Regio- and *endo*-Selective [2 + 2] Photocycloadditions of Homobenzoquinones with Ethyl Vinyl Ether

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Irradiation of various *meta*- and *para*-substituted homobenzoquinones with ethyl vinyl ether gave the [2 + 2] photoadducts, tricyclic diones, regio- and *endo*-selectively and in good yields. The tricyclic skeleton has an *anti*-form built by the addition of ethyl vinyl ether from the less hindered side of homoquinones. All of the CH_3, Cl, Br, and CH_3O substituents at the reacting C═C double bond afforded head-to-head (HH) addition predominantly. In the case of CH_3, Cl, and Br, the ethoxy group was oriented in the *endo*-position, while the CH_3O substituent led to a 1/5 mixture with the *exo*-isomer. It was also found that the Br-substituted [2 + 2] adducts undergo a facile skeletal rearrangement, being converted into dihydro-*o*-benzoquinone monomethide derivatives for *para*-substitution and dihydrobenzofuran derivatives for *meta*-substitution, probably under the influence of the in situ generated HBr. Intramolecular [2 + 2] photocycloaddition of an alkenylhomobenzoquinone afforded a tetracyclic dione.

Introduction

Photocycloaddition of cyclic conjugated enones with alkenes is a convenient method to construct a cyclobutane-containing polycyclic system. This reaction has been also applied to the synthesis of a number of naturally occurring substances[1,2] and has attracted much attention from the mechanistic viewpoint.[3,4] The general mechanism for the [2 + 2] photocycloaddition of α,β-conjugated enones to alkenes is known as the Corey−de Mayo mechanism. The generally accepted mechanistic picture, which was recently somewhat modified by Schuster et al., suggests a reaction sequence involving a photoexcitation of the enone, a rapid intersystem crossing to the triplet state (or accompanied by exciplex formation[3a−c]), the formation of a triplet 1,4-biradical with the alkene, and collapse to the coupling adduct after spin inversion.[3d,e,4] One of the most important concerns for synthetic application of the [2 + 2] photocycloaddition is the control of stereochemistry.[4,5] The photoaddition of α,β-conjugated enones to alkenes gives two regioisomers, viz., head-to-head (HH) and head-to-tail (HT) adducts. Although many examples of the [2 + 2] photocycloaddition of conjugated cyclopentenones and cyclohexenones to alkenes have been reported, there is some difficulty in properly predicting the regiochemistry. This is because the regiochemistry is dependent on the steric and electronic nature of both the enones and the alkenes.

On the other hand, quinones occupy a very important position in the photoreactions with alkenes in which the conjugated C═C and C═O double bonds competitively take part in the [2 + 2] photoaddition to provide cyclobutane derivatives[6] and Paternò−Büchi adducts,[7] respectively, depending on the identities of the quinone as well as the alkene.

In the context of our study of quinonoid compounds, we have investigated the photoinduced electron transfer[8] and the thermal[9] reaction of homoquinones. These compounds have a fused cyclopropane ring in the quinone frame. Photoexcitation of the strained bicyclic enedione structure is of interest in view of the formation of

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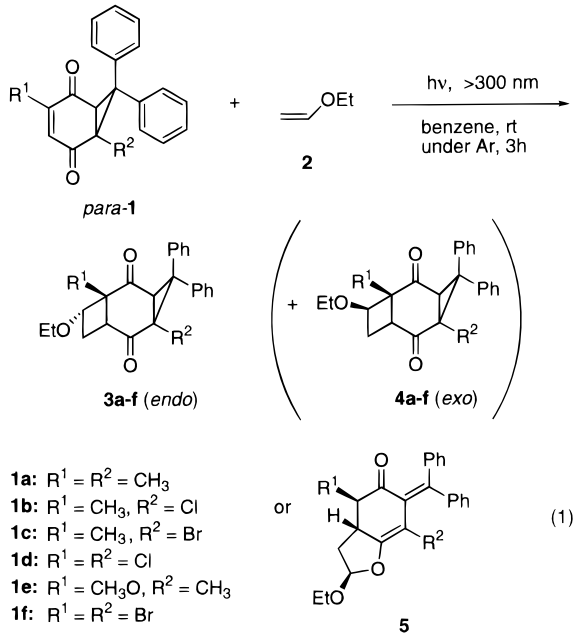
polycyclic diones via [2 + 2] cycloaddition with alkenes and their possible skeletal rearrangements. In this paper, we report the regio- and *endo*-selective [2 + 2] photocycloaddition of variously *para*- or *meta*-substituted homobenzoquinones **1a**−**j** with ethyl vinyl ether to get a deeper insight into the factor controlling the stereochemistry of these photoadditions. We also focus attention on a new tandem acid-catalyzed skeletal transformation of dibromo-substituted adducts.

Results and Discussion

Reaction of *para*-Substituted Homobenzoquinones 1a−f. The photoreaction of *para*-substituted homobenzoquinones **1a**−**f** (30 mM) with a 5-fold excess of ethyl vinyl ether **2** was carried out under an argon atmosphere in benzene solution by irradiation with a high-pressure mercury lamp through a Pyrex filter (>300 nm) for 3 h at room temperature (eq 1). The product yields were determined by ^{1}H NMR using an internal standard after evaporation of the solvent and the unreacted **2**.



The reaction of **1a**−**d** gave [2 + 2] photocycloadducts **3a**−**d** in 69−89% yields (Table 1). Unidentified products, possibly due to the photodegradation of the primary adducts, were also detected. However, no indication of the formation of Paternò−Büchi adducts, spirooxetanes, was found in the careful NMR analysis. Compounds **3a**−**d** were isolated by flash column chromatography, and their structures were elaborately determined by IR and ^{13}C and ^{1}H NMR with the aid of NOE for **3a**. The assignment of **3a** is as follows. All of the coupling constants around the cyclobutane ring are consistent with the structure for the HH adduct[10] (Figure 1). The cyclobutane ring is considered to be constructed with a *cis*-fusion to the homoquinone six-membered ring. This occurs by an *anti*-attack of **2** with respect to the cyclopropane ring,

Table 1. Photocycloaddition of Homoquinones 1 with Ethyl Vinyl Ether 2

Entry	1	Product, %yield
1	1a	**3a:** $R^2 = CH_3$ 69
2	1b	**3b:** $R^2 = Cl$ 72
3	1c	**3c:** $R^2 = Br$ 80
4	1d	**3d** 89
5	1e	**3e** 63 (77:23) **4e** 19
6	1f	**5f** 56
7	1g	**3g:** $R^1 = R^2 = CH_3$ 89
8	1h	**3h:** $R^1 = R^2 = Cl$ 85
9	1i	**3i** 72 (82:18) **4i** 16
10	1j	**6j** 51

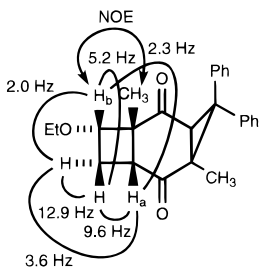


Figure 1. Selected ^{1}H NMR coupling constants of **3a**.

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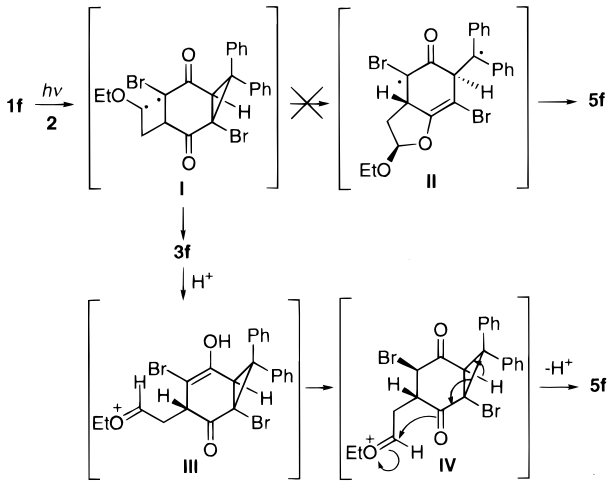
Scheme 1

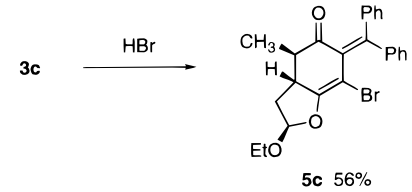


since the bridgehead methine proton H_a appears to be shifted to a higher magnetic field (δ 1.86) than expected due to the shielding effect of the facing *endo*-aromatic nucleus. The bulky *endo*-phenyl group apparently plays a significant role in the exclusive *anti*-approach of **2**. Indeed, the steric congestion due to the *endo*-phenyl ring can be seen in the X-ray structure analysis of the representative diphenylbromohomonaphthoquinone.[11] The NOE enhancement between the ethoxy-substituted methine proton H_b and the adjacent bridgehead CH_3 group indicates that the ethoxy group is located on the *endo*-side of the cyclobutane ring.

As shown in Table 1, homoquinones **1a**−**d** exclusively provided the *endo*-isomer of the HH adducts **3a**−**d** irrespective of the substituent variation both at the cyclopropane ring (entries 1−3; $R_1 = CH_3$, $R_2 = CH_3$, Cl, and Br) and at the C=C double bond carbon (entry 2 and 4; $R_1 = CH_3$, Cl, $R_2 = Cl$). However, the methoxy-substituted homobenzoquinone **1e** ($R_1 = CH_3O$, $R_2 = CH_3$) gave an appreciable amount of *exo*-isomer **4e** (19%) along with the *endo*-isomer **3e** (63%, entry 5), although the addition mode was found to be HH as in the cases of **1a**−**d**.

It is of interest that the reaction of dibromo-substituted homobenzoquinone **1f** gave the dihydro-*o*-benzoquinone monomethide **5f** (entry 6). The structure of **5f** was based on the detailed ^1H and ^{13}C NMR analyses (see Experimental Section). The stereochemistry of **5f** was identical to that of the methyl,bromo-substituted analog **5c** derived from the skeletal rearrangement of **3c** (vide infra). Here, two possible mechanisms may account for the formation of **5f**. The first explanation involves a cyclization of the initially formed 1,4-biradical **I** to the carbonyl oxygen rather than to the adjacent carbon atom, followed by β-fission of cyclopropane ring (**II**), and the 1,3-hydrogen shift into the Br-substituted spin center (Scheme 1). However, we cannot find any reason the other substituents, CH_3 and Cl, do not bring about such a consecutive radical process. The second path suggests an acid-catalyzed skeletal rearrangement[12] of the [2 + 2] adduct **3f** in such a way that protonation on the carbonyl oxygen initiates the heterolytic cleavage of the cyclobutane bond (**III**). The ethoxy-substituted carbocation then attacks the homoquinone carbonyl oxygen to afford the **5f** via a simultaneous ring opening of the cyclopropane ring and proton release (**IV**).

To assess the possibility of the latter ionic process, we treated a benzene solution of methyl,bromo-substituted **3c** with HBr gas and obtained **5c** in 56% yield (eq 2).



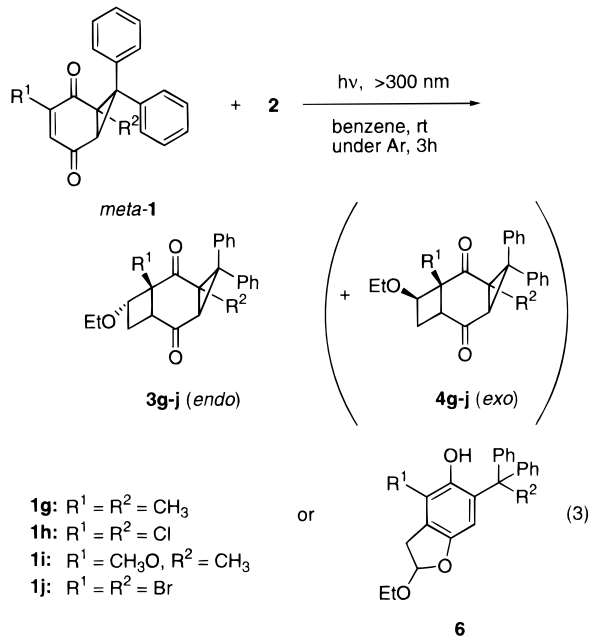
(2)

5c 56%

The structure of **5c** was confirmed by X-ray crystal structure analysis. It is notable that **5c** adopts the most stable geometry in which the methyl group lies on the *trans*-side against the five-membered oxa ring and the ethoxy group is located in *exo*-position. These findings strongly suggest the occurrence of an acid-catalyzed rearrangement of the [2 + 2] adduct **3f** into **5f**.

As to the nature of the acid species generated in situ, the detail is so far unclear. However, the Br substituent at the C=C double bond may be regarded as a most probable candidate for the photochemical generation of HBr, since the monobromo-substituted **1c** did give [2 + 2] adduct **3c**.

Reaction of *meta*-Substituted Homobenzoquinones 1 g−j. To obtain further information regarding the substituent effects affecting the stereochemistry of the [2 + 2] photoaddition, *meta*-substituted homobenzoquinones **1g**−**j** were employed to react with **2** (eq 3, Table 1).



(3)

1g: $R^1 = R^2 = CH_3$
1h: $R^1 = R^2 = Cl$
1i: $R^1 = CH_3O$, $R^2 = CH_3$
1j: $R^1 = R^2 = Br$

meta-**1**

3g-j (*endo*)

4g-j (*exo*)

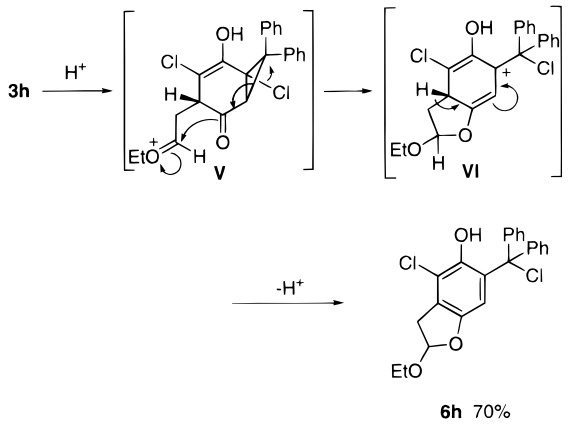
6

The reaction of *m*-dimethyl- and *m*-dichloro-substituted homobenzoquinones **1g** and **1h** produced HH *endo*-adducts[10] **3g** and **3h** stereoselectively in 89% and 85% yields, respectively (entries 7 and 8). However, the product **3h** readily decomposed on silica gel so that it was

(10) In general, in the field of [2 + 2] photoaddition of enones, the term head-to-head means the relative position between an alkyl group of an alkene and the carbonyl group of the enone. In this paper, we define it as the relative position between the ethoxy group of the alkene and a substituent at the double bond of the homoquinone since there are two carbonyl groups.

(11) Oshima, T.; Fukushima, K.; Kawamoto, T. *Acta Crystallogr.* **1999**, *C55*, 608.

Scheme 2



isolated as a solid by washing the crude product mixture with hexane after evaporation of the solvent and **2**. The methoxy-substituted **1j** led to the formation of an almost 1/5 ratio of minor HH *exo*-adduct **4i** (16%) as in the case of *para*-substituted homologue **1e** (entry 9). Coupled with the results of *para*-substituted homobenzoquinones, it was found that the regiochemistry of [2 + 2] addition is only determined by the substituents at the C=C double bond of homobenzoquinones and not by the cyclopropane substituents, although the *endo*-selectivity is appreciably reduced by the introduction of a methoxy substituent.

It should be also noted that the reaction of *m*-dibromo-substituted **1j** afforded a dihydrobenzofuran derivative **6j** in a yield of 51% (entry 10). This product seems to be produced via the acid-induced skeletal rearrangement of the expected [2 + 2] HH adduct **3j** in a similar manner as described for the formation of **5f**. Indeed, treatments of the isolated HH adduct **3h** with HBr gas yielded the corresponding dihydrobenzofuran **6h** in 70% yield (Scheme 2). This rearrangement can be characterized by the reaction pathway involving the acid-initiated cyclobutane ring opening (**V**), cyclization using the carbonyl oxygen, cyclopropane cleavage, followed by the 1,2-halide migration (**VI**), and the proton-releasing aromatization. Incidentally, it is well-known that a similar type of dihydrobenzofurans were formed from the Paternò−Büchi adducts, spirooxetanes, of benzoquinones with alkenes via the acid-catalyzed dienone−phenol rearrangement.[13]

Intramolecular [2 + 2] Photocycloaddition of Alkenyl-Substituted Homobenzoquinone. Intramolecular photocycloaddition of alkenes to α,β-conjugated enones was first reported by Ciamician.[14] Since then, the reaction has received much attention in view of its utility for the synthesis of polycyclic systems incorporating a cyclobutane ring.[15] In general, the intramolecular [2 + 2] photocycloaddition has been recognized to proceed via

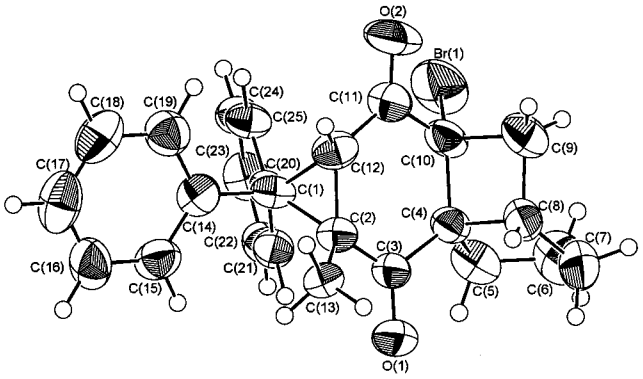
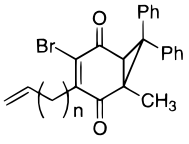


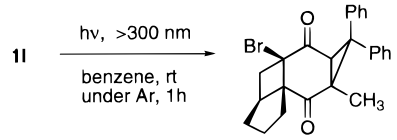
Figure 2. ORTEP drawing of the structure **7l**.

biradical intermediates as in the case of the intermolecular reaction, highly depending on the ring strain of the cyclic systems. For these cyclization reactions, the so-called "rule of five", which postulates that the cyclopentyl fused [2 + 2] adduct is formed preferentially,[16,17] can be applied.

Homobenzoquinones **1k** and **1l** bearing alkenyl side chains were synthesized by 1,3-dipolar addition of diphenyldiazomethane to the corresponding 2-bromo-3-alkenyl-5-methylbenzoquinones. As a result of the short chain length, 3-butenyl-substituted homobenzoquinone **1k** ($n = 2$) was recovered quantitatively when irradiated with a high-pressure mercury lamp in benzene for 1 h. Elongation of side chain by one methylene unit made it possible for 4-pentenyl-substituted **1l** ($n = 3$) to successfully achieve the intramolecular reaction, obeying the "rule of five" (eq 4). The [2 + 2] adduct **7l** (78%) was



n=2: **1k**
n=3: **1l**



(4)

7l 78%

submitted for X-ray crystal structure analysis (Figure 2). The compound has a unique tetracyclic dione structure containing three-, four-, five-, and six-membered rings. All the rings are *cis*-fused and the three- and four-membered rings adopt the *anti*-structure. Because of the high steric strain, the bridging bonds C(4)−C(10) (1.566(10) Å) and C(4)−C(8) (1.583(10) Å) of the cyclobutane ring are relatively longer than normal C−C bonds. Additionally, this X-ray structure clearly shows that the photoaddition of the alkene moiety still takes place in

(12) Protic acid or Lewis acid catalyzed skeletal rearrangement of cyclobutanes: (a) Liu, H.-J.; Chan, W. H. *Can. J. Chem.* **1980**, *58*, 2196. (b) Naito, T.; Makita, Y.; Kaneko, C. *Chem. Lett.* **1984**, 921. (c) Engler, T. A.; Combrink, K. D.; Ray, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 7931. (d) Engler, E. A.; Combrink, K. D.; Letavic, M. A.; Lynch, K. O., Jr.; Ray, J. E. *J. Org. Chem.* **1994**, *59*, 6567. (e) Engler, E. A.; Wei, D.; Letavic, M. A.; Combrink, K. D.; Reddy, J. P. *J. Org. Chem.* **1994**, *59*, 6588. (f) Engler, E. A.; Iyengar, R. *J. Org. Chem.* **1998**, *63*, 1929.

(13) Oshima, T.; Nakajima, Y.; Nagai, T. *Heterocycles* **1996**, *43*, 619.

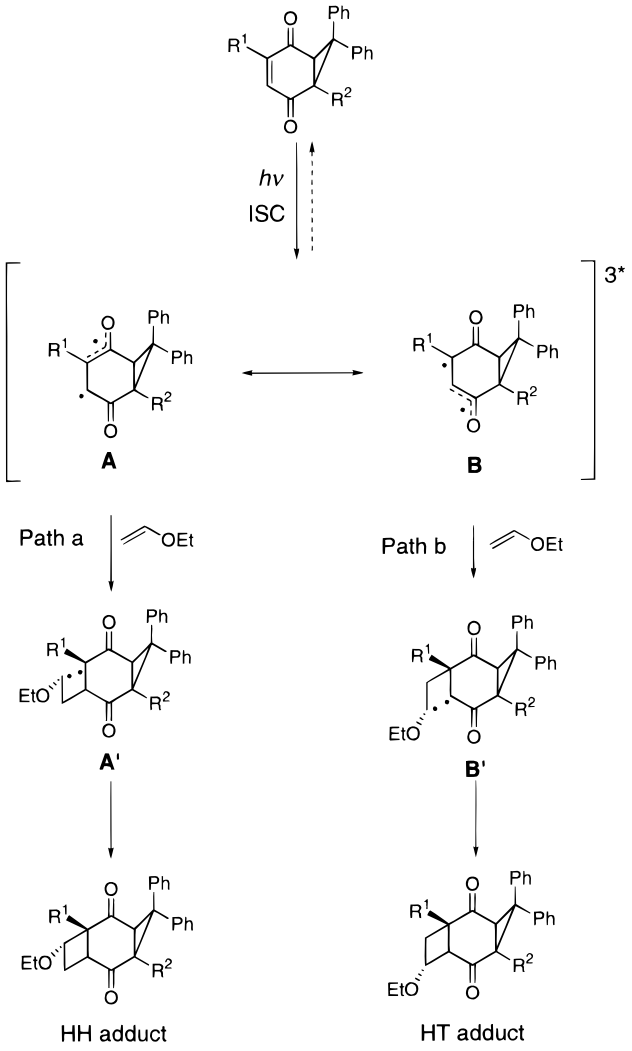
(14) Ciamician, G.; Silber, P. *Ber. Dtsch. Chem. Ges.* **1908**, *41*, 1928.

(15) For example: (a) Conrads, R.; Mattay, J.; Hoffmann, R. *Stereoselective Synthesis*; Helmchen, G., Ed.; Georg Thieme: Stuttgart, 1996; Vol. E21, Chapter 1.6.1.4, p 3119. (b) Crimmins, M. T. *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 5, Chapter 2.3.

(16) See reviews: (a) Becker, D.; Haddad, N. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1989; Vol. 10, Chapter 1. (b) Mattay, J. *Organic Photochemistry and Photobiology*; Horspool, W. M., Ed.; CRC Press: Boca Raton, 1995; p 618.

(17) Original publications such as photosensitized internal cycloaddition of dienes: (a) Srinivasan, R.; Carlough, K. H. *J. Am. Chem. Soc.* **1967**, *89*, 4932. (b) Liu, R. S. H.; Hammond, G. S. *J. Am. Chem. Soc.* **1967**, *89*, 4936.

Scheme 3



the less hindered *anti*-side of quinone plane as in the case of intermolecular reaction.

Mechanistic Consideration for the Regio- and *endo*-Selective Photocycloaddition. Taking into account that homoquinone **1a** shows an absorption peak at λ_{max} = 372 nm ($\epsilon = 2.1 \times 10^2$ in acetonitrile), the excited triplet state of **1a** must be formed by an intersystem crossing (ISC) from its excited singlet state. As Schuster et al. proposed,[3d,e,4] the [2 + 2] photocycloaddition appears to proceed similarly through an addition of alkene to the excited triplet state of homobenzoquinones and the collapse of generated triplet biradical intermediates to the corresponding [2 + 2] cycloadducts as represented for the *para*-substituted homologues (Scheme 3).

The excited triplet state of homobenzoquinones can be envisaged as possessing the biradical character depicted in its canonical structures **A** and **B**. An attack of ethyl vinyl ether on **A** at the unsubstituted spin center will lead to the HH adducts **3** via the more stable substituted 1,4-biradicals **A′** (path a), while the attack on **B** at the substituted spin center leads to the less stable biradical **B′**, responsible for the HT adducts (path b). Since it appears that the transformation of **A′** or **B′** to a final adduct via intersystem crossing is fast and irreversible step, the preferential formation of HH adducts in the present reactions is likely to be determined by the higher reactivity of **A** compared to that of **B** toward alkene,

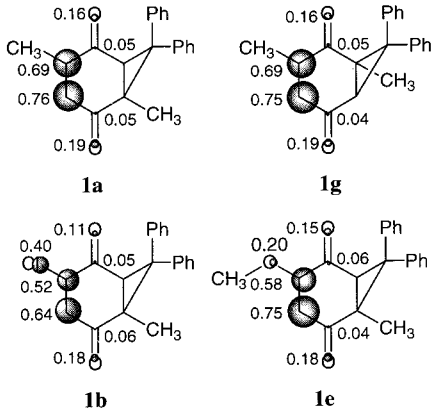
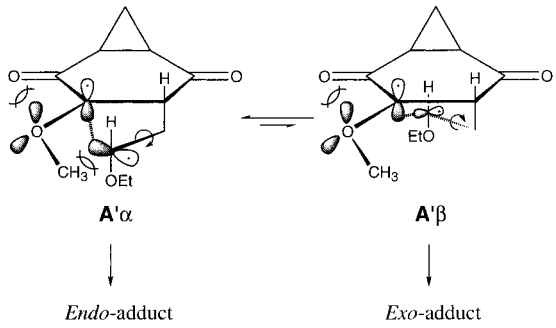


Figure 3. Calculated spin density for the excited triplet states of **1a**, **1g**, **1b,** and **1e** by MOPAC PM3.

Scheme 4



which can be explained by considering two factors: (a) the canonical structure **A** is expected to be more reactive toward the alkene than **B** because of the reduced steric repulsion, and (b) the calculated spin density for the lowest triplet states indicates rather a high value on the unsubstituted carbon atom as compared to the substituted carbon atom irrespective of the substituent variation or the *para*- and *meta*-substitution pattern (Figure 3).[18] These points are responsible for the occurrence of the preferential HH addition.

The *endo*/*exo*-selectivity must be determined at the recombination step of the HH 1,4-biradical **A′**. As representatively shown for the CH_3O substituted-biradical in Scheme 4, there can be two possible equilibrated conformers **A′**α and **A′**β that lead to product. In **A′**α the vinyl ether moiety is located in the less hindered outward position of the homoquinone frame, while in **A′**β the vinyl ether moiety is under the six-membered ring; both orient the ethoxy group far from the homoquinone moiety to avoid the severe steric repulsion. In such conformations, the two radical p-orbitals are likely to interact orthogonally to maximize their spin−orbit coupling[19] and then form the *endo*-adduct from **A′**α and the *exo*-adduct from the **A′**β conformer by way of the requisite bond rotation. Apparently, the equilibration between **A′**α and **A′**β is shifted to the left-hand side as a result of the steric interactions described above. This is probably the reason for the exclusive formation of *endo*-adducts for the spherical CH_3, Cl, and Br substituents.

(18) The calculations using the PM3 method were performed with the MOPAC program using a CS MOPAC Pro software (ver 4.0).

(19) Griesbeck, A. G.; Buhr, S.; Fiege, M.; Schmickler, H.; Lex, J. *J. Org. Chem.* **1998**, *63*, 3847.

Why did the CH_3O-substituted **1e** and **1l** provide ca. 1/5 amounts of the *exo*-isomer along with the major *endo*-adduct? As depicted in Scheme 4, the CH_3O substituent will adopt an *anti*-orientation with respect to the adjacent quinone carbonyl group to minimize the steric repulsion. In such geometry, it seems possible that the radical p-orbital would preferably interact with the quasiperiplanar lone pair orbital of the CH_3O group.[20] These geometrical situations will endow this nonspherical substituent with more effective steric hindrance than that expected from Taft's E_s parameter.[21] We can therefore explain some participation of the *exo*-process for **1e** and **1l** on the basis of the intrinsic spatial structure of the methoxy substituent.[22] To obtain further insight concerning this stereochemistry, additional [2 + 2] photocycloadditions of homoquinones and various alkenes are now in progress. The results will be published elsewhere.

Conclusions

Irradiation of *meta*- and *para*-substituted homobenzoquinones with ethyl vinyl ether gave the [2 + 2] photoadducts, *anti*-tricyclic diones, regio- and *endo*-selectively in good yields. The CH_3, Cl, and Br substituents at the reacting C=C double bond of homobenzoquinones induced the predominant head-to-head (HH) addition with the exclusive formation of the *endo*-orientation for the ethoxy group. On the other hand, the CH_3O substituent, though also bringing about the HH addition, permitted the formation of an appreciable amount (ca 20%) of *exo*-adducts. Coupled with the PM3 calculations, it is concluded that the spin density and the steric nature of the excited triplet state, as well as the relative stability of the head-to-head 1,4-biradicals, play a crucial role in the stereochemical course of these reactions. The reduced *endo*-selectivity for the CH_3O substituent is ascribed to the characteristic steric effect of the nonspherical methoxy substituent on the 1,4-biradical recombination. It was also found that the Br-substituted [2 + 2] adducts undergo the acid-catalyzed skeletal rearrangement to afford the dihydro-*o*-benzoquinone monomethide derivatives for the *para*-substituted homobenzoquinones and dihydrobenzofuran derivatives for the *meta*-substituted homobenzoquinones, depending on the mode of the subsequent cyclopropane ring cleavage.

Experimental Section

Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 270 MHz using $CDCl_3$ as solvent. The light source for all photo experiments was Eikohsha EHB W1-300 300 W high-pressure Hg lamp.

Materials. Ethyl vinyl ether (**2**) was used as purchased. Benzene, for preparative runs, was refluxed over lithium aluminum hydride for 1 day and fractionated. Homoquinones **1a**−**j** were synthesized by 1,3-dipolar addition of diphenyldiazomethane to the corresponding quinones as previously reported.[23] 2,5-Dimethyl-, 2-chloro-5-methyl-, 2-bromo-5-methyl-, 2,5-dichloro-, 2,5-dibromo-, 2,6-dimethyl-, 2,6-dichloro-, and 2,6-dibromo-1,4-benzoquinone were commercially available. 2-Methoxy-5-methyl- and 2-methoxy-6-methyl-1,4-benzoquinone were prepared according to the literature methods.[24] The compounds **1b**, **1e**, and **1i** were also identified as follows.

1-Chloro-4-methyl-7,7-diphenylbicyclo[4.1.0]hept-3-ene-2,5-dione (1b): 67% yield, mp 181−183 °C, pale yellow prisms (benzene/hexane); ^1H NMR δ 1.63 (d, 3H, J = 1.3 Hz), 3.54 (s, 1H), 6.22 (q, 1H, J = 1.3 Hz), 7.10−7.50 (m, 10H); IR (KBr) 1674 cm^{-1}. Anal. Calcd for $C_{20}H_{15}ClO_2$: C, 74.42; H, 4.68. Found: C, 74.58; H, 4.96.

4-Methoxy-1-methyl-7,7-diphenylbicyclo[4.1.0]hept-3-ene-2,5-dione (1e): 65% yield, mp 147−148 °C, pale yellow prisms (benzene/hexane); ^1H NMR δ 1.28 (s, 3H), 3.07 (s, 1H), 3.32 (s, 3H), 5.43 (s, 1H), 7.10−7.50 (m, 10H); IR (KBr) 1692, 1647 cm^{-1}. Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70. Found: C, 79.45; H, 5.91.

3-Methoxy-1-methyl-7,7-diphenylbicyclo[4.1.0]hept-3-ene-2,5-dione (1i): 63% yield, mp 225−226 °C, pale yellow prisms (benzene/hexane); ^1H NMR δ 1.28 (s, 3H), 3.06 (d, 1H, J = 1.7 Hz), 3.32 (s, 3H), 5.30 (d, 1H, J = 1.7 Hz), 7.10−7.40 (m, 10H); ^{13}C NMR δ 16.9, 38.3, 42.8, 53.4, 56.2, 110.7, 127.2, 127.6, 128.5, 128.9, 129.4, 139.6, 139.1, 161.4, 192.1, 193.6; IR (KBr) 1684, 1650 cm^{-1}; MS *m/e* 318 (M^+). Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70. Found: C, 79.13; H, 5.78.

General Procedure for the Photoreaction of 1 with 2. A mixture of **1a** (45.3 mg, 0.15 mmol) and **2** (216 mg, 3 mmol) in benzene (5 mL) was irradiated under argon atmosphere at room temperature for 3 h. After removal of the solvent and excess **2** under reduced pressure, 1,1,1,2-tetrachloroethane was added as an internal standard for ^1H NMR analysis. The reaction mixture was also column chromatographed on silica gel to give **3a** (38.7 mg, 69% yield), with a mixture of hexane and benzene as an eluent. The products were purified by recrystallization from benzene/hexane. HPLC with a semifractionation column was also used for the purification of some products. For the reactions for **1f** and **1j**, a spontaneous skeletal rearrangement of the initially formed labile photoadducts **3f** and **3j** took place to yield **5f** and **6j**, respectively. These secondary products were isolated by silica gel column chromatography with a mixture of hexane and benzene as an eluent. The structures of **3a**−**e**, **3g**−**i**, **4e**, **4i**, **5f**, and **6j** were confirmed by the ^1H and ^{13}C NMR, IR, and mass spectra, as well as the elemental analyses as follows.

***endo*-5-Ethoxy-1,6-dimethyl-9,9-diphenyl-*anti*-tricyclo[6.1.0.0^{3,6}]nonan-2,7-dione (3a):** mp 105−106 °C (dec), pale yellow prisms; ^1H NMR δ 0.66 (s, 3H), 1.16 (t, 3H, J = 6.9 Hz), 1.20 (s, 3H), 1.86 (ddd, 1H, J = 9.6, 3.6, 2.3 Hz), 2.09 (ddd, 1H, J = 12.9, 3.6, 2.0 Hz), 2.50 (ddd, 1H, J = 12.9, 9.6, 5.2 Hz), 3.00 (s, 1H), 3.29−3.39 (m, 2H), 3.61 (ddd, 1H, J = 5.2, 2.3, 2.0 Hz), 7.20−7.50 (m, 10H); ^{13}C NMR δ 15.2, 18.7, 20.0, 32.1, 42.6, 48.3, 49.2, 49.5, 53.5, 64.2, 84.0, 127.2, 127.8, 128.4, 128.9, 129.9, 139.3, 141.4, 207.2, 210.1; IR (KBr) 1681 cm^{-1}; MS (EI) *m/e* 374 (M^+). Anal. Calcd for $C_{25}H_{26}O_3$: C, 80.21; H, 6.95. Found: C, 80.09; H, 7.06.

6-Chloro-*endo*-5-ethoxy-1-methyl-9,9-diphenyl-*anti*-tricyclo[6.1.0.0^{3,6}]nonan-2,7-dione (3b): mp 128−130 °C, pale yellow prisms; ^1H NMR δ 1.14 (t, 3H, J = 7.7 Hz), 1.90 (ddd, 1H, J = 9.7, 3.0, 3.0 Hz), 2.20 (ddd, 1H, J = 12.9, 3.0, 1.7 Hz), 2.55 (ddd, 1H, J = 12.9, 9.7, 5.0 Hz), 3.33 (dd, 1H, J = 15.8, 7.7 Hz), 3.38 (dq, 1H, J = 15.8, 7.7 Hz), 3.48 (s, 1H), 3.68 (ddd, 1H, J = 5.0, 3.0, 1.7 Hz), 7.20−7.50 (m, 10H); IR (KBr) 1698 cm^{-1}. Anal. Calcd for $C_{24}H_{23}ClO_2$: C, 73.00; H, 5.87. Found: C, 73.11; H, 6.20.

6-Bromo-*endo*-5-ethoxy-1-methyl-9,9-diphenyl-*anti*-tricyclo[6.1.0.0^{3,6}]nonan-2,7-dione (3c): mp 75−76 °C (dec), colorless needles; ^1H NMR δ 0.71 (s, 3H), 1.17 (t, 3H, J = 7.3 Hz), 1.96 (ddd, 1H, J = 9.9, 2.6, 2.6 Hz), 2.21 (ddd, 1H, J =

(20) Kirby, A. J. *Stereoelectronic Effects*; Oxford University Press: New York, 1996.

(21) Taft, R. W., Jr. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956.

(22) In fact, Gallo et al. reported the larger *ortho*-steric effect of the CH_3O substituent as compared with those of the above spherical substituents for the *N*-methylation of *o*-substituted pyridines: Berg, U.; Gallo, R.; Klatte, G.; Metzger, J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1350. The *ortho*-steric parameters ($S°$) for the *N*-methylation of *o*-substituted pyridines are 0 (H), −0.54 (Cl), −0.73 (CH_3), −0.82 (Br), and −1.28 (CH_3O), respectively.

(23) (a) For homoquinones **1a**, **1f**, and **1j**; ref 8d. (b) For **1c** and **1g**; ref 7e. (c) For **1d** and **1h**; Oshima, T.; Nagai, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2507.

(24) (a) Stevens, R. V.; Angle, S. R.; Kloc, K.; Mak, K. F.; Trueblood, K. N.; Liu, Y.-X. *J. Org. Chem.* **1986**, *51*, 4347. (b) Adam, W.; Shimizu, M. *Synthesis* **1994**, 560.

12.2, 2.6, 2.6 Hz), 2.56 (ddd, 1H, J = 12.2, 9.9, 5.0 Hz), 3.35 (dq, 1H, J = 8.6, 7.3 Hz), 3.38 (dq, 1H, J = 8.6, 7.3 Hz), 3.54 (s, 1H), 3.68 (ddd, 1H, J = 5.0, 2.6, 2.6 Hz), 7.20−7.50 (m, 10H); ^{13}C NMR δ 14.5, 15.1, 19.7, 47.7, 49.1, 50.4, 51.4, 53.7, 64.2, 83.9, 127.7, 128.3, 128.4, 128.6, 129.5, 137.1, 141.7, 201.5, 204.4; MS (EI) *m/e* 438 (M^+, Cl = 35). Anal. Calcd for $C_{24}H_{23}$ Br O_3: C, 65.61; H, 5.28. Found: C, 65.78; H, 5.38.

1,6-Dichloro-*endo*-5-ethoxy-9,9-diphenyl-*anti*-tricyclo-[6.1.0.0^{3,6}]nonan-2,7-dione (3d): mp 127−129 °C, colorless prisms; ^{1}H NMR δ 1.16 (t, 3H, J = 6.9 Hz), 2.27 (dd, 1H, J = 10.6, 1.3 Hz), 2.27 (ddd, 1H, J = 13.2, 2.6, 1.3 Hz), 2.86 (ddd, 1H, J = 13.2, 10.6, 5.3 Hz), 3.47 (dd, 1H, J = 13.9, 6.9 Hz), 3.48 (dd, 1H, J = 13.9, 6.9 Hz), 3.56 (s, 1H), 4.10 (dd, 1H, J = 5.3, 2.6 Hz), 7.20−7.50 (m, 10H); ^{13}C NMR δ 14.9, 32.7, 50.5, 51.9, 52.2, 57.2, 65.4, 67.5, 85.4, 128.0, 128.5, 128.6, 128.8, 129.4, 129.5, 136.4, 139.9, 197.0, 198.2; IR (KBr) 1708 cm^{-1}; MS (EI) *m/e* 414 (M^+, Cl = 35). Anal. Calcd for $C_{23}H_{20}$ Cl_2O_3: C, 66.51; H, 4.85. Found: C, 66.74; H, 4.90.

***endo*-5-Ethoxy-6-methoxy-1-methyl-9,9-diphenyl-*anti*-tricyclo[6.1.0.0^{3,6}]nonan-2,7-dione (3e):** mp 98−100 °C, colorless prisms; ^{1}H NMR δ 1.22 (s, 3H), 1.14 (t, 3H, J = 6.9 Hz), 2.13 (ddd, 1H, J = 12.2, 5.6, 4.6 Hz), 2.41 (s, 3H), 2.50 (ddd, 1H, J = 9.9, 5.6, 2.3 Hz), 2.72 (ddd, 1H, J = 12.2, 9.9, 6.9 Hz), 2.93 (s, 1H), 3.42 (dq, 1H, J = 9.2, 6.9 Hz), 3.52 (dq, 1H, J = 9.2, 6.9 Hz), 3.84 (ddd, 1H, J = 6.9, 4.6, 2.3 Hz), 7.10−7.40 (m, 10H); ^{13}C NMR δ 15.2, 19.9, 31.3, 41.0, 44.7, 45.6, 48.5, 52.4, 65.3, 80.7, 85.3, 127.1, 127.6, 128.3, 128.6, 128.7, 130.6, 138.3, 141.3, 203.1, 208.3; IR (KBr) 1740, 1698 cm^{-1}. HRMS *m/z* (M^+) Calcd for $C_{25}H_{26}O_4$: 390.1831. Found: 390.1831.

***exo*-5-Ethoxy-6-methoxy-1-methyl-9,9-diphenyl-*anti*-tricyclo[6.1.0.0^{3,6}]nonan-2,7-dione (4e):** mp 102−104 °C, colorless prisms; ^{1}H NMR δ 1.21 (s, 3H), 1.16 (t, 3H, J = 6.9 Hz), 2.34 (ddd, 1H, J = 10.2, 2.6, 1.6 Hz), 2.42−2.51 (m, 1H), 2.48 (s, 3H), 2.68 (ddd, 1H, J = 11.2, 10.2, 9.9 Hz), 2.95 (s, 1H), 3.33 (dq, 1H, J = 9.2, 6.9 Hz), 3.63 (dq, 1H, J = 9.2, 6.9 Hz), 4.07 (ddd, 1H, J = 9.9, 7.6, 1.6 Hz), 7.10−7.40 (m, 10H); ^{13}C NMR δ 15.1, 18.8, 36.8, 40.4, 42.2, 43.8, 49.4, 52.4, 65.6, 74.6, 86.0, 127.3, 127.9, 128.2, 128.8, 128.9, 130.3, 137.4, 140.8, 202.0, 209.8; IR (KBr) 1722, 1642 cm^{-1}. HRMS *m/z* (M^+) Calcd for $C_{25}H_{26}O_4$: 390.1831. Found: 390.1826.

***endo*-4-Ethoxy-1,3-dimethyl-9,9-diphenyl-*anti*-tricyclo-[6.1.0.0^{3,6}]nonan-2,7-dione (3g):** mp 95−96 °C, colorless needles; ^{1}H NMR δ 0.67 (s, 3H), 1.09 (t, 3H, J = 6.9 Hz), 1.22 (s, 3H), 1.85 (dd, 1H, J = 9.9, 2.3 Hz), 2.12 (ddd, 1H, J = 12.9, 2.3, 2.0 Hz), 2.45 (ddd, 1H, J = 12.9, 9.9, 5.0 Hz), 2.87 (s, 1H), 3.21 (dd, 1H, J = 15.8, 6.9 Hz), 3.36 (dd, 1H, J = 15.8, 6.9 Hz), 3.59 (dd, 1H, J = 5.0, 2.0 Hz), 7.10−7.40 (m, 10H); ^{13}C NMR δ 15.1, 18.3, 20.0, 31.3, 46.8, 46.9, 48.6, 49.7, 53.3, 63.9, 84.8, 127.1, 127.7, 128.5, 128.8, 128.9, 129.9, 139.2, 141.5, 208.5, 209.2; IR (KBr) 1684 cm^{-1}; MS (EI) *m/e* 374 (M^+). Anal. Calcd for $C_{25}H_{26}O_3$: C, 80.21; H, 6.95. Found: C, 80.07; H, 7.05.

1,3-Dichloro-*endo*-4-ethoxy-9,9-diphenyl-*anti*-tricyclo-[6.1.0.0^{3,6}]nonan-2,7-dione (3h): mp 97−99 °C, pale yellow prisms; ^{1}H NMR δ 1.14 (t, 3H, J = 6.9 Hz), 2.20 (dd, 1H, J = 10.6, 1.3 Hz), 2.25 (ddd, 1H, J = 13.9, 2.3, 1.3 Hz), 2.81 (ddd, 1H, J = 13.9, 10.6, 5.3 Hz), 3.44 (dd, 1H, J = 13.9, 6.9 Hz), 3.45 (dd, 1H, J = 13.9, 6.9 Hz), 3.46 (s, 1H), 4.10 (dd, 1H, J = 5.3, 2.3 Hz), 7.20−7.50 (m, 10H); ^{13}C NMR δ 15.1, 31.8, 48.9, 52.0, 53.1, 58.7, 65.7, 67.3, 86.7, 127.9, 128.4, 128.5, 128.7, 129.4, 129.5, 135.9, 139.8, 194.9, 201.0; IR (KBr) 1702 cm^{-1}. Slightly high value of carbon (∼1%) was obtained for the combustion analysis, probably because of the trace amount of concomitant impurity.

***endo*-4-Ethoxy-3-methoxy-1-methyl-9,9-diphenyl-*anti*-tricyclo[6.1.0.0^{3,6}]nonan-2,7-dione (3i):** mp 102−104 °C, colorless prisms; ^{1}H NMR δ 1.12 (t, 3H, J = 6.9 Hz), 1.29 (s, 3H), 2.19 (ddd, 1H, J = 12.5, 5.3, 4.3 Hz), 2.40 (ddd, 1H, J = 9.9, 5.3, 2.3 Hz), 2.51 (s, 3H), 2.67 (ddd, 1H, J = 12.5, 9.9, 6.6 Hz), 2.83 (s, 1H), 3.44 (q, 2H, J = 6.9 Hz), 3.87 (ddd, 1H, J = 6.6, 4.3, 2.3 Hz), 7.10−7.31 (m, 6H), 7.40 (d, 2H, J = 6.9 Hz), 7.48 (d, 2H, J = 6.9 Hz); ^{13}C NMR δ 15.2, 18.5, 30.7, 42.7, 44.5, 46.3, 48.6, 52.6, 64.9, 80.6, 85.3, 127.1, 127.6, 128.5, 128.7, 130.6, 138.5, 141.7, 205.6, 206.0; IR (KBr) 1725, 1634 cm^{-1}. HRMS *m/z* (M^+) Calcd for $C_{25}H_{26}O_4$: 390.1831. Found: 390.1835.

***exo*-4-Ethoxy-3-methoxy-1-methyl-9,9-diphenyl-*anti*-tricyclo[6.1.0.0^{3,6}]nonan-2,7-dione (4i):** mp 164−166 °C, colorless prisms; ^{1}H NMR δ 1.15 (t, 3H, J = 6.9 Hz), 1.34 (s, 3H), 2.26 (d, 1H, J = 10.9 Hz), 2.54 (s, 3H), 2.48−2.71 (m, 2H), 2.89 (s, 1H), 3.30 (dq, 2H, J = 8.9, 6.9 Hz), 3.62 (dq, 2H, J = 8.9, 6.9 Hz), 4.12 (dd, 1H, J = 9.2, 7.9 Hz), 7.14−7.45 (m, 8H), 7.48 (d, 2H, J = 6.9 Hz); ^{13}C NMR δ 15.1, 19.4, 36.3, 41.7, 42.1, 15.9, 49.3, 52.5, 65.7, 74.6, 86.2, 127.4, 128.0, 128.4, 128.9, 129.0, 130.2, 137.7, 141.1, 204.2, 207.1; IR (KBr) 1698, 1687 cm^{-1}. HRMS *m/z* (M^+) Calcd for $C_{25}H_{26}O_4$: 390.1831. Found: 390.1829.

4,7-Dibromo-6-(diphenylmethylene)-2-ethoxy-5-oxo-2,-3a-*trans*-3a,4-*trans*-2,3,3a,4,5,6-hexahydrobenzofuran (5f): mp 105−106 °C, yellow prisms; ^{1}H NMR δ 1.26 (t, 3H, J = 7.3 Hz), 2.13 (ddd, 1H, J = 13.2, 10.3, 5.3 Hz), 2.65 (dd, 1H, J = 13.2, 7.9 Hz), 3.50 (dq, 1H, J = 9.6, 6.9 Hz), 3.72 (ddd, 1H, J = 11.9, 10.3, 7.9 Hz), 3.75 (dq, 1H, J = 9.6, 6.9 Hz), 4.59 (d, 1H, J = 11.9 Hz), 5.63 (d, 1H, J = 5.3 Hz), 7.00−7.40 (m, 10H); ^{13}C NMR δ 15.0 (CH_3), 39.9 (CH_2), 44.6 (CH), 58.4 (CH), 64.8 (CH_2), 91.3, 106.3 (CH), 126.6, 127.8, 127.9, 128.3, 129.1, 129.9, 131.2, 142.3, 143.3, 154.2, 157.7, 188.5; IR (KBr) 1694, 1633 cm^{-1}. Anal. Calcd for $C_{23}H_{20}$ Br_2O_3: C, 54.78; H, 4.00. Found: C, 54.66; H, 4.08.

4-Bromo-6-(bromodiphenylmethyl)-2-ethoxy-5-hydroxy-2,3-dihydrobenzofuran (6j): compound **6j** could not be purified because of the intrinsic liability; however, the structure was confirmed by the comparison of the ^{1}H NMR spectra with those of the dichloro analogue **6h**; ^{1}H NMR δ 1.21 (t, 3H, J = 7.3 Hz), 3.05 (dd, 1H, J = 17.6, 2.6 Hz), 3.45 (dd, 1H, J = 17.6, 6.6 Hz), 3.57 (dq, 1H, J = 9.4, 7.3 Hz), 3.85 (dq, 1H, J = 9.4, 7.3 Hz), 4.26 (s, 1H), 5.70 (dd, 1H, J = 6.6, 2.6 Hz), 7.10−7.50 (m, 10H).

Acid-Catalyzed Rearrangement of 3c and 3h. To a benzene solution (3 mL) of **3c** (39.5 mg, 0.09 mmol) was introduced HBr gas evolved by the treatment of NaBr with sulfuric acid, and the solution was stirred at room temperature for 1 h. The reaction mixture was column chromatographed on silica gel to give **5c** (22.1 mg, 56% yield) with a mixture of hexane and benzene as an eluent. The reaction of **3h** was also carried out in the same manner. The products were characterized as follows.

7-Bromo-6-(diphenylmethylene)-2-ethoxy-4-methyl-5-oxo-2,3a-*trans*-3a,4-*trans*-2,3,3a,4,5,6-hexahydrobenzofuran (5c): mp 95−97 °C, yellow prisms; ^{1}H NMR δ 1.09 (d, 3H, J = 6.3 Hz), 1.25 (t, 3H, J = 6.9 Hz), 1.97 (ddd, 1H, J = 12.5, 10.6, 5.3 Hz), 2.38 (dq, 1H, J = 11.7, 6.3 Hz), 2.48 (dd, 1H, J = 12.5, 7.9 Hz), 3.05 (ddd, 1H, J = 11.7, 10.6, 7.9 Hz), 3.61 (dq, 1H, J = 9.7, 6.9 Hz), 3.89 (dq, 1H, J = 9.7, 6.9 Hz), 5.62 (d, 1H, J = 5.3 Hz), 7.00−7.40 (m, 10H); IR (KBr) 1700, 1620 cm^{-1}. Anal. Calcd for $C_{24}H_{23}$ Br O_3: C, 65.61; H, 5.28. Found: C, 65.48; H, 5.34.

4-Chloro-6-(chlorodiphenylmethyl)-2-ethoxy-5-hydroxy-2,3-dihydrobenzofuran (6h): colorless oil; ^{1}H NMR δ 1.22 (t, 3H, J = 7.3 Hz), 3.09 (dd, 1H, J = 17.5, 2.3 Hz), 3.36 (dd, 1H, J = 17.5, 6.6 Hz), 3.58 (dq, 1H, J = 14.2, 7.3 Hz), 3.86 (dq, 1H, J = 14.2, 7.3 Hz), 4.28 (s, 1H), 5.70 (dd, 1H, J = 6.6, 2.3 Hz), 5.97 (s, 1H), 7.20−7.30 (m, 10H); ^{13}C NMR δ 15.0, 37.1, 64.4, 83.5, 106.3, 109.7, 118.3, 124.6, 127.7, 127.8, 128.1, 128.3, 131.9, 144.9, 150.6; IR (neat) 3443, 2921, 1443, 1355, 1214, 1088, 944, 700 cm^{-1}; MS (EI) *m/e* 414 (M^+, Cl = 35). Anal. Calcd for $C_{23}H_{20}$ Cl_2O_3: C, 66.51; H, 4.85. Found: C, 66.48; H, 4.87.

Intramolecular Photoreaction of Alkenylhomoquinones 1k and 1l. Alkenyl-substituted **1k** and **1l** were synthesized by addition of the corresponding alkenyl bromide to 2-bromo-5-methyl-1,4-benzoquinone according to the literature method.[25] The compounds **1k** and **1l** were identified as follows.

4-Bromo-3-(3-butenyl)-1-methyl-7,7-diphenylbicyclo-[4.1.0]hept-3-ene-2,5-dione (1k): mp 141−142 °C, pale yel-

(25) McKinley, J.; Aponick, A.; Raber, J. C.; Fritz, C.; Montgomery, D.; Wigel, C. T. *J. Org. Chem.* **1997**, *62*, 4874.

low prisms; ^{1}H NMR δ 1.30 (s, 3H), 1.59−1.93 (m, 2H), 2.26−2.41 (m, 2H), 3.27 (s, 1H), 4.92−5.02 (m, 2H), 5.60−5.80 (m, 1H), 7.10−7.50 (m, 10H); ^{13}C NMR δ 17.5, 31.2, 31.3, 40.0, 41.9, 53.6, 115.2, 127.6, 128.3, 128.9, 129.0, 129.1, 129.2, 137.1, 138.7, 138.9, 140.0, 152.0, 187.3, 192.9; IR (KBr) 1665 cm^{-1}. Anal. Calcd for $C_{24}H_{21}$ BrO_2: C, 68.42; H, 5.02. Found: C, 68.50; H, 5.14.

4-Bromo-1-methyl-3-(4-pentenyl)-7,7-diphenylbicyclo-[4.1.0]hept-3-ene-2,5-dione (1l): mp 117−118 °C, pale yellow prisms; ^{1}H NMR δ 1.00−1.10 (m, 2H), 1.22 (s, 3H), 1.95−2.01 (m, 2H), 2.15−2.35 (m, 2H), 3.26 (s, 1H), 5.02 (dd, 2H, J = 1.65, 1.65 Hz), 5.60−5.80 (m, 1H), 7.10−7.80 (m, 10H); ^{13}C NMR δ 17.6, 26.4, 31.3, 33.8, 39.9, 41.8, 52.5, 115.0, 127.6, 128.9, 129.0, 129.1, 129.2, 137.8, 138.6, 138.7, 140.1, 152.7, 187.3, 193.0; IR (KBr) 1669 cm^{-1}. Anal. Calcd for $C_{25}H_{23}$ Br O_2: C, 68.97; H, 5.32. Found: C, 68.72; H, 5.37. Irradiation of **1l** (65.3 mg, 0.15 mmol) in benzene (5 mL) for 1 h provided the intramolecularly cyclized tetracyclic dione **7l** (78% by NMR); however, compound **1k** was quantitatively recovered intact.

***rel*-(1*R*,3*S*,5*S*,7*S*,11*S*)-1-Bromo-5-methyl-4,4-diphenyltetracyclo[5.5.0^{3,5}.0^{7,11}]dodeca-2,6-dione (7l):** mp 184−186 °C, colorless prisms; ^{1}H NMR δ 1.24 (s, 3H), 1.30−2.00 (m, 5H), 2.17 (dd, 1H, J = 10.88, 7.36 Hz), 2.41−2.53 (m, 1H), 2.81−2.95 (m, 2H), 3.20 (s, 1H), 7.10−7.50 (m, 10H); ^{13}C NMR δ 20.0, 26.5, 32.6, 36.4, 41.5, 43.3, 45.8, 46.3, 50.1, 58.6, 65.5, 127.3, 128.1, 128.3, 128.9, 129.0, 130.8, 137.4, 141.1, 202.9, 207.7; IR (KBr) 1678 cm^{-1}.

X-ray Crystal and Molecular Structure Analyses. All X-ray data were measured on a Mac Science MXC3 diffractometer using graphite-monochromated Mo Kα radiation at room temperature. The structures were solved by SIR92 and refined by full-matrix least-squares. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were constrained to geometrically calculated positions.

Crystal Data for 5c. $C_{24}H_{23}$ Br O_3, M = 439.40, monoclinic, space group $C2/c$, a = 18.092(5), b = 13.206(4), c = 17.721(6) Å, β = 97.92(2)°, V = 4194(2) Å^3, Z = 8, R = 0.071, and Rw = 0.064 for 1947 reflections with $I > 1.0\sigma(I)$.

Crystal Data for 7l. $C_{25}H_{23}$ Br O_2, M = 435.40, triclinic, space group $P1$, a = 9.446(4), b = 12.389(8), c = 9.113(6) Å, α = 103.39(5)°, β = 94.99(2)°, γ = 97.00(4)°, V = 1022(1) Å^3, Z = 2, R = 0.082, and Rw = 0.078 for 1994 reflections with $I > 2.0\sigma(I)$.

Supporting Information Available: Tables of crystallographic data, atom coordinates, and bond distances and angles for **5c** and **7l**. This material is available free of charge via the Internet at http://pubs.acs.org.

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