Reduction of 3-Aminoquinoline-2,4(1*H*,3*H*)-diones and Deamination of the Reaction Products

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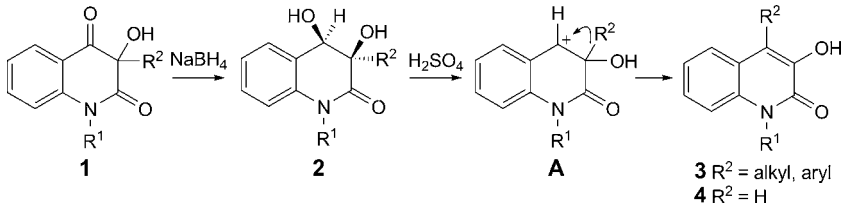
3-Aminoquinoline-2,4-diones were stereoselectively reduced with $NaBH_4$ to give *cis*-3-amino-3,4-dihydro-4-hydroxyquinolin-2(1*H*)-ones. Using triphosgene (= bis(trichloromethyl) carbonate), these compounds were converted to 3,3a-dihydrooxazolo[4,5-*c*]quinoline-2,4(5*H*,9b*H*)-diones. The deamination of the reduction products using HNO_2 afforded mixtures of several compounds, from which 3-alkyl/aryl-2,3-dihydro-1*H*-indol-2-ones and their 3-hydroxy and 3-nitro derivatives were isolated as the products of the molecular rearrangement.

Introduction. – Recently, we reported that the reduction of 3-hydroxyquinoline-2,4-diones **1** with $NaBH_4$ proceeds in a highly stereoselective manner to give *cis*-diols **2**. These compounds undergo rearrangement through the action of H_2SO_4 *via* an intermediate carbocation **A** to 4-alkyl/aryl-3-hydroxy-1*H*-quinolin-2-ones **3**. Starting with the 3-benzyl derivatives of **1**, 4-unsubstituted 3-hydroxy-1*H*-quinolin-2-ones **4** can be obtained (*Scheme 1*) [1].

Scheme 1

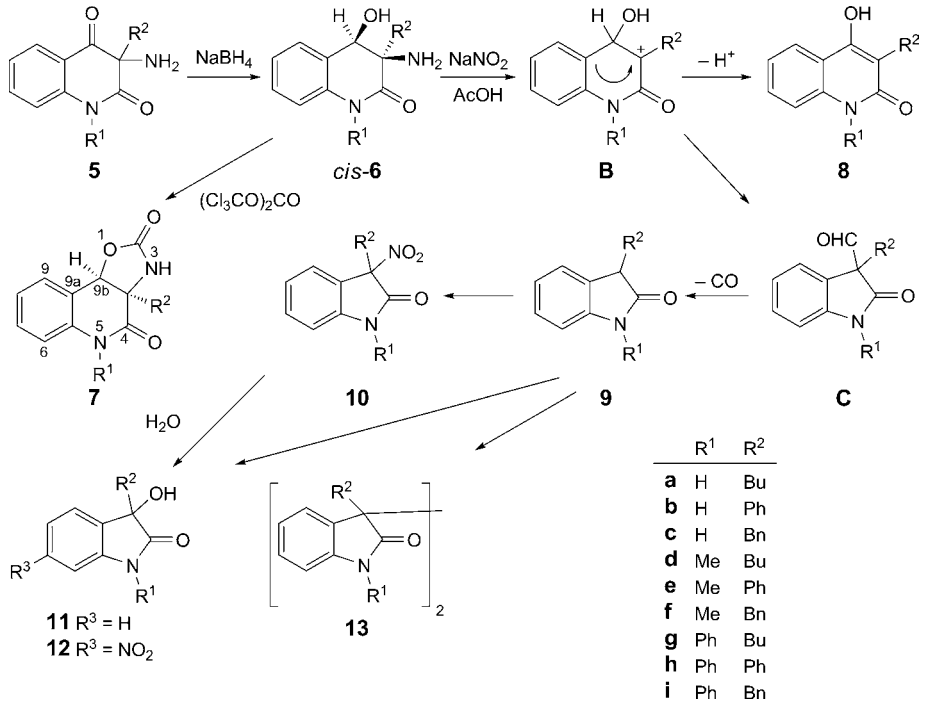


The ease and high stereoselectivity of the reduction of diones **1** to diols **2**, and their facile pinacol-pinacoline-type rearrangement to compounds **3** or **4**, which pertains to the synthesis of biologically active viridicatin alkaloids [2–6] (if R^2 = aryl), prompted us to study the analogous reactions of 3-aminoquinoline-2,4(1*H*,3*H*)-diones **5** (*cf. Scheme 2*). We found that the reduction of **5** with $NaBH_4$ also proceeds with high stereoselectivity and in high yields, but the subsequent deamination of **6** with HNO_2 is a complex reaction leading to a mixture of several products.

Results and Discussion. – For our experiments, we selected $NaBH_4$ as the reduction agent. The starting 3-aminoquinoline-2,4(1*H*,3*H*)-diones **5a**–**5i** were prepared by the reaction of the corresponding 3-chloroquinoline-2,4(1*H*,3*H*)-diones with NH_3 generated *in situ* according to a well-tested protocol [7]. In addition to the seven known compounds **5**, two novel amines **5f** and **5i** were prepared. Notably, the yields of these amines with a Bn group at C(3) were much lower than those of the amines with a Ph or Bu group at C(3) [7], and a considerable quantity of 3-hydroxy derivatives **1** was simultaneously obtained from this reaction.

Although many 3-aminoquinoline-2,4(1*H*,3*H*)-diones **5** are known, their reduction to the corresponding amino alcohols **6** (*cf. Scheme 2*) had not been described in the literature until recently. According to the literature, 25 reductions of α-amino ketones bearing a NH_2 group at a tertiary C-atom to the corresponding 2-amino alcohols were accomplished using different reagents; however, primarily the reactions with $NaBH_4$ [8–13] were successful. To determine the influence of the R^2 substituent on the transformation of diones **5**, we selected compounds with the Ph, Bu, and Bn groups in this position. The H, Me, and Ph groups were selected as the R^1 substituents.

Scheme 2



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

The results of the reduction of compounds **5** with $NaBH_4$ are compiled in *Table 1*. All of the reductions exhibited only one spot in TLC in several solvent systems. In the NMR spectra of the reaction products, only one set of signals was observed, indicating that the reaction proceeded with high stereoselectivity to give only one of the two

Table 1. *Reduction of Compounds* **5a**–**5i**.

Entry	Starting compound	R^1	R^2	Product (yield [%])[a])
1	**5a**	H	Bu	**6a** (75)
2	**5b**	H	Ph	**6b** (80)
3	**5c**	H	Bn	**6c** (75)
4	**5d**	Me	Bu	**6d** (73)
5	**5e**	Me	Ph	**6e** (90)
6	**5f**	Me	Bn	**6f** (75)
7	**5g**	Ph	Bu	**6g** (69)
8	**5h**	Ph	Ph	**6h** (78)
9	**5i**	Ph	Bn	**6i** (80)

[a]) The yields of pure recrystallized compounds.

possible diastereoisomers. This situation was completely analogous to that reported in our previous publication [1] for the derivatives with OH instead of NH_2 at C(3) (compare *Schemes 1* and *2*). The NOESY spectra of compounds **6** were recorded to determine the mutual orientation of the substituents at C(3) and C(4). The results strongly supported the through-space proximity of the H-atom at C(4) with the H-atoms of the R^2 substituent, evidenced by the appropriate cross-peaks in the NOESY spectra. However, additional cross-peaks were also observed, because compounds **6** are not completely rigid, and the dynamic behavior of the substituents at C(3) and C(4) (rotamers) give rise to additional cross-peaks. The reactions of compounds **6** with triphosgene (= bis(trichloromethyl) carbonate) afford compounds **7**, confirming the *cis*-configuration of the NH_2 and OH groups in **6**.

Compounds **6** were analyzed by two MS methods with differing ionization techniques, electron impact (EI) and electrospray ionization (ESI). In the first-order EI-mass spectra of compounds **6a**, **6d**, and **6g** (R^2 = Bu), and **6b**, **6e**, and **6h** (R^2 = Ph), the peak of the molecular radical cation, $M^{+\bullet}$, was unambiguously detected. On the other hand, in the EI-mass spectra of compounds with a Bn group at C(3), *i.e.*, **6c**, **6f**, and **6i**, the peak of the molecular ion, $M^{+\bullet}$, was not observed, and the most abundant peak was at the *m*/*z* corresponding to the $[M-Bn]^{+\bullet}$ fragment. The ESI-MS experiments of compounds **6** were performed in the positive-ion mode. In the first-order mass spectra, one dominant signal at *m*/*z* corresponding to the $[M+H]^+$ ion was observed for all of the examined compounds. In most of the cases, this signal was accompanied by that for the Na^+ adduct $[M+Na]^+$ and signals approximately twice as high for $[2M+H]^+$ and/or $[2M+Na]^+$. Moreover, in the first-order mass spectra of compounds **6a**, **6d**, and **6g** (R^2 = Bu), and **6b**, **6e**, and **6h** (R^2 = Ph), additional signals were detected. Using tandem mass spectrometry (under collision-induced dissociation conditions) of the $[M+H]^+$ ion, these signals were attributed to the singly charged fragments of the precursor ion originating from consecutive neutral losses of NH_3 ($[M+H-NH_3]^+$) and CO ($[M+H-NH_3-CO]^+$). While the latter product ion peak was observed in the ESI-mass spectra of compounds bearing both Bu and Ph substituents at C(3), the $[M+H-NH_3]^+$ ion peak was detected only in the spectra of compounds **6b**, **6e** and **6h** (R^2 = Ph). These signals were completely absent in the first-order mass spectra of compounds with a Bn group at C(3) (**6c**, **6f** and **6i**).

When a substituted α-amino alcohol is treated with HNO_2, its deamination is accompanied by rearrangement to form a ketone or an aldehyde; in some cases, the glycol corresponding to the amino alcohol is produced in varying yields [14]. The deamination of α-amino alcohols bearing a primary NH_2 group at the secondary C-atom to provide an intermediate carbocation is called the 'semipinacolinic' deamination [15]. The deamination of these types of α-amino alcohols with HNO_2 was studied in detail from 1923 to 1960, and this topic has been well-reviewed [16]. However, we were not able to find any analogous reaction involving the deamination of a compound with a OH group at the secondary C-atom and an NH_2 group at the tertiary C-atom. In this sense, the rearrangement of compounds **6** is exceptional.

In contrast to diols **2**, for which two different carbocations can form in the reaction with H_2SO_4 [1], the deamination of amino alcohols **6** with HNO_2 can result in only one carbocation **B** (*Scheme 2*). This carbocation can react with a nucleophile (possibly H_2O, or AcO^- or NO_2^- ions) to generate the corresponding 3,4-dihydro-4-hydroxyquinolin-2(1*H*)-ones substituted with OH, AcO, or NO_2 group at C(3). A further possibility is its deprotonation to yield 4-hydroxy-1*H*-quinolin-2-ones **8**. The molecular rearrangement of **B** can proceed through the migration of the aryl group in **B** (C(4a)) to C(3) to form aldehyde **C**. However, preliminary analyses of the products of the molecular rearrangement of **6** indicated that none of the molecules contain an aldehyde function.

Unfortunately, the deamination of compounds **6** yielded complex mixtures of several compounds according to TLC, and their separation was very difficult. This result is the main reason for the relatively low yields of isolated compounds (*Table 2*). The main reaction products were identified as 3-alkyl/aryl-2,3-dihydro-1*H*-indol-2-ones **9**, indicating that decarbonylation of the primarily formed intermediate **C** occured during the rearrangement. All of the isolated compounds **9** are known, but some of them have been insufficiently described. Therefore, we determined their spectroscopic characteristics (*Exper. Part*). In only one case, **6h**, the rearranged product **9h** was not isolated.

In addition to compounds **9** and starting compounds **6**, 4-hydroxy-1*H*-quinolin-2-ones **8** were obtained (*Table 2*). In *Scheme 2*, it is shown that the reaction pathway also proceeds through deprotonation of intermediate **B**. Compounds **8** do not form when the substituent R^2 in **6** is a Ph group. Through deamination of these compounds (*i.e.*, **6b**, **6e**, and **6h**), additional compounds were isolated (*Table 2*). According to elemental analysis, compounds containing an ONO or NO_2 group are present. Differentiation between these two possibilities was accomplished by studying the chemical shifts of C(3) in their ^{13}C-NMR spectra. In the literature, the signal of an sp^3-C-atom bearing both a C=O and a ONO group appears in the region of 82–84 ppm [17]. In analogous compounds, bearing a NO_2 group instead of a ONO group, the chemical shift of the sp^3-C-atom is detected in the region of 92–96 ppm [18][19]. The compounds that we isolated exhibit signals in the region from 94.4–94.9 ppm, which is consistent with structure **10**. Only two compounds of this type are known in the literature [20]. These compounds were prepared by oxidation of the corresponding 3-alkylindoles with thallium(III) trinitrate, but their NMR spectra were not reported. Structure **10** was finally confirmed through X-ray diffraction analysis of compound **10h**; the ORTEP view of this compound shows a NO_2 group at C(3) (*Fig.*). Compound **10h** crystallizes as

Table 2. *Rearrangement of Compounds* **6**

Entry	Starting compound	R^1	R^2	*Method*[a])	Products (yield [%])[b])
1	**6a**	H	Bu	*A*	**8a** (11)[c]), **9a** (24)
2				*B*	**8a** (13)[c]), **9a** (23)
3	**6b**	H	Ph	*A*	**9b** (3), **10b** (31), **13b** (4)
4				*B*	**6b** (21)[d]), **9b** (9), **10b** (7), **11b** (8)
5	**6c**	H	Bn	*A*	**8c** (11)[c]), **9c** (28)
6				*B*	**8c** (15)[c]), **9c** (35)
7	**6d**	Me	Bu	*A*	**6d** (10)[d]), **9d** (51)
8				*B*	**6d** (13)[d]), **9d** (42)
9	**6e**	Me	Ph	*A*	**2e** (1)[c]), **9e** (5), **10e** (28), **13e** (2)
10				*B*	**2e** (2)[c]), **9e** (11), **10e** (12), **13e** (2)
11	**6f**	Me	Bn	*A*	**8f** (4)[c]), **9f** (40)
12				*B*	**6f** (7)[d]), **8f** (7)[c]), **9f** (28)
13	**6g**	Ph	Bu	*A*	**6g** (28)[d]), **9g** (46)
14				*B*	**2g** (3)[c]), **6g** (27)[d]), **9g** (39)
15	**6h**	Ph	Ph	*A*	**10h** (4), **11h** (13), **12h** (3), **13h** (6)
16				*B*	**2h** (3)[c]), **6h** (5)[d]), **10h** (16), **11h** (9), **12h** (8), **13h** (3)
17	**6i**	Ph	Bn	*A*	**6i** (21)[d]), **8i** (16)[c]), **9i** (23)
18				*B*	**6i** (13)[d]) **8i** (9)[c]), **9i** (26)

[a]) *Method A:* $NaNO_2$ in AcOH, urea was added at the end of the reaction; *Method B:* as *Method A*, but without urea addition. [b]) The yields of pure recrystallized or distilled compounds. [c]) Identical in all respects to the authentic sample. [d]) Recovered starting material.

a racemic mixture in the triclinic space group $P\bar{1}$ with two molecules within the unit cell. From the selected bond distances and angles, the typical features of the aromatic C(3)–C(4) bond, as well those showing the peptidic character of N–C(=O) moiety and NO_2 group were deduced. Unfortunately, the only slightly similar but comparable molecules are two 7-nitro-6-oxo-3,4,6,7,8,9-hexahydroimidazo[4,5-*f*]indolizin-8a-carboxylates [21], in which the same arrangement of the NO_2 group at the aliphatic stereogenic center of a five-membered ring is present.

In the first-order positive-ion-mode ESI-MS spectra of compounds **10**, the most abundant peak was attributed to the $[M+H-NO_2]^{+\bullet}$ ion originating from in-source fragmentation of the $[M+H]^+$ ion, of which the peak was not observed in the mass spectra. On the other hand, other even-electron ions such as $[M+Na]^+$ and $[M+K]^+$ were formed under ESI conditions. Additionally, the last two ions undergo in-source fragmentation to give the $[M+Na-NO_2]^{+\bullet}$ and $[M+K-NO_2]^{+\bullet}$ ions.

Further isolated compounds, indicating the presence of a OH group in their IR spectra, were identified as **11**, mainly from the chemical shifts of C(3) at 77.2 and 77.4 ppm. In the ESI-mass spectra of compounds **11**, five significant signals were observed. The base peak, which we assigned to the $[M+H-H_2O]^+$ ion, was accompanied by those of the $[M+Na]^+$ and $[M+K]^+$ ions. Moreover, peaks of two types of singly charged dimeric $[2M+Na]^+$ and doubly charged trimeric $[3M+Ca]^{2+}$ ions were also detected.

These results indicate that the primary products of the rearrangement of compound **6** are most likely compounds **9**, which result from decarbonylation of intermediate **C**

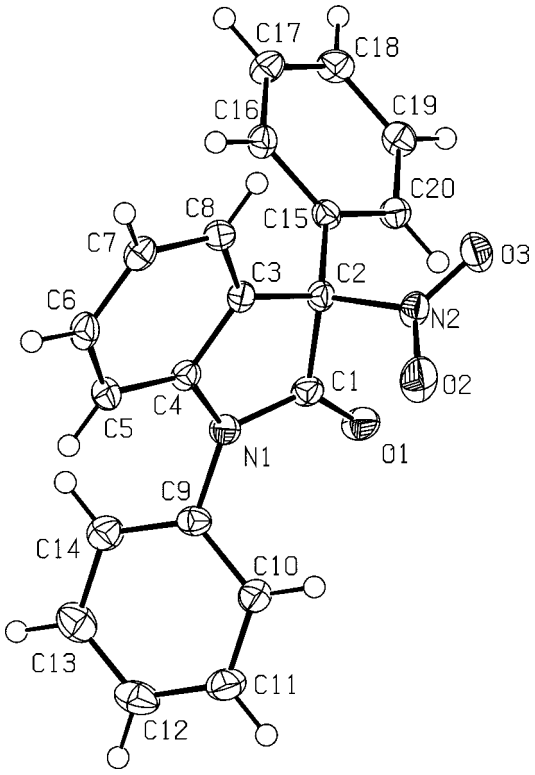


Figure. *The molecular structure of compound* **10h**, *ORTEP view* (50% probability level). Selected interatomic distances [Å] and angles [°]: O1–C1, 1.2063(16); C1–C2, 1.5588(18); C2–C3, 1.5047(16); C3–C4, 1.3935(17); N1–C4, 1.4162(16); N1–C1, 1.3697(17); N2–C2, 1.5510(16); N2–O2, 1.2220(15); N2–O3, 1.2112(15); O1–C1–N1, 127.06(12); C1–N1–C4, 110.89(11); O2–N2–O3, 124.66(12).

(*Scheme 2*). Independent of the method, compounds **10** are formed from nitration of **9** with HNO_3, which is the product of the decomposition of HNO_2 with H_2O [22][23]. However, these compounds originate only from **9b**, **9e**, and **9h**, which have a Ph group at C(3), which facilitates the replacement of an H-atom with the NO_2 group. Compounds **11** are hydrolytic products of **10**. Nucleophilic replacement of the aliphatic tertiary NO_2 group in α-position to the C=O group with a OH moiety proceeds easily not only under alkaline conditions [24], but also by heating in AcOH [25][26]. However, we cannot exclude that at least a portion of **11** is formed by direct oxidation of **9**.

Interestingly, compounds **12h** and **13h** were also obtained in low yields from the rearrangement of **6h**. The occurrence of compound **12h** evidences that nitration of the aromatic nucleus can proceed under the given reaction conditions not only at C(3), but also at C(6). In the literature, only one compound of this type, namely 1,3-dimethyl-3-[β-(dimethylamino)ethyl]-6-nitroindolinone, has been described as the product from nitration of the corresponding indolinone [27].

Dimeric compounds **13b**, **13e**, and **13h** resulted from dehydrogenation of the corresponding compounds **9**. The spontaneous dimerization of crude 3-substituted 2,3-dihydro-1*H*-indol-2-ones to produce a 3,3′-leucoisoindigo such as **13** has been described [17]. Several compounds **13**, including **13b** and **13e**, were prepared, in addition to dioxindoles **11**, by oxidation of the corresponding oxindoles **9** with O_2 in the presence of Co^{II} *Schiff*'s base complexes [28]. A dimer similar to **13** was also prepared by the reaction of 3-[(ethoxycarbonyl)methyl]indolin-2-one enolate with CI_4 and was used as a starting material for the synthesis of the alkaloid (±)-folicanthine [29]. Both the ^{1}H- and ^{13}C-NMR spectra of dimeric compounds **13b**, **13e**, and **13h** were very complex. They consisted of very broad signals that became narrower when the spectra were recorded at 360 K, and the original shape was observed again after cooling to 300 K. Hindered rotation due to the presence of bulky substituents is most likely responsible for this behavior.

Two methods were applied for the deamination of compounds **6** (*Table 2*). These methods differ only in that the addition of urea, which was used in *Method A* ($NaNO_2$ in AcOH) to quench the excess HNO_2, was omitted in *Method B.* However, as shown in *Table 2*, there are no substantial differences between the methods in most cases. Our presumption about the potential reduction of **10** with urea proved to be groundless.

To establish the origin of compounds **10** and **11**, we performed additional experiments. Compound **9h**, which we prepared as described in [30], was reacted with HNO_2 under the conditions of *Method C* (procedure as in *Method A*, but the charge of $NaNO_2$ was doubled, and the reaction time was prolonged). After separation of the crude reaction product by column chromatography (CC; SiO_2), the starting compound **9h** and three additional compounds, identified as **10h**, **12h**, and **13h**, were obtained. This result confirmed our assumption that compounds **10** result from **9** *via* nitration with HNO_3 produced from HNO_2 decomposition. Interesting results were obtained when the reaction of **9h** was performed in the presence of HNO_3 (*Method D*, procedure as in *Method A*, but concentrated HNO_3 was added instead of H_2O, and the reaction time was prolonged). Starting compound **9h** was not isolated, and, in addition to compound **11h**, which was the main reaction product, compound **10h** and a considerable quantity of 6-NO_2 derivative **12h** were obtained. The formation of compounds **11** from **10** was established by hydrolyzing **10h** with aqueous AcOH in the presence of urea. In addition to **11h**, a small quantity of **9h** was obtained, evidencing that the reduction of **10h** with urea also occurs, but only to a small extent at an elevated temperature.

Conclusions. – The described diastereoselective reduction of 3-aminoquinoline-2,4(1*H*,3*H*)-diones **5** represents an straightforward access to the previously unknown *cis*-amino alcohols **6**. The molecular rearrangement during their deamination with HNO_2 offered an alternative pathway to not only 3-alkyl/aryl-2,3-dihydro-1*H*-indol-2-ones **9**, but also 3-OH and 3-NO_2 derivatives **11** and **10**, respectively. Because many biologically active compounds and natural products possess a 3-hydroxy-oxindole framework with a tetrasubstituted stereogenic center C(3) [31][32], 3-NO_2 derivatives **10** are interesting structures for further study. In addition, compounds **10** are potential precursors for the synthesis of their 3-NH_2 analogs.

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Experimental Part

1. *General.* TLC: *Alugram® -SIL-G/UV$_{254}$* foils (*Macherey-Nagel*); elution with benzene/AcOEt 4:1, $CHCl_3$/EtOH 9:1 and/or 19:1, 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: *Smart OMNI-Transmission Nicolet iS10* spectrophotometer; KBr; in cm^{-1}. NMR Spectra: *Bruker Avance* spectrometer operating at 500.13 (^1H), 125.76 (^{13}C), and 50.68 MHz (^{15}N), and *Bruker Avance II 400* spectrometer operating at 400.13 (^1H), 100.56 (^{13}C), and 40.55 MHz (^{15}N); in (D_6)DMSO; δ in ppm rel. to TMS as an internal standard or to $MeNO_2$ as an external standard in a co-axial capillary; *J* in Hz; manufacturer's software for all 2D experiments (gradient-selected gs-COSY, gs-NOESY, gs-HMQC, and gs-HMBC). EI-MS (pos.): *Shimadzu QP-2010* instrument within *m/z* 50–600 using direct inlet probe (DI); analysis of samples in CH_2Cl_2 (30 µg/ml), 10 µl of the soln. 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 source as MeOH/H_2O 1:1 (*v/v*) solns. *via* a syringe pump at a constant flow rate of 4 µl/min; other instrumental conditions: *m/z* range 50–1500, electrospray voltage, −4.2 kV; drying gas temp., 220°; drying gas flow, 6.0 dm^3/min, nebulizer pressure, 55.16 kPa, cap. exit, 140 V; N_2 used as nebulizing as well as drying gas. Elemental analysis (C, H, N): *Flash EA 1112* elemental analyzer (*Thermo Fisher Scientific*).

Crystallography. Single crystals of **10h** were prepared by liquid diffusion method [33] with AcOEt/hexane as solvent/precipitant pair. The X-ray data were obtained at 150 K using *Oxford Cryostream* low-temperature device on a *Nonius KappaCCD 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 [34]. The absorption was corrected by integration methods [35]. Structures were solved by direct methods (SIR92) [36] and refined by full matrix least-square based on F^2 (SHELXL97) [37]. The H-atoms were mostly localized on a difference *Fourier* map; however, to ensure uniformity of treatment of crystal, all H-atoms were recalculated into idealized positions (riding model) and assigned temp. factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) with C–H = 0.93 Å for H-atoms in aromatic rings. $R_{int} = \Sigma | F_o^2 - F_{o,mean}^2 | / \Sigma F_o^2$, $GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$ 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. All X-ray diffraction experiments, refinement, and analysis of the obtained XRD data were carried out by *A. R.*

Crystallographic data have been deposited with the *Cambridge Crystallographic Data Centre*, No. CCDC-944756 for **10h**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

2. *General Procedure for the Preparation of 3-Aminoquinoline-2,4(1*H*,3*H*)-diones* **5f** *and* **5i**. Compounds were prepared by modifying the procedure described in [7]. The soln. of appropriate 3-chloroquinoline-2,4(1*H*,3*H*)-dione (40 mmol) in DMF (120 ml) was added during 15 min to the stirred and cooled (0°) suspension of NH_4Cl (4.27 g, 80 mmol) and K_2CO_3 (22.11 g, 160 mmol) in DMF (100 ml). The mixture was stirred for 48 h and then poured onto crushed ice (800 ml). In the case of **5f**, an oily product was obtained, which was extracted with $CHCl_3$ (3 × 30 ml), and the dried extract was separated by CC (SiO_2) to give **5f**. In the case of **5i**, the deposited precipitate was filtered with suction and suspended in HCl (10%, 160 ml). After 2 h intensive stirring, the soluble portion was extracted with benzene (3 × 15 ml), alkalized with aq. NH_3, and the precipitate of **5i** was filtered with suction and crystallized from benzene. The insoluble portion was filtered off, collected with the evaporation residue of benzene extract, and crystallized from AcOEt to give compound **5i**.

2.1. *3-Amino-3-benzyl-1-methylquinoline-2,4(1*H,*3*H*)-dione* (**5f**). Prepared from 3-benzyl-3-chloro-1-methylquinoline-2,4(1*H*,3*H*)-dione besides 2.36 g (21%) of *3-benzyl-3-hydroxy-1-methylquinoline-2,4(1*H,*3*H*)-dione* (**1f**). Yield: 3.584 g (32%). White solid. M.p. 101–104° (benzene/hexane). IR: 3392, 3319, 3059, 3025, 2917, 1697, 1654, 1601, 1546, 1473, 1373, 1298, 1242, 1109, 1016, 943, 899, 852, 771, 735, 698, 663, 624, 582, 513. ^{1}H- and ^{13}C-NMR: see *Table 3*. EI-MS: 281 (8), 280 (43, M^+), 190 (11), 189 (90), 162 (13), 161 (92), 133 (5), 118 (18), 116 (10), 106 (12), 105(5), 104 (10), 91 (11), 90 (7), 79 (6), 78 (9), 77 (23), 65 (20), 63 (6), 51 (10). ESI-MS (pos.): 561.2 (23, $[2M+H]^+$), 303.2 (4, $[M+Na]^+$), 281.2 (100, $[M+H]^+$), 264.2 (4, $[M+H-NH_3]^+$). Anal. calc. for $C_{17}H_{16}N_2O_2$ (280.32): C 72.84, H 5.75, N 9.99; found: C 72.86, H 5.75, N 9.63.

2.2. *3-Amino-3-benzyl-1-phenylquinoline-2,4(1*H,*3*H*)-dione* (**5i**). Prepared from 3-benzyl-3-chloro-1-phenylquinoline-2,4(1*H*,3*H*)-dione besides 4.94 g (36%) of *3-benzyl-3-hydroxy-1-phenylquinoline-2,4(1*H,*3*H*)-dione* (**1i**). Yield: 4.241 g (31%). White solid. M.p. 174–178° (benzene). IR: 3394, 3321, 3062, 3027, 2925, 1708, 1673, 1598, 1494, 1463, 1344, 1300, 1288, 1245, 1209, 1136, 1105, 1072, 980, 933, 831, 798, 758, 712, 702, 667, 646, 592, 521, 501. ^{1}H- and ^{13}C-NMR: see *Table 3*. EI-MS: 343 (11), 342 (45, M^+), 252 (16), 251 (94), 224 (17), 223 (100), 196 (18), 195 (13), 167 (24), 166 (8), 143 (9), 139 (6), 92 (9), 91 (56), 77 (24), 65 (7), 51 (13). ESI-MS (pos.): 685.2 (25, $[2M+H]^+$), 343.2 (100, $[M+H]^+$). Anal. calc. for $C_{22}H_{18}N_2O_2$ (342.39) : C 77.17, H 5.30, N 8.18; found: C 77.06, H 5.31, N 7.96.

Table 3. *^{1}H- and ^{13}C-NMR Data* ((D$_6$)DMSO) *of Compounds* **5** *and* **7** (δ in ppm)

Position	**5f**		**5i**		**7e**		**7h**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
2	–	171.9	–	176.1	–	158.5	–	158.3
3	–	69.7	–	69.9	9.26	–	9.34	–
3a	–	–	–	–	–	66.0	–	66.3
3-NH$_2$	2.25	–	2.24	–	–	–	–	–
4	–	194.8	–	194.8	–	167.2	–	167.1
4a	–	120.3	–	120.1	–	–	–	–
5	7.83	127.0	7.90	127.1	–	–	–	–
5a	–	–	–	–	–	137.6	–	137.7
6	7.25	123.0	7.22	123.2	7.17	116.2	6.23	117.4
7	7.71	136.2	7.51	135.7	7.15	123.6	7.14	123.9
8	7.28	115.6	6.31	116.5	7.30	128.4	7.09	128.2
8a	–	142.6	–	143.6	–	–	–	–
9	–	–	–	–	7.41	121.5	7.52	121.9
9a	–	–	–	–	–	124.5	–	124.5
9b	–	–	–	–	6.01	7.82	6.39	78.2
Substituent at N(1)								
1	3.38	29.7	–	137.7	3.40	29.9	–	–
2,6	–	–	7.38	129.3	–	–	7.34	129.0
			7.31	129.1				
3,5	–	–	7.82	130.1	–	–	7.63	130.1
			7.28	130.4				
4	–	–	7.57	129.0	–	–	7.55	128.9
Substituent at C(3)								
1	2.98	40.3	3.17	48.6	–	135.5	–	135.4
2	–	134.1	–	134.2	7.18	126.7	7.40	126.8
3,7	6.95	130.0	7.10	130.3	7.24	128.8	7.34	128.8
4,6	7.18	127.7	7.24	127.8	7.24	128.8	7.34	128.9
5	7.18	126.9	7.24	127.0	–	–	–	–

3. *General Procedure for the Reduction of Compounds* **5**. $NaBH_4$ (85 mg, 2.5 mmol) was added in four portions during 5 min to the stirred soln. of compound **5** (2 mmol) in MeOH (10 ml). After 20 min, crushed ice (up to 20 g), conc. HCl (0.25 ml), and H_2O (4 ml) were added in successive steps under cooling with crushed ice. The soln. was filtered, and the filtrate was alkalized with 6% $NaHCO_3$. Precipitated product was filtered off, washed with H_2O, and recrystallized from an appropriate solvent. The filtrate was extracted with $CHCl_3$ (3×20 ml). The dried extract was evaporated to dryness, and the residue was recrystallized from appropriate solvent. The yields are compiled in *Table 1*.

3.1. cis-*3-Amino-3-butyl-3,4-dihydro-4-hydroxyquinolin-2(1*H*)-one* (**6a**). Prepared from **5a**. Yield: 351 mg (75%). White solid. M.p. 175–177° (AcOEt). IR: 3365, 3073, 2958, 1681, 1596, 1565, 1486, 1390, 1307, 1251, 1201, 1072, 1033, 1004, 941, 840, 752, 698, 669, 520. ^{1}H- and ^{13}C-NMR: see *Table 4*. EI-MS: 234 (24, M^+), 160 (5), 132 (15), 122 (28), 121 (6), 113 (58), 105 (9), 104 (8), 94 (12), 93 (13), 85 (27), 77 (18), 71 (10), 57 (21), 56 (100), 55 (9), 43 (44). ESI-MS (pos.): 491.3 (5, $[2M+Na]^+$), 462.2 (4, $[2M+H]^+$), 257.2 (4, $[M+Na]^+$), 235.2 (100, $[M+H]^+$), 190.2 (15, $[M+H-NH_3-CO]^+$). Anal. calc. for $C_{13}H_{18}N_2O_2$ (234.29): C 66.64, H 7.74, N 11.96; found: C 66.42, H 7.72, N 11.86.

3.2. cis-*3-Amino-3,4-dihydro-4-hydroxy-3-phenylquinolin-2(1*H*)-one* (**6b**). Prepared from **5b**. Yield: 406 mg (80%). White solid. M.p. 248–254° (EtOH). IR: 3361, 3197, 3079, 2908, 1673, 1596, 1550, 1483, 1382, 1184, 1130, 1079, 1018, 975, 939, 817, 752, 694, 663, 568, 538. ^{1}H- and ^{13}C-NMR: see *Table 4*. EI-MS: 254 (24, M^+), 133 (31), 122 (15), 106 (13), 105 (100), 104 (48), 94 (8), 93 (8), 77 (28), 51 (8). ESI-MS (pos.): 277.2 (5, $[M+Na]^+$), 255.2 (100, $[M+H]^+$), 238.2 (29, $[M+H-NH_3]^+$), 210.2 (9, $[M+H-NH_3-CO]^+$). Anal. calc. for $C_{15}H_{14}N_2O_2$ (254.28): C 70.85, H 5.55, N 11.02; found: C 70.70, H 5.47, N 10.79.

3.3. cis-*3-Amino-3-benzyl-3,4-dihydro-4-hydroxyquinolin-2(1*H*)-one* (**6c**). Prepared from **5c**. Yield: 402 mg (75%). White solid. M.p. 184–194° and then 234–235° (AcOEt). IR: 3347, 3207, 3153, 3095, 2958, 2896, 2726, 1689, 1614, 1596, 1556, 1494, 1479, 1454, 1392, 1357, 1324, 1272, 1243, 1203, 1128, 1072, 1004, 935, 908, 755, 721, 700, 659, 592, 491. ^{1}H- and ^{13}C-NMR: see *Table 4*. EI-MS: 178 (11), 177 (100, $[M-Bn]^+$), 176 (43), 175 (6), 160 (40), 159 (13), 149 (10), 147 (13), 132 (75), 131 (14), 122 (13), 120 (15), 119 (42), 118 (11), 117 (9), 105 (9), 104 (36), 94 (8), 93 (16), 92 (17), 91 (58), 77 (33), 65 (23), 51 (11). ESI-MS (pos.): 307.2 (4, $[M+K]^+$), 291.2 (10, $[M+Na]^+$), 269.2 (100, $[M+H]^+$). Anal. calc. for $C_{16}H_{16}N_2O_2$ (268.31): C 71.62, H 6.01, N 10.44; found: C 71.73, H 6.04, N 10.39.

3.4. cis-*3-Amino-3-butyl-3,4-dihydro-4-hydroxy-1-methylquinolin-2(1*H*)-one* (**6d**). Prepared from **5d**. Yield: 362 mg (73%). White solid. M.p. 117–120° (benzene/hexane). IR: 3357, 3297, 2954, 2869, 1672, 1604, 1575, 1457, 1363, 1309, 1232, 1122, 1081, 1006, 950, 759, 673, 607. ^{1}H- and ^{13}C-NMR: see *Table 4*. EI-MS: 248 (10, M^+), 220 (11), 191 (12), 189 (9), 174 (14), 163 (9), 160 (7), 147 (7), 146 (31), 137 (11), 136 (100), 135 (19), 119 (8), 118 (51), 117 (8), 113 (69), 106 (20), 93 (8), 91 (22), 86 (13), 85 (20), 78 (7), 77 (20), 57 (11), 56 (88), 43 (34). ESI-MS (pos.): 491.3 (4, $[2M+Na]^+$), 271.3 (4, $[M+Na]^+$), 249.3 (100, $[M+H]^+$), 204.3 (11, $[M+H-NH_3-CO]^+$). Anal. calc. for $C_{14}H_{20}N_2O_2$ (248.32): C 67.71, H 8.12, N 11.28; found: C 67.94, H 8.14, N 11.31.

3.5. cis-*3-Amino-3,4-dihydro-4-hydroxy-1-methyl-3-phenylquinolin-2(1*H*)-one* (**6e**). Prepared from **5e**. Yield: 482 mg (90%). White solid. M.p. 199–203° (benzene). IR: 3353, 3288, 3066, 2881, 2817, 1668, 1604, 1548, 1473, 1365, 1259, 1201, 1124, 1076, 1039, 987, 848, 757, 703, 684, 615, 568, 545. ^{1}H- and ^{13}C-NMR: see *Table 4*. EI-MS: 268 (30, M^+), 136 (37), 135 (10), 134 (6), 133 (31), 118 (28), 106 (29), 105 (100), 104 (44), 91 (12), 77 (30), 51 (9). ESI-MS (pos.): 291.2 (5, $[M+Na]^+$), 269.3 (100, $[M+H]^+$), 252.2 (20, $[M+H-NH_3]^+$), 224.3 (8, $[M+H-NH_3-CO]^+$). Anal. calc. for $C_{16}H_{16}N_2O_2$ (268.31): C 71.62, H 6.01, N 10.44; found: C 71.78, H 6.11, N 10.45.

3.6. cis-*3-Amino-3-benzyl-3,4-dihydro-4-hydroxy-1-methylquinolin-2(1*H*)-one* (**6f**). Prepared from **5f**. Yield: 423 mg (75%). White solid. M.p. 137–140° (AcOEt). IR: 3350, 3281, 3059, 3028, 2884, 2816, 2718, 1665, 1604, 1591, 1495, 1472, 1415, 1371, 1207, 1117, 1071, 1048, 971, 871, 761, 730, 701, 643, 587, 508. ^{1}H- and ^{13}C-NMR: see *Table 4*. EI-MS: 192 (12), 191 (100, $[M-Bn]^+$), 190 (33), 174 (70), 173 (9), 147 (15), 146 (83), 145 (13), 136 (13), 119 (24), 118 (36), 117 (14), 106 (15), 104 (23), 92 (11), 91 (72), 77 (25), 65 (22), 51 (10). ESI-MS (pos.): 321.2 (4, $[M+K]^+$), 305.2 (5, $[M+Na]^+$), 283.3 (100, $[M+H]^+$). Anal. calc. for $C_{17}H_{18}N_2O_2$ (282.34): C 72.32, H 6.43, N 9.92; found: C 72.26, H 6.42, N 9.78.

3.7. cis-*3-Amino-3-butyl-3,4-dihydro-4-hydroxy-1-phenylquinolin-2(1*H*)-one* (**6g**). Prepared from **5g**. Yield: 428 mg (69%). White solid. M.p. 192–195° (AcOEt). IR: 3376, 3342, 3288, 2954, 2929, 2859, 1674,

Table 4. *^{1}H- and ^{13}C-NMR Data* ((D_6)DMSO) *of Compounds* **6** (δ in ppm)

Position	**6a**		**6b**		**6c**		**6d**		**6e**		**6f**		**6g**		**6h**		**6i**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
2	–	173.2	–	172.8	–	172.1	–	172.4	–	172.4	–	171.4	–	172.7	–	172.7	–	171.6
3	–	59.4	–	63.2	–	60.3	–	59.6	–	63.6	–	60.6	–	60.0	–	60.0	–	60.8
3-NH_2	1.84	–	2.46	–	1.75	–	1.85	–	2.48	–	1.79	–	1.95	–	1.95	–	1.90	–
4	4.62	72.9	4.93	73.4	4.54	72.3	4.62	72.1	4.95	72.4	4.56	71.5	4.83	72.2	4.83	72.2	4.73	71.7
4-OH	5.61	–	5.94	–	5.83	–	5.67	–	6.06	–	5.89	–	5.79	–	5.79	–	6.01	–
4a	–	127.3	–	127.8	–	127.0	–	128.8	–	129.3	–	128.4	–	128.4	–	128.4	–	128.1
5	7.39	126.0	7.34	125.2	7.38	126.0	7.46	125.8	7.37	124.7	7.46	126.1	7.52	126.3	7.52	126.3	7.50	126.3
6	7.01	122.1	6.98	122.5	7.03	122.1	7.13	122.8	7.06	123.1	7.14	122.8	7.10	122.9	7.10	122.9	7.11	123.0
7	7.21	127.9	7.19	127.8	7.22	128.1	7.34	128.1	7.29	127.9	7.37	128.3	7.14	127.7	7.14	127.8	7.18	128.1
8	6.86	114.4	6.93	114.6	6.93	114.5	7.11	114.1	7.15	114.3	7.16	114.3	6.20	115.4	6.20	115.4	6.27	115.9
8a	–	135.7	–	135.3	–	136.0	–	137.9	–	137.5	–	138.0	–	138.8	–	138.8	–	139.1
Substituent at N(1)																		
1	10.12	–	10.53	–	10.26	–	3.31	29.6	3.44	29.9	3.31	29.6	–	138.7	–	138.7	–	138.8
2,6	–	–	–	–	–	–	–	–	–	–	–	–	7.22	129.9	7.22	129.2	7.28	129.2
3,5	–	–	–	–	–	–	–	–	–	–	–	–	7.59	129.2	7.59	129.9	7.59	129.8
4	–	–	–	–	–	–	–	–	–	–	–	–	7.49	128.1	7.50	128.2	7.50	128.1
Substituent at C(3)																		
1	1.59, 1.27	31.0	–	140.4	2.86, 2.69	37.3	1.50, 1.22	31.1	–	140.4	2.80, 2.68	37.7	1.62, 1.44	31.0	1.64, 1.45	31.0	2.96, 2.84	37.5
2	1.35, 1.10	24.9	7.44	127.7	–	137.0	1.34, 1.08	24.9	7.26	127.7	–	136.8	1.44, 1.23	25.0	1.47, 1.23	25.0	–	136.8
3,7	1.17	22.8	7.17	127.4	7.18	130.6	1.16	22.8	7.13	127.4	7.07	130.5	1.23	22.8	1.23	22.8	7.26	130.8
4,6	0.83	14.1	7.17	126.9	7.26	127.6	0.81	14.1	7.13	126.9	7.26	127.7	0.88	14.1	0.86	14.1	7.31	127.8
5	–	–	–	–	7.21	126.1	–	–	–	–	7.22	126.3	–	–	–	–	7.26	126.8

1604, 1591, 1575, 1492, 1456, 1377, 1346, 1257, 1199, 1170, 1155, 1070, 1012, 989, 837, 756, 700, 646, 532, 501. ^{1}H- and ^{13}C-NMR: see *Table 4*. EI-MS: 310 (21, M^+), 236 (6), 235 (7), 223 (6), 208 (12), 198 (21), 197 (64), 196 (21), 181 (14), 180 (61), 169 (7), 168 (31), 167 (17), 152 (6), 150 (7), 149 (69), 113 (54), 105 (10), 104 (11), 97 (14), 93 (15), 86 (33), 85 (27), 84 (9), 83 (14), 81 (9), 77 (25), 71 (20), 70 (12), 69 (24), 67 (12), 65 (13), 57 (54), 56 (100), 55 (31), 51 (12), 43 (65), 42 (25), 41 (52). ESI-MS (pos.): 621.3 (5, $[2M+H]^+$), 311.3 (100, $[M+H]^+$), 266.3 (7, $[M+H-NH_3-CO]^+$). Anal. calc. for $C_{19}H_{22}N_2O_2$ (310.39): C 73.52, H 7.14, N 9.03; found: C 73.54, H 7.11, N 8.80.

3.8. cis-*3-Amino-3,4-dihydro-1,3-diphenyl-4-hydroxyquinolin-2(1*H*)-one* (**6h**). Prepared from **5h**. Yield: 515 mg (78%). White solid. M.p. 197–199° (AcOEt). IR: 3357, 3303, 3224, 3058, 1685, 1589, 1493, 1459, 1446, 1349, 1297, 1261, 1197, 1122, 1072, 1035, 947, 893, 852, 762, 721, 698, 679, 650, 555, 509. ^{1}H- and ^{13}C-NMR: see *Table 4*. EI-MS: 331 (5), 330 (20, M^+), 198 (13), 197 (53), 196 (18), 181 (9), 180 (41), 169 (6), 168 (28), 167 (12), 133 (26), 106 (32), 105 (100), 104 (51), 93 (8), 77 (32), 65 (6), 57 (6), 51 (13). ESI-MS (pos.): 683.3 (7, $[2M+Na]^+$), 661.2 (10, $[2M+H]^+$), 369.2 (5, $[M+K]^+$), 353.2 (10, $[M+Na]^+$), 331.2 (100, $[M+H]^+$), 314.2 (31, $[M+H-NH_3]^+$), 286.2 (24, $[M+H-NH_3-CO]^+$). Anal. calc. for $C_{21}H_{18}N_2O_2$ (330.38): C 76.34, H 5.49, N 8.48; found: C 76.44, H 5.52, N 8.51.

3.9. cis-*3-Amino-3-benzyl-3,4-dihydro-4-hydroxy-1-phenylquinolin-2(1*H*)-one* (**6i**). Prepared from **5i**. Yield: 550 mg (80%). White solid. M.p. 200–201° (AcOEt). IR: 3355, 3278, 3060, 2917, 2724, 1676, 1585, 1489, 1454, 1358, 1346, 1292, 1255, 1201, 1128, 1072, 975, 955, 877, 856, 759, 729, 698, 640, 598, 503. ^{1}H- and ^{13}C-NMR: see *Table 4*. EI-MS: 254 (17), 253 (100, $[M-Bn]^+$), 252 (24), 236 (45), 235 (16), 208 (42), 197 (13), 196 (9), 180 (43), 168 (19), 167 (14), 120 (9), 119 (28), 118 (9), 104 (22), 92 (11), 91 (41), 77 (27), 65 (18), 51 (13). ESI-MS (pos.): 689.3 (11, $[2M+H]^+$), 345.3 (100, $[M+H]^+$). Anal. calc. for $C_{22}H_{20}N_2O_2$ (344.41): C 76.72, H 5.85, N 8.13; found: C 76.83, H 5.90, N 8.13.

4. *Reaction of Compounds* **6** *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 **6** (0.4 mmol), Et_3N (0.121 ml, 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 1 h, and 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 benzene (3×20 ml). Collected extracts were dried, evaporated, and the residue was crystallized from appropriate solvent or subjected to CC (SiO_2).

4.1. *3,3a,5,9b-Tetrahydro-5-methyl-3a-phenyl[1,3]oxazolo[4,5-*c*]quinoline-2,4-dione* (**7e**). Prepared from **6e**. Yield: 82 mg (70%). White solid. M.p. 267–273° (EtOH). IR: 3232, 3123, 2971, 1754, 1690, 1614, 1584, 1492, 1465, 1448, 1395, 1346, 1304, 1265, 1209, 1191, 1160, 1131, 1092, 1021, 976, 949, 939, 896, 768, 722, 700, 679, 639, 581, 548. ^{1}H- and ^{13}C-NMR: see *Table 3*. EI-MS: 295 (19), 294 (100, M^+), 266 (18), 250 (13), 221 (15), 207 (12), 206 (11), 205 (7), 194 (16), 165 (11), 163 (18), 152 (10), 147 (21), 146 (13), 135 (61), 134 (58), 118 (64), 117 (16), 107 (33), 106 (89), 105 (36), 104 (82), 103 (34), 91 (30), 90 (13), 89 (22), 78 (21), 77 (96), 76 (18), 65 (14), 63 (17), 51 (43). ESI-MS (pos.): 333.2 (27, $[M+K]^+$), 317.2 (84, $[M+Na]^+$), 295.3 (51, $[M+H]^+$), 251.3 (100, $[M+H-CO_2]^+$). Anal. calc. for $C_{17}H_{14}N_2O_3$ (294.30): C 69.38, H 4.79, N 9.52; found: C 69.43, H 4.91, N 9.37.

4.2. *3,3a,5,9b-Tetrahydro-3a,5-diphenyl[1,3]oxazolo[4,5-*c*]quinoline-2,4-dione* (**7h**). Prepared from **6h**. Yield: 92 mg (65%). White solid. M.p. 260–270° (EtOH). IR: 3292, 3062, 2972, 1778, 1702, 1612, 1492, 1459, 1324, 1257, 1200, 1132, 1095, 1025, 948, 935, 896, 765, 752, 723, 696, 638, 596, 582. ^{1}H- and ^{13}C-NMR: see *Table 3*. EI-MS: 357 (22), 356 (89, M^+), 328 (23), 285 (9), 284 (36), 283 (28), 256 (18), 208 (7), 207 (21), 205 (7), 197 (29), 196 (44), 181 (17), 180 (100), 179 (10), 168 (36), 152 (15), 127 (14), 104 (34), 103 (21), 89 (14), 77 (72), 63 (10), 51 (39). ESI-MS (pos.): 735.2 (5, $[2M+Na]^+$), 395.2 (7, $[M+K]^+$), 379.3 (28, $[M+Na]^+$), 357.3 (31, $[M+H]^+$), 313.3 (100, $[M+H-CO_2]^+$). Anal. calc. for $C_{22}H_{16}N_2O_3$ (356.37): C 74.15, H 4.53, N 7.86; found: C 74.22, H 4.75, N 7.76.

5. Rearrangement of Compounds **6**. *Method A.* Under intensive stirring, compound **6** (0.75 mmol) was dissolved in AcOH (4.5 ml). After cooling to 0°, H_2O (0.45 ml) and then solid $NaNO_2$ (103 mg, 1.5 mmol) were added during 5 min, and stirring was continued for 2 h 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 and washed with H_2O (10 ml). The filtrate was extracted with $CHCl_3$ (3×20 ml). The extract was dried and evaporated *in vacuo* to dryness. Both portions were collected and subjected to CC (SiO_2). In the cases when the crude product was pasty,

the reaction mixture was extracted with $CHCl_3$ (3×20 ml), the collected extracts were evaporated to dryness and purified by CC (SiO_2). *Method B:* The reaction was carried out in the same way as *Method A*, merely the addition of urea was omitted. The yields are collected in *Table 2*.

5.1. *3-Butyl-1,3-dihydro-2*H-*indol-2-one* (**9a**). Prepared from **6a.** Yields: 34 (24%, *Method A*) and 33 mg (23%; *Method B*). White solid. M.p. 62–64° ([38]: 62–63° (hexane)). IR: 2956, 2931, 2867, 1705, 1618, 1469, 1411, 1376, 1340, 1317, 1228, 1172, 1153, 1101, 1020, 1002, 941, 929, 868, 831, 795, 748, 727, 704, 667, 580, 557, 492. ^{1}H- and ^{13}C-NMR: see *Table 5*. EI-MS: 189 (21, M^+) , 146 (49), 133 (100), 132 (29), 128 (7), 119 (7), 118 (8), 117 (10), 105 (7), 104 (19), 91 (6), 90 (5), 78 (7), 77 (21), 51 (9). ESI-MS (pos.): 401.2 (8, $[2M+Na]^+$), 379.3 (23, $[2M+H]^+$), 228.1 (5, $[M+K]^+$), 212.2 (19, $[M+Na]^+$), 190.2 (100, $[M+H]^+$). Anal. calc. for $C_{12}H_{15}NO$ (189.25): C 76.16, H 7.99, N 7.40; found: C 76.22, H 8.05, N 7.49.

5.2. *1,3-Dihydro-3-phenyl-2*H-*indol-2-one* (**9b**). Prepared from **6b**. Yields: 5 (3%; *Method A*) and 14 mg (9%; *Method B*). White solid. M.p. 190–195° ([39]: 190–192° (benzene/hexane)). IR: 3185, 3085, 3031, 1704, 1616, 1469, 1322, 1224, 1182, 1097, 1074, 1035, 939, 871, 836, 752, 709, 684, 663, 593. ^{1}H- and ^{13}C-NMR: see *Table 5*. EI-MS: 210 (14), 209 (87, M^+), 181 (15), 180 (100), 179 (6), 165 (8), 152 (15), 96 (16), 90 (15), 89 (6), 77 (14), 76 (12), 63 (6), 51 (9). ESI-MS (pos.): 441.2 (14, $[2M+Na]^+$), 438.2 (5, $[4M+Ca]^{2+}$), 419.2 (25, $[2M+H]^+$), 333.7 (13, $[3M+Ca]^{2+}$), 232.2 (17, $[M+Na]^+$), 229.2 (8, $[2M+Ca]^{2+}$), 210.2 (100, $[M+H]^+$), 132.2 (38, $[M+H-C_6H_6]^+$). Anal. calc. for $C_{14}H_{11}NO$ (209.24): C 80.36, H 5.30, N 6.69; found C 80.20, H 5.12, N 6.45.

5.3. *3-Benzyl-1,3-dihydro-2*H-*indol-2-one* (**9c**). Prepared from **6c**. Yields: 47 (28%; *Method A*) and 58 mg (35%; *Method B*). White solid. M.p. 129–131° ([40]: 129–130° (AcOEt/hexane)). IR: 3033, 2920, 2895, 2850, 1708, 1622, 1496, 1471, 1340, 1311, 1236, 1151, 1078, 1016, 962, 937, 854, 808, 748, 694, 665, 613, 588, 550. ^{1}H- and ^{13}C-NMR: see *Table 5*. EI-MS: 223 (19, M^+), 132 (17), 104 (6), 92 (8), 91 (100), 77 (10), 65 (10), 51 (6). ESI-MS (pos.): 485.2 (6, $[2M+K]^+$), 469.2 (12, $[2M+Na]^+$), 466.2 (6, $[4M+Ca]^{2+}$), 447.2 (5, $[2M+H]^+$), 354.7 (9, $[3M+Ca]^{2+}$), 262.1 (6, $[M+K]^+$), 246.2 (32, $[M+Na]^+$), 243.2 (17, $[2M+Ca]^+$), 224.2 (100, $[M+H]^+$), 196.2 (19, $[M+H-CO]^+$). Anal. calc. for $C_{15}H_{13}NO$ (223.27): C 80.69, H 5.87, N 6.27; found: C 80.25, H 5.95, N 6.52.

5.4. *3-Butyl-1,3-dihydro-1-methyl-2*H-*indol-2-one* (**9d**). Prepared from **6d**. Yields: 78 (51%; *Method A*) and 64 mg (42%; *Method B*). Yellowish oil, b.p. 110–120°/0.5 Torr ([41]: 120–122°/0.6 Torr). IR: 3055, 2956, 2931, 1712, 1614, 1494, 1469, 1376, 1346, 1259, 1130, 1085, 1020, 925, 750, 701, 611, 541. ^{1}H- and ^{13}C-NMR: see *Table 5*. EI-MS: 203 (58, M^+), 202 (54), 174 (11), 161 (16), 160 (100), 148 (10), 147 (50), 132 (15), 131 (11), 130 19), 104 (8). ESI-MS (pos.): 429.3 (19, $[2M+Na]^+$), 426.3 (7, $[4M+Ca]^{2+}$), 407.3 (5, $[2M+H]^+$), 242.2 (13, $[M+K]^+$), 226.2 (44, $[M+Na]^+$), 204.2 (100, $[M+H]^+$). Anal. calc. for $C_{13}H_{17}NO$ (203.28): C 76.81, H 8.43, N 6.89; found: C 76.65, H 8.41, N 6.79.

5.5. *1,3-Dihydro-1-methyl-3-phenyl-2*H-*indol-2-one* (**9e**). Prepared from **6e**. Yields: 8 (5%; *Method A*) and 18 mg (11%; *Method B*). White solid. M.p. 117–120° ([42]: 117–119° (cyclohexane)). IR: 3052, 3023, 2933, 2908, 1693, 1610, 1496, 1465, 1374, 1346, 1263, 1170, 1124, 1085, 1020, 931, 877, 752, 730, 703, 642, 543. ^{1}H- and ^{13}C-NMR: see *Table 5*. EI-MS: 224 (18), 223 (100, M^+), 195 (13), 194 (73), 180 (6), 179 (10), 167 (11), 165 (15), 153 (7), 152 (12), 150 (7), 149 (52), 139 (8), 127 (11), 125 (11), 118 (13), 113 (14), 111 (19), 109 (9), 99 (13), 97 (26), 95 (13), 85 (31), 84 (10), 83 (32), 82 (13), 81 (16), 77 (11), 76 (11), 71 (53), 70 (20), 69 (32), 57 (69), 56 (14), 55 (33), 43 (51). ESI-MS (pos.): 469.2 (36, $[2M+Na]^+$), 447.2 (5, $[2M+H]^+$), 354.7 (9, $[3M+Ca]^{2+}$), 262.1 (36, $[M+K]^+$), 246.2 (100, $[M+Na]^+$), 243.2 (30, $[2M+Ca]^+$), 224.2 (78, $[M+H]^+$). Anal. calc. for $C_{15}H_{13}NO$ (223.27): C 80.69, H 5.87, N 6.27; found: C 80.27, H 5.82, N 6.14.

5.6. *3-Benzyl-1,3-dihydro-1-methyl-2*H-*indol-2-one* (**9f**). Prepared from **6f**. Yields: 71 (40%; *Method A*) and 50 mg (28%; *Method B*). White solid. M.p. 65–68° ([43]: 67–68° (hexane)). IR: 3055, 3027, 2917, 1700, 1610, 1492, 1469, 1454, 1371, 1355, 1338, 1265, 1232, 1157, 1120, 1087, 991, 894, 850, 792, 755, 750, 725, 703, 622, 584, 539. ^{1}H- and ^{13}C-NMR: see *Table 5*. EI-MS: 238 (7), 237 (39, M^+), 160 (8), 147 (8), 146 (75), 118 (8), 117 (7), 92 (8), 91 (100), 77 (5), 65 (13). ESI-MS (pos.): 497.2 (26, $[2M+Na]^+$), 494.3 (9, $[4M+Ca]^{2+}$), 375.8 (18, $[3M+Ca]^{2+}$), 276.2 (13, $[M+K]^+$), 260.2 (82, $[M+Na]^+$), 257.2 (35, $[2M+Ca]^+$), 238.3 (100, $[M+H]^+$), 210.3 (5, $[M+H-CO]^+$). Anal. calc. for $C_{16}H_{15}NO$ (237.30): C 80.98, H 6.37, N 5.90; found: C 80.68, H 6.34, N 5.84.

5.7. *3-Butyl-1,3-dihydro-1-phenyl-2*H-*indol-2-one* (**9g**). Prepared from **6g**. Yields: 91 (46%; *Method A*) and 78 mg (39%; *Method B*). Yellowish oil. B.p. 165–185°/0.5 Torr ([30]: 170–190°/0.5 Torr). IR:

Table 5. *^{1}H- and ^{13}C-NMR Data* ((D_6)DMSO) *of Rearrangement Products of* **6***: Compounds* **9** (δ in ppm)

Position	**9a**		**9b**		**9c**		**9d**		**9e**		**9f**		**9g**		**9h**		**9i**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
2	–	179.0	–	176.9		178.2	–	177.0	–	175.4	–	176.2	–	176.6	–	175.0	–	175.9
3	3.45	45.1	4.77	51.7	3.84	46.5	3.53	44.6	4.87	51.2	3.91	46.0	3.78	44.8	5.11	51.5	4.14	46.2
3a	–	129.9	–	129.9	–	129.0	–	129.0	–	129.2	–	128.1	–	128.9	–	129.3	–	129.7
4	7.27	124.0	7.08	124.6	6.90	124.4	7.33	123.7	7.13	124.5	6.91	124.0	7.44	124.3	7.22	125.1	7.16	124.7
5	6.98	121.3	6.99	121.4	6.87	121.0	7.07	122.0	7.07	122.4	6.95	121.7	7.14	122.6	7.13	123.0	7.04	122.3
6	7.20	127.6	7.27	127.9	7.14	127.7	7.32	127.7	7.38	128.3	7.25	127.0	7.26	127.8	7.31	128.2	7.17	128.0
7	6.85	109.2	6.97	109.3	6.77	109.2	7.02	108.2	7.13	108.7	6.92	108.2	6.76	108.7	6.84	109.1	6.60	108.6
7a	–	142.9	–	142.7	–	142.7	–	144.3	–	144.3	–	144.1	–	144.0	–	144.0	–	144.0
Substituent at N(1)																		
1	10.38	–	10.43	–	10.36	–	3.16	25.9	3.23	26.2	3.10	25.9	–	134.6	–	134.5	–	134.5
2,6	–	–	–	–	–	–	–	–	–	–	–	–	7.44	126.7	7.53	127.0	7.25	126.7
3,5	–	–	–	–	–	–	–	–	–	–	–	–	7.62	129.7	7.64	129.7	7.58	129.7
4	–	–	–	–	–	–	–	–	–	–	–	–	7.49	128.0	7.51	128.3	7.48	127.9
Substituent at C(3)																		
1	1.90, 1.82	29.6	–	137.6	3.36, 2.99	35.3	1.92, 1.82	29.6	–	144.3	3.38, 2.97	35.5	2.02, 1.97	29.8	–	137.6	3.46, 3.21	35.8
2	1.23	27.4	7.20	128.1	–	138.2	1.22	27.4	7.18	128.5	–	138.0	1.34	27.3	7.33	128.6	–	137.5
3, 7	1.29	22.3	7.39	128.5	7.18	129.4	1.29	22.2	7.38	128.8	7.18	129.3	1.34	22.2	7.43	128.9	7.17	129.4
4, 6	0.87	13.9	7.32	126.9	7.25	128.1	0.86	13.8	7.33	127.3	7.27	128.1	0.88	13.8	7.37	127.4	7.23	128.1
5	–	–	–	–	7.21	126.4	–	–	–	–	7.20	126.4	–	–	–	–	7.21	126.6

2956, 2929, 2857, 1720, 1612, 1502, 1481, 1463, 1373, 1326, 1220, 1170, 1101, 1025, 752, 700, 644, 626, 590, 566. ^{1}H- and ^{13}C-NMR: see *Table 5*. EI-MS: 266 (9), 265 (44, M^+), 223 (12), 222 (67, 210 (16), 209 (100), 196 (14), 181 (8), 180 (47), 167 (12), 152 (12), 115 8), 91 (14), 77 (28), 51 (19). ESI-MS (pos.): 553.3 (6, $[2M+Na]^+$), 531.2 (6, $[2M+H]^+$), 304.2 (7, $[M+K]^+$), 288.3 (19, $[M+Na]^+$), 266.3 (100, $[M+H]^+$). Anal. calc. for $C_{18}H_{19}NO$ (265.35): C 81.47, H 7.22, N 5.28; found: C 81.21, H 7.13, N 5.13.

5.8. *1,3-Dihydro-1,3-diphenyl-2*H-*indol-2-one* (**9h**). Prepared according to [30]. White solid. M.p. 110–112° ([30]: 111–113° (hexane)). IR: 3068, 3028, 2998, 1713, 1610, 1594, 1501, 1467, 1454, 1366, 1325, 1298, 1251, 1215, 1178, 1168, 1099, 1074, 1026, 980, 883, 868, 795, 756, 739, 697, 659, 638, 619, 601, 505. ^{1}H- and ^{13}C-NMR: see *Table 5*. EI-MS: 286 (13), 285 (59, M^+), 257 (21), 256 (100), 254 (16), 180 (13), 152 (8), 128 (7), 127 (13), 77 (10), 51 (8). ESI-MS (pos.): 593.2 (14, $[2M+Na]^+$), 571.2 (4, $[2M+H]^+$), 324.2 (20, $[M+K]^+$), 308.2 (58, $[M+Na]^+$), 286.2 (100, $[M+H]^+$). Anal. calc. for $C_{20}H_{15}NO$ (285.34): C 84.19, H 5.30, N 4.91; found: C 84.29, H 5.30, N 4.76.

5.9. *3-Benzyl-1,3-dihydro-1-phenyl-2*H-*indol-2-one* (**9i**). Prepared from **6i**. Yields: 52 (23%; *Method A*) and 58 mg (26%; *Method B*). White solid. M.p. 90–94° ([30]: 90–94° (i-PrOH)). IR: 3060, 3035, 2917, 2865, 1722, 1608, 1592, 1496, 1479, 1463, 1452, 1371, 1327, 1275, 1225, 1171, 1101, 1078, 1024, 914, 845, 752, 733, 700, 645, 633, 594, 561. ^{1}H- and ^{13}C-NMR: see *Table 5*. EI-MS: 300 (13), 299 (54, M^+), 222 (10), 209 (13), 208 (81), 181 (7), 180 (49), 179 (12), 178 (8), 152 (19), 92 (8), 91 (100), 77 (22), 65 (13), 51 (19). ESI-MS (pos.): 621.2 (11, $[2M+Na]^+$), 599.2 (7, $[2M+H]^+$), 338.2 (10, $[M+K]^+$), 322.2 (24, $[M+Na]^+$), 300.2 (100, $[M+H]^+$). Anal. calc. for $C_{21}H_{17}NO$ (299.37): C 84.25, H 5.72, N 4.68; found: C 84.02, H 5.71, N 4.50.

5.10. *1,3-Dihydro-3-nitro-3-phenyl-2*H-*indol-2-one* (**10b**). Prepared from **6b**. Yields: 59 (31%; *Method A*) and 13 mg (7%; *Method B*). Yellowish solid. M.p 140–142° (benzene/hexane). IR: 3208, 3178, 3108, 1727, 1617, 1552, 1471, 1448, 1411, 1340, 1328, 1295, 1218, 1101, 1083, 1002, 948, 821, 748, 698, 674, 644, 620, 611, 485. ^{1}H- and ^{13}C-NMR: see *Table 6*. EI-MS: 210 (14), 209 (93), 208 (32), 181 (17), 180 (100), 179 (11), 178 (6), 152 (17), 90 (17), 89 (7), 77 (12), 76 (12), 63 (5), 51 (6). ESI-MS (pos.): 531.1 (5, $[2M+Na]^+$), 293.1 (20, $[M+K]^+$), 277.2 (16, $[M+Na]^+$), 247.1 (17, $[M+K-NO_2]^+$), 231.2 (24, $[M+Na-NO_2]^+$), 208.2 (100, $[M+H-NO_2]^+$), 180.2 (8, $[M+H-NO_2-CO]^+$). Anal calc. for $C_{14}H_{10}N_2O_3$ (254.24): C 66.14, H 3.96, N 11.02; found: C 66.08, H 3.80, N 10.93.

5.11. *3,4-Dihydro-1-methyl-3-nitro-3-phenylquinolin-2(1*H*)-one* (**10e**). Prepared from **6e**. Yields: 56 (28%; *Method A*) and 24 mg (12%; *Method B*). Yellow solid, m.p. 123–128° (cyclohexane). IR: 3060, 2975, 2937, 1727, 1610, 1558, 1492, 1469, 1336, 1245, 1128, 1089, 952, 806, 752, 738, 696, 684, 538. ^{1}H- and ^{13}C-NMR: see *Table 6*. EI-MS: 224 (15), 223 (100), 222 (68), 208 (8), 207 (14), 195 (11), 194 (69), 193 (11), 179 (10), 178 (6), 166 (7), 165 (26), 153 (6), 152 (17), 151 (8), 118 (12), 116 (7), 89 (8), 76 (7). ESI-MS (pos.): 559.2 (5, $[2M+Na]^+$), 307.1 (45, $[M+K]^+$), 291.2 (62, $[M+Na]^+$), 261.1 (37, $[M+K-NO_2]^+$), 245.2 (98, $[M+Na-NO_2]^+$), 222.2 (100, $[M+H-NO_2]^+$), 194.2 (4, $[M+H-NO_2-CO]^+$). Anal. calc. for $C_{15}H_{12}N_2O_3$ (268.27): C 67.16, H 4.51, N 10.44; found: C 66.99, H 4.47, N 10.45.

5.12. *1,3-Dihydro-3-nitro-1,3-diphenyl-2*H-*indol-2-one* (**10h**). Prepared from **6b**. Yields: 10 (4%; *Method A*) and 40 mg (16%; *Method B*). Yellowish solid, M.p. 133–138° (benzene/hexane). IR: 3066, 3043, 2924, 1739, 1610, 1594, 1556, 1498, 1465, 1446, 1371, 1340, 1324, 1309, 1213, 1180, 1099, 1076, 1025, 962, 948, 835, 808, 757, 732, 694, 651, 622, 588. ^{1}H- and ^{13}C-NMR: see *Table 6*. EI-MS: 286 (11), 285 (50), 284 (8), 257 (21), 256 (100), 254 (20), 180 (16), 179 (6), 178 (6), 152 (11), 151 (6), 128 (8), 127 (15), 51 (9), 44 (7). ESI-MS (pos.): 683.1 (3, $[2M+Na]^+$), 369.1 (16, $[M+K]^+$), 353.2 (24, $[M+Na]^+$), 323.2 (30, $[M+K-NO_2]^+$), 307.2 (66, $[M+Na-NO_2]^+$), 285.2 (100, $[M+H-NO_2]^+$). Anal. calc. for $C_{20}H_{14}N_2O_3$ (330.34): C 72.72, H 4.27, N 8.48; found: C 72.29, H 4.26, N 8.26.

Crystallographic Data for **10h**. $C_{20}H_{14}N_2O_3$, M_r 330.33, triclinic, $P\bar{1}$, $a=8.7901(5)$, $b=9.5950(4)$, $c=9.9790(3)$ Å, $\alpha=91.935(4)$, $\beta=101.309(6)$, $\gamma=106.188(5)°$, $Z=2$, $V=789.07(7)$ Å^3, $D_c=1.390$ g cm^{-3}, $\mu=0.095$ mm^{-1}, $T_{min}/T_{max}=0.973/0.982$; $-11\le h\le 11$, $-12\le k\le 12$, $-12\le l\le 12$; 14684 reflections measured ($\theta_{max}=27.5°$), 14644 independent ($R_{int}=0.0229$), 3073 with $I>2\sigma(I)$, 226 parameters, $S=1.077$, R_1 (obs. data) $=0.0388$, wR_2 (all data) $=0.0971$; max., min. residual electron density $=0.303$, -0.227 eÅ^{-3}.

5.13. *1,3-Dihydro-3-hydroxy-3-phenyl-2*H-*indol-2-one* (**11b**). Prepared from **6b**. Yield: 14 mg (8%, *Method B*). White solid. M.p. 211–216° ([44]: 211–214° (benzene)). IR: 3415, 3214, 3072, 1708, 1617, 1469, 1340, 1303, 1184, 1120, 1066, 939, 900, 781, 755, 738, 690, 665, 609, 497. ^{1}H- and ^{13}C-NMR: see

Table 6. *^{1}H-, ^{13}C-, and ^{15}N-NMR Data* ((D_6)DMSO) *of Rearrangement Products of* **6***: Compounds* **10**, **11**, *and* **12** (δ in ppm)

Position	**10b**		**10e**		**10h**		**11b**		**11h**		**12h**	
	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	–	246.0[a])	–	–	–	–	–	–	–	–	–	–
2	–	168.8	–	167.4	–	166.9	–	178.6	–	176.4	–	176.0
3	–	94.9	–	94.4	–	94.6	–	77.4	–	77.2	–	76.8
3-OH	–	–	–	–	–	–	6.67	–	6.99	–	7.33	–
3a	–	124.9	–	123.4	–	123.2	–	133.8	–	133.1	–	133.5
4	7.63	126.1	7.69	125.9	7.81	126.5	7.15	124.9	7.30	125.1	7.57	126.0
5	7.24	123.2	7.32	123.8	7.38	124.4	7.01	122.1	7.16	123.5	8.06	119.2
6	7.55	132.4	7.66	132.5	7.59	132.6	7.29	129.3	7.35	129.5	–	148.4
7	7.11	111.4	7.33	110.6	6.97	110.9	6.95	109.9	6.68	109.4	7.47	103.9
7a	–	143.0	–	144.3	–	144.2	–	142.0	–	143.2	–	144.3
Substituent at N(1)												
1	11.38[b])	–	3.30	27.0	–	133.0	10.45	–	–	134.3	–	139.9
2, 6	–	–	–	–	7.55	126.9	–	–	7.51	126.8	7.59	126.8
3, 5	–	–	–	–	7.66	130.1	–	–	7.64	129.8	7.68	130.2
4	–	–	–	–	[c])	129.2	–	–	7.53	128.3	7.59	129.0
Substituent at C(3)												
1	–	131.8	–	131.6	–	131.6	–	141.6	–	141.3	–	139.9
2	7.53	129.0	7.52	129.0	[c])	129.1	7.33	125.5	7.43	125.5	7.53	125.5
3, 7	7.51	128.3	7.52	128.4	[c])	128.4	7.36	128.2	7.44	128.4	7.50	128.7
4, 6	7.55	130.2	7.55	130.3	[c])	130.5	7.31	127.5	7.35	127.8	7.50	128.3

[a]) $\delta(^{15}N)$. [b]) $^1J(^{15}N,^1H) = 95.1$ Hz. [c]) 7.57 – 7.64.

Table 6. EI-MS: 225 (38, M^+), 198 (8), 197 (61), 196 (100, $[M-29]^+$), 180 (13), 167 (8), 120 (29), 105 (15), 98 (12), 92 (18), 77 (31), 76 (11), 65 (12), 51 (12), identical to that of (*R*)-**11b** [45]. ESI-MS (pos.): 489.1 (5, $[2M+K]^+$), 473.1 (43, $[2M+Na]^+$), 470.2 (10, $[4M+Ca]^{2+}$), 357.7 (64, $[3M+Ca]^{2+}$), 264.1 (53, $[M+K]^+$), 248.2 (100, $[M+Na]^+$), 208.2 (98, $[M+H-H_2O]^+$), 180.2 (10, $[M+H-H_2O-CO]^+$). Anal. calc. for $C_{14}H_{11}NO_2$ (225.24): C 74.65, H 4.92, N 6.22; found C 74.50, H 4.97, N 5.95.

5.14. *1,3-Dihydro-3-hydroxy-1,3-diphenyl-2*H-*indol-2-one* (**11h**). Prepared from **6h**. Yields: 29 (13%; *Method A*) and 20 mg (9%; *Method B*). Colorless solid. M.p. 170 – 175° ([46]: 172 – 173° (benzene/cyclohexane)). IR: 3419, 3027, 1708, 1612, 1594, 1498, 1465, 1454, 1374, 1355, 1282, 1172, 1112, 1068, 1025, 989, 927, 902, 827, 779, 755, 725, 700, 647, 611, 576, 489 cm^{-1}. ^{1}H- and ^{13}C-NMR: see *Table 6*. EI-MS: 302 (7), 301 (31, M^+), 274 (6), 273 (35), 272 (100), 256 (8), 196 (9), 191 (13), 167 (18), 166 (6), 105 (17), 77 (43), 57 (26), 51 (15). ESI-MS (pos.): 625.1 (22, $[2M+Na]^+$), 471.7 (14, $[3M+Ca]^{2+}$), 340.2 (12, $[M+K]^+$), 324.2 (33, $[M+Na]^+$), 302.2 (5, $[M+H]^+$), 284.2 (100, $[M+H-H_2O]^+$). Anal. calc. for $C_{20}H_{15}NO_2$ (301.34): C 79.72, H 5.02, N 4.65; found: C 79.59, H 4.94), N 4.63.

5.15. *1,3-Dihydro-3-hydroxy-6-nitro-1,3-diphenyl-2*H-*indol-2-one* (**12h**). Prepared from **6h**. Yields: 8 (3%; *Method A*) and 21 mg (8%; *Method B*). Colorless solid. M.p. 301 – 305° (AcOEt). IR: 3335, 3092, 1705, 1609, 1527, 1453, 1434, 1376, 1345, 1260, 1210, 1177, 1119, 1060, 1032, 958, 918, 870, 858, 837, 779, 731, 714, 697, 656, 643, 505. EI-MS: 347 (7), 346 (31, M^+), 319 (7), 318 (37), 317 (57), 301 (11), 285 (12), 273 (7), 272 (20), 271 (17), 256 (21), 167 (10), 166 (6), 135 (11), 105 (37), 77 (49), 51 (11), 45 (13), 44 (100). ESI-MS (pos.): 385.1 (10, $[M+K]^+$), 369.2 (100, $[M+Na]^+$), 347.2 (25, $[M+H]^+$), 329.2 (75, $[M+H-H_2O]^+$). Anal. calc. for $C_{20}H_{14}N_2O_4$ (346.34): C 69.36, H 4.07, N 8.09; found: C 69.45, H 4.19, N 7.94.

5.16. *1,1′,3,3′-Tetrahydro-3,3′-diphenyl-2*H,*2′*H-*3,3′-biindole-2,2′-dione* (**13b**). Prepared from **6b**. Yield: 12.5 mg (4%; *Method A*). White solid. M.p. 187 – 206° ([47]: 188 – 192°, [28]: 234 – 236°

(AcOEt/hexane). IR: 3416, 3203, 3057, 1705, 1673, 1618, 1595, 1472, 1448, 1374, 1326, 1296, 1239, 1201, 1104, 1067, 1026, 1002, 926, 873, 846, 758, 750, 696, 658, 608, 589, 570, 537. ESI-MS (pos.): 455.1 (12, $[M+K]^+$), 439.2 (37, $[M+Na]^+$), 417.2 (100, $[M+H]^+$), 208.2 (100, $[M+H-209]^+$). Anal. calc. for $C_{28}H_{20}N_2O_2$ (416.67): C 80.75, H 4.84, N 6.73; found C 80.50, H 4.97, N 6.95.

5.17. *1,1′,3,3′-Tetrahydro-1,1′-dimethyl-3,3′-diphenyl-2*H,*2′*H-*3,3′-biindole-2,2′-dione* (**13e**). Prepared from **6e**. Yields: 7 (2%; *Method A*) and 7 mg (2%; *Method B*). White solid. M.p. 212–220° ([28]: 215–217° (benzene/cyclohexane)). IR: 3048, 2962, 2929, 2881, 1708, 1608, 1492, 1471, 1373, 1347, 1259, 1133, 1081, 1027, 973, 757, 736, 701, 646, 603, 541, 526. EI-MS: 223 (81), 222 (100), 208 (8), 207 (26), 195 (12), 194 (68), 193 (16), 192 (9), 181 (11), 179 (11), 166 (11), 165 (37), 153 (11), 152 (26), 151 (13), 127 (11), 126 (10), 118 (9), 116 (12), 113 (10), 111 (24), 99 (12), 98 (9), 97 (22), 96 (10), 95 (8), 91 (12), 89 (11), 85 (23), 84 (12), 83 (24), 82 (14), 77 (12), 76 (14), 71 (39), 70 (16), 69 (24), 57 (46), 55 (20), 43 (40), 41 (15). ESI-MS (pos.): 911.3 (26, $[2M+H]^+$), 483.2 (4, $[M+K]^+$), 467.2 (100, $[M+Na]^+$), 445.3 (7, $[M+H]^+$). Anal. calc. for $C_{30}H_{24}N_2O_2$ (444.52): C 81.06, H 5.44, N 6.30; found: C 80.98, H 5.43, N 6.21.

5.18. *1,1′,3,3′-Tetrahydro-1,1′,3,3′-tetraphenyl-2*H,*2′*H-*3,3′-biindole-2,2′-dione* (**13h**). Prepared from **6h**. Yields: 26 (6%; *Method A*) and 13 mg (3%; *Method B*). White solid. M.p. 220–223°(EtOH). IR: 3059, 2922, 1720, 1607, 1589, 1498, 1464, 1372, 1324, 1297, 1239, 1203, 1179, 1105, 1073, 1033, 1011, 912, 879, 758, 732, 698, 654, 633, 612, 597, 521. EI-MS: 286 (10), 285 (50), 284 (36), 257 (21), 256 (100), 255 (10), 254 (35), 181 (7), 180 (14), 179 (8), 178 (10), 152 (16), 151 (11), 128 (9), 127 (23), 126 (10), 77 (23), 51 (23). ESI-MS (pos.): 607.2 (8, $[M+K]^+$), 591.2 (16, $[M+Na]^+$), 569.2 (55, $[M+H]^+$), 324.2 (12, $[M+K-283]^+$), 308.2 (33, $[M+Na-283]^+$), 286.3 (100, $[M+H-283]^+$). Anal. calc. for $C_{40}H_{28}N_2O_2$ (568.66): C 84.48, H 4.96, N 5.63; found: C 84.68, H 5.06, N 5.63.

6. *Transformations of Compounds* **9** *and* **10**. 6.1. *Reaction of* **9h** *with* HNO_2. *Method C.* The reaction was carried out in the same way as described for *Method A*, merely the charge of $NaNO_2$ was doubled, and the reaction time was prolonged to 3 h. CC (SiO_2) of the crude reaction product provided compounds **9h** (66 mg, 31%), **10h** (37 mg, 15%), **12h** (16 mg, 6%) and **13h** (30 mg, 7%).

6.2. *Reaction of* **9h** *with* $NaNO_2$ *and* HNO_3. *Method D.* The reaction was carried out in the same way as described for *Method A*, merely the addition of H_2O was omitted, conc. HNO_3 (0.2 ml) was added, and the reaction time was prolonged to 3 h. CC (SiO_2) of the crude reaction product furnished compounds **10h** (37 mg, 15%), **11h** (59 mg, 26%), and **12h** (41 mg, 16%).

6.3. *Reaction of* **10h** *with Urea.* The soln. of **10h** (42 mg, 0.126 mmol) and urea (11 mg, 0.18 mmol) in AcOH (2 ml) and H_2O (0.1 ml) was heated to 50° for 3 h. The reaction mixture was diluted with H_2O and extracted with $CHCl_3$. After evaporation, the residue was purified by CC (SiO_2), to yield **10h** (19 mg, 62%), **11h** (7 mg, 24%) and **9h** (0.3 mg, 1%).

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