Mechanism of Photoinduced Reactions between 1-Acetylisatin and Aldehydes

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Hydrogen atom abstraction from aliphatic (**2a**, **2b**) and aromatic (**2c**, **2d**, **2e**) aldehydes by the triplet $n\pi^*$ state of 1-acetylisatin (**1**) yielded triplet (isatin ketyl-aldehyde acyl) radical pairs, which follow an out-of-cage pathway in subsequent reactions to give a series of radical coupling products **4**–**7**. This out-of-cage mechanism is supported by examination of the primary products at various degrees of conversions during the course of the reaction, by the results of addition reactions of thermally generated isatin acyl radical with neutral **1,** and by calculation of the charge density distribution in the acyl radicals and in ground state **1**. Therefore, the oxygen-philic attack of the acyl radical, which had escaped out of cage from the triplet radical pair, at the C(3) carbonyl oxygen atom of a ground state **1** selectively afforded the thermodynamically more stable addition radical **B**. The recombination of two radicals **B** gave the 3-indolinone dimers **4** and **5** as diastereomers, while coupling of **B** with the isatin ketyl furnished the dihydroisoindigo derivative **6**. Isatide **7** was also formed by ketyl radical recombination. The product ratio is dependent on the structure of the aldehyde. For **2d** and **2e**, each with an electron-donating substituent in the benzene ring, the corresponding acyl radicals are less electrophilic because of a diminished positive charge density at the carbonyl carbon atom, and the formation of the addition radical **B** is a slow process relative to the encounter and recombination of the isatin ketyl radicals. As a result, products **6d** and **6e** from cross-coupling of the isatin ketyl and radical B are formed in much lower yields than **6a**, **6b**, and **6c**. The 3-acetyloxy-2-indolinone **3** turned out to be a secondary product derived from the decomposition of **6** during the workup procedures. Since all the primary products are formed by out-of-cage radical pair combination processes, no chain mechanism is involved.

Introduction

Aldehydes each have a weak C(O)−H bond with a dissociation enthalpy of 86±1[1a] (or 89.3±0.4[1b,1c]) kcal·mol^{-1}, similar to that in benzylic (88±1 kcal·mol^{-1})[1a] and allylic (86±1 kcal·mol^{-1})[1a] C−H bonds. As a result, aldehydes serve as good hydrogen atom donors for $n\pi^*$ triplet excited carbonyl compounds. There have been several investigations on hydrogen abstraction reactions of triplet *p*-quinones[2−4] and *o*-quinones[5−7] from aldehydes from synthetic and mechanistic viewpoints. These reactions are of special synthetic value because they provide straightforward and efficient routes to acetylquinones (the photo-Friedel−Crafts reaction) and acetyloxyarenes. Mechanistically, two distinct reaction pathways for the triplet semiquinone-acyl radical pairs formed in the hydrogen abstraction step have been suggested. They could either undergo in-cage radical pair recombination after intersystem crossing (ISC) to give an adduct, or else the two radicals in the pair might escape out of cage and take part in subsequent reactions in the bulk solution. Which pathway is taken may depend on the structures of the quinone and the aldehyde, as well as on reaction conditions, and may have to be clarified from case to case. There are still confusions and controversies in this respect. In an early study, Waters suggested an out-of-cage free radical chain mechanism for the photoaddition between benzaldehyde and phenanthrenequinone to give 9-benzoyloxy-10-hydroxyphenanthrene.[5] Bruce later put forward a similar out-of-cage free radical mechanism, based on trapping of the radical intermediates by styrene and 1,1-diphenylethylene, to account for the formation of 2-acetylhydroquinone in the photoreaction between 1,4-benzoquinone and acetaldehyde.[6] In addition, in triplet benzophenone-sensitized photoinduced reductive acylation reactions of benzoquinone (BQ), the acyl moiety formed by hydrogen abstraction from the aldehyde by the triplet benzophenone obviously adds to the BQ by an out-of-cage pathway.[2] On the other hand, from product studies and photo-CIDNP measurements, Maruyama suggested that photoinduced reactions of *o*-quinones (phenanthrenequinone[7a,7c] and 1,2-naphthoquinone[7d]) and *p*-quinone (1,4-naphthoquinone[3]) with aliphatic and aromatic aldehydes predominately follow the in-cage pathway.

1-Acetylisatin (**1**) has an $n\pi^*$ triplet state with a triplet energy of about 64 kcal·mol^{-1}.[8,9a] We have recently investigated photoinduced [2+2] cycloadditions (the Paterno−Büchi reaction) between **1** and a series of alkenes[9a,9b] and alkynes.[10] In the photoinduced reaction

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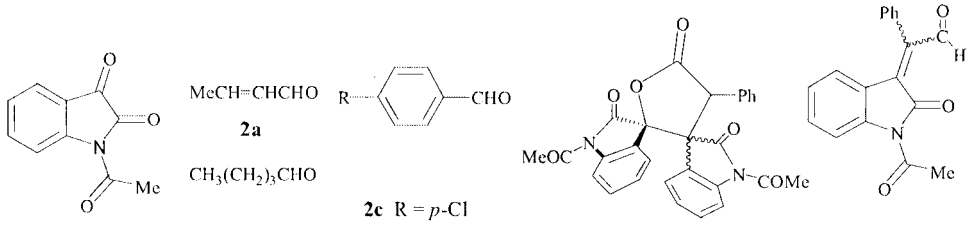
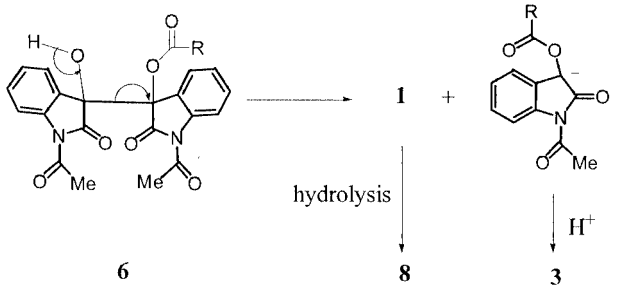


1 2b I II

between **1** and phenylacetylene,[10] a pair of diastereoisomeric 2:1 addition products **I** is derived from a secondary reaction by the hydrogen abstraction from the aldehyde functionality of the primary product **II** by triplet excited **1**. To gain more insight into the mechanistic details of the triplet hydrogen abstraction of *o*-quinones from aldehydes, we investigated photoinduced reactions between **1** and both aliphatic and aromatic aldehydes **2a**−**2e**.

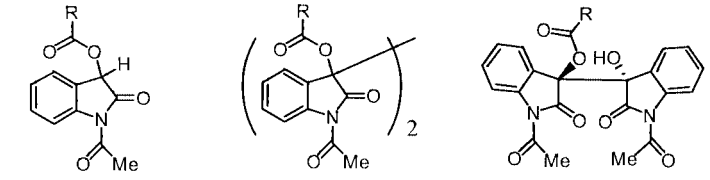
Results and Discussion

The longest-wavelength absorption band in the UV spectrum of 1-acetylisatin (**1**),[8] at 347−379 nm ($\varepsilon = 2.84 \times 10^3$ $L \cdot mol^{-1} \cdot cm^{-1}$), shows a hypsochromic shift with increasing solvent polarity and is assigned as an $n\pi^*$ band. This long-wavelength absorption tails well into the visible region. Photoinduced reactions between **1** and compounds **2** were therefore carried out in dry benzene solution with light of $\lambda > 400$ nm for selective excitation of **1**. The reactions proceeded rapidly, with gradual fading of the yellow color of **1**. In the case of the photoreaction between **1** and **2a**, complete conversion of **1** was reached in 4 hr. Chromatographic separation of the reaction mixture gave the 3-acyloxy-2-indolinone **3a** (11%), two 3,3′-dihydroisoindigo derivatives − 3,3′-diacyloxy-3,3′-bi-2*H*-indole-2,2′-dione **4** (27%) and the 3-acyloxy-3′-hydroxy-3,3′-bi-2*H*-indole-2,2′-dione **6** (36%), isatide **7** (5%), and *N*-acylanthranilic acid (**9**) (15%). However, ^{1}H NMR spectral monitoring of the reaction course at different time intervals during the photolysis indicated that only products **4**, **6** and **7** were the primary products formed in the photoreactions, while **3** and **9** were absent in the photolysate throughout the reaction course and were derived during the subsequent workup procedures. A control experiment on the thermal reactions of **6c** (vide infra) further showed that **6c** is thermally labile when absorbed on silica gel and gave **3c** (58%) and **8** (21%) as the main decomposition products when heating on silica gel (see Exp. Sect.). In another control experiment, the pinacol **7** was also found to be thermally labile, decomposing quantitatively into **8** when heated in the presence of silica gel. The reaction pathway resulting in the thermal conversion of **6** to **3** and **8** is outlined in Scheme 1. Deprotonation of the hydroxy group in **6** resulted in its decomposition to isatin **1**



6 8 3

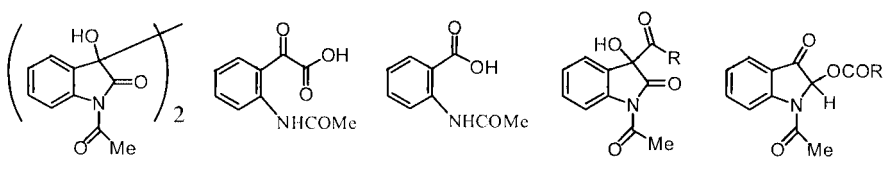
Scheme 1



3a R = MeCH=CH-
3b R = $Me(CH_2)_3$-
3c R = *p*-ClPh-
3d R = *p*-MeOPh-
3e R = *o*-OHPh-

4 and **5**
4a R = MeCH=CH-
4b, **5b** R = $Me(CH_2)_3$-
4c, **5c** R = *p*-ClPh-
4d, **5d** R = *p*-MeOPh-
4e R = *o*-OHPh-

6a R = MeCH=CH-
6b R = $Me(CH_2)_3$-
6c R = *p*-ClPh-



7 8 9 10 11

Table 1. Photoinduced reactions between **1** and **2**

2	Irradiation time (h)	Conversion (%)[a]	Products and yield (%)[b]
2a	4	100	**3a** (11), **4a** (27), **6a** (36), **7** (5), **9** (15)
2b	1.5	100	**3b** (15), **4b** (11), **5b** (14), **6b** (30), **7** (16), **9** (12)
2c	3	100	**3c** (9), **4c** (11), **5c** (17), **6c** (34), **7** (19), **8**(6)
2d	3	100	**3d** (15), **4d** (17), **5d** (24), **7** (22), **8** (14), **9** (3)
2e	9	100	**3e** (33), **4e** (25), **7** (21)

[a] All the reactions were carried out in benzene solution under nitrogen. [**1**] = 0.05 mol·L^{-1}, [RCHO] = 0.5 mol·L^{-1}. [b] Yield of isolated pure product.

and 3-acyloxy-3-oxindolyl anion, which on protonation gave **3**. Meanwhile, a separate experiment showed that the isatin adsorbed on silica gel containing trace amounts of water is hydrolyzed into **8** upon heating (Scheme 1).

Photoinduced reactions between **1** and **2b**−**2e** in benzene solution were also investigated, and these gave results similar to the reaction between **1** and **2a**, with the corresponding compounds **4**, **5**, **6**, and **7** as the primary products directly formed in the photoreaction. During the workup procedures, various quantities of **3**, **8**, and **9** were obtained (Table 1). The structures of compounds **3**−**7** were mainly determined by spectral (^{1}H NMR, IR, MS) and elemental analysis data. However, since it is difficult to establish unambiguously merely from the spectral data whether the acyl moiety in the primary products **4**−**6** is linked to the C(2) or C(3) carbonyl oxygen atom of **1**, an X-ray crystallographic analysis of **6a** was undertaken, and showed that the acyl is linked to the C(3)-carbonyl oxygen atom of **1** (Figure 1). Figure 1 also showed that **6a** is a *dl* isomer with the two chiral atoms having (*R*,*R*) configuration. The structure of **4d** (the *dl*-diastereomer) was also established by X-ray crystallographic analysis.[11]

Unlike in phenanthrenequinone, the non-equivalence of the two carbonyl groups in **1** allows unequivocal differentiation between the in-cage and out-of-cage products from their structures. In these reactions we have not found any products that may be derived from an in-cage process. Had any in-cage mechanism played any role, intersystem crossing (ISC) followed by radical pair recombination should have resulted in the formation of the adducts **10** and/or **11**. The absence of these products clearly indicates that no in-cage mechanism is involved in the reactions between **1** and **2a**−**2e**. At the same time, the structures of the primary products **4**−**7** show that they are all formed in out-of-cage reactions by radical pair combination in the bulk solution. The initially formed isatin ketyl-aldehyde acyl radical pair **A** (Scheme 2) is of triplet multiplicity, and escape out of cage is favored for these long-lived triplet radical pairs.[12] As electrophilic radicals, the acyl moieties have shown special "oxygen-philic' reactivity in several reactions with aldehydes and ketones,[13] being apt to attack the carbonyl at the oxygen atom, resulting in homolytic cleavage of the C=O bond, giving radical **B** (Scheme 2). This oxygen-philic reactivity of the acyl group toward the carbonyl oxygen atom in **1** can be best interpreted by inspection of the charge density distribution in the acyl radicals and in ground state **1**, as shown in Figure 2. The atomic charges were calculated by the DFT method at the UB3LYP/6−31G* level for the acyl radicals derived from **1a**−**1e** and at the B3LYP/6−31G* level for **1**. The two carbonyl oxygen atoms in **1** are both seen to be heavily negatively charged, while the acyl radicals are positively charged at the carbonyl carbon atom. However, although the two carbonyl oxygen atoms in **1** have similar negative charge densities, electrophilic attack by the acyl radical takes place exclusively at the C(3) carbonyl oxygen in **1**. The reason for this profound selectivity in the reaction site can be looked for in the different thermodynamic stabilities of the two addition radicals **B** and **C** (Scheme 2). Semiempirical AM1 calculation of the formation enthalpy (ΔH_f) indicated that radicals **B** and **C** derived from **2c** have ΔH_f values of −53.022 and −49.233 kcal·mol^{-1}, respectively, and that **B** is 3.789 kcal·mol^{-1} more stable than **C**. This means a higher activation enthalpy for the addition of acyl at the C(2) carbonyl oxygen atom. The acyl attack on **1** is therefore directed at the C(3) carbonyl oxygen atom in **1**.

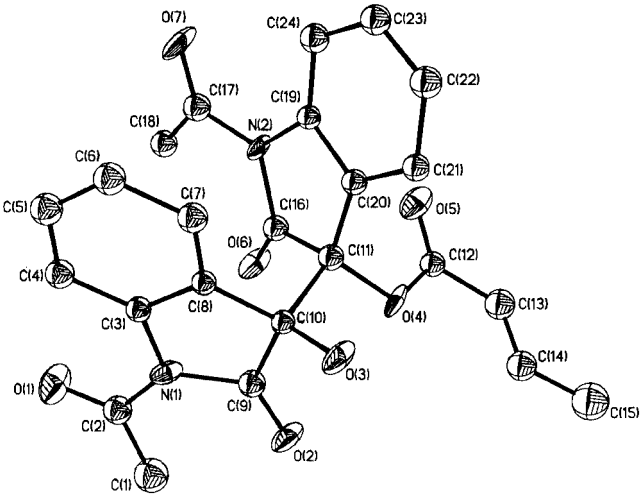
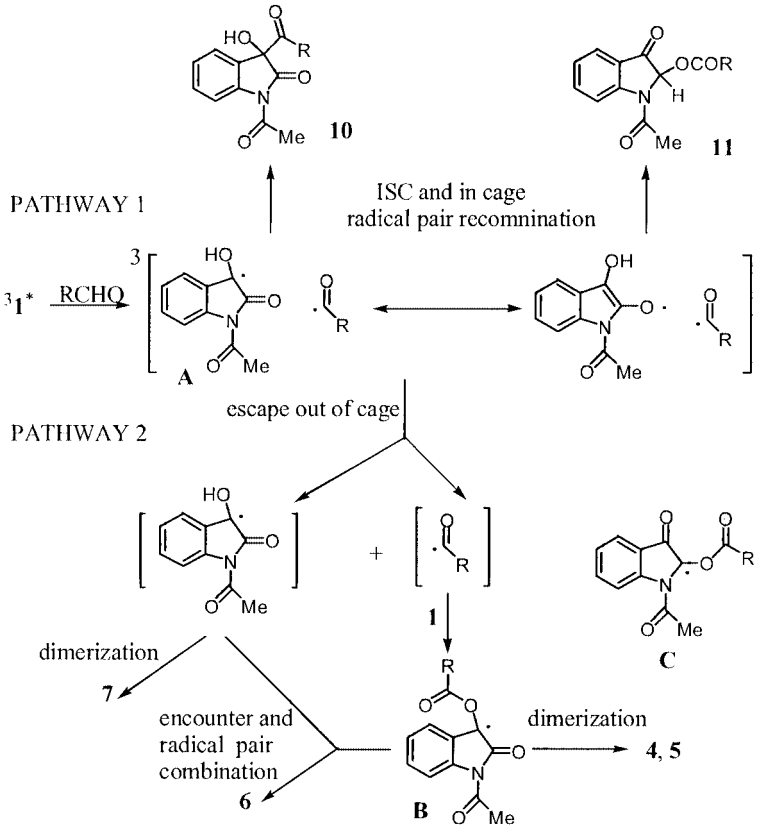


Figure 1. X-ray structure of **6a**

An alternative pathway resulting in the addition radical **B** would be through initial single-electron transfer (SET) from the acyl radical to the ground state **1** to give isatin ketyl anion radical and acylium cation, followed by ion radical pair recombination, as first suggested by Bruce as a mechanistic possibility to account for the *o*-acylation product in the photoreactions of benzoquinone with acetaldehyde.[6b] This concept is a product of early studies on acyl



Scheme 2

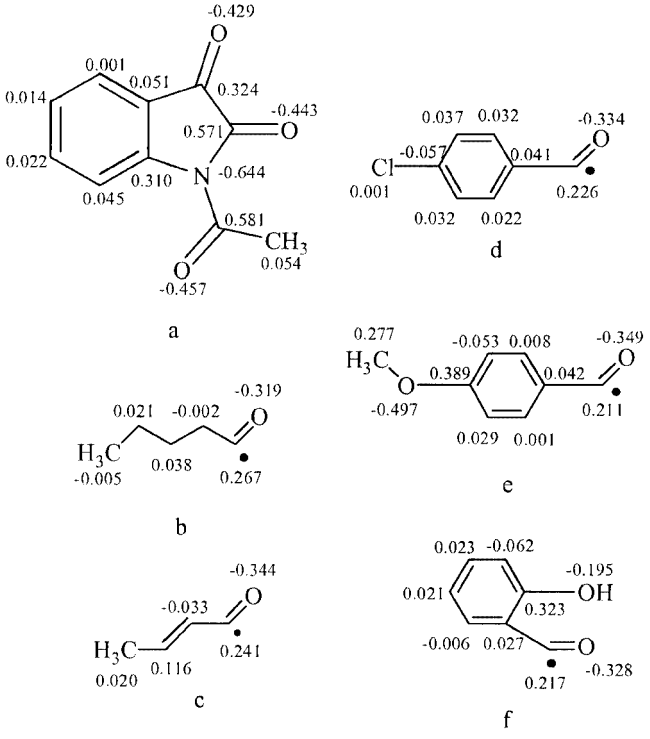


Figure 2. Atomic charges in: (a) ground state **1,** (b) valeroyl radical, (c) crotonyl radical, (d) *p*-chlorobenzoyl radical, (e) *p*-methoxybenzoyl radical, and (f) *o*-hydroxybenzoyl radical (charge density at the hydrogen atoms has been summed up to their attached carbon atom)

radical additions to aldehydes and ketones at the carbonyl oxygen,[13] in which the contribution of a polar transition state is postulated. SET from aliphatic acyl radical to high-valent metal cations such as Cu^{II},[14] Mn^{III},[15] Fe^{III} [16], Pb^{IV},[17] etc. has long been established. We calculated the vertical and adiabetic ionization potentials of the acyl radicals at the UB3LYP/6−31G* level, and the results are given in Table 2. For comparison, the adiabetic IPs of formyl and acetyl radicals were also calculated, and their calculated IPs are in good agreement with the experimentally measured values (8.2[18] and 7 eV,[19] respectively). Although the aliphatic and aromatic acyl radicals have similar IPs, it is noted that SETs from aromatic acyl radicals to these metal cations are unknown at present. These metal cations are also much stronger electron acceptors than neutral organic electron acceptors. As an example, the half-wave reduction potential of the Cu^{II}/Cu^{I} couple is in the 0.4−0.8 V range (SCE, MeCN),[20] while most neutral organic molecules have negative $E^{red}_{1/2}$ values.[21] As a result, SET from acyl radicals to neutral organic electron acceptors has seldom been reported. Russell suggested that acyl radicals may be oxidized to acylium cations in DMSO by SET to *tert*-butylmercury chloride,[22] which has an $E^{red}_{1/2}$ more positive than −0.6V (SCE).[23] The $E^{red}_{1/2}$ of **1** is −0.75V (SCE, MeCN).[9a] Unfortunately, the half-wave oxidation potentials of the acyl radicals are unknown, and estimation of the enthalpy for SET between the acyl radicals and ground state **1** by the Weller equation[24] is not possible. Although the more negative $E^{red}_{1/2}$ value of **1** in relation to *t*BuHgCl and the non-

polarity of the solvent (PhH) used in the photoreactions between **1** and **2a**−**2e** would not favor the SET process and the formation of the (acylium cation − ketyl anion) ion pair, the SET involvement could not be definitely excluded, especially in the photoreactions between **1** and the aliphatic aldehydes **2a** and **2b**.

Table 2. Ionization potentials of the acyl radicals derived from **2a**−**2e**[a]

	Formyl	Acetyl	**2a**	**2b**	**2c**	**2d**	**2e**
Vertical IP (eV)			7.90	8.11	7.93	7.44	7.43
Adiabatic IP (eV)	8.29(8.2)[b]	6.97(7.1)[c]	6.40	6.51	6.36	5.82	5.91

[a] Calculated at the UB3LYP/6−31G* level. [b] Experimental value, ref.[18] [c] Experimental value, ref.[19]

Encounter and combination of two isatin ketyls furnish the isatide **7**. Products **4** and **5** are diastereomers, formed by encounter and recombination of the addition radicals **B** in solution. Product **6**, on the other hand, is derived from encounter and recombination of the addition radical **B** with isatin ketyl, having escaped out of cage following the initial hydrogen abstraction of ^{3}**1*** from the aldehyde. It is notable that, in the reactions between **1** and **2d** or **2e**, each of which has an electron-donating substituent in the benzene ring, the cross-coupling products (**6d** and **6e**) are absent. Although the presence of **3d** and **3e** indicates the formation of **6d** and **6e** during the photoreaction, their yields are significantly lower than those of the corresponding **6a**−**6c**. This phenomenon can be interpreted by the acyl radicals of **2d** and **2e**, with the presence of the electron-releasing substituents, being less electrophilic than the acyls from **2a**−**2c**, and therefore more reluctant to add to the carbonyl oxygen in **1**. As a result, after the dissociation of the isatin ketyl-aldehyde acyl radical pairs and diffusion of the two types of radicals into the solution, the formation of the addition radical **B** would be a rather slow process in relation to the encounter and recombination of the ketyl radicals resulting in the isatide **7**, and the formation of **6d** and **6e** would occur only in the later stage of the whole reaction sequence when most of the ketyl radicals had been consumed in self-coupling to give **7**, the yields of **6d** and **6e** therefore being decreased. This argument is supported by the calculated charge density distribution in the acyl radicals derived from **2d** and **2e**. Indeed, the carbonyl carbon atom in these two acyl radicals is less positively charged than in the acyl radicals derived from **2a**−**2c**. Since all the primary products **4**−**7** are derived from radical pair recombination processes, which eliminate free radicals from the solution, no chain mechanism could be involved in the photoreactions between **1** and **2a**−**2e**. Although radical **B** may serve as a potential chain carrier by abstracting a hydrogen atom from the aldehyde **2** to give **3** and an acyl radical to initiate a new chain, careful examination of the high-resolution ^{1}H NMR spectra of the reaction mixture at various conversions indicated that product **3** is not a primary product in the photoreactions, being formed by thermal decomposition of product **6** during the workup procedures. This fact also excludes a chain mechanism.

To give more insight into the mechanism of the formation of **3**−**7** in photoreactions between **1** and **2**, we investigated reactions between **1** and **2c** induced by thermal decomposition of benzoyl peroxide (BP). Heating of a benzene solution of BP (20.4 mmol), **1** (7.2 mmol), and **2c** (26.8 mmol) at reflux for 48 h resulted in total consumption of **1** and gave, after chromatographic separation of the reaction mixture, in addition to biphenyl and benzoic acid derived from BP, **3c** (0.69 mmol, 10%), **4c** (0.41 mmol, 12%), **5c** (0.21 mmol, 6%), **6c** (1.80 mmol, 50%), **8** (0.31 mmol, 4%), and **9** (0.18 mmol, 3%). In this case, the *p*-chlorobenzoyl radical is generated by hydrogen abstraction from the aldehyde **2c** by the benzoyloxy radical formed in the decomposition of BP. A geminate isatin ketyl-acyl radical pair (as **A** in Scheme 2) is bypassed, and an out-of-cage mechanism for the formation of the products is imposed, the *p*-chlorobenzoyl radical attacking a ground state **1** to furnish radical **B**. The formation of the same products (**3**−**7**) in the BP-induced reactions as in the photoreactions between **1** and **2c** lent further support to the photoreaction mechanism as outlined in Scheme 2.

Conclusion

In summary, photoinduced reactions between 1-acetylisatin (**1**) and the aldehydes **2a**−**2e** give the 3,3′-bi-2*H*-indole-2,2′-dione derivatives **4**−**7** as primary products in high total yield. These reactions follow an out-of-cage mechanism after initial hydrogen abstraction from the aldehyde by ^{3}**1*** , with the isatin ketyl radicals and the 3-acyloxy-2-oxo-3-indolinyl radical **B** formed by an oxygen-philic attack of the escaped acyl at the C(3) carbonyl of a ground state **1** as the intervening radical species. All the primary products **4**−**7** are formed by self- and cross-coupling reactions of these two radical species, with the product ratio depending on the relative rates of the formation of the addition radical **B** and the radical coupling reactions.

Experimental Section

General Remarks: Melting points are uncorrected. ^{1}H NMR spectra were recorded with a Bruker DPX 300 at 300 MHz in $CDCl_3$ as solvent. Chemical shifts are reported in δ (ppm). *J* values are given in Hz. Infrared spectra were taken with a Shimadzu IR 440 spectrometer in KBr pellets. Mass spectra were recorded with a VG ZAB-HS spectrometer. Elemental analyses were performed with a Perkin−Elmer-240C analyzer. Benzene (AR grade) was dried with sodium and distilled before use. 1-Acetylisatin was recrystallized from benzene. The aldehydes **2a**−**2e** were distilled under reduced pressure or recrystallized before use.

Calculation Method: The geometry optimization and total energies of the acyl radicals were calculated by UB3LYP/6−31G*. In calculation of the vertical IP, the acyl radical geometry was used for the acylium cations and the total energy was calculated by B3LYP/

6−31G*. In calculation of the adiabetic IPs, the geometry of the cation was optimized by B3LYP/6−31G*. The formation enthalpies of the radicals **B** and **C** were calculated by the AM1 method (Gaussian 98)[25]

Preparative Photolyses: The light source was a medium-pressure mercury lamp (500 W) in a cooling water jacket, which was further surrounded by a layer of solution filter (20% aqueous sodium nitrite, 1 cm thick) to cut off light of wavelengths shorter than 400 nm. The solution of 1-acetylisatin (**1**) and an excess amount of aldehyde in benzene was purged with dry nitrogen for 20 min and then irradiated with continuous nitrogen purging. At the end of the reaction, the solution had turned from yellow to colorless. The solvent was removed in vacuo and the residue was separated by flash chromatography on a silica gel column with petroleum ether (b.p. 60−90 °C)/ethyl acetate as eluent.

Photolysis of 1 with Crotonaldehyde 2a: A solution of **1** (570 mg, 3 mmol) and **2a** (1.05 g, 15 mmol) in benzene (60 mL) was photolyzed for 4 h to reach complete conversion of **1**. Workup as described above gave **3a** (85 mg, 11%), **4a** (210 mg, 27%), **6a** (240 mg, 36%), **7** (30 mg, 5%), and **9** (85 mg, 16%).

1-Acetyl-3-(2-butenoyl)-1,3-dihydro-2*H*-indol-2-one (3a): White powder (from petroleum ether and ethyl acetate), m.p. 92−93 °C. IR (KBr): $\tilde{\nu}$ = 2890, 1780, 1710, 1650, 1600, 1450, 1360, 1340, 1260, 1150, 1090, 1020, 950, 750 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.94 (dd, *J* = 6.9, 1.7 Hz, 3 H), 2.71 (s, 3 H), 5.97 (dd, *J* = 12.1, 1.7 Hz, 1 H), 6.10 (s, 1 H), 6.92−7.29 (m, 2 H), 7.38−7.62 (m, 2 H), 8.27 (d, *J* = 8.2 Hz, 1 H). MS: *m*/*z* (%) = 259 [M^+] (14), 217 (8), 191 (14), 149 (23), 132 (17), 69 (100). $C_{14}H_{13}NO_4$ (259.3): calcd. C 64.86, H 5.02, N 5.34; found C 64.85, H 5.21, N 5.34.

(3*R*,3′*R*)-1,1′-Diacetyl-1,1′,3,3′-tetrahydro-3,3′-dibutenoyl-3,3′-bi-2*H*-indole-2,2′-dione (4a): Colorless blocks (from petroleum ether and ethyl acetate), m.p. 190−192 °C. IR (KBr): $\tilde{\nu}$ = 1780, 1720, 1650, 1600, 1450, 1380, 1340, 1280, 1170, 1100, 1000, 760, 600 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.94 (dd, *J* = 6.9, 1.7 Hz, 6 H), 2.48 (s, 6 H), 6.03 (dd, *J* = 15.6, 1.7 Hz, 2 H), 6.80 (br., 1 H), 7.06−7.45 (m, 8 H), 8.17 (d, *J* = 8.2 Hz, 2 H). MS: *m*/*z* (%) = 516 [M^+] (0.4), 327 (14), 259 (8), 146 (5), 69 (100). $C_{28}H_{24}N_2O_8$ (516.5): calcd. C 65.12, H 4.65, N 5.43; found C 65.26, H 4.71, N 5.21.

(3*R*,3′*R*)-1,1′-Diacetyl-1,1′,3,3′-tetrahydro-3-(2-butenoyl)-3′-hydroxy-3,3′-bi-2*H*-indole-2,2′-dione (6a): Colorless prisms (from petroleum ether and ethyl acetate) m.p. 130−131 °C. IR (KBr): $\tilde{\nu}$ = 3500, 1760, 1720, 1690, 1650, 1600, 1460, 1380, 1300, 1260, 1160, 1040, 1020, 960, 900, 750, 630 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.97 (dd, *J* = 6.9, 1.7 Hz, 3 H), 2.32 (s, 3 H), 2.69 (s, 3 H), 6.03 (dd, *J* = 15.6, 1.7 Hz, 1 H), 6.33 (br., 1 H), 6.95 (t, *J* = 7.4 Hz, 1 H), 7.10 (qd, *J* = 15.6, 6.9 Hz, 1 H), 7.30−7.40 (m, 3 H), 7.49 (t, *J* = 7.8 Hz, 3 H), 8.13 (d, *J* = 8.1 Hz, 1 H), 8.20 (d, *J* = 8.2 Hz, 1 H) ppm. MS: *m*/*z* (%) = 259 (10), 217 (9), 191 (14), 149 (22), 146 (55), 132 (9), 90 (18), 69 (100). $C_{24}H_{20}N_2O_7$ (448.4): calcd. C 64.29, H 4.46, N 6.25; found C 64.48, H 4.61, N 6.36.

Photolysis of 1 with Valeraldehyde 2b: A solution of **1** (700 mg, 3.7 mmol) and **2b** (0.8 mL, 8 mmol) in benzene (80 mL) was photolyzed for 1.5 h to reach a complete conversion of **1**. Workup as described above gave **3b** (150 mg, 15%), **4b** (110 mg, 11%), **5b** (140 mg, 14%), **6b** (260 mg, 30%), **7** (110 mg, 16%), and **9** (80 mg, 12%).

1-Acetyl-1,3-dihydro-3-pentanoyl-2*H*-indol-2-one (3b): Colorless oil. IR (KBr): $\tilde{\nu}$ = 2900, 1780, 1760, 1720, 1600, 1460, 1380, 1340, 1280, 1160, 1100, 1020, 760 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.93 (t, *J* = 7.3 Hz, 3 H), 1.38 (m, 2 H), 1.67 (m, 2 H), 2.47 (t, *J* = 7.5 Hz, 2 H), 2.68 (s, 3 H), 6.03 (s, 1 H), 7.22 (td, *J* = 7.5, 0.9 Hz, 1 H), 7.36 (d, *J* = 7.5 Hz, 1 H), 7.37−7.43 (m, 2 H), 8.25 (d, *J* = 8.2 Hz, 1 H) ppm. MS: *m*/*z* (%) = 275 [M^+] (7), 233 (10), 191 (80), 149 (100), 132 (62), 104 (23), 93 (12), 57 (65), 43 (54). $C_{15}H_{17}NO_4$ (275.3): calcd. C 65.45, H 6.18, N 5.09; found C 65.79, H 6.36, N 4.85.

(3*R*,3′*R*)-1,1′-Diacetyl-1,1′,3,3′-tetrahydro-3,3′-dipentanoyl-3,3′-bi-2*H*-indole-2,2′-dione (4b): Colorless oil. IR (KBr): $\tilde{\nu}$ = 2900, 1780, 1750, 1720, 1600, 1460, 1330, 1270, 1170, 1000, 770 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.94 (t, *J* = 7.3 Hz, 6 H), 1.31−1.43 (m, 4 H), 1.59- 1.70 (m, 4 H), 2.40−2.60 (m, 10 H), 6.75 (br., 1 H), 7.08 (t, *J* = 7.5 Hz, 2 H), 7.41 (td, *J* = 8.0, 1.4 Hz, 2 H), 8.16 (d, *J* = 8.1 Hz, 2 H) ppm. MS: *m*/*z* (%) = 359 (6), 321 (3), 275 (45), 191 (77), 149 (23), 85 (100). $C_{30}H_{32}N_2O_8$ (548.6): calcd. C 65.69, H 5.84, N 5.11; found C 65.87, H 6.05, N 4.87.

(3*R*,3′*S*)-1,1′-Diacetyl-1,1′,3,3′-tetrahydro-3,3′-dipentanoyl-3,3′-bi-2*H*-indole-2,2′-dione (5b): Colorless oil. IR (KBr): $\tilde{\nu}$ = 2900, 1780, 1760, 1720, 1600, 1460, 1370, 1330, 1270, 1170, 1080, 1010, 910, 760 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.92 (t, *J* = 7.5 Hz, 6 H), 1.23−1.44 (m, 4 H), 1.55−1.65 (m, 4 H), 2.46 (t, *J* = 7.5 Hz, 4 H), 2.61 (s, 6 H), 7.20 (t, *J* = 7.5 Hz, 2 H), 7.29−7.42 (m, 6 H), 8.11 (d, *J* = 8.2 Hz, 2 H) ppm. MS: *m*/*z* (%) = 275 (7), 256 (7), 233 (10), 191 (12), 149 (44), 129 (69), 105 (7), 97 (12), 85 (40), 43 (100). $C_{30}H_{32}N_2O_8$ (548.6): calcd. C 65.69, H 5.84, N 5.11; found C 65.90, H 5.90, N 4.92.

(3*R*,3′*R*)-1,1′-Diacetyl-1,1′,3,3′-tetrahydro-3′-hydroxy-3-pentanoyl-3,3′-bi-2*H*-indole-2,2′-dione (6b): Colorless oil. IR (KBr): $\tilde{\nu}$ = 3400, 2900, 1780, 1760, 1720, 1600, 1460, 1370, 1330, 1270, 1160, 1090, 1040, 940, 910, 870, 760, 600 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.93 (t, *J* = 7.5 Hz, 3 H), 1.29−1.41 (m, 2 H), 1.60−1.70 (m, 2 H), 2.32 (s, 3 H), 2.41−2.65 (m, 3 H), 2.69 (s, 3 H), 6.96 (t, *J* = 7.5 Hz, 1 H), 7.24−7.53 (m, 5 H), 8.13 (d, *J* = 8.0 Hz, 1 H), 8.20 (d, *J* = 7.2 Hz, 1 H) ppm. MS: *m*/*z* (%) = 275 (6), 233 (9), 191 (80), 149 (100), 132 (53), 119 (14), 104 (18), 93 (11), 90 (39), 57 (58), 43 (85). $C_{25}H_{24}N_2O_7$ (464.5): calcd. C 64.66, H 5.17, N 6.03; found C 64.72, H 5.52, N 6.11.

Photolysis of 1 with 4-Chlorobenzaldehyde 2c: A solution of **1** (750 mg, 4 mmol) and **2c** (562 mg, 4 mmol) in benzene (80 mL) was photolyzed for 3 h to reach a complete conversion of **1**. The solvent was removed in vacuo and the residue was dissolved in acetone/petroleum ether. Most of the unstable **6c** (352 mg, 34%) crystallized and the mixture remaining in solution was further separated by flash chromatography as described above to give **3c** (112 mg, 9%), **4c** (139 mg, 11%), **5c** (225 mg, 17%), and **7** (146 mg, 19%).

1-Acetyl-3-(*p*-chlorobenzoyl)-1,3-dihydro-2*H*-indol-2-one (3c): White powders (from acetone and petroleum ether), m.p. 146−148 °C. IR (KBr): $\tilde{\nu}$ = 1778, 1719, 1592, 1467, 1371, 1328, 1261, 1169, 1117, 1106, 1014, 758 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.73 (s, 3 H), 6.28 (s, 1 H), 7.24 (d, *J* = 7.4 Hz, 1 H), 7.42−7.47 (m, 4 H), 8.01−8.05 (m, 2 H), 8.31 (d, *J* = 8.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 172.92, 170.79, 165.16, 141.34, 140.87, 131.89, 131.21, 129.37, 127.41, 126.04, 125.30, 123.69, 117.37, 77.83, 77.40, 76.98, 70.98, 26.92 ppm. MS: *m*/*z* (%) = 329 [M^+] (6), 287 (8), 149 (19), 139 (100), 111 (16), 77 (9), 43 (33). $C_{17}H_{12}ClNO_4$ (329.7): calcd. C 61.91, H 3.64, N 4.25; found C 61.82, H 3.46, N 4.51.

(3*R*,3′*R*)-1,1′-Diacetyl-3,3′-bis(*p*-chlorobenzoyl)-1,1′,3,3′-tetrahydro-3,3′-bi-2*H*-indole-2,2′-dione (4c): Colorless crystals (from

acetone and petroleum ether), m.p. 262−264 °C. IR (KBr): ṽ = 1775, 1728, 1595, 1488, 1464, 1370, 1335, 1269, 1172, 1117, 1091, 1014, 847, 762, 754, 682 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.51 (s, 6 H), 6.89 (s, 2 H), 7.11 (t, *J* = 7.5 Hz, 2 H), 7.45−7.52 (m, 6 H), 8.10 (d, *J* = 8.4 Hz, 4 H), 8.24 (d, *J* = 8.2 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.35, 170.21, 164.00, 141.72, 141.27, 132.43, 131.88, 129.69, 127.24, 125.70, 124.48, 121.21, 117.17, 81.61, 77.85, 77.43, 77.01, 26.49 ppm. MS: *m*/*z* (%) = 467 (4), 262 (5), 156 (7), 149 (6), 139 (100), 111 (15), 90 (4), 75 (12), 43 (24). $C_{34}H_{22}Cl_2N_2O_8$ (657.5): calcd. C 62.10, H 3.35, N 4.26; found C 62.23, H 3.21, N 4.27.

(3*R*,3′*S*)-1,1′-Diacetyl-3,3′-bis(*p*-chlorobenzoyl)-1,1′,3,3′-tetrahydro-3,3′-bi-2*H*-indole-2,2′-dione (5c): Colorless crystals (from acetone and petroleum ether), m.p. 244−246 °C. IR (KBr): ṽ = 1774, 1730, 1594, 1466, 1370, 1333, 1275, 1068, 1016, 941, 852, 756, 686 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.80 (s, 6 H), 7.09 (t, *J* = 7.5 Hz, 2 H),8.08 (m, 4 H), 7.19 (dd, *J* = 7.5, 1.0 Hz,2 H), 7.31 (td, *J* = 8.4, 1.0 Hz, 2 H), 7.44−7.47 (m, 4 H), 8.03 (d, *J* = 8.3 Hz, 2 H) ppm. MS: *m*/*z* (%) = 469 (3), 262 (4), 234 (3), 149 (6), 139 (100), 111 (15), 104 (6), 75 (12), 50 (9). $C_{34}H_{22}Cl_2N_2O_8$ (657.5): calcd. C 62.10, H 3.35, N 4.26; found C 62.05, H 3.42, N 4.27.

(3*R*,3′*R*)-1,1′-Diacetyl-3-(*p*-chlorobenzoyl)-1,1′,3,3′-tetrahydro-3′-hydroxy-3,3′-bi-2*H*-indole-2,2′-dione (6c): Colorless crystals (from acetone and petroleum ether), m.p. 136−138 °C. IR (KBr): ṽ = 3409, 1760, 1717, 1595, 1464, 1402, 1269, 1169, 1092, 1014, 756 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.78 (s, 3 H), 2.81 (s, 3 H), 7.06 (t, *J* = 7.5 Hz, 1 H), 7.14 (t, *J* = 7.5 Hz, 2 H), 7.24−7.34 (m, 2 H), 7.49 (d, *J* = 8.7 Hz, 2 H), 7.92−8.06 (m, 3 H), 8.13 (d, *J* = 8.7 Hz, 2 H) ppm. MS: *m*/*z* (%) = 329 (1), 287 (2), 189 (2), 161 (2), 146 (33), 141(8), 139 (16), 119 (10), 104 (10), 90 (59), 77 (13), 64 (21), 43 (100). $C_{27}H_{19}ClN_2O_7$ (518.9): calcd. C 62.49, H 3.67, N 5.40; found C 62.4, H 3.67, N 5.37.

Photolysis of 1 with Anisaldehyde 2d: A solution of **1** (760 mg, 4 mmol) and **2d** (1.36 g, 10 mmol) in benzene (80 mL) was photolyzed for 3 h to reach a complete conversion of **1**. Workup as described above gave the products **3d** (197 mg, 15%), **4d** (219 mg, 17%), **5d** (314 mg, 24%), **7** (167 mg, 22%), **8** (117 mg, 14%), and **9** (24 mg, 3%).

1-Acetyl-1,3-dihydro-3-(*p*-methoxybenzoyl)-2*H*-indol-2-one (3d): White powder (from petroleum ether and acetone), m.p. 138−139 °C. IR (KBr): ṽ = 2920, 1775, 1720, 1605, 1580, 1512, 1460, 1425, 1372, 1325, 1255, 1170, 1100, 1030, 1010, 915, 855, 800, 765, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.75 (s, 3 H), 3.89 (s, 3 H), 6.26 (s, 1 H), 6.96 (d, *J* = 8.6 Hz, 2 H), 7.22−7.47 (m, 3 H), 8.06 (d, *J* = 8.6 Hz, 2 H), 8.31 (d, *J* = 8.3 Hz, 1 H) ppm. MS: *m*/*z* (%) = 325 [M$^+$] (3), 152 (6), 135 (100), 132 (16), 104 (5), 92 (5), 77 (11), 43 (9). $C_{18}H_{15}NO_5$ (325.3): calcd. C 66.46, H 4.62, N 4.31; found C 66.42, H 4.60, N 4.46.

(3*R*,3′*R*)-1,1′-Diacetyl-1,1′,3,3′-tetrahydro-3,3′-bis(*p*-methoxybenzoyl)-3,3′-bi-2*H*-indole-2,2′-dione (4d): Colorless crystals (from petroleum ether and ethyl acetate) m.p. 147−148 °C. IR (KBr): ṽ = 2900, 1760, 1720, 1600, 1520, 1450, 1370, 1330, 1260, 1170, 1100, 1020, 940, 850, 760, 700, 600 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.52 (s, 6 H), 3.88 (s, 6 H), 6.95−7.02 (m, 6 H), 7.10 (t, *J* = 7.5 Hz, 2 H), 7.45 (td, *J* = 7.8, 1.4 Hz, 2 H), 8.07−8.16 (m, 6 H), 8.24 (d, *J* = 8.2 Hz, 2 H) ppm. MS: *m*/*z* (%) = 459 (1), 304 (1), 262 (4), 220 (2), 152 (9), 135 (100), 107 (5), 92 (4). $C_{36}H_{28}N_2O_{10}$ (648.6): calcd. C 66.67, H 4.32, N 4.32; found C 66.76, H 4.63, N 4.45.

(3*R*,3′*S*)-1,1′-Diacetyl-1,1′,3,3′-tetrahydro-3,3′-bis(*p*-methoxybenzoyl)-3,3′-bi-2*H*-indole-2,2′-dione (5d): White powder (from petroleum ether and ethyl acetate), m.p. 133−135 °C. IR (KBr): ṽ = 1760, 1720, 1600, 1500, 1460, 1380, 1330, 1260, 1170, 1100, 1020, 940, 850, 760, 700, 600 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.79 (s, 6 H), 3.88 (s, 6 H), 6.96 (d, *J* = 8.5 Hz, 4 H), 7.10 (t, *J* = 7.4 Hz, 2 H), 7.22 (d, *J* = 7.3 Hz, 2 H), 7.34 (t, *J* = 7.7 Hz, 2 H), 8.08 (d, *J* = 8.4 Hz, 6 H) ppm. MS: *m*/*z* (%) = 459 (0.4), 304 (3), 262 (9), 220 (6), 152 (11), 146 (10), 135 (100), 107 (14), 92 (9). $C_{36}H_{28}N_2O_{10}$ (648.6): calcd. C 66.67, H 4.32, N 4.32; found C 66.71, H 4.57, N 4.61.

Photolysis of 1 with Salicylaldehyde 2e: A solution of **1** (380 mg, 2 mmol) and **2e** (0.4 mL, 4 mmol) in benzene (40 mL) was photolyzed for 9 h to reach complete conversion of **1**. Workup as described above gave the products **3e** (205 mg, 33%), **4e** (155 mg, 25%), and **7** (80 mg, 21%).

1-Acetyl-1,3-dihydro-3-(*o*-hydroxybenzoyl)-2*H*-indol-2-one (3e): Colorless needles (from acetone and petroleum ether), m.p. 153−154 °C. IR (KBr): ṽ = 3200, 1760, 1720, 1680, 1600, 1580, 1470, 1450, 1360, 1330, 1270, 1240, 1160, 1140, 1120, 1070, 1000, 760, 690, 650, 580 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.75 (s, 3 H), 6.32 (s, 1 H), 6.93 (t, *J* = 7.8 Hz, 1 H), 7.03 (d, *J* = 8.4 Hz, 1 H), 7.24−7.29 (m, 1 H), 7. 45−7.56 (m, 3 H), 7.93 (dd, *J* = 8.0, 1.7 Hz, 1 H), 8.32 (d, *J* = 8.3 Hz, 1 H), 10.27 (s, 1 H) ppm. MS: *m*/*z* (%) = 311 (2), 269 (1), 251 (2), 174 (21), 132 (100), 121 (38), 104 (7), 93 (5), 77 (7), 65 (7), 43 (17). $C_{17}H_{13}NO_5$ (311.3): calcd. C 65.59, H 4.18, N 4.50; found C 65.66, H 4.13, N 4.63.

(3*R*,3′*R*)-1,1′-Diacetyl-1,1′,3,3′-tetrahydro-3,3′-bis(*o*-hydroxybenzoyl)-3,3′-bi-2*H*-indole-2,2′-dione (4e): Colorless crystals (from acetone and petroleum ether), m.p. 203−204 °C. IR (KBr): ṽ = 3300, 1760, 1720, 1680, 1600, 1570, 1470, 1360, 1320, 1260, 1150, 1120, 1080, 930, 900, 860, 750, 690, 650, 580 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.82 (s, 6 H), 6.96−7.01 (m, 4 H), 7.13 (t, *J* = 7.5 Hz, 2 H), 7.25 (d, *J* = 7.5 Hz, 2 H), 7.35 (td, *J* = 7.8, 1.4 Hz, 2 H), 7.54 (td, *J* = 7.9, 1.8 Hz, 2 H), 8.05 (d, *J* = 8.2 Hz, 2 H), 8.18 (dd, *J* = 8.2, 1.6 Hz, 2 H), 9.66 (s, 2 H) ppm. MS: *m*/*z* (%) = 483 (4), 346 (8), 304 (16), 278 (6), 262 (45), 234 (31), 220 (24), 163 (13), 146 (31), 138 (24), 121 (100), 92 (41), 64 (17), 43 (66). $C_{34}H_{24}N_2O_{10}$ (620.6): calcd. C 65.80, H 3.87, N 4.52; found C 65.82, H 4.18, N 4.43.

Thermal Decomposition of 6c: Heating of **6c** (100 mg, 0.19 mmol) absorbed on silica gel (10 g) on a steam bath and chromatographic separation of the reaction mixture on a silica gel column afforded **3c** (55 mg, 0.167 mmol, 58%) and **8** (20 mg, 0.097 mmol, 21%).

Reaction of 1 with 2c Induced by Thermal Decomposition of Benzoyl Peroxide (BP): Heating of a benzene solution of BP (4.9368 g, 20.4 mmol), **1** (1.3608 g, 7.2 mmol), and **2c** (3.7654 g, 26.8 mmol) at reflux for 48 h resulted in the total conversion of **1**, and the mixture was separated by chromatography on a silica gel column with petroleum ether and ethyl acetate as eluents and gave, in addition to biphenyl and benzoic acid derived from BP, **3c** (0.69 mmol, 10%), **4c** (0.41 mmol, 12%), **5c** (0.21 mmol, 6%), **6c** (1.80 mmol, 50%), **8** (0.31 mmol, 4%), and **9** (0.18 mmol, 3%).

X-ray Crystallographic Study. Crystal Data for 6a: $C_{24}H_{20}N_2O_7$, *M* = 448.42, colorless prisms, Enraf−Nonius CAD4 diffractometer, Mo-K_α radiation (λ = 0.71073 Å), 0.45 × 0.25 × 0.05 mm, *T* = 293(2) K. Monoclinic, space group *P*21/*c*, *a* = 7.6033(15), *b* = 35.579(7), *c* = 8.1527(16) Å, α = 90, β = 104.19(3), γ = 90°, *V* = 2138.1(7) Å^3, *Z* = 4, $D_{calcd.}$ = 1.393 g·cm^{-3}, μ = 0.104 mm^{-1}, *F*(000) = 936.00. The structure was solved by direct methods (SHELXL) and refined on F^2 by full-matrix, least-squares. A total of 4409 independent reflections [*R*(int) = 0.1495] were used

in the refinement, which converged with $R = 0.1410$ and $wR = 0.2764$ (GOF = 1.057). CCDC-215369 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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