Photoinduced Molecular Transformations. 140.[1] New One-Step General Synthesis of Naphtho[2,3-*b*]furan-4,9-diones and Their 2,3-Dihydro Derivatives by the Regioselective [3 + 2] Photoaddition of 2-Hydroxy-1,4-naphthoquinones with Various Alkynes and Alkenes: Application of the Photoaddition to a Two-Step Synthesis of Maturinone[2,3]

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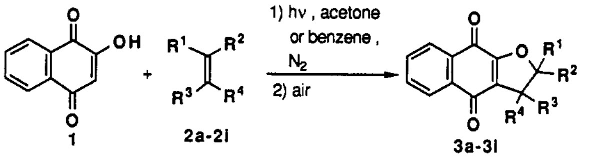
2,3-Dihydronaphtho[2,3-*b*]furan-4,9-diones can now be produced in one step in 41–83% yields by an unprecedented regioselective [3 + 2] photoaddition of 2-hydroxy-1,4-naphthoquinones with a variety of alkenes. The dihydronaphthofurandiones can be readily transformed into naphtho[2,3-*b*]furan-4,9-diones. This new photoaddition reaction has been successfully applied to a two-step synthesis of maturinone, a constituent of *Cacalia decomposita A* Gray. Naphtho[2,3-*b*]furan-4,9-diones can also be obtained directly by a new [3 + 2] photoaddition of 2-hydroxy-1,4-naphthoquinone with various alkynes in acetone. The photoaddition between 2-hydroxy-1,4-naphthoquinones and alkenes in acetone involves an initial formation of furanohydroquinones, which are oxidized to furanoquinones. A quenching experiment together with the regioselective nature of photoaddition indicate that the photoaddition is a two-step process from a triplet of excited quinones and involves more stabilized polar biradicals or ionic intermediates generated from them by an intramolecular electron transfer from which the furanohydroquinones are formed.

Naphtho[2,3-*b*]furan-4,9-diones and their 2,3-dihydro derivatives comprise an important group of heterocyclic quinones. A number of biologically interesting natural product and their derivatives having this skeleton have recently been found in nature.[4]

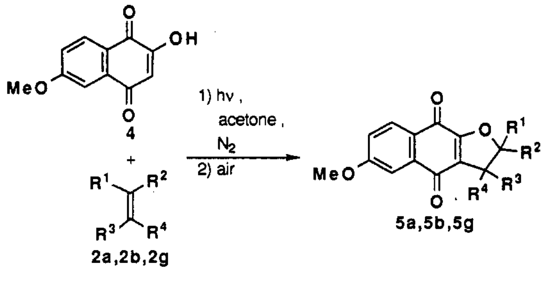
A variety of methods for synthesizing this class of molecules has been reported since the 1950s,[5,6] although Hooker[7] reported the synthesis of the first representative of this group of molecules (2-isopropylnaphtho[2,3-*b*]-furan-4,9-dione) by the annelation of 2-hydroxy-1,4-naphthoquinone (lawsone) as early as 1896. Most of these methods, however, are not necessarily of general application, since they require either several reaction steps or rather strong conditions.

We have found the 2,3-dihydronaphtho[2,3-*b*]furan-4,9-diones can be formed in high yields by an unprecedented regioselective [3 + 2] photoaddition of 2-hydroxy-1,4-naphthoquinone with a variety of alkenes (eqs 1 and 2). 2,3-Dihydronaphtho[2,3–*b*]furan-4,9-diones, thus obtained, can be readily transformed into naphtho[2,3-*b*]-furan-4,9-diones with either DDQ[4c] or by a basic elimi-



1 2a-2i 3a-3i (1)

Substituent; **a:** $R^1=R^2=Me, R^3=R^4=H$ **b:** $R^1=R^2=R^3=Me, R^4=H$
c: $R^1=R^2=R^3=R^4=Me$ **d:** $R^1=R^3=H, R^2, R^4=-(CH_2)_3-$
e: $R^1=Bu, R^2=R^3=H, R^4=Me$ **e'**: $R^1=Me, R^2=R^3=H, R^4=Bu$
f: $R^1=Ph, R^2=R^3=R^4=H$ **g:** $R^1=OAc, R^2=R^3=R^4=H$
h: $R^1=OEt, R^2=R^3=R^4=H$ **i:** $R^1=Me, R^2=CO_2Me, R^3=R^4=H.$



4 2a,2b,2g 5a,5b,5g (2)

Substituent; **a:** $R^1=R^2=Me, R^3=R^4=H$ **b:** $R^1=R^2=R^3=Me, R^4=H$
g: $R^1=OAc, R^2=R^3=R^4=H.$

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[1] Part 139: Kobayashi, K.; Konishi, A.; Minakawa, H.; Sakurai, H.; and Suginome, H. *J. Chem. Soc., Chem. Commun.* **1993**, 807.

[2] Presented at 13th International Congress of Heterocyclic Chemistry, Corvallis, OR, 1991; Abstr. GE12, p 140.

[3] Preliminary communication: Kobayashi, K.; Shimizu, H.; Sasaki, H.; and Suginome, H. *J. Org. Chem.* **1991**, *56*, 3204.

[4] (a) Romo, J.; Nathan, P. *Tetrahedron* **1964**, *20*, 2331. Correa, J.; Romo, J. *Ibid.* **1966**, *22*, 685. (b) Kakisawa, H.; Inouye, Y. *Tetrahedron Lett.* **1969**, 1929. (c) Brown, P. M.; Thomson, R. H. *J. Chem. Soc. C.* **1969**, 1184. (d) Mathieson, J. W.; Thomson, R. H. *J. Chem. Soc. C.* **1971**, 153. (e) Adams, J. H.; Lewis, J. R. *J. Chem. Res., Synop.* **1978**, 3; *J. Chem. Res., Miniprint* **1978**, 189. (f) Kingston, D. G. I.; Rao, M. M. *Planta Med.* **1980**, *39*, 230. Rao, M. M.; Kingston, D. G. I. *J. Nat. Prod.* **1982**, *45*, 600. (g) Inoue, K.; Chen, C.-C.; Inouye, H.; Kuriyama, K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2764. (h) Inoue, K.; Inouye, H.; Chen, C. C. *Phytochemistry* **1981**, *20*, 2271. (i) Dominguez, X. A. *Planta Med.* **1983**, *49*, 578. (j) Joshi, K. C.; Singh, P.; Sharma, M. C. *J. Nat. Prod.* **1985**, *48*, 145. (k) Chen, C. C. *Hua Hsuh* **1983**, *41*, 9. (l) Chen, C. C.; Lee, M. H. *Hua Hsuh* **1986**, *44*, 61. (m) Toshimitsu, H.; Smith, F. T.; Lee, K. H. *J. Med. Chem.* **1987**, *30*, 2005. (n) Wang, M.; Liu, W. *Phytochemistry* **1987**, *26*, 578. (o) Girard, M.; Kindack, D.; Dawson, B. A.; Ethier, J. C.; Awang, D. V. C. *J. Nat. Prod.* **1988**, *51*, 1023. (p) Wagner, H.; Kreher, B.; Lotter, H.; Hamburger, M. O.; Cordell, G. A. *Helv. Chim. Acta* **1989**, *72*, 659.

[5] For a review on early work, see: Sartori, M. F. *Chem. Rev.* **1963**, *63*, 279.

[6] (a) Hooker, S. C. *J. Am. Chem. Soc.* **1936**, *58*, 1168. (b) Hooker, S. C.; Steyermark, A. *Ibid.* **1936**, *58*, 1202. (c) Ettlinger, M. G. *Ibid.* **1950**, *72*, 3666. (d) Reynolds, G. A.; VanAllan, J. A.; Adel, R. E. *J. Org. Chem.* **1965**, *30*, 3819. (e) Huot, R.; Brassard, P. *Can. J. Chem.* **1974**, *52*, 88. (f) Ghera, E.; Maurya, R.; Ben-David, Y. *Tetrahedron Lett.* **1986**, *27*, 3935. (g) Zani, C. L.; de Oliveira, A. B.; Snieckus, V. *Ibid.* **1987**, *28*, 6561. (h) Otsuki, T. *Bull. Chem. Soc. Jpn.* 1976, *49*, 3713. (i) Kang, W. B.; Nan'ya, S.; Toru, T.; Ueno, Y. *Chem. Lett.* **1988**, 1415. (j) Kang, W. B.; Sekiya, T.; Toru, T.; Ueno, Y. *J. Chem. Soc., Perkin Trans.* **1990**, 441. (k) de Oliveira, A. B.; Raslan, D. S.; Khuong-Huu, F. *Tetrahedron Lett.* **1990**, *31*, 6873.

[7] Hooker, S. C. *J. Chem. Soc.* **1896**, *69*, 1355.

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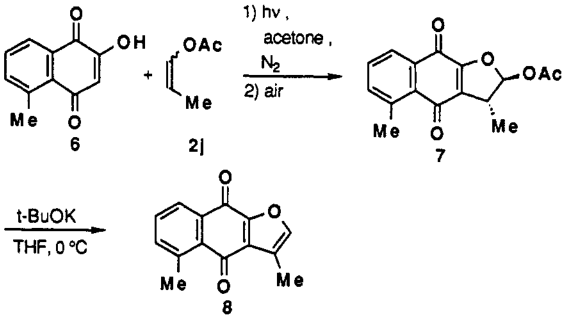
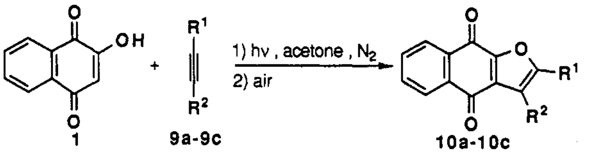
nation of alcohol from 2-alkoxy-2,3-dihydronaphtho[2,3-*b*]furan-4,9-diones. This new one-step photochemical annelation of naphthoquinones was then applied to a two-step synthesis of maturinone,[4a-c] a constituent of *Cacalia decomposita* A Gray (eq 3).



(3)

An additional study of ours regarding this new reaction has also shown that naphtho[2,3-*b*]furan-4,9-diones can directly and exclusively be formed by an unprecedented regioselective [3 + 2] photoaddition of 2-hydroxy-1,4-naphthoquinone with alkynes (eq 4).



(4)

Substituent; a: R^1=Ph,R^2=H b: R^1=Ph,R^2=Me c:R^1=Bu,R^2=H.

The reaction of excited enones[8] and quinones[9,10] with alkenes and alkynes, which are the most extensively studied photoreactions, mostly led to the [2 + 2] photoadducts. We thus believe that the present reaction is not only of value in synthesis but is also of considerable mechanistic interest. We give here a full report of the results.

[3 + 2] Photoaddition of 2-Hydroxy-1,4-naphthoquinones with Alkenes. Typically, the irradiation of a 2.5 × 10^{-2} M solution of 2-hydroxy-1,4-naphthoquinone (**1**) (Lawsone) in acetone containing an excess of isobutene (**2a**) through a Pyrex filter with a 500-W high-pressure Hg arc under a nitrogen atmosphere for 15 h at room temperature gave 2,2-dimethyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (**3a**) as an exclusive product (92%).[6b]

Similary, a photoaddition between hydroxynaphthoquinone 1 and 2-methyl-2-butene (**2b**) in acetone gave 2,2,3-trimethyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (**3b**) as an exclusive product in 65% yield. While this photoaddition in benzene gave the furanonaphthoquinone **3b** in enhanced yield (77%), photoaddition in a protic solvent, such as methanol, was found to markedly reduce (17%) the yield of the adduct **3b**.

Table I. Results of Photoadditions of 2-Hydroxy-1,4-naphthoquinone (1) and 2-Hydroxy-6-methoxy-1,4-naphthoquinone (4) with Alkenes 2

quinone	alkene 2	solvent[a]	2,3-dihydronaphthofurandione 3	yield (%)
1	2a	A	3a	92
1	2b	A	3b	65
1	2b	B	3b	77
1	2b	C	3b	17
1	2c	A	3c	48
1	2c	B	3c	47
1	2d	A	3d	60
1	2e	A	R^1; R^4 trans 3e + 3e′[b]	29
1	2f	A	3f	83
1	2g	A	3g	53
1	2h	A	3h	41
1	2h	B	3h	46
1	2i	A	3i	49
1	2i	B	3i	58
4	2a	A	5a	69
4	2b	A	5b	74
4	2g	A	5g	52

[a] Key: A, acetone; B, benzene; C, methanol. [b] 3e:3e′ = 55:45.

The results of a photoaddition between hydroxynaphthoquinone 1 and a variety of olefins (**2a**–**2i**) under similar conditions are summarized in Table I. It is remarkable that the photoaddition of 1 with styrene (**2f**), vinyl acetate (**2g**), ethyl vinyl ether (**2h**), and methyl methacrylate (**2i**) in both acetone and benzene all took place regioselectively to give the corresponding 2-substituted 2,3-dihydro[2,3-*b*]furan-4,9-diones (**3f**, **3g**, **3h**, and **3i**) in 41–83% yields as single products.

As in the case of the photoaddition between hydroxynaphthoquinone 1 and olefin **3b**, photoaddition in either acetone or benzene gave a similar yield of each adduct. No photoadducts between 1 and electron-deficient olefins, such as acrylonitrile and ethyl acrylate, have been obtained, although the photoaddition took place with methyl methacrylate (**2i**). The results of the photoadditions between 2-hydroxy-6-methoxynaphthalene-1,4-dione (4)[11] and olefins **2a**, **2b**, and **2g** were entirely parallel and gave regioselective [3 + 2] photoadducts in 52–69% yields (eq 2).

New Synthesis of Maturinone (8) by the Photoannelation. The [3 + 2] photoaddition was then successfully applied to a two-step synthesis of maturinone 8,[4a-c] a constituent of *Cacalia decomposita* A Gray (eq 2); the photoaddition of 2-hydroxy-5-methyl-1,4-naphthoquinone (6)[12] with 1-propenyl acetate (**2i**) in acetone under the above-mentioned conditions gave *trans*-2-acetoxy-2,3-dihydro-3,5-dimethylnaphtho[2,3-*b*]furan-4,9-dione (**7**) in 40% yield. The *trans* disposition of the acetoxyl group attached to the C-2 position and the methyl group attached to the C-3 position of photoadduct 7 was confirmed by its ^{1}H-NMR spectrum (J_{2H-3H} = 1.98 Hz). Treatment of naphthofurandione 7 with potassium *tert*-butoxide in THF at 0 °C resulted in an elimination of acetic acid to give maturinone 8 in 52% yield.

[3 + 2] Photoaddition of 2-Hydroxy-1,4-naphthoquinone (1) with Alkynes. The formation of [2 + 2] photoadducts between excited quinones and alkynes has been reported.[9,10] We then found that the regioselective [3 + 2] photoadducts can be obtained when 2-hydroxy-1,4-naphthoquinone (1) with various alkynes in acetone

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(8) For reviews, see: (a) Baldwin, S. W. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, pp 123–225. (b) Weedon, A. C. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum: New York, 1980; pp 91–143. (c) Schuster, D. I.; Lem, G.; Kaprinidis, N. A. *Chem. Rev.* **1993**, *93*, 22.

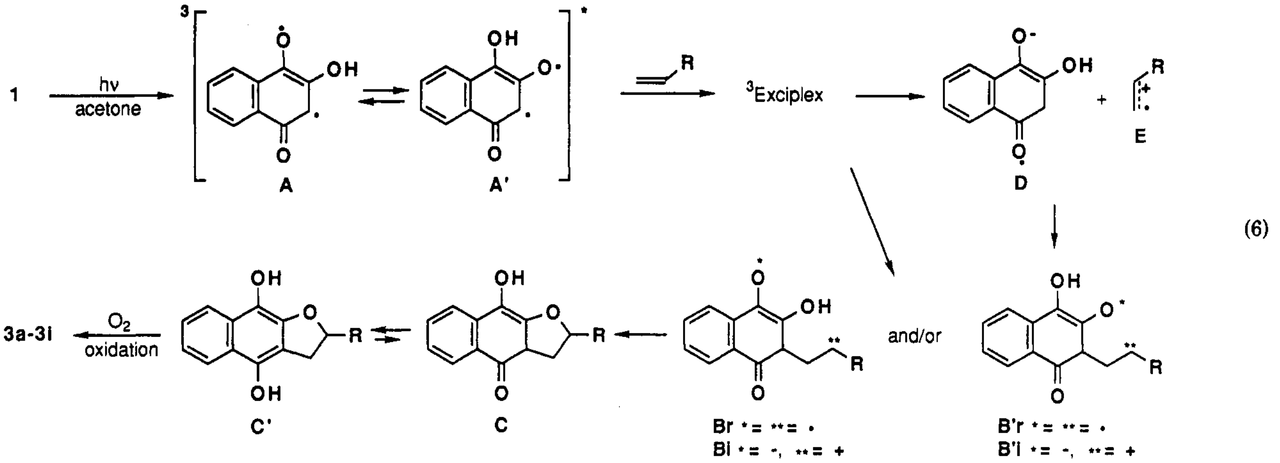
(9) *E.g.* (a) Otsuki, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2596. (b) Maruyama, K.; Narita, N. *Ibid.* **1980**, *53*, 757. (c) Ochiai, M.; Arimoto, M.; Fujita, E. *J. Chem. Soc., Chem. Commun.* **1981**, 460. (d) Liu, H. J.; Chan, W. H. *Can. J. Chem.* **1980**, *58*, 2196. (e) Maruyama, K.; Otsuki, T.; Tai, S. *J. Org. Chem.* **1985**, *50*, 52. (f) Pappas, S. P.; Pappas, B. C.; Portnoy, N. A. *Ibid.* **1969**, *34*, 520.

(10) For reviews: (a) Bruce, J. M. *Quart. Rev.* **1968**, *21*, 405. (b) Bruce, J. M. In *The Chemistry of Quinonoid Compounds, Part 1*; Patai, S., Ed.; Wiley: New York, 1974; p 465.

(11) Baillie, A. C.; Thomson, R. H. *J. Chem. Soc., C* **1966**, 2184.

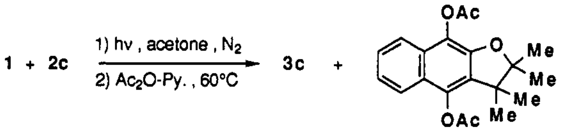
(12) MacLeod, J. W.; Thomson, R. H. *J. Org. Chem.* **1960**, *25*, 36.

Scheme I



are irradiated; irradiation of a 3.3 × 10^{-2} M solution of 2-hydroxy-1,4-naphthoquinone (**1**) in acetone containing an excess phenylacetylene (**9a**) for 7.5 h under the conditions described for the photoadditions with alkenes gave 2-phenylnaphtho[2,3-*b*]furan-4,9-dione (**10a**)[6b,g,i] in 54% yield. Similar photoadditions of 2-hydroxy-1,4-naphthoquinone with methylphenylacetylene (**9b**) and 1-hexyne (**9c**) regioselectively gave 2-phenyl-3-methylnaphtho[2,3-*b*]furan-4,9-dione (**10b**) and 2-butylnaphtho[2,3-*b*]furan-4,9-dione (**10c**) in 15 and 5.5% yields.

Pathway Leading to the [3 + 2] Photoadducts. The foregoing photoadditions are new types of photoreactions in both quinone and enone photochemistry. We have confirmed that the initial products in the present photoaddition are furanohydroquinones; when the crude products from the photoaddition between hydroxynaphthoquinone **1** (1 mmol) and 2,3-dimethyl-2-butene (10 mmol) in acetone (40 mL) are treated with acetic anhydride (1 mL) and pyridine (1 mL) under nitrogen for 2 h at 60 °C, 4,9-diacetoxy-2,3-dihydro-2,2,4,4-tetramethylnaphtho[2,3-*b*]furan (**11**) could be isolated in 36% yield, together with 2,2,4,4-tetramethylnaphtho[2,3-*b*]furan (**3c**) (18%) (eq 5).



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The photoaddition is quenched by a triplet quencher; when the photoaddition of 2-hydroxynaphthoquinone (**1**) (1 mmol) with 2-methyl-2-butene (**2b**) (10 mmol) in benzene is carried out in the presence of piperylene (1 mmol), only a trace of dihydrofuranoquinone **3b** was obtained.

The probable gross reaction pathway of the addition leading to the hydroquinones is outlined in Scheme I, eq 6. A comparison of the electronic absorption spectrum of 2-hydroxy-1,4-naphthoquinone (**1**) with that of 2-methoxy-1,4-naphthoquinone[13] indicates that no orthoquinone form of 2-hydroxynaphthoquinone exists in the solution. The initial stages in this photochemical addition can be explained within the framework of an accepted model of [2 + 2] photochemical additions.[8] The irradiation of **1** in acetone or benzene generates tautomeric excited triplets (A) and (A′) which react with an alkene through an exciplex to give biradical, (B_r) and/or (B_r'). The involvement of a triplet species of the quinone was proved by a quenching experiment. In view of the strong electron-accepting character of naphthoquinone,[14] it seems likely that these biradical intermediates have an appreciable polar character, or are ionic intermediates (B_i) and (B_i') generated by electron transfer. Alternatively, ionic intermediates B_i and/or B'_i may be formed through a pair of radical ions D and E.[15-18] The regioselectivity found in the present addition clearly indicates that the photoaddition is a two-step process involving a more stabilized polar biradical or ionic intermediate, such as B_i and B'_i. An intramolecular cyclization of the intermediate gives hydroquinones (C) and (C′). In contrast to the photoaddition[9] of 1,4-naphthoquinone with alkenes, no trace of [2 + 2] photoadducts was observed in the present photoadditions. 2,3-Dihydronaphthofuran-4,9-dione was then formed by air oxidation of the hydroquinone during the workup and isolation procedure.

The photoaddition of hydroxynaphthoquinone with alkynes leading to naphtho[2,3-*b*]furan-4,9-diones may proceed in a manner parallel to the photoaddition of alkenes and may also involve vinyl cations B_i and/or B'_i.

Experimental Section

General Method. Regarding the instruments used and a description of the general photolysis procedure, see ref 19.

2,3-Dihydro-2,2-dimethylnaphtho[2,3-*b*]furan-4,9-dione (3a). A solution of 2-hydroxy-1,4-naphthoquinone (**1**) (0.17 g, 1 mmol) and isobutene (0.56 g, 10 mmol) in acetone (40 mL) was irradiated through a Pyrex filter with a 500-W high-pressure Hg arc at room temperature for 15 h. After excess isobutene and acetone were removed under reduced pressure, the residue was subjected to preparative TLC on silica gel (1:3 ethyl acetate–

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(13) Singh, I.; Ogata, R. T.; Moore, R. E.; Chang, C. W. J.; Scheuer, P. J. *Tetrahedron* **1968**, *24*, 6053.

(14) *E.g.*: Chatterjee, S. *J. Chem. Soc. B* 1971, 2194. Rao, P. S. *Nature* **1973**, *243*, 344. Rao, P. S.; Hayon, E. *J. Am. Chem. Soc.* **1974**, *96*, 1287. Rao, P. S., Hauyon, E. *J. Am. Chem. Soc.* **1974**, *96*, 1295. Chen, E. C. M.; Wentworth, W. E. *J. Chem. Phys.* **1975**, *63*, 3183.

(15) Bryce-Smith, D.; Dechpande, R.; Gilbert, A.; Gtzanka, J. *J. Chem. Soc., Chem. Commun.* **1970**, 561.

(16) Wilson, R. M.; Gardner, E. J.; Elder, R. C.; Squire, R. H.; Florian, L. R. *J. Am. Chem. Soc.* **1974**, *96*, 2955.

(17) Wilson, R. M.; Musser, A. U. *J. Am. Chem. Soc.* **1980**, *102*, 1720.

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

(19) Suginome, H.; Liu, C. F., Seco, S.; Kobayashi, K.; Furusaki, A. *J. Org. Chem.* **1988**, *53*, 5952.

hexane) to give **3a** (0.21 g, 92%), mp 188–190 °C (ether–hexane) (lit.[6b] mp 185.5-188.5 °C).

2,3-Dihydro-2,2,3-trimethylnaphtho[2,3-*b*]furan-4,9-dione (3b). (a) The photoreaction of **1** (0.17 g, 1 mmol) and 2-methyl-2-butene (0.70 g, 10 mmol) in acetone (40 mL) for 5 h under the conditions described above gave dihydronaphthofurandione **3b** (0.16 g, 65%): mp 168–169 °C (from ether–hexane); IR (Nujol) 1687, 1643, 1611, 1596, 1575 cm^{-1}; ^{1}H NMR (90 MHz) δ 1.31 (3H, d, J = 7.25 Hz), 1.49 (3H, s), 1.51 (3H, s), 3.26 (1H, q, J = 7.25 Hz), 7.55–7.8 (2H, m), 7.95–8.15 (2H, m); MS (rel intensity) m/z 242 (M$^+$, 99), 227 [(M − Me)$^+$, 100]. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.27; H, 5.76.

(b) The photoaddition in benzene (40 mL) for 5 h gave **3b** (0.19 g, 77%).

(c) The photoaddition in methanol (40 mL) for 5 h gave **3b** (41 mg, 17%).

2,3-Dihydro-2,2,3,3-tetramethylnaphtho[2,3-*b*]furan-4,9-dione (3c). (a) The photoreaction of **1** (1 mmol) with 2,3-dimethyl-2-butene (0.84 g, 10 mmol) in acetone (40 mL) for 15 h gave dihydronaphtho[2,3-*b*]furan-4,9-dione (**3c**) (0.122 g, 48%): mp 101–102 °C (from ether–hexane); IR (Nujol) 1677, 1645, 1612, 1594, 1574 cm^{-1}; ^{1}H NMR (90 MHz) δ 1.36 (6H, s), 1.44 (6H, s), 7.6–7.7 (2H, m), 8.0–8.1 (2H, m); MS (rel intensity) m/z 256 (M$^+$, 100). Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.87; H, 6.29.

(b) The photoaddition in benzene (40 mL) for 15 h gave dihydronaphthofurandione **3c** (0.121 g, 47%).

Dihydronaphthofurandione 3d. The photoaddition of **1** (1 mmol) with cyclopentene (0.14 g, 2 mmol) in acetone (40 mL) for 4 h gave adduct **3d** (0.14 g, 60%): mp 132–134 °C (from ether-hexane); IR (Nujol) 1682, 1652, 1624, 1597, 1575 cm^{-1}; ^{1}H NMR (270 MHz) δ 1.45–1.65 (1H, m), 1.75–2.1 (4H, m), 2.2–2.3 (1H, m), 3.94 (1H, td, J = 8.43 and 1.83 Hz), 5.48 (1H, dd, J = 8.43 and 5.13 Hz), 7.65–7.75 (2H, m), 8.05–8.1 (2H, m); MS (rel intensity) m/z 240 (M$^+$, 100). Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 75.01; H, 4.94.

***trans*-2,3-Dihydro-2-butyl-3-methylnaphtho[2,3-*b*]furan-4,9-dione (3e) and *trans*-2,3-Dihydro-2-methyl-3-butylnaphtho[2,3-*b*]furan-4,9-dione (3e′).** The photoreaction of **1** (0.17 g, 1 mmol) and 2-heptene (0.49 g, 5 mmol) in acetone (40 mL) for 20 h under the conditions described above gave a mixture of dihydronaphthofurandione **3e** and **3e′** (55:45) (79 mg, 29%): an oil, IR (neat) 1683, 1650, 1621, 1597, 1575 cm^{-1}; ^{1} NMR (270 MHz) δ 0.89–0.96 (3H, m, Me of Bu of **3e** and **3e′**), 1.2–2.0 (9H, m), 3.15 (0.45 H, ddd, J = 9.16, 5.86, and 3.67 Hz), 3.29 (0.55 H, q, J = 6.96 Hz), 4.51 (0.55 H, q, J = 6.96 Hz), 4.80 (0.45 H, dq, J = 6.21 and 5.86 Hz), 7.6–7.75 (2H, m), and 8.05–8.1 (2H, m); MS (rel intensity) m/z 270 (M$^+$, 100). Anal. Calcd for $C_{17}H_{18}O_3$: m/z 270.1256. Found: m/z 270.1262.

2,3-Dihydro-2-phenylnaphtho[2,3-*b*]furan-4,9-dione (3f). The photoaddition of **1** (1 mmol) with styrene (0.21 g, 2 mmol) in acetone (40 mL) for 18 h under the conditions described above gave dihydronaphthofuranedione (**3f**) (0.23 g, 83%): mp 163–165 °C (from ether–hexane); IR (Nujol) 1675, 1650, 1642, 1631, 1595, 1575 cm^{-1}; ^{1}H NMR (90 MHz) δ 3.24 (1H, dd, J = 17.84 and 8.79 Hz), 3.68 (1H, dd, J = 17.84 and 10.76 Hz), 6.00 (1H, dd, J = 10.77 and 8.79 Hz), 7.39 (5H, s), 7.65–7.8 (2H, m), 8.0–8.15 (2H, m); MS (rel intensity) m/z 276 (M$^+$, 3.9), 104 (100). Anal. Calcd for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38. Found: C, 78.20; H, 4.32.

2-Acetoxy-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (3g). The photoaddition of **1** (1 mmol) with vinyl acetate (0.86 g, 10 mmol) in acetone (40 mL) for 7 h gave 2,3-dihydronaphthofurandione (**3g**) (0.14 g, 53%): mp 193–195 °C (from diethyl ether–hexane); IR (Nujol) 1764, 1679, 1661, 1638, 1594, 1575 cm^{-1}; ^{1}H NMR (90 MHz) δ 2.12 (3H, s), 3.14 (1H, dd, J = 18.68 and 7.26 Hz), 6.98 (1H, dd, J = 7.26 and 3.07 Hz), 7.55–7.8 (2H, m), 7.9–8.15 (2H, m); MS (rel intensity) m/z 258 (M$^+$, 0.3), 188 [(M − AcOH)$^+$, 41], 43 (100). Anal. Calcd for $C_{14}H_{10}O_5$: C, 65.12; H, 3.90. Found: C, 64.98; H, 3.79.

2-Ethoxy-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (3h). (a) The photoaddition of **1** (1 mmol) with ethyl vinyl ether (0.72 g, 10 mmol) in acetone (40 mL) for 15 h gave 2,3-dihydronaphthofurandione **3h** (0.10 g, 41%): mp 119–120 °C (from ether–hexane) after separation by column chromatography (1:5 ethyl acetate–hexane) on silica gel; IR (Nujol) 1686, 1656, 1631, 1597, 1575 cm^{-1}; ^{1}H NMR (90 MHz) δ 1.27 (3H, t, J = 7.03 Hz), 3.03 (1H, dd, J = 18.24 and 3.73 Hz), 3.34 (1H, dd, J = 18.24 and 6.81 Hz), 3.55–4.15 (2H, m), 5.97 (1H, dd, J = 6.81 and 3.73 Hz), 7.55–7.8 (2H, m), 8.0–8.15 (2H, m); MS (rel intensity) m/z 244 (M$^+$, 44), 187 (100). Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.71; H, 4.97.

(b) The photoaddition in benzene (40 mL) for 15 h gave **3h** (0.1 g, 46%).

2-Carbomethoxy-2,3-dihydro-2-methylnaphtho[2,3-*b*]furan-4,9-dione (3i). (a) The photoaddition of **1** (1 mmol) with methyl methacrylate (1.0 g, 10 mmol) in acetone (40 mL) for 5 h gave dihydronaphthofuranedione **3i** (0.13 g, 49%): mp 168–169 °C (from ether–hexane–dichloromethane); IR (Nujol) 1752, 1686, 1650, 1633, 1594, 1573 cm^{-1}; ^{1}H NMR (90 MHz) δ 1.78 (3H, s), 3.08 (1H, d, J = 17.58 Hz), 3.62 (1H, d, J = 17.58 Hz), 3.81 (3H, s), 7.6–7.75 (2H, m), 8.0–8.15 (2H, m); MS (rel intensity) m/z 272 (M$^+$, 7.9), 213 [(M − COOMe)$^+$, 100]. Anal. Calcd for $C_{15}H_{12}O_5$: C, 66.17; H, 4.44. Found: C, 66.04; H, 4.33.

(b) The photoaddition in benzene (40 mL) for 34 h gave **3i** (0.16 g, 58%).

2,3-Dihydro-6-methoxy-2,2-dimethylnaphtho[2,3-*b*]furan-4,9-dione (5a). The photoreaction of **4** (45 mg, 0.22 mmol) and isobutene **2a** (0.12 g, 22 mmol) in acetone (15 mL) for 1 h gave **5a** (39 mg, 69%): mp 216–218 °C (from hexane–dichloromethane); IR (Nujol) 1673, 1643, 1622, 1589 cm^{-1}; ^{1}H NMR (90 MHz) δ 1.58 (6H, s), 2.98 (2H, s), 3.94 (3H, s), 7.09 (1H, dd, J = 8.57, 2.64 Hz), 7.52 (1H, d, J = 2.64 Hz), 8.02 (1H, d, J = 8.57 Hz); MS m/z 258 (M$^+$, 79), 230 [(M − CO),$^+$ 100]. Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.74; H, 5.47.

2,3-Dihydro-6-methoxy-2,2,3-trimethylnaphtho[2,3-*b*]furan-4,9-dione (5b). The photoreaction of **4** (0.12 g, 0.56 mmol) and 2-methyl-2-butene (**2b**) (0.39 g, 5.6 mmol) in acetone for 4.5 h gave **5b** (0.11 g, 74%): mp 133–134.5 °C (from hexane–dichloromethane); IR (Nujol) 1671, 1640, 1614, 1594 cm^{-1}; ^{1}H NMR (90 MHz) δ 1.30 (3H, d, J = 7.03 Hz), 1.48 (3H, s), 1.50 (3H, s), 3.24 (1H, q, J = 7.03 Hz), 3.94 (3H, s), 7.80 (1H, dd, vinyl J = 8.57, 2.64 Hz), 7.52 (1H, d, J = 2.64 Hz), 8.01 (1H, dd, J = 8.57 Hz); MS m/z 272 (M$^+$, 100). Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92. Found: C, 70.39; H, 6.01.

2-Acetoxy-2,3-dihydro-6-methoxynaphtho[2,3-*b*]furan-4,9-dione (5g). The photoreaction of hydroxyquinone **4** (55 mg, 0.27 mmol) and vinyl acetate (**2g**) (0.23 g, 2.7 mmol) in acetone (15 mL) for 7 h gave furonaphthoquinone **5g** (40 mg, 52%): mp 193–194 °C (from hexane–dichloromethane); IR (Nujol) 2.12 (3H, s), 3.12 (1H, dd, J = 18.45, 3.07 Hz), 3.47 (1H, dd, J = 18.45, 7.04 Hz), 3.95 (3H, s), 6.99 (1H, dd, J = 7.04, 3.07 Hz), 7.13 (1H, dd, J = 8.57, 2.63 Hz), 7.54 (1H, d, J = 2.63 Hz), 8.05 (1H, d, J = 8.57 Hz); MS m/z 288 (M,$^+$ 1.4), 246 [(M − CH_2CO),$^+$ 19], 228 [(M − AcOH)$^+$, 28), 218 (93), 43 (100). Anal. Calcd for $C_{15}H_{12}O_6$: C, 62.50; H, 4.20. Found: C, 62.43; H, 4.16.

Synthesis of Maturinone (8). A solution of 2-hydroxy-5-methyl-1,4-naphthoquinone (**6**)[12] (96 mg, 0.51 mmol) and 1-propenyl acetate (**2j**) (0.51 g, 5.1 mmol) in acetone (23 mL) was irradiated as mentioned above. The solution was worked up, and the product was purified as described above to give *trans*-2-acetoxy-3,5-dimethyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (**7**) (58 mg, 40%): IR (neat) 1766, 1680, 1650, 1629, 1588, 1567 cm^{-1}; ^{1}H NMR (90 MHz) 1.43 (3H, d, J = 7.48 Hz), 2.11 (3H, s), 2.77 (3H, s), 3.50 (1H, dq, J = 7.48 and 1.98 Hz), 6.50 (1H, d, J = 1.98 Hz), 7.5–7.65 (2H, m), 8.08 (1H, dd, J = 7.69 and 1.32 Hz); MS (rel intensity) m/z 286 (M$^+$, 2.1), 226 [(M − AcOH)$^+$, 60], 216 (90), 43 (100). Anal. Calcd for $C_{16}H_{14}O_5$: m/z 286.0841. Found: m/z 286.0856.

To a stirred suspension of potassium *tert*-butoxide (7 mg, 0.06 mmol) in THF (2 mL) was added the adduct **7** (16 mg, 0.055 mmol) in THF (1 mL) at 0 °C. After being stirred for 10 min, the mixture was quenched with aqueous ammonium chloride and extracted with ether. The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and then evaporated in *vacuo*. The residue was subjected to preparative TLC on silica gel to afford maturinone (**8**) (6.7 mg, 52%), mp 167–169 °C (ether–hexane) (lit.[4a] mp 168–169 °C).

2-Phenylnaphtho[2,3-*b*]furan-4,9-dione (10a). The photoreaction of **1** (0.17 g, 1 mmol) and phenylacetylene (**9a**) (1.0 g, 10 mmol) in acetone (30 mL) for 7.5 h gave furonaphthoquinone **10a** (0.15 g, 54%), mp 245–249 °C (from dichloromethane) (lit.[6b] mp 246.5–247.5 °C; lit.[6g] mp 250.0–251.0 °C).

3-Methyl-2-Phenylnaphtho[2,3-*b*]furan-4,9-dione (10b). The photoreaction of 1 (0.17 g, 1 mmol) and methylphenylacetylene (**9b**) (0.35 g, 3 mmol) in acetone (30 mL) for 22 h gave furonaphthoquinone **10b** (42 mg, 15%): mp 199–201 °C (from dichloromethane); IR (Nujol) 1675 and 1663 cm^{-1}; ^{1}H NMR (90 MHz) δ 2.66 (3H, s), 7.4–7.5 (3H, m), 7.6–7.9 (4H, m), 8.1–8.3 (2H, m); MS *m/z* 288 (M$^+$, 100). Anal. Calcd for $C_{19}H_{12}O_3$: C, 79.15; H, 4.19. Found: C, 79.26; H, 4.13.

2-Butylnaphtho[2,3-*b*]furan-4,9-dione (10c). The irradiation of 1 (0.17 g, 1 mmol) and 1-hexyne (**9c**) (0.25 g, 3 mmol) in acetone (30 mL) for 30 h gave furonaphthoquinone **10c** (14 mg, 5.5%): mp 94–97 °C (from dichloromethane); IR (Nujol) 1658 cm^{-1}; ^{1}H NMR (90 MHz) δ 0.96 (3H, t, J = 6.37 Hz), 1.2–1.8 (4H, m), 2.82 (2H, t, J = 7.25 Hz), 6.61 (1H, s), 7.6–7.8 (2H, m), 8.1–8.3 (2H, m); MS *m/z* 254 (M$^+$, 94), 212 (100). Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; C, 5.55. Found: C, 75.37; H, 5.60.

Isolation of 4,9-Diacetoxy-2,3-dihydro-2,2,4-tetramethylnaphtho[2,3-*b*]furan (11) in the Photoaddition. After a solution of 1 (1 mmol, 174 mg) and 2,3-dimethyl-2-butene (**2c**, 840 mg, 10 mmol) in acetone (40 mL) was irradiated for 15 h, the solvent was removed. Treatment of the residue with acetic anhydride (1 mL) and pyridine (1 mL) at 60 °C for 2 h under nitrogen gave a mixture of products. After excess acetic anhydride and pyridine were removed, the mixture was subjected to preparative TLC on silica gel (1:3 ethyl acetate–hexane) to give **3c** (46 mg, 18%) and 4,9-diacetoxy-2,3-dihydro-2,2,4,4-tetramethylnaphtho[2,3-*b*]furan (**11**) (123 mg, 36%): mp 173–174 °C (from ether–hexane); IR (Nujol) 1769, 1760, 1660 cm^{-1}; ^{1}H NMR (90 MHz) δ 1.30 (s, 6H, s), 1.35 (6H, s), 2.43 (3H, s), 2.47 (3H, s), 7.2–7.75 (4H, m); MS (rel intensity) *m/z* 342 (M$^+$, 15), 300 [(M − CH_2CO)$^+$, 31], 258 [(M − 2CH_2CO)$^+$, 100]; HRMS found *m/z* 342.1459, calcd for $C_{20}H_{22}O_5$ 342.1468.

Quenching Experiment of the Photoaddition of 2-Hydroxy-1,4-naphthoquinone (1) with 2-Methyl-2-butene (2b). Irradiation of a benzene solution (30 mL) of 2-hydroxy-1,4-naphthoquinone (1) (0.18 g, 1.0 mmol) and 2-methyl-2-butene (**2b**) (0.70 g, 10 mmol) containing piperylene (68 mg, 1.0 mmol) for 8 h gave furonaphthoquinone **3b** (4.4 mg, 1.8%).