Synthesis of 4,7-Indolequinones by Photoinduced Reaction of Azidoquinones

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Various azidoquinones were prepared from methyl 3-substituted 2,3-dihydro-5-hydroxy-6-methylbenzofuran-2-carboxylate. Irradiation of these azidoquinones gave methyl 3-substituted 6-methyl-4,7-dioxoindole-2-carboxylates, a model of mitomycin analogs, in a moderate yield.

Recently, the author found that *p*-benzoquinones having an ester group in the α position of alkyl side chains have a high reactivity toward γ-hydrogen abstraction reaction to give the rearranged product, *i.e.*, methyl 3-substituted 2,3-dihydro-5-hydroxybenzofuran-2-carboxylate derivatives **1**, in fairly good yields.[1] In this paper, as a further extension of these reactions, the present author reports a reaction of the corresponding azidoquinone **4** derived from the dihydrobenzofuran **1**. The investigations of the photolysis of azidoquinones have been centered on the exploitation of a new general synthetic method of 4,7-indolequinones, which are related to some natural products.[2] Pharmacologically interesting functionalized 4,7-indolequinones **5a**—**i** were obtained by photoinduced cyclization of the corresponding azidoquinones **4a**—**i** having a suitable side chain.

In general, the intramolecular cyclization of ortho-substituted aryl azide could be one of the most important synthetic routes to five-memberd nitrogen heterocycles.[3] However, research studies on simple alkyl-substituted azidoquinones so far reported have revealed that the reactions of azidoquinones were highly dependent upon the reaction conditions (acidic or thermal), and rearrangement products[4] or ring contraction products[5] were the major components of the reactions.[6] On the contrary, in the photoreaction of functionalized alkylazidoquinones as described in the following text, it was found that an intramolecular photoinduced cyclization reaction occurs without any difficulties to give 4,7-indolequinone derivatives **5**.

Results and Discussion

Preparation of Azidoquinones. All of the azidoquinones **4** were usually obtained from methyl 3-substituted 2,3-dihydro-5-hydroxy-6-methylbenzofuran-2-carboxylates **1**[1] by the subsequent reaction (Scheme 1). The dihydrobenzofuran **1** was treated with bromine in chloroform to give methyl 3-substituted 4-bromo-2,3-dihydro-5-hydroxy-6-methylbenzofuran-2-carboxylate **2**. Oxidation of this bromide **2** with ceric ammonium nitrate (CAN) in an aqueous acetonitrile[7] afforded bromoquinone **3**, which was reacted with sodium azide[8] in an aqueous methanol to provide azidoquinone **4** in an excellent overall yield from **1**. The structures of bromodihydrobenzofuran **2**, bromoquinone **3**, and azidoquinone **4** were identified on the basis of its spectroscopic properties (Table 2).

Table 1. Photoinduced formation of 4,7-indolequinone **5** from azidoquinone **4**

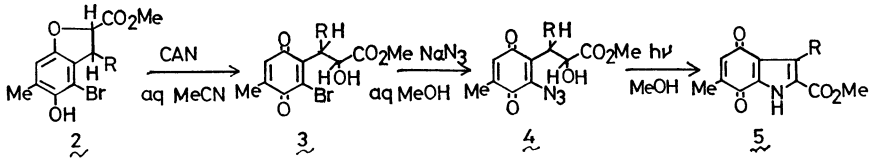
Entry	Azidoquinone	R	Product	Yield/%[a]
1	**4a**	H	**5a**	42
2	**4b**	Me	**5b**	62
3	**4c**	Et	**5c**	61
4	**4d**	$(CH_2)_2CH_3$	**5d**	60
5	**4e**	CO_2Me	**5e**	40
6	**4f**	$(CH_2)_2CO_2Me$	**5f**	64
7	**4g**	$(CH_2)_3NPht$	**5g**	56
8	**4h**	$(CH_2)_3NHCOCF_3$	**5h**	42
9	**4i**	$CH_2OCO_2C_6H_5$	**5i**	37

a) Reported yields are for isolated, purified products.

Irradiation of Azidoquinones. On irradiation of a solution of azidoquinone **4** (1 mmol) in methanol with a high pressure Hg arc lamp (300 W), the orange yellow color of the solution rapidly turned purple red with the evolution of nitrogen, and then gradually changed to dark yellow. The photochemical reaction was complete in several hours (2—5 h) at room temperature and gave methyl 3-substituted 6-methyl-4,7-dioxoindole-2-carboxylate **5** in a good yield after purification by column chromatography (Table 1). Methanol was the best solvent for the photochemical reaction. Although the same product was taken in benzene, hexane, and chloroform, the yield of the 4,7-indolequinone **5** was rather poor.

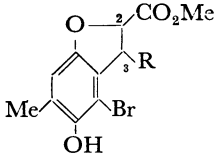
The salient feature of this result indicated that the formation of functionalized 4,7-indolequinones **5e**—**i** easily occures on irradiation of azidoquinone **4e**—**i** having various functional groups (ester, amide, imide, and protected alcohol) in the alkyl side chain.

The structures of the irradiation product **5** were established by their IR and ^1H NMR spectra and by their chemical reactions (Experimental). For ex-



Scheme 1.

Table 2. ^{1}H NMR Spectra[a] of intermediates **2**, **3**, and **4**



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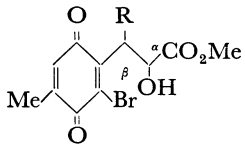

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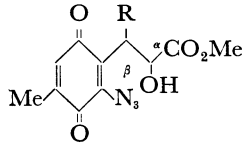
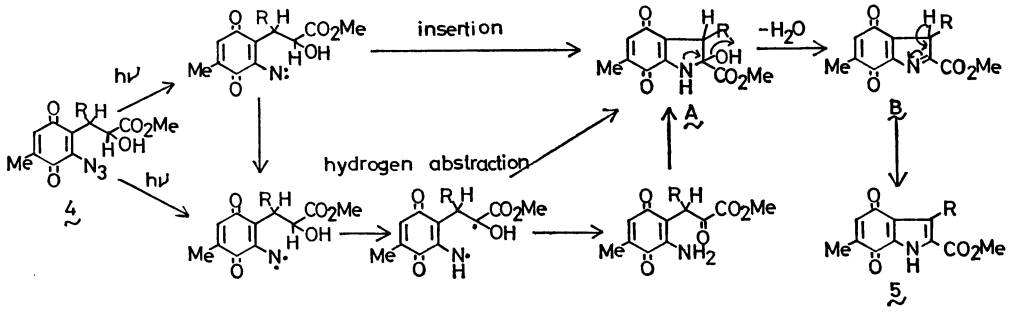


4

	R	C_2-H	C_3-H	OH	C_α-H	C_β-H	OH	C_α-H	C_β-H	OH
a	H	5.18(dd) J=7.2 Hz J=10 Hz	b)	3.92(s)	4.43(t) J=7 Hz	3.10(d) J=7 Hz	2.83(d) J=7 Hz	4.36(t) J=7 Hz	2.87(d) J=7 Hz	2.96(bs)
b	Me	4.68(d) J=4 Hz	3.62(m)	5.14(s)	4.64(t) J=8 Hz	3.53(m)	3.39(bd) J=8 Hz	4.46(d)	3.46(dq)	c)
c	Et	4.85(d) J=3.2 Hz	3.52(m)	5.17(s)	4.56(dd) J=7.5 Hz J=10 Hz	3.61(m)	3.70(d) J=10 Hz	4.47(t) J=8 Hz	3.34(dq) J=7.5 Hz J=8 Hz	3.94(bs)
d	$(CH_2)_2CH_3$	4.85(d) J=3.2 Hz	3.52(m)	5.16(s)	4.55(dd) J=7.5 Hz J=10 Hz	3.74(m)	3.74(d) J=10 Hz	4.45(dd) J=7 Hz J=9.5 Hz	3.43(m)	c)
e	CO_2Me	5.35(d) J=4.6 Hz	4.40(d) J=4.6 Hz	5.22(s)	4.84(dd) J=6 Hz J=8 Hz	4.55(d) J=6 Hz	3.39(d) J=8 Hz	4.83(dd) J=5.5 Hz J=7.5 Hz	4.32(d) J=5.5 Hz	3.38(bd) J=7.5 Hz
f	$(CH_2)_2CO_2Me$	4.83(d) J=3.3 Hz	3.52— 3.88(m)	5.23(s)	4.57(dd) J=7.5 Hz J=10 Hz	c)	c)	4.48(dd) J=7.5 Hz J=10 Hz	c)	c)
g	$(CH_2)_3NPht$	4.86(d) J=3.5 Hz	3.50— 3.90(m)	5.19(s)	4.52(dd) J=8 Hz J=10 Hz	c)	3.56(d) J=10 Hz	4.44(t) J=7.5 Hz	3.32— 3.80(m)	c)
h	$(CH_2)_3NHCOCF_3$	4.78(d) J=3 Hz	3.54(m)	5.13(s)	4.54(dd) J=8 Hz J=10 Hz	c)	c)	4.45(t) J=8 Hz	3.34(m)	3.92(bd) J=8 Hz
i	$CH_2OCO_2C_6H_5$	5.18(d) J=3.2 Hz	4.02(m)	5.19(s)	4.44— 4.85(m)	4.12(m)	3.59(d) J=8 Hz	4.35— 4.82(m)	c)	c)

a) ^{1}H NMR spectra were run on a 100 MHz instrument. b) ABX type: 3.29(dd, J=7.2 and 16 Hz, 1H); 3.53(dd, J=10 and 16 Hz, 1H). c) Chemical shifts and coupling constants were not determined due to overlap with the signal of other protons.



Scheme 2.

ample, evidence for the presence of N–H bond in photoproduct **5** was shown by the fact that the reaction of **5b** with 1 equiv of potassium *t*-butoxide in dry dimethyl sulfoxide,[9] followed by addition of the excess methyl iodide, gave methyl 1,3,6-trimethyl-4,7-dioxoindole-2-carboxylate **6a** in an excellent yield (90%). Additional evidence for the presence of the quinone ring in the product **5** was obtained by reduction-acetylation[10] of **5f** to methyl 4,7-diacetoxy-5-methylindole-2-carboxylate derivative **7** in an 80% yield. The structure of **5f** was further supported by the Thiele oxidation[11] to methyl 4,5,7-triacetoxy-6-methylindole 2-carboxylate **8**.

Thermal cyclization of azidoquinone **4** in benzene or toluene gave indolequinone **5** in a low yield (5—10%). The yield of **5** decreased further when **4** was heated in a high boiling solvent (xylene or decalin), and tars were obtained.

The photochemical conversion from **4** to **5** can be rationalized as proceeding *via* nitrene[12] (Scheme 2), but it is not clear whether the cyclization step takes place by direct intramolecular insertion of the singlet nitrene into a C–H bond or by intramolecular 1,5-hydrogen abstraction of the triplet nitrene.

The evidence for the reaction pathway outlined in Scheme 2 was obtained by studying UV spectra analysis during irradiation of **4b**. Irradiation of **4b** in methanol caused a rapid change in the absorption spectrum. The absorption maximum at 405 nm (**4b**) was shifted initially to 510 nm (**A** or **B**), but finally moved 346 nm (**5b**). That is to be expected for the intermediate corresponding to **A** or **B**.

In summary, these photochemical ring formations from the azidoquinone under mild conditions allow the facile synthesis of highly functionalized 4,7-indolequinones which have mitosane ring systems.

Experimental

Melting points were measured on a Yanagimoto micro melting point apparatus and are uncorrected. Infrared spectra were run on a JASCO IRA-1 spectrophotometer. Nuclear magnetic resonance spectra were obtained with JEOL PS-100 spectrometer with tetramethylsilane as an internal standard and the chemical shifts are recorded in δ values. Mass spectra were measured with Hitachi M-52 instrument (20 eV). Column chromatography was performed using Wako reagent grade silica gel (200 mesh). Preparative thin layer chromatography was performed using Merck silica gel F-254. Elemental analyses were performed by the Microanalytical Laboratory of Kyoto University. UV irradiations were carried out in a Pyrex tube at room temperature with an Eikosha 300 W high pressure Hg lamp.

Preparation of Starting Materials. All of the compounds **1a**—**i** described below were prepared according to the previously reported methods.[1] Methyl 2,3-dihydro-5-hydroxy-6-methylbenzofuran-2-carboxylate (**1a**), methyl 2,3-dihydro-5-hydroxy-3,6-dimethylbenzofuran-2-carboxylate (**1b**), methyl 3-ethyl-2,3-dihydro-5-hydroxy-6-methylbenzofuran-2-carboxylate (**1c**), methyl 2,3-dihydro-5-hydroxy-6-methyl-3-propylbenzofuran-2-carboxylate (**1d**), dimethyl 2,3-dihydro-5-hydroxy-6-methylbenzofuran-2,3-dicarboxylate (**1e**), methyl 2,3-dihydro-5-hydroxy-3-[2-(methoxycarbonyl)ethyl]-6-methylbenzofuran-2-carboxylate (**1f**), methyl 2,3-dihydro-5-hydroxy-3-[3-(phthalimido)propyl]-6-methylbenzofuran-2-carboxylate (**1g**), methyl 2,3-dihydro-5-hydroxy-6-methyl-3-[3-trifluoroacetamido)propyl]benzofuran-2-carboxylate (**1h**), and methyl 2,3-dihydro-5-hydroxy-3-(phenoxycarbonyloxymethyl)benzofuran-2-carboxylate (**1i**).

Methyl 4-Bromo-2,3-dihydro-5-hydroxy-6-methylbenzofuran-2-carboxylate (2a). (General Procedure for Bromination). To a well-stirred solution of **1a** (389 mg, 1.87 mmol) in chloroform (20 ml) at 0 °C was added dropwise (30 min) 1 M (1 M=1 mol dm^{-3}) bromine in chloroform (2 ml). After stirring for 30 min, the reaction mixture was treated with a diluted solution of sodium thiosulfate. The organic layer was washed twice with water, dried over $MgSO_4$, evaporated, and chromatographed (silica gel, benzene solvent) to give **2a** (484 mg, 90%): Mp 81.5—82.5 °C (dichloromethane–petroleum ether); IR (KBr): 3350 and 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.25 (s, 3H), 3.29 (dd, J=7.2 and 16 Hz, 1H), 3.53 (dd, J=10 and 16 Hz, 1H), 3.81 (s, 3H), 3.92 (bs, 1H), 5.18 (dd, J=7.2 and 10 Hz, 1H), and 6.62 (s, 1H); Found: C, 45.81; H, 3.94; Br, 28.17%. Calcd for $C_{11}H_{11}O_4Br$: C, 46.01; H, 3.86; Br, 27.83%.

Methyl 4-Bromo-2,3-dihydro-5-hydroxy-3,6-dimethylbenzofuran-2-carboxylate (2b). Reaction of **1b** (641 mg, 2.88 mmol) with bromine by the method described above gave **2b** (702 mg, 81%): Mp 70—73 °C (dichloromethane–petroleum ether); IR (KBr): 3420 and 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.46 (d, J=7 Hz, 3H), 2.23 (s, 3H), 3.72 (s, 3H), 3.62 (m, 1H), 4.68 (d, J=4 Hz, 1H), 5.14 (s, 1H), and 6.62 (s, 1H); Found: C, 47.62; H, 4.43; Br, 26.77%. Calcd for $C_{12}H_{13}O_4Br$: C, 47.86; H, 4.35; Br, 26.54%.

Methyl 4-Bromo-3-ethyl-2,3-dihydro-5-hydroxy-6-methylbenzofuran-2-carboxylate (2c). Reaction of **1c** (236 mg, 1 mmol) with bromine gave **2c** (230 mg, 73%): Mp 80—81 °C (petroleum ether); IR (KBr): 3460 and 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 0.96 (t, J=7 Hz, 3H), 1.66 (m, 2H), 2.26 (s, 3H), 3.52 (m, 1H), 3.78 (s, 3H), 4.85 (d, J=3.2 Hz, 1H), 5.17 (s, 1H), and 6.67 (s, 1H); Found: C, 49.26; H, 4.92; Br, 25.29%. Calcd for $C_{13}H_{15}O_4Br$: C, 49.54; H, 4.80; Br, 25.36%.

*Methyl 4-Bromo-2,3-dihydro-5-hydroxy-6-methyl-3-propylbenzofuran-2-carboxylate (**2d**).* Bromination of **1d** (250 mg, 1 mmol) gave **2d** as an oil (263 mg, 80%). IR (neat): 3460 and 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 0.96 (t, J=7 Hz, 3H), 1.20—2.20 (m, 4H), 2.25 (s, 3H), 3.52 (m, 1H), 3.76 (s, 3H), 4.85 (d, J=3.2 Hz, 1H), 5.16 (s, 1H), and 6.64 (s, 1H). Found: C, 50.94; H, 5.40%. Calcd for $C_{14}H_{17}O_4Br$: C, 51.08; H, 5.21%.

*Dimethyl 4-Bromo-2,3-dihydro-5-hydroxy-6-methylbenzofuran-2,3-dicarboxylate (**2e**).* A solution of **1e** (476 mg, 1.79 mmol) in chloroform was treated with bromine to give **2e** (405 mg, 66%): Mp 182—185 °C (methanol–petroleum ether); IR (KBr): 3340 and 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.27 (s, 3H), 3.80 (s, 3H), 3.82 (s, 3H), 4.40 (d, J=4.6 Hz, 1H), 5.22 (s, 1H), 5.35 (d, J=4.6 Hz, 1H), and 6.71 (s, 1H). Found: C, 45.10; H, 3.94%. Calcd for $C_{13}H_{13}O_6Br$: C, 45.24; H, 3.80%.

*Methyl 4-Bromo-2,3-dihydro-5-hydroxy-3-[2-(methoxycarbonyl)-ethyl]-6-methylbenzofuran-2-carboxylate (**2f**).* Reaction of **1f** (589 mg, 2 mmol) with bromine afforded **2f** (642 mg, 86%): Mp 91—92 °C (petroleum ether–dichloromethane); IR (KBr): 3470, 1745, and 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.90—2.51 (m, 4H), 2.26 (s, 3H), 3.52—3.88 (m, 1H), 3.66 (s, 3H), 3.75 (s, 3H), 4.83 (d, J=3.3 Hz, 1H), 5.23 (s, 1H), and 6.64 (s, 1H). Found: C, 47.97; H, 4.76; Br, 21.59%. Calcd for $C_{15}H_{17}O_6Br$: C, 48.27; H, 4.59; Br, 21.41%.

*Methyl 4-Bromo-2,3-dihydro-5-hydroxy-3-[3-(phthalimido)propyl]-6-methylbenzofuran-2-carboxylate (**2g**).* Reaction of **1g** (395 mg, 1 mmol) with bromine gave **2g** (337 mg, 71%): Mp 153—154 °C (methanol–dichloromethane); IR (KBr): 3490, 1765, and 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.60—2.20 (m, 4H), 2.24 (s, 3H), 3.50—3.90 (m, 3H), 3.77 (s, 3H), 4.86 (d, J=3.5 Hz, 1H), 5.19 (s, 1H), 6.65 (s, 1H), and 7.66—7.90 (m, 4H). Found: C, 55.44, H, 4.17; N, 2.83; Br, 17.07%. Calcd for $C_{22}H_{20}O_6NBr$: C, 55.71; H, 4.25; N, 2.95; Br, 16.85%.

*Methyl 4-Bromo-2,3-dihydro-5-hydroxy-6-methyl-3-[3-(trifluoroacetamido)propyl]benzofuran-2-carboxylate (**2h**).* Prepared from **1h** (860 mg, 2.38 mmol) and bromine; (628 mg, 60%): Mp 93—94 °C (petroleum ether–dichloromethane); IR (KBr): 3420, 3290, 1735, and 1700 cm^{-1}; ^1H NMR ($CDCl_3$)δ: 1.45—2.20 (m, 4H), 2.25 (m, 3H), 3.40 (t, J= 7 Hz, 2H), 3.54 (m, 1H), 3.75 (s, 3H), 4.78 (d, J=3 Hz, 1H), 5.13 (s, 1H), 6.41 (bs, 1H), and 6.61 (s, 1H). Found: C, 43.50; H, 3.87; N, 3.30%. Calcd for $C_{16}H_{17}O_5NBr$: C, 43.65; H, 3.89; N, 3.18%.

*Methyl 4-Bromo-2,3-dihydro-5-hydroxy-6-methyl-3-(phenoxycarbonyloxymethyl)benzofuran-2-carboxylate (**2i**).* Treatment of **1i** (117 mg, 0.327 mmol) with bromine afforded **2i** (140 mg, 98%): Mp 103—104 °C (petroleum ether–dichloromethane); IR (KBr): 3470, 1760, and 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.27 (s, 3H), 3.79 (s, 3H), 4.02 (m, 1H), 4.31 (dd, J= 8.2 and 11 Hz, 1H), 4.72 (dd, J=3.8 and 11 Hz, 1H), 5.18 (d, J=3.2 Hz, 1H), 5.19 (s, 1H), 6.71 (s, 1H), and 7.20—7.44 (m, 5H). Found: C, 52.24; H, 4.09%. Calcd for $C_{19}H_{17}O_7Br$: C, 52.19; H, 3.92%.

*Methyl 3-(2-Bromo-4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-2-hydroxypropionate (**3a**).* (General Procedure for Oxidation). To a solution of **2a** (287 mg, 1 mmol) in 70% aq acetonitrile (10 ml) at 0 °C was added dropwise over 15 min a solution of ceric ammonium nitrate (CAN)[7] (1.21 g, 2.2 mmol) in water (5 ml). The mixture was stirred for 15 min and then poured into water (100 ml). The aq suspension was extracted with chloroform (3×20 ml) and the organic phases were washed with water (3×20 ml), dried, passed through a short pad of silica gel using chloroform, and evaporated to give **3a** (220 mg, 98%): Mp 77—78 °C (dichloromethane–petroleum ether); IR (KBr): 3480, 1735, 1660, and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.11 (d, J=1.6 Hz, 3H), 2.83 (d, J=7 Hz, 1H), 3.10 (d, J=7 Hz, 2H), 3.78 (s, 3H), 4.43 (q, J=7 Hz, 1H), and 6.61 (q, J=1.6 Hz, 1H). Found: C, 43.78; H, 3.69; Br, 26.60%. Calcd for $C_{11}H_{11}O_5Br$: C, 43.58; H, 3.66; Br, 26.37%.

*Methyl 3-(2-Bromo-4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-2-hydroxybutyrate (**3b**).* (CAN Oxidation of **2b**): (86%); mp 116—118 °C (hexane–dichloromethane); IR (KBr): 3470, 1740, 1675, and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.32 (d, J=7 Hz, 3H), 2.12 (d, J=1.6 Hz, 3H), 3.39 (bd, J=8 Hz, 1H), 3.53—3.80 (m, 1H), 3.80 (s, 3H), 4.64 (t, J=8 Hz, 1H), and 6.62 (q, J=1.6 Hz, 1H). Found: C, 45.53; H, 4.16; Br, 25.43%. Calcd for $C_{12}H_{13}O_5Br$: C, 45.44; H, 4.13; Br, 25.19%.

*Methyl 3-(2-Bromo-4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-2-hydroxypentanoate (**3c**).* (CAN Oxidation of **2c**): (88%); IR (neat): 3460, 1740, 1670, and 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 0.90 (t, J=7 Hz, 3H), 1.70—1.92 (m, 2H), 2.12 (d, J=1.6 Hz, 3H), 3.61 (m, 1H), 3.70 (d, J=10 Hz, 1H), 3.74 (s, 3H), 4.56 (dd, J=7.5 and 10 Hz, 1H), and 6.63 (q, J=1.6 Hz, 1H). Found: C, 47.10; H, 4.66; Br, 24.38%. Calcd for $C_{13}H_{15}O_5Br$: C, 47.15; H, 4.57; Br, 24.13%.

*Methyl 3-(2-Bromo-4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-2-hydroxyhexanoate (**3d**).* (CAN Oxidation of **2d**): (90%); mp 82—83 °C (petroleum ether); IR (KBr): 3460, 1735, 1670, and 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 0.90 (t, J=7 Hz, 3H), 1.28 (m, 2H), 1.77 (m, 2H), 2.16 (d, J=1.6 Hz, 3H), 3.74 (s, 3H and m, 2H), 4.55 (dd, J=7.5 and 10 Hz, 1H), and 6.63 (q, J=1.6 Hz, 1H). Found: C, 48.51; H, 5.01; Br, 23.43%. Calcd for $C_{14}H_{17}O_5Br$: C, 48.71; H, 4.96; Br, 23.15%.

*Dimethyl 3-(2-Bromo-4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-2-hydroxysuccinate (**3e**).* (CAN Oxidation of **2e**): (96%); IR (neat): 3460, 1735, 1670, and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.13 (d, J=1.6 Hz, 3H), 3.39 (d, J=8 Hz, 1H), 3.70 (s, 3H), 3.76 (s, 3H), 4.55 (d, J=6 Hz, 1H), 4.84 (dd, J=6 and 8 Hz, 1H), and 6.65 (q, J=1.6 Hz, 1H). Found: C, 43.02; H, 3.75%. Calcd for $C_{13}H_{13}O_7Br$: C, 43.23; H, 3.63%.

*Dimethyl 3-(2-Bromo-4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-2-hydroxyhexanedioate (**3f**).* (CAN Oxidation of **2f**): (92%); mp 91—92 °C (hexane–dichloromethane); IR (KBr): 3440, 1735, 1725, 1665, and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.13 (d, J=1.6 Hz, 3H), 2.13—2.46 (m, 4H), 3.64 (s, 3H), 3.75 (s, 3H and m, 2H), 4.57 (dd, J=8 and 10 Hz, 1H), and 6.64 (q, J=1.6 Hz, 1H). Found: C, 46.55; H, 4.44; Br, 20.68%. Calcd for $C_{15}H_{17}O_7Br$: C, 46.29; H, 4.40; Br, 20.53%.

*Methyl 3-(2-Bromo-4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-2-hydroxy-6-phthalimidohexanoate (**3g**).* (CAN Oxidation of **2g**): (89%); mp 153—155 °C (dichloromethane–petroleum ether); IR (KBr): 3460, 3400, 1770, 1735, and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.40—2.10 (m, 4H), 2.10 (d, J=1.6 Hz, 3H), 3.62—3.76 (m, 2H), 3.72 (s, 3H), 4.52 (dd, J= 8 and 10 Hz, 1H), 6.60 (q, J=1.6 Hz, 1H), and 7.69—7.82 (m, 4H). Found: C, 53.67; H, 4.34; N, 2.76%. Calcd for $C_{22}H_{20}O_7NBr$: C, 53.89; H, 4.11; N, 2.86%.

*Methyl 6-Trifluoroacetamido-3-(2-bromo-4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-2-hydroxyhexanoate (**3h**).* (CAN Oxidation of **2h**): (42%); mp 124—125 °C (dichloromethane–petroleum ether); IR (KBr): 3450, 3330, 1750, 1700, and 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.30—2.10 (m, 4H), 2.12 (d, J=1.6 Hz, 3H), 3.35 (q, J=7 Hz, 2H), 3.73 (s, 3H and m, 1H), 4.54 (dd, J=4 and 5 Hz, 1H), and 6.60 (q, J=1.6 Hz, 1H). Found: C, 41.83; H, 3.82; N, 3.03; Br, 17.78%.

Calcd for $C_{16}H_{17}O_6NF_3Br$: C, 42.12; H, 3.76; N, 3.07; Br, 17.52%.

*Methyl 3-(2-Bromo-4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-2-hydroxy-4-(phenoxycarbonyloxy)butyrate (**3i**).* (CAN Oxidation of **2i**): (80%); IR (neat): 3460, 1750, and 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.12 (d, J=1.6 Hz, 3H), 3.59 (d, J=8 Hz, 1H), 3.79 (s, 3H), 4.12 (m, 1H), 4.44—4.85 (m, 2H and m, 1H), 6.65 (q, J=1.6 Hz, 1H), and 7.05—7.51 (m, 5H). Found: C, 50.19; H, 5.97%. Calcd for $C_{19}H_{17}O_8Br$: C, 50.35; H, 5.84%.

*Methyl 3-(2-Azido-4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-2-hydroxypropionate (**4a**).* (General Procedure for Azidoquinone Formation). To a solution of **3a** (303 mg, 1 mmol) in methanol (10 ml) at 0 °C was added sodium azide (78 mg, 1.2 mmol) in water (2 ml). The resulting mixture gradually became red. After stirring for 1 h at room temperature, the solvent was removed under reduced pressure at a temperature below 40 °C, water (50 ml) was added and the mixture was extracted with chloroform (3×25 ml). The combined chloroform extracts were washed with water (3×25 ml), dried ($MgSO_4$), evaporated, and chromatographed (silica gel, chloroform solvent) to give **4a** (238 mg, 90%). IR (neat): 3460, 2120, 1735, and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.07 (d, J=1.6 Hz, 3H), 2.87 (d, J=7 Hz, 2H), 2.96 (bs, 1H), 3.80 (s, 3H), 4.36 (t, J=7 Hz, 1H), and 6.61 (q, J=1.6 Hz, 1H). Anal.[13]

Compounds **4b—i** were prepared from the corresponding **3b—i** by the same procedure. The spectral data of these compounds are given below.

*Methyl 3-(2-Azido-4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-2-hydroxybutyrate (**4b**).* (Oil, 90%); IR (neat): 3440, 2110, 1735, and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.24 (d, J=7 Hz, 3H), 2.07 (d, J=1.6 Hz, 3H), 3.49 (m, 1H), 3.74 (s, 3H and m, 1H), 4.46 (d, J=8 Hz, 1H), and 6.55 (q, J=1.6 Hz, 1H). Anal.[13]

*Methyl 3-(2-Azido-4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-2-hydroxypentanoate (**4c**).* (Oil, 98%); IR (neat): 3440, 2110, 1740, 1670, and 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 0.84 (t, J=7 Hz, 3H), 1.74 (m, 2H), 2.07 (d, J=1.6 Hz, 3H), 3.34 (dt, J=8 and 7.5 Hz, 1H), 3.72 (s, 3H), 3.94 (bs, 1H), 4.47 (t, J=8 Hz, 1H), and 6.60 (q, J=1.6 Hz, 1H). Anal.[13]

*Methyl 3-(2-Azido-4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-2-hydroxyhexanoate (**4d**).* (88%); mp 93—94 °C (petroleum ether); IR (KBr): 3460, 2120, 2100, 1735, 1670, and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 0.88 (t, J=7 Hz, 3H), 1.22 (m, 2H), 1.73 (m, 2H), 2.05 (d, J=1.6 Hz, 3H), 3.43 (m, 1H), 3.72 (s, 3H), 3.78 (d, J=9.5 Hz, 1H), 4.45 (dd, J=7 and 9.5 Hz, 1H), and 6.55 (q, J=1.6 Hz, 1H). Found: C, 54.60; H, 5.64%. Calcd for $C_{14}H_{17}O_5N_3$: C, 54.72; H, 5.58%.

*Dimethyl 3-(2-Azido-5-methyl-3,6-dioxo-1,4-cyclohexadienyl)-2-hydroxysuccinate (**4e**).* (Oil, 88%); IR (neat): 3460, 2120, 1735, and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.10 (d, J=1.6 Hz, 3H), 3.38 (bd, J=7 Hz, 1H), 3.70 (s, 3H), 3.76 (s, 3H), 4.32 (d, J=5.5 Hz, 1H), 4.83 (dd, J=5.5 and 7 Hz, 1H), and 6.59 (q, J=1.6 Hz, 1H). Anal.[13]

*Dimethyl 3-(2-Azido-4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-2-hydroxyhexanedioate (**4f**).* (Oil, 80%); IR (neat): 3440, 2110, 2095, 1745, 1730, 1670, and 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.13 (d, J=1.6 Hz, 3H), 2.13—2.46 (m, 4H), 3.64 (s, 3H), 3.75 (s, 3H and m, 2H), 4.57 (dd, J=8 and 10 Hz, 1H), and 6.64 (q, J=1.6 Hz, 1H). Found: C, 51.11; H, 4.75%. Calcd for $C_{15}H_{17}O_7N_3$: C, 51.28; H, 4.88%.

*Methyl 3-(2-Azido-4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-2-hydroxy-6-phthalimidohexanoate (**4g**).* (71%); mp 117—120 °C (petroleum ether–dichloromethane); IR (KBr): 3460, 2110, 2100, 1770, 1735, 1705, and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.30—2.07 (m, 4H), 2.07 (d, J=1.6 Hz, 3H), 3.32—3.80 (m, 2H and m, 2H), 3.70 (s, 3H), 4.44 (m, 1H), 6.51 (q, J=1.6 Hz, 1H), and 7.60—7.80 (m, 4H). Anal.[13]

*Methyl 3-(2-Azido-4-methyl-3,6-dioxo-1,4-cyclohexadienyl)-6-trifluoroacetamido-2-hydroxyhexanoate (**4h**).* (Oil, 85%); IR ($CHCl_3$): 3430, 2110, 1720, and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.30—2.00 (m, 4H), 2.09 (d, J=1.6 Hz, 3H), 3.34 (m, 2H), 3.67 (m, 1H), 3.73 (s, 3H), 3.92 (bd, J=10 Hz, 1H), 4.45 (dd, J=7 and 10 Hz, 1H), 6.55 (q, J=1.6 Hz, 1H), and 6.95 (bs, 1H). Anal.[13]

*Methyl 3-(2-Azido-5-methyl-3,6-dioxo-1,4-cyclohexadienyl)-2-hydroxy-4-(phenoxycarbonyloxy)butyrate (**4i**).* (Oil, 68%); IR (neat): 3440, 2120, 1750, and 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.10 (d, J=1.6 Hz, 3H), 3.81 (s, 3H and m, 1H), 4.35—4.82 (m, 3H), 6.61 (q, J=1.6 Hz, 1H), and 7.09—7.53 (m, 5H). Anal.[13]

*Irradiation of **4a**.* (General Photochemical Procedure for 4,7-Indolequinone Formation). A solution of **4a** (265 mg, 1 mmol) in methanol (200 ml) was purged with nitrogen for 15 min and irradiated in a Pyrex tube for 5 h with a 300-W high pressure Hg lamp. After removal of the solvent, the crude residue was chromatographed on silica gel using chloroform to give methyl 6-methyl-4,7-dioxoindole-2-carboxylate (**5a**) (92 mg, 42%): Mp 249—250 °C (methanol–dichloromethane); IR (KBr): 3260, 1710, and 1660 cm^{-1}; ^1H NMR (DMSO-d_6) δ: 2.02 (d, J=1.6 Hz, 3H), 3.82 (s, 3H), 6.55 (q, J=1.6 Hz, 1H), 6.97 (s, 1H), and 13.49 (bs, 1H); MS, *m/e* (rel intensity), 219 (M^+, 92), 187 (82), 159 (78), 151 (48), and 131 (100). Found: C, 60.01; H, 4.32; N, 6.25%. Calcd for $C_{11}H_9O_4N$: C, 60.27; H, 4.14; N, 6.39%.

Physical properties of the other photoproducts **5b—i** are given below.

*Methyl 3,6-Dimethyl-4,7-dioxoindole-2-carboxylate (**5b**) from **4b**.* (62%); mp 275—277 °C (decomp); IR (KBr): 3250, 1700, and 1655 cm^{-1}; ^1H NMR (DMSO-d_6) δ: 2.01 (d, J=1.6 Hz, 3H), 2.47 (s, 3H), 3.81 (s, 3H), 6.50 (q, J=1.6 Hz, 1H), and 13.10 (bs, 1H). Found: C, 62.02; H, 4.77; N, 5.94%. Calcd for $C_{12}H_{11}O_4N$: C, 61.80; H, 4.75; N, 6.01%.

*Methyl 3-Ethyl-6-methyl-4,7-dioxoindole-2-carboxylate (**5c**) from **4c**.* (61%); mp 221—222 °C; IR (KBr): 3250, 1695, and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.17 (t, J=7.5 Hz, 3H), 2.08 (d, J=1.6 Hz, 3H), 3.09 (q, J=7.5 Hz, 2H), 3.95 (s, 3H), 6.49 (q, J=1.6 Hz, 1H), and 9.97 (bs, 1H). Found: C, 63.30; H, 5.42; N, 5.64%. Calcd for $C_{13}H_{13}O_4N$: C, 63.15; H, 5.30; N, 5.67%.

*Methyl 6-Methyl-4,7-dioxo-3-propylindole-2-carboxylate (**5d**) from **4d**.* (60%); mp 183—184 °C; IR (KBr): 3260, 1695, and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 0.95 (t, J=7.5 Hz, 3H), 1.61 (m, 2H), 2.08 (d, J=1.6 Hz, 3H), 3.07 (t, J=7.5 Hz, 2H), 3.94 (s, 3H), 6.47 (q, J=1.6 Hz, 1H), and 9.92 (bs, 1H); MS, *m/e* (rel intensity), 261 (M^+, 7), 260 (40), 229 (91), and 201 (100). Found: C, 64.45; H, 5.83; N, 5.26%. Calcd for $C_{14}H_{15}O_4N$: C, 64.36; H, 5.79; N, 5.36%.

*Dimethyl 6-Methyl-4,7-dioxoindole-2,3-dicarboxylate (**5e**) from **4e**.* (40%); mp 200—201 °C; IR (KBr): 3220, 1735, 1695, and 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.13 (d, J=1.6 Hz, 3H), 3.96 (s, 3H), 4.00 (s, 3H), 6.57 (q, J=1.6 Hz, 1H), and 8.70 (bs, 1H). Found: C, 56.54; H, 4.18; N, 4.91%. Calcd for $C_{13}H_{11}O_6N$: C, 56.32; H, 4.00; N, 5.05%.

*Methyl 3-[2-(Methoxycarbonyl)ethyl]-6-methyl-4,7-dioxoindole-2-carboxylate (**5f**) from **4f**.* (64%); mp 195—196 °C; IR (KBr): 3260, 1740, 1700, and 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.10 (d, J=1.6 Hz, 3H), 2.65 (t, J=7 Hz, 2H), 3.43 (t, J=7 Hz, 2H), 3.69 (s, 3H), 3.97 (s, 3H), 6.53 (q, J=1.6 Hz, 1H), and 10.15 (bs, 1H); MS, *m/e* (rel intensity),

305 (M^+, 8), 273 (35), 245 (94), and 213 (100). Found: C, 58.89; H, 4.77; N, 4.39%. Calcd for $C_{15}H_{15}O_6N$: C, 59.01; H, 4.95; N, 4.59%.

*Methyl 6-Methyl-4,7-dioxo-3-[3-(phthalimido)propyl]indole-2-carboxylate (**5g**) from **4g**.* (56%); mp 242—243 °C; IR (KBr): 3240, 1770, 1700, and 1650 cm $^{-1}$; H NMR (DMSO-d_6) δ: 1.90 (m, 2H), 1.99 (d, J=1.6 Hz, 3H), 3.03 (t, J=7 Hz, 2H), 3.61 (t, J=7 Hz, 2H), 3.76 (s, 3H), 6.48 (q, J=1.6 Hz, 1H), 7.83 (s, 4H), and 13.02 (bs, 1H); MS, *m/e* (rel intensity), 406 (M^+, 40), 373 (15), 329 (13), 233 (44), and 227 (100). Found: C, 64.93; H, 4.49; N, 6.85%. Calcd for $C_{22}H_{18}O_6N_2$: C, 65.02; H, 4.46; N, 6.89%.

*Methyl 6-Methyl-4,7-dioxo-3-[3-(trifluoroacetamido)propyl]indole-2-carboxylate (**5h**) from **4h**.* (42%); mp 241—242 °C; IR (KBr): 3240, 1700, and 1650 cm $^{-1}$; ^{1}H NMR (DMSO-d_6) δ: 1.79 (m, 2H), 2.04 (d, J=1.6 Hz, 3H), 3.13 (m, 4H), 3.86 (s, 3H), 6.43 (q, J=1.6 Hz, 1H), 8.85 (bs, 1H), and 12.74 (bs, 1H); MS, *m/e* (rel intensity), 372 (M^+, 5), 258 (75), 244 (19), and 227 (100). Found: C, 51.55; H, 4.28; N, 7.41%. Calcd for $C_{16}H_{15}O_5N_2F_3$: C, 51.16; H, 4.06; N, 7.53%.

*Methyl 6-Methyl-4,7-dioxo-3-(phenoxycarbonyloxymethyl)indole-2-carboxylate (**5i**) from **4i**.* (37%); mp 155—156 °C; IR (neat): 3240, 1760, 1700, and 1650 cm $^{-1}$; ^{1}H NMR ($CDCl_3$) δ: 2.10 (d, J=1.6 Hz, 3H), 3.98 (s, 3H), 5.70 (s, 2H), 6.53 (q, J=1.6 Hz, 1H), 7.10—7.40 (m, 5H), and 10.60 (bs, 1H). Found: C, 62.02; H, 4.18; N, 3.65%. Calcd for $C_{19}H_{15}O_7N$: C, 61.79; H, 4.09; N, 3.79%.

*Methyl 1,3,6-Trimethyl-4,7-dioxoindole-2-carboxylate (**6a**).* To a solution of **5b** (116 mg, 0.5 mmol) in dry DMSO (20 ml) at 20 °C was added under argon potassium *t*-butoxide (68 mg, 0.6 mmol). The resulting red solution was stirred for 10 min, and methyl iodide (156 μl, 2.5 mmol) was added. After stirring for 1 h at room temperature, the reaction mixture was poured into cold 0.1 M hydrochloric acid (100 ml) and the resulting suspension was extracted with chloroform (3×20 ml). The organic layer was washed with water and dried ($MgSO_4$). Removal of the solvent and chromatography gave **6a** (111 mg, 90%): Mp 141—143 °C; IR (KBr): 1705 and 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.08 (d, J=1.6 Hz, 3H), 2.58 (s, 3H), 3.92 (s, 3H), 4.25 (s, 3H), and 6.45 (q, J=1.6 Hz, 1H); MS, *m/e* (rel intensity), 247 (M^+, 100). Found: C, 63.00; H, 5.41; N, 5.50%. Calcd for $C_{13}H_{13}O_4N$: C, 63.15; H, 5.30; N, 5.67%.

*Methyl 1-Allyl-3,6-dimethyl-4,7-dioxoindole-2-carboxylate (**6b**).* Reaction of **5b** (116 mg, 0.5 mmol), potassium *t*-butoxide (75 mg, 0.67 mmol), and allyl bromide (0.5 ml, 5.76 mmol) in dry DMSO (20 ml) solution by the procedure described for the preparation of **6a** gave after chromatography **6b** (123 mg, 90%): Mp 144—145 °C; IR (KBr): 1700, 1650, and 1645 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.05 (d, J=1.6 Hz, 3H), 2.59 (s, 3H) 3.91 (s, 3H), 4.91—6.19 (m, 5H), and 6.46 (q, J=1.6 Hz, 1H); MS, *m/e* (rel intensity), 273 (M^+, 26), 258 (63), 215 (65), and 71 (100). Found: C, 65.82; H, 5.49; H, 4.89%. Calcd for $C_{15}H_{15}O_4N$: C, 65.92; H, 5.53; N, 5.13%.

*Methyl 4,7-Diacetoxy-3-[2-(methoxycarbonyl)ethyl]-6-methylindole-2-carboxylate (**7**).* A solution of **5f** (153 mg, 0.5 mmol) in ether was reduced with excess aq sodium dithionite[10] to give methyl 4,7-dihydroxy-3-[2-(methoxycarbonyl)-ethyl]-6-methylindole-2-carboxylate, which was acetylated with acetic anhydride (2 ml) in the presence of pyridine (0.1 ml) to afford **7** (156 mg, 80%); mp 171—172 °C (methanol–petroleum ether); IR (KBr): 3340, 1750, 1720, and 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.24 (s, 3H), 2.40 (s, 6H), 2.58 (t, J=7 Hz, 2H), 3.38 (t, J=7 Hz, 2H), 3.68 (s, 3H), 3.92 (s, 3H), 6.70 (s, 1H), and 8.62 (bs, 1H). Found: C, 58.11; H, 5.38; N, 3.35%. Calcd for $C_{19}H_{21}O_8N$: C, 58.31; H, 5.41; N, 3.58%.

*Methyl 4,5,7-Triacetoxy-3-[2-(methoxycarbonyl)ethyl]-6-methylindole-2-carboxylate (**8**)* was prepared by the Thiele oxidation of **5f** (153 mg, 0.5 mmol) with acetic anhydride (5 ml) in the presence of conc H_2SO_4 (0.1 ml).[11] (79 mg, 35%); mp 238—239 °C (dichloromethane–petroleum ether); IR (KBr): 3350, 1770; 1750, 1735, and 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.07 (s, 3H), 2.32 (s, 3H), 2.42 (s, 6H), 2.56 (t, J=8 Hz, 2H), 3.34 (t, J=8 Hz, 2H), 3.70 (s, 3H), 3.94 (s, 3H), and 8.75 (bs, 1H); MS, *m/e* (rel intensity), 449 (M^+, 5), 409 (23), 366 (48), 334 (21), 324 (49), and 292 (100). Found: C, 55.90; H, 5.29; N, 3.23%. Calcd for $C_{21}H_{23}O_{10}N$: C, 56.12; H, 5.16; N, 3.12%.

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