.9	7.83	126.6	7.33	127.6	7.64	128.0
C(9a)	–	123.4	–	122.9	–	122.2	–	124.0	–	123.1	–	122.3
C(9b)	–	85.9	–	86.9	–	88.5	–	88.0	–	85.5	–	86.5
OH	6.58	–	6.41	–	6.92	–	6.52	–	7.02	–	6.59	–
Me or C(1′) (R^1)	3.06	29.7	3.46	30.0	3.54	30.1	3.30	30.8	3.39	29.6	3.48	29.8
H–C(2′) (R^1)	–	–	–	–	–	–	–	–	–	–	–	–
H–C(3′) (R^1)	–	–	–	–	–	–	–	–	–	–	–	–
H–C(4′) (R^1)	–	–	–	–	–	–	–	–	–	–	–	–
CH_2(1′) or C(1′) (R^2)	1.75, 1.69	31.3	–	135.1	–	135.4	1.94, 1.88	30.8	2.04, 2.01	30.9	–	132.7
CH_2(2′) or H–C(2′) (R^2)	0.98	25.0	7.21	126.7	7.27	126.7	1.01, 0.74	24.6	1.02, 0.78	24.6	7.25	128.4
CH_2(3′) or H–C(3′) (R^2)	1.14	22.6	7.26	128.0	7.31	128.2	1.15	22.6	1.20	22.6	7.34	128.1
Me(4′) or H–C(4′) (R^2)	0.74	13.5	7.26	128.4	7.31	128.3	0.75	13.6	0.72	13.6	7.34	128.5
NH or CH_2(1′)	7.30	–	7.87	–	8.39	–	3.66, 347	40.8	3.66, 3.47	41.1	3.37, 3.23	44.5
CH_2(2′) (R^3)	–	–	–	–	–	–	1.72, 1.61	32.5	1.72, 1.61	32.5	2.04, 1.66	31.2
CH_2(3′) (R^3)	–	–	–	–	–	–	1.41	20.0	1.41	20.0	1.26, 1.21	20.2
Me(4′) (R^3)	–	–	–	–	–	–	0.98	14.0	0.98	14.0	0.89	13.9
CH_2(1′) or C(1′) (R^4)	3.04, 2.86	37.4	3.14, 2.87	37.7	–	134.9	3.11, 2.85	37.5	–	135.6	3.01, 2.86	38.1
CH_2(2′) or H–C(2′) (R^4)	0.82, 0.77	31.0	0.81	30.8	6.92	129.5	0.77	31.0	6.88	129.3	0.95, 0.75	30.8
CH_2(3′) or H–C(3′) (R^4)	0.90, 0.75	18.9	0.90	8.9	7.22	128.1	0.85, 0.75	18.9	7.23	127.9	0.95, 0.85	18.8
Me(4′) or H–C(4′) (R^4)	0.59	13.7	0.61	13.5	7.20	128.4	0.57	13.5	7.20	126.6	0.60	13.5

(*Table 6*). The structure of **12Al** was confirmed by X-ray diffraction analysis (*Figs. 2* and *3*). The corresponding ORTEP views indicate that the direction of the C(5) → OH bond in **12Al** is opposite to that of the C(2′) → O group of the indolone moiety. Hence, it follows that the relative configuration of **12Al** is (4*R**,5*S**). From the analysis and mutual comparison of NMR spectra (*Table 6*) of the rearrangement products from **3g**,**h**,**k**,**l** follows that also **12Ag**, **12Ah**, and **12Ak** are pure racemic diastereoisomers with (4*R**,5*S**) configuration.

Besides **12Ag**,**h**,**k**,**l**, also **12Bg**,**h**,**k**,**l** were isolated (*Table 4*). According to TLC in several solvent systems, the corresponding pairs **12A**/**12B** differ in their R_f values, and the compounds are chromatographically pure. The TLC spots of compounds **12B** are

Table 3 (cont.)

3h		**3i**		**3j**		**3k**		**3l**	
δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
–	158.6	–	158.7	–	157.1	–	160.3	–	158.6
–	74.9	–	68.4	–	69.1	–	74.6	–	75.4
–	169.9	–	171.0	–	170.7	–	170.3	–	170.1
–	137.2		138.1	–	137.9	–	137.8	–	137.8
7.33	115.2	6.20	115.6	6.19	115.7	6.39	116.3	6.38	116.5
7.42	130.5	7.27	129.9	7.16	129.9	7.31	130.2	7.20	130.3
6.93	122.8	7.21	123.5	6.93	122.8	7.14	123.5	6.91	123.1
7.20	126.6	7.90	127.2	7.40	128.0	7.72	128.4	7.33	128.4
–	121.4	–	123.3	–	122.6	–	122.0	–	121.2
–	88.0	–	85.5	–	87.1	–	86.8	–	88.4
7.09	–	6.65	–	7.16	–	6.76	–	7.31	–
3.59	29.9	–	137.7	–	137.6	–	138.2	–	138.0
–	–	7.13	128.7	7.22	129.3	7.34[a])	[a])	7.44[a])	[a])
–	–	7.64	130.3	7.65	130.3	7.70	130.6	7.51	130.4
–	–	7.55	128.4	7.57	128.7	7.59	128.9	7.61	128.9
–	135.7	2.03, 2.00	30.8	2.12, 2.09	30.8	–	132.6	–	132.3
7.39	128.2	1.17	24.7	1.20	24.7	7.51	128.4	7.60	128.4
7.29	128.4	1.25	22.7	1.28	22.7	7.45	128.4	7.70	128.4
7.36	128.6	0.80	13.6	0.82	13.7	7.37	128.6	7.44	128.9
3.47, 3.10	44.8	3.50, 3.38	41.0	3.59, 3.46	41.3	3.31, 2.94	44.5	3.44, 3.05	44.8
2.11, 1.74	31.0	1.62, 1.52	32.7	1.72, 1.60	32.6	2.02, 1.66	31.1	2.08, 1.74	31.0
1.34, 1.25	20.3	1.33, 1.28	19.9	1.39, 1.32	20.0	1.26, 1.22	20.2	1.29, 1.21	20.2
0.92	13.9	0.93	13.9	0.97	14.0	0.86	13.8	0.89	13.8
–	132.7	3.25, 2.95	37.5	–	135.7	3.33, 2.97	38.1	–	135.9
6.96	128.7	0.85	31.1	7.06	129.3	0.0.95	31.2	7.18	128.4
7.23	128.1	0.92	19.0	7.26	128.1	1.08, 1.02	19.1	7.32	128.4
7.19	128.8	0.66	13.4	7.06	129.0	0.70	13.4	7.23	128.9

[a]) Broadened δ(H), δ(C) not observed.

yellow after exposition to I_2, in contrast to those of **12A**. The MS of corresponding pairs **12A**/**12B** are almost identical, but their IR spectra are quite different. The IR absorption bands of the C(2′) lactam group of **12B** are shifted to lower wavenumbers compared to those of **12A**, which is caused by the intramolecular H-bond formation [9]. Thus, compounds **12B** are epimeric (4*R**,5*R**) racemates, in which an intramolecular H-bond occurs between C(2′)=O and OH−C(5). However, the NMR data of compounds **12B** were surprising. The composition of the solutions of these compounds in (D_6)DMSO was not constant but changed with time. For instance, immediately after dissolution, the chromatographically pure **12Bg** showed NMR

Table 4. *Molecular Rearrangement of Compounds* **2** *and* **3** *in Boiling AcOH* (*Method A*) *and Concentrated HCl Solution* (*Method B*) (*Scheme 2*)[a])

Entry	Starting compound	Method	Reaction time [h]	Product(s) (yield [%])
1	**3a**	*A*	1.5	**10a** (38)
2	**3a**	*B*	1.5	**10a** (6), MeIs[b]) (6)
3	**2b**	*A*	2	**10b** (9)
4	**2b**	*B*	2	**10b** (40)
5	**2c**	*A*	1	**11c** (92)
6	**2c**	*B*	0.5	**11c** (90)
7	**3c**	*A*	1	**11c** (91)
8	**3c**	*B*	1.5	**11c** (37)
9	**2d**	*A*	2	**11d** (41)
10	**2d**	*B*	0.5	**11d** (45)
11	**3d**	*A*	2.5	**11d** (38)
12	**3d**	*B*	0.5	**11d** (53)
13	**3e**	*A*	2	**10e** (79)
14	**3e**	*B*	1	**10e** (77)
15	**3f**	*A*	1	**10f** (83)
16	**3f**	*B*	1	**10f** (52)
17	**3g**	*A*	3	**12Ag** (33), **12Bg** (46)
18	**3g**	*B*	1	**12Ag** (51)
19	**3h**	*A*	3	**12Ah** (33), **12Bh** (37)
20	**3h**	*B*	2	**12Ah** (83)
21	**3i**	*A*	1	**10i** (81)
22	**3i**	*B*	0.5	**10i** (72)
23	**3j**	*A*	1	**10j** (84)
24	**3j**	*B*	0.5	**10j** (84)
25	**3k**	*A*	6	**12Ak** (47), **12Bk** (11)
26	**3k**	*B*	4	**12Ak** (31), **12Bk** (24)
27	**3l**	*A*	3	**12Al** (42), **12Bl** (19)
28	**3l**	*B*	2	**12Al** (80)

[a]) For substituents, see *Scheme 1*. [b]) MeIs = *N*-Methylisatin (= 1-methyl-1*H*-indole-2,3-dione), identical to authentic compound (*Aldrich*, Cat. No. 183075).

signals indicating the presence of *ca.* 40% of **12Ag**. In the course of time, the (4*R**,5*S**) diastereoisomer **12Ag** started to dominate and, after 30 h, the solution contained *ca.* 80% of **12Ag**. A similar behavior was observed in the case of **12Bh**; the starting content of *ca.* 50% of the (4*R**,5*R**) diastereoisomer **12Bh** in the mixture with **12Ah** diminished with time to *ca.* 15%. Though, we were able to assign most of the signals of (4*R**,5*R**) diastereoisomer **12Bg** and also some signals of the (4*R**,5*R**) diasteroisomer **12Bh** (*Table 6*). The differences between the ^{1}H-NMR spectra of epimeric racemates **12A** and **12B** (*Table 6*) are probably due to the ring-current effect of the Ph group and H-bonding.

The solutions of compounds **12Bk** and **12Bl** in (D_6)DMSO exhibited, according to ^{1}H-NMR, only a small content (*ca.* 5%) of (4*R**,5*R**) diastereoisomers, and no signals of these compounds could be found in the ^{13}C-NMR spectra. However, from TLC we have arguments for diastereoisomer purity of **12Bk** and **12Bl** in the crystalline state. It

Table 5. *^{1}H- and ^{13}C-NMR Data* ((D$_6$)DMSO) *of Compounds* **10**[a]) *and* **11**. δ in ppm.

Position	**10b**		**10f**		**10i**[b])		**10j**		**11c**		**11d**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
C(2)	–	156.9	–	155.5	–	157.7	–	155.5	–	166.2	–	164.7
C(4)	–	70.9	–	68.8	–	67.8	–	69.0	–	76.2	–	77.8
C(5)	–	135.2	–	135.0	–	136.2	–	134.9	–	181.3	–	181.5
C(2′)	–	173.2	–	172.2	–	172.7	–	171.7	–	169.7	–	169.3
C(3a′)	–	127.7	–	126.5	–	126.8	–	126.5	–	122.8	–	122.6
H–C(4′)	7.39	124.4	7.40	124.7	7.33	125.3	7.53	125.4	7.29	125.0	7.28	125.1
H–C(5′)	7.11	123.6	7.14	123.7	7.22	124.1	7.23	124.5	7.17	124.2	7.13	124.2
H–C(6′)	7.41	130.4	7.41	130.8	7.39	130.2	7.38	130.9	7.60	131.8	7.52	131.7
H–C(7′)	7.11	109.6	7.09	109.5	6.94	109.9	6.74	109.8	7.41	111.0	7.48	110.7
C(7a′)	–	143.8	–	143.8	–	143.9	–	143.5	–	144.0	–	143.7
Me of C(1′) (R^1)	3.19	26.7	3.17	26.6	–	134.0	–	133.4	3.39	29.9	3.32	27.20
H–C(2′) (R^1)	–	–	–	–	7.47	126.0	7.18	126.6	–	–	–	–
H–C(3′) (R^1)	–	–	–	–	7.63	129.8	7.63	130.2	–	–	–	–
H–C(4′) (R^1)	–	–	–	–	7.52	128.4	7.55	128.9	–	–	–	–
H–C(1′) or C(1′) (R^2)	3.78	97.3	4.70	99.8	4.61	99.7	4.82	100.2	–	128.8	–	128.7
CH$_2$(2′) or H–C(2′) (R^2)	1.97	27.2	1.43, 1.26	26.7	1.68, 1.46	27.6, –	1.62, 1.46	27.3	7.56	128.0	7.62	128.0
CH$_2$(3′) or H–C(3′) (R^2)	1.24	22.3	1.07, 0.96	22.5	1.17, 1.05	23.1	1.11, 1.02	22.6	7.47	129.6	7.50	129.5
Me(4′) or H–C(4′) (R^2)	0.80	13.3	0.56	13.5	0.68	13.5	0.61	13.5	7.62	134.0	7.66	134.1
NH or CH$_2$(1′) (R^3)	9.99	–	3.63, 3.61	39.7	3.53, 3.50	40.4	3.64, 3.61	39.8	–	–	–	–
CH$_2$(2′) (R^3)	–	–	1.62	28.1	1.63	28.5	1.65	28.1	–	–	–	–
CH$_2$(3′) (R^3)	–	–	1.44	19.4	1.48	19.9	1.44	19.4	–	–	–	–
Me(4′) (R^3)	–	–	0.99	13.9	0.88	13.5	1.00	13.9	–	–	–	–
C(1′) or CH$_2$(1′) (R^4)		136.6	–	135.8	3.16, 2.95	41.0	–	135.7	3.15, 3.04	40.2	–	134.5
H–C(2′) or CH$_2$(2′) (R^4)	7.06	124.1	6.94	126.2	1.45	28.5	7.01	126.0	1.20	29.9	7.11	125.6
H–C(3′) or CH$_2$(3′) (R^4)	7.23	128.8	7.24	128.9	1.30	19.9	7.31	129.0	1.20	19.2	7.35	129.2
H–C(4′) or Me(4′) (R^4)	7.09	125.5	7.16	126.7	1.05	13.8	7.23	127.0	0.76	13.4	7.27	127.5

[a]) Due to instability of **10a** and **10e** solutions, we were not able to assign NMR signals unambigously. The following signals (in $CDCl_3$) were assigned: **10a**: δ(H) 3.33 (Me (R^1)) and 3.87 (H–C(1′) (R^2)); δ(C) 70.4 (C(4)), 174.0 (C(2′)), 144.1 (C(7a′)), 26.7 (Me (R^1)), and 98.7 (CH(1′) (R^2)). **10e**: δ(H) 3.23 (Me (R^1)) and 4.54 (H–C(1′) (R^2)); δ(C) 157.1 (C(2)), 70.2 (C(4)), 173.3 (C(2′)), 143.8 (C(7a′)), 27.2 (Me (R^1)), and 99.6 (CH(1′) (R^2)). [b]) Measured in $CDCl_3$.

is plausible that compounds **12B** epimerize to **12A** in (D$_6$)DMSO solution *via* the opening and subsequent closing of the imidazoline ring.

The comparison of the rearrangement results obtained by *Method A* and *Method B* (*Table 4*) shows that it is generally impossible to decide which one provides better yields (see, *e.g.*, *Entries 25–28*). In case of compounds **3g**,**h**,**l**, it is worth mentioning that only the more stable racemates **12Ag**,**h**,**l** were obtained by *Method B*. Therefore,

Table 6. *^{1}H- and ^{13}C-NMR Data* ((D_6)DMSO) *of Compounds* **12**. δ in ppm.

	12Ag		**12Bg**		**12Ah**		**12Bh**		**12Ak**		**12Al**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
C(2)	–	161.6	–	160.0	–	159.3	–	157.5	–	161.5	–	159.2
C(4)	–	75.8	–	74.8	–	76.4	–	75.5	–	75.6	–	76.1
C(5)	–	91.4	–	93.0	–	91.5	–	93.4	–	91.7	–	91.6
C(2′)	–	173.8	–	174.0	–	173.2	–	173.4	–	173.5	–	172.8
C(3′a)	–	121.7	–	121.0	–	121.3	–	121.2	–	121.3	–	121.0
H–C(4′)	7.71	128.4	5.67	125.8	7.64	128.4	5.63	125.5	7.82	129.0	7.72	127.6
H–C(5′)	7.17	121.6	6.57	123.0	7.10	121.9	6.46	122.8	7.24	122.4	7.14	122.6
H–C(6′)	7.41	130.2	7.26	129.9	7.36	130.2	7.24	129.9	7.38	130.4	7.34	130.4
H–C(7′)	6.85	108.2	6.98	108.5	6.82	108.3	6.96	108.6	6.51	108.6	6.49	108.7
C(7′a)	–	144.4	–	145.0	–	144.1	–	144.6	–	144.2	–	143.9
OH	6.91	–	6.80	–	7.28	–	[a])	–	7.07	–	7.06	–
Me or C(1′) (R^1)	2.54	25.5	3.18	26.3	2.53	25.6	3.21	26.5	–	133.4	–	133.2
H–C(2′) (R^1)	–	–	–	–	–	–	–	–	6.52	126.2	6.53	126.1
H–C(3′) (R^1)	–	–	–	–	–	–	–	–	7.43	129.5	7.43	129.6
H–C(4′) (R^1)	–	–	–	–	–	–	–	–	7.36	128.3	7.35	128.4
C(1′) (R^2)	–	136.1	–	139.1	–	135.3	–	[a])	–	136.3	–	135.6
H–C(2′) (R^2)	6.99	127.3	[a])	[a])	7.03	127.4	[a])	[a])	7.08	127.7	[b])	127.8
H–C(3′) (R^2)	7.21	127.1	[a])	[a])	7.26	127.2	[a])	[a])	7.31	127.5	[b])	127.6
H–C(4′) (R^2)	7.28	128.4	[a])	[a])	7.32	128.7	[a])	[a])	7.33	128.6	[b])	128.8
CH_2(1′) (R^3)	3.10, 3.01	42.0	[a])	40.5	3.22, 3.12	42.0	3.49, 2.86	40.7	3.12, 3.04	41.8	3.25, 3.16	42.1
CH_2(2′) (R^3)	1.86, 1.71	31.2	[a])	31.7	1.91, 1.80	31.2	1.63	31.5	1.89, 1.78	31.2	1.95, 1.84	31.0
CH_2(3′) (R^3)	1.29	20.2	[a])	19.8	1.33	20.2	1.37	19.8	1.32	20.3	1.34	20.2
Me(4′) (R^3)	0.91	13.9	[a])	13.9	0.93	13.9	0.93	13.9	0.92	13.7	0.94	13.9
CH_2(1′) or C(1′) (R^4)	3.16, 2.68	41.8	[a])	41.7	–	137.5	[a])	[a])	3.19, 2.93	41.8	–	137.4
CH_2(2′) or H–C(2′) (R^4)	1.18	30.7	[a])	30.8	7.06	124.2	[a])	[a])	1.20	30.8	[b])	123.9
CH_2(3′) or H–C(3′) (R^4)	1.18	19.4	[a])	19.3	7.21	128.5	[a])	[a])	1.20	19.5	[b])	128.6
Me (4′) or H–C(4′) (R^4)	0.74	13.6	[a])	13.6	7.06	124.9	[a])	[a])	0.78	13.7	[b])	124.9

[a]) Due to instability of **12Bg** and **12Bh** solutions, we were not able to assign NMR signals unambigously. [b]) Strong overlap of signals, the assignment would be uncertain.

we treated pure compounds **12Bg**,**h**,**k**,**l** in a boiling mixture of HCl and AcOH and actually obtained pure compounds **12Ag**,**h**,**k**,**l** in moderate yields; the existence of a mixture **12A**/**12B** in the mother liquors was evidenced by TLC. Under the same reaction conditions, pure compounds **12A** yielded mixtures **12A**/**12B**, *i.e.*, the reaction is reversible and the equilibrium between both components depends on the solvent. In DMSO, the equilibrium is shifted to compounds **12A**, which causes problems during NMR spectra measuring. In $CDCl_3$, compounds **12B** are only slightly soluble.

2.2. *Solid-State Structures.* Both compounds **11c** and **12Al** crystallize in the triclinic space group P_1, but the unit cell for **12Al** contains two geometrically independent molecules. Relevant crystallographic details for both compounds are given in *Table 7*. Although there are many structures of spiro-indole derivatives determined by X-ray

Table 7. *Crystallographic Data of* **11c** *and* **12Al**

	11c	**12Al** · 0.5 acetone
Empirical formula	$C_{21}H_{21}N_3O_2$	$C_{33}H_{26}N_3O_3$
Crystal system	triclinic	triclinic
Space group	P_1	P_1
a [Å]	9.0351(7)	13.4822(10)
b [Å]	10.1110(8)	14.4551(9)
c [Å]	10.9844(13)	14.8441(12)
α [°]	83.026(7)	85.294(6)
β [°]	77.807(7)	80.916(6)
γ [°]	65.868(6)	71.245(6)
Z	2	4
V [Å^3]	894.38(14)	2703.4(3)
D_c [g cm^{-3}]	1.290	1.380
Crystal size [mm]	0.512 × 0.132 × 0.122	0.32 × 0.28 × 0.19
Crystal shape	colorless block	colorless block
μ [mm^{-1}]	0.085	0.091
F (000)	368	1192
h; k; l (range)	−10, 11; −12, 13; −14, 14	−17, 17; −18, 18; −19, 19
θ range [°]	2.97; 27.5	2.07; 27.5
Reflections measured	14849	48211
independent (R_{int})[a])	4042 (0.0786)	12232 (0.1043)
observed ($I > 2\sigma(I)$)	2671	8610
Parameters refined	235	686
Max., min. $\Delta\rho$/e [Å^{-3}]	0.456, −0.485	0.626, −0.611
G.o.f.[b])	1.063	0.811
R[c]) wR[c])	0.0725, 0.1521	0.0949, 0.2592

[a]) $R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$. [b]) G.o.f. $= [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$ for all data. [c]) $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for observed data, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$ for all data.

techniques, these compounds are the first examples of spiro[imidazolidine-4,3′-oxindoles]. The ORTEP views of **11c** and **12Al** (*Figs. 1* and *2*) show an almost planar arrangement of each five-membered ring with interplanar angles being 88.3(2)° for **11c** and 89.3(2) and 85.9(1)° for **12Al**. The C(2)–N(2) distance (1.283(3) Å) in compound **11c** reveals a typical double-bond character with respect to the standard single-bond N(sp^3)–C(sp^2) distance of 1.44 Å [10] (atom numbering of *Fig. 1*). Both C(1)–O(1) and C(4)–O(2) distances and the geometry of the respective groups are characteristic for C=O groups. On the other hand, in **12Al**, O(3)–C(2) (1.402(4) Å) and O(3′)–C(2′) (1.398(4) Å) are single bonds (atom numberings of *Figs. 2* and *3*). The classical H-bonding patterns operate through these groups (O(3′)–H(3′)–O(1) 169.7°, O(3′)–O(1) 2.710(3) Å) in the structure of **12Al** (*Fig. 3*). There is also an additional π–π stacking interaction between almost coplanar Ph rings in the crystal unit cell (distance 3.568 Å).

3. Conclusions. – The elaborated methods allow to prepare spiro-oxindoles **10**–**12** from 3-aminoquinolinediones **1** in good to very good yields. The molecular rearrangement of compounds **2** and **3** is not only of theoretical importance but enables, through a

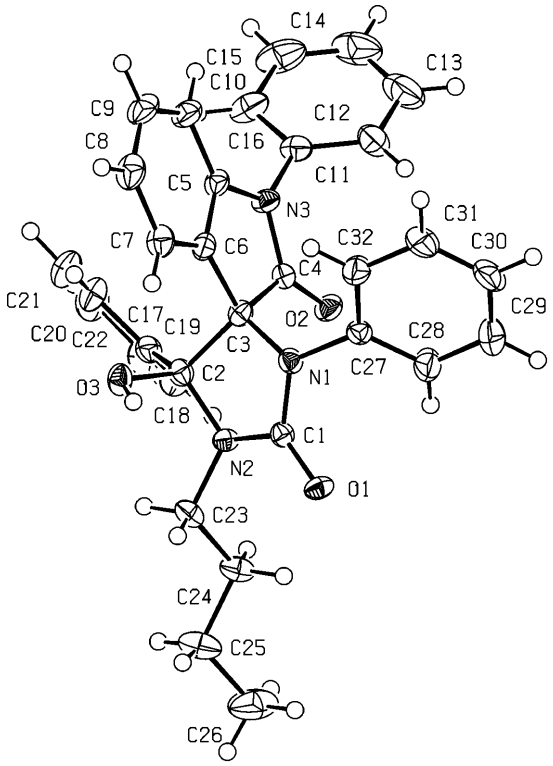


Fig. 2. *ORTEP View of one of two independent molecules of compound* **12Al** *showing the thermal ellipsoids at 50% probability* (arbitrary spheres for H-atoms). Arbitrary atom numbering: C(2)–C(3)–H corresponds to C(5)–OH and C(4)–C(2) to C(2′)=O in *Scheme 2*.

simple procedure, a targeted preparation of new types of spiro-oxindoles suitable both for biological testing as well as for studying further transformations. Spiro[imidazolidine-4,3′-oxindoles] have not been described so far, except for two compounds of type **5** mentioned in our earlier reports [2][4]. One of these compounds, bearing a Ph group at position 1′, exhibits high toxicity against K-562 (chronic myeloid leukemia) and MCF 7 (breast carcinoma) [2]. The presented work extends the set of compounds containing a spiro-oxindole structural motif which is a component in some indole alkaloids [11] as well as in other compounds presumed to display significant biological activities [12][13].

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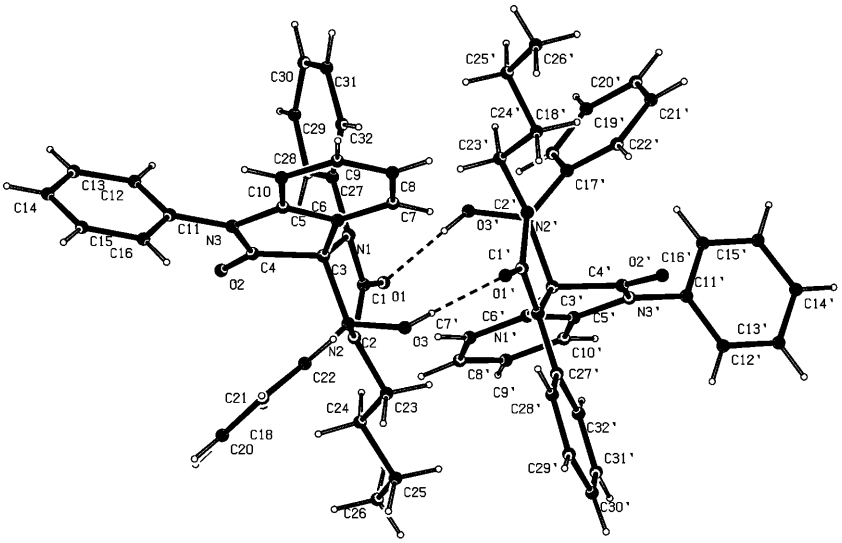

Fig. 3. *View of hydrogen bridging in* **12Al**. Arbitrary atom numbering: C(2)–C(3)–H corresponds to C(5)–OH and C(4)–C(2) to C(2′)=O in *Scheme 2*.

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), and $CHCl_3$/AcOEt 7:3. 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: *Mattson-3000* spectrophotometer; KBr pellets; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker Avance-500* spectrometer at 500.13 MHz (^1H) and 125.76 MHz (^{13}C); (D_6)DMSO or $CDCl_3$ solns.; δ in ppm rel. to Me_4Si as internal standard, J in Hz; manufacturer's software for all 2D experiments (gradient-selected (gs)-COSY, gs-NOESY, gs-TOCSY, gs-HMQC, and gs-HMBC); δ(H) assignments by gs-COSY and gs-TOCSY; δ(C) assignments of protonated C-atoms by gs-HMQC and of quaternary C-atoms by gs-HMBC. Atmospheric-pressure chemical-ionization (APCI) MS: positive- and negative-ion mode with an ion-trap analyzer *Agilent LC-MSD Trap XCT-Ultra* (*Agilent*, Palo Alto, CA, USA) within *m/z* 50–500; analysis of samples in MeCN by direct infusion (10 µl) at the flow rate of 400 µl/min; ion-source temp. 350°, APCI-probe temp. 350°, flow rate and N_2 pressure 4 l/min and 45 psi, resp.; MS/MS: isolation width of precursor ions 4 *m/z* and collision amplitude 0.8 V; the MS of **2a** and **2c** were measured with an *MS-Trio-1000-Fisons* instrument within *m/z* 50–500, ion source 200°, 70 eV. Elemental analyses (C, H, N): *EA-1108* elemental analyzer (*Fisons Instrument*).

2. *X-Ray Analysis.* The X-ray data for colorless crystals of **11c** and **12Al** (grown from *ca.* 5% Et_2O and acetone) were obtained at 150° K with an *Oxford-Cryostream* low-temperature device and a *Nonius-KappaCCD* diffractometer with MoK_α radiation (λ 0.71073 Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN [14]. The absorption was corrected by integration methods [15]. Structures were solved by direct methods (Sir92) [16] and refined by full-matrix least squares based on F^2 (SHELXL97) [17]. H-Atoms were mostly localized on a difference *Fourier* map; however, to ensure uniformity of treatment of the crystal (form), all H-atoms were recalculated into idealized positions (riding model) and assigned temp. factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or 1.5 U_{eq} for C–H = 0.96, 0.97, and 0.93 Å of Me, CH_2, and H-atoms at aromatic rings, resp., and for O–H = 0.82 Å of the OH group. There is disordered solvent (acetone) in the structure of **12Al**. Attempts to model this disorder or split it into two positions were unsuccessful. PLATON/

SQUEZZE [18] was used to correct the data for the presence of disordered solvent. A potential solvent volume of 188 Å^3 was found. Per unit cell, 61 electrons worth of scattering were located in the void. The calculated stoichiometry of solvent was calculated to be two molecules of acetone per unit cell which results in 64 electrons per unit cell[1]).

3. *3-Aminoquinoline-2,4(1*H,*3*H*)-diones* **1** were prepared from the corresponding 3-chloroquinoline-2,4(1*H*,3*H*)-diones according to the protocol described in [8].

4. *3-Ureidoquinoline-2,4(1*H,*3*H*)-diones* **2** *and 3,3a,5,9b-Tetrahydro-9b-hydroxy-1*H*-imidazo[4,5-*c*]quinoline-2,4-diones* **3**: *General Procedure.* Phenyl isocyanate (0.130 ml, 1.2 mmol) or butyl isocyanate (0.135 ml, 1.2 mmol) was added to the cooled (0°) and stirred soln. of **1** (1 mmol) in $CHCl_3$ (5 ml). After stirring at r.t. for the time given in *Table 1*, the precipitate was collected by filtration with suction and recrystallized from an appropriate solvent. In cases of mixtures **2**/**3**, these were separated by repeated fractional crystallization or by CC. When the product was soluble in $CHCl_3$, the soln. was concentrated, and the residue was crystallized from an appropriate solvent. In some cases, the mother liquors were worked up by CC (SiO_2). Yields of **2** and **3** are given in *Table 1*.

*3-Butyl-3-(3′-butylureido)-1-methylquinoline-2,4(1*H,*3*H*)-dione* (= N-*Butyl*-N′*-(3-butyl-1,2,3,4-tetrahydro-1-methyl-2,4-dioxoquinolin-3-yl)urea*; **2a**). Prepared from **1a** (besides **3a**). Colorless crystals. M.p. 152–157° (benzene/hexane). IR: 3374, 3146, 3087, 2958, 2931, 2871, 1703, 1665, 1628, 1602, 1565, 1474, 1361, 1301, 1280, 1227, 1146, 1114, 1089, 1018, 945, 761, 731, 655, 603, 560, 521. ^{1}H- and ^{13}C-NMR: *Table 2*. EI-MS: 345 (5, M^+), 327 (98), 298 (85), 256 (78), 244 (95), 216 (83), 200 (79), 187 (100), 160 (51), 131 (41), 104 (22), 89 (13), 77 (19), 57 (16), 55 (22). Anal. calc. for $C_{19}H_{27}N_3O_3$ (345.44): C 66.06, H 7.88, N 12.16; found: C 66.22, H 7.92, N 12.31.

*3-Butyl-1-methyl-3-(3′-phenylureido)quinoline-2,4(1*H,*3*H*)-dione* (= N-*(3-Butyl-1,2,3,4-tetrahydro-1-methyl-2,4-dioxoquinolin-3-yl)*-N′*-phenylurea*; **2b**). Prepared from **1b**. Colorless crystals. M.p. 195–200° (AcOEt/hexane). IR: 3347, 3145, 3094, 3027, 2954, 2926, 2868, 1674, 1652, 1600, 1553, 1498, 1474, 1441, 1373, 1363, 1315, 1185, 1119, 1083, 1049, 1014, 951, 896, 849, 752, 691, 660, 582, 504. ^{1}H- and ^{13}C-NMR: *Table 2*. APCI-MS (pos.): 366 (100, $[M+H]^+$), 247 (59, $[M+H-C_6H_5NCO]^+$). APCI-MS/MS (pos.) of 366: 247 (100, $[M+H-C_6H_5NCO]^+$), 230 (15, $[M+H-C_6H_5NHCO-NH_2]^+$). APCI-MS (neg.): 364 (100, $[M-H]^-$). APCI-MS/MS (neg.) of 364: 245 (100, $[M-H-C_6H_5NCO]^-$), 188 (14, $[M-H-C_6H_5NCO-C_4H_9]^-$). Anal. calc. for $C_{21}H_{23}N_3O_3$ (365.43): C 69.02, H 6.34, N 11.50; found: C 69.14, H 6.42, N 11.39.

*3-(3′-Butylureido)-1-methyl-3-phenylquinoline-2,4(1*H,*3*H*)-dione* (= N-*Butyl*-N′*-(1,2,3,4-tetrahydro-1-methyl-2,4-dioxo-3-phenylquinolin-3-yl)urea*; **2c**). Prepared from **1c** (besides **3c** and 3-hydroxy-1-methyl-3-phenylquinoline-2,4(1*H*,3*H*)-dione). Colorless crystals. M.p. 186–190° (benzene). IR: 3382, 3061, 2957, 2931, 2869, 1707, 1667, 1626, 1601, 1557, 1472, 1418, 1356, 1302, 1275, 1257, 1204, 1171, 1135, 1059, 1038, 870, 770, 697, 660, 581, 562, 528. ^{1}H- and ^{13}C-NMR: *Table 2*. EI-MS: (3, M^+), 348 (12), 276 (5), 244 (100), 216 (42), 188 (14), 187 (50), 160 (32), 132 (12), 131 (21), 117 (6), 104 (17), 103 (9), 77 (14), 57 (5). Anal. calc. for $C_{21}H_{23}N_3O_3$ (365.43): C 69.02, H 6.34, N 11.50; found: C 69.17, H 6.48, N 11.28.

*1-Methyl-3-phenyl-3-(3′-phenylureido)quinoline-2,4(1*H,*3*H*)-dione* (= N-*Phenyl*-N′*-(1,2,3,4-tetrahydro-1-methyl-2,4-dioxo-3-phenylquinolin-3-yl)urea*; **2d**). Prepared from **1d** (besides **3d**). Colorless crystals. M.p. 218–222° (EtOH). IR: 3373, 3335, 3209, 3148, 3086, 3062, 1705, 1680, 1649, 1599, 1554, 1495, 1474, 1417, 1368, 1314, 1246, 1227, 1190, 1175, 1126, 1061, 1032, 953, 888, 868, 848, 766, 746, 687, 660, 640, 574, 531, 505. ^{1}H- and ^{13}C-NMR: *Table 2*. APCI-MS (pos.): 386 (100, $[M+H]^+$), 267 (38, $[M+H-C_6H_5NCO]^+$). APCI-MS/MS (pos.) of 386: 267 (100, $[M+H-C_6H_5NCO]^+$), 250 (11, $[M+H-C_6H_5NHCO-NH_2]^+$). APCI-MS (neg.): 384 (100, $[M-H]^-$), 265 (18, $[M-H-C_6H_5NCO]^-$), 250 (80, $[M-H-C_6H_5NCO-CH_3]^-$). APCI-MS/MS (neg.) of 384: 265 (100, $[M-H-C_6H_5NCO]^-$), 208 (21). Anal. calc. for $C_{23}H_{19}N_3O_3$ (385.42): C 71.67, H 4.97, N 10.90; found: C 71.35, H 5.13, N 10.76.

*1,3a-Dibutyl-3,3a,5,9b-tetrahydro-9b-hydroxy-5-methyl-1*H*-imidazo[4,5-*c*]quinoline-2,4-dione* (**3a**). Prepared from **1a** (besides **2a**). Colorless crystals. M.p. 162–167° (AcOEt/hexane). IR: 3268, 2957, 2931, 2870, 1704, 1690, 1656, 1605, 1476, 1449, 1415, 1366, 1315, 1267, 1223, 1170, 1115, 1079, 1051, 1030, 992,

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[1]) CCDC-684114 and 684115 for **11c** and **12Al**, resp., contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

949, 937, 767, 739, 654, 609, 579, 546. ^{1}H- and ^{13}C-NMR: *Table 3*. APCI-MS (pos.): 346 (100, $[M+H]^+$), 328 (27, $[M+H-H_2O]^+$), 302 (23, $[M+H-C_3H_8]^+$), 247 (38, $[M+H-C_4H_9NCO]^+$). APCI-MS/MS (pos.) of 346: 247 (100, $[M+H-C_4H_9NCO]^+$). APCI-MS (neg.): 344 (100, $[M-H]^-$), 326 (4, $[M-H-H_2O]^-$), 245 (3, $[M-H-C_4H_9NCO]^-$). APCI-MS/MS (neg.) of 344: 245 (100, $[M-H-C_4H_9NCO]^-$), 211 (23), 188 (8, $[M-H-C_4H_9NCO-C_4H_9]^-$). Anal. calc. for $C_{19}H_{27}N_3O_3$ (345.44): C 66.06, H 7.88, N 13.89; found: C 66.19, H 7.99, N 13.62.

*1-Butyl-3,3a,5,9b-tetrahydro-9b-hydroxy-5-methyl-3a-phenyl-1*H-*imidazo[4,5-*c*]quinoline-2,4-dione* (**3c**). Prepared from **1c** (besides **2c** and 3-hydroxy-1-methyl-3-phenylquinoline-2,4(1*H*,3*H*)-dione). Colorless crystals. M.p. 175–177° (benzene). IR: 3285, 3067, 3032, 2953, 2931, 2868, 1712, 1699, 1674, 1658, 1604, 1474, 1408, 1374, 1304, 1267, 1230, 2934, 2870, 1692, 1664, 1602, 1500, 1470, 1417, 1371, 1356, 1300, 1264, 1238, 1206, 1173, 1137, 1114, 1094, 1054, 1019, 966, 913, 880, 855, 760, 738, 704, 691, 679, 664, 652, 604, 557, 540, 505. ^{1}H- and ^{13}C-NMR: *Table 3*. APCI-MS (pos.): 366 (100, $[M+H]^+$), 348 (34, $[M+H-H_2O]^+$), 267 (78, $[M+H-C_4H_9NCO]^+$). APCI-MS/MS (pos.) of 366: 267 (100, $[M+H-C_4H_9NCO]^+$). APCI-MS (neg.): 364 (100, $[M-H]^-$), 265 (9, $[M-H-C_4H_9NCO]^-$). APCI-MS/MS (neg.) of 364: 265 (100, $[M-H-C_4H_9NCO]^-$), 245 (8, $[M-H-C_6H_5NCO]^-$), 231 (8, $[M-H-C_6H_5-C_4H_8]^-$), 208 (5). Anal. calc. for $C_{21}H_{23}N_3O_3$ (365.43): C 69.02, H 6.34, N 11.50; found: C 69.10, H 6.38, N 11.35.

*3,3a,5,9b-Tetrahydro-9b-hydroxy-5-methyl-1,3a-diphenyl-1*H-*imidazo[4,5-*c*]quinoline-2,4-dione* (**3d**). Prepared from **1d** (besides **2d**). Colorless crystals. M.p. 188–192° (EtOH). IR: 3386, 3284, 3086, 3063, 2942, 1711, 1669, 1657, 1604, 1497, 1472, 1384, 1300, 1271, 1224, 1148, 1131, 1110, 1052, 992, 933, 859, 833, 756, 697, 655, 631, 554, 532. ^{1}H- and ^{13}C-NMR: *Table 3*. APCI-MS (pos.): 386 (64, $[M+H]^+$), 368 (12, $[M+H-H_2O]^+$), 267 (100, $[M+H-C_6H_5NCO]^+$). APCI-MS/MS (pos.) of 386: 267 (100, $[M+H-C_6H_5NCO]^+$), 250 (11, $[M+H-C_6H_5NHCO-NH_2]^+$). APCI-MS (neg.): 384 (67, $[M-H]^-$), 265 (8, $[M-H-C_6H_5NCO]^-$), 250 (100, $[M-H-C_6H_5NCO-CH_3]^-$). APCI-MS/MS (neg.) of 384: 265 (100, $[M-H-C_6H_5NCO]^-$), 208 (4). Anal. calc. for $C_{23}H_{19}N_3O_3$ (385.42): C 71.67, H 4.97, N 10.90; found: C 71.50, H 4.89, N 10.81.

*1,3,3a-Tributyl-3,3a,5,9b-tetrahydro-9b-hydroxy-5-methyl-1*H-*imidazo[4,5-*c*]quinoline-2,4-dione* (**3e**). Prepared from **1e**. Colorless crystals. M.p. 117–120° (hexane). IR: 3319, 3086, 3052, 2957, 2931, 2871, 1694, 1669, 1604, 1501, 1470, 1420, 1369, 1312, 1267, 1213, 1171, 1134, 1113, 1088, 1052, 1017, 937, 900, 828, 757, 691, 653, 631, 606, 576, 547, 515. ^{1}H- and ^{13}C-NMR: *Table 3*. APCI-MS (pos.): 384 (100, $[M+H-H_2O]^+$), 303 (23, $[M+H-C_4H_9NCO]^+$). APCI-MS/MS (pos.) of 384: 328 (100, $[M+H-H_2O-C_4H_8]^+$), 285 (19, $[M+H-H_2O-C_4H_9NCO]^+$), 272 (36, $[M+H-2\,C_4H_8]^+$). APCI-MS (neg.): 400 (100, $[M-H]^-$). APCI-MS/MS (neg.) of 400: 356 (94, $[M-H-C_3H_7]^-$), 301 (43, $[M-H-C_4H_9NCO]^-$), 267 (41), 244 (100, $[M-H-C_4H_9NCO-C_4H_9]^-$). Anal. calc. for $C_{23}H_{35}N_3O_3$ (401.54): C 68.80, H 8.79, N 10.46; found: C 68.57, H 8.86, N 10.29.

*3,3a-Dibutyl-3,3a,5,9b-tetrahydro-9b-hydroxy-5-methyl-1-phenyl-1*H-*imidazo[4,5-*c*]quinoline-2,4-dione* (**3f**). Prepared from **1f**. Colorless crystals. M.p. 172–180° (AcOEt). IR: 3316, 3063, 3037, 2959, 2934, 2870, 1692, 1664, 1602, 1500, 1470, 1417, 1371, 1356, 1300, 1264, 1206, 1173, 1137, 1114, 1094, 1054, 1019, 966, 913, 880, 855, 812, 760, 704, 691, 679, 664, 552, 604, 570, 557, 537, 503. ^{1}H- and ^{13}C-NMR: *Table 3*. APCI-MS (pos.): 422 (4, $[M+H]^+$), 404 (47, $[M+H-H_2O]^+$), 303 (100, $[M+H-C_6H_5NCO]^+$. APCI-MS/MS (pos.) of 422: 303 (100, $[M+H-C_6H_5NCO]^+$). APCI-MS/MS (pos.) of 404: 348 (100, $[M+H-H_2O-C_4H_8]^+$), 305 (48, $[M+H-H_2O-C_4H_9NCO]^+$, 292 (29), 285 (19, $[M+H-H_2O-C_6H_5NCO]^+$). APCI-MS (neg.): 420 (100, $[M-H]^-$), 402 (24, $[M-H-H_2O]^-$). APCI-MS/MS (neg.) of 420: 376 (8, $[M-H-C_3H_8]^-$), 321 (14, $[M-H-C_4H_9NCO]^-$), 301 (15, $[M-H-C_6H_5NCO]^-$), 244 (100, $[M-H-C_4H_9NCO-C_6H_5]^-$). Anal. calc. for $C_{25}H_{31}N_3O_3$ (421.53): C 71.23, H 7.41, N 9.97; found: C 71.40, H 7.53, N 9.72.

*1,3-Dibutyl-3,3a,5,9b-tetrahydro-9b-hydroxy-5-methyl-3a-phenyl-1*H-*imidazo[4,5-*c*]quinoline-2,4-dione* (**3g**). Prepared from **1g**. Colorless crystals. M.p. 125–128° (benzene/hexane). IR: 3417, 3284, 2958, 2931, 2871, 1686, 1604, 1501, 1471, 1406, 1368, 1312, 1268, 1210, 1142, 1109, 1052, 1020, 966, 934, 879, 837, 757, 708, 695, 631, 596, 548, 514. ^{1}H- and ^{13}C-NMR: *Table 3.* APCI-MS (pos.): 422 (6, $[M+H]^+$), 404 (100, $[M+H-H_2O]^+$, 323 (30, $[M+H-C_4H_9NCO]^+$). APCI-MS/MS (pos.) of 422: 323 (100, $[M+H-C_4H_9NCO]^+$). APCI-MS/MS of 404 (pos.): 348 (100, $[M+H-H_2O-C_4H_8]^+$), 292 (37, $[M+H-H_2O-2\,C_4H_8]^+$). APCI-MS (neg.): 420 (100, $[M-H]^-$). APCI-MS/MS (neg.) of 420: 376 (30,

$[M - H - C_3H_8]^-$), 363 (46, $[M - H - C_4H_9]^-$), 346 (7, $[M - H - H_2O - C_4H_8]^-$), 321 (71, $[M - H - C_4H_9NCO]^-$), 288 (82), 264 (35, $[M - H - C_4H_9NCO - C_4H_9]^-$), 244 (83, $[M - H - C_4H_9NCO - C_6H_5]^-$), 230 (100, $[M - H - C_4H_9 - C_4H_8 - C_6H_5]^-$). Anal. calc. for $C_{25}H_{31}N_3O_3$ (421.53): C 71.23, H 7.41, N 9.97; found: C 71.35, H 7.46, N 9.59.

*3-Butyl-3,3a,5,9b-tetrahydro-9b-hydroxy-5-methyl-1,3a-diphenyl-1*H-*imidazo[4,5-*c*]quinoline-2,4-dione* (**3h**). Prepared from **1h**. Colorless crystals. M.p. 214–222° (benzene). IR: 3302, 3065, 2954, 2872, 1692, 1674, 1605, 1498, 1472, 1404, 1370, 1352, 1266, 1218, 1190, 1147, 1104, 1051, 1023, 965, 882, 825, 755, 726, 698, 679, 651, 633, 528. ^{1}H- and ^{13}C-NMR: *Table 3*. APCI-MS (pos.): 442 (5, $[M + H]^+$), 424 (41, $[M + H - H_2O]^+$), 323 (100, $[M + H - C_6H_5NCO]^+$). APCI-MS/MS (pos.) of 442: 323 (100, $[M + H - C_6H_5NCO]^+$). APCI-MS/MS (pos.) of 424: 368 (100, $[M + H - H_2O - C_4H_8]^+$), 325 (19, $[M + H - H_2O - C_4H_9NCO]^+$. APCI-MS (neg.): 440 (82, $[M - H]^-$), 321 (69, $[M - H - C_6H_5NCO]^-$), 250 (100). APCI-MS/MS (neg.) of 440: 396 (4, $[M - H - C_3H_8]^-$), 341 (47, $[M - H - C_4H_9NCO]^-$), 321 (100, $[M - H - C_6H_5NCO]^-$), 264 (26, $[M - H - C_6H_5NCO - C_4H_9]^-$). Anal. calc. for $C_{27}H_{27}N_3O_3$ (441.52): C 73.45, H 6.16, N 9.52; found: C 73.52, H 6.29, N 9.38.

*1,3,3a-Tributyl-3,3a,5,9b-tetrahydro-9b-hydroxy-5-phenyl-1*H-*imidazo[4,5-*c*]quinoline-2,4-dione* (**3i**). Prepared from **1i**. Colorless crystals. M.p. 137–142° (benzene/hexane). IR: 3284, 2958, 2931, 2871, 1678, 1603, 1592, 1497, 1465, 1422, 1370, 1335, 1304, 1271, 1211, 1167, 1129, 1071, 1059, 1021, 960, 936, 862, 828, 765, 756, 737, 700, 680, 627, 517. ^{1}H- and ^{13}C-NMR: *Table 3*. APCI-MS (pos.): 464 (10, $[M + H]^+$), 446 (100, $[M + H - H_2O]^+$), 365 (13, $[M + H - C_4H_9NCO]^+$). APCI-MS/MS (pos.) of 464: 365 (100, $[M + H - C_4H_9NCO]^+$). APCI-MS/MS (pos.) of 446: 390 (100, $[M + H - H_2O - C_4H_8]^+$), 347 (19, $[M + H - C_4H_9NCO]^+$), 334 (26, $[M + H - H_2O - 2\ C_4H_8]^+$), 291 (10, $[M + H - 2\ C_4H_8 - NHCO]^+$). APCI-MS (neg.): 462 (100, $[M - H]^-$), 444 (15, $[M - H - C_6H_5NCO]^-$). APCI-MS/MS (neg.) of 462: 363 (61, $[M - H - C_4H_9NCO]^-$), 267 (100, $[M - H - C_4H_9NCO - C_6H_6 - H_2O]^-$). Anal. calc. for $C_{28}H_{37}N_3O_3$ (463.61): C 72.54, H 8.04, N 9.06; found: C 72.68, H 8.22, N 8.91.

*3,3a-Dibutyl-3,3a,5,9b-tetrahydro-9b-hydroxy-1,5-diphenyl-1*H-*imidazo[4,5-*c*]quinoline-2,4-dione* (**3j**). Prepared from **1j**. Colorless crystals. M.p. 173–176° (AcOEt/hexane). IR: 3343, 3061, 3039, 2956, 2931, 2871, 1692, 1681, 1603, 1495, 1461, 1412, 1362, 1334, 1605, 1273, 1254, 1182, 1130, 1091, 1077, 1023, 957, 919, 871, 857, 806, 770, 752, 735, 703, 654, 633, 598, 547, 517. ^{1}H- and ^{13}C-NMR: *Table 3*. APCI-MS (pos.): 484 (7, $[M + H]^+$), 466 (39, $[M + H - H_2O]^+$) , 365 (100), $[M + H - C_6H_5NCO]^+$). APCI-MS/MS (pos.) of 484: 365 (100, $[M + H - C_6H_5NCO]^+$). APCI-MS/MS (pos.) of 466: 410 (100, $[M + H - H_2O - C_4H_8]^+$), 367 (54, $[M + H - H_2O - C_4H_9NCO]^+$). APCI-MS (neg.): 482 (100, $[M - H]^-$), 464 (17, $[M - H - H_2O]^-$), 438 (26, $[M - H - C_3H_8]^-$), 363 (6, $[M + H - C_6H_5NCO]^+$). APCI-MS/MS (neg.) of 482: 438 (100, $[M - H - C_3H_8]^-$). Anal. calc. for $C_{30}H_{33}N_3O_3$ (483.60): C 74.51, H 6.88, N 8.69;.found: C 74.58, H 6.98, N 8.51.

*1,3-Dibutyl-3,3a,5,9b-tetrahydro-9b-hydroxy-3a,5-diphenyl-1*H-*imidazo[4,5-*c*]quinoline-2,4-dione* (**3k**). Prepared from **1k**. Colorless crystals. M.p. 108–115° (benzene/hexane). IR: 3308, 3067, 3034, 2957, 2931, 2871, 1690, 1604, 1593, 1496, 1461, 1407, 1368, 1332, 1259, 1216, 1186, 1134, 1099, 1054, 1028, 1007, 941, 872, 832, 802, 759, 745, 700, 683, 658, 633, 615, 547, 522. ^{1}H- and ^{13}C-NMR: *Table 3*. APCI-MS (pos.): 466 (100, $[M + H - H_2O]^+$), 385 (53, $[M + H - C_4H_9NCO]^+$). APCI-MS/MS (pos.) of 466: 410 (100, $[M + H - H_2O - C_4H_8]^+$), 354 (30, $[M + H - H_2O - 2\ C_4H_8]^+$). APCI-MS (neg.): 482 (100, $[M - H]^-$), 312 (24). APCI-MS/MS (neg.) of 482: 438 (9, $[M - H - C_3H_8]^-$), 287 (100, $[M - H - C_4H_9NCO - C_6H_6 - H_2O]^-$), 230 (34). Anal. calc. for $C_{30}H_{33}N_3O_3$ (483.60): C 74.51, H 6.88, N 8.69; found: C 74.65, H 6.93, N 8.59.

*3-Butyl-3,3a,5,9b-tetrahydro-9b-hydroxy-1,3a,5-triphenyl-1*H-*imidazo[4,5-*c*]quinoline-2,4-dione* (**3l**). Prepared from **1l**. Colorless crystals. M.p. 207–212° (benzene/cyclohexane). IR: 3424, 3064, 3037, 2959, 2931, 2872, 1709, 1682, 1603, 1495, 1460, 1396, 1366, 1329, 1261, 1157, 1135, 1107, 1084, 1054, 1025, 1008, 942, 913, 875, 827, 755, 699, 653, 636, 615, 585, 535, 500. ^{1}H- and ^{13}C-NMR: *Table 3*. APCI-MS (pos.): 504 (3, $[M + H]^+$), 486 (25, $[M + H - H_2O]^+$), 466 (10), 385 (100, $[M + H - C_6H_5NCO]^+$). APCI-MS/MS (pos.) of 504: 385 (81, $[M + H - C_6H_5NCO]^+$), 309 (100, $[M + H - C_4H_9NCO - C_6H_6 - H_2O]^+$), 196 (21). APCI-MS/MS (pos.) of 486: 430 (100, $[M + H - H_2O - C_4H_8]^+$). APCI-MS (neg.): 502 (52, $[M - H]^-$), 482 (7), 458 (6, $[M - H - C_3H_8]^-$), 383 (26, $[M - H - C_6H_5NCO]^-$), 312 (100, $[M - H - C_6H_5NCONC_4H_9]^-$). APCI-MS/MS (neg.) of 502: 458 (43, $[M - H - C_3H_8]^-$), 383 (100, $[M - H -$

$C_6H_5NCO]^-$), 307 (23, $[M - H - C_4H_9NCO - C_6H_6 - H_2O]^-$). Anal. calc. for $C_{32}H_{29}N_3O_3$ (503.59): C 76.32, H 5.80, N 8.34; found: C 76.47, H 6.03, N 8.14.

5. Molecular Rearrangement of Compounds **2** *and* **3**: *General Procedures. Method A:* A soln. of **2** or **3** (1 mmol) in AcOH (8 ml) was heated to reflux for the time given in *Table 4*. After cooling, the mixture was concentrated, and the residue was crystallized from an appropriate solvent or separated by CC (SiO_2).

Method B: A soln. of **2** or **3** (1 mmol) in conc. HCl soln. (5 ml) was heated to reflux for the time given in *Table 4*. A small quantity of AcOH was added to dissolve the starting compound. After cooling, the precipitated product was filtrated off with suction and recrystallized from an appropriate solvent. When the mixture was homogeneous, it was concentrated, and the residue was crystallized from an appropriate solvent or separated by CC (SiO_2).

*(5*E*)-3-Butyl-5-butylidene-1′-methylspiro[imidazolidine-4,3′-[3*H*]indole]-2,2′(1′*H*)-dione* (**10a**). Prepared from **3a** (besides *N*-methylisatin). Colorless crystals. M.p. 117–121° (cyclohexane). IR: 3177, 3050, 2957, 2930, 2872, 1722, 1688, 1613, 1493, 1474, 1449, 1416, 1364, 1350, 1317, 1277, 1242, 1169, 1128, 1098, 1045, 958, 877, 763, 685, 643, 537, 487. ^{1}H- and ^{13}C-NMR: *Table 5*. APCI-MS (pos.): 328 (100, $[M + H]^+$). APCI-MS/MS (pos.) of 328: 311 (5, $[M + H - NH_3]^+$), 285 (19, $[M + H - NHCO]^+$), 272 (100, $[M + H - C_4H_8]^+$), 255 (90), 229 (98, $[M + H - C_4H_9NCO]^+$). APCI-MS (neg.): 326 (100, $[M - H]^-$). APCI-MS/MS (neg.) of 326: 283 (4, $[M - H - NHCO]^-$), 269 (26, $[M - H - C_4H_9]^-$), 240 (5, $[M - H - C_5H_8 - CO]^-$), 227 (100, $[M - H - C_4H_9NCO]^-$). Anal. calc. for $C_{19}H_{25}N_3O_2$ (327.42): C 69.70, H 7.70, N 12.83; found: C 69.85, H 7.85, N 12.71.

*(5*E*)-5-Butylidene-1′-methyl-3-phenyl-1′*H*-spiro[imidazolidine-4,3′-[3*H*]indole]-2,2′(1′*H*)-dione* (**10b**). Prepared from **2b**. Colorless crystals. M.p. 186–191° (benzene/hexane). IR: 3447, 3193, 3071, 2951, 2928, 2867, 1733, 1697, 1613, 1494, 1469, 1391, 1367, 1304, 1250, 1190, 1156, 1127, 1088, 1020, 969, 902, 876, 826, 779, 746, 702, 678, 553, 539, 504. ^{1}H- and ^{13}C-NMR: *Table 5*. APCI-MS (pos.): 348 (100, $[M + H]^+$). APCI-MS/MS (pos.) of 348: 305 (11, $[M + H - NHCO]^+$), 292 (17, $[M + H - C_4H_8]^+$), 255 (100, $[M + H - C_6H_5NH_2]^+$), 229 (79, $[M + H - C_6H_5NCO]^+$). APCI-MS (neg.): 346 (100, $[M - H]^-$). APCI-MS/MS (neg.) of 346: 318 (32, $[M - H - CO]^-$), 303 (100, $[M - H - NHCO]^-$), 287 (10), 260 (19, $[M - H - C_5H_8 - CO]^-$), 254 (56), 227 (57, $[M - H - C_6H_5NCO]^-$). Anal. calc. for $C_{21}H_{21}N_3O_2$ (347.16): C 72.60, H 6.09, N 12.10; found: C 72.31, H 6.13, N 11.84.

*(5*E*)-1,3-Dibutyl-5-butylidene-1′-methylspiro[imidazolidine-4,3′-[3*H*]indole]-2,2′(1′*H*)-dione* (**10e**). Prepared from **3e**. Yellowish oil. IR: 3056, 2957, 2931, 2871, 1728, 1674, 1611, 1491, 1468, 1418, 1366, 1342, 1311, 1255, 1191, 1128, 1096, 1021, 938, 814, 753, 695, 676, 538. ^{1}H- and ^{13}C-NMR: *Table 5*. APCI-MS (pos.): 384 (100, $[M + H]^+$). APCI-MS/MS (pos.) of 384: 328 (100, $[M + H - C_4H_8]^+$), 285 (17, $[M + H - C_4H_9NCO]^+$), 272 (30, $[M + H - 2\ C_4H_8]^+$). APCI-MS (neg.): 382 (21, $[M - H]^-$), 414 (100). APCI-MS/MS (neg.) of 382: 325 (100, $[M - H - C_4H_9]^-$), 308 (22, $[M - H - C_4H_8 - H_2O]^-$), 268 (47, $[M - H - 2\ C_4H_9]^-$). Anal. calc. for $C_{23}H_{33}N_3O_2$ (383.53): C 72.03, H 8.67, N 10.96; found: C 72.11, H 8.52, N 10.89.

*(5*E*)-1-Butyl-5-butylidene-1′-methyl-3-phenylspiro[imidazolidine-4,3′-[3*H*]indole]-2,2′(1′*H*)-dione* (**10f**). Prepared from **3f**. Colorless crystals. M.p. 118–122° (benzene/hexane). IR: 3053, 2959, 2933, 2871, 2833, 1728, 1711, 1671, 1611, 1492, 1469, 1419, 1358, 1341, 1259, 1241, 1202, 1123, 1085, 1032, 982, 944, 920, 892, 812, 771, 760, 743, 692, 674, 654, 621, 538, 511. ^{1}H- and ^{13}C-NMR: *Table 5*. APCI-MS (pos.): 404 (100, $[M + H]^+$). APCI-MS/MS (pos.) of 404: 348 (100, $[M + H - C_4H_8]^+$), 305 (47, $[M + H - C_4H_9NCO]^+$), 292 (35, $[M + H - 2\ C_4H_8]^+$). APCI-MS (neg.): 402 (100, $[M - H]^-$). APCI-MS/MS (neg.) of 402: 316 (100, $[M - H - C_5H_8 - CO]^-$), 303 (29, $[M - H - C_4H_9NCO]^-$), 260 (86, $[M - H - C_5H_8 - CO - C_4H_8]^-$). Anal. calc. for $C_{25}H_{29}N_3O_2$ (403.52): C 74.41, H 7.24, N 10.41; found: C 74.57, H 7.32, N 10.29.

*(5*E*)-1,3-Dibutyl-5-butylidene-1′-phenylspiro[imidazolidine-4,3′-[3*H*]indole]-2,2′(1′*H*)-dione* (**10i**). Prepared from **3i**. Colorless crystals. M.p. 52–55° (hexane). IR: 3066, 2953, 2927, 2867, 1742, 1722, 1674, 1611, 1594, 1529, 1500, 1465, 1454, 1420, 1371, 1312, 1296, 1263, 1226, 1194, 1179, 1158, 1104, 1088, 954, 937, 869, 819, 809, 766, 757, 702, 678, 661, 626, 522. ^{1}H- and ^{13}C-NMR: *Table 5*. APCI-MS (pos.): 446 (100, $[M + H]^+$). APCI-MS/MS (pos.) of 446: 390 (100, $[M + H - C_4H_8]^+$), 372 (7, $[M + H - H_2O - C_4H_8]^+$), 347 (21, $[M + H - C_4H_9NCO]^+$), 334 (23, $[M + H - 2\ C_4H_8]^+$). APCI-MS (neg.): 444 (100, $[M - H]^-$). APCI-MS/MS (neg.) of 444: 387 (100, $[M - H - C_4H_9]^-$), 358 (9, $[M - H - C_5H_8 - CO]^-$),

330 (23, $[M - H - 2\ C_4H_9]^-$). Anal. calc. for $C_{28}H_{35}N_3O_2$ (445.60): C 75.47, H 7.92, N 9.43; found: C 75.61, H 7.83, N 9.13.

*(5*E*)-1-Butyl-5-butylidene-1′,3-diphenylspiro[imidazolidine-4,3′-[3*H*]indole]-2,2′(1′*H*)-dione* (**10j**). Prepared from **3j**. Colorless crystals. M.p. 86–88° (hexane). IR: 3060, 3032, 2959, 2931, 2904, 2867, 1722, 1680, 1612, 1592, 1495, 1465, 1453, 1417, 1361, 1324, 1294, 1252, 1222, 1204, 1187, 1175, 1125, 1072, 1043, 1025, 1002, 972, 947, 896, 858, 809, 759, 745, 698, 678, 666, 644, 622, 537. ^{1}H- and ^{13}C-NMR: *Table 5*. APCI-MS (pos.): 466 (100, $[M+H]^+$). APCI-MS/MS (pos.) of 466: 410 (100, $[M+H-C_4H_8]^+$), 367 (55, $[M+H-C_4H_9NCO]^+$), 354 (27, $[M+H-2\ C_4H_8]^+$), 347 (20, $[M+H-C_6H_5NCO]^+$). APCI-MS (neg.): 464 (100, $[M-H]^-$). APCI-MS/MS (neg.) of 464: 378 (100, $[M-H-C_5H_8-CO]^-$), 365 (16, $[M-H-C_4H_9NCO]^-$), 322 (32, $[M-H-C_5H_8-CO-C_4H_8]^-$). Anal. calc. for $C_{30}H_{31}N_3O_2$ (465.59): C 77.39, H 6.71, N 9.03; found: C 77.23, H 6.97, N 9.00.

*3-Butyl-1′-methyl-5-phenylspiro[4*H*-imidazol-4,3′-[3*H*]indole]-2,2′(1′*H*,3*H*)-dione* (**11c**). Prepared from **2c** and from **3c**. Colorless crystals. M.p. 163–165° (benzene/hexane). IR: 2959, 2931, 2872, 1737, 1724, 1714, 1611, 1591, 1563, 1492, 1473, 1446, 1365, 1348, 1326, 1263, 1181, 1132, 1103, 1083, 1043, 1022, 964, 930, 840, 772, 699, 685, 589, 539. ^{1}H- and ^{13}C-NMR: *Table 5*. APCI-MS (pos.): 348 (100, $[M+H]^+$). APCI-MS/MS (pos.) of 348: 292 (100, $[M+H-C_4H_8]^+$), 306 (3, $[M+H-NCO]^+$), 249 (8, $[M+H-C_4H_9NCO]^+$), 217 (14, $[M+H-C_6H_5-CNCO]^+$), 160 (19, $[M+H-C_6H_5-CNCO-C_4H_9]^+$). Anal. calc. for $C_{21}H_{21}N_3O_2$ (347.41): C 72.60, H 6.09, N 12.10; found: C 72.55, H 6.17, N 11.87.

*1′-Methyl-1,5-diphenylspiro[4*H*-imidazol-4,3′-[3*H*]indole]-2,2′(1′*H*,3*H*)-dione* (**11d**). Prepared from **2d** and from **3d**. Colorless crystals. M.p. 290–291° (benzene). IR: 1738, 1721, 1611, 1589, 1555, 1492, 1471, 1447, 1416, 1359, 1295, 1254, 1206, 1127, 1066, 1024, 974, 949, 835, 771, 702, 682, 589, 538. ^{1}H- and ^{13}C-NMR: *Table 5*. APCI-MS (pos.): 368 (100, $[M+H]^+$). APCI-MS/MS (pos.) of 368: 325 (16, $[M+H-NHCO]^+$), 237 (19, $[M+H-C_6H_5-CNCO]^+$), 180 (100, $[M+H-C_6H_5-CNCO-C_4H_9]^+$). Anal. calc. for $C_{23}H_{17}N_3O_2$ (367.40): C 75.19, H 4.66, N 11.44; found: C 75.31, H 4.47, N 11.17.

*(4*R**,5*S**)-1,3-Dibutyl-5-hydroxy-1′-methyl-5-phenylspiro[imidazolidine-4,3′-[3*H*]indole]-2,2′(1′*H*)-dione* (**12Ag**). Prepared from **3g** and **12Bg**. Colorless crystals. M.p. 165–171° (benzene). IR: 3383, 3056, 2959, 2934, 2872, 1721, 1704, 1613, 1493, 1469, 1451, 1403, 1370, 1310, 1263, 1200, 1177, 1134, 1108, 1094, 1063, 1050, 1024, 930, 885, 830, 755, 704, 672, 655, 640, 539, 516. ^{1}H- and ^{13}C-NMR: *Table 6*. APCI-MS (pos.): 422 (2, $[M+H]^+$), 404 (100, $[M+H-H_20]^+$), 378 (10, $[M+H-C_3H_8]^+$). APCI-MS/MS (pos.) of 422: 404 (5, $[M+H-H_2O]^+$), 323 (100, $[M+H-C_4H_9NCO]^+$), 300 (26). APCI-MS/MS (pos.) of 404: 348 (100, $[M+H-H_2O-C_4H_8]^+$), 292 (44, $[M+H-H_2O-2\ C_4H_8]^+$). APCI-MS (neg.): 420 (100, $[M-H]^-$). APCI-MS/MS (neg.) of 420: 363 (75, $[M-H-C_4H_9]^-$), 321 (100, $[M-C_4H_9NCO]^-$), 264 (80, $[M-H-C_4H_9NCO-C_4H_9]^-$), 176 (14), 121 (68). Anal. calc. for $C_{25}H_{31}N_3O_3$ (421.53): C 71.23, H 7.41, N 9.97; found: C 71.45, H 7.30, N 9.83.

*(4*R**,5*R**)-1,3-Dibutyl-5-hydroxy-1′-methyl-5-phenylspiro[imidazolidine-4,3′-[3*H*]indole]-2,2′(1′*H*)-dione* (**12Bg**). Prepared from **3g**. Yellowish oil. IR: 3386, 3059, 2957, 2931, 2870, 1710, 1612, 1492, 1468, 1414, 1370, 1348, 1258, 1176, 1133, 1108, 1094, 1073, 1023, 880, 831, 751, 698, 667, 579, 539. ^{1}H- and ^{13}C-NMR: *Table 6*. APCI-MS (pos.): 404 (100, $[M+H-H_20]^+$), 378 (4, $[M+H-C_3H_8]^+$), 348 (4, $[M+H-H_2O-C_4H_8]^+$). APCI-MS/MS (pos.) of 404: 348 (100, $[M+H-H_2O-C_4H_8]^+$), 292 (39, $[M+H-H_2O-2\ C_4H_8]^+$). APCI-MS (neg.): 420 (100, $[M-H]^-$). APCI-MS/MS (neg.) of 420: 363 (66, $[M-H-C_4H_9]^-$), 321 (100, $[M-C_4H_9NCO]^-$), 287 (26, $[M-H-C_6H_5-C_4H_8]^-$), 264 (65, $[M-H-C_4H_9NCO-C_4H_9]^-$), 230 (34), 176 (15), 121 (56). Anal. calc. for $C_{25}H_{31}N_3O_3$ (421.53): C 71.23, H 7.41, N 9.97; found: C 71.54, H 7.57, N 10.03.

(*4*R**,5*S**)-1-Butyl-5-hydroxy-1′-methyl-3,5-diphenylspiro[imidazolidine-4,3′-[3*H*]indole]-2,2′(1′*H*)-dione* (**12Ah**). Prepared from **3h** and **12Bh**. Colorless crystals. M.p. 234–238° (benzene). IR: 3315, 3065, 3031, 2957, 2934, 2869, 1728, 1698, 1616, 1555, 1499, 1473, 1453, 1394, 1360, 1323, 1267, 1251, 1206, 1179, 1123, 1094, 1051, 1028, 935, 895, 843, 820, 752, 699, 661, 645, 542, 515. ^{1}H- and ^{13}C-NMR: *Table 6*. APCI-MS (pos.): 442 (6, $[M+H]^+$), 424 (100, $[M+H-H_2O]^+$). APCI-MS/MS (pos.) of 442: 424 (7, $[M+H-H_2O]^+$), 343 (100, $[M+H-C_4H_9NCO]^+$), 325 (83, $[M+H-H_2O-C_4H_9NCO]^+$). APCI-MS/MS (pos.) of 424: 368 (100, $[M+H-H_2O-C_4H_8]^+$), 325 (19, $[M+H-H_2O-C_4H_9NCO]^+$). APCI-MS (neg.): 440 (100, $[M-H]^-$), 502 (15). APCI-MS/MS (neg.) of 440: 396 (3, $[M-H-C_3H_8]^-$), 341 (100, $[M-H-C_4H_9NCO]^-$). Anal. calc. for $C_{27}H_{27}N_3O_3$ (441.52): C 73.45, H 6.16, N 9.52; found: C 73.26, H 6.27, N 9.38.

*(4*R*,5*R**)-1-Butyl-5-hydroxy-1′-methyl-3,5-diphenylspiro[imidazolidine-4,3′-[3*H*]indole]-2,2′(1′*H*)-dione* (**12Bh**). Prepared from **3h**. Colorless crystals. M.p. 171–175° and then 231–234° (benzene/hexane). IR: 3356, 3057, 2974, 2948, 2868, 1713, 1702, 1613, 1600, 1500, 1470, 1445, 1412, 1368, 1341, 1315, 1204, 1264, 1221, 1176, 1123, 1088, 1058, 1042, 1026, 1002, 957, 936, 916, 844, 822, 786, 764, 752, 695, 657, 639, 542, 517. ^{1}H- and ^{13}C-NMR: *Table 6*. APCI-MS (pos.): 442 (1, $[M+H]^+$), 424 (100, $[M+H-H_2O]^+$), 320 (7). APCI-MS/MS (pos.) of 442: 424 (33, $[M+H-H_2O]^+$), 398 (38, $[M+H-C_3H_8]^+$), 343 (100, $[M+H-C_4H_9NCO]^+$), 325 (90, $[M+H-H_2O-C_4H_9NCO]^+$). APCI-MS/MS (pos.) of 424: 368 (100, $[M+H-H_2O-C_4H_8]^+$), 325 (16, $[M+H-H_2O-C_4H_9NCO]^+$), 237 (30). APCI-MS (neg.): 440 (100, $[M-H]^-$), 250 (16). APCI-MS/MS (neg.) of 440: 396 (3, $[M-H-C_3H_8]^-$), 341 (100, $[M-H-C_4H_9NCO]^-$). Anal. calc. for $C_{27}H_{27}N_3O_3$ (441.52): C 73.45, H 6.16, N 9.52; found: C 73.31, H 6.34, N 9.40.

*(4*R*,5*S**)-1,3-Dibutyl-5-hydroxy-1′,5-diphenylspiro[imidazolidine-4,3′-[3*H*]indole]-2,2′(1′*H*)-dione* (**12Ak**). Prepared from **3k** and **12Bk**. Colorless crystals. M.p. 142–146° (benzene/cyclohexane). IR: 3447, 3305, 3057, 2957, 2925, 2872, 1736, 1682, 1611, 1595, 1500, 1468, 1419, 1374, 1333, 1248, 1209, 1176, 1111, 1058, 1029, 992, 938, 892, 851, 831, 817, 771, 754, 736, 699, 670, 610, 527, 512. ^{1}H- and ^{13}C-NMR: *Table 6*. APCI-MS (pos.): 466 (100, $[M+H-H_2O]^+$). APCI-MS/MS (pos.) of 466: 410 (100, $[M+H-H_2O-C_4H_8]^+$), 354 (32, $[M+H-H_2O-2\,C_4H_8]^+$). APCI-MS (neg.): 482 (100, $[M-H]^-$). APCI-MS/MS (neg.) of 482: 438 (100, $[M-H-C_3H_8]^-$), 383 (47, $[M-C_4H_9NCO]^-$), 339 (29, $[M-H-C_4H_9NCO-C_3H_8]^-$), 176 (18). Anal. calc. for $C_{30}H_{33}N_3O_3$ (483.60): C 74.51, H 6.88, N 8.69; found: C 74.57, H 6.93, N 8.48.

*(4*R*,5*R**)-1,3-Dibutyl-5-hydroxy-1′,5-diphenylspiro[imidazolidine-4,3′-[3*H*]indole]-2,2′(1′*H*)-dione* (**12Bk**). Prepared from **3k**. Colorless crystals. M.p. 111–114° (hexane). IR: 3440, 3059, 2957, 2930, 2870, 1725, 1705, 1611, 1594, 1501, 1466, 1413, 1371, 1330, 1306, 1237, 1207, 1183, 1161, 1135, 1115, 1074, 1027, 1001, 926, 880, 752, 701, 670, 619, 578, 530, 511. APCI-MS (pos.): 484 (2, $[M+H]^+$), 466 (100, $[M+H-H_2O]^+$). APCI-MS/MS (pos.) of 484: 466 (16, $[M+H-H_2O]^+$), 385 (100, $[M+H-C_4H_9NCO]^+$), 362 (65). APCI-MS (neg.): 482 (100, $[M-H]^-$), 312 (38). APCI-MS/MS (neg.) of 482: 438 (100, $[M-H-C_3H_8]^-$), 383 (45, $[M-H-C_4H_9NCO]^-$), 339 (26, $[M-H-C_4H_9NCO-C_3H_8]^-$), 326 (16, $[M-H-C_4H_9NCO-C_4H_9]^-$). Anal. calc. for $C_{30}H_{33}N_3O_3$ (483.60): C 74.51, H 6.88, N 8.69; found: C 74.27, H 7.01, N 8.53.

*(4*R*,5*S**)-1-Butyl-5-hydroxy-1′,3,5-triphenylspiro[imidazolidine-4,3′-[3*H*]indole]-2,2′(1′*H*)-dione* (**12Al**). Prepared from **3l** and **12Bl**. Colorless crystals. M.p. 194–196° (benzene/hexane). IR: 3419, 3287, 3064, 2959, 2932, 2870, 1735, 1690, 1672, 1610, 1500, 1466, 1452, 1408, 1368, 1306, 1246, 1210, 1177, 1125, 1093, 1061, 1028, 993, 941, 896, 843, 803, 753, 699, 665, 620, 581, 522. ^{1}H- and ^{13}C-NMR: *Table 6*. APCI-MS (pos.): 486 (100, $[M+H-H_2O]^+$, 382 (3). APCI-MS/MS (pos.) of 486: 430 (100, $[M+H-H_2O-C_4H_8]^+$), 387 (21, $[M+H-H_2O-C_4H_9NCO]^+$), 299 (58). APCI-MS (neg.): 502 (95, $[M-H]^-$), 312 (100). APCI-MS/MS (neg.) of 502: 458 (13, $[M-H-C_3H_8]^-$), 403 (100, $[M-H-C_4H_9NCO]^-$), 359 (4, $[M-H-C_4H_9NCO-C_3H_8]^-$). Anal. calc. for $C_{32}H_{29}N_3O_3$ (503.59): C 76.32, H 5.80, N 8.34; found: C 76.16, H 6.01, N 8.55.

*(4*R*,5*R**)-1-Butyl-5-hydroxy-1′,3,5-triphenylspiro[imidazolidine-4,3′-[3*H*]indole]-2,2′(1′*H*)-dione* (**12Bl**). Prepared from **3l**. Colorless crystals. M.p. 139–146° (cyclohexane). IR: 3433, 3061, 3034, 2959, 2929, 2870, 1732, 1707, 1611, 1595, 1497, 1467, 1451, 1401, 1356, 1326, 1299, 1253, 1206, 1177, 1125, 1099, 1067, 1026, 939, 874, 843, 812, 796, 751, 701, 622, 583. APCI-MS (pos.): 504 (10, $[M+H]^+$), 486 (100, $[M+H-H_2O]^+$). APCI-MS/MS (pos.) of 504: 486 (6, $[M+H-H_2O]^+$), 460 (5, $[M+H-C_3H_8]^+$), 405 (100, $[M+H-C_4H_9NCO]^+$), 387 (23, $[M+H-C_4H_9NCO-H_2O]^+$). APCI-MS (neg.): 502 (100, $[M-H]^-$). APCI-MS/MS (neg.) of 502: 458 (14, $[M-H-C_3H_8]^-$), 403 (100, $[M-H-C_4H_9NCO]^-$). Anal. calc. for $C_{32}H_{29}N_3O_3$: C 76.32, H 5.80, N 8.34; found: C 76.12, H 5.97, N 8.41.

6. Interconversion of Compounds **12B** *and* **12A**: *General Procedure.* A soln. of pure **12B** (0.1 mmol) in a mixture of conc. HCl soln. (1.5 ml) and AcOH (1 ml) was heated to reflux for 4 h. After cooling, the mixture was concentrated, and the residue was crystallized from an appropriate solvent. The following compounds **12A**, identical in all respects to those prepared from **3** (see *Sect. 5*) were prepared (yields in [%]): **12Ag** (48), **12Ah** (64), **12Ak** (37), and **12Al** (63). In the mother liquors, the presence of both compounds **12A** and **12B** was evidenced by TLC. Under the same conditions, but starting from **12A**,

mixtures **12A**/**12B** were obtained (verified by TLC). Due to a small content of **12B** in these mixtures, their isolation failed.

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