212. Photoinduced Molecular Transformations

Part 142[1])

One-Step Syntheses of 1*H*-Benz[*f*]indole-4,9-diones and 1*H*-Indole-4,7-diones by a New Regioselective Photoaddition of 2-Amino-1,4-naphthoquinones and 2-Amino-1,4-benzoquinones with Alkenes

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The 2,3-dihydro-1*H*-benz[*f*]indole-4,9-diones **3a–d, h** were formed in a one-step reaction in 13–82% yield by an unprecedented [3 + 2] regioselective photoaddition of 2-amino-1,4-naphthoquinone (**1**) with various electron-rich alkenes **2** (*Scheme 1*, *Table*). The [3 + 2] photoadducts derived from **1** with vinyl ethers and vinyl acetate gave 1*H*-benz[*f*]indole-4,9-diones **4e, f, i**, in 33–72% yield, by spontaneous loss of the corresponding alcohol or AcOH from the resulting adducts; **4i** has a kinamycin skeleton. The [3 + 2] photoaddition also took place on irradiation of the differently substituted amino-1,4-benzoquinones **6**, **7**, and **12** and excess alkenes **2** in benzene, giving 1*H*-indole-4,7-dione derivatives **13** and **14** (*Scheme 3*), **15a** and **16** (*Scheme 4*), and **18** (*Scheme 4*), respectively. The initial products in these photoadditions were proved to be hydroquinones, the air oxidation of which yielded the heterocyclic quinones; 2,3-dihydro-2-methoxy-2-methyl-5-phenyl-1*H*-indole-1,4,7-triyl triacetate (**19**) was isolated after treatment of the crude photoaddition mixture obtained from 2-amino-5-phenyl-1,4-benzoquinone (**7**) and 2-methoxyprop-1-ene (**2f**) with Ac_2O and pyridine under N_2. A pathway leading to the annelated hydroquinones involving ionic intermediates arising from an electron transfer in these photoadditions is proposed (*Scheme 5*).

In previous papers, we reported on a one-step synthesis of 2,3-dihydronaphtho-[2,3-*b*]furan-4,9-diones [2] [3] and 2,3-dihydrobenzo[2,3-*b*]furan-1,4-diones [1] in good yields by new regioselective [3 + 2] photoadditions of 2-hydroxy-1,4-naphthoquinones and 2-hydroxy-1,4-benzoquinones with a variety of alkenes. In a subsequent communication [4], we reported on a new one-step synthesis of 2,3-dihydro-1*H*-benz[*f*]indole-4,9-diones in 45–82% yield by a similar regioselective [3 + 2] photoaddition of 2-amino-1,4-naphthoquinones with various electron-rich alkenes. The [3 + 2] photoadducts derived from the aminonaphthoquinones with vinyl ethers and vinyl acetate spontaneously lost an alcohol or AcOH to give 1*H*-benz[*f*]indole-4,9-diones, including a benz[*f*]indoledione with a kinamycin skeleton.

In this paper, we describe the full details concerning this work [4]. We also describe an extention of the [3 + 2] photoaddition to the one-step formation of 1*H*-indole-4,7-diones from 2-amino-1,4-benzoquinone and various alkenes.

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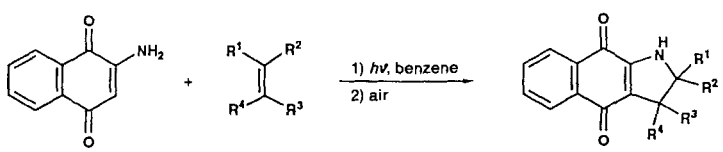
The 1*H*-benz[*f*]indole-4,9-diones and 1*H*-indole-4,7-diones comprise important groups of heterocyclic quinones. Among them are several physiologically active quinones such as kinamycins [5] and biologically important natural products such as mitosens and others [6], respectively. The synthetic methods so far reported for these classes of compounds, however, are not necessarily simple and require several reaction steps [7]. A number of synthetic approaches to the 1*H*-indole-4,7-diones that are common to the mitosens were developed [7c, d, h] [8].

Results and Discussion. – *1*H-*Benz[f]indole-4,9-diones by Photoaddition of 2-Amino-1,4-naphthoquinone* (**1**) *with Alkenes* **2**. Irradiation for 1 h at room temperature (N_2) of $7 \cdot 10^{-2}$M 2-aminonaphthoquinone [9] (**1**) in benzene containing isobutene (**2a**) with a 500-W high-pressure Hg arc through a *Pyrex* filter gave 2,3-dihydro-2,2-dimethyl-1*H*-benz[*f*]indole-4,9-dione (**3a**) in 82% isolated yield as a single product (*Scheme 1*). Simi-

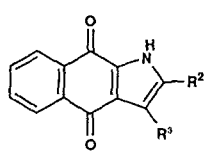
Scheme 1



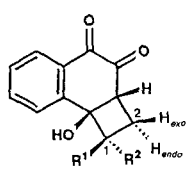
1

2a $R^1 = R^2 = Me$, $R^3 = R^4 = H$
b $R^1 = R^2 = R^3 = Me$, $R^4 = H$
c $R^1 = R^2 = R^3 = R^4 = Me$
d $R^1 = Me$, $R^2 = Ph$, $R^3 = R^4 = H$
e $R^1 = EtO$, $R^2 = R^3 = R^4 = H$
f $R^1 = MeO$, $R^2 = Me$, $R^3 = R^4 = H$
g $R^1 = AcO$, $R^2 = Me$, $R^3 = R^4 = H$
h $R^2, R^3 = -(CH_2)_3-$, $R^1 = R^4 = H$
i $R^1 = MeO$, $R^2, R^3 = -(CH_2)_4-$, $R^4 = H$

3a $R^1 = R^2 = Me$, $R^3 = R^4 = H$
b $R^1 = R^2 = R^3 = Me$, $R^4 = H$
c $R^1 = R^2 = R^3 = R^4 = Me$
d $R^1 = Me$, $R^2 = Ph$, $R^3 = R^4 = H$
e $R^1 = EtO$, $R^2 = R^3 = R^4 = H$
f $R^1 = MeO$, $R^2 = Me$, $R^3 = R^4 = H$
g $R^1 = AcO$, $R^2 = Me$, $R^3 = R^4 = H$
h $R^2, R^3 = -(CH_2)_3-$, $R^1 = R^4 = H$, *cis*
i $R^1 = MeO$, $R^2, R^3 = -(CH_2)_4-$, $R^4 = H$



4e $R^2 = R^3 = H$
f $R^2 = Me$, $R^3 = H$
i $R^2, R^3 = -(CH_2)_4-$



5 $R^1 = Me$, $R^2 = Ph$
$R^1 = Ph$, $R^2 = Me$

larly, the photoaddition of **1** with alkenes **2b–d**, **h** took place regioselectively to give the dihydro-1*H*-benz[*f*]indole-4,9-diones **3b–d**, **h**. The yields of **3c** and **3h**, however, were rather low (18 and 13%, after isolation by prep. TLC; see *Table*). In the case of **3d**, by-product **5** was isolated in 23% yield and identified by spectroscopic means as a 1:1 epimer mixture (at C(1)) of a tetrahydro-1-methyl-1-phenylcyclobuta[*a*]naphthalene-3,4-dione.

On the other hand, the photoaddition of naphthoquinone **1** with vinyl ethers **2e**, **f** and vinyl acetate **2g** under the above mentioned conditions gave 1*H*-benz[*f*]indole-4,9-dione **4e**, **f** in 33–72% isolated yield (*Scheme 1*, *Table*). These benz[*f*]indolediones were formed

Table. *Photoaddition of 2-Amino-1,4-naphthoquinone* (**1**) *with Alkenes* **2**

Alkene[a])	Irradiation time [h]	Product **3** or **4**	Yield[b]) [%]
2a	1	**3a**	82
2b	12	**3b**	66
2c	3	**3c**	18
2d	2	**3d**[c])	45
2e	1.5	**4e**	33
2f	3	**4f**	72
2g	4.5	**4f**	47
2h	10	**4h**	13
2i	2.5	**4i**	68

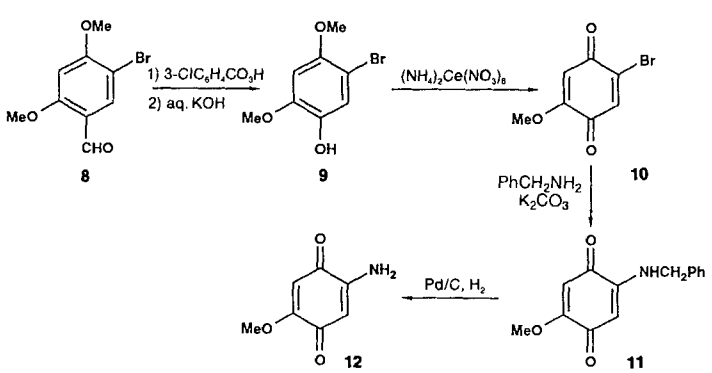
[a]) Molar ratio alkene **2**/**1** 20:1.
[b]) Isolated product.
[c]) [2 + 2] Adduct **5** (23%) as by-product.

by spontaneous elimination of either an alcohol or AcOH from the initially generated adducts **3e–g**, during the reaction or on separation by prep. TLC. A similar photoaddition of naphthoquinone **1** with 1-methoxycyclohexene (**2i**) gave 2,3,4,5-tetrahydro-1*H*-benzo[*b*]carbazole-6,11-dione (**4i**), a framework of kynamycin [5], in one step in 68% yield.

No photoaddition took place with electron-deficient olefins, such as methyl methacrylate, or with *N*-substituted 2-aminonaphthoquinones, such as commercially available 2-(phenylamino)-1,4-naphthoquinone and 2-(benzylamino)-1,4-naphthoquinone [10].

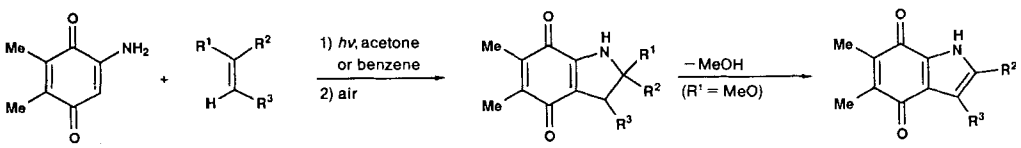
*2,3-Dihydro-1*H*-indole-4,7-diones and 1*H*-Indole-4,7-diones by Photoaddition of Amino-1,4-benzoquinones with Alkenes* (**2**). Of the three amino-1,4-benzoquinones examined, 6-amino-2,3-dimethyl-1,4-benzoquinone [11] (**6**) and 2-amino-5-phenyl-1,4-benzoquinone [11] (**7**) were prepared according to published methods. The unknown 2-amino-5-methoxy-1,4-benzoquinone (**12**) was prepared in 4 steps from 5-bromo-2,4-dimethoxybenzaldehyde [12] (**8**) *via* **9–11** (see *Scheme 2* and *Exper. Part*).

Scheme 2



The irradiation of **6** in the presence of a five-molar excess of α-methylstyrene (**2d**) in benzene (N_2) with a 100-W high-pressure mercury arc afforded an oily product **13d** in 30% yield (*Scheme 3*). Its high-resolution mass spectrum was in accord with the molecular formula $C_{17}H_{17}NO_2$, and the IR and ^{1}H-NMR spectra established the structure of the [3 + 2] adduct to be 2,3-dihydro-2,5,6-trimethyl-2-phenyl-1*H*-indole-4,7-dione (**13d**).

Scheme 3



6

2d R^1 = Me, R^2 = Ph, R^3 = H
f R^1 = MeO, R^2 = Me, R^3 = H
i R^1 = MeO, R^2,R^3 = –$(CH_2)_4$–
j R^1 = R^2 = Ph, R^3 = H

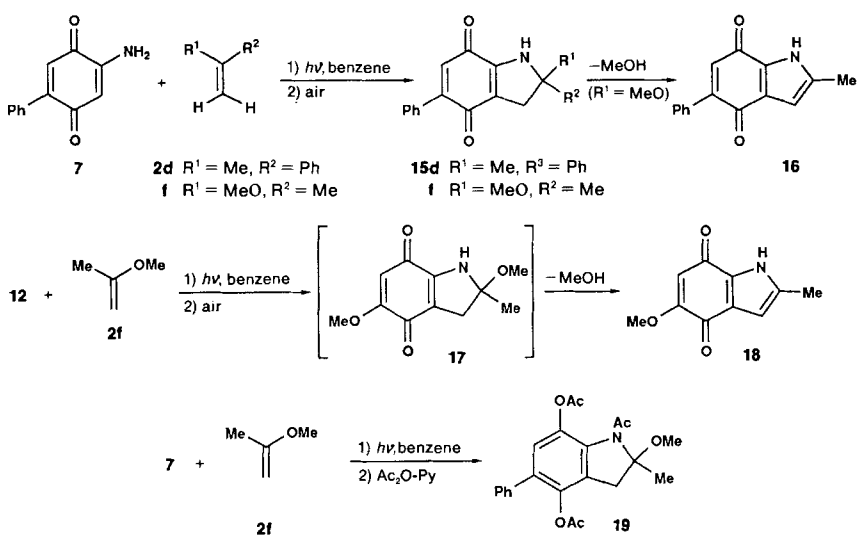
13d R^1 = Me, R^2 = Ph, R^3 = H
f R^1 = MeO, R^2 = Me, R^3 = H
i R^1 = MeO, R^2,R^3 = –$(CH_2)_4$–
j R^1 = R^2 = Ph, R^3 = H

14f R^2 = Me, R^3 = H
i R^2,R^3 = –$(CH_2)_4$–

The photoaddition of **6** with 1,1-diphenylethene (**2j**) and with the vinyl ethers **2f** and **2i** in benzene under the same conditions gave **13j** (30%), **14f** (43%), and **14i** (16%), respectively. In the latter two cases, the initial adducts **13f** and **13i** spontaneously lost MeOH to give the indolediones, as in the case of the photoaddition of 2-hydroxynaphthoquinone with vinyl ethers [2] [3].

The photoadditions of aminobenzoquinones **7** and **12** with α-methylstyrene (**2d**) and 2-methoxypropene (**2f**) took place in a similar manner as that of **6**, to give 2,3-dihydro-1*H*-indole-4,7-dione **15d** and 1*H*-indole-4,7-diones **16** and **18**, the latter *via* the initial adducts **15f** and **17** (*Scheme 4*).

Scheme 4



7

2d R^1 = Me, R^2 = Ph
f R^1 = MeO, R^2 = Me

15d R^1 = Me, R^3 = Ph
f R^1 = MeO, R^2 = Me

16

12 + **2f**

17

18

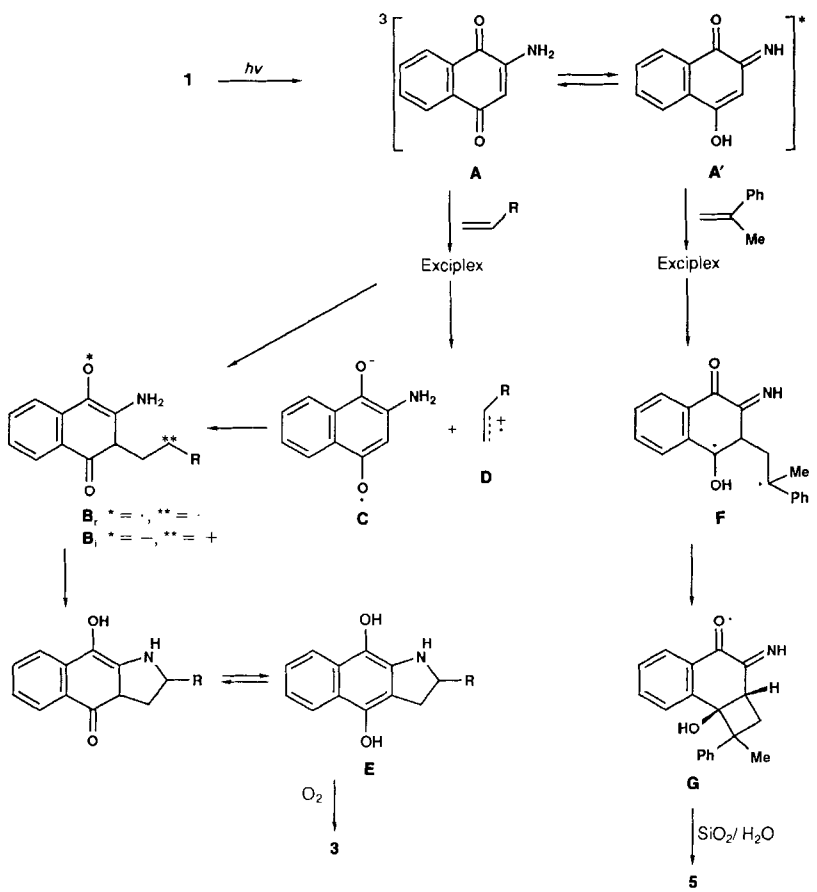
7 + **2f**

19

The very initial products in the present photoadditions were 2,3-dihydro-1*H*-benz-[*f*]indole-4,9-diols or 2,3-dihydro-1*H*-indole-4,7-diols. Thus, 2,3-dihydro-2-methoxy-2-methyl-5-phenyl-1*H*-indole-1,4,7-triyl triacetate (**19**) could be isolated in 41 % yield when the crude photoaddition mixture from amino benzoquinone **7** and **2f** was treated with Ac_2O and pyridine under N_2 for 22 h at 50° (*Scheme 4*). The isolation of 2,3-dihydro-1*H*-benz[*f*]indole-1,4,9-triyl triacetate was, however, unsuccessful in similar acetylations of crude photoaddition mixtures from aminonaphthoquinone **1** and alkenes, the oxidation of the initial hydroquinones to quinones by air being apparently more readily than in the case of 2,3-dihydro-1*H*-indole-4,7-diols. Indeed, we found that a yellow hydroquinone corresponding to **3a**, prepared by reduction of quinone **3a** by catalytic hydrogenation over Pd/C, rapidly turned into the purple quinone **3a** on exposure to air.

Pathways Leading to the [3 + 2] Photoadducts **3**, **4**, **13**–**18**. A number of studies concerning the photoaddition of 1,4-naphthoquinones with alkenes [13] revealed that the excited 1,4-naphthoquinones mostly add to the alkenes to give [2 + 2] photoadducts, as in

Scheme 5



the case of enone [2 + 2] cycloaddition [14]. Some photochemical behaviours of 2-amino-1,4-naphthoquinone and 2-(alkylamino)- and 2-(dialkylamino)-substituted 1,4-naphthoquinones were also reported [10] [15].

The probable reaction path of the present photoaddition leading to 2,3-dihydro-1*H*-benz[*f*]indole-4,9-diones **3** (*Scheme 1*) and 2,3-dihydro-1*H*-indole-4,7-diones **13** (*Scheme 3*) is outlined for the photoaddition of 2-amino-1,4-naphthoquinone (**1**; *Scheme 5*). The initial stage corresponds to an accepted model for enone [2 + 2] photoadditions [14]. Irradiation of naphthoquinone **1** in benzene may well generate a tautomeric excited triplet, **A** and **A′**. The excited tautomer **A** may then form preferentially an exciplex with the alkene to give a biradical $\mathbf{B}_r$ or a zwitterion $\mathbf{B}_i$, generated by an electron transfer; biradical $\mathbf{B}_r$ may well have an appreciable polar character. Alternatively, $\mathbf{B}_i$ can be generated from the exciplex *via* the pair of radical ions **C** and **D** [16] [17]. The regioselectivity of the present photoaddition is an indication of the involvement of a more stabilized biradical or ionic intermediate, such as $\mathbf{B}_r$ and $\mathbf{B}_i$, on the way to 2,3-dihydro-1*H*-benz[*f*]-indole-4,9-diones **3′**: cyclization of $\mathbf{B}_r$ or $\mathbf{B}_i$ gives a hydroquinone **E**. This cyclization is analogous to the one proposed for the photoaddition of 2-hydroxy-1,4-naphthoquinones with alkenes leading to dihydronaphtho[2,3-*b*]furan-4,9-diones [1–3].

The path to by-product **5** was already discussed in detail [18]: **5** may be formed by a [2 + 2] addition of the excited enol form **A′** *via* **F** and imino ketone **G**, which would be hydrolysed.

Experimental Part

General. See [19], also for the general photolysis procedure. M.p.: uncorrected. Prep. TLC: *Merck 60 PF 254.* ^{1}H-NMR and IR spectra were measured in $CDCl_3$ and in Nujol, resp., unless stated otherwise.

2-Aminonaphthalene-1,4-dione (**1**) was prepared according to [9]. UV: see [18].

*2,3-Dihydro-2,2-dimethyl-1*H*-benz[f]indole-4,9-dione* (**3a**) (*General Procedure*). A soln. of **1** (85 mg, 0.49 mmol) and isobutene (= 2-methylprop-1-ene; **2a**; 0.55 g, 9.8 mmol) in benzene (70 ml) was irradiated through a *Pyrex* filter with a 500-W high-pressure Hg arc under N_2 for 1 h at r.t. The solvent and excess **2a** were evaporated. Purification of the residue by prep. TLC (silica gel, AcOEt/hexane 1:3, R_f 0.47) gave **3a** (91 mg, 82%). M.p. 200° (dec.; from hexane/Et_2O). IR: 3270, 1678, 1616, 1593, 1566. ^{1}H-NMR (90 MHz): 1.40 (*s*, Me_2C); 2.95 (*s*, 2H–C(3)); 5.0–5.15 (br., NH); 7.4–7.8 (*m*, 2 arom. H), 7.9–8.15 (*m*, 2 arom. H). MS: 227 (31, M^+), 212 (100, $[M - Me]^+$). Anal. calc. for $C_{14}H_{13}NO_2$: C 73.99, H 5.77, N 6.16; found: C 73.99, H 5.73, N 6.11.

*2,3-Dihydro-2,2,3-trimethyl-1*H*-benz[f]indole-4,9-dione* (**3b**). As described for **3a**, with **1** (20 mg, 0.12 mmol), 2-methyl-but-2-ene (**2b**; 0.16 g, 2,4 mmol), and benzene (40 ml; for 12 h): **3b** (19 mg, 66%). R_f 0.34 (AcOEt/hexane 1:3). M.p. 205–207° (from hexane/CH_2Cl_2). IR: 3270, 1674, 1614, 1592, 1564. ^{1}H-NMR (90 MHz): 1.29 (*d*, J = 7.25, Me–C(3)); 1.28 (*s*, 1 Me–C(2)); 1.33 (*s*, 1 Me–C(2)); 3.17 (*q*, J = 7.25, H–C(3)), 5.0 (br., NH); 7.4–7.7 (*m*, 2 arom. H); 7.8–8.1 (*m*, 2 arom. H). MS: 24 (34, M^+), 226 (100, $[M - Me]^+$). HR-MS: 241.1108 ($C_{15}H_{15}NO_2$, calc. 241.1102).

*2,3-Dihydro-2,2,3,3-tetramethyl-1*H*-benz[f]indole-4,9-dione* (**3c**). As described for **3a**, with **1** (70 mg, 0.40 mmol), 2,3-dimethyl-but-2-ene (**2c**; 0.67 g, 8 mmol), and benzene (140 ml; 3 h): **3c** (18 mg, 18%). R_f 0.56 (AcOEt/hexane 1:5). M.p. 165–167° (from hexane). IR: 3330, 1674, 1615, 1590, 1566. ^{1}H-NMR (90 MHz): 1.24 (*s*, Me_2C); 1.32 (*s*, Me_2C); 4.9 (br., NH); 7.2–8.1 (*m*, 4 arom. H). MS: 255 (41, M^+), 240 (100, $[M - Me]^+$). HR-MS: 255.1251 ($C_{16}H_{17}NO_2^+$, calc. 255.1258).

*2,3-Dihydro-2-methyl-2-phenyl-1*H*-benz[f]indole-4,9-dione* (**3d**) *and (1*RS,*8b*SR*)- and (1*RS,*8b*RS*)-1,2,2a,8b-Tetrahydro-8b-hydroxy-1-methyl-1-phenylcyclobuta[a]naphthalene-3,4-dione* (**5**). As described for **3a**, with **1** (70 mg, 0.40 mmol), α-methylstyrene (**2d**; 0.94 g, 8 mmol), and benzene (70 ml; 2 h): **3d** (52 mg, 45%) and **5** (29 mg, 23%).

3d: R_f 0.52 (AcOEt/hexane 1:3). M.p. 162–165° (from hexane/CH_2Cl_2). IR: 3300 (OH), 1673, 1619, 1594, 1567. ^{1}H-NMR (90 MHz): 1.73 (*s*, Me–C(2)); 3.31 (*s*, 2H–C(3)); 5.5 (br. *s*, NH); 7.25–7.7 (*m*, 7 arom. H); 7.9–8.1 (2 arom. H). MS: 289 (33, M^+), 274 (100, $[M - Me]^+$). HR-MS: 289.1090. ($C_{19}H_{15}NO_2^+$, calc. 289.1102).

5: Oil; 1:1 epimer mixture. R_f 0.63. IR (neat): 3450, 1771, 1690. ^{1}H-NMR (270 MHz): 1.21 (*s*, 1.5 H, Me–C(1)); 1.51 (*s*, 1.5 H, Me–C(1)); 1.88 (*dd*, J = 15.02, 2.20, 0.5 H, H_{endo}–C(2) (R^1 = Me, R^2 = Ph)); 2.44 (*s*, 0.5 H); 2.47 (*dd*, J = 14.92, 8.06, 0.5 H, H_{exo}–C(2) (R^1 = Ph, R^2 = Me)); 2.57 (*dd*, J = 14.92, 1.83, 0.5 H, H_{endo}–C(2) (R^1 = Ph, R^2 = Me)); 3.16 (*dd*, J = 15.02, 8.79, 0.5 H, H_{exo}–C(2) (R^1 = Me, R^2 = Ph)); 3.55 (*s*, 0.5 H); 3.907, 3.914 (2*dd*, J = 2.20, 8.79 and J = 8.06, 1.83, 1 H, H–C(2a)); 7.1–7.4 (*m*, 6.5 H); 7.54 (*tdd*, J = 7.69, 1.73, 1.09, 0.5 H, arom. H), 7.75 (*tdd*, J = 7.69, 1.73, 1.47, 0.5 H, arom. H); 7.93, 7.96 (2*dd*, J = 7.69, 1.47 and J = 7.69, 1.09, 1 H, arom. H); 8.12 (*dd*, J = 7.69, 1.73, 0.5 H, arom. H). MS: 292 (10, M^+), 118 (100, $[CH_2{=}CMePh]^+$). HR-MS: 292.1077 ($C_{19}H_{16}O_3^+$, calc. 292.1100).

*1*H-*Benz[*f*]indole-4,9-dione* (**4e**). As described for **3a**, with **1** (70 mg, 0.40 mmol), 1-ethoxyethene (**2e**; 0.58 g, 8 mmol), and benzene (70 ml; 1.5 h): **4e** (26 mg, 33%). R_f 0.46 (AcOEt/hexane 1:3). M.p. 297–299° (from $CHCl_3$). IR: 3250, 1655, 1587. ^{1}H-NMR (90 MHz): 7.2–8.0 (*m*, 7, arom. H). MS: 197 (100, M^+). HR-MS: 197.0465 ($C_{12}H_7NO_2^+$, calc. 197.0475).

*2-Methyl-1*H-*benz[*f*]indole-4,9-dione* (**4f**). As described for **3a**, with **1** (70 mg, 0.40 mmol), 2-methoxyprop-1-ene (**2f**; 0.58 g, 8 mmol), and benzene (70 ml; 3 h). Purification by recrystallization from $CHCl_3$ instead of TLC: **4f** (70 mg, 72%). M.p. 300° (dec.; from $CHCl_3$; [6c]: M.p. 304–305° (dec.)).

Similarly, **4f** (40 mg, 47%) was obtained from **1** (70 mg, 0.40 mmol) and isopropenyl acetate (**2g**; 0.80 g, 8 mmol) in benzene (140 ml) after 4.5 h. Purification by prep. TLC (silica gel, AcOEt/hexane 1:3; R_f 0.53).

*cis-1,2,3,3aα,4,10bα-Hexahydrobenzo[*f*]cyclopenta[*b*]indole-5,10-dione* (**3h**). As described for **3a**, with **1** (70 mg, 0.40 mmol), cyclopentene (**2h**; 0.54 g, 8.0 mmol), and benzene (70 ml; 10 h): **3h** (12 mg, 13%). R_f 0.28 (AcOEt/hexane 1:3). M.p. 205–207° (from hexane/CH_2Cl_2). IR: 3350, 1676, 1618, 1593, 1565. ^{1}H-NMR (270 MHz): 1.5–2.1 (*m*, CH_2)$_3$); 3.96 (*ddd*, J = 9.53, 8.06, 3.29, H_α–C(10b)); 4.5–4.6 (*m*, H_α–C(3a)); 5.2 (br. *s*, NH); 7.5–7.7 (*m*, 2 arom. H); 7.95 (*dd*, J = 7.69, 1.10, 1 arom. H); 8.06 (*dd*, J = 7.69, 1.10, 1 arom. H). MS: 239 (83, M^+), 210 ($[M - CO]^+$, 100). HR-MS: 239.0958 ($C_{15}H_{13}NO_2^+$, calc. 239.0946).

*2,3,4,5-Tetrahydro-1*H-*benzo[*b*]carbazole-6,11-dione* (**4i**). As described for **3a**, with **1** (70 mg, 0.40 mmol), 1-methoxycyclohexene (**2i**; 0.90 g, 8.0 mmol), and benzene (70 ml; 2.5 h): **4i** (68 mg, 68%). R_f 0.15 ($CHCl_3$). M.p. 290° (dec.; from $CHCl_3$). IR: 3200, 1654, 1587. ^{1}H-NMR (270 MHz): 1.75–1.95 (*m*, CH_2(1), CH_2(4)); 2.71 (*t*, J = 5.86 CH_2); 2.89 (*t*, J = 5.86, CH_2); 7.6–7.75 (*m*, 2 arom. H); 8.1–8.2 (*m*, 2 arom. H), 9.3 (br., NH). MS: 251 (100, M^+). HR-MS: 251.0930 ($C_{16}H_{13}NO_2^+$, calc. 251.0945).

5-Bromo-2,4-dimethoxyphenol (**9**). A soln. of **8** [12] (1.73 g, 7.06 mmol) and 3-chloroperbenzoic acid (1.83 g, 10.6 mmol) in CH_2Cl_2 (30 ml) was heated under reflux under N_2 for 6 h. After evaporation, AcOEt (50 ml) was added, the resulting mixture washed with sat. $NaHCO_3$ soln. and brine, dried (Na_2SO_4), and evaporated. The residue was dissolved in MeOH (3 ml) and treated with 10% aq. KOH soln. (8 ml) at r.t. with stirring for 45 min. The mixture was neutralized with conc. HCl soln. and the solvent removed by evaporation. The residue was extracted with CH_2Cl_2, the extract dried ($MgSO_4$) and evaporated, and the residue recrystallized: **9** (1.31 g, 80%). M.p. 93–94° (from Et_2O/hexane). IR: 3300, 1661, 1599. ^{1}H-NMR (90 MHz): 3.83, 3.88 (2*s*, 2 MeO); 6.52 (*s*, H–C(3)); 7.10 (*s*, H–C(6)). MS: 234 (98, $[M + 2]^+$), 232 (100, M^+). HR-MS: 231.9763 ($C_8H_9Br^+$, calc. 231.9735).

2-Bromo-5-methoxycyclohexa-2,5-diene-1,4-dione (**10**). To a stirred soln. of **9** (812 mg, 3.5 mmol) in MeCN (6 ml) at r.t. was added dropwise a soln. of ceric ammonium nitrate (4.77 g, 8.7 mmol) in H_2O (6 ml). The mixture was stirred for 1.5 h at r.t., then diluted with H_2O, and extracted with CH_2Cl_2. The extract was washed successively with H_2O, aq. $NaHCO_3$ soln. and brine, dried ($MgSO_4$), and evaporated and the residue recrystallized from Et_2O: **10** (570 mg, 74%). M.p. 195–196° ([20]: m.p. 190–191°).

2-Methoxy-5-[(phenylmethyl)amino]cyclohexa-2,5-diene-1,4-dione (**11**). A mixture of **10** (200 mg, 0.92 mmol), benzylamine (107 mg, 1.0 mmol), and K_2CO_3 (373 mg) in benzene (10 ml) was stirred for 24 h under N_2. The resulting mixture was filtered through a *Celite* pad. After evaporation of the filtrate, the residue was subjected to prep. TLC (silica gel, CH_2Cl_2): **11** (97 mg, 43%). M.p. 285° (dec.; from hexane/CH_2Cl_2). IR: 3378, 3274, 1647, 1632, 1599. ^{1}H-NMR (90 MHz): 3.84 (*s*, MeO); 4.30 (*d*, J = 5.71, PhCH_2); 5.46 (*s*, H–C(3) or H–C(6)); 5.77 (*s*, H–C(6) or H–C(3)); 6.0–6.4 (br. NH); 7.32 (*s*, 5 arom. H). MS: 243 (58, M^+), 91 (100, $[PhCH_2]^+$). HR-MS: 243.0879 ($C_{14}H_{13}NO_3^+$, calc. 243.0895).

2-Amino-5-methoxycyclohexa-2,5-diene-1,4-dione (**12**). A mixture of **11** (123 mg, 0.51 mmol) and 10% Pd/C (53 mg, 0.05 mmol) in AcOEt under H_2 was stirred overnight at r.t. After filtering through a *Celite* pad and removing the solvent, the residue was subjected to prep. TLC (silica gel, hexane/AcOEt 1:3): **12** (31 mg, 40%). M.p. 185° (dec.; from EtOH). IR: 3424, 3306, 1669, 1625, 1576, 1560. ^{1}H-NMR (90 MHz): 3.84 (*s*, MeO); 5.0–5.4 (br., NH_2); 5.66 (*s*, H–C(3) or H–C(6)); 5.77 (*s*, H–C(6) or H–C(3)). MS: 153 (91, M^+), 124 (100, $[M - HCO]^+$). Anal. calc. for $C_7H_7NO_2$: C 54.90, H 4.61, N 9.15; found: C 54.81, H 4.64, N 9.07.

*2,3-Dihydro-2,5,6-trimethyl-2-phenyl-1*H-*indole-4,7-dione* (**13d**). A soln. of **6** (30 mg, 0.20 mmol) and **2d** (118 mg, 1.0 mmol) in benzene (20 ml) was irradiated under N_2 for 8 h with a 100-W high-pressure mercury arc through

a *Pyrex* filter. After evaporation the product was subjected to prep. TLC (silica gel): **13d** (16 mg, 30%). Oil. R_f 0.42 (AcOEt/hexane 1:3). IR (neat): 3350, 1662, 1633, 1591. ^{1}H-NMR (90 MHz): 1.66 (*s*, Me–C(2)); 1.97, 2.06 (2*s*, Me–C(5), Me–C(6)); 3.15 (*s*, 2H–C(3)); 5.15–5.25 (br., NH); 7.1–7.5 (*m*, 5 arom. H). MS: 267 (52, M^+), 252 (100, $[M - Me]^+$). HR-MS: 267.1244 ($C_{16}H_{17}NO_2$, calc. 267.1259).

*2,3-Dihydro-5,6-dimethyl-2,2-diphenyl-1*H*-indole-4,7-dione* (**13j**). As described for **13d**, with **6** (30 mg, 0.20 mmol), 1,1-diphenylethene (**2j**; 180 mg, 1.0 mmol), and benzene (20 ml; 7 h): **13j** (20 mg, 30%). Oil. R_f 0.48 (AcOEt/hexane 1:3). IR (neat): 1655, 1632, 1592. ^{1}H-NMR (90 MHz): 1.95, 2.03 (2*s*, Me–C(5), Me–C(6)); 3.66 (*s*, 2H–C(3)); 5.3–5.5 (br., NH); 7.25–7.35 (*m*, 10 arom. H). MS: 329 (71, M^+), 167 (100). HR-MS: 329.1432 ($C_{22}H_{19}NO_2^+$, 329.1415).

*2,5,6-Trimethyl-1*H*-indole-4,7-dione* (**14f**). As described for **13d**, with **6** (24 mg, 0.16 mmol), **2f** (231 mg, 3.2 mmol), and benzene (10 ml; 5 h): **14f** (13 mg, 43%). M.p. 239° (sublimation). IR: 3240, 1655, 1637, 1603. ^{1}H-NMR: 2.04 (*s*, Me–C(5), Me–C(6)); 2.35 (*s*, Me–C(2)); 6.31 (br. *s*, H–C(3)); 8.9–9.9 (br., NH). MS: 189 (100, M^+). HR-MS: 189.0771 ($C_{11}H_{11}NO_2^+$, calc. 189.0790).

Use of acetone instead of benzene gave **14f** in a lower yield (7.6 mg, 25%).

*6,7,8,9-Tetrahydro-2,3-dimethyl-5*H*-carbazole-1,4-dione* (**14i**). As described for **13d**, with **6** (30 mg, 0.20 mmol), **2i** (112 mg, 1.0 mmol), and benzene (20 ml; 30 h): **14i** (7.3 mg, 16%). M.p. 229–230° (from hexane/CH_2Cl_2). IR: 3208, 3126, 1650, 1626, 1603. ^{1}H-NMR (90 MHz): 1.7–1.9 (*m*, CH_2(6), CH_2(7)); 2.02 (*s*, Me–C(2), Me–C(3)); 2.1–2.8 (*m*, CH_2(5), CH_2(8)); 8.5–9.5 (br., NH). MS: 229 (100, M^+). HR-MS: 229.1095 ($C_{14}H_{15}NO_2^+$, calc. 229.1102).

*2,3-Dihydro-2-methyl-2,5-diphenyl-1*H*-indole-4,7-dione* (**15d**). As described for **13d**, with **7** (40 mg, 0.23 mmol), **2d** (0.12 g, 1.1 mmol), and benzene (27 ml; 7.5 h): **15d** (25 mg, 35%). M.p. 124° (from hexane/Et_2O). IR: 3310, 1661, 1617, 1578, 1561. ^{1}H-NMR (90 MHz): 1.72 (*s*, Me–C(2)); 3.23 (*s*, 2H–C(3)); 5.45–5.35 (br., NH); 6.56 (*s*, H–C(6)); 7.3–7.5 (*m*, 10 arom. H). MS: 315 (81, M^+), 300 (100, $[M - Me]^+$). HR-MS: 315.1259 ($C_{21}H_{17}NO_2^+$, calc. 315.1239).

*2-Methyl-5-phenyl-1*H*-indole-4,7-dione* (**16**). As described for **13d**, with **7** (25 mg, 0.13 mmol), **2f** (0.18 g, 2.6 mmol), and benzene (17 ml; 4.5 h): **16** (12 mg, 38%). M.p. 245–247° (from hexane/Et_2O/$CHCl_3$). IR: 3250, 1657, 1638, 1585, 1562. ^{1}H-NMR (90 MHz): 2.39 (*s*, Me–C(2)); 6.43 (*s*, H–C(3)); 6.63 (*s*, H–C(6)); 7.44 (*s*, 5 arom. H); 9.2–9.8 (br., NH). MS: 237 (100, M^+). HR-MS: 237.0779 ($C_{15}H_{11}NO_2^+$, calc. 237.0790).

*2,3-Dihydro-2-methoxy-2-methyl-5-phenyl-1*H*-indole-1,4,7-triyl Triacetate* (**19**). After irradiation of **7** (52 mg, 0.26 mmol) and **2f** (0.38 g, 5.2 mmol) in benzene (35 ml) for 6.5 h (see above), the solvent and excess **2f** were removed *in vacuo*. To the residue was added pyridine/Ac_2O 1:1 (2 ml). The mixture was stirred at 50° for 22 h and then evaporated and the residue subjected to prep. TLC (silica gel, AcOEt/$CHCl_3$ 1:10): **19** (42 mg, 41%). R_f 0.56. IR (neat): 1768, 1718. ^{1}H-NMR (90 MHz): 1.70 (*s*, Me–C(2)); 2.24, 2.26, 2.41 (3*s*, 3 Ac); 3.19 (*s*, 2H–C(3)); 3.33 (*s*, MeO); 7.20 (*s*, H–C(6)); 7.3–7.5 (*m*, 3 arom. H); 7.6–7.75 (*m*, 2 arom. H). MS: 397 (12, M^+), 355 (22, $[M - CH_2CO]^+$), 239 (77), 43 (100). HR-MS: 397.1500 ($C_{22}H_{23}NO_6^+$, 397.1525).

*5-Methoxy-2-methyl-1*H*-indole-4,7-dione* (**18**). As described for **13d**, with **12** (15 mg, 0.10 mmol), **2f** (72 mg, 1.0 mmol), benzene (10 ml), and acetone (1 ml; 6 h): **18** (4.2 mg, 22%): M.p. 120° (dec.). IR: 3228, 3136, 1684, 1635, 1594. ^{1}H-NMR (90 MHz): 2.36 (*s*, Me–C(2)); 3.82 (*s*, MeO); 5.64 (*s*, H–C(6)); 6.35 (br. *s*, H–C(3)); 8.9–9.9 (br., NH). MS: 191 (100, M^+). HR-MS: 191.0568 ($C_{10}H_9NO_3^+$, calc. 191.0583).

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