Pergamon

Tetrahedron Vol. 50, No. 28, pp. 8293-8300, 1994
Copyright © 1994 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4020/94 $7.00+0.00

0040-4020(94)00454-4

Photoinduced Molecular Transformations. Part 151.[1] One-Pot Synthesis of 1*H*-Benz[*g*]indole-4,5-diones by a Regioselective (3+2) Photoaddition of 4-Amino-1,2-naphthoquinones with Alkenes

Hiroshi Suginome*, Hideo Sakurai, Akiyoshi Sasaki, Hiroyasu Takeuchi, and Kazuhiro Kobayashi

Organic Synthesis Division, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

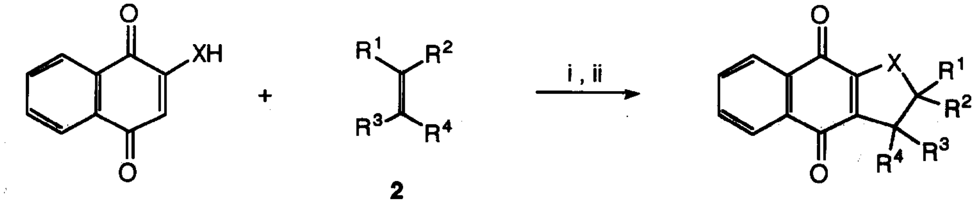
Abstract: 1*H*-Benz[*g*]indole-4,5-diones are formed in up to 82% yields by the (3+2) photoaddition of 4-amino-1,2-naphthoquinone with alkyl vinyl ethers in acetone with Pyrex-filtered light, while a 1:1 mixture of 2,3-dihydro-1*H*-benz[*g*]indole-4,5-dione and 2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione is formed in 32% yield by the (3+2) photoaddition of 4-amino-1,2-naphthoquinone with isobutene in acetone. On the other hand, the irradiation of 4-phenylamino-1,2-naphthoquinone with alkenes, such as ethyl vinyl ether or isobutene, in acetone gave 2,3-dihydro-4-phenyliminonaphtho[2,3-*b*]furan-9-ones, arising from the (3+2) photoaddition in up to 34% yields. The intermediacy of the hydroquinones in these (3+2) photoadditions was confirmed by the formation of acetates of the intermediate hydroquinones upon treating of the initial photoadducts with acetic anhydride.The formation mechanism of these (3+2) photoadducts is discussed.

In previous papers[2] we reported that 2,3-dihydronaphtho[2,3-*b*]furan-4,9-diones **3** are formed in high yields by a new regioselective (3+2) photoaddition of 2-hydroxy-1,4-naphthoquinones **1** with a variety of alkenes **2** in acetone or benzene with Pyrex-filtered light. Our subsequent studies have disclosed that 2,3-dihydro-1*H*-benz[*f*]indole-4,9-diones **5**[3] and 2,3-dihydronaphtho[2,3-*b*]thiophene-4,9-diones[4] can be obtained in a single procedure by a similar (3+2) photoaddition of 2-aminonaphthoquinone, such as **4**, and of photogenerated 2-mercapto-1,4-naphthoquinone **6** with various electron-rich alkenes **2**, respectively, as outlined in Scheme 1. We have reported since that these (3+2) photoadditions are a general reaction of 2-hydroxy-, 2-amino- and 2-mercapto-1,4-quinones which take place between 2-hydroxy- or 2-amino-1,4-anthraquinone,[5] 2-hydroxy-1,4-benzoquinones,[6] and 2-hydroxy-1,4-phenanthrenequinone[7] with alkenes.

In this paper we report that similar (3+2) photoadducts are formed when 4-amino-1,2-naphthoquinones with alkenes in solution are irradiated. There have been some reports concerning the photochemical reactions of 1,2-naphthoquinone and their derivatives: a photoinduced intramolecular hydrogen abstraction of 3-alkoxy-1,2-naphthoquinones[8a] and photoadditions of 1,2-naphthoquinone with alkenes[8b] and aliphatic aldehydes.[8c] No reaction analogous to the present (3+2) photoaddition involving amino group has, however, been reported in the area of the photochemistry of 1,2-naphthoquinones.

RESULTS AND DISCUSSION

Substrates and their Electronic Spectra.——Known 4-amino-1,2-naphthoquinone **8**[9] and 4-anilino-1,2-naphthoquinone **14**[10] were used as substrates for the present work. The tautomerism of these quinones in solution has been studied by several groups.[10] Based on their studies of the ^{13}C NMR spectra of 4-amino- and 4-



1 X=O; **4** X=NH; **6** X=S

2

3 X=O; **5** X=NH; **7** X=S

R^1=alkyl, aryl, OAc, OMe or OEt; R^2=alkyl, aryl, H or CO_2Me; R^3=H or alkyl; R^4=H or alkyl

i, hν, acetone ; ii, air

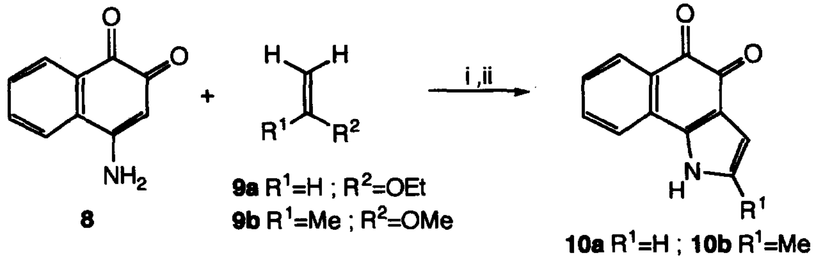
Scheme 1

arylamino-1,2-naphthoquinones in neutral and basic solvents, Yano and colleagues have concluded that the predominant tautomers of these quinones in neutral solvents are the orthoquinone forms.[10c] These results have also been supported by their studies of the electronic spectra of these quinones, which exhibited intense absorption maxima in the UV and visible regions [4-amino-1,2-naphthoquinone: 235 (log ε 4.20), 273 (log ε: 4.31) and 456 (log ε; 3.56)].[10c,11]

The (3+2)Photoadditions of 4-Amino- or 5-Anilino-1,2-naphthoquinones with Alkenes.—The photoadditions of 4-amino- or 4-anilino-1,2-naphthoquinones with alkenes were carried out in a 6 x 10^{-3} M acetone solution under the conditions described for the (3+2) photoaddition of 2-amino-1,4-naphthoquinones with alkenes by us.[3] Thus, the irradiation of a solution of 4-aminonaphthoquinone **8** and ethyl vinyl ether **9a** in acetone with Pyrex-filtered light generated by a 500-W high-pressure Hg arc for 75 h gave a single crystalline product **10a** in 82% yield. The high-resolution mass spectrum of product **10a** indicated the molecular formula to be $C_{12}H_7NO_2$. The IR spectrum exhibited a series of absorption bands assignable to NH and orthoquinone carbonyl groups. The ^1H NMR spectrum in DMSO-d_6 showed two doublets at 6.78 and 7.30 (*J* 3.08) assignable to 3- and 2-H of the pyrrole nucleus. These results indicated that product **10a** was 1*H*-benz[*g*]indole-4,5-dione, arising from the (3+2) photoaddition of 4-amino-1,2-quinone with alkenes, followed by a spontaneous elimination of ethanol from the adducts. The photoaddition of 4-aminoquinone **8** with 2-methoxypropene **9b** took place in a manner parallel to the reaction mentioned above and gave 2-methyl-1*H*-benz[*g*]indole-4,5-dione **10b** in 60% yield. (Scheme 2)

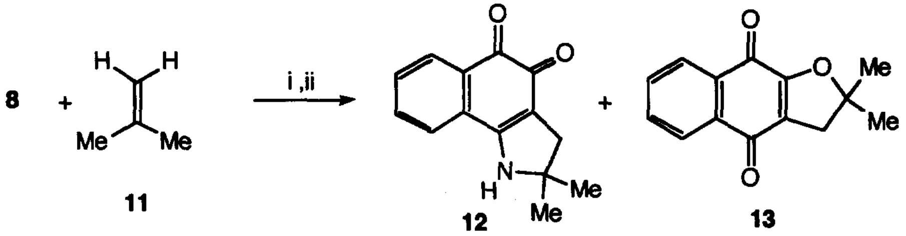
The irradiation of 4-aminoquinone **8** and isobutene **11** in acetone for 2.5 h under the conditions mentioned above, on the other hand, gave two products, **12** and **13**, in modest yields. High-resolution mass spectrometry indicated the molecular formula of product **12** (14 %) to be $C_{14}H_{13}NO_2$. The IR spectrum indicated a series of absorption bands due to the NH and orthoquinone carbonyl groups. The ^1H NMR spectrum indicated that a 6H singlet at δ 1.59 and a 2H singlet at δ 3.04 assignable to the dihydroindole nucleus. These spectral results indicated that product **12** was 2,3-dihydro-2,2-dimethyl-1*H*-benz[*g*]indole-4,5-dione. Product **13** (18%) was identical to 2,3-dihydro-2,2-dimethylnaphtho[2,3-*b*]furan-4,9-dione obtained by the (3+2) photoaddition of 2-hydroxy-1,4-naphthoquinone with isobutene by us.[2] (Scheme 3)

The photoaddition of 4-anilino-1,2-naphthoquinone **14** with vinyl ethers **9a** and **11** under the above-mentioned conditions gave 2-ethoxy-2,3-dihydro-4-phenyliminonaphtho[2,3-*b*]furan-9-one **15a** and 2,3-



i, hν, acetone ; ii, air

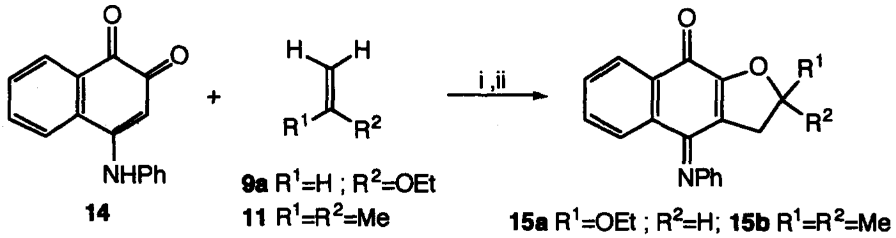
Scheme 2



i, hν, acetone ; ii, air

Scheme 3

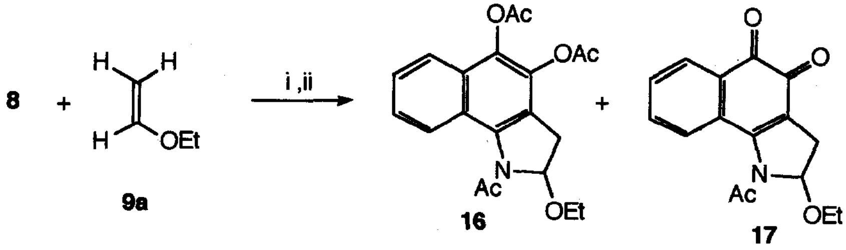
dihydro-2,2-dimethyl-4-phenyliminonaphtho[2,3*b*]furan-9-one **15b** in 15 and 34%, respectively. (Scheme 4) These structures were deduced by spectroscopic analysis, the details of which are described in the experimental section.



i, hν, acetone ; ii, air

Scheme 4

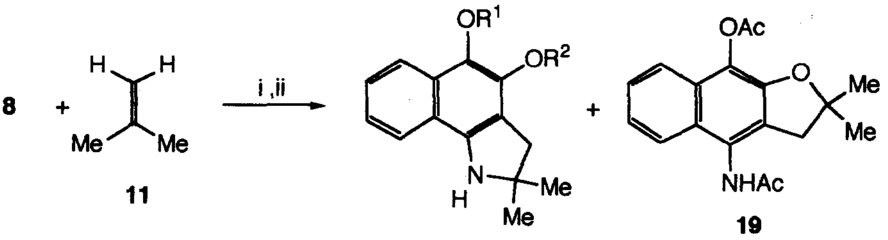
The initial products leading to 1*H*-benz[*g*]indole-4,5-diones **10a** and **10b** in the present photoadditions were proved to be the corresponding hydroquinones. Thus, 1-acetyl-4,5-bis(acetoxy)-2-ethoxy-2,3-dihydro-1*H*-benz[*g*]indole **16** could be isolated in 32% yield together with 1-acetyl-2-ethoxy-2,3-dihydro-1H-benz[g]indole-4,5-dione **17** in 15% yield when the crude products from the photoaddition of 4-amino-1,2-naphthoquinone **8** and ethyl vinyl ether **9a** were treated with acetic anhydride and pyridine under a nitrogen atmosphere for 3h at 70°C (Scheme 5). A similar treatment of the crude products obtained from the photoaddition of



i, hν, acetone ; ii, Ac_2O, py., 70°C

Scheme 5

aminonaphthoquinone **8** and isobutene **11** with acetic anhydride and pyridine gave a mixture of 4 (or 5)-acetoxy-2,3-dihydro-5 (or 4)-hydroxy-2,2-dimethyl-1*H*-benz[*g*]indole **18** and 4-acetylamino-9-acetoxy-2,3-dihydro-2,2-dimethylnaphtho[2,3-*b*]furane **19** in 17 and 19% yield, respectively,as outlined in Scheme 6.



18 R^1=Ac ; R^2=H or R^1=H ; R^2=Ac

i, hν, acetone ; ii, Ac_2O, py., r.t.

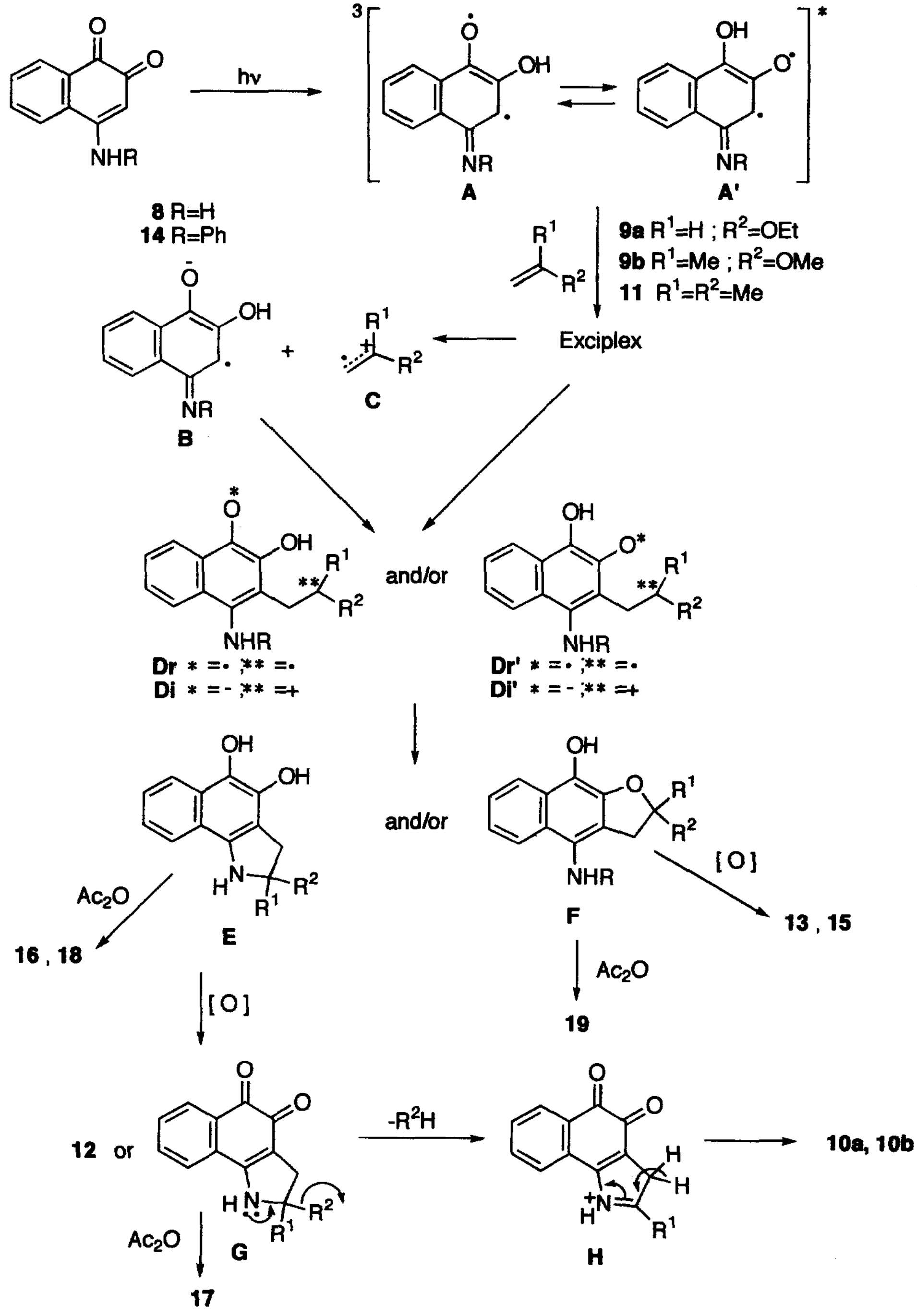
Scheme 6

Pathways leading to the (3+2) Photoadducts **10a, 10b, 12, 13, 15a** *and* **15b**.(Scheme 7)——The foregoing experiments have shown that the irradiation of 4-amino-1,2-naphthoquinone **8** with alkyl vinyl ethers **9a** or **9b** in acetone resulted in an exclusive formation of 1*H*-benz[*g*]indole-4,5-diones **10** arising from a regioselective (3+2) photoaddition, followed by an elimination of alcohols. The irradiation of the aminonaphthoquinone **8** with alkene such as isobutene **12** in acetone, however, gave a 4.4 : 5.6 mixture of an orthoquinone, 2,3-dihydro-1*H*-benz[*g*] indole-4,5-diones and a paraquinone, 2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione **13** arising from a (3+2) photoaddition.

The aforementioned experiments have also shown that, in contrast to the above-mentioned results concerning the photoaddition of 4-amino-1,2-naphthoquinone **8**, the photoreaction of 4-anilino-1,2-naphthoquinone **14** with either alkyl vinyl ether **9a** or alkene **11** afforded 2,3-dihydro-4-phenylaminonaphtho [2,3-*b*]furan-9-ones **15a** or **15b** as the regioselective (3+2) photoadduct in lower yield, respectively.

We also confirmed the intermediacy of the hydroquinones in these (3+2) photoadditions by trapping the hydroquinones as their acetates by treating the initial photoadducts with acetic anhydride.

One of the suggested gross reaction pathways of the photoaddition leading to the (3+2) photoadducts,


hν
8 R=H
14 R=Ph
A
A'
9a R¹=H ; R²=OEt
9b R¹=Me ; R²=OMe
11 R¹=R²=Me
Exciplex
B
C
Dr * =• ;** =•
Di * =- ;** =+
and/or
Dr' * =• ;** =•
Di' * =- ;** =+
E
and/or
F
Ac₂O
16 , 18
[O]
13 , 15
Ac₂O
19
[O]
12 or
G
Ac₂O
17
-R²H
H
10a, 10b

Scheme 7

(**10a**, **10b**, **12**, **13**, **15a**, and **15b**), is outlined in Scheme 7. The irradiation of quinones **8** and **14** in acetone generates tautomeric excited triplets, **A** and **A**,' which are species analogous to the tautomeric-excited triplets generated from 2-hydroxy- or 2-amino-1,4-naphthoquinones by irradiation, as reported by us previously.[2,3,5-7] These excited species then react with an alkene through an exciplex to give biradical **Dr** and **Dr'**. These biradical species may either have an appreciable polar character or be ionic intermediates **Di** and **Di'**, analogous to the biradical species generated in the (3+2) photoaddition of 2-hydroxy- or 2-aminonaphthoquinones with alkenes.[3] Alternatively, the ionic intermediates, **Di** and **Di'**, may be formed through a pair of radical ions, **B** and **C**.[12,13] The regioselectivity found in the present photoaddition may suggest that the photoaddition is a two-step process involving a more stabilized polar radical or ionic intermediates, such as **Di** and **Di'**. An intramolecular cyclization of the intermediate gives either hydroquinone **E** or **F**. The oxidation of **E** by air gives 1,2-naphthoquinone **12**, while the oxidation of **F** gives para species **13** and **15**. As mentioned previously, 1-acetyl-4,5-bis(acetoxy)-2-ethoxy-2,3-dihydro-1*H*-benz[*g*]indole **16** and the corresponding orthoquinone **17** are isolated when the products obtained from the photoaddition of 4-amino-1,2-naphthoquinone **8** and ethyl vinyl ether **9a** are treated with acetic anhydride and base and the 2-ethoxyl groups attached to products **16** and **17** are not eliminated under the conditions of the acetylation. These results indicates that 1*H*-benz[*g*]indole-4,5-diones **10a** and **10b** are formed by elimination of an element of alcohol from an intermediate **G** through a species **H**, as outlined in Scheme 7.

The aforementioned experiments have also shown that, in contrast to the exclusive formation of 1*H*-benz[*g*]indole-4,5-diones **10**, arising from an elimination of an element of alcohol from the initial adducts, the photoaddition of anilinoquinone **14** gave exclusively 2-alkoxy-2,3-dihydro-4-phenyliminonaphtho[2,3-*b*]furan-9-one **15** without the loss of an alcohol. These results indicates that the enamino nitrogen played a role to facilitate the elimination of alcohols in the photoaddition of 4-aminoquinone **8**.

The above-mentioned product difference in the photoaddition between 4-aminoquinone **8** and 4-anilinoquinone **14** suggest that the relative base strength and bulkiness of the amino and anilino substituents attached to the 4-position of quinones **8** and **14** seem to be of importance in directing whether the photoadditions lead to orthoquinones, such as **10**, or paraquinones, such as **15**; the photoaddition of 4-aminoquinone **8** goes exclusively through intermediate **Di**, while the photoaddition of 4-anilinoquinone **14** gives exclusively the paraquinones **15**. Cyclization of intermediate **Di** with more bulky and less basic 4-anilino nitrogen should be more hindered than cyclization of intermediate **Di** with a less bulky and more basic 4-amino group.

The photoaddition described in this paper should be of value in organic molecular transformations.

EXPERIMENTAL

General Method. Regarding the instruments used and a general photolysis procedure, see the previous paper[7] of this series.

***1H-Benz[g]indole-4,5-diones* 10a.**——A solution of 4-amino-1,2-naphthoquinone **8** (200 mg, 1.15 mmol) and ethyl vinyl ether **9a** (1.68 g, 23 mmol) in acetone (200 cm^3, 5.8 × 10^{-3}M) was irradiated with a 500-W high-pressure Hg arc through a Pyrex filter under nitrogen for 75 h. After evaporation of the solvent, the residue was subjected to PLC on silica gel (1:1 dichloromethane-acetone). The orange band (Rf 0.5-0.6) was collected and eluted with acetone. The eluent was evaporated to give a crude material which was recrystallized from diethyl ether-hexane to give pure indoledione **10a** (186 mg, 82%): m.p. 197 °C (dec.); νmax/cm^{-1} 3220, 1684, 1639 and 1601; δ_H (90 MHz, DMSO-d$_6$) 6.78 (1H, d, *J* 3.08, 3-H), 7.30 (1H, d, *J* 3.08, 2-H) and 7.5-8.6 (5H, m, ArH and NH); *m/z* 197 (M,$^+$ 64) and 169 [(M-CO),$^+$ 100%] (Found: M,$^+$ 197.0504. $C_{12}H_7NO_2$ requires *M*, 197.0477).

***2-Methyl-1H-Benz[g]indole-4,5-dione* 10b.**—The irradiation of a solution of **8** (86 mg, 0.5 mmol) and 2-methoxypropene, **9b** (360 mg, 5 mmol) in acetone (85 cm^3, 5.9 × 10^{-3}M) for 7 days and separation of the product in a similar way to that described above gave indoledione **10b** (43 mg, 60%): m.p. 290 °C (diethyl edther-hexane); νmax/cm^{-1} 3156, 1687, 1634 and 1611; δH (90 MHz, DMSO-d$_6$) 2.26 (3H, s, 2-Me), 6.18 (1H, s, 3-H) and 7.15-8.1 (5H, m, ArH and NH); *m/z* 211 (M,$^+$ 72) and 182 [(M-CO),$^+$ 100%] (Found: M,$^+$ 211.0614. $C_{13}H_9NO_2$ requires *M*, 211.0633).

***2,3-Dihydro-2,2-dimethyl-1H-Benz[g]indole-4,5-dione* 12 and *2,3-dihydro-2,2-dimethylnaphtho[2,3-b]furan-4,9-dione* 13.**—A solution of **8** (49 mg, 0.28 mmol) and isobutene, **11** (157 mg, 2.8 mmol) in acetone (50 cm^3, 5.6 × 10^{-3}M) was irradiated as mentioned above for 2.5 h. The crude product was subjected to PLC on silica gel (10 : 1 dichloromethane-acetone) to give *ortho-* and *paraquinones* **12**$^{3)}$ (8.9 mg, 14%) and **13** (11 mg, 18 %): **12** Rf 0.58; m.p. 135-137 °C (hexane-dichloromethane); νmax/cm^{-1} 3260, 1671, 1629 and 1603; δH (90 MHz), 1.59 (6H, s, 2-Me), 3.04 (2H, s, 3-H) 7.55-7.75 (2H, m, 7- and 8-H) and 8.1-8.35 (3H, m, 6-, 9-H and NH); *m/z* 227 (M,$^+$ 100%) (Found: M,$^+$ 227.0949. $C_{14}H_{13}NO_2$ requires *M*, 227.0946).

***2-Ethoxy-2,3-dihydro-4-phenyliminonaphtho[2,3-b]furan-9-one* 15a.**—A solution of 4-phenylamino-1,2-naphthoquinone **14** (200 mg, 0.80 mmol) and ethyl vinyl ether **9a** (580 mg, 8.0 mmol) in acetone (150 cm^3, 5.5 × 10^{-3}M) was irradiated for 41 h and the product was subjected to PLC on silica gel to give **15a** (38 mg, 15%): an oil; Rf 0.86 (1:1 THF-hexane); νmax/cm^{-1} (neat) 1669, 1603 and 1591; δH (270 MHz), 1.17 (3H, t, *J* 6.93, -OCH_2CH_3), 2.23 (1H, dd, *J* 18.47 and 2.97, 3-H), 2.68 (1H, dd, *J* 18.47 and 7.26, 3-H), 3.57 (1H, dq, *J* 9.24 and 6.93, -OC*H*HCH_3), 3.94 (1H, dq, *J* 9.24 and 6.93, OC*H*HCH_3), 5.57 (1H, dd, *J* 7.26 and 2.97, 2-H), 6.82 (2H, d, *J* 7.59), 7.14 (1H, dd, J 7.59 and 7.26), 7.35 (2H, dd, *J* 7.91 and 7.59), 7.4-7.75 (2H, m, 6- and 7-H), 8.19 (1H, d, *J* 7.26) and 8.46 (1H, d, *J* 7.59); *m/z* 319 (M,$^+$ 100%) (Found: M,$^+$ 319.1210. $C_{20}H_{17}NO_4$ requires *M*, 319.1208).

***2,3-Dihydro-2,2-dimethyl-4-phenyliminonaphtho[2,3-b]furan-9-one* 15b.**—The irradiation of aminonaphthoquinone **14** (150 mg, 0.6 mmol) and isobutene **11** (336 mg, 6 mmol) in acetone (110 cm^3, 5.5 × 10^{-3}M) for 70 h gave, after purification by PLC on silica gel (1:1 THF-hexane), **15b** (62 mg, 34 %): Rf 0.82; m.p. 105-107 °C (hexane-chloroform); νmax/cm^{-1} 1670, 1602 and 1591; δH (90 MHz) 1.35 (6H, s, 2-Me), 2.25 (2H, s, 3-H), 6.75-7.75 (7H, m), 8.1-8.5 (1H, m) and 8.4-8.55 (1H, m); *m/z* 303 (M,$^+$ 100%) (Found: M,$^+$ 303.1257. $C_{20}H_{17}NO_2$ requires *M*, 303.1259).

***1-Acetyl-4,5-bis(acetoxy)-2-ethoxy-2,3-dihydro-1H-benz[g]indole* 16 *and 1-acetyl-2-ethoxy-2,3-dihydro-1H-benz[g]indole-4,5-dione* 17.**—A solution of **8** (200 mg, 1.15 mmol) and ethyl vinyl ether **9** (840 mg, 11.5 mmol) in acetone (200 cm^3, 5.8 × 10^{-3}M) was irradiated as mentioned above for 23 h; the solvent was then evaporated. To the residue was added acetic anhydride and pyridine (each 3 cm^3), and the resulting mixture was heated at 70 °C for 3h in an atmosphere of nitrogen. After removal of excess acetic anhydride and pyridine in vacuo the residue was subjected to PLC on silica gel (1:5 EtOAc-hexane) to give hydroquinone diacetate **16** (137 mg, 32 %) and orthoquinone **17** (49 mg, 15 %). **16:** Rf 0.64; an oil; νmax/cm^{-1} (neat) 1775, 1718 and 1658; δH (270 MHz) 1.22 (3H, t, *J* 6.93, -OCH_2CH_3), 2.18 (3H, s, Ac), 2.43 (3H, s, Ac), 2.48 (3H, s, Ac), 3.02 (1H, dd, *J* 17.16 and 1.98, 3-H), 3.35 (1H, dd, *J* 17.16 and 6.27, 3-H), 3.66 (1H, dq, *J* 9.57 and 6.93, -OC*H*HCH_3), 3.93 (1H, dq, *J* 9.57 and 6.93, -OC*H*HCH_3), 5.91 (1H, dd, *J* 6.27 and 1.98, 2-H), 7.35-7.6 (3H, m) and 7.84 (1H, d, *J* 7.58); *m/z* 371 (M,$^+$ 15), 329 [(M-CH_2O),$^+$ 32] and 199 (100 %) (Found: M,$^+$ 371.1362. $C_{20}H_{21}NO_6$ requires *M*, 371.1369). **17:** Rf 0.67; m.p. 103-106 °C (from dichloromethane-hexane); νmax/cm^{-1} 3370, 1672, 1650 (sh) and 1613; δH (270 MHz) 1.25 (3H, t, *J* 6.93, -OCH_2CH_3), 2.38 (3H, s, Ac), 2.89 (1H, dd, *J* 17.49 and 2.97, 3-H), 3.34 (1H, dd, *J* 17.49 and 7.26, 3-H), 3.71 (1H, dq, *J* 9.57 and 6.93, -OC*H*HCH$_3$), 4.03 (1H, dq, *J* 9.57 and 6.93, -OC*H*HCH$_3$), 5.87 (1H, dd, *J* 7.26 and 2.97, 2-H), 7.6-7.75 (2H, m, 7- and 8-H) and 8.1-8.2 (2H, m, 6- and 9-H); *m/z* 285 (M,$^+$ 8.7), 257 [(M-CO),$^+$ 35], 186 (48) and 43 (100 %) (Found: M,$^+$ 285.0980. $C_{16}H_{15}NO_4$ requires *M*, 285.1001).

***4 (or 5)-Acetoxy-2,3-dihydro-5(or 4)-hydroxy-2,2-dimethyl-1H-benz[g]indole* 18 *and 4-acetylamino-9-acetoxy-2,3-dihydro-2,2-dimethylnaphtho[2,3-b]furan* 19.**——The irradiation of a solution of **8** (48 mg, 0.28 mmol) and isobutene (157 mg, 2.8 mmol) in acetone (50 cm^3, 5.6 × 10^{-3}M) for 2.5 h according to the manner mentioned above, followed by evaporation of the solvent, gave a residue which was treated with acetic anhydride and pyridine (2 cm^3 each) overnight at room temperature. After removing excess acetic anhydride and pyridine the crude product was subjected to by PLC on silica gel (1:2 THF-hexane) to give **18** (13 mg, 17 %) and **19** (18 mg, 19 %). **18**: Rf 0.26; an oil; ν_{max}/cm^{-1} (neat) 3370, 1765 and 1654; δ_H (270 MHz) 1.54 (6H, s, 2-Me), 2.43 (3H, s, Ac), 3.00 (2H, s, 3-H), 4.0 (1H, br. s, NH) and 7.2-7.7 (5H, m, ArH and OH); *m/z* 271 (M,$^+$ 27) and 229 [(M-CH_2CO),$^+$ 100 %) (Found: M,$^+$ 271.1119. $C_{16}H_{17}NO_3$ requires *M*, 271.1209). **19**: Rf 0.39; an oil; ν_{max}/cm^{-1} (neat) 3350, 1777, 1675, 1643 and 1612; δ_H (270 MHz, $CDCl_3$) 1.55 (6H, s, 2-Me), 2.36 and 2.37 (6H, each s, Ac), 2.94 (2H, s, 3-H), 7.65-7.75 (2H, m, 6- and 7-H) and 8.1-8.25 (3H, m, 5-, 8-H and NH); *m/z* 313 (M,$^+$ 1.8), 269 (61) and 43 (100 %) (Found: M,$^+$ 313.1324. $C_{18}H_{19}NO_4$ requires *M*, 313.1315).

REFERENCES

1 Part 150. Suginome, H.; Nakayama, Y. *Tetrahedron*, in press.

2 Kobayashi, K.; Shimizu, H.; Sasaki, A.; Suginome, H. *J. Org. Chem.*, **1991**, *56*, 3204. Kobayashi, K.; Shimizu, H.; Sasaki, A.; Suginome, H.; *J. Org. Chem.*, **1993**, *58*, 4614.

3 Kobayashi, K.; Takeuchi, H.; Seko, S.; Suginome, H. *Helv. Chim. Acta.*, **1991**, *74*, 1091. Kobayashi, K.; Takeuchi, H.; Seko, S.; Kanno, Y.; Kujime, S.; Suginome, H. *Helv. Chim. Acta.*, **1993**, *76*, 2942.

4 Suginome, H.; Kobayashi, K.; Konishi, A.; Minakawa, H.; Sakurai, H. *J. Chem. Soc. Chem. Commun.*, **1993**, 807.

5 Kobayashi, K.; Kujime, A.; Suginome, H.; *Heterocycles*, **1992**, *33*, 553.

6 Kobayashi, K.; Kanno, Y.; Suginome, H. *J. Chem. Soc., Perkin Trans. 1*, **1993**, 1449.

7 Suginome, H.; Kamekawa, H.; Sakurai, H.; Kobayashi. K; *J. Chem. Soc. Perkin Trans. 1*, **1994**, 471.

8 a) Takuwa, A.; Soga, O.; Itoh, M.; and Maruyama, K. *Chem. Lett.*, **1987**, 727. b) Takuwa, A.; Sumikawa, M. *Chem. Lett.*, **1989**, 9. c) Takuwa, A.; Kai, R.; *Bull, Chem. Soc. Jpn.*, **1990**, *63*, 623.

9 Fieser, L. F.; Hartwell, J. L. *J. Am. Chem. Soc.*, 1935, **57**, 1482. Fieser, L. F.; Fieser, M. *J. Am. Chem. Soc.*, **1934**, *57*, 1565.

10 a) Harmon, R. E.; Phipps, L. M.; Howell, J. A.; Gupta, S. K. *Tetrahedron*, **1969**, *25*, 5807. b) Biggs, I. D.; Tedder, J. M. *Tetrahedron*, **1978**, *34*, 1377. c) Yano, H.; Yamasaki, M.; Shimomura,Y. ; Iwasaki, M.; Ohta, M.; Furuno, Y.; Kouno, K.; Ono, Y.; Ueda, Y. *Chem. Pharm. Bull.*, **1980**, *28*, 1207.

11 For electronic spectrum of 1,2-naphthoquinone, see a) Nagakura, S.; Kuboyama, A. *J. Am. Chem. Soc.*, **1954**, *76*, 1003. b) Kuboyama, A.; Yamazaki, R.; Yabe, S.; Uehara, Y. *Bull. Chem. Soc. Jpn.*, **1969**, *42*, 10. c) Bruce, J. M. in *The Chemistry of the Quinonoid Compounds, Part 1.* Ed. Patai, Wiley, New York, 1974, p.465.

12 Bryce-Smith, D.; Dechpande, R.; Gilbert, A.; Gtzanka, J. *J. Chem. Soc., Chem. Commun.*, **1970**, 561. Wilson, R. M.; Gardner, E. J.; Elder, R. C.; Squire, R. H.; Florian, L. R. *J. Am. Chem. Soc.*, **1974**, *96*, 2955. Wilson, R. M.; Musser, A. U. *J. Am Chem. Soc.*, **1980**, *102*, 1720.

13 For a review, see Mariano, P. S.; Stevinoha, J. L. in *Synthetic Organic Photochemistry;* Ed. Horspool, W. M. Plenum Press, New York, 1984, p. 189.

(*Received in Japan* 18 *April* 1994; *accepted* 18 *May* 1994)