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Cycloadditions in Syntheses. XXVI.[1] 1,2-Dihydrocyclobuta[*b*]-naphthalene-3,8-diones: Synthesis by Photochemical Means and Their Reactions *via* 2,3-Dimethylene-1,4-dioxo-1,2,3,4-tetrahydronaphthalenes

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2-Chloro-1,4-naphthoquinone undergoes photochemical 2+2 addition to alkenes. Elimination of hydrogen chloride from the adducts provides a facile and general synthetic method for 1,2-dihydrocyclobuta[*b*]naphthalene-3,8-diones. Heating of the latter compounds affords 2,3-dimethylene-1,2,3,4-tetrahydronaphthalene-1,4-diones, which react *in situ* with alkenes to give the 4+2 adducts. 1-Formyl-1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione obtained by the use of the above two-step procedure using acrolein dimethylacetal as the alkene in the first step affords upon heating 1*H*-naphtho[2,3-*c*]pyran-5,10-dione *via* electrocyclization of the corresponding dimethylene compound. If an enone is used as the alkene in the first step, the addition occurs in a 4+2 manner to give directly 4*H*-naphtho[2,3-*b*]pyran-5,10-diones.

Keywords——1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione; 1*H*-naphtho[2,3-*c*]pyran-5,10-dione; 4*H*-naphtho[2,3-*b*]pyran-5,10-dione; benzocyclobutene method; cyclobutane annelation; photochemical synthesis; naphthopyrandione; pyran annelation

Since 1979, we have developed a novel photochemical method for the synthesis of cyclobutane-fused heteroaromatics starting from heteroaromatics containing a β-alkoxy (or its equivalent group) enone function in their ring system. The general scheme of this method is summarized in Chart 1. The enone function involved in a heteroaromatic ring (A) adds photochemically to a variety of olefins to give the 2+2 adduct (B). This addition reaction proceeds in most cases in a regiospecific manner and the head-to-tail adducts are formed exclusively or at least as major products, irrespective of the olefin used. Treatment of the adducts with base (or acid) then affords the heteroaromatics annelated with a cyclobutane ring on the ene function of the starting enone system (C). Though such cyclobutane annelation was originally found for the synthesis of cyclobutane-fused cyclohexanones using 3-acetoxy-2-cyclohexenones as starting materials,[3] this two-step procedure was first used by Kaneko and Naito for the annelation of the 2-quinolone series[4] and applied successfully to 2-pyridone,[5] coumarin,[6] and uracil derivatives.[7] This two-step cyclobutane annelation method to heteroaromatics (Kaneko–Naito method) has several useful characteristics, *e.g.*, elimination of the alcohol under mild conditions, regioselective addition giving only the head-to-tail adducts, and high overall yields. Later, the method was extended to 3-alkoxy-1-isoquinolone having a δ-alkoxy dienone function in the ring system.[8] Since the synthesis of a 4-membered ring fused to heteroaromatic compounds (C) had become readily attainable, the benzocyclobutene method[9,10] (generation of so-called *ortho*-xylylene or -quinodimethane intermediates and their subsequent inter- or intramolecular cycloaddition reactions) was then extended successfully to heteroaromatic compounds (D→E).[11]

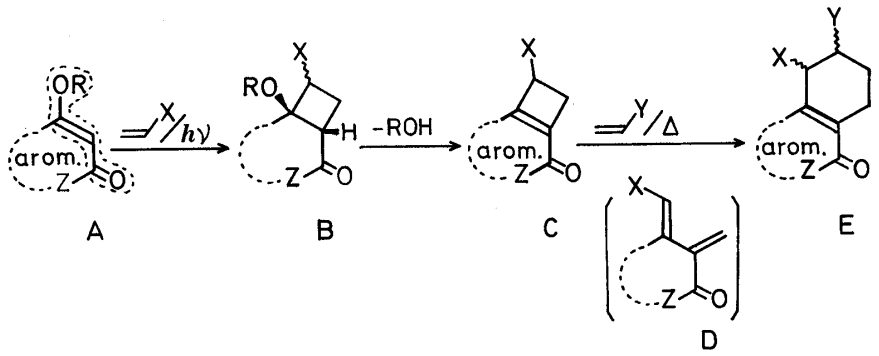


Chart 1

Quite recently, the synthesis of 1,2-dihydrocyclobuta[*b*]naphthalene-3,8-diones was achieved starting from 2-chloro-1,4-naphthoquinone by an application of the above-mentioned two-step procedure.[12]

In this paper, we present the experimental details of the synthesis of 1,2-dihydrocyclobuta[*b*]naphthalene-3,8-diones as well as their thermal cycloaddition reactions with $_{\pi}2$ components *via* the 2,3-dimethylene intermediates. Synthesis of 1*H*-naphtho[2,3-*c*]pyran-5,10-dione from 1-formyl-1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione by electrocyclization of the latter type of intermediate is also reported. Further, a novel photochemical addition of 2-chloro-1,4-naphthoquinone to enones in a 4+2 manner to give 4*H*-naphtho[2,3-*b*]-pyran-5,10-diones is described.

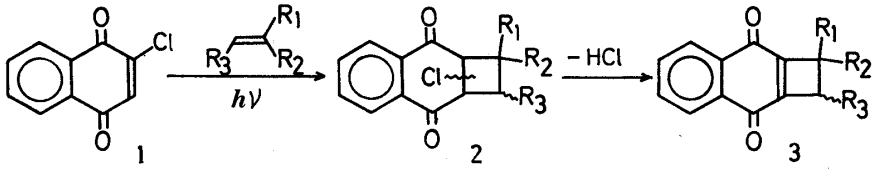
Synthesis of 1,2-Dihydrocyclobuta[*b*]naphthalene-3,8-diones

The ready 2+2 photoadditions of 1,4-naphthoquinone derivatives to olefins[13] prompted us to synthesize 1,2-dihydrocyclobuta[*b*]naphthalene-3,8-diones by an application of the Kaneko–Naito method from 1,4-naphthoquinone having a leaving group at the 2-position. We have obtained two important results concerning the second step (B→C) in this method. These are i) the elimination of an alcohol from the adducts is possible only when a gain of aromaticity is attained in this step[14] and ii) the elimination of hydrogen chloride occurs spontaneously from the adducts obtained from 6-chlorouracils and alkenes.[7] In the case of application of the Kaneko–Naito method to the nonaromatic 1,4-naphthoquinone series, these considerations clearly indicate that chlorine is a more suitable leaving group than an alkoxy group. Hence, we have chosen 2-chloro-1,4-naphthoquinone (**1**)[15] as the starting material.

Irradiation of **1** in benzene at ≥300 nm under bubbling of ethylene afforded 2a-chloro-1,2,2a,8a-tetrahydrocyclobuta[*b*]naphthalene-3,8-dione (**2a**) and 1,2-dihydrocyclobuta[*b*]-naphthalene-3,8-dione (**3a**) in yields of 53 and 8%, respectively. The former (**2a**) was converted to **3a** in 90% yield merely by treatment with triethylamine in chloroform at room temperature. More conveniently, **3a** was obtained as a sole product in higher overall yield (81%) by base treatment of the photoproducts obtained from **1** and ethylene without separation of **2a** and **3a**.

1,2-Dihydrocyclobuta[*b*]naphthalene-3,8-dione (**3a**) was found to react with methanol under basic conditions (NaOMe–MeOH) to give 2a-methoxy-1,2,2a,8a-tetrahydrocyclobuta[*b*]naphthalene-3,8-dione (**4a**).[16] Under basic conditions, **4a** did not eliminate methanol. However, the elimination of methanol from **4a** was achieved under acidic conditions (*p*-TsOH–benzene), though the yield of **3a** was rather low (53%).

Previously, **3a** was synthesized either from 2,3-bis-(bromomethyl)-naphthalene[17] or from dimethyl cyclobutane-1,2-dicarboxylate.[18] The present method for the synthesis of **3a** is superior to those reported not only in its small number of steps and higher overall yield, but



	R_1	R_2	R_3
a	H	H	H
b	CO_2Me	Me	H
c	CO_2Me	H	H
d	CO_2Me	H	Me
e	Me	H	H
f	CH_2OAc	H	H
g	$CH(OMe)_2$	H	H
h	Me	Me	H

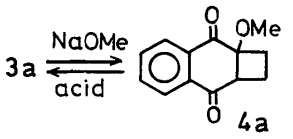


Chart 2

TABLE I. Formation of Naphthocyclobutenes (**3**) by Photoaddition of **1** to Olefins Followed by Base Treatment

	R_1	R_2	R_3	Yield of **3** (%) A	B
a	H	H	H	81	—
b	CO_2Me	Me	H	74[a]	—
c	CO_2Me	H	H	27[b]	—
d	CO_2Me	H	Me	72	—
e	Me	H	H	35	—
f	CH_2OAc	H	H	33	—
g	$CH(OMe)_2$	H	H	37	50
h	Me	Me	H	5[c]	35

A, irradiation with a 450 W high-pressure mercury lamp equipped with a Pyrex filter. B, irradiation with a 15 W fluorescent lamp (visible light). *a*) The ene product (**5**) was obtained in 4% yield. *b*) The dimer of **3c** was obtained in 68% yield. *c*) The yield was increased to 32% by the use of a 100 W high-pressure mercury lamp.

also in its applicability to the synthesis of a variety of 1-substituted and/or 1,2-disubstituted derivatives of **3a** by the use of substituted ethylenes in the photoaddition step. Thus, **1** was irradiated in the presence of various olefins, electron-rich or electron-deficient, and the resultant crude adducts (**2b**—**h**) were treated with triethylamine in chloroform at room temperature for 10 min to give the substituted derivatives of **3a** (**3b**—**h**). The results are summarized in Table I. Though the photoaddition step proceeded at ≥ 300 nm in all cases, the same addition also proceeded on exposure to visible light[19] in some cases with better overall yields (**3g** and **3h**).

The stereochemistries of $\mathbf{3d}_{cis}$ and $\mathbf{3d}_{trans}$ were elucidated by comparison of the proton nuclear magnetic resonance (^{1}H-NMR) spectra. Thus, the coupling constant between the C_1- and C_2-protons was smaller in $\mathbf{3d}_{trans}$ ($J = 2.0$ Hz) than in $\mathbf{3d}_{cis}$ ($J = 5.0$ Hz). This assignment was also supported by base-catalyzed equilibration between $\mathbf{3d}_{cis}$ and $\mathbf{3d}_{trans}$, in which the major isomer was $\mathbf{3d}_{trans}$ (thermodynamically more stable than $\mathbf{3d}_{cis}$).

Thus, we have now established an efficient synthetic method for 1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione (**3a**) and its substituted derivatives (**3b**—**h**) by an application of the Kaneko–Naito method starting from 2-chloro-1,4-naphthoquinone (**1**) without isolation of the photoadducts.

In the synthesis of **3h** by the above one-pot procedure the head-to-tail adduct ($\mathbf{2h}_{H\text{-}T}$) was

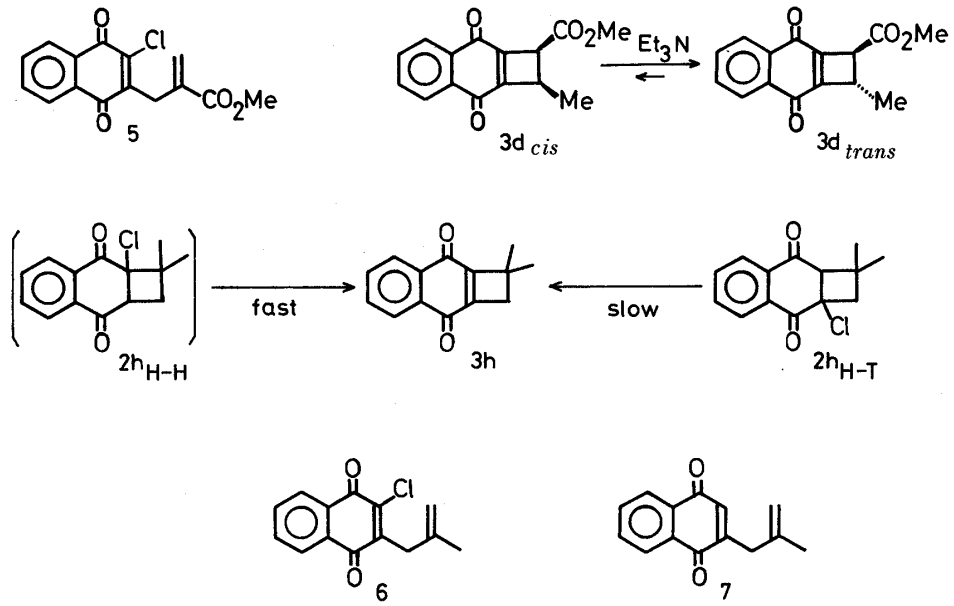


Chart 3

obtained in 8% yield, together with **3h** (35%). Since the elimination of hydrogen chloride from $\mathbf{2h}_{H\text{-}T}$ was very slow (completed by 72 h at room temperature) under the same basic conditions, it is clear that the presence of *gem*-dimethyl groups results in a large steric hindrance toward the active methine proton in $\mathbf{2h}_{H\text{-}T}$, whose elimination is the essential requisite for the formation of **3h**. Consequently, **3h** obtained in the above one-pot synthesis should be formed directly from the other isomer ($\mathbf{2h}_{H\text{-}H}$), because the corresponding proton may be eliminated readily without any steric hindrance. In this reaction, the ene-type products (**6** and **7**) were also obtained in yields of 10 and 11%, respectively, only when the irradiation was performed with visible light.

Two unexpected products (**8** and **9**[20]) were obtained in addition to the 2+2 adduct (**2i**) by irradiation of **1** in presence of ethyl vinyl ether followed by chromatographic separation on silica gel. The yields of these products differed markedly according to both the irradiation

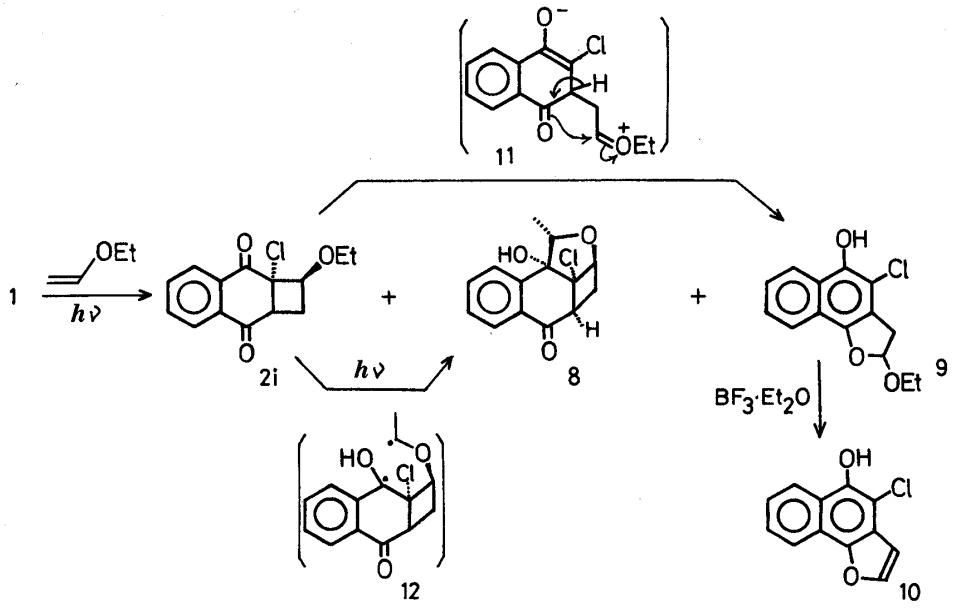


Chart 4

TABLE II. Products of Photoaddition of **1** to Ethyl Vinyl Ether

Irradiation condition	Solvent	Yield of product (%) **2i**	**8**	**9**
A	Benzene	0	21	38
A	1% pyridine–benzene	5	32	4
B	1% pyridine–benzene	46	10	0

A, irradiation with a 450 W high-pressure mercury lamp equipped with a Pyrex filter. B, irradiation with a 15 W fluorescent lamp.

solvent and light source (Table II).

Both **2i** and **9** were transformed to the naphthofuran (**10**) by treatment with $BF_3 \cdot Et_2O$ in benzene. This clearly shows that **9** was a secondary product derived from **2i** under acidic conditions *via* a zwitterionic intermediate (**11**). Actually, when the irradiation was carried out in a 1% pyridine–benzene solution, the yield of **9** decreased remarkably. The other product (**8**) is also a secondary product derived from **2i**, because irradiation (≥ 300 nm) of the latter in benzene afforded the former (**8**) in 72% yield. This finding suggests not only that a δ-hydrogen abstraction process (*cf.*, **12**) participates in the formation of **8**, but also that the *endo* structure (ethoxy and chlorine groups are *trans* to each other) of **2i** is involved. When the irradiation was carried out with visible light, the δ-hydrogen abstraction process was suppressed appreciably and **2i** was obtained as the major product. In an attempt to obtain **3i**, **2i** was treated with base (Et_3N–$CHCl_3$). Instead of the desired product (**3i**), only the dimeric product was obtained.[21,22]

Thermal Ring-Opening Reactions of 1,2-Dihydrocyclobuta[*b*]naphthalene-3,8-diones to 2,3-Dimethylene-1,2,3,4-tetrahydronaphthalene-1,4-diones

The dimerization reaction of **3a** to **13** under pyrolytic conditions was reported by Cava and Shirley.[17] However, the structure of **13** was only deduced from the ultraviolet (UV) spectrum, and hence was not definitive. Also, vigorous conditions (185—190 °C) were applied for this reaction. We have found that the ring opening reaction of **3a** to the quinodimethane species (**16a**) occurs under relatively mild conditions (reflux in toluene) and confirmed the correctness of the assigned structure (**13**) by analysis of the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum (see Experimental). The formation of **13** probably occurs by the initial formation of **16a** followed by its subsequent addition to **3a**, as is evident from the structure of the dimer (**13**). Different types of dimer were obtained, however, from either **3b** or **3d**. Their structures (**15** and **14d**) were deduced from the ^{1}H-NMR spectra (see Experimental). A large coupling constant ($J = 9.0$ Hz) between two vicinal methine protons in **14d** indicates clearly that both methoxycarbonyl groups are in a *trans* relationship. As is evident from their structures, these dimers are formed by cycloaddition between two molecules of the corresponding dimethylene intermediates (such as **16d**), both of which are stabilized by a methoxycarbonyl group and hence are more stable than the corresponding unsubstituted compound (**16a**). Possible mechanisms for the formation of **14d** and **15** are shown in Chart 5.

Under refluxing in toluene, **3a** underwent 4+2 cycloaddition to dimethyl fumarate to give **17** in 78% yield. A small amount of dimer (**13**) was formed in this reaction. In contrast, 3,8-dimethoxy-1,2-dihydrocyclobuta[*b*]naphthalene (**18**)[23] was stable under the same conditions, probably because the ring opening of **18** to the corresponding dimethylene compound necessarily loses the aromaticity of the starting material (**18**).

One application of the benzocyclobutene method is to synthesize benzo[*c*]pyran derivatives by heating benzocyclobutenes having an aldehyde or acyl group at the 1-position.[24] We also succeeded in the synthesis of 1*H*-pyrano[3,4-*c*]pyridin-8(7*H*)-ones from 1,2-

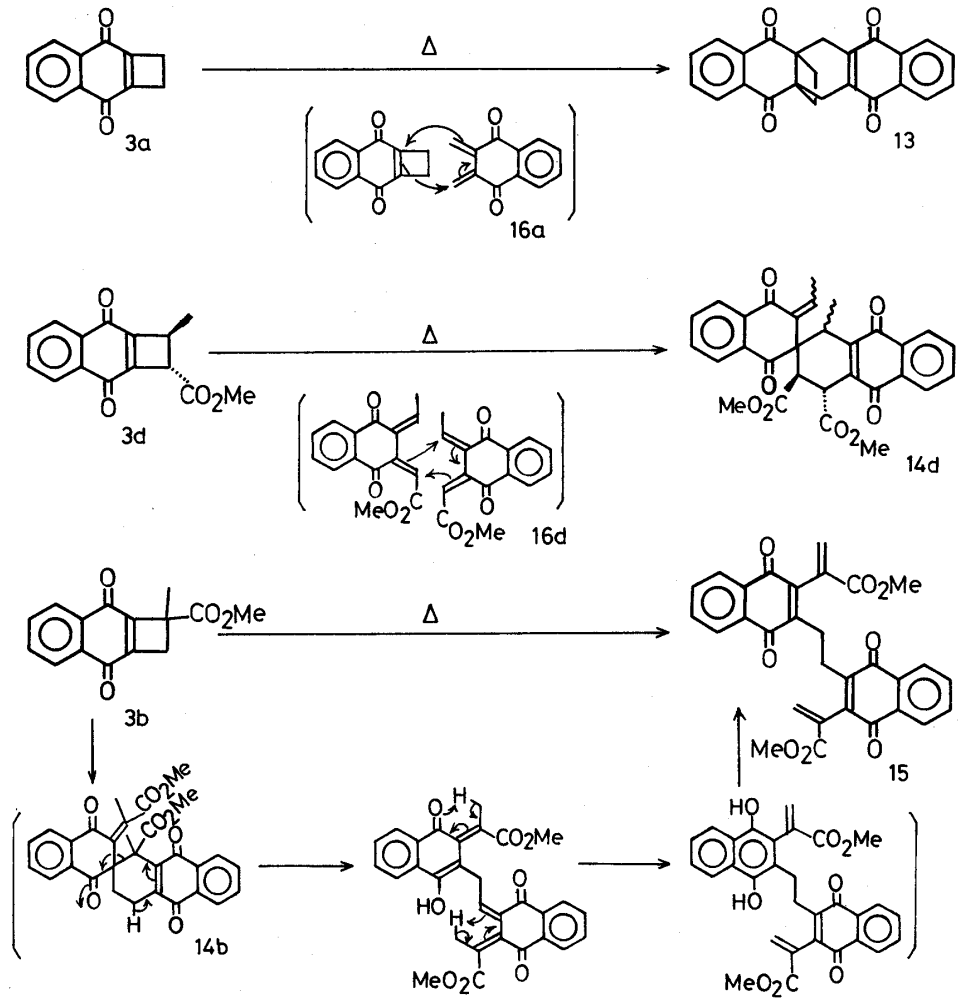


Chart 5

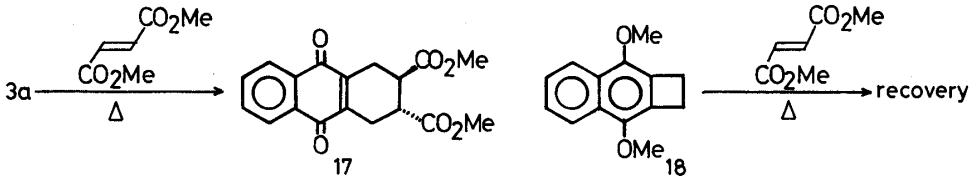


Chart 6

dihydrocyclobuta[*c*]pyridin-3(4*H*)-ones having an acetal function at the 1-position by heating in aq. acetic acid. The reaction clearly proceeded by the initial hydrolysis of the acetal group, formation of the 2-pyridone-3,4-quinodimethane intermediate, and 6π-electrocyclization *via* its *Z*-form.[25] Based on the above results, we have applied this method to 1-dimethoxymethyl-1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione (**3g**) in order to synthesize 1*H*-naphtho[2,3-*c*]-pyran-5,10-dione (**19**), a basic skeleton of some naphthopyran antibiotics.[26]

After several attempts, it was found that **3g** was converted to **19** in 55% yield by treatment with *p*-TsOH in refluxing acetone.

Photochemical 4+2 Cycloaddition of 2-Chloro-1,4-naphthoquinone (1) to Enones

In addition to the above mentioned photochemical cycloaddition reactions, 1,4-naphthoquinone and its derivatives undergo thermal 4+2 addition to dienes.[27] However, the

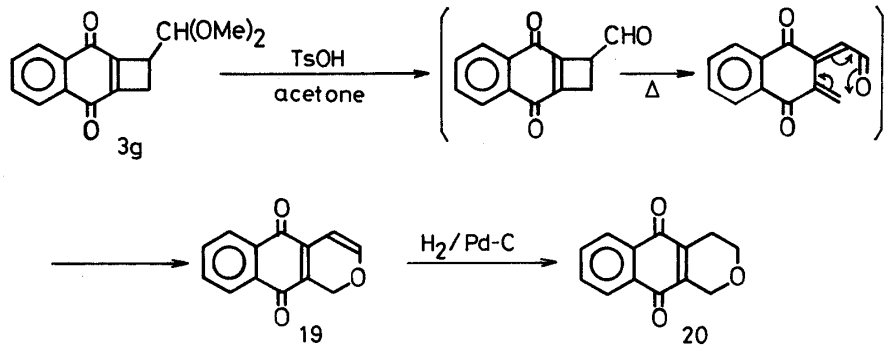


Chart 7

addition reactions to heterodienes have not yet been reported. We found that **1** added to acrolein or methyl vinyl ketone in a 4+2 manner only under irradiation. Thus, irradiation of **1** with visible light in the presence of these enones afforded 4+2 adducts which on subsequent base treatment gave directly 4*H*-naphtho[2,3-*b*]pyran-5,10-diones (**21a** and **21b**). Though the overall yields are poor (the yields of **21a** and **21b** are 9 and 27%, respectively), these photoreactions are the first examples of this type of photocycloaddition reaction.

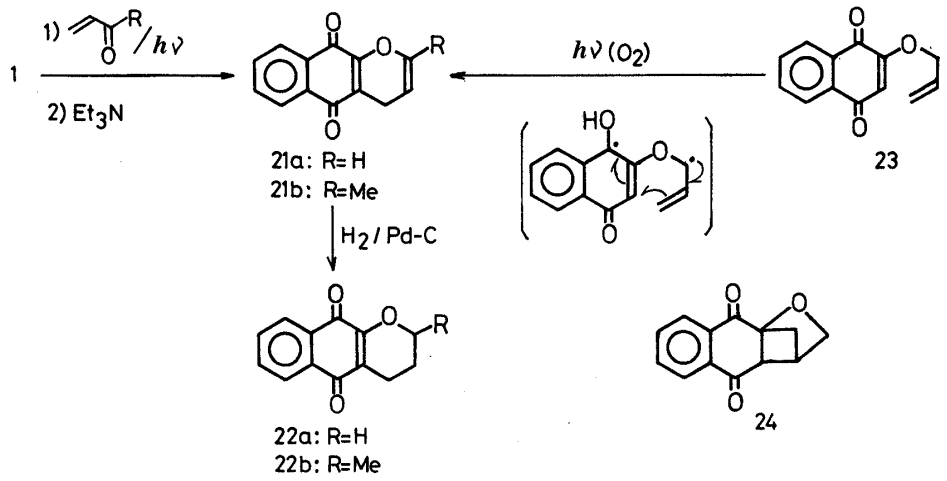


Chart 8

The same naphthopyran (**21a**) was also obtained by irradiation of 2-allyloxy-1,4-naphthoquinone (**23**) *via* hydrogen abstraction, cyclization, and subsequent air-oxidation. In this case, the corresponding intramolecular 2+2 adduct (**24**) was also obtained concomitantly. The cross structure of the adduct was deduced by comparison of the ^{1}H-NMR spectrum with that of the cross adduct obtained by the photolysis of 4-allyloxy-2-quinolone.[28] The selective formation of the cross adduct (**24**) is in good accordance with the so-called "rule of five."[29] These naphthopyrans (**21a** and **21b**) were hydrogenated to dihydro derivatives (**22a** and **22b**[30]). This type of dihydronaphthopyrandione system is also a structural moiety present in a variety of naturally occurring quinones, *e.g.*, α-lapachone.[31]

Conclusion

In summary, we have successfully applied our two-step procedure (the Kaneko–Naito method, which was originally developed for cyclobutane annelation to heteroaromatics) to the carbocyclic series and have elaborated a simple synthetic method for 1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione and its substituted derivatives. A novel photo-

chemical 4+2 cycloaddition of 2-chloro-1,4-naphthoquinone to enones has also been disclosed. These findings provide novel routes to two types of dihydronaphthopyrandione system (*e.g.*, **20** and **22**, structural moieties present in a variety of naturally occurring quinones).

Experimental

All melting points are uncorrected. Infrared (IR) spectra were recorded on a Shimadzu IR-420 spectrometer, UV spectra were taken on a Hitachi 320 spectrometer, and NMR spectra were obtained on a JEOL JNM-60H or JEOL JNM-FX-100 spectrometer (with tetramethylsilane as an internal standard). High-resolution mass spectra (MS) were taken with a Hitachi M-80 spectrometer.

Column chromatography was done on 100—200 mesh silica gel, purchased from Kanto Chemical Co., Inc. Preparative thin-layer chromatography (PTLC) was performed on Silica gel GF_{254} (type 60, Merck). The Chromatotron (Model 7924, Harrison Research) is a preparative, centrifugally accelerated, radial, thin-layer chromatography performed on Silica gel GF_{254}.

Irradiation was carried out through a Pyrex filter with a Ushio 450 W high-pressure mercury lamp (UV; $\geq$300 nm) or a Toshiba FL 15 W fluorescent lamp[18] (visible).

Photoaddition of 2-Chloro-1,4-naphthoquinone (1) to Ethylene——A solution of **1** (183.1 mg) in 155 ml of benzene was irradiated (UV) for 15 min under bubbling of ethylene gas. The residue after evaporation of the solvent was chromatographed over silica gel (50 g). Elution with CH_2Cl_2–hexane (1 : 1) gave 112.0 mg (53%) of the adduct (**2a**) and 14.4 mg (8%) of 1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione (**3a**). **2a**: mp 80—81 °C (hexane–ether), colorless prisms. UV λ_{max}^{MeOH} nm: 231, 258.5, 303. IR (KBr): 1693, 1677 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.70—3.10 (m, 4H), 3.55—4.05 (m, 1H), 7.50—7.85 (m, 2H), 7.85—8.20 (m, 2H). MS *m/z*: 220 (M^+ for ^{35}Cl), 222 (M^+ for ^{37}Cl). *Anal.* Calcd for $C_{12}H_9ClO_2$: C, 65.32; H, 4.11. Found: C, 65.03; H, 3.90. **3a**: 195—200 °C (resolidified immediately and melted again at 259—264 °C) (MeOH–CH_2Cl_2), yellow needles. UV λ_{max}^{MeOH} nm: 244.5, 249.5, 264, 271.5, 336. IR (KBr): 1670 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.05 (s, 4H), 7.50—7.80 (m, 2H), 7.80—8.10 (m, 2H). High-resolution MS *m/z*: M^+ Calcd for $C_{12}H_8O_2$: 184.0523. Found: 184.0523.

Elimination of Hydrogen Chloride from the Adduct (2a)——The adduct (**2a**) (50.0 mg) was added to a solution of 5 ml of 1% Et_3N–$CHCl_3$, and the whole was stirred for 10 min at room temperature. The reaction mixture was evaporated to dryness and purified by PTLC (CH_2Cl_2) to give 37.6 mg (90%) of **3a**.

Addition of Methanol to 1,2-Dihydrocyclobuta[*b*]naphthalene-3,8-dione (3a)——A solution of **3a** (100.0 mg) in 5% NaOMe–MeOH was stirred at room temperature for 10 min. After addition of water, the mixture was extracted with CH_2Cl_2 and the organic layer was washed with water then dried over Na_2SO_4. The residue after evaporation of the solvent was chromatographed over silica gel (15 g). Elution with hexane–CH_2Cl_2 (2 : 1) afforded 98.5 mg (84%) of 2a-methoxy-1,2,2a,8a-tetrahydrocyclobuta[*b*]naphthalene-3,8-dione (**4a**) as colorless prisms, mp 62—63 °C (hexane). UV λ_{max}^{MeOH} nm: 228, 254, 300. IR (KBr): 1685, 1670 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.62—2.10 (m, 1H), 2.10—2.75 (m, 3H), 3.20 (s, 3H), 3.33—3.75 (m, 1H), 7.50—7.85 (m, 2H), 7.85—8.20 (m, 2H). *Anal.* Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 71.98; H, 5.45.

Elimination of Methanol from 4a——A solution of **4a** (58.2 mg) in 15 ml of benzene was treated with 25 mg of *p*-toluenesulfonic acid and the mixture was refluxed for 1 h with azeotropic removal of water. The mixture was washed with water, dried over Na_2SO_4, and purified with the Chromatotron (2% MeOH–CH_2Cl_2) to give 26.1 mg (53%) of **3a**.

General Procedure for the Synthesis of 1,2-Dihydrocyclobuta[*b*]naphthalene-3,8-diones without Isolation of the Adducts——A solution of 2-chloro-1,4-naphthoquinone (**1**) in benzene was irradiated in the presence of a large excess of alkene with visible or UV light until **1** disappeared on TLC. After removal of the solvent, a solution of 1—3% Et_3N–$CHCl_3$ was added to the residue and the whole was stirred for 10 min at room temperature. The reaction mixture was washed with water and the products were separated by column chromatography, by PTLC, or by use of the Chromatotron.

1,2-Dihydrocyclobuta[*b*]naphthalene-3,8-dione (3a)——Irradiation (UV) of **1** (331.0 mg) in 236 ml of benzene under bubbling of ethylene for 20 min and treatment with Et_3N gave 241.8 mg (81%) of **3a**.

1-Methoxycarbonyl-1-methyl-1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione (3b)——Irradiation (UV) of **1** (201.1 mg) and 30 ml of methyl methacrylate in 160 ml of benzene for 30 min and treatment with Et_3N gave 12.9 mg (4%) of the ene product (**5**) and 196.8 mg (74%) of **3b**. **3b**: mp 89.5—90.5 °C (MeOH), yellow prisms. UV λ_{max}^{MeOH} nm: 245, 250, 270, 338. IR (KBr): 1730, 1670 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.73 (s, 3H), 2.88 (d, J=14.5 Hz, 1H), 3.39 (d, J=14.5 Hz, 1H), 3.68 (s, 3H), 7.40—7.75 (m, 2H), 7.75—8.10 (m, 2H). *Anal.* Calcd for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.01; H, 4.63. **5**: mp 76—77 °C (MeOH), yellow needles. UV λ_{max}^{MeOH} nm: 245.5, 251.5, 273, 333. IR (KBr): 1725, 1663 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.78 (s, 3H), 3.85 (br s, 2H), 5.49 (br s, 1H), 6.27 (br s, 1H), 7.60—7.85 (m, 2H), 8.00—8.25 (m, 2H). MS *m/z*: 290 (M^+ for ^{35}Cl), 292 (M^+ for ^{37}Cl).

1-Methoxycarbonyl-1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione (3c)——Irradiation (UV) of **1** (297.7 mg) and 30 ml of methyl acrylate in 172 ml of benzene for 20 min and treatment with Et_3N gave 101.5 mg (27%) of **3c** and 253.8 mg (68%) of its dimeric product. **3c**: mp 158—159 °C (MeOH), yellow prisms. UV λ_{max}^{MeOH} nm: 245, 250.5, 270, 340. IR (KBr): 1736, 1674 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.11 (dd, J=16.0, 2.8 Hz, 1H), 3.40 (dd, J=16.0, 4.0 Hz, 1H), 3.73 (s, 3H), 4.13 (dd, J=4.0, 2.8 Hz, 1H), 7.40—7.75 (m, 2H), 7.75—8.10 (m, 2H). High-resolution MS *m/z*: M^+ Calcd for $C_{14}H_{10}O_4$: 242.0579. Found: 242.0587.

1-Methoxycarbonyl-2-methyl-1,2-dihydrocyclobuta[*b*]naphthalene-3,8-diones (3d$_{cis}$ and 3d$_{trans}$)——Irradiation (UV) of **1** (128.3 mg) and 5 ml of methyl crotonate in 25 ml of benzene for 20 min and treatment with Et_3N gave 123.4 mg (72%) of **3d** (mixture of *trans* and *cis* isomers in a ratio of *ca.* 18 : 5) which afforded 62.1 mg of **3d**$_{trans}$ as pale orange prisms, mp 106—107 °C (MeOH). UV λ_{max}^{MeOH} nm: 245, 250.5, 270, 339. IR (KBr): 1730, 1672 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.54 (d, J=6.8 Hz, 3H), 3.42 (qd, J=6.8, 2.0 Hz, 1H), 3.67 (d, J=2.0 Hz, 1H), 3.71 (s, 3H), 7.50—7.80 (m, 2H), 7.80—8.10 (m, 2H). High-resolution MS *m/z*: M^+ Calcd for $C_{15}H_{12}O_4$: 256.0735. Found: 256.0736.

The ^{1}H-NMR spectrum of the crude products obtained from the mother liquor showed the characteristic signals of **3d**$_{cis}$ at δ 1.35 (d, J=6.8 Hz, 3H) and 4.18 (d, J=5.0 Hz, 1H), in addition to those of **3d**$_{trans}$.

1-Methyl-1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione (3e)——Irradiation (UV) of **1** (200.1 mg) in 160 ml of benzene under bubbling of propene gas for 20 min and treatment with Et_3N gave 71.9 mg (35%) of **3e** as yellow needles, mp 56—57 °C (hexane–ether). UV λ_{max}^{MeOH} nm: 244, 249, 265, 272, 335. IR (KBr): 1660, 1650 sh cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.44 (d, J=7.2 Hz, 3H), 2.55 (dd, J=14.7, 1.5 Hz, 1H), 3.23 (dd, J=14.7, 4.5 Hz, 1H), 7.37—7.72 (m, 2H), 7.72—8.10 (m, 2H). MS *m/z*: 198 (M^+). *Anal.* Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.09. Found: C, 78.62; H, 5.00.

1-Acetoxymethyl-1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione (3f)——Irradiation (UV) of **1** (26.4 mg) and 10 ml of allylacetate in 20 ml of benzene for 10 min gave 17.1 mg of **2f**, which on treatment with Et_3N afforded 11.8 mg (33%) of **3f**. **3f**: mp 109—109.5 °C (hexane–ether), yellow prisms. UV λ_{max}^{MeOH} nm: 244.5, 249.5, 263 sh, 271, 335. IR (KBr): 1735, 1665 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.05 (s, 3H), 2.76 (dd, J=15.0, 2.2 Hz, 1H), 3.36 (dd, J=15.0, 4.0 Hz, 1H), 3.50—3.90 (m, 1H), 4.22 (dd, J=11.2, 5.8 Hz, 1H), 4.44 (dd, J=11.2, 6.7 Hz, 1H), 7.45—7.70 (m, 2H), 7.70—8.05 (m, 2H). MS *m/z*: 256 (M^+). *Anal.* Calcd for $C_{15}H_{12}O_4$: C, 70.30; H, 4.72. Found: C, 70.25; H, 4.80.

1-Dimethoxymethyl-1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione (3g)——a) Irradiation (UV) of 1 (202.0 mg) and 10 ml of acrolein dimethyl acetal in 154 ml of benzene for 15 min and treatment with Et_3N gave 91.3 mg (34%) of **3g** and 17.2 mg (9%) of **1**. The yield of **3g** was 37% based on the consumed **1**.

b) Irradiation (visible light) of **1** (497.7 mg) and 15.3 ml of acrolein dimethyl acetal in 265 ml of benzene in the presence of 1.5 ml of pyridine for 26 h and treatment with Et_3N gave 264.3 mg (44%) of **3g** and 54.6 mg (11%) of **1**. The yield of **3g** was 50% based on the consumed **1**. **3g**: mp 100—101 °C (hexane–ether), yellow prisms. UV λ_{max}^{MeOH} nm: 244.5, 250, 265, 272 sh, 335. IR (KBr): 1672 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.03 (d, J=4.2 Hz, 2H), 3.36 (s, 3H), 3.41 (s, 3H), 3.65 (dt, J=4.8, 4.2 Hz, 1H), 4.61 (d, J=4.8 Hz, 1H), 7.40—7.70 (m, 2H), 7.70—8.10 (m, 2H). High-resolution MS *m/z*: M^+ Calcd for $C_{15}H_{14}O_4$: 258.0890. Found: 258.0886.

1,1-Dimethyl-1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione (3h)——a) Irradiation (UV) of **1** (200.6 mg) in 150 ml of benzene under bubbling of isobutene gas for 20 min and treatment with Et_3N gave 11.6 mg (5%) of **3h** and 4.3 mg (2%) of the head-to-tail adduct (**2h**$_{H\text{-}T}$). When the irradiation was carried out with a 100 W high-pressure mercury lamp, the yields of **3h** and **2h**$_{H\text{-}T}$ were 32 and 5%, respectively. **2h**$_{H\text{-}T}$: colorless oil. UV λ_{max}^{MeOH} nm: 230, 255, 303. IR (film): 1695, 1682 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.87 (s, 3H), 1.45 (s, 3H), 2.52 (d, J=12.3 Hz, 1H), 2.88 (dd, J=12.3, 0.8 Hz, 1H), 3.60 (d, J=0.8 Hz, 1H), 7.45—7.85 (m, 2H), 7.85—8.20 (m, 2H). **3h**: mp 133—134 °C (MeOH), yellow needles. UV λ_{max}^{MeOH} nm: 245, 249.5, 266, 273, 336. IR (KBr): 1675, 1660 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.48 (s, 6H), 2.80 (s, 2H), 7.40—7.75 (m, 2H), 7.75—8.10 (m, 2H), MS *m/z*: 212 (M^+). *Anal.* Calcd for $C_{14}H_{12}O_4$: C, 79.22; H, 5.70. Found: C, 79.05; H, 5.81.

b) Irradiation (visible light) of **1** (195.5 mg) in 150 ml of benzene under bubbling of isobutene gas for 20 h and treatment with Et_3N gave 25.7 mg (10%) of **6**, 22.8 mg (11%) of **7**, 75.4 mg (35%) of **3h**, and 20.0 mg (8%) of **2h**$_{H\text{-}T}$. **6**: mp 85—86.5 °C (MeOH), pale yellow prisms. UV λ_{max}^{MeOH} nm: 245, 251, 265 sh, 274, 333. IR (KBr): 1665 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.81 (s, 3H), 3.49 (br s, 2H), 4.63 (br s, 1H), 4.77 (br s, 1H), 7.50—7.80 (m, 2H), 7.80—8.10 (m, 2H). High-resolution MS *m/z*: M^+ Calcd for $C_{14}H_{11}ClO_2$: 246.0447 (for ^{35}Cl), 248.0418 (for ^{37}Cl). Found: 246.0455, 248.0404. **7**: mp 67—69 °C (MeOH), pale yellow prisms. UV λ_{max}^{MeOH} nm: 245.5, 251, 265 sh, 330. IR (KBr): 1662 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.75 (s, 3H), 3.25 (br s, 2H), 4.76 (br s, 1H), 4.88 (br s, 1H), 6.68 (t, J=1.2 Hz, 1H), 7.45—7.80 (m, 2H), 7.80—8.10 (m, 2H). High-resolution MS *m/z*: M^+ Calcd for $C_{14}H_{12}O_2$: 212.0837. Found: 212.0837.

Elimination of Hydrogen Chloride from 2h$_{H\text{-}T}$——A mixture of 3% Et_3N–$CHCl_3$ and 10.2 mg of **2h**$_{H\text{-}T}$ was stirred for 72 h at room temperature. The reaction mixture was washed with water and dried over Na_2SO_4, and evaporation of the solvent gave 8.7 mg (quant.) of **3h**.

Photoadditions of 2-Chloro-1,4-naphthoquinone (1) to Ethyl Vinyl Ether——a) A solution of **1** (202.1 mg) in 30 ml of ethyl vinyl ether and 142 ml of benzene was irradiated (UV) for 15 min. The reaction mixture was concentrated to *ca.* 50 ml, then washed with water and dried over Na_2SO_4. The residue obtained after evaporation of the solvent was separated by column chromatography (SiO_2, 15 g). Elution with hexane–CH_2Cl_2 (1 : 1) afforded 106.4 mg (38%) of 4-chloro-2-ethoxy-5-hydroxy-2,3-dihydronaphtho[1,2-*b*]furan (**9**).

A fraction eluted with 9% MeOH–CH_2Cl_2 was further purified by PTLC (2% MeOH–CH_2Cl_2) to give 58.9 mg (21%) of 9-chloro-4-hydroxy-3-methyl-5,6-benzo-2-oxatricyclo[6.1.1.$0^{4,9}$]dec-5-en-7-one (**8**).

b) A solution of **1** (201.7 mg) in 30 ml of ethyl vinyl ether and 140 ml of 1% pyridine–benzene was irradiated (UV) for 15 min. The reaction mixture was concentrated to *ca.* 50 ml, then washed with water and dried over Na_2SO_4. The residue obtained after removal of the solvent was separated as above to give 10.6 mg (4%) of **9**, 12.4 mg (5%) of the adduct, 8a-chloro-1-ethoxy-1,2,2a,8b-tetrahydrocyclobuta[*b*]naphthalene-3,8-dione (**2i**), and 87.4 mg (32%) of **8**.

c) A solution of **1** (200.0 mg) in 30 ml of ethyl vinyl ether and 160 ml of 1% pyridine–benzene was irradiated (visible) for 12 h. The reaction mixture was concentrated to *ca.* 50 ml, then washed with water and dried over Na_2SO_4. The residue obtained after evaporation of the solvent was separated as above to give 33.7 mg (17%) of the starting material, 105.6 mg (38%; conversion yield of 46%) of **2i**, and 23.0 mg (conversion yield of 10%) of **8**. **2i**: mp 99.5—100 °C (hexane–ether), colorless prisms. UV λ_{max}^{MeOH} nm: 229, 255, 300. IR (KBr): 1685 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.15, (t, J=7.2 Hz, 3H), 2.03 (ddd, J=11.5, 9.8, 8.5 Hz, 1H), 2.90 (ddd, J=11.5, 9.8, 8.0 Hz, 1H), 3.43 (t, J=9.8 Hz, 1H), 3.53 (dq, J=8.8, 7.2 Hz, 1H), 3.97 (dq, J=8.8, 7.2 Hz, 1H), 4.29 (dd, J=8.5, 8.0 Hz, 1H), 7.50—7.90 (m, 2H), 7.90—8.30 (m, 2H). MS *m/z*: 264 (M^+ for ^{35}Cl), 266 (M^+ for ^{37}Cl). *Anal.* Calcd for $C_{14}H_{13}ClO_3$: C, 63.69; H, 4.89. Found: C, 63.52; H, 4.95. **8**: mp 129.5—130 °C (hexane–ether), colorless prisms. UV λ_{max}^{MeOH} nm: 204.5, 248, 290. IR (KBr): 3520, 1678 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.25 (d, J=6.5 Hz, 3H), 2.17 (ddd, J=13.2, 4.8, 3.0 Hz, 1H), 2.70 (s, 1H), 3.08 (td, J=13.2, 7.2 Hz, 1H), 3.52 (ddd, J=13.2, 4.8, 2.5 Hz, 1H), 4.00 (q, J=6.5 Hz, 1H), 4.63—4.93 (m, 1H), 7.20—8.00 (m, 4H). High-resolution MS *m/z*: M^+ Calcd for $C_{14}H_{13}ClO_3$: 264.0552 (for ^{35}Cl), 266.0522 (for ^{37}Cl). Found: 264.0552, 266.0521. **9**: mp 122—122.5 °C (hexane), colorless prisms. UV λ_{max}^{MeOH} nm: 211, 245.5, 327, 341. IR (KBr): 3430 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.26 (t, J=7.3 Hz, 3H), 3.22 (dd, J=16.5, 2.8 Hz, 1H), 3.54 (dd, J=16.5, 6.5 Hz, 1H), 3.72 (dq, J=10.0, 7.3 Hz, 1H), 4.04 (dq, J=10.3, 7.3 Hz, 1H), 5.56 (s, 1H), 5.92 (dd, J=6.5, 2.8 Hz, 1H), 7.30—7.55 (m, 2H), 7.75—7.95 (m, 1H), 8.05—8.25 (m, 1H). High-resolution MS *m/z*: M^+ Calcd for $C_{14}H_{13}ClO_3$: 264.0552 (for ^{35}Cl), 266.0522 (for ^{37}Cl). Found: 264.0554, 266.0528.

Photolysis of 2i to 8——A solution of **2i** (38.3 mg) in 60 ml of 1% pyridine–benzene was irradiated with a 100 W high-pressure mercury lamp for 0.5 h. The reaction mixture was evaporated to dryness and the residue was separated by PTLC (15% ether–CH_2Cl_2) to give 27.5 mg (72%) of **8**.

4-Chloro-5-hydroxynaphtho[1,2-*b*]furan (10)——a) A solution of **9** (46.5 mg) in 5 ml of benzene was treated with 0.06 ml of 47% $BF_3 \cdot Et_2O$–ether, and the mixture was stirred at room temperature for 10 min. The product was extracted with CH_2Cl_2 after addition of water and the residue obtained after evaporation of the solvent was purified by column chromatography (SiO_2, 5 g; hexane–CH_2Cl_2 (2:1)) to give 29.4 mg (77%) of **10**.

b) The adduct (**2i**, 4.7 mg) was treated with $BF_3 \cdot Et_2O$ as above to give 3.8 mg of **10** as colorless needles, mp 82—83 °C (hexane–ether). UV λ_{max}^{MeOH} nm: 223.5, 255, 325, 341. IR (KBr): 3420 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 5.73 (s, 1H), 6.79 (d, J=2.0 Hz, 1H), 7.59 (d, J=2.0 Hz, 1H), 7.30—7.60 (m, 2H), 8.00—8.30 (m, 2H). High-resolution MS *m/z*: M^+ Calcd for $C_{12}H_7ClO_2$: 218.0134 (for ^{35}Cl), 220.0104 (for ^{37}Cl). Found: 218.0090, 220.0060.

Dimerization of 3a——A solution of **3a** (25.6 mg) in 10 ml of toluene was refluxed for 2 h. The residue obtained after evaporation of the solvent was chromatographed over silica gel (3 g). By elution with hexane–CH_2Cl_2 (1:2), 7.0 mg (27%) of **3a** was recovered. Elution with 2% MeOH–CH_2Cl_2 afforded 12.9 mg (50%) of the dimer (**13**). Recrystallization from MeOH–CH_2Cl_2 furnished yellow needles, mp 249—252 °C (lit.,[17] mp 255—260 °C). UV λ_{max}^{MeOH} nm: 225, 245, 250, 330. IR (KBr): 1677, 1655 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.70—2.75 (m, 2H), 3.40—3.85 (m, 6H), 7.50—7.85 (m, 4H), 7.85—8.25 (m, 4H). ^{13}C-NMR (CF_3CO_2D) δ: 30.2 (t), 30.5 (t), 51.6 (s), 129.2 (d), 130.2 (d), 133.7 (s), 136.4 (s), 137.0 (d), 138.1 (d), 147.2 (d), 187.6 (s), 205.0 (s). MS *m/z*: 368 (M^+).

Dimerization of 3g$_{trans}$——A solution of **3g**$_{trans}$ (14.3 mg) in 1 ml of xylene was refluxed for 2 h. The residue obtained after evaporation of the solvent was purified by PTLC (3.5% MeOH–CH_2Cl_2) to give 12.9 mg (90%) of the dimer (**14**) as a colorless oil. UV λ_{max}^{MeOH} nm: 237, 260 sh, 310 sh, 335. IR (film): 1732, 1690, 1665 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.17 (d, J=7.0 Hz, 3H), 2.08 (d, J=7.0 Hz, 3H), 3.40 (q, J=7.0 Hz, 1H), 3.62 (d, J=9.0 Hz, 1H), 3.67 (s, 3H), 3.77 (s, 3H), 4.84 (d, J=9.0 Hz, 1H), 6.00 (q, J=7.0 Hz, 1H), 7.45—8.15 (m, 8H). High-resolution MS *m/z*: M^+ Calcd for $C_{30}H_{24}O_8$: 512.1470. Found: 512.1481.

Dimerization of 3b——A solution of **3b** (48.0 mg) in 10 ml of toluene was refluxed for 40 min. The residue obtained after evaporation of the solvent was separated by PTLC (3% ether–CH_2Cl_2) to give 20.4 mg (42%) of the dimer (**15**) and 17.2 mg (36%) of the starting material. **15**: mp 214—215 °C (CCl_4–MeOH), orange prisms. UV λ_{max}^{MeOH} nm: 246.5, 252 sh, 270 sh, 331. IR (KBr) 1713, 1655 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.75 (s, 4H), 3.62 (s, 6H), 5.70 (d, J=1.0 Hz, 2H), 6.60 (d, J=1.0 Hz, 2H), 7.50—7.70 (m, 4H), 7.90—8.10 (m, 4H). MS *m/z*: 510 (M^+).

***trans*-2,3-Dimethoxycarbonyl-1,2,3,4-tetrahydroanthracene-9,10-dione (17)**——A solution of **3a** (43.5 mg) and 1.38 g (40 mol eq) of dimethyl fumarate in 10 ml of xylene was refluxed for 1 h. After removal of excess dimethyl fumarate and xylene, the residue was chromatographed over silica gel (25 g). A fraction eluted with CH_2Cl_2 was separated by PTLC (8% ether–CH_2Cl_2) to give 2.6 mg (6%) of the dimer (**13**) and 60.5 mg (78%) of the 4+2 adduct **17** as yellow prisms, mp 162—163 °C (EtOH). UV λ_{max}^{MeOH} nm: 244.5, 250 sh, 262, 269, 330. IR (KBr): 1730, 1657 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.50—3.35 (m, 6H), 3.69 (s, 6H), 7.50—7.80 (m, 2H), 7.80—8.10 (m, 2H). High-resolution MS *m/z*: M^+ Calcd for $C_{18}H_{16}O_6$: 328.0945. Found: 328.0913. *Anal.* Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91. Found: C, 66.08; H, 4.81.

3,8-Dimethoxy-1,2-dihydrocyclobuta[*b*]naphthalene (18)——A solution of 1,2,2a,8a-tetrahydrocyclobuta[*b*]-naphthalene-3,8-dione[17] (40.3 mg, obtained by irradiation (≥300 nm) of 1,4-naphthoquinone in benzene under bubbling of ethylene) in tetrahydrofuran (THF) (5 ml) was treated with 50% NaH (59 mg) and Me_2SO_4 (0.08 ml), and the whole was refluxed for 3 h under Ar. After usual work-up, 32.7 mg (71%) of **18** was obtained as colorless prisms, mp 146.5—147 °C (hexane–ether). ^{1}H-NMR ($CDCl_3$) δ: 3.48 (s, 4H), 3.99 (s, 6H), 7.10—7.40 and 7.75—8.05 (an A_2B_2 pattern, each 2H). *Anal.* Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.56; H, 6.75.

Reaction of **18** with dimethyl fumarate under the same conditions as used in the formation of **17** resulted in recovery of the starting material.

1*H*-Naphtho[2,3-*c*]pyran-5,10-dione (19)——A solution of **3d** (100.0 mg) in 15 ml of acetone in the presence of 15 mg of *p*-TsOH (as hydrate) was refluxed for 10 h. A large excess of CH_2Cl_2 was added to the reaction mixture, which was washed with water and dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed over silica gel (15 g). Elution with 0.5% MeOH–CH_2Cl_2 gave 45.4 mg (55%) of **19** as dark red prisms, which melted and resolidified at about 130—137 °C, and decomposed at 155—156 °C (hexane). UV λ_{max}^{MeOH} nm ($\log\varepsilon$): 260 (4.16), 445 (3.38). IR (KBr): 1668, 1645, 1542 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 5.07 (s, 2H), 5.98 (d, J=5.5 Hz, 1H), 6.83 (d, J=5.5 Hz, 1H), 7.45—7.75 (m, 2H), 7.75—8.10 (m, 2H). MS *m/z*: 212 (M^+). *Anal.* Calcd for $C_{13}H_8O_3$: C, 73.58; H, 3.80. Found: C, 73.33; H, 3.65.

Catalytic Hydrogenation of 19——Compound **19** (28.2 mg) was hydrogenated in the presence of PtO_2 (7 mg) in MeOH (11 ml) at room temperature under atmospheric pressure for 1.5 h. The catalyst was filtered off, and the filtrate was evaporated to dryness. The residue was separated by PTLC (ether–hexane (3:2)) to give 1.6 mg, (6%) of the starting material and 17.4 mg (61%) of 1*H*-3,4-dihydronaphtho[2,3-*c*]pyran-5,10-dione (**20**) as yellow prisms, mp 127—129 °C (hexane–ether). UV λ_{max}^{MeOH} nm: 244, 261, 267, 330. IR (KBr): 1655, 1635 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.65 (tt, J=5.5, 2.5 Hz, 2H), 3.92 (t, J=5.5 Hz, 2H), 4.60 (t, J=2.5 Hz, 2H), 7.52—7.82 (m, 2H), 7.82—8.15 (m, 2H). MS *m/z*: 214 (M^+). *Anal.* Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found: C, 72.67; H, 4.58.

Photochemical 4+2 Cycloaddition of 1 to Acrolein——A solution of **1** (203.3 mg) and 9 ml of acrolein in 170 ml of benzene was irradiated (visible light) for 24 h. The reaction mixture was evaporated to dryness and treated with 20 ml of 0.2% Et_3N–$CHCl_3$ at room temperature for 1 h. The residue obtained after evaporation of the solvent was chromatographed over silica gel (20 g). Elution with hexane–CH_2Cl_2 (1:3) afforded 45.2 mg (22%) of the starting material (**1**) and 16.5 mg (7%) of 4*H*-naphtho[2,3-*b*]pyran-5,10-dione (**21a**) as yellow needles, mp 210—211 °C (dec.) (MeOH–CH_2Cl_2). UV λ_{max}^{MeOH} nm ($\log\varepsilon$): 253 (4.36), 294 (3.59). IR (KBr): 1673 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.15 (dd, J=3.2, 1.5 Hz, 2H), 5.15 (dt, J=6.2, 3.2 Hz, 1H), 6.52 (dt, J=6.2, 1.5 Hz, 1H), 7.50—7.85 (m, 2H), 7.85—8.20 (m, 2H). MS *m/z*: 212 (M^+). *Anal.* Calcd for $C_{13}H_8O_3$: C, 73.58; H, 3.80. Found: C, 73.51; H, 3.59.

Catalytic Hydrogenation of 21a——Compound **21a** (8.5 mg) was hydrogenated by 10% Pd–C (11 mg) in MeOH (2 ml) at room temperature under atmospheric pressure for 1 h. The catalyst was filtered off, and the solvent was evaporated to give 7.5 mg of 2*H*-3,4-dihydronaphtho[2,3-*b*]pyran-5,10-dione (**22a**) as yellow prisms, mp 229—231 °C (MeOH). UV λ_{max}^{MeOH} nm: 250, 280, 330. IR (KBr): 1673, 1613 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.00 (tt, J=6.5, 5.2 Hz, 2H), 2.58 (t, J=6.5 Hz, 2H), 4.28 (t, J=5.2 Hz, 2H), 7.40—7.75 (m, 2H), 7.75—8.10 (m, 2H). High-resolution MS *m/z*: M^+ Calcd for $C_{13}H_{10}O_3$: 214.0630. Found: 214.0630.

Synthesis of 2-Allyloxy-1,4-naphthoquinone (23)——2-Hydroxy-1,4-naphthoquinone (1.086 g) was added to a solution of 10 ml of allyl alcohol and 100 ml of benzene containing 0.4 ml of conc. H_2SO_4, and the mixture was refluxed for 1.5 h. The reaction mixture was washed with water, dried over Na_2SO_4, and evaporated to dryness. The residue was chromatographed over silica gel (30 g) to give 1.229 g (92%) of **23** as pale yellow needles by elution with CH_2Cl_2–hexane (3:1), mp 103—104 °C (hexane–ether). UV λ_{max}^{MeOH} nm: 242, 247, 276, 330. ^{1}H-NMR ($CDCl_3$) δ: 4.52 (br d, J=5.0 Hz, 2H), 5.15—5.60 (m, 2H), 5.65—6.30 (m, 1H), 7.45—7.80 (m, 2H), 7.80—8.10 (m, 2H). *Anal.* Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found: C, 72.79; H, 4.60.

Photolysis of 23——A solution of **23** (205.3 mg) in 182 ml of CH_3CN was irradiated with a 100 W high-pressure mercury lamp for 30 min. The residue obtained after removal of the solvent was separated by column chromatography (SiO_2, 10 g; hexane–CH_2Cl_2 (3:2)) and PTLC (7% ether–CH_2Cl_2) to give 25.8 mg (13%) of the intramolecular 2+2 adduct (**24**) and 7.5 mg (4%) of **21a**. **24**: mp 138—139 °C (MeOH–ether), colorless prisms. UV λ_{max}^{MeOH} nm: 229, 251.5, 300. IR (KBr): 1693 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.10 (dd, J=9.2, 8.0 Hz, 1H), 2.43 (dd, J=8.0, 2.8 Hz, 1H), 3.08 (d, J=9.2 Hz, 1H), 3.53 (d, J=2.8 Hz, 1H), 4.04 (s, 2H), 7.40—7.80 (m, 2H), 7.80—8.20 (m, 2H). High-resolution MS *m/z*: M^+ Calcd for $C_{13}H_{10}O_3$: 214.0629. Found: 214.0629.

Photochemical 4+2 Cycloaddition of 1 to Methyl Vinyl Ketone——A solution of **1** (199.8 mg) and 10 ml of methyl vinyl ketone in 170 ml of benzene was irradiated (visible light) for 45 h. The residue obtained after evaporation of the solvent was treated with 20 ml of 0.2% Et_3N–$CHCl_3$ for 1 h at room temperature. The reaction mixture was diluted by addition of CH_2Cl_2, washed with water, and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the residue was chromatographed over silica gel (30 g). Elution with hexane–CH_2Cl_2 (2:3) gave 64.1 mg (27%) of 4*H*-2-methylnaphtho[2,3-*b*]pyran-5,10-dione (**21b**) as yellow prisms, mp 178—179 °C (dec.) (MeOH). UV λ_{max}^{MeOH} nm: 253, 320. IR (KBr): 1715, 1683, 1647, 1625, 1595, 1575 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.93 (br s, 3H), 3.05 (dq, J=3.2, 1.5 Hz, 2H), 4.70—4.93 (m, 1H), 7.50—7.80 (m, 2H), 7.80—8.15 (m, 2H). MS *m/z*: 226 (M^+). *Anal.* Calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46. Found: C, 74.25; H, 4.20.

Catalytic Hydrogenation of 21b——Compound **21b** (18.2 mg) was hydrogenated for 1 h in the presence of PtO_2 (4 mg) in MeOH (6 ml) at room temperature under atmospheric pressure. The catalyst was filtered off, and the solvent was removed *in vacuo*. The residue was separated by PTLC (hexane–CH_2Cl_2 (2:1)) to give 6.1 mg (34%) of the starting material and 7.3 mg (40%) of 2*H*-2-methyl-3,4-dihydronaphtho[2,3-*b*]pyran-5,10-dione (**22b**) as yellow needles, mp 126—127 °C (hexane–ether) (lit.,[30] mp 121—122 °C). UV λ_{max}^{MeOH} nm: 250, 280, 330. IR (KBr): 1665, 1642, 1612, 1590, 1575 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.48 (d, J=6.5 Hz, 3H), 1.50—2.35 (m, 2H), 2.40—2.80 (m, 2H), 4.23 (dqd, J=8.8, 6.5, 2.8 Hz, 1H), 7.40—7.73 (m, 2H), 7.73—8.05 (m, 2H). High-resolution MS m/z: M^+ Calcd for $C_{14}H_{12}O_3$: 228.0786. Found: 228.0788.

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