FULL PAPER

Reduction of N-Nitrosaminoquinolinediones with $LiAlH_4$ – an Easy Path to New Tricyclic Benzoxadiazocines

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3-Butylaminoquinolinediones (**1**) react with $NaNO_2$ in AcOH to give the corresponding N-nitrosoderivatives (**2**). The analogous reactions of 4-hydroxy-3-butylaminoquinolinediones (**5**), prepared by the reduction of **1** with $NaBH_4$, produce the corresponding nitrosamines (**4**). The reduction of both **2** and **4** with Zn under different conditions was non-productive, but the reduction of both compounds with $LiAlH_4$ at the oxo and lactame groups yielded impure products, generating new tricyclic benzoxadiazocines (**9**) by a reaction with HNCO. All compounds were characterized by IR, ^{1}H-, and ^{13}C-NMR (in some cases, ^{15}N-NMR also) spectroscopy and EI and/or ESI mass spectrometry. The X-ray structure of compound **9g** was determined.

Introduction. – In our laboratory, we have paid much attention to the reactivity of 3-alkyl/aryl-3-hydroxyquinolinediones and 3-alkyl/aryl-3-aminoquinolinediones. Recently, we described the stereoselective reduction of 3-hydroxyquinoline-2,4-diones with $NaBH_4$ to the corresponding *cis*-diols. In conc. H_2SO_4, these diols can undergo pinacol rearrangement giving 3-hydroxy-2-quinolones [1], which frequently occur as secondary metabolites of fungi of the genus *Penicillium* [2]. Primary 3-aminoquinoline-2,4-diones were also stereoselectively reduced with $NaBH_4$ to give *cis*-3-amino-3,4-dihydro-4-hydroxyquinolin-2(1*H*)-ones [3]. The deamination of the reduction products using HNO_2 produced mixtures of several compounds, from which new indolin-2-ones and their 3-hydroxy and 3-nitro derivatives were isolated as the products of the molecular rearrangement [3]. In our last article, we also demonstrated that 3-hydroxyquinolinediones can be converted to their 3-aminoanalogues by a reaction with ammonium or alkylammonium ions [4].

Primary and secondary 3-aminoquinolinediones are very reactive compounds and can easily be converted to novel heterocyclic compounds, mostly in the course of molecular rearrangement. These rearrangements mainly occur by a reaction with urea, thiourea, isocyanic, and isothiocyanic acids in an acidic environment [5]. Similar rearrangements were also observed during acid treatment of the addition products of 3-aminoquinolinediones with organic isocyanates or thiocyanates [6][7].

We aimed to prepare 3-hydrazino derivatives **3**, which might be suitable compounds to study cyclization to triazinoquinolinones with HNCO. For that purpose, we prepared the 3-nitrosoamino derivatives **2** of the 3-alkylaminoquinolinediones **1** and studied their reduction to the corresponding 3-hydrazino derivatives **3**.

Results and Discussion. – According to the literature, the optimal route for the preparation of hydrazines **3** from amines **1** should be through nitrosamines **2** (*Scheme 1*). The nitrosation of **1** with $NaNO_2$ in AcOH proceeded smoothly, giving high yields of compounds **2** (*Table 1*). The ^{15}N-NMR spectra of compounds **2** (*Table 2*) showed three ^{15}N-NMR signals. Two of them (at *ca.* −115 and +146 ppm) correspond to NBu and NO groups, which is in accord with the published values of −128.5 (N) and +152.4 (NO) ppm for Et_2NNO [8][9].

Many reductions of nitrosamines to hydrazines are described in the literature, mostly using Zn in acidic media. We studied this reaction using **2b**, **2e**, and **2g**. However, the reduction of these nitrosamines to hydrazines **3** was unsuccessful. We found that compounds **2b**, **2e**, and **2g** react with Zn in AcOH in an unexpected manner. At temperatures of approximately 0°, the reaction did not proceed even with very long reaction times. At temperatures approximately of 60° the reduction occurred, but the reaction products were identified as 3-alkyl-4-hydroxyquinolin-2-(1*H*)-ones in all cases. Analogous results were obtained from experiments using Zn and AcOH in MeOH [10], Zn and NH_4Cl in MeOH [11], or in EtOH in the presence of $(NH_4)_2CO_3$ [12]. On the other hand, only the starting compound was obtained by treatment of **2f** with $Na_2S_2O_4$ in an aqueous base [13]. The expected compounds **3** were never isolated. It is interesting that during the reduction of compounds **2** not only the N–N bond, but the entire N(NO)Bu group is cleaved.

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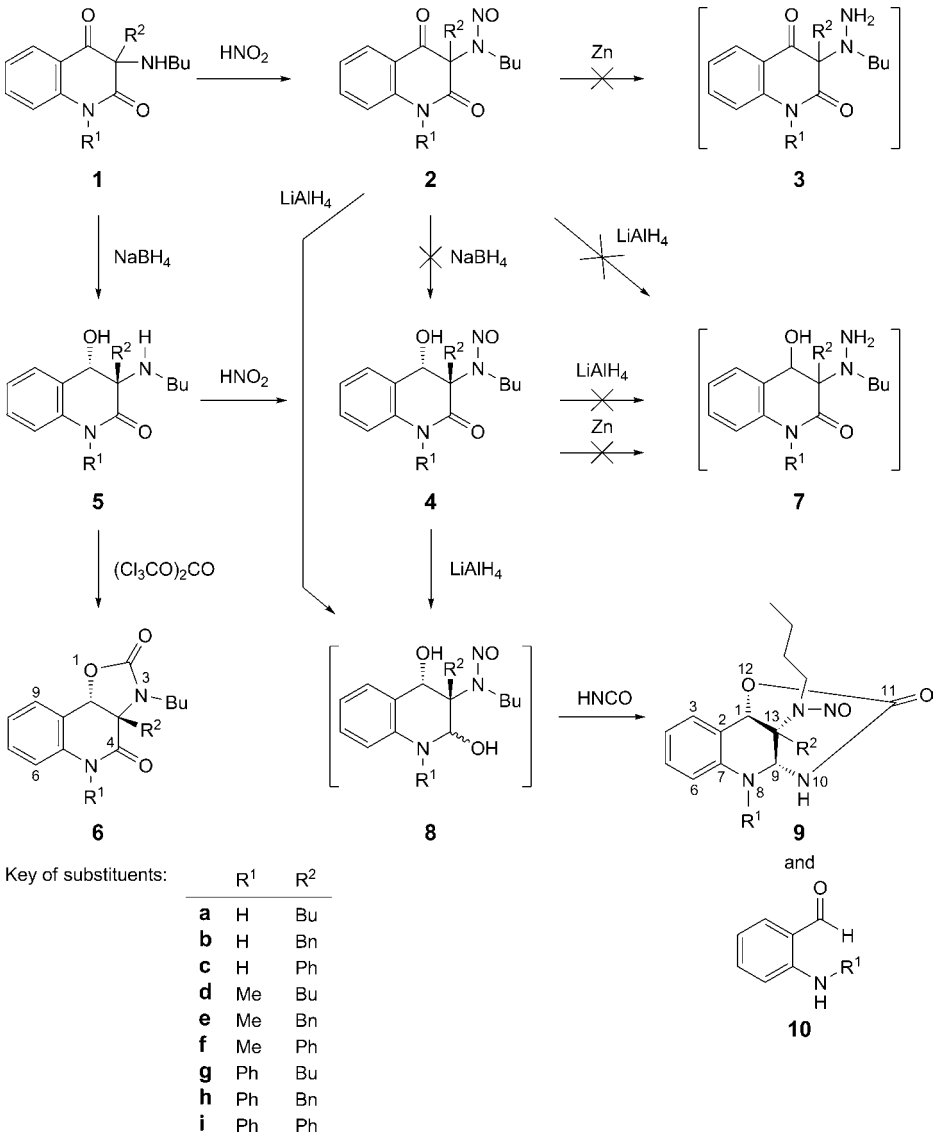
Scheme 1



Key of substituents:

	R^1	R^2
a	H	Bu
b	H	Bn
c	H	Ph
d	Me	Bu
e	Me	Bn
f	Me	Ph
g	Ph	Bu
h	Ph	Bn
i	Ph	Ph

Therefore, we carried out experiments with the Zn reduction of compounds **4**. These compounds were prepared by the nitrosation of compounds **5** (*Table 1*), which we acquired by the reduction of amines **1** with $NaBH_4$ (*Table 3*). The CO group is reduced in compounds **1** to give compounds **5** and thus, ^{13}C resonances at *ca.* 184 – 191 ppm belonging to CO groups are shifted to *ca.* 68 – 72 ppm corresponding to the CHOH moiety (*Table 4*). Coupling constants $^3J(O^1H,C(4)^1H) = 5.9 \pm 0.3$ Hz were observed in the ^1H-NMR for compounds **5**. The *cis*-configuration of the

Table 1. *Nitrosation of Compounds* **1** *and* **5**

Starting material	Substituents		Product (yield [%])	Starting material	Product (yield [%])
	R^1	R^2			
1a	H	Bu	**2a** (86)	**5a**	**4a** (91)
1b	H	Bn	**2b** (75)	**5b**	**4b** (62)
1c	H	Ph	**2c** (96)	**5c**	**4c** (97)
1d	Me	Bu	**2d** (74)	**5d**	**4d** (91)
1e	Me	Bn	**2e** (92)	**5e**	**4e** (71)
1f	Me	Ph	**2f** (92)	**5f**	**4f** (80)
1g	Ph	Bu	**2g** (98)	**5g**	**4g** (80)
1h	Ph	Bn	**2h** (83)	**5h**	**4h** (71)
1i	Ph	Ph	**2i** (89)	**5i**	**4i** (85)

Table 2. *^{1}H-, ^{13}C-, and ^{15}N-NMR Chemical Shifts and $^{1}J(^{15}N,^{1}H)$ Coupling Constants* ((D_6)DMSO) *of Compounds* **2**

Position	**2a**		**2b**		**2c**		**2d**		**2e**		**2f**		**2g**		**2h**		**2i**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
1	–	–	–	−241.1[a]) 90.9[b])	–	–	–	−249.2[a])	–	−247.8[a])	–	–	–	−233.3[a])	–	−227.4[a])	–	–
2	–	166.9	–	166.4	–	168.0	–	166.6	–	166.1	–	164.1	–	166.5	–	165.9	–	164.0
3	–	72.9	–	73.2	–	83.7	–	72.8	–	73.2	–	78.0	–	73.2	–	73.2	–	78.3
4	–	188.6	–	188.8	–	190.6	–	187.7	–	187.8	–	184.4	–	187.2	–	188.3	–	184.4
4a	–	120.1	–	120.5	–	119.4	–	121.2	–	121.7	–	120.2	–	120.8	–	121.5	–	119.9
5	7.79	126.6	7.60	126.0	7.90	127.7	7.93	127.0	7.74	127.7	7.97	128.3	7.98	127.2	7.81	126.6	8.00	128.5
6	7.17	122.8	6.94	122.3	7.21	123.6	7.32	121.2	7.11	121.6	7.28	123.5	7.30	123.5	7.10	123.1	7.24	123.8
7	7.69	136.3	7.38	135.6	7.67	137.0	7.84	136.6	7.52	135.9	7.77	136.8	7.62	136.3	7.33	136.7	7.58	136.5
8	7.20	116.7	6.72	116.1	7.15	116.7	7.52	116.2	6.97	115.2	7.43	116.1	6.48	116.9	5.98	116.3	6.42	116.9
8a	–	141.3	–	140.7	–	140.6	–	142.2	–	141.4	–	141.6	–	143.1	–	142.4	–	142.4
1′(R^1)	11.31	–	11.04	–	11.62	–	3.47	29.6	3.19	29.4	3.54	30.3	–	136.9	–	136.9	–	136.8
2′(R^1)	–	–	–	–	–	–	–	–	–	–	–	–	7.41	128.9	7.03	128.8	7.34	128.8
													7.19	128.8	6.98	128.3	7.30	128.6
3′(R^1)	–	–	–	–	–	–	–	–	–	–	–	–	7.65	130.7	7.56	130.7	7.70	130.8
														130.5		130.2		130.6
4′(R^1)	–	–	–	–	–	–	–	–	–	–	–	–	7.60	129.3	7.64	129.1	7.63	129.4
1′(R^2)	2.19	32.7	3.56	39.2	–	130.4	2.22	33.1	3.60	39.8		126.2	2.32	32.9	3.68	39.5		125.8
	2.15		3.49				2.12		3.49				2.25		3.62			
2′(R^2)	1.49	23.9	–	130.1	7.47	129.1	1.13	24.0	–	130.0	7.41	129.8	1.49	24.2	–	130.1	7.53	129.9
	1.07						0.94						1.17					
3′(R^2)	1.23	22.2	7.02	127.6	7.52	129.6	1.23	22.1	7.02	127.5	7.54	129.8	1.33	22.2	7.15	128.0	7.63	130.1
4′(R^2)	0.78	13.6	6.83	130.3	7.57	130.3	0.75	13.6	6.83	129.9	7.54	130.7	0.84	13.5	7.01	130.6	7.63	130.9
5′(R^2)	–	–	7.02	127.6	–	–	–	–	7.02	127.7	–	–	–	–	7.15	128.1	–	–
N	–	–	–	−115.6[a])	–	–	–	−114.9[a])	–	−116.2[a])	–	–	–	−115.3[a])	–	−116.0[a])	–	–
NO	–	–	–	+147.3[a])	–	–	–	+147.3[a])	–	+146.1[a])	–	–	–	+146.3[a])	–	+146.2[a])	–	–
1′NBu)	4.41	49.6	4.58	49.9	3.39	46.7	4.47	49.7	4.62	49.9	4.04	50.7	4.48	49.7	4.62	50.0	4.12	50.7
											3.99						3.97	
2′(NBu)	1.97	32.2	2.07	32.3	1.46	28.1	2.10	32.1	2.10	32.2	1.54	30.9	1.98	32.2	2.07	32.3	1.51	30.9
3′(NBu)	1.49	19.3	1.55	19.3	1.16	19.9	1.51	19.2	1.58	19.3	1.27	18.9	1.49	19.2	1.54	19.3	1.26	18.9
4′(NBu)	1.01	13.6	1.05	13.7	0.79	13.5	1.03	13.4	1.07	13.3	0.76	13.2	1.01	13.6	1.04	13.6	0.74	13.2

[a]) $\delta(^{15}N)$. [b]) $^{1}J(^{15}N,^{1}H)$.

Table 3. *Reduction of Compounds* **1** *with* $NaBH_4$

Starting material	Substituents		Product (yield [%])
	R^1	R^2	
1a	H	Bu	**5a** (91)
1b	H	Bn	**5b** (71)
1c	H	Ph	**5c** (41)
1d	Me	Bu	**5d** (87)
1e	Me	Bn	**5e** (80)
1f	Me	Ph	**5f** (91)
1g	Ph	Bu	**5g** (80)
1h	Ph	Bn	**5h** (82)
1i	Ph	Ph	**5i** (75)

OH and amino groups in **5** was demonstrated by their reaction with triphosgene ($CCl_3OCOOCCl_3$), yielding the cyclic carbamates **6**. The subsequent nitrosation of **5** to compounds **4** occurred easily. A proton signal in –NHBu in compounds **5** was not detectable in compounds **4**, and the corresponding ^{15}N resonances in –NHBu (*ca.* -336 ± 3 ppm) were shifted to *ca.* -126 ± 3 ppm, corresponding to a –*N*(NO)Bu fragment (*Table 5*). However, experiments on the reduction of **4** with Zn were unsuccessful just as for compounds **2**. From the reaction of **4g**, **4h**, and **4i** with Zn in AcOH at 60°, only the starting compounds were recovered. Additionally, only the starting compounds were recovered from **4h** in the reaction with $Na_2S_2O_4$ in an alkaline medium and, surprisingly, also from **4e** and **4g** by the reaction with $NaBH_4$. The corresponding hydrazines **7** were never found.

In preliminary experiments, we found that the reduction of compounds **2** with $LiAlH_4$ gave a mixture of products which did not crystallize and complete separation by column chromatography (CC, SiO_2) was infeasible. These experiments also showed that the crude mixtures from the reduction reacted with HNCO to give crystalline compounds. Therefore, in subsequent experiments (*Table 6*), we carried out the reduction of compounds **2** and **4** using three different methods. In *Method A*, crude products of the reduction of **2** or **4** with $LiAlH_4$ in THF were separated by CC (SiO_2) and their IR, MS, and NMR spectra were examined. In *Method B*, crude products of the reduction of **2** or **4** were reacted with HNCO without isolation and separated by CC (SiO_2). In *Method C*, some selected crude products **8** obtained by *Method A* were reacted with HNCO and then treated under the same conditions as in *Method B*. The results are given in *Table 6*. While the results of the reduction of compounds **2a** – **2c** are not very interesting because only the starting compounds **2a** – **2c** and compounds **4a** – **4c** were isolated, the reduction of compounds **2d** – **2i** gave surprising results.

Our attention was primarily focused on the determination of the structure of crystalline compounds obtained by *Method B* and *Method C*. These compounds had an elemental composition and MW corresponding to **2** + 4 H + HNCO–H_2O, which means that the primary product of the reduction of **2** with four H-atoms reacted with HNCO and eliminated H_2O. Initially, we were convinced that the reduction proceeds at the C(4)-carbonyl and N=O groups. However, in the ^{13}C-NMR spectra, the presence of the signal corresponding to the lactame group was absent and the signal at the highest frequency was at approximately 151 ppm, which is characteristic for carbamates. In comparison with starting compound **2**, the product showed the signal of the quaternary C-atom at approximately the same value, but a new signal from a tertiary C-atom at approx. 62 ppm appeared. Further study of the NMR spectra showed that, after the reduction of the carbonyl and lactame groups in **2** with four H-atoms, compounds **8** containing the configurationally unstable hemiaminal group were produced (*Scheme 1*). Despite to repeated CC (SiO_2), we were unable to purify the waxy compounds **8** sufficiently so that we could assign ^1H- and ^{13}C-NMR chemical shifts and coupling constants. The OH group at C(4) was subsequently reacted with HNCO to give the corresponding carbamic acid, which eliminated H_2O in the reaction with the second OH group at C(2) and formed an isolable tricyclic compound **9**. For the formation of **9**, the relative position *cis* of O-atoms at C(2) and C(4) in compound **8** is necessary. However, this orientation is not mandatory in compounds **8**. Due to the presence of the hemiacetal group at C(2), the creation of interconverting diastereoisomers is possible. The $^1H,^1H$-COSY spectrum revealed in compound **9** the existence of an NHCH ··· CH fragment and ^{13}C- as well as ^{15}N-NMR chemical shifts that strongly supported the reduction of two CO groups in the original C(2) and C(4) positions in compounds **2**. Unfortunately, we observed only two instead of four ^{15}N chemical shifts in compounds **9** (*Table 7*). That is why we could not support the structure **9** absolutely because we had no information about the N–NO group. The presumptions mentioned were validated by X-ray crystallography of compound **9gA** (*Fig.*).

We obtained a single crystal of compound **9gA** using the liquid diffusion method [14] with CH_2Cl_2 and benzene as the solvent-precipitant pair. The molecular structure of compound **9gA**, as determined by single-crystal X-ray diffraction, is shown in the *Figure*. The structure of **9gA** is composed of a bicyclic unsaturated central motif, where one of the rings is the six-membered carbamate ring. The second ring is connected to the N–NO moiety that resembles the known structures of several N–NO species

Table 4. *^{1}H-, ^{13}C-, and ^{15}N-NMR Chemical Shifts and ^{1}J(^{15}N,^{1}H)Coupling Constants* ((D$_6$)DMSO) *of Compounds* **5**

Position	**5a**		**5b**		**5c**		**5d**		**5e**		**5f**		**5g**		**5h**		**5i**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
1	–	–	–	–	–	−247.7[a]) 90.3[b])	–	−257.7[a])	–	−256.5[a])	–	−254.3[a])	–	–	–	−233.7[a])	–	–
2	–	171.9	–	171.1	–	170.8	–	171.1	–	170.4	–	171.0	–	171.3	–	170.6	–	170.3
3	–	62.8	–	63.8	–	67.8	–	63.0	–	64.1	–	68.6	–	63.4	–	64.4	–	68.4
4[c])	4.54	69.8	4.25	69.3	4.72	72.3	4.53	69.1	4.28	68.5	4.86	71.0	4.64	69.5	4.35	69.0	4.99	71.6
OH[c])	5.34	–	5.53	–	5.64	–	5.41	–	5.62	–	5.82	–	5.60	–	5.81	–	5.98	–
4a	–	126.2	–	125.9	–	127.1	–	127.7	–	127.5	–	129.3	–	127.1	–	127.0	–	128.6
5	7.32	128.3	7.26	128.4	7.30	126.9	7.38	128.1	7.30	128.1	7.35	126.3	7.44	128.9	7.34	128.7	7.43	126.6
6	6.97	121.9	6.96	121.9	6.97	122.1	7.08	122.4	7.06	122.5	7.05	123.1	7.07	122.6	7.04	122.7	7.04	122.9
7	7.20	128.3	7.24	128.4	7.19	126.8	7.36	128.5	7.35	128.6	7.29	128.4	7.16	128.3	7.16	128.7	7.10	127.9
8	6.85	114.4	6.89	114.5	6.89	114.5	7.10	114.1	7.11	114.2	7.12	114.5	6.19	115.5	6.23	115.7	6.20	115.6
8a	–	136.3	–	136.5	–	138.1	–	138.3	–	138.4	–	138.6	–	139.0	–	138.9	–	138.6
1′(R^1)	10.04	–	10.21	–	11.4	–	3.29	29.4	3.32	29.4	3.41	30.1	–	139.4	–	139.5	–	138.6
2′(R^1)	–	–	–	–	–	–	–	–	–	–	–	–	7.19	129.3	7.33	129.2	7.34	129.2
3′(R^1)	–	–	–	–	–	–	–	–	–	–	–	–	7.59	129.9	7.61	129.9	7.63	130.0
4′(R^1)	–	–	–	–	–	–	–	–	–	–	–	–	7.49	128.0	7.51	128.1	7.53	128.3
1′(R^2)	1.66	26.7	3.09	33.0	–	135.8	1.66	27.4	3.06	34.0	–	138.0	1.78	26.9	3.18	33.5	–	138.1
			2.97				1.63		2.94						3.04			
2′(R^2)	1.21	24.0	–	137.1	7.50	127.0	1.20	24.0	–	136.9	7.38	129.2	1.20	24.0	–	136.9	7.58	129.1
							1.12						1.12					
3′(R^2)	1.21	22.9	7.28	130.8	7.24	129.1	1.12	22.9	7.19	130.8	7.18	127.4	1.12	22.9	7.24	130.9	7.28	127.2
4′(R^2)	0.89	14.2	7.28	127.7	7.19	128.1	0.90	14.2	7.29	127.7	7.21	127.2	0.94	14.3	7.33	127.8	7.22	127.2
5′(R^2)	–	–	7.26	126.1	–	–	–	–	7.23	126.1	–	–	–	–	7.27	126.2	–	–
NH	1.40	–	1.08	–	2.12	−334.7[a])	1.38	n.o.	1.08	−339.5[a])	2.17	−333.4[a])	1.51	–	1.29	−339.3[a])	2.27	–
1′(NBu)	2.48	42.0	2.74	42.4	2.49	43.2	2.41	41..9	2.68	42.3	2.58	42.6	2.56	42.1	2.83	42.6	2.62	43.4
	2.40		2.48		2.42		2.30		2.43		2.43		2.49		2.61		2.47	
2′(NBu)	1.26	32.3	1.27	32.1	1.37	32.4	1.21	32.2	1.23	32.1	1.39	32.8	1.25	32.3	1.32	32.1	1.42	32.4
							1.18											
3′(NBu)	1.20	19.9	1.18	19.9	1.26	19.9	1.14	19.8	1.15	19.7	1.28	20.3	1.16	19.9	1.22	19.9	1.29	20.0
4′(NBu)	0.84	13.9	0.83	13.9	0.84	14.0	0.82	13.7	0.81	13.8	0.86	14.3	0.85	13.9	0.85	13.9	0.86	14.0

[a]) $\delta(^{15}N)$. [b]) $^{1}J(^{15}N,^{1}H)$. [c]) $^{3}J(O^{1}H,C^{1}H) = 5.9 \pm 0.3$ Hz.

Table 5. *^{1}H-, ^{13}C- and ^{15}N-NMR Chemical Shifts and $^{1}J(^{15}N,^{1}H)$ Coupling Constants* ((D_6)DMSO) *of Compounds* **4**

Position	**4a**		**4b**		**4c**		**4d**		**4e**		**4f**		**4g**		**4h**		**4i**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
1	–	–	–	–	–	–	–	254.3[a])	–	254.2[a])	–	–	–	232.9[a])	–	235.6[a])	–	–
2	–	167.2	–	166.5	–	167.5	–	166.4	–	165.8	–	167.5	–	166.7	–	166.1	–	164.2
3	–	72.4	–	70.6	–	75.1	–	71.9	–	63.0	–	75.7	–	72.8	–	71.7		70.0
4[c])	5.33	68.8	5.02	68.1	5.70	71.2	5.32	68.2	5.03	67.6	5.83	70.1	5.43	68.8	5.20	68.2	6.14	67.6
OH[b])	6.07	–	6.18	–	6.52	–	6.11	–	6.33	–	6.67	–	6.29	–	6.57	–	6.83	–
4a	–	126.3	–	126.8	–	127.5	–	127.4	–	126.9	–	126.9	–	127.3	–	127.2	–	127.5
5	7.38	127.8	7.14	126.8	7.43	125.9	7.40	128.1	7.18	129.0	7.47	126.8	7.49	128.3	7.31	129.1	7.56	128.9
6	7.06	122.7	6.89	122.6	7.02	122.8	7.13	123.2	7.03	123.2	7.08	123.5	7.12	123.3	7.04	123.5	7.08	123.6
7	7.26	128.6	7.26	128.7	7.15	128.2	7.36	128.9	7.32	129.0	7.28	129.0	7.17	128.7	7.13	128.8	7.08	128.1
8	6.92	115.0	6.84	115.1	6.87	114.9	7.17	114.9	7.15	115.0	7.12	114.9	6.27	116.3	6.32	117.0	6.21	116.1
8a	–	135.4	–	135.6	–	134.7	–	137.6	–	137.8	–	137.0	–	138.7	–	138.9	–	138.2
1′(R^1)	10.66	–	10.78	–	10.87	–	3.41	30.1	3.40	30.3	3.49	30.5	–	138.5	–	138.7	–	138.2
2′(R^1)	–	–	–	–	–	–	–	–	–	–	–	–	7.27	128.8	7.19	131.0	7.38	128.1
3′(R^1)	–	–	–	–	–	–	–	–	–	–	–	–	7.62	130.0	7.28	128.1	7.62	130.8
4′(R^1)	–	–	–	–	–	–	–	–	–	–	–	–	7.52	128.4	7.29	126.9	7.53	128.1
1′(R^2)	2.28	27.9	3.47	34.1	–	133.7	2.25	28.7	3.54	35.0	–	133.6	2.29	29.0	3.60	35.4	–	133.6
	2.01						2.07		3.50				2.15		3.55			
2′(R^2)	1.39	25.0	–	135.1	7.57	129.8	1.22	24.9	–	135.0	7.49	128.6	1.30	25.3	–	134.9	7.72	129.9
	1.06						0.98					128.3	1.20					
3′(R^2)	1.22	22.6	7.10	130.9	7.33	127.8	1.34	22.5	7.14	130.9	7.29	129.7	1.30	22.5	7.26	128.5	7.38	128.9
4′(R^2)	0.88	14.1	7.25	128.0	7.33	128.5	0.86	14.0	7.28	128.0	7.29	129.0	0.88	14.0	7.64	130.1	7.38	128.6
5′(R^2)	–	–	7.19	128.7	–	–	–	–	7.25	126.8	–	–	–	–	7.54	128.5	–	–
NH/N	–	–	–	–	–	–	–	−122.8[a])	–	−128.7[a])	–	–	–	n.o.	–	−126.5[a])	–	–
NO	–	–	–	–	–	–	–	n.o.	–	n.o.	–	–	–	n.o.	–	165.8	–	–
1′NBu)	3.52	44.4	3.72	43.9	3.37	45.5	3.53	44.9	3.76	43.5	3.39	45.7	3.48	44.5	3.68	44.6	3.68	45.5
	3.29		3.20		3.26		3.18		3.14		3.28		3.40		3.27		3.27	
2′(NBu)	1.30	27.9	1.10	27.8	1.20	28.0	1.17	27.8	1.06	27.8	1.05	28.0	1.28	28.0	1.18	28.0	1.18	28.0
			0.90				1.02		0.79				1.24					
3′(NBu)	1.22	20.2	1.10	20.0	1.05	19.9	1.06	20.0	1.06	19.8	1.01	19.9	1.15	20.1	1.18	20.1	1.18	19.9
4′(NBu)	0.88	13.6	0.79	13.5	0.71	13.4	0.79	13.6	0.79	13.5	0.68	13.4	0.84	13.6	0.75	13.5	0.75	13.3

[a]) $\delta(^{15}N)$. [b]) $^{3}J(O^{1}H, C^{1}H) = 5.9 \pm 0.3$ Hz.

Table 6. *Reduction of Compounds* **2** *and* **4** *with* $LiAlH_4$ – Methods A, B, *and Conversion of Crude Compounds* **8** *to Pure* **9** (*Method C*)

Starting compound	Substitution		*Method*	Product(s) (yield [%])
	R^1	R^2		
2a	H	Bu	*A*	**2a** (49)[a]), **4a** (1)
			B	**2a** (21)[a]), **4a** (3)
2b	H	Bn	*A*	**2b** (49)[a])
			B	**2b** (36)[a])
2c	H	Ph	*A*	**4c** (17)
			B	**4c** (42)
2d	Me	Bu	*A*	**2d** (5)[a]), **4d** (15), **8d** (43)[b])
			B	**4d** (19), **9d** (43)
2e	Me	Bn	*A*	**4e** (5), **8e** (51)[b]), **10e** (3)
			B	**4e** (8), **9e** (43), **10e** (3)
2f	Me	Ph	*A*	**4f** (5), **8f** (49)[b]), **10f** (5)
			B	**9fA** (16), **9fB** (10), **10f** (10)
2g	Ph	Bu	*A*	**8g** (42)[b]), **10g** (13)
			B	**9gA** (21), **10g** (14)
2h	Ph	Bn	*A*	**8h** (20)[b]), **10h** (21)
			B	**9h** (20), **10h** (13)
2i	Ph	Ph	*A*	**8i** (13)[b]), **10i** (29)
			B	**4i** (6), **10i** (27), **9i** (1)
4f	Me	Ph	*B*	**9fA** (9), **10f** (10)
4g	Ph	Bu	*B*	**9gB** (32), **10g** (13)
8d	Me	Bu	*C*	**9d** (71)
8e	Me	Bn	*C*	**9e** (18)
8g	Ph	Bu	*C*	**9gA** (31)
8h	Ph	Bn	*C*	**9h** (27)

[a]) Recovered starting compound. [b]) Products pure according to TLC, but impure according to ^{1}H- and ^{13}C-NMR.

found in the literature [15][16]. To the best of our knowledge, there is not even a remotely similar structure present in the literature. On the other hand, all of the other interatomic distances and angles are in line with previous findings for the appropriate functional groups [17]. A H-bond typical for an amido group, was found between two pairs of N–H···C=O groups, moreover a weak intramolecular H-bond was observed between the N–H and N=O groups. Three chiral C-atoms are present in the molecule of compound **9gA**. From the X-ray results of compound **9gA** (*Fig.*), it follows that configurations of the atoms in position C(1) and C(9) are (1*S**,9*S**). The third chiral atom at position C(13) has the configuration (13*R**). The directions of the N=O bond and C-butyl chain are antiparallel (*i.e.*, a H-bond between NH and N=O groups). However, these findings should not be present in all compounds **9**, as it especially depends on the orientation of the N=O group. The NMR spectra of compounds **9** are given in *Table 7*. For **9f** and **9g**, two couples of individual compounds, designated as **9fA**, **9fB**, and **9gA**, **9gB**, were isolated. With high probability, these couples are two conformers differentiated by the orientation of the –N=O group.

In the molecule of compounds **9**, a 1,3,5-oxadiazocine ring is present. Even more than 1500 1,3,5-oxadiazocines are described in the literature, only some few of them contain a CH_2 bridge between C(2) and C(6) atoms, but the benzene ring and oxo group are joined in other positions [18][19].

Mostly, minor products were isolated from the reduction of compounds **2** and **4** and identified as (2-butylamino)- (**10d**) and (2-phenylamino)benzaldehyde (**10g**). These compounds are formed mostly as late as AcOH and KNCO were added to the mixture. Therefore, they must arise from the ring opening and following retroaldolization of the compounds **8** (*Scheme 2*) under catalysis of very strong HNCO.

Conclusions. – The described reduction of 3-nitrosaminoquinoline-2,4-diones **2** with $LiAlH_4$ does not have an analogy in the literature. Above all, the very high stability of the nitroso group to reduction is surprising. The

Scheme 2

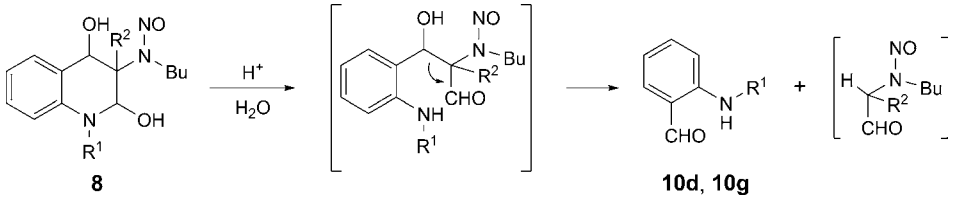


Table 7. *^{1}H- and ^{13}C-NMR Chemical Shifts* ((D$_6$)DMSO) *of Compounds* **6** *and* **9**

Position	**6d**		**6f**		**9d**		**9e**		**9fA**[a])		**9fB**[a])		**9gA**[a])		**9gB**[a])		**9h**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
1	–	–	–	–	5.69	74.3	5.74	74.4	6.46	74.6	6.60	73.0	5.79	73.6	5.88	72.6	5.87	73.8
2	–	156.2	–	158.2	–	119.7	–	119.5	–	120.3	–	119.9	–	120.2	–	120.9	–	119.7
3	–	–	–	–	7.42	131.7	7.52	131.7	7.46	130.9	7.58	131.4	7.50	132.2	7.47	131.6	7.66	132.3
3a	–	64.1	–	68.4	–	–	–	–	–	–	–	–	–	–	–	–	–	–
4	–	168.0	–	167.1	6.89	118.6	6.98	118.9	6.87	118.5	6.85	118.6	6.98	120.0	6.86	119.6	7.06	120.1
5	–	–	–	–	7.38	131.2	7.45	131.5	7.31	130.7	7.24	131.4	7.27	130.8′	7.13	130.1	7.34	131.1
5a	–	138.5	–	137.4	–	–	–	–	–	–	–	–	–	–	–	–	–	–
6	7.28	115.4	7.17	116.1	6.82	113.1	7.02	113.5	6.79	112.8	6.62	113.0	6.78	115.0	6.57	114.3	6.87	114.8
7	7.57	131.6	7.28	128.4	–	142.7	–	142.6	–	142.0	–	142.8	–	144.0	–	143.5	–	143.8
8	7.25	123.7	7.12	123.7	–	– 308.0[b])	–	–	–	– 307.7[b])	–	– 308.8[b])	–	n.o.	–	n.o.	–	–
9	7.54	131.1	7.38	121.4	5.33	67.7	4.98	67.7	5.97	66.9	6.06	68.7	5.70	67.7	5.52	69.0	5.53	68.3
9a	–	117.7	–	124.2	–	–	–	–	–	–	–	–	–	–	–	–	–	–
9b	5.58	76.6	6.06	76.9	–	–	–	–	–	–	–	–	–	–	–	–	–	–
10	–	–	–	–	8.31	– 288.7[b]) 93.0[c])	8.31		8.66	– 288.8[b]) 93.2[c])	8.59	– 286.0[b]) 93.2[c])	8.72	– 285.1[b]) 93.4[c])	8.83	– 286.3[b]) 93.4[c])	8.79	–
11	–	–	–	–	–	151.4		151.2		151.7	–	151.8	–	151.2	–	151.9		151.0
13	–	–	–	–	–	62.2	–	62.7	–	62.4	–	63.8	–	62.7	–	60.9	–	62.7
1′(R^1)	3.35	29.4	3.42	29.8	3.08	37.2	3.12	37.4	3.09	36.8	2.98	37.2	–	139.9	–	139.5	–	140.3
2′(R^1)	–	–	–	–	–	–			–	–	–	–	7.50	124.8	7.46	125.4	7.59	126.3
3′(R^1)	–	–	–	–	–	–			–	–	–	–	7.50	131.1	7.20	131.6	7.59	130.1
4′(R^1)	–	–	–	–	–	–			–	–	–	–	7.29	125.8	7.27	125.6	7.42	126.3
N	–	–	–	–	–	n.o.			–	n.o.	–	n.o.	–	n.o.	–	n.o.	–	–
NO	–	–	–	–	–	n.o.			–	n.o.	–	n.o.	–	n.o.	–	n.o.		
1′(R^2)	2.15	34.1	–	133.0	1.72	30.4	2.95	36.4	–	135.2	–	135.1	1.93	30.1	2.08	30.4	3.28	36.6
	1.90				1.64								1.79		2.00			
2′(R^2)	1.65	24.4	7.13	127.3	1.21	25,2	–	134.2	7.79	127.1	7.52	126.9	0.86	25.2	1.14	24.6	–	134.2
	1.60				1.00													
3′(R^2)	1.02	22.3	7.27	129.0	1.17	22.0	6.88	130.3	7.55	128.9	7.28	128.6	1.13	21.7	1.48	22.1	6.80	130.0
															1.35			
4′(R^2)	0.80	13.8	7.27	129.3	0.79	13.7	7.28	128.4	7.50	129.0	7.28	129.0	0.67	13.7	0.93	13.9	7.20	128.3
5′(R^2)	–	–	–	–	–	–	7.28	127.3	–	–	–	–	–	–	–	–	7.20	127.2
1′(Bu)	3.69	41.6	3.15	43.5	3.68	42.5	3.73	43.2	3.35	43.3	3.43	43.1	3.73	42.8	3.55	43.7	3.69	43.2
	3.40		3.00		3.64				3.23		3.39		3.63		3.16			
2′(Bu)	1.65	31.1	1.67	30.7	1.47	28.1	1.47	28.2	1.02	27.8	1.25	28.3	1.51	27.9	1.35	27.7	1.43	28.2
	1.60		1.52		1.44				0.57		0.95		1.42					
3′(Bu)	1.30	19.7	1.29	19.6	1.17	20.2	1.38	20.3	1.02	19.9	1.23	20.4	1.36	20.2	1.13	20.1	1.34	20.2
															0.82			
4′(Bu)	0.94	13.7	0.88	13.7	0.97	13.7	0.97	13.8	0.69	13.5	0.81	14.0	0.86	13.7	0.75	13.5	0.96	13.7

[a]) The couples of compounds **9fA/9fB** and **9gA/9gB** – see Results and Discussion. [b]) $\delta(^{15}N)$. [c]) $^1J(^{15}N,^1H)$.

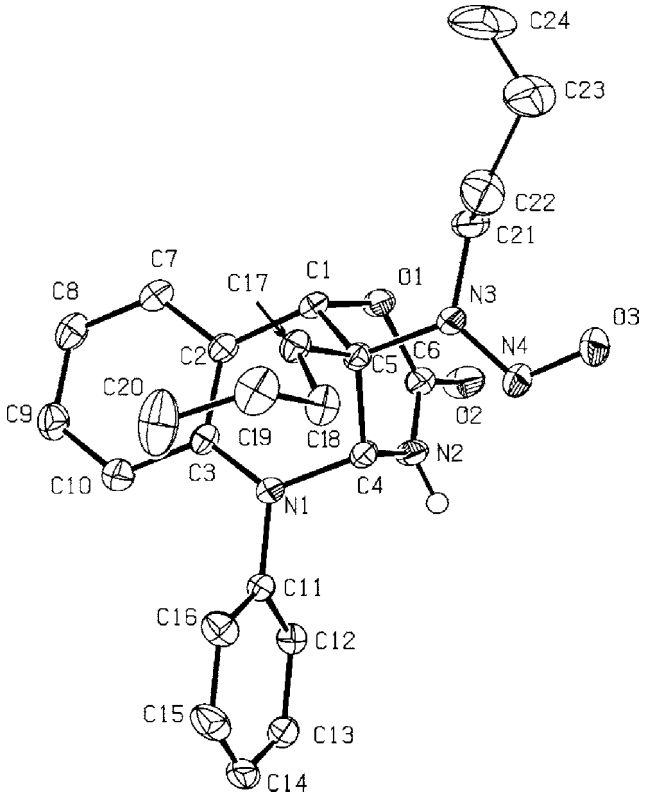


Figure. *Molecular Structure* (ORTEP 50% probability level) *of* **9gA**. Selected Interatomic Distances [Å] and Angles [°]: O1 C6 1.3535(18), O1 C1 1.4553(18), O3 N4 1.2469(19), N3 N4 1.3145(19), N3 C21 1.474(2), N3 C5 1.484(2), N1 C3 1.4011(19), N1 C11 1.4402(19), N1 C4 1.455(2), N2 C6 1.344(2), N2 C4 1.462(2), O2 C6 1.219(2), C1 C2 1.507(2), C1 C5 1.533(2), O3 N4 N3 114.20(14). Arbitrary atom numbering: O(1)–C(6) corresponds to O(12)–C(11)=O and N(1)–C(4) to N(8)–C(9) in *Scheme 1*.

cis-1,3-diols primarily formed react smoothly with HNCO to form interesting tricyclic compounds **9**, which have not been described in the literature. Therefore, this reaction is not merely interesting from a theoretical view-point, but because of the simple reaction protocol, this reaction presents an easy pathway for the preparation of novel heterocyclic systems that might be interesting structures for the study of biological activity due to the presence of the 1,3,5-diazocine skeleton.

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Experimental Part

1. *General.* TLC: *Alugram® SIL G/UV$_{254}$* foils (*Macherey–Nagel*); elution with benzene/AcOEt 4:1, $CHCl_3$/EtOH 9:1 and 1:1, 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. IR Spectra: *Smart OMNI-Transmission Nicolet iS10 spectrophotometer*; KBr; in cm^{-1}. NMR Spectra: *Bruker Avance 500* spectrometer operating at 500.13 (^{1}H), 125.76 (^{13}C), and 50.68 (^{15}N) MHz; (D_6)DMSO soln.; δ in ppm rel. to Me_4Si as an internal standard or to $MeNO_2$ as an external standard in co-axial capillary; *J* in Hz; manufacturer's software for all 2D experiments (gradient-selected (gs)-COSY, gs-TOCSY, gs-HMQC, gs-HMQC-RELAY, and gs-HMBC). EI-MS (pos.): *Shimadzu QP-2010* instrument within the range of *m*/*z* 50–600 using a direct inlet probe (DI); analysis of samples in CH_2Cl_2 (30 µg/ml), a sample of 10 µl of the soln. was evaporated in DI cuvette at 50°; ion-source temp., 200°; the energy of electrons, 70 eV; only signals exceeding rel. abundance of 5% are listed. ESI-MS (pos.): *amaZon X* ion-trap mass spectrometer (*Bruker Daltonics*, DE-Bremen), equipped with an ESI source; individual samples infused into the ion as MeOH/H_2O 1:1soln. *via* a syringe pump at a constant flow rate of 4 µl/min; further experimental conditions: *m*/*z* range, 50–1500, electrospray voltage, −4.2 kV, drying gas temp., 220°, drying gas flow, 6.0 dm^3/min; nebulizer pressure, 55.16 kPa, cap. exit, 140 V; N_2 used as nebulizing as well as drying gas. Elemental analyses (C, H, N); *Flash EA 1112* elemental analyzer (*Thermo Fisher Scientific*); in %.

Crystallography. Single crystals of **9gA** were prepared by the liquid diffusion method [14] with CH_2Cl_2/benzene as the solvent-precipitant pair. The X-ray data were obtained at 150 K using *Oxford Cryostream* low-temperature device on a *Nonius Kappa CCD* diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN [20]. The absorption was corrected by integration methods [21]. Structure was solved by direct method (SIR92) [22] and refined by full matrix least-square based on F^2 SHELXL97 [23]. The H-atoms were mostly localized on a difference *Fourier* map; however, to ensure uniformity of treatment of the crystal, all H-atoms were recalculated into idealized positions (riding model) and assigned temp. factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or of $1.5\ U_{eq}$ (Me). H-atoms in CH, CH_2, and Me moieties and H-atoms in aromatic rings were placed with C–H distances of 0.98, 0.97, 0.96, and 0.93 Å, N–H bond being 0.86 Å. $R_{int} = \Sigma|F_o^2 - F_{o,mean}^2|/\Sigma F_o^2$, $GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$ for all data, $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ 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.

No. CCDC-1054592 for **9gA**, deposited with the *Cambridge Crystallographic Data Centre*, contains the supplementary crystallographic data for this article. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

2. *Starting 3-Amino-1*H,*3*H*-quinoline-2,4-diones* **2**. Compounds **2** were prepared from corresponding 3-Cl derivatives as described in [24].

3. *General Procedure for the Nitrosation of Compounds* **1** *and* **5**. Under intensive stirring, the starting compound **1** or **5** (2 mmol) was dissolved in AcOH (10 ml). After cooling to 0°, H_2O (1 ml) and then solid $NaNO_2$ (206 mg, 3 mmol) was added during 5 min, and stirring was continued for 15 min at r.t. Solid urea (45 mg, 0.75 mmol) was added to quench redundant HNO_2, and after 15 min, the mixture was blended with crushed ice (15 g). The deposited precipitate was filtered with suction, washed with H_2O (10 ml), dried, and crystallized from an appropriate solvent. In the cases when the crude product was pasty, the mixture was extracted with $CHCl_3$ (3 × 20 ml), collected extracts were evaporated to dryness and worked-up by CC (SiO_2). The yields are given in *Table 1*. ^{1}H-, ^{13}C-, and ^{15}N-NMR spectra are given in *Tables 2* and *5*.

*3-Butyl-3-[butyl(nitroso)amino]quinoline-2,4(1*H,*3*H*)-dione* (**2a**). Prepared from **1a**. Yield: 86%. Colorless solid. M.p. 118–120° (cyclohexane). IR: 3188, 3079, 2956, 2931, 2873, 1698, 1662, 1614, 1597, 1509, 1487, 1441, 1415, 1369, 1342, 1280, 1255, 1232, 1176, 1162, 1123, 1098, 870, 842, 770, 750, 720, 687, 666, 651. ESI-MS (pos.): 673.1 (5, $[2M + K]^+$), 657.3 (13, $[2M + Na]^+$), 495.7 (10, $[3M + Ca]^{2+}$), 356.2 (49, $[M + K]^+$), 340.2 (100, $[M + Na]^+$), 318.2 (6, $[M + H]^+$), 287.2 (17, $[M + H - HNO]^+$). Anal. calc. for $C_{17}H_{23}N_3O_3$ (317.38): C 64.33, H 7.30, N 13.24; found C 64.31, H 7.34, N 12.94.

*3-Benzyl-3-[butyl(nitroso)amino]quinoline-2,4(1*H,*3*H*)-dione* (**2b**). Prepared from **1b**. Yield 75%. Colorless solid. M.p. 150–152°

(benzene/hexane). IR: 3193, 3067, 2964, 2934, 2867, 1702, 1662, 1616, 1598, 1487, 1440, 1421, 1381, 1330, 1254, 1233, 1159, 1092, 1034, 929, 829, 782, 762, 719, 702, 687, 667, 510. EI-MS 321 (12, $[M-NO]^+$), 265 (6), 251 (10), 250 (46), 249 (13), 248 (9), 230 (8), 187 (14), 175 (7), 146 (6), 119 (9), 118 (22), 92 (16), 91 (100), 90 (6), 65 (9), 57 (11), 41 (14). ESI-MS (pos.): 741.2 (6, $[2M+K]^+$), 725.3 (15, $[2M+Na]^+$), 390.2 (65, $[M+K]^+$), 374.3 (100, $[M+Na]^+$), 352.3 (5, $[M+H]^+$), 321.3 (31, $[M+H-HNO]^+$). Anal. calc. for $C_{20}H_{21}N_3O_3$ (351.40): C 68.36, H 6.02, N 11.96; found C 68.18, H 5.98, N 11.86.

*3-[Butyl(nitroso)amino]-3-phenylquinoline-2,4(1*H*,3*H*)-dione* (**2c**). Prepared from **1c**. Yield 96%. Colorless solid. M.p. 143 – 146° (benzene). IR: 3202, 3142, 3085, 2996, 2956, 2931, 2872, 1719, 1681, 1615, 1596, 1485, 1467, 1447, 1437, 1421, 1361, 1328, 1245, 1227, 1185, 1158, 1118, 1082, 930, 870, 839, 776, 756, 746, 713, 667, 615. ESI-MS (pos.) 697.2 (17, $[2M+Na]^+$), 525.7 (13, $[3M+Ca]^{2+}$), 376.1 (25, $[M+K]^+$), 360.1 (100, $[M+Na]^+$), 338.1 (5, $[M+H]^+$), 330.1 (10, $[M+Na-NO]^+$), 307.1 (28, $[M-NO]^+$). Anal. calc. for $C_{19}H_{19}N_3O_3$ (337.37): C 67.64, H 5.68, N 12.46; found C 67.52, H 5.75, N 12.50.

*3-Butyl-3-[butyl(nitroso)amino]-1-methylquinoline-2,4(1*H*,3*H*)-dione* (**2d**). Prepared from **1d**. Yield 74%. Colorless solid. M.p. 98 – 100° (cyclohexane). IR: 2951, 2872, 1693, 1655, 1600, 1473, 1417, 1397, 1361, 1345, 1300, 1243, 1171, 1145, 1106, 1049, 1031, 960, 925, 869, 775, 752, 723, 697, 683, 663, 630, 491. EI-MS: 331 (4, M^+), 301 (11), 246 (5), 245 (26), 231 (11), 230 (61), 229 (10), 202 (10), 201 (10), 200 (9), 189 (18), 188 (12), 176 (9), 162 (14), 160 (9), 146 (10), 140 (31), 134 (9), 133 (7), 132 (6), 105 (9), 104 (8), 84 (100), 77 (8), 57 (15), 41 (18). ESI-MS (pos.): 701.1 (6, $[2M+K]^+$), 685.3 (11, $[2M+Na]^+$), 370.2 (100, $[M+K]^+$), 354.2 (78, $[M+Na]^+$), 332.2 (16, $[M+H]^+$), 301.2 (35, $[M+H-HNO]^+$). Anal. calc. for $C_{18}H_{25}N_3O_3$ (331.41): C 65.23, H 7.60, N 12.68; found: C 65.23, H 7.77, N 12.64.

*3-Benzyl-3-[butyl(nitroso)amino]-1-methylquinoline-2,4(1*H*,3*H*)-dione* (**2e**). Prepared from **1e**. Yield 92% yield. Colorless solid. M.p. 114 – 117° (hexane). IR: 3031, 2955, 2870, 1692, 1662, 1601, 1474, 1456, 1412, 1367, 1336, 1304, 1245, 1190, 1175, 1143, 1100, 1041, 986, 930, 841, 777, 757, 730, 701, 683, 663, 610, 523. EI-MS 365 (2, M^+), 336 (7), 335 (29), 279 (6), 265 (20), 264 (86), 263 (32), 262 (17), 244 (18), 243 (7), 202 (5), 201 (34), 190 (7), 189 (15), 175 (9), 162 (13), 146 (6), 134 (9), 132 (7), 118 (32), 105 (12), 104 (14), 91 (100), 78 (7), 77 (13). ESI-MS (pos.): 753.2 (5, $[2M+Na]^+$), 567.7 (11, $[3M+Ca]^{2+}$), 404.1 (51, $[M+K]^+$), 388.2 (100, $[M+Na]^+$), 385.2 (44, $[2M+Ca]^{2+}$), 366.2 (5), $[M+H]^+$), 267.1 (8, $[M+Na-Bn]^+$), 245.1 (11, $[M+H-Bn]^+$). Anal. calc. for $C_{21}H_{23}N_3O_3$ (365.43): C 69.02, H 6.34, N 11.50; found: C 69.30, H 6.38, N 11.64.

*3-[Butyl(nitroso)amino]-1-methyl-3-phenylquinoline-2,4(1*H*,3*H*)-dione* (**2f**). Prepared from **1f**. Yield 92%. Yellowish solid. M.p. 98 – 100° (cyclohexane). IR: 2956, 2873, 1710, 1674, 1601, 1472, 1415, 1355, 1301, 1264, 1234, 1178, 1143, 1079, 1035, 958, 939, 874, 813, 775, 757, 720, 701, 665, 613, 531. EI-MS 351 (10, M^+), 321 (15), 252 (10), 251 (61), 250 (100), 244 (12), 223 (8), 222 (45), 207 (6), 160 (14), 134 (9), 117 (7), 105 (16), 104 (92), 91 (6), 77 (17), 57 (9), 41 (13). ESI-MS (pos.): 725.3 (12, $[2M+Na]^+$), 546.7 (8, $[3M+Ca]^{2+}$), 390.1 (61, $[M+K]^+$), 374.2 (100, $[M+Na]^+$), 352.2 (9, $[M+H]^+$), 321.2 (35, $[M+H-HNO]^+$). Anal. calc. for $C_{20}H_{21}N_3O_3$ (351.39): C 68.36, H 6.02, N 11.96; found: C 68.13, H 6.10, N 11.98.

*3-Butyl-3-[butyl(nitroso)amino]-1-phenylquinoline-2,4(1*H*,3*H*)-dione* (**2g**). Prepared from **1g**. Yield 98%. Yellowish solid. M.p. 142 – 146° (cyclohexane). IR: 3062, 3037, 2963, 2933, 2863, 1700, 1666, 1600, 1491, 1463, 1416, 1346, 1328, 1304, 1280, 1260, 1241, 1183, 1161, 1119, 1092, 1069, 1026, 960, 853, 791, 774, 751, 726, 705, 691, 661, 629, 523, 508. EI-MS: 363 (4, $[M-NO]^+$), 307 (6), 292 (14), 251 (6), 250 (5), 224 (6), 199 (10), 196 (28), 195 (100), 167 (8), 140 (10), 84 (48), 77 (7), 57 (16), 41 (19). ESI-MS (pos.): 825.2 (9, $[2M+K]^+$), 809.4 (49, $[2M+Na]^+$), 787.0 (11, $[2M+H]^+$), 609.9 (5, $[3M+Ca]^{2+}$), 432.2 (30, $[M+K]^+$), 416.3 (72, $[M+Na]^+$), 394.3 (19, $[M+H]^+$), 363.4 (100, $[M+H-HNO]^+$). Anal. calc. for $C_{23}H_{27}N_3O_3$ (393.48): C 70.21, H 6.92, N 10.68; found: C 69.84, H 6.82, N 10.66.

*3-Benzyl-3-[butyl(nitroso)amino]-1-phenylquinoline-2,4(1*H*,3*H*)-dione* (**2h**). Prepared from **1h**. Yield 83%. Colorless solid. M.p. 140 – 143° (cyclohexane). IR: 3027, 2955, 2870, 1697, 1665, 1602, 1493, 1465, 1408, 1330, 1268, 1239, 1184, 1163, 1102, 1070, 1028, 1001, 925, 865, 816, 765, 755, 748, 723, 710, 703, 663, 638, 529. EI-MS: 427 (4, M^+), 398 (9), 397 (31), 327 (27), 326 (97), 325 (34), 324 (15), 306 (12), 298 (6), 264 (8), 263 (35), 251 (11),237 (11), 233 (10), 224 (13), 196 (34), 195 (100), 167 (18), 166 (8), 118 (29), 103 (8), 92 (13), 91 (93), 77 (19), 57 (13), 41 (20). ESI-MS (pos.): 877.3 (8, $[2M+Na]^+$), 466.2 (64, $[M+K]^+$), 450.2 (100, $[M+Na]^+$), 447.2 (16, $[2M+Ca]^{2+}$), 428.2 (7, $[M+H]^+$), 397.3 (48, $[M-NO]^+$). Anal. calc. for $C_{26}H_{25}N_3O_3$ (427.49): C 73.05, H 5.89, N 9.83; found: C 72.87, H 5.95, N 9.54.

*3-[Butyl(nitroso)amino]-1,3-diphenylquinoline-2,4(1*H*,3*H*)-dione* (**2i**). Prepared from **1i**. Yield 89%. Colorless solid. M.p. 158 – 161° (benzene/hexane). IR: 2960, 2875, 1710, 1676, 1602, 1491, 1461, 1418, 1342, 1251, 1239, 1187, 1175, 1160, 1116, 1083, 1038, 1002, 976, 925, 868, 777, 763, 756, 748, 701, 689, 665, 634, 597, 557, 539, 512. ESI-MS (pos.): 865.1 (7, $[2M+K]^+$), 849.3 (24, $[2M+Na]^+$), 827.2 (6, $[2M+H]^+$), 639.7 (11, $[3M+Ca]^{2+}$), 452.2 (55, $[M+K]^+$), 436.2 (100, $[M+Na]^+$), 414.2 (13, $[M+H]^+$), 383.2 (37, $[M-NO]^+$). Anal. calc. for $C_{25}H_{23}N_3O_3$ (413.47): C 72.62, H 5.61, N 10.16; found: C 72.88, H 5.61, N 10.12.

*3-Butyl-3-[butyl(nitroso)amino]-3,4-dihydro-4-hydroxyquinolin-2(1*H*)-one* (**4a**). Prepared from **5a**. Yield 91%. Colorless solid. M.p. 165 – 167° (cyclohexane). IR: 3238, 2959, 2933, 2874, 1673, 1600, 1491, 1459, 1388, 1331, 1298, 1242, 1203, 1146, 1121, 1047, 959, 846, 757, 711, 663, 618, 605. ESI-MS (pos.): 661.3 (15, $[2M+Na]^+$), 498.7 (7, $[3M+Ca]^{2+}$), 358.1 (36, $[M+K]^+$), 342.2 (100, $[M+Na]^+$), 320.2 (9, $[M+H]^+$), 289.2 (9, $[M+H-HNO]^+$). Anal. calc. for $C_{17}H_{25}N_3O_3$ (319.40): C 63.93, H 7.89, N 13.16; found: C 63.76, H 7.96, N 12.80.

*3-Benzyl-3-[butyl(nitroso)amino]-3,4-dihydro-4-hydroxyquinolin-2(1*H*)-one* (**4b**). Prepared from **5b**. Yield 62%. Colorless solid. M.p. 83 – 86° (hexane). IR: 3562, 3210, 3086, 2959, 2929, 2871, 1678, 1617, 1599, 1495, 1467, 1456, 1390, 1336, 1319, 1263, 1213, 1170, 1085, 1041, 1030, 965, 940, 871, 813, 752, 707, 677, 650, 606, 578, 527, 497. ESI-MS (pos.): 729.3 (7, $[2M+Na]^+$), 392.2 (54, $[M+K]^+$), 376.2 (100, $[M+Na]^+$), 354.2 (25, $[M+H]^+$). Anal. calc. for $C_{20}H_{23}N_3O_3$ (353.41): C 67.97, H 6.56, N 11.89; found: C 68.13, H 6.82, N 11.63.

*3-[Butyl(nitroso)amino]-3,4-dihydro-4-hydroxy-3-phenylquinolin-2(1*H*)-one* (**4c**). Prepared from **5c**. Yield 97%. Colorless solid. M.p. 219 – 229° (benzene). IR: 3368, 3199, 3079, 2954, 2927, 2870, 1682, 1613, 1598, 1488, 1452, 1404, 1365, 1334, 1248, 1175, 1134, 1084, 957, 928, 823, 756, 701, 669, 611, 586, 536. ESI-MS (pos.): 528.7 (8, $[3M+Ca]^{2+}$), 378.1 (47, $[M+K]^+$, 362.2 (100, $[M+Na]^+$), 359.2 (44, $[2M+Ca]^{2+}$), 340.2 (8, $[M+H]^+$, 309.2 (30, $[M-NO]^+$). Anal. calc. for $C_{19}H_{21}N_3O_3$ (339.39): C 67.24, H 6.24, N 12.38; found: C 67.02, H 6.21, N 12.24.

*3-Butyl-3-[butyl(nitroso)amino]-3,4-dihydro-4-hydroxy-1-methylquinolin-2(1*H*)-one* (**4d**). Prepared from **5d**. Yield 91%. Yellow oil. IR: 3423, 2959, 2872, 1678, 1605, 1498, 1468, 1416, 1376, 1306, 1272, 1202, 1129, 1037, 953, 825, 755, 684, 639, 619, 602, 553, 509. ESI-MS (pos.): 689.3 (11, $[2M+Na]^+$), 519.8 (10, $[3M+Ca]^{2+}$), 372.2 (100, $[M+K]^+$), 356.2 (99, $[M+Na]^+$), 334.2 (22, $[M+H]^+$, 326.2 (7, $[M+Na-NO]^+$), 303.2 (8, $[M+H-HNO]^+$). Anal. calc. for $C_{18}H_{27}N_3O_3$ (333.43): C 64.84, H 8.16, N 12.60; found: C 64.72, H 8.03, N 12.42.

*3-Benzyl-3-[butyl(nitroso)amino]-3,4-dihydro-4-hydroxy-1-methylquinolin-2(1*H*)-one* (**4e**). Prepared from **5e**. Yield 71%. Colorless solid. M.p. 185 – 188° (benzene/cyclohexane). IR: 3497, 3034, 2958, 2871, 1668, 1605, 1498, 1475, 1439, 1405, 1365, 1341, 1270, 1182, 1130, 1037, 962, 877, 846, 800, 754, 730, 706, 685, 633, 598, 565, 505. EI-MS: 337 (8, $[M-NO]^+$), 279 (8), 266 (22), 265 (100), 264 (6), 248 (8), 236 (7), 229 (15), 175 (5), 174 (14), 167 (21), 149 (44), 132 (6), 118 (34), 113 (8), 106 (11), 92 (7), 91 (78), 71 (15), 70 (12), 57 (21), 43 (12). ESI-MS (pos.): 757.3 (7, $[2M+Na]^+$), 570.7 (31, $[3M+Ca]^{2+}$), 406.2 (76, $[M+K]^+$), 390.2 (100, $[M+Na]^+$), 387.2 (51, $[2M+Ca]^{2+}$), 368.2 (6, $[M+H]^+$), 337.2 (38, $[M+H-HNO]^+$). Anal. calc. for $C_{21}H_{25}N_3O_3$ (367.44): C 68.64, H 6.86, N 11.44; found: C 68.34, H 6.89, N 11.42.

*3-[Butyl(nitroso)amino]-3,4-dihydro-4-hydroxy-1-methyl-3-phenylquinolin-2(1*H*)-one* (**4f**). Prepared from **5f**. Yield 80%. Colorless solid. M.p. 209 – 211° (benzene). IR: 3327, 2956, 2930, 2872, 1673, 1606, 1493, 1467, 1451, 1438, 1396, 1360, 1310, 1250, 1213, 1192, 1140, 1100, 1041, 952, 929, 853, 809, 756, 750, 708, 683, 636, 595, 572, 536. ESI-MS (pos.): 729.2 (15, $[2M + Na]^+$), 549.7 (14, $[3M + Ca]^{2+}$), 392.1 (51, $[M + K]^+$), 376.2 (100, $[M + Na]^+$), 373.2 (19, $[2M + Ca]^{2+}$), 323.2 (6, $[M - NO]^+$). Anal. calc. for $C_{20}H_{23}N_3O_3$ (353.42): C 67.97, H 6.56, N 11.89; found: C 67.97, H 6.57, N 11.86.

*3-Butyl-3-[butyl(nitroso)amino]-3,4-dihydro-4-hydroxy-1-phenylquinolin-2(1*H*)-one* (**4g**). Prepared from **5g**. Yield 80%. Colorless solid. M.p. 126 – 128° (cyclohexane). IR: 3426, 2956, 2872, 1665, 1605, 1494, 1465, 1411, 1334, 1297, 1254, 1205, 1151, 1065, 1050, 1039, 956, 926, 836, 749, 696, 658, 612, 585, 553, 515. EI-MS: 365 (8, $[M - NO]^+$), 294 (11), 293 (30), 278 (7), 276 (12), 266 (6), 264 (12), 252 (18), 251 (100), 250 (10), 198 (7), 197 (41), 196 (15), 180 (9), 168 (21), 167 (8), 140 (24), 85 (6), 84 (81), 77 (6), 57 (19), 55 (5), 41 (21). ESI-MS (pos.): 813.4 (18, $[2M + Na]^+$), 612.9 (10, $[3M + Ca]^{2+}$), 434.3 (41, $[M + K]^+$), 418.3 (100, $[M + Na]^+$), 396.3 (7, $[M + H]^+$), 388.2 (10, $[M + Na - NO]^+$), 365.4 (7, $[M + H - HNO]^+$). Anal. calc. for $C_{23}H_{29}N_3O_3$ (395.49): C 69.85, H 7.39, N 10.62; found: C 69.81, H 7.40, N 10.52.

*3-Benzyl-3-[butyl(nitroso)amino]-3,4-dihydro-4-hydroxy-1-phenylquinolin-2(1*H*)-one* (**4h**). Prepared from **5h**. Yield 71%. Colorless solid. M.p. 242 – 246° (benzene). IR: 3435, 3028, 2953, 2872, 1662, 1605, 1494, 1466, 1453, 1411, 1334, 1295, 1264, 1188, 1086, 1051, 1041, 964, 925, 886, 854, 751, 729, 702, 695, 680, 637, 612, 589, 549, 516. EI-MS: 399 (7, $[M - NO]^+$), 328 (27), 327 (100), 326 (6), 291 (11), 197 (22), 196 (10), 180 (8), 174 (9), 168 (17), 167 (7), 118 (30), 92 (6), 91 (62), 77 (6), 71 (6), 57 (13), 41 (11). ESI-MS (pos.): 897.1 (6, $[2M + K]^+$), 881.3 (6, $[2M + Na]^+$), 468.2 (35, $[M + K]^+$), 452.1 (100, $[M + Na]^+$), 430.2 (6, $[M + H]^+$), 399.3 (7, $[M - NO]^+$). Anal. calc. for $C_{26}H_{27}N_3O_3$ (429.51): C 72.71, H 6.33, N 9.78; found: C 72.85, H 6.35, N 9.73.

3-[Butyl(nitroso)amino]-3,4-dihydro-4-hydroxy-1,3-diphenylquinolin-2(1 H)-one (**4i**). Prepared from **5i**. Yield 85%. Colorless solid. M.p. 201 – 204° (benzene/hexane). IR: 3272, 3064, 2961, 2869, 1686, 1604, 1592, 1492, 1457, 1396, 1335, 1295, 1260, 1216, 1179, 1131, 1091, 1080, 958, 935, 862, 832, 803, 767, 737, 722, 697, 615, 590, 526, 504. EI-MS: 386 (12), 385 (43, $[M - NO]^+$), 314 (14), 313 (31), 312 (21), 286 (8), 208 (12), 197 (14), 196 (8), 180 (12), 168 (11), 167 (6), 160 (23), 105 (12), 104 (100), 77 (12), 57 (9), 41 (12). ESI-MS (pos.): 869.2 (6, $[2M + K]^+$), 853.3 (19, $[2M + Na]^+$), 642.8 (14, $[3M + Ca]^{2+}$), 454.2 (55, $[M + K]^+$), 438.2 (100, $[M + Na]^+$), 435.2 (27, $[2M + Ca]^{2+}$), 408.2 (10, $[M + Na - NO]^+$). Anal. calc. for $C_{25}H_{25}N_3O_3$ (415.48): C 72.27. H 6.06, N 10.11; found: C 72.43, H 6.14, N 9.98.

4. *General Procedure for the Reduction of Compounds* **1** *with NaBH*$_4$. To the stirred soln. of **1** (1 mmol) in MeOH (5 ml) was added $NaBH_4$ (42 mg, 1.1 mmol) at 0° in small portions during 15 min and the stirring was continued for 20 min. Then, crushed ice (7.5 ml) was added, the mixture was acidified with conc. HCl, and 6% soln. of $NaHCO_3$ (4.5 ml) was added. The deposited precipitate was filtered with suction, dried, and crystallized from appropriate solvent. In some cases, the precipitate was separated by CC (SiO_2). The results are given in *Table 2*, ^{1}H- and ^{13}C-NMR spectra are given in *Table 4*.

cis-*3-Butyl-3-(butylamino)-3,4-dihydro-4-hydroxyquinolin-2(1*H*)-one* (**5a**). Prepared from **1a**. Yield 91%. Colorless solid. M.p. 119 – 121° (benzene/cyclohexane). IR: 3433, 3305, 3020, 2952, 2930, 2858, 1681, 1657, 1595, 1488, 1438, 1371, 1351, 1300, 1249, 1233, 1151, 1076, 830, 753, 716, 670, 660, 630. ESI-MS (pos.): 291.2 (100, $[M + H]^+$). Anal. calc. for $C_{17}H_{26}N_2O_2$ (290.40): C 70.31, H 9.02, N 9.65; found: C 69.92, H 9.20, N 9.54.

cis-*3-Benzyl-3-(butylamino)-3,4-dihydro-4-hydroxyquinolin-2(1*H*)-one* (**5b**). Prepared from **1b**. Yield 71%. Colorless solid. M.p. 189 – 194° (hexane). IR: 3192, 3062, 2954, 2928, 2872, 1679, 1597, 1493, 1471, 1438, 1376, 1339, 1253, 1226, 1200, 1119, 1070, 1030, 1017, 868, 807, 757, 718, 700, 683, 587, 504. ESI-MS (pos.): 325.2 (100, $[M + H]^+$). Anal. calc. for $C_{20}H_{24}N_2O_2$ (324.42): C 74.04, H 7.46, N 8.64; found: C 73.83, H 7.51, N 8.54.

cis-*3-(Butylamino)-3,4-dihydro-4-hydroxy-3-phenylquinolin-2(1*H*)-one* (**5c**). Prepared from **1c**. Yield 41%. Colorless solid. M.p. 144 – 146° (hexane). IR: 3201, 3079, 2958, 2923, 2867, 1681, 1616, 1598, 1486, 1454, 1365, 1253, 1205, 1132, 1078, 1041, 1004, 970, 904, 867, 829, 781, 757, 701, 682, 667, 634, 586, 545, 520, 480. EI-MS: 310 (8, M^+), 221 (7), 189 (13), 162 (6), 161 (10), 160 (9), 132 (11), 122 (9), 120 (12), 119 (100), 118 (33), 105 (8), 104 (53), 77 (20). ESI-MS (pos.): 311.3 (100, $[M + H]^+$). Anal. calc. for $C_{19}H_{22}N_2O_2$ (310.39): C 73.52, H 7.14, N 9.03; found: C 73.76, H 7.21, N 8.97.

cis-*3-Butyl-3-(butylamino)-3,4-dihydro-4-hydroxy-1-methylquinolin-2(1*H*)-one* (**5d**). Prepared from **1d**. Yield 87%. Colorless solid. M.p. 100 – 102°. IR: 3289, 2960, 2929, 2868, 1672, 1602, 1496, 1474, 1458, 1413, 1377, 1352, 1301, 1262, 1238, 1204, 1137, 1111, 1068, 1044, 972, 916, 900, 882, 852, 836, 807, 754, 695, 672, 619, 561, 532, 450. EI-MS: 304 (2, M^+), 247 (19), 233 (6), 217 (6), 216 (39), 215 (23), 174 (7), 173 (9), 146 (11), 142 (24), 118 (8), 98 (17), 84 (100), 72 (10), 57 (9), 41 (10). ESI-MS (pos.): 305.2 (100, $[M + H]^+$). Anal. calc. for $C_{18}H_{28}N_2O_2$ (304.43): C 71.02, H 9.27, N 9.20; found: C 71.28, H 9.38, N 9.11.

cis-*3-Benzyl-3-(butylamino)-3,4-dihydro-4-hydroxy-1-methylquinolin-2(1*H*)-one* (**5e**). Prepared from **1e**. Yield 80%. Colorless solid. M.p. 113 – 116° (cyclohexane). IR: 3408, 3028, 2954, 2925, 2871, 1664, 1604, 1496, 1477, 1460, 1413, 1350, 1320, 1303, 1238, 1207, 1124, 1080, 1060, 1048, 1031, 995, 936, 881, 783, 754, 738, 721, 698, 687, 664, 645, 594, 504. ESI-MS (pos.): 339.3 (100, $[M + H]^+$). Anal. calc. for $C_{21}H_{26}N_2O_2$ (338.44): C 74.52, H 7.74, N 8.28; found: C 74.51, H 7.64, N 8.13.

cis-*3-(Butylamino)-3,4-dihydro-4-hydroxy-1-methyl-3-phenylquinolin-2(1*H*)-one* (**5f**). Prepared from **1f**. Yield 91%. Colorless solid. M.p. 134 – 136°. IR: 3268, 2961, 2867, 2746, 1663, 1603, 1494, 1477, 1460, 1453, 1418, 1354, 1309, 1264, 1195, 1119, 1082, 1042, 1008, 952, 885, 864, 840, 773, 755, 721, 707, 681, 654, 626, 576, 549, 512. EI-MS: 324 (1, M^+), 253 (8), 237 (6), 236 (34), 235 (50), 222 (7), 189 (9), 162 (15), 161 (11), 160 (9), 146 (11), 120 (11), 119 (100), 118 (38), 106 (6), 105 (8), 104 (47), 91 (9), 77 (14), 72 (7). ESI-MS (pos.): 325.2 (100, $[M + H]^+$). Anal. calc. for $C_{20}H_{24}N_2O_2$ (324.42): C 74.04, H 7.46, N 8.54; found: C 74.30, H 7.55, N 8.32.

cis-*3-Butyl-3-(butylamino)-3,4-dihydro-4-hydroxy-1-phenylquinolin-2(1*H*)-one* (**5g**). Prepared from **1g**. Yield 80%. Colorless solid. M.p. 127 – 130° (hexane). IR: 3309, 3064, 3039, 2948, 2861, 1673, 1604, 1590, 1492, 1459, 1382, 1332, 1294, 1265, 1232, 1203, 1159, 1124, 1074, 1024, 1002, 958, 921, 865, 840, 809, 782, 765, 740, 696, 663, 651, 619, 532, 514, 499, 435. EI-MS: 366 (3, M^+), 279 (5), 278 (23), 180 (11), 169 (8), 168 (5), 142 (32), 98 (16), 85 (7), 84 (100), 70 (6), 57 (18), 41 (19). ESI-MS (pos.): 367.4 (100, $[M + H]^+$). Anal. calc. for $C_{23}H_{30}N_2O_2$ (366.49): C 75.37, H 8.25, N 7.64; found: C 75.26, H 8.27, N 7.64.

cis-*3-Benzyl-3-(butylamino)-3,4-dihydro-4-hydroxy-1-phenylquinolin-2(1*H*)-one* (**5h**). Prepared from **1h** in yield 82% besides 4-hydroxy-2-quinolone (4%). Colorless solid. M.p. 64 – 68° (hexane); IR: 3426, 3065, 3031, 2956, 2927, 2870, 1688, 1602, 1591, 1494, 1458, 1327, 1299, 1266, 1236, 1196, 1157, 1128, 1072, 1020, 961, 795, 760, 725, 697, 652, 596, 508. EI-MS: 310 (22), 309 (100, $[M - Bn]^+$), 291 (9), 236 (12), 208 (18), 180 (11), 118 (8), 91 (24), 84 (25). ESI-MS (pos.): 401.3 (100, $[M + H]^+$). Anal calc. for $C_{26}H_{28}N_2O_2$ (400.51): C 77.97, H 7.05, N 6.99; found: C 77.63, H 7.28, N 6.65.

cis-*3-(Butylamino)-3,4-dihydro-4-hydroxy-1,3-diphenylquinolin-2(1*H*)-one* (**5i**). Prepared from **1i**. Yield 75%. Colorless solid. M.p. 139 – 143° (benzene). IR: 3065, 2956, 2858, 1683, 1674, 1604, 1493, 1457, 1338, 1297, 1261, 1182, 1133, 1087, 1004, 944, 892, 776, 763, 720, 704, 694, 660, 595, 515. EI-MS: 386 (4, M^+), 315 (11), 299 (7), 298 (29), 297 (16), 189 (4), 180 (13), 162 (26), 161 (13), 120 (10), 119 (100), 118 (26), 105 (7), 104 (47), 77 (12). ESI-MS (pos.): 387.3 (100, $[M + H]^+$). Anal. calc. for $C_{25}H_{26}N_2O_2$ (386.49): C 77.69, H 6.78, N 7.25; found: C 77.41, H 6.95, N 7.26.

5. *General Procedure for the Reduction of Compounds* **2** *and* **4** *with LiAlH*$_4$ *and Following Reaction with HNCO. Method A.* To the soln. of **2** or **4** (0.75 mmol) in anh. THF (8 ml) was added $LiAlH_4$ (86 mg, 2.1 mmol) in a small portions during 1.5 h at r.t. The mixture was heated to reflux for 1 – 3 h according to results of TLC. After cooling, H_2O

(75 µl), 15% NaOH (75 µl), and once again H_2O (75 µl), were gradually added. The suspension was filtered with suction; the precipitate was washed with THF (5 ml). The filtrate was evaporated to dryness and worked-up by CC (SiO_2).

Method B. The reduction was carried out by the same manner as in *Method A*. After filtration of the suspension and washing of precipitate, the filtrates were evaporated to dryness. After addition of AcOH (2 ml) and KNCO (81 mg, 1 mmol), the mixture was stirred at r.t. for 1.5 h, evaporated to a small volume and, after addition of H_2O (5 ml), three times extracted with $CHCl_3$. The collected extracts were dried with K_2CO_3 and evaporated to dryness. The oily residue was separated by column chromatography.

Method C. Some selected oily fractions from the CC of the products of *Method A*, pure according to TLC, were dissolved in AcOH (2 ml) and then treated by *Method B*. The yields are given in *Table 6*.

*11-Butyl-11-[butyl(nitroso)amino]-1,2,3,6-tetrahydro-1-methyl-4*H*-2,6-methano-5,1,3-benzoxadiazocin-4-one* (**9d**). Prepared from **2d** by *Method B* in 43% yield and from **8d** by *Method C* in 71% yield. Colorless solid. M.p. 271 – 273° (AcOEt). IR: 3274, 2957, 2930, 2871, 1708, 1673, 1608, 1579, 1504, 1463, 1420, 1394, 1335, 1256, 1220, 1199, 1155, 1127, 1092, 1071, 1021, 993, 948, 927, 857, 837, 750, 628, 616, 586, 543. ESI-MS (pos.): 759.3 (8, $[2M + K]^+$), 743.4 (18, $[2M + Na]^+$), 721.4 (5, $[2M + H]^+$), 560.3 (6, $[3M + Ca]^{2+}$), 399.2 (100, $[M + K]^+$), 383.2 (66, $[M + Na]^+$), 361.3 (24, $[M + H]^+$). Anal. calc. for $C_{19}H_{28}N_4O_3$ (360.45): C 63.31, H 7.83, N 15.54; found: C 63.25, H 7.91, N 15.60.

*11-Benzyl-11-[butyl(nitroso)amino]-1,2,3,6-tetrahydro-1-methyl-4*H*-2,6-methano-5,1,3-benzoxadiazocin-4-one* (**9e**). Prepared from **2e** by *Method B* in 43% yield and from **8e** by *Method C* in 18% yield. Colorless solid. M.p. 276 – 278° (AcOEt). IR: 3272, 3029, 2958, 2872, 1709, 1676, 1606, 1580, 1502, 1465, 1418, 1393, 1264, 1217, 1112, 1086, 1023, 947, 883, 857, 838, 749, 702, 635, 618, 566. ESI-MS (pos.): 811.3 (9, $[2M + Na]^+$), 433.1 (32, $[M + K]^+$), 417.2 (100, $[M + Na]^+$), 395.2 (5, $[M + H]^+$). Anal. calc. for $C_{22}H_{26}N_4O_3$ (394.47): C 66.99, H 6.54, N 14.20; found: C 66.65, H 6.52, N 14.30).

*11-[Butyl(nitroso)amino]-1,2,3,6-tetrahydro-1-methyl-11-phenyl-4*H*-2,6-methano-5,1,3-benzoxadiazocin-4-one* (**9fA**). Prepared from **2f** by *Method B* in 26% yield and from **4f** by *Method B* in 9% yield. It rises also from **9fB** by its heating over m.p. Colorless solid. M.p. 235 – 240° (AcOEt). IR: 3287, 2960, 2874, 1721, 1695, 1604, 1503, 1444, 1411, 1337, 1248, 1216, 1150, 1100, 1084, 1001, 964, 915, 860, 827, 761, 750, 698, 678, 609, 555, 508. ESI-MS (pos.): 783.3 (25, $[2M + Na]^+$), 761.3 (5, $[2M + H]^+$), 419.1 (61, $[M + K]^+$), 403.2 (100, $[M + Na]^+$), 381.2 (6, $[M + H]^+$). Anal. calc. for $C_{21}H_{24}N_4O_3$ (380.44): C 66.30, H 6.36, N 14.73; found: C 65.98, H 6.39, N 14.80.

*11-[Butyl(nitroso)amino]-1,2,3,6-tetrahydro-1-methyl-11-phenyl-4*H*-2,6-methano-5,1,3-benzoxadiazocin-4-one* (**9fB**). Prepared from **2f** by *Method B* in 11% yield. Colorless solid. M.p. 155 – 161 and then 229 – 235° (AcOEt/cyclohexane). IR: 3396, 3229, 3125, 2959, 1738, 1713, 1607, 1581, 1500, 1447, 1421, 1339, 1249, 1213, 1197, 1153, 1101, 1079, 1044, 1016, 973, 942, 920, 821, 764, 708, 698, 632, 615, 557, 512. ESI-MS (pos.): 783.3 (15, $[2M + Na]^+$), 590.2 (44, $[3M + Ca]^{2+}$), 419.1 (47, $[M + K]^+$), 403.2 (100, $[M + Na]^+$), 400.2 (48, $[2M + Ca]^{2+}$), 381.2 (23, $[M + H]^+$). Anal. calc. for $C_{21}H_{24}N_4O_3$ (380.44): C 66.30, H 6.36, N 14.73; found: C 66.13, H 6.32, N 14.71.

*11-Butyl-11-[butyl(nitroso)amino]-1,2,3,6-tetrahydro-1-phenyl-4*H*-2,6-methano-5,1,3-benzoxadiazocin-4-one* (**9gA**). Prepared from **2g** *by Method B* in 21% yield and from **8g** by *Method C* in 31% yield. Colorless solid. M.p. 218 – 227° (benzene/hexane). IR: 3243, 3134, 2958, 2932, 2871, 1720, 1608, 1595, 1581, 1496, 1432, 1412, 1381, 1338, 1243, 1206, 1158, 1090, 1002, 906, 871, 837, 757, 736, 704, 631, 607, 546, 500. EI-MS: 423 (20), 422 (70, M^+), 350 (11), 349 (41), 348 (6), 291 (14), 278 (8), 277 (13), 275 (6), 266 (11), 263 (11), 262 (10), 250 (23), 249 (33), 248 (15), 234 (16), 233 (7), 208 (24), 207 (91), 206 (22), 196 (11), 195 (15), 194 (17), 193 (8), 180 (17), 167 (8), 140 (21), 131 (12), 98 (12), 85 (9), 84 (100), 77 (10), 59 (7), 57 (28), 55 (10), 43 (10), 41 (24). ESI-MS (pos.): 867.4 (8, $[2M + Na]^+$), 845.3 (5, $[2M + H]^+$), 461.2 (67, $[M + K]^+$), 445.2 (100, $[M + Na]^+$), 423.3 (44, $[M + H]^+$). Anal. calc. for $C_{24}H_{30}N_4O_3$ (422.52): C 68.22, H 7.16, N 13.26; found C 68.24, H 7.26, N 13.27.

*11-Butyl-11-[butyl(nitroso)amino]-1,2,3,6-tetrahydro-1-phenyl-4*H*-2,6-methano-5,1,3-benzoxadiazocin-4-one* (**9gB**). Prepared from **4g** by *Method B* in 32% yield. Colorless solid. M.p. 202 – 205° (benzene/hexane). IR: 3235, 3130, 2958, 2931, 2871, 1712, 1606, 1596, 1579, 1497, 1465, 1450, 1415, 1396, 1332, 1302, 1252, 1205, 1158, 1129, 1092, 1069, 993, 961, 910, 823, 757, 728, 697, 660, 611, 551, 499. EI-MS: 423 (28), 422 (99, M^+), 392 (11), 350 (9), 349 (35), 348 (8), 321 (29), 320 (100), 291 (7), 277 (8), 264 (16), 263 (39), 262 (31), 248 (10), 246 (9), 234 (11), 233 (7), 221 (14), 220 (6), 219 (8), 208 (12), 207 (19), 206 (10), 196 (11), 195 (9), 194 (14), 193 (8), 180 (16), 140 (17), 131 (12), 98 (11), 84 (56), 77 (10), 57 (12), 41 (15). ESI-MS (pos.): 867.4 (9, $[2M + Na]^+$), 653.3 (19, $[3M + Ca]^{2+}$), 461.2 (21, $[M + K]^+$), 445.2 (62, $[M + Na]^+$), 423.3 (100, $[M + H]^+$). Anal. calc. for $C_{24}H_{30}N_4O_3$ (422.52): C 68.22, H 7.16, N 13.26, found: C 68.51, H 7.28, N 13.15.

*11-Benzyl-11-[butyl(nitroso)amino]-1,2,3,6-tetrahydro-1-phenyl-4*H*-2,6-methano-5,1,3-benzoxadiazocin-4-one* (**9h**). Prepared from **2h** by *Method B* in 20% yield and from **8h** by *Method C* in 27% yield. Colorless solid. M.p. 220 – 229° (benzene/hexane). IR: 3399, 3237, 3130, 2958, 2872, 1721, 1607, 1495, 1463, 1416, 1382, 1340, 1244, 1204, 1109, 1084, 998, 892, 867, 756, 729, 702, 629, 593. ESI-MS (pos.): 935.4 (10, $[2M + Na]^+$), 913.3 (6, $[2M + H]^+$), 495.2 (6, $[M + K]^+$), 479.2 (100, $[M + Na]^+$), 457.3 (27, $[M + H]^+$). Anal. calc. for $C_{27}H_{28}N_4O_3$ (456.54): C 71.03, H 6.18, N 12.27; found: C 70.95, H 6.51, N 11.90.

*11-[Butyl(nitroso)amino]-1,2,3,6-tetrahydro-1,11-diphenyl-4*H*-2,6-methano-5,1,3-benzoxadiazocin-4-one* (**9i**). Prepared from **2i** by *Method B* in 1% yield. Colorless solid. M.p. 260 – 264° (benzene/cyclohexane). IR: 3447, 3266, 2961, 1739, 1606, 1577, 1498, 1445, 1409, 1382, 1337, 1291, 1235, 1207, 1105, 1081, 1014, 880, 758, 722, 695, 632. ESI-MS (pos.): 907.4 (8, $[2M + Na]^+$), 885.3 (5, $[2M + H]^+$), 683.3 (5, $[3M + Ca]^{2+}$, 481.2 (26, $[M + K]^+$), 465.2 (100, $[M + Na]^+$), 443.3 (15, $[M + H]^+$). Anal. calc. for $C_{26}H_{26}N_4O_3$ (442.51): C 70.57, H 5.92, N 12.66; found C 70.95, H 5.71, N 12.5.

2-(Methylamino)benzaldehyde (**10d**). Isolated from the reduction of **2e** (*Method A*, yield 3%; *Method B*, yield 3%), **2f** (*Method A*, yield 5%; *Method B*, yield 13%), and **4f** (*Method B*, yield 10%). Yellow oil. B.p. 128°/15 Torr. IR and ^{1}H-NMR data were identical with those published [25].

2-(Phenylamino)benzaldehyde (**10g**). Isolated from the reduction of **2g** (*Method A*, yield 13%; *Method B*, yield 14%), **4g** (*Method B*, 13%), **2h** (*Method A*, yield 21%; *Method B*, yield 14%), and **2i** (*Method A*, yield 29%; *Method B*, yield 27%). Yellow solid. M.p. 70 – 72° (hexane). For **10g**, a m.p. of 70 – 71° was published. The ^{1}H-NMR data were identical with those reported [26].

6. *General Procedure for the Conversion of Impure Compounds* **8** *to* **9**. *Method C.* To the soln. of selected crude compound **8**, obtained by reduction of **2** by *Method A* (0.25 mmol) in AcOH (2 ml), KNCO (27 mg, 0.33 mmol) was added. The mixture was stirred at r.t. for 2 h, crushed ice (15 ml) was added, and the sediment was filtered with suction. If oily compound arose, the mixture was extracted three times with $CHCl_3$. The collected extracts were dried with K_2CO_3 and evaporated to dryness. The oily residue was separated by CC (SiO_2). The following compounds **9**, identical in all respects to those prepared from corresponding compounds **2** by *Method B*, were prepared: **9d** (yield 71%), **9e** (yield 18%), **9gA** (yield 31%), and **9h** (yield 21%).

7. *General Procedure for the Reaction of Compounds* **5** *with Triphosgene.* Triphosgene (= bis(trichloromethyl)carbonate; 43 mg, 0.145 mmol) was added in several portions during 1 h to the well-stirred soln. of **5** (0.4 mmol), Et_3N (120 µl, 0.87 mmol), and 4-(dimethylamino)pyridine (DMAP; 20 mg, 0.18 mmol) in benzene (10 ml). The soln. was stirred at r.t. for 4 h, and the progress of the reaction was monitored by TLC. The suspension was filtered, and the filtrate was evaporated to dryness. H_2O (15 ml) was added to the residue, and the suspension was extracted with $CHCl_3$ (3 × 20 ml).

Collected extracts were washed with HCl (2.5%), dried, evaporated, and the residue was crystallized from the appropriate solvent. The mother liquors were subjected to CC (SiO_2).

3,3a-Dibutyl-3,3a,5,9b-tetrahydro-5-methyl[1,3]oxazolo[4,5-c]quinoline-2,4-dione (**6d**). Prepared from **5d**. Yield 22%. Colorless solid. M.p. 125 – 127° (benzene/hexane). IR: 3060, 2957, 2930, 2871, 1763, 1692, 1614, 1465, 1356, 1332, 1287, 1262, 1207, 1180, 1105, 1069, 1040, 1025, 1007, 979, 958, 916, 860, 825, 779, 755, 667, 636, 528. ESI-MS (pos.): 683.3 (31, $[2M + Na]^+$, 369.2 (27, $[M + K]^+$), 353.2 (99, $[M + Na]^+$), 331.2 (100, $[M + H]^+$), 287.2 (17, $[M + H - CO_2]^+$). Anal. calc. for $C_{19}H_{26}N_2O_3$ (330.42): C 69.06, H 7.93, N 8.48; found: C 68.88, H 8.15, N 8.54.

3-Butyl-3,3a,5,9b-tetrahydro-5-methyl-3a-phenyl[1,3]oxazolo[4,5-c]quinoline-2,4-dione (**6f**). Prepared from **5f**. Yield 42%. Colorless solid. M.p. 151 – 155° (benzene/hexane). IR: 3517, 3071, 2977, 2958, 2932, 2897, 2855, 1769, 1686, 1615, 1491, 1465, 1448, 1388, 1344, 1296, 1264, 1203, 1114, 1077, 1040, 1023, 975, 722, 870, 777, 764, 750, 714, 700, 684, 662, 637, 580, 544. ESI-MS (pos.): 723.3 (28, $[M + Na]^+$), 389.1 (17, $[M + K]^+$), 373.2 (89, $[M + Na]^+$), 351.2 (100, $[M + H]^+$), 307.2 (40, $[M + H - CO_2]^+$). Anal. calc. for $C_{21}H_{22}N_2O_3$ (350.16): C 71.98, H 6.33, N 7.99; found: C 72.09, H 6.34, N 8.05.

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