New One-Step General Synthesis of 2,3-Dihydronaphtho[2,3-*b*]furan-4,9-diones by Regioselective Photoaddition of 2-Hydroxy-1,4-naphthoquinones with Various Alkenes and Its Application to a Two-Step Synthesis of Maturinone[1,2]

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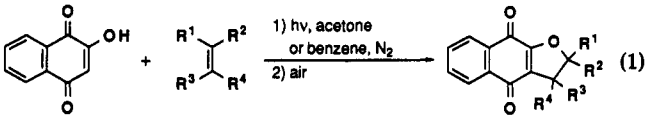
Summary: A one-step formation of 2,3-dihydronaphtho-[2,3-*b*]furan-4,9-diones in 41–83% by a new 2 + 3 type regioselective photoaddition of 2-hydroxy-1,4-naphthoquinones with a variety of alkenes is reported. The dihydronaphthofurandiones can readily be transformed into naphtho[2,3-*b*]furan-4,9-diones including a natural quinone, maurinone.

Naphtho[2,3-*b*]furan-4,9-diones are an important class of heterocyclic quinones.[3] Several biologically important natural products and their derivatives belong to this group.[4]

Since the first synthesis of this system by Hooker,[5] a variety of methods for the synthesis of this class of molecule has been reported.[3,4b-d,6] Most of these methods, however, are not necessarily generally applicable and require several steps.

In this paper, we report a novel one-step synthesis of 2,3-dihydronaphtho[2,3-*b*]furan-4,9-diones based on a new type of regioselective photoaddition of 2-hydroxy-1,4-naphthoquinones with a variety of cyclic and acyclic alkenes (eq 1). 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.



(1)

1 2a-2h 3a-3h

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; $R^1=Ph$,$R^2=R^3=R^4=H$: f; $R^1=OAc$, $R^2=R^3=R^4=H$: g; $R^1=OEt$, $R^2=R^3=R^4=H$: h; $R^1=Me$, $R^2=COOMe$, $R^3=R^4=H$

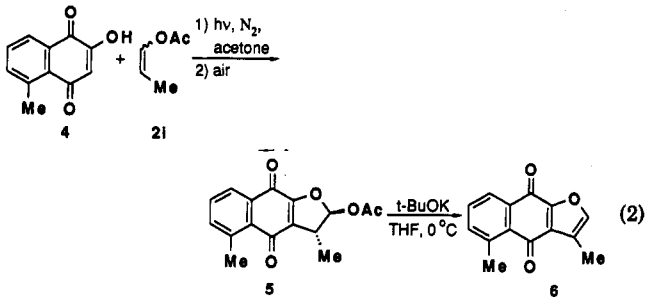
Table I. Results of Photoadditions of 2-Hydroxy-1,4-naphthoquinone (1) with Alkenes

alkene	solvent[a]	time of irradn (h)	2,3-dihydro-naphtho-quinone[b]	yield (%)
2a	A	15	3a	92
2b	A	5	3b	65
2b	B	5	3b	77
2b	C	5	3b	17
2c	A	15	3c	48
2c	B	15	3c	47
2d	A	4	3d	60
2e	A	18	3e	83
2f	A	10	3f	53
2g	A	15	3g	41
2g	B	15	3g	46
2h	A	5	3h	49
2h	B	24	3h	58

[a] A, acetone; B, benzene; C, methanol. [b] Satisfactory analytical and spectral data were obtained.

The results of a photoaddition between hydroxynaphthoquinone (1) and a variety of olefines (2b–h) under a similar set of conditions are summarized in Table I.[7] The photoaddition of 1 with styrene (2e), vinyl acetate (2f), ethyl vinyl ether (2g), and methyl methacrylate (2h) in acetone or benzene took place regioselectively to give the corresponding 2-substituted 2,3-dihydronaphtho[2,3-*b*]-furan-4,9-diones (3e–h) in 41–83% yields as single products. The yield of adduct decreased appreciably when the photoaddition was conducted in methanol. No photoadducts between 1 and olefins such as acrylonitrile and ethyl acrylate have been obtained.

The present photoaddition reaction was successfully applied to a two-step synthesis of maturinone (6),[4a-c] a constituent of *Cacalia decomposita A. Gray* (eq 2). Thus,



(2)

the photoaddition of 2-hydroxy-5-methyl-1,4-naphthoquinone (4)[8] with 1-propenyl acetate (2i) in acetone gave *trans*-2-acetoxy-2,3-dihydro-3,5-dimethylnaphtho[2,3-*b*]-furan-4,9-dione (5)[9] in 40% yield under our standard

(1) Photoinduced Molecular Transformations. Part 120. Part 119. Suginome, H.; Furukawa, K.; Orito, K. *J. Chem. Soc., Perkin Trans. 1*, in press.

(2) Presented at 20th Congress of Heterocyclic Chemistry, Gifu, Japan, 1989; Abstr. P.67.

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(7) Typically, a solution of commercially available 2-hydroxy-1,4-naphthoquinone (1) (Lawsone) (0.17 g, 1 mmol) and isobutene (2a) (0.56 g, 10 mmol) in acetone (40 mL) was irradiated through a Pyrex filter with a 500-W high-pressure Hg arc lamp under a nitrogen atmosphere for 15 h at room temperature. The usual workup and purification by preparative TLC (silica gel) gives 2,3-dihydro-2,2-dimethylnaphtho[2,3-*b*]furan-4,9-dione (3a)[6b] as the exclusive product (0.21 g, 92%).

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(9) Satisfactory analytical and spectral results were obtained for these compounds.

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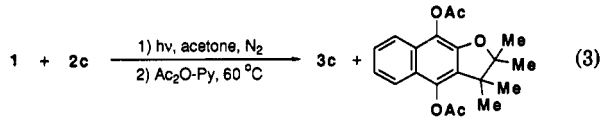
conditions.[7] The trans disposition of the acetoxyl and methyl groups attached to C-2 and C-3 of photoproduct **5** was assigned by its ^{1}H NMR spectrum ($J_{2\text{-H-3-H}}$ = 1.98 Hz). Treatment of naphthofurandione **5** with potassium *tert*-butoxide in THF at 0 °C resulted in the elimination of acetic acid, giving maturinone (**6**) in 52% yield.

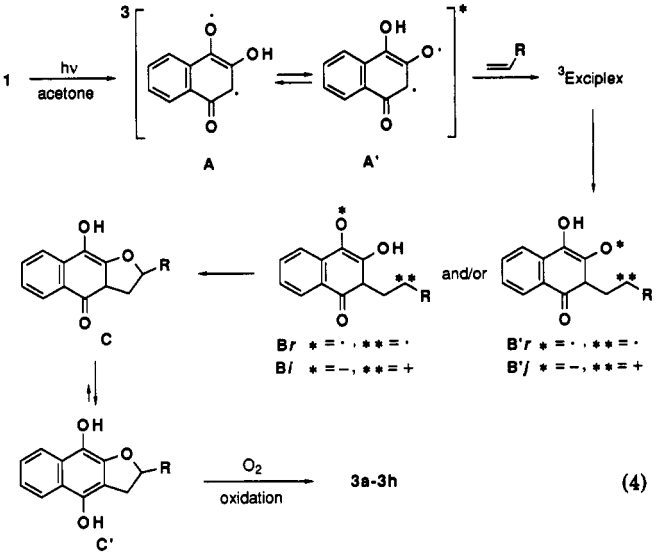
The initial products in the present photoaddition are furanohydroquinones; 4,9-diacetoxy-2,3-dihydro-2,2,4,4-tetramethylnaphtho[2,3-*b*]furan (**7**)[9] can be isolated in 36% yield together with 2,2,4,4-tetramethylnaphtho[2,3-*b*]furan (**3c**) (18%) when the crude products from the photoaddition between 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 (eq 3).



(3)

7

The probable gross reaction pathway of the addition leading to the hydroquinones is outlined in eq 4. A comparison of the electronic absorption spectrum of 2-hydroxy-1,4-naphthoquinone (**1**) with that of 2-methoxy-1,4-naphthoquinone[10] indicates that no orthoquinone form of 2-hydroxynaphthoquinone exists in solution. The initial events in this photochemical addition can be explained within the framework of an accepted model of $[2 + 2]_\pi$ photochemical additions.[11] Irradiation of **1** in acetone or benzene generates tautomeric exited triplets (A) and (A'), which react with an alkene through a triplet exciplex to give biradical (B_r) and/or (B_r'). In view of the strong electron-accepting character of naphthoquinone,[12] it seems likely that the exciplex or these biradical intermediates have appreciable polar character or are ionic intermediates (B_i) and (B_i') generated by electron transfer. The regioselectivity found in the present addition is a clear in-



(4)

dication of the involvement of a more stabilized polar biradical or ionic intermediate, such as B_i and B_i', in the formation of dihydronaphtho[2,3-*b*]furan-4,9-diones. Intramolecular cyclization of the intermediate gives hydroquinones (C) and (C'). In contrast to the photoaddition[13] of 1,4-naphthoquinone with alkenes, no trace of $[2 + 2]_\pi$ cycloadducts were observed in the present photoadditions. 2,3-Dihydronaphthofuran-4,9-dione is then formed by air oxidation of the hydroquinone during the workup and isolation procedures.

Additional mechanistic and synthetic aspects of the present *formal* [2 + 3] photoaddition are presently under investigation and will be reported in a forthcoming full paper.

Supplementary Material Available: Experimental details for the synthesis of **3a-g** and maturinone (**6**) and for isolation of diacetoxyfuranohydroquinone **7** from the photoaddition between hydroxynaphthoquinone **1** and 2,3-dimethyl-2-butene (4 pages). Ordering information is given on any current masthead page.

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Highly Efficient Synthesis of 13-Dehydroprostaglandins by 1,4-Addition Reaction of Alkynyl ω Side-Chain Unit onto Cyclopentenone Framework

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Summary: Optically active 2-((diethylamino)methyl)-4-siloxy-2-cyclopentenone (**2**) reacts with a diethyl(3-(*tert*-butyldimethylsiloxy)-1-alkynyl)aluminum compound via 1,4-addition pathway to afford the enone **5**, useful intermediate for synthesis of PGs via two-component coupling process, in excellent yield, thus making it easy to synthesize 13-dehydro-PGs.

The synthesis of analogues of prostaglandins (PGs) has attracted much interest for use in biological and clinical investigations.[1] A number of analogues in which the double bond at C-13 (PG numbering) has been replaced by triple bond have been prepared and some of which have deserved particular attention as promising therapeutic agents.[2]

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